

***Environmental
Engineering
and Management
Journal***

An International Journal

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Dedicated to Our Senior Professors



"Gheorghe Asachi" Technical University of Iasi

Environmental Engineering and Management Journal

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OBJECTIVES

Development in the XXI Century is a complex process that relies on different perspectives, strategies and actions, all of them important for its sustainability dimension. Action plans for sustainable development, such as Agenda 21 or the Millennium Development Goals (MDGs), adopted at the UN Millennium Summit 2000, can only be successful if all involved stakeholders make efforts to find effective long-term solutions that link environment and natural resources with patterns of production and consumption, social development. In recent years, it has become increasingly clear that sustainable economies must be built around sustainable products, services, and consumption patterns, not just sustainable industrial processes. Production-oriented strategies can effectively reduce the environmental impacts associated with the design and manufacture of products and the consumption of materials and resources in the production process. Sustainable production and sustainable consumption are complementary strategies for making economies more sustainable. Multidisciplinary, international cooperation and effective communication of the scientific, technological and managerial achievements in the environmental field are of a great importance for promoting sustainable development. Already at its 5th edition, the ICEEM conference is designed to bring together engineers, scientists and managers, active in the field of Environmental Protection, in the unique landscape of the most famous Danube Delta in Romania.

CONFERENCE FEES

- **until 20th of July 2009:**
450 Euro/person (single room) or **400 euro/person** (double room) – all inclusive
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600 Euro/person (single room) or **550 euro/person** (double room) – all inclusive

LOCATION

The ICEEM05 conference will be held between **15 -19 September 2009** in the outstanding landscapes of the Romanian Danube Delta. The Danube Delta Biosphere Reservation is a labyrinth of water and land, made up of countless lakes, channels, islands at the end of a 2,860 km long river. The Danube Delta is the largest European wetland and reed bed, forming also Europe's largest water purification system. The area is particularly well known for the abundance of birdlife: 312 important bird species are present in the Delta, which is an important stopover and breeding area for many bird species. About 90 fish species are found here, including populations of sturgeon. It is also one of the last refuges for the European mink, the wildcat, the freshwater otter and the globally threatened monk seal. The biosphere reserve was declared as both Natural World Heritage and Ramsar site in 1991.

You may find more information about the Danube Delta at www.ddbra.ro

The Conference will be held in 3 locations of the Danube Delta:

- 15 – 16 September 2009 at the Delta Hotel, Tulcea
- 17 September 2009 – Crisan, Danube Delta
- 18 – 19 September - Sulina, Danube Delta

ACCOMODATION

For 15 and 16 September accommodation will be provided at the Delta Hotel in Tulcea. For the remaining days of the Conference, accommodation will be provided at hostels in Crisan and Sulina, Danube Delta.

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• The abstracts (maximum 1 page A4) can be submitted until **1st of May 2009**, and will be published in the conference proceedings (ISBN abstracts book).

• Selected papers by the International Scientific Committee will be published in special issue of *Environmental Engineering and Management Journal* (ISI quoted journal).

• More information about ICEEM/05 can be found at: www.ch.tuiasi.ro/ICEEM05



EDITORIAL

A SPECIAL ISSUE

DEDICATED TO OUR SENIOR PROFESSORS

The *Gheorghe Asachi* Technical University of Iasi is the modern quintessence of the Romanian tradition of higher technical education. It originated at the beginning of the 19th century under the leadership of one of Romania’s great scholars, Gheorghe Asachi, who founded the first Romanian school of engineers. Through the enthusiastic contributions of visionaries with foresight in technical sciences, this school has continually evolved, and has achieved official recognition in the mid 20th Century.

In 1937 the *Gheorghe Asachi* Polytechnic School was founded by transforming the two technico-applicative sections of the University, which became faculties in the new higher Institution.

With a much enlarged sphere of activity, the Polytechnic Institute of Iasi became the *Gheorghe Asachi* Technical University in 1993.

Ever since its beginnings, our university has benefited from a valuable team of professors, dedicated to carrying forward the academic spirit, and driven by the will to found and develop a higher technical school in Iasi, following the European models. The University maintains a world-class, comprehensive program for teaching, research and research training.

We aim for international standards of excellence across the spectrum of research, from fundamental, curiosity-driven work that builds knowledge and leads to new research questions to applied research and innovation with direct commercial application.

The thoughts, desires and dreams of the forefathers of the higher technical education from Iasi were put into practice and developed by an elite of professors who formed the bases of branches with numerous specializations in the more significant technical fields.

These professors were founders and driving forces for the Romanian academic education in fields such as chemistry, electronics and electrotechnics, mechanics, computer technology, hydrotechnics, construction and architecture, textiles, environmental protection.

The *Gheorghe Asachi* Technical University trains engineers in a multitude of domains, all offering the opportunity for individual specialization. It is recognized that excellence in research means both excellence in teaching and the ability to interact with and to provide benefit for our community. We also acknowledge that leading infrastructure attracts and retains high quality staff.

The good training of the future engineers is ensured by the distinguished teaching staff of the University. They represent true role models for our younger colleagues, researchers and students, and their continued advice has continually proven invaluable to the progress of our educational and research activities. Each, in their respective field, has left an imprint on our learning institution, through contributions such as the founding and equipping of new laboratories, publishing scientific papers and books which would serve as valuable documentation for younger generations.

By organizing international symposiums and founding scientific journals they have decisively contributed to the increased international visibility of our university. Our strategies invoke the benefits of collaboration and interdisciplinary research, and the importance of rewarding excellence.

The academic staff plays a key role in promoting graduate study, fostering intellectual and professional academic growth, and developing initiatives to enhance the graduate student experience.

Our professors coordinate skills development programs for both graduate research students and their advisors, and focus on initiatives to enhance the quality of our research training programs, such as travel, exchanges, internships, and industry collaboration.

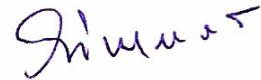
Every November, the academic staff and students celebrate the Days of the University.

This year, in 2008, the festivities had a particularly special attribute. Recognizing exceptional, research, creativity and service to the University community, the university has shown high respect for its senior professors, who, with devotion, remain faithful to the university even after a carrier full of accomplishments.

With the same enthusiasm, this issue of the *Environmental Engineering and Management Journal* pays homage to our esteemed senior professors who, for decades, have trained generations of young engineers, have rendered distinguished service to the university, have significant records in teaching, research, and scholarship and have made significant contributions in the advancement of scientific research in our university.

We are all grateful for the contributions of our senior professors to the continuing progress of higher technical education in Iasi, and wish for this special issue of *Environmental Engineering and Management Journal* to be a symbol of our respect and appreciation for their entire activity in education and research.

Professor Ion GIURMA



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of Iași, Romania*



COMPOSITE MEMBRANES WITH CROSS-LINKED MATRIMID SELECTIVE LAYER FOR GAS SEPARATION

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Abstract

In the present work, composite membranes were developed for separation of hydrogen from its mixtures with other gases. The composite membranes were characterized by single gas permeation and scanning electron microscopy. Gas transport properties have been determined for four gases (H₂, CH₄, N₂, CO₂). The influence of cross-linking on transport was measured. H₂/CH₄ selectivity values up to 115 were obtained. The resulting membranes have a selectivity of H₂/CH₄ close to intrinsic selectivity of Matrimid 5218.

Keywords: composite membranes, cross-linking, gas separation, Jeffamine T403, Matrimid

1. Introduction

Due to the fear of the depletion of resources and the growth of environmental awareness more and more researches have set out for seeking alternative energy sources in recent days. Among the alternative energy carriers, hydrogen is preferred because it burns to waste-free water vapour when utilized („clean fuel”).

One of the larger applications of composite hydrogen permeable membranes is hydrogen recovery in refineries. A typical application is the recovery of hydrogen from waste gas streams that would otherwise be used as a fuel (Baker, 2002).

Over the past 20 years, there has been an increasing interest for polyimides as membrane materials for gas separation purposes.

Polyimides have proven useful for the formation of gas separation membranes because of their attractive combination properties: high gas permeability as well as high intrinsic permselectivity in comparison to polycarbonate, polysulfone and other materials (Hayes, 1988; Koros et al., 1988; Ohya et al., 1996; Pinnau and Freeman, 2000, Shao et al., 2004).

The gas transport performance of polyimides can be improved by cross-linking modification. Cross-linking of a polymer matrix may influence physical properties and the ability of the material to transport and separate gases. Because cross-linking restricts the mobility of polymer chains by the formation of covalent bonds, it stabilizes the material against thermal and chemical degradations as well as impacting gas transport.

The restriction of the polymer chain mobility can impede gas transport since the diffusion of gas molecules through a polymer involves the cooperative motion of chain segments (Dudley et al., 2001; Liu et al., 2001; Sullivan, 2005; Tin, 2003).

This work presents the development and optimization of Matrimid composite membranes. It's focus is to investigate the influence of the polymer concentration, the type of solvent and non-solvent used, the cross-linking agent and its concentration, the influence of the support, and the speed used for coating. The prepared membranes were evaluated for gas separation.

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2. Experimental

2.1 Materials

The Matrimid 5218 (polyimide of 3, 3', 4, 4'-benzophenonetetracarboxylic dianhydride and diamino-phenylindane) was purchased from Ciba Specialty Chemicals and Huntsman in powder form (<http://www.huntsman.com>). Matrimid 5218 has an attractive combination of gas permeability and selectivity properties accompanied by excellent mechanical properties, high glass transition temperature (Bateman and Gordon, 1974). It has the structure from Fig.1.

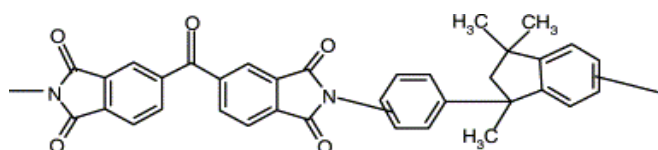


Fig.1. Chemical structure of Matrimid

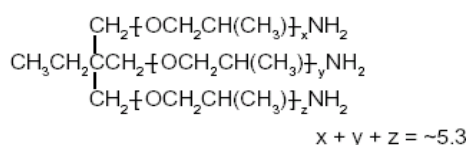


Fig.2. Chemical structure of Jeffamine

Buthylenediamine, chloroform, dichloromethane, toluene, cyclohexane were supplied by Aldrich, and used as received. Polyacrylonitrile (PAN), PAN+ γ butirolactone(γ BL) and poly(dimethylsiloxane),(PDMS) were used as a support material for composite membranes. The support was prepared at GKSS-Research Center.

2.2 Preparation of composite membrane

2.2.1 Matrimid membrane

A 0.5 (w/w) of polymer solution was prepared by dissolving Matrimid powder in solvent (chloroform, dichloromethane). The casting solution was filtered using a 20 μ m metal mesh filter.

2.2.2 Matrimid cross-linked membrane

A solution of 5 % Matrimid, solvent and cross-linked agent was prepared and mixed for 24 hours at 24 $^{\circ}$ C. With this solution, solutions with different concentrations of Matrimid (0.25 %, 0.5%, 1%) were prepared. The casting solutions were filtered using a 20 μ m metal mesh filter.

Membranes were prepared on PAN and PDMS support by hand or on PAN and PAN+ γ BL support in a pilot scale membrane casting machine. Further it was cast another solution 1% PDMS in isoctane.

The deposition of PDMS layer on the surface of Matrimid has a drastic effect on selectivity. PDMS

blocks the defects of the selective layer. The gas flow through the PDMS blocked pores becomes then negligible compared to the quantity of gas penetrated through the total surface of the membrane and membrane's selectivity turns to be controlled by the properties of the selective layer material (Shishatskiy et al., 2006). For coating different speeds were used.

2.3 Gas permeability and selectivity

The membranes were tested for gas permeation using the semi-automatic apparatus based on the barometric method. The set up allows to program of the testing sequence up to 8 individual gases at a feed pressure up to 1.3 bar within the temperature range 20-80 $^{\circ}$ C. In the current study membranes were tested at 30 $^{\circ}$ C in the range of feed pressures 0.3 – 2 bar using the measurement cell with the active membrane area of 34.2 cm 2 . The selectivity (α) was obtained calculating the ratio between permeability values for different gases.

2.4. Scanning electron microscopy

The morphology of the prepared membranes was analyzed by Scanning Electron Microscopy (SEM). Samples were immersed in isopropanol and fractured in liquid nitrogen, coated with Au/Pd by sputtering and observed in a field emission scanning electron microscope Leo Gemini1550 VP.

3. Result and discussion

The chemical mechanism of the cross-linking may be described as follows: the amino groups in buthlyenediamine or Jeffamine react with imide groups of Matrimid to form amide groups, and thus the cross-linked is formed. The reaction and the final product structure should be that depicted in Figs. 3 and 4.

3.1 Permeation transport of simple gas

The results presented in Table 1 suggest that the crosslinking may have a significant influence on gas permeation properties.

Table 1. Gas transport properties for membranes prepared without and with cross-linking agent (Jeffamine)

Solution	H_2 Permeance, m^3/m^2h*bar	$\alpha(H_2/CH_4)$
0.5% Matrimid in $CHCl_3$	0.1562	86.71
	0.1478	82.28
	0.164	83.13
	0.1686	81.78
2% Jeffamine to Matrimid, 0.5% $CHCl_3$	0.2781	88.74
	0.2842	82.00
	0.289	85.57
	0.247	92.65

The improvement of H₂/CH₄ selectivity was mainly resulted by the reduced chain mobility and increased the packing density of the polymer chains after cross-linking.

Table 2 show the permeance and selectivity values measured for membranes with butylenediamine and Jeffamine like cross-linking agent. For membranes preparation solutions of 1% Jeffamine to 1% Matrimid in CH₂Cl₂ and 0.1% (CH₂)₄(NH₂)₂ to 1% matrimid in CH₂Cl₂. were used. PAN dry support was used as support.

Consequently, Jeffamine will ensure a more advanced degree of cross-linking, which in turn will determine a more intense passing a smaller molecules, such as hydrogen, leading to a better selectivity of membranes. Therefore, Jeffamine was chosen as a cross-linking agent for further experiments. Some influence of the casting solvent on the permeation properties has been reported in the literature. As it can be seen in Fig. 5, the cast film of Matrimid from chloroform has higher permeability coefficients than the film cast from dichloromethane.

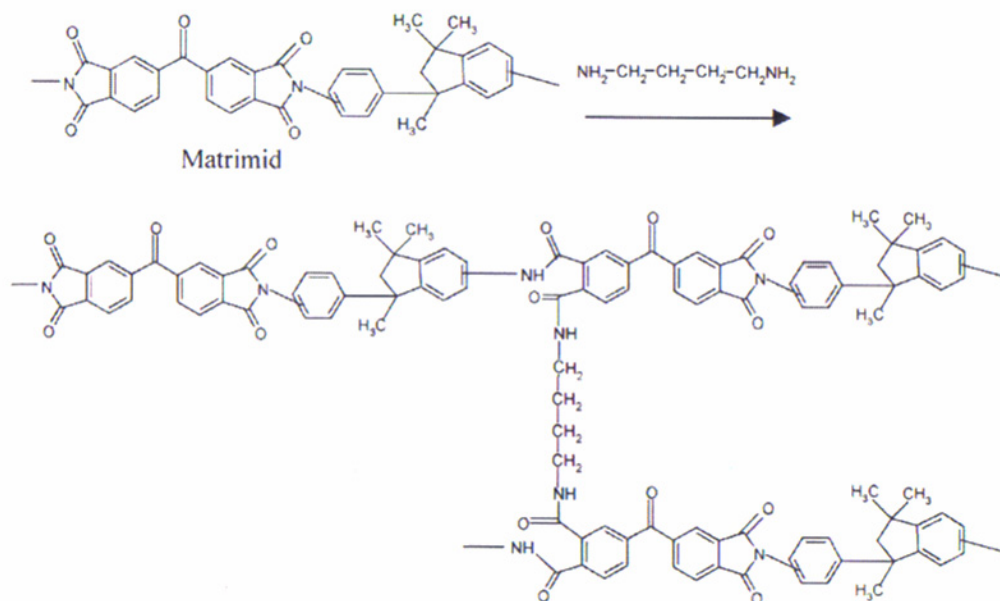


Fig.3. Mechanism of chemical cross-linking of Matrimid with butylenediamine

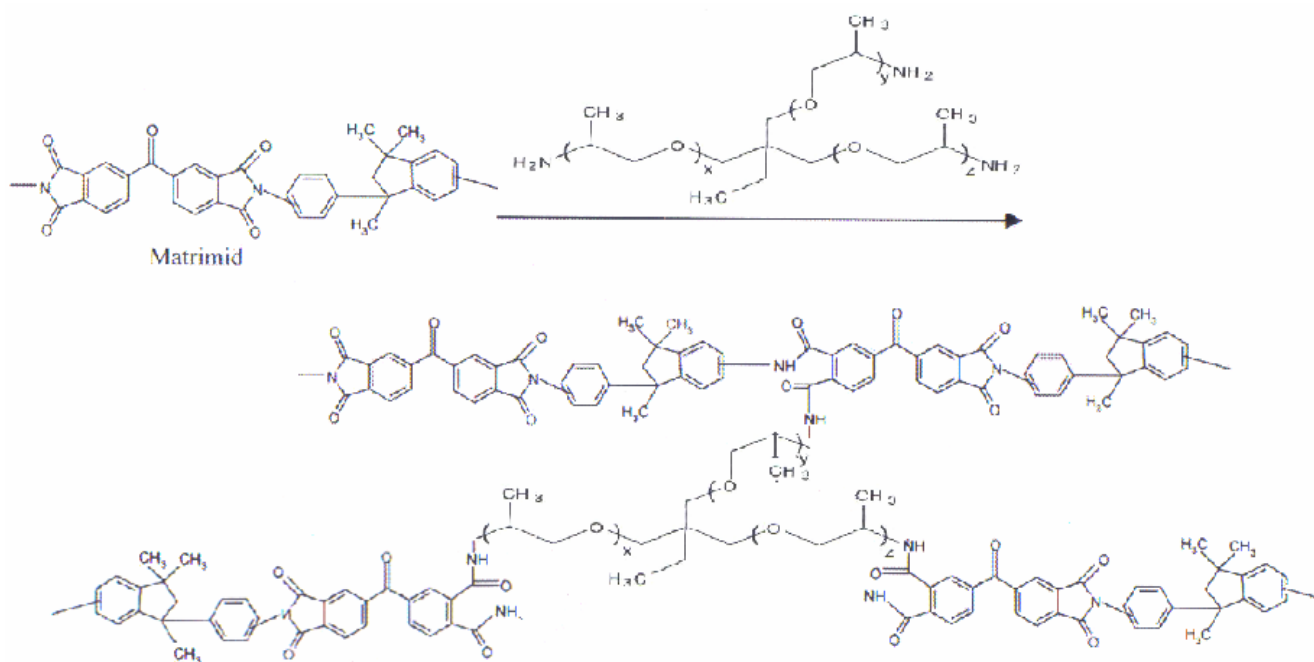


Fig. 4. Mechanism of chemical cross-linking of Matrimid with Jeffamine

This can be explained by the volatility of chloroform. The drying of the solution cast films is faster if chloroform is used instead of dichloromethane. It is possible that due to this fast drying process a large free volume arises in the dry film. It was also found that the permeability increases with increasing free volume.

Table 2. Permeance and selectivity of membranes prepared from Jeffamine (buthylenediamine)/Matrimid/ dichloromethane (manually prepared)

Sample	H ₂ Permeance, m ³ /m ² h*bar	A (H ₂ /CH ₄)
with Jeffamine	0.0029	76.46
with Jeffamine	0.0593	74.25
with buthlyenediamine	0.0590	45.59
with buthlyenediamine	0.0454	57.20

It is well known that the flux is dependent on selective skin thickness. Therefore, to decrease the thickness it can be use a non-solvent for dry phase separation and asymmetric structure formation. As non-solvents, cyclohexane, buthanol, and toluene were tested.

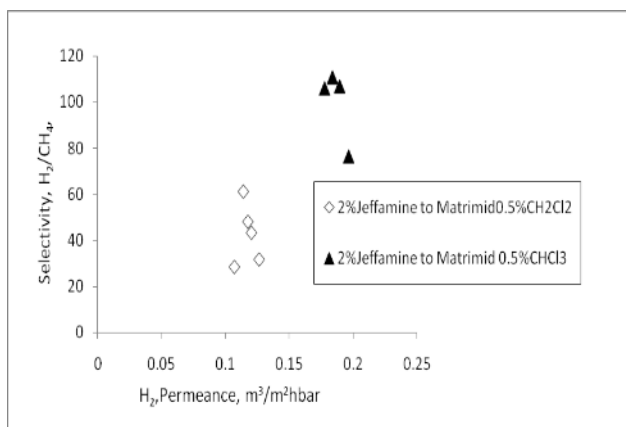


Fig. 5. Gas transport properties for membranes prepared with CH₂Cl₂ and for membranes prepared with CHCl₃

Knowing the position of the cloud point line in the phase diagram of Matrimid/CHCl₃/non-solvent, several casting solution were prepared with the Matrimid 5218 concentration 0.35 to 2% and concentration of non-solvent 0.2 to 10 % wt. For exemplification, Fig.6 presents the phase diagram of Matrimid/ CHCl₃/Bu-OH system. The obtained membranes exhibit reasonable permeances and selectivities (Table 3).

Different kinds of support were tested for membrane preparations. PAN and PDMS supports were tried out for the membranes manually prepared. For non-coated samples, the results are more or less comparable, but after the deposition of the PDMS layer it can be seen that for the membranes prepared on PAN support the selectivity increases about 4 times whereas for the membranes prepared on PDMS

support the selectivity doesn't increase significantly (Table 4).

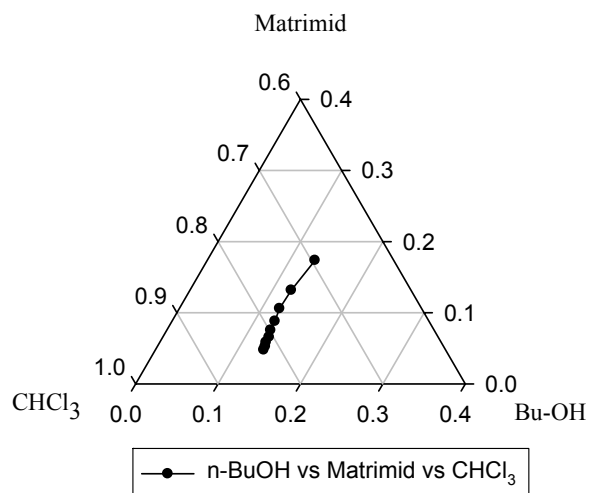


Fig. 6. Phase diagram of Matrimid/ CHCl₃/Bu-OH

Table 3. Gas transport properties of Matrimid membranes prepared with non-solvent

Membrane	H ₂ Permeance, m ³ /m ² h*bar	α (H ₂ /CH ₄)
2% Jeffamine to 0.5% Matrimid in CHCl ₃ +0.5% Cyclohexane	0.1918	83.84
2% Jeffamine to 0.5% Matrimid in CHCl ₃ +0.5% Toluene	0.2036	73.00
2% Jeffamine to 0.5% Matrimid in CHCl ₃ +0.5% Buthanol	0.2531	82.11

For the membranes prepared on lab scale machine, PAN and PAN+γBL supports were tested. From Table 5, it can be observed that the selectivity is higher when PAN+γBL support is used, but the flux is higher in the case of PAN support.

Table 4. Gas transport properties for membranes manually prepared using different types of support

Membrane	H ₂ Permeance, m ³ /m ² h*bar	α (H ₂ /CH ₄)
1% Jeffamine to 1% Matrimid in CH ₂ Cl ₂ (PAN support, non-coated with PDMS)	0.0758	22.37
1% Jeffamine to 1% Matrimid in CH ₂ Cl ₂ (PDMS support, non-coated with PDMS)	0.1268	22.24
1% Jeffamine to 1% Matrimid in CH ₂ Cl ₂ (PAN support, coated with PDMS)	0.0593	74.25
1% Jeffamine to 1% Matrimid in CH ₂ Cl ₂ (PDMS support, coated with PDMS)	0.1130	30.11

In order to see if the membranes are reproducible, the same samples were tested at different intervals: after two days, after one week and after two months. The obtained membranes using

PAN and γ BL dry support exhibit very interesting results in comparison to membranes prepared on PAN and γ BL wet support.

Table 5. Gas transport properties for membranes prepared in a pilot scale membrane casting machine using different types of support

Membrane	H ₂ Permeance, m ³ /m ² h*bar	α (H ₂ /CH ₄)
2% Jeffamine to 0.5% Matrimid in CHCl ₃ (PAN support, coated with PDMS)	0.1404	90.94
	0.1854	92.19
2% Jeffamine to 0.5% Matrimid in CHCl ₃ (PAN+ γ BL support, coated with PDMS)	0.0723	112.32
	0.0727	109.57

It can be seen from the Fig. 7 that the selectivity of membranes prepared on wet support is decreasing and the selectivity of membranes prepared on dry support is increasing unexpectedly (Fig. 8).

This could be explained because of the different structure of membranes prepared on wet support in comparison to the membranes prepared on dry support as can be seen from the SEM photomicrographs.

3.2 Morphology

Fig. 9 shows the SEM photomicrographs of cross-sections of Matrimid membranes prepared with different solutions and different supports. The morphology investigation of membranes by electron microscopy demonstrates a well developed open porosity. By using wet support for membrane preparation (Fig. 9c, 9d) it can be observed that a microcrystalline structure is formed.

By using dichloromethane as a solvent, a microcrystalline structure is formed in both cases: for wet and also for dry support (Fig. 9b, 9d). Utilizing a dry support leads to a structure with more closed pores as compared to wet support. These different structures obviously explain the higher selectivity noted when utilizing dry support.

2%Jeffamine to Matrimid 0,5%CHCl₃-wet-support

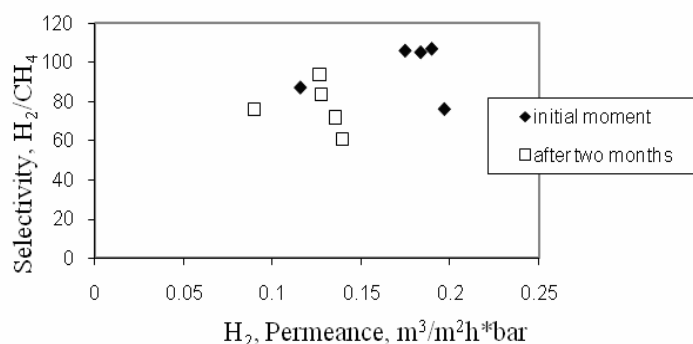


Fig 7. Gas transport properties for membranes prepared on wet support measured after two months

2%Jeffamine to Matrimid 0,5%CHCl₃-dry support

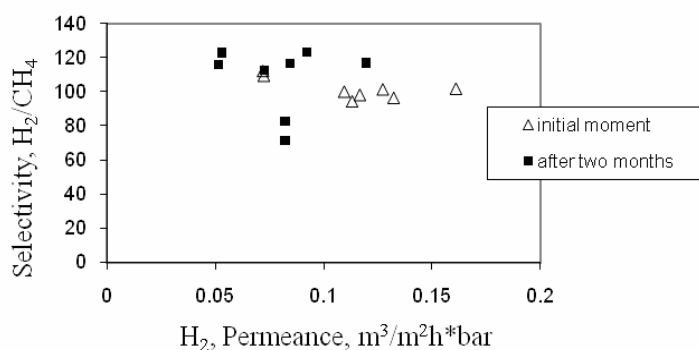


Fig. 8. Gas transport properties for membranes prepared on dry support measured after two months

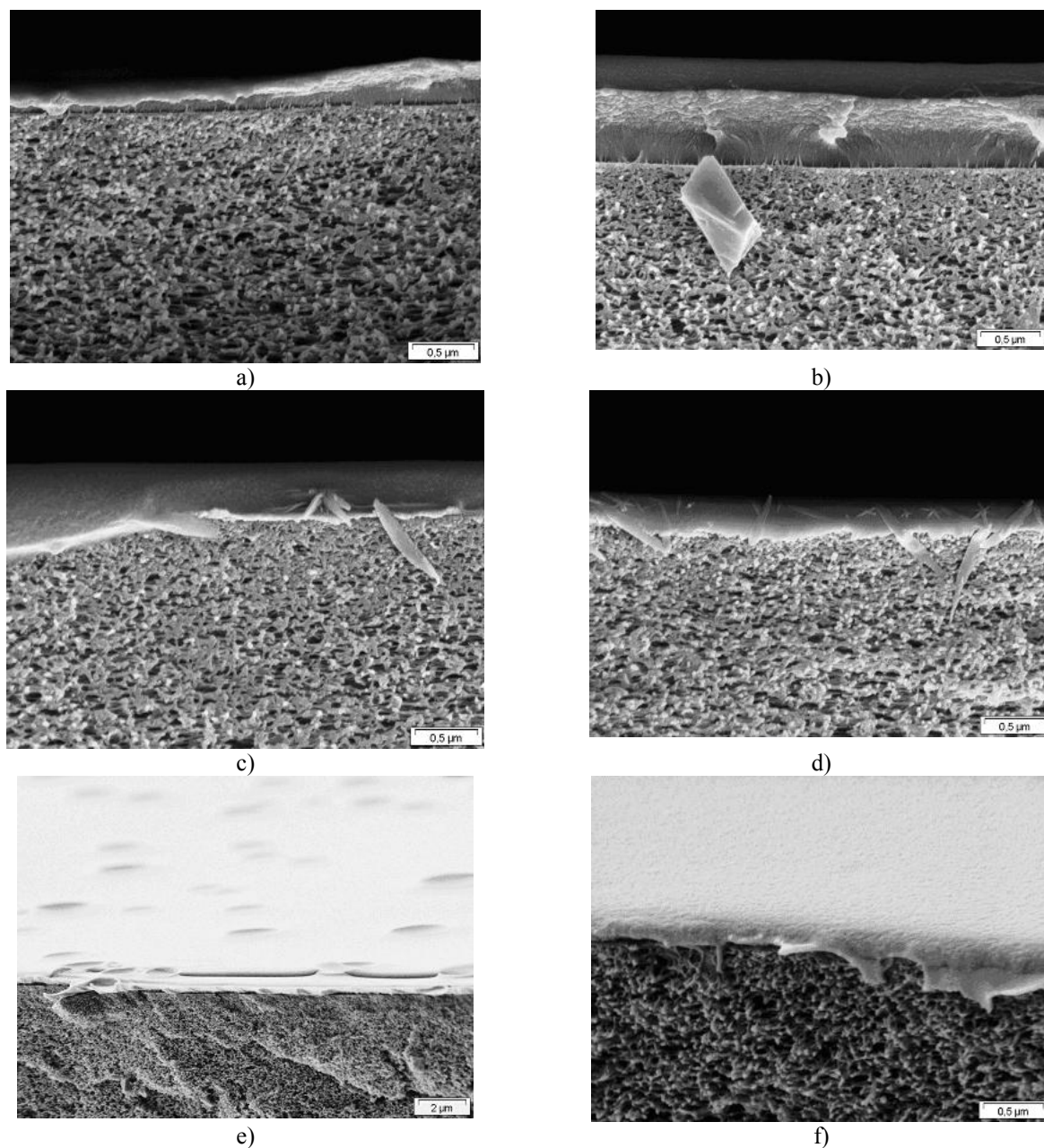


Fig. 9. SEM micrographs of cross-sections of: a) 2% Jeffamine to Matrimid 0.5% in CHCl_3 (PAN support, dry); b) 2% Jeffamine to Matrimid 0.5% in CH_2Cl_2 (PAN support, dry); c) 2% Jeffamine to Matrimid 0.5% in CHCl_3 (PAN support, wet); d) Jeffamine to Matrimid 0.5% in CH_2Cl_2 (PAN support, wet); e) 0.5% Matrimid in CHCl_3 (PAN support, dry); f) 2% Jeffamine to Matrimid 0.5% in CHCl_3 +0.35% cyclohexane (PAN support, wet)

4 Conclusions

H_2/CH_4 selectivity of membranes could be increased by cross-linking. The gas permeation properties of these composite membranes depend on the type and concentration of the cross-linking agent, on the type and concentration of solvent and non-solvent used and also on the type of support used. Cross-linking modification is an effective method to develop next generation gas separation membranes for rigorous environments. Cross-linked membranes may exhibit higher selectivity, because the material is

stabilized against plasticization and becomes more resistant to chemicals.

Acknowledgements

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INTEGRATED STUDIES ON THE BEHAVIOUR OF PERSISTENT POLLUTANTS AND RISKS ASSOCIATED WITH THEIR PRESENCE IN THE ENVIRONMENT

PERSENVIR - Research Grant no. 132 / 2007 of Idei Programe PNCDI-II, Project ID _595

The research project is conceived within the PNCDI-Ideas Program, being an exploratory research project oriented through generation of knowledge for enhancing the contribution of Romanian scientific research to establishment of a solid base of applicative research and technological development by innovatory ideas and by formation of highly qualified researcher. At the same time, the international excellence and visibility are considered by approaching some advanced researches that are interdisciplinary and complex in a field where Romania has a research potential and where a series of results that are comparable to that from European Union were achieved.

Project objectives:

Main objective:

The project aims to contribute to a deep understanding of the environmental behaviour and effects of persistent pollutants (PCs), through elaboration and performing of experiments in the view of development of quantitative relationships and models on their fate, transport and behaviour and on the remediation alternatives of environmental components affected by pollution. The research as well as information on the ways to evaluate the risks associated with the impacts induced in the environment by PCs presence in various environmental matrices will combine both analytical methods and multivariate modeling. Based on experimental and calculated data, methods for various pollutants characterization and ranking will be developed, which facilitate the risk assessment process as well as the decisional process for risk management and remediation of the environmental components affected by the contamination with persistent pollutants.

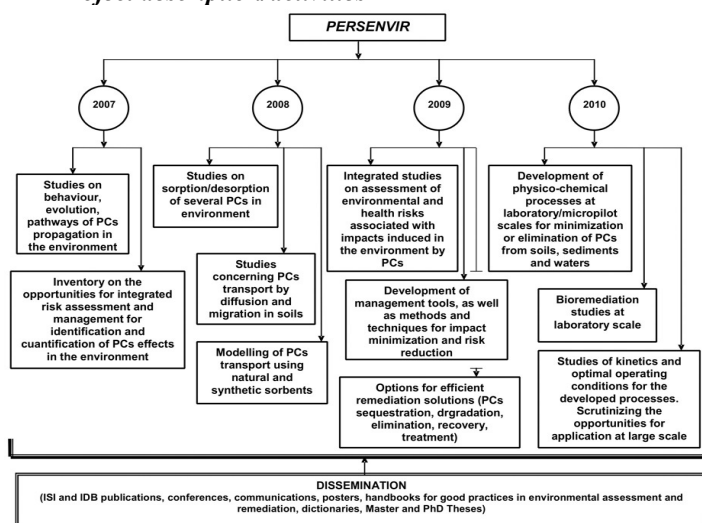
Specific objectives:

- examine physical, chemical, and biological processes resulting in the migration of persistent pollutants through the individual environmental compartments
- describe chemical, physical, and biological parameters affecting the mobility of PCs in the environment,
- describe and possibly explain observed spatial patterns and temporal trends in the fluxes, concentrations, and relative compositions of various persistent contaminants
- evaluate the relative importance of degradation, sediment burial, export in the atmosphere and outflow to various environmental matrices, bioavailability of PCs in soils and waters and implications for risk assessment
- assess environmental impacts and risks that gather, integrate, and evaluate site-specific information regarding:
 1. environmental fate and transport of contaminants
 2. modes of action of each contaminant under evaluation (effects information)
 3. contaminant uptake by biota from the environment and subsequent movement through food webs
 4. responses of the ecological resources under evaluation to the contaminant exposure

Under this context, the project proposes a coherent, conceptual framework for integrated environmental risk assessment and management, generated by the presence of persistent pollutants (persistent contaminants, PCs) able to compare, evaluate and develop a set of methods and indicators to represent the links between source and exposure, for use in the assessment procedure, based on scientific concepts and methods. They are devoted to improve the use made of the data and knowledge that is already in force in order to obtain more integrated assessments of risks and impacts. These advances will be brought together, in order to identify and fill key gaps in the existing knowledge and methodologies, and develop the tools needed to make them operational. In this context, three key gaps are addressed:

- data and knowledge are spread across disciplines, through different networks and in different databases – tools, methods and collaborative research are needed to bring together and link these different areas of data and knowledge more effectively to inform integrated assessments;
- in many areas, a large gap between science and policy remains – methods are needed to bridge this gap by translating the science that exists into information that is of direct relevance to policy;
- in specific contexts, there are key gaps in data or knowledge that break the continuity of current understanding.

Project description/activities



For more information on the PERSENVIR Project, please visit: <http://persenvir.xhost.ro>

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DETERMINATION OF ORGANIC COMPOUNDS FROM DIFFERENT TYPES OF COFFEE BY HPLC AND GC-ECD ANALYSIS

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Abstract

A study was conducted to investigate the organic compounds residues in different types of coffee from market in Romania. High pressure liquid chromatography with fluorescence detector (HPLC), respectively gas chromatography with electron capture detection (GC-ECD) was used for the determination of 7 polycyclic aromatic hydrocarbons (PAHs) and 9 organochlorine pesticides (OCPs) in coffee samples. It was found that concentrations of PAHs in coffee samples varied from 0.001 µg/Kg to 90.732 µg/Kg. B[a]P was absent in the green coffee samples. The detection limits ranged from 0.02 ng/kg to 0.04 ng/kg and quantification limits were 0.2 ng/kg. Calibration and recovery studies gave satisfactory results. Concentrations of OCPs in coffee samples varied from 0.001 mg/Kg to 0.007 mg/Kg. The methods provide a rapid and accurate determination of these organic compounds in coffee samples.

Key words: coffee samples, HPLC, GC-ECD, PAH, OCP

1. Introduction

It was about a decade ago that scientists started to pay great attention to the significance of vegetation in environmental pollution processes (Paterson et al., 1990). Polycyclic aromatic hydrocarbons (PAHs) are well-known environmental pollutants, even at low concentrations. PAHs are included in the European Community (EC) and in the Environmental Protection Agency (EPA) priority pollutant list due to their mutagenic and carcinogenic properties (Cooke and Dennis, 1986). On the other hand organochlorine pesticides (OCPs) are ubiquitous and persistent pollutants. They have been worldwide contaminants in 1969, but nowadays their use has been prohibited in most countries. Among the OCPs that have become globally enriched in food chains are included the insecticides DDT, lindane (γ -HCH), aldrin, dieldrin and the fungicide hexachlorobenzene (HCB). The

latter is also a product of rapid, high temperature combustion.

Vegetables are essential constituents of the human diet. Monitoring of PAHs and OCPs in vegetables is nowadays a priority objective in order to get an extensive evaluation of vegetable quality to avoid possible risks to human health.

Numerous research papers have been published on PAHs and OCPs in environmental samples, such soil (Kulhanek et al., 2005), plants (Ho and Hsieh, 2001; Soceanu et al., 2006), water (Dobrinas et al., 2008; Reddy and Quinn, 2001; Dobrinas et al., 2002; Reddy and Quinn, 2001), marine sediments (Gong et al., 2007; Zaghden et al., 2007), organisms (Carls et al., 2006) and zooplankton (Covaci et al., 2002). Although few foods have been analyzed to date, PAHs have been detected in vegetable oils, fruits, sea food, tea, coffee, potato, toasted bread (Nieva-Cano et al., 2001; Stall and Einsenbrand, 1988; Vinas et al., 2007; Vo-Dinh,

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1989) and OCPs have been detected in fish and fish oil, vegetable oil, vegetables, fruits, baby food and meat (Colume et al., 2001; Chuang et al., 2001; Di Bella et al., 2006; Garrido-Frenich et al., 2006; Zawiyah et al., 2007). Food pollution is due to the deposition of PAHs from air or water, or as a result of preservation, drying and cooking procedures (Vo-Dinh, 1989).

OCPs are nonsystemic, as they cannot penetrate into the plant. They form a deposition on the surface of the leaf or other plant organ; their potential absorption depends on the formulation, lipophilicity and concentration of the active ingredients and therefore the extraction of these pesticides is rather simple compared to the systemic organophosphate and carbamate pesticides. Most of the methods applied to the determination of PAHs and OCPs in vegetables are based on solvent extraction (the extract is cleaned up in a silica, alumina or florisil column) followed by gas chromatography with various detectors.

The studies for the contamination of food are enclosed on the JECFA (Joint FAO/WHO Expert Committee on Food Additives) list and the European Commission limited the Benzopyrene content in food (Report 1996; EC 2005).

Since only a few research studies on the PAHs and OCPs content in food samples, and in vegetables in particular, have been undertaken, in this paper we report a simple method for the determination of 7 PAHs and 9 OCPs in different types of coffee, by HPLC and GC-ECD.

2. Experimental

2.1. Chemicals and reagents

There were used the following PAHs and OCPs analytical standards: benzo[a]anthracene ((B[a]An), benzo[a]anthracene; benzo[k]fluoranthene (B[k]Fl), benzo[b]fluoranthene (B[b]Fl), (B[a]Py), benzo[a]pyrene; (B[ghi]P), benzo[ghi]perylene; (dB[α,h]An), dibenzo[α,h]anthracene; (I[1,2,3-cd]Py), indeno[1,2,3-cd]pyrene) from Supelco (Belefonte PA, SUA) and HCB, Lindane, heptachlor, p,p'- DDT, p,p'- DDE, p,p'- DDD, Aldrin, Dieldrin, Endrin from International Atomic Energy Agency, Monaco laboratory.

As sorbent materials: silica gel, florisil and aluminium oxide were assayed for preconcentration step. Silica gel 60 (0.2 – 0.5 mm) and aluminium oxide 90 (0.063 – 0.200 mm) were obtained from Merck, Darmstadt, Germany. Florisil (60 – 100 mesh) was obtained from Fluka (packed in Switzerland) and was activated overnight (12h) at 130°C before use. Silica gel and aluminium oxide were activated at 420°C for 4h before use. Anhydrous sodium sulphate (granulated for residue analysis – Merck) was activated at 200°C for 2h before use.

There were used the following solvents: n-hexane and acetonitrile, supplied by Merck,

Darmstadt, Germany, petroleum ether and ethylic ether supplied by J.T. Baker.

From the PAH mix solution (PAH Calibration Mix – Supelco), a new PAH solution at levels from 10 µg/ml to 100 µg/ml was prepared into acetonitrile and this solution was diluted to construct calibration lines for the PAHs.

2.2. Sampling

Samples of green coffee bean, roasted coffee bean, instant coffee granules and coffee without caffeine (all being registered to the same producer), all available at supermarkets were analyzed. No indication as regards the country of origin was given on the label.

2.3. Sample extraction and clean-up

Approximately, 10 g of each coffee type was used for Soxhlet extraction over a period of 4 h with hexane as solvent. Coffee samples were extracted in triplicate. The solvent was removed under reduced pressure at 40° C. The lipid extracts were mixed with petroleum ether and the mixture was transferred to a separatory funnel where was shaken with acetonitrile and then was separated the layers.

The extracts were then evaporated under vacuum using a rotary evaporator and then the concentrated extract was purified by column chromatography. A home-made glass column containing a piece of glass wool on a glass frit was filled with 5 g of activated aluminium oxide, 5 g of activated silica-gel and about 1 g of anhydrous sodium sulfate on the top to fractionate the aliphatic and aromatic fractions. For OCPs fractions was used a home-made glass column containing a piece of glass wool on a glass frit filled with 5 g of Florisil and about 1 g of anhydrous sodium sulfate on the top. The PAHs and OCPs residues were eluted with petroleum ether: ethylic ether (94:6) mixture and the eluate was collected in a conical evaporating flask. The sorbent was not allowed to dry during the conditioning and sample loading steps. The eluate was finally concentrated in a Kuderna–Danish concentrator to approximately 1 mL and the concentrated aliquots were blown down under a gentle stream of nitrogen gas.

2.4. Instruments

2.4.1. HPLC

All HPLC measurements were assayed using a Varian device equipped with ProStar 240 Quaternary pump, a ProStar autosempler and ProStar 363 fluorescence detector. The optimized instrumental parameters were as follows: injection loop: 20µL; a ChromSep HPLC Column SS 100x4.6 mm; elution conditions: 32 min linear gradient elution from 70:30 acetonitrile/water to 93:03 acetonitrile/water, followed by 3 min linear gradient to 100% acetonitrile and held for 5 min; elution temperature:

30 °C; fluorescence detection: 16 min λ_{ex} at 274nm and λ_{em} at 414 nm, followed by 7 min λ_{ex} at 296 nm and λ_{em} at 406nm followed by 9 min at λ_{ex} at 300nm and λ_{em} at 470 nm.

2.4.2. GC-ECD

A Varian gas chromatograph equipped with an electron capture detector (ECD) and a fused-silica capillary column HP-5, 30m×0.32mm×0.25µm film thickness were used for OCPs analysis. Operating conditions were as follows: initial temperature 60°C (1 min), increased at a rate of 20°C/min to 300°C and finally held for 10 min; injector temperature: 250°C; carrier gas: He; column flow-rate: 1.36mL/min; detector temperature: 300°C; make-up gas: N₂; operation mode: splitless (electronic pressure control); purge off time: 2 min; injection volume: 1 µL.

3. Results and discussion

Limits of detection (LOD) and limits of quantitation (LOQ) for PAHs were evaluated on the basis of the noise obtained with the analysis of blank coffee samples. LOD and LOQ were defined as the concentration of the analyte that produced a signal-noise ratio of three and ten, respectively.

The noise values were determined by measuring the amplitude signal by fluorescence analysis of a blank reagent (n = 7). The performance of the proposed method for the determination of PAHs in coffee samples is summarized in Table 1.

Table 1. Data on performance of the method

PAH _s	Instrument linearity Range[µg/l]	r ²	LOD ^a [ng/kg]	LOQ [ng/kg]
B[a]A	0.2-10	0.9993	0.04	0.2
B[b]F	0.2-10	0.9946	0.04	0.2
B[k]F	0.2-10	0.9968	0.02	0.2
B[a]P	0.2-10	0.9966	0.02	0.2
D[a,h]A	0.2-10	0.9977	0.04	0.2
B[ghi]P	0.2-10	0.9976	0.04	0.2
I[1,2,3-cd]P	0.2-10	0.9989	0.04	0.2

a- 7 determinations

A green coffee sample was enriched with PAH solutions. The theoretical concentration that enriched the sample was of 2 µg/kg. The recovery percent for the PAHs varied between 83-105 %.

Table 2 gives the results obtained from coffee samples and representative chromatogram of coffee samples are presented in Fig. 1.

In Table 2: (B[a]An), benzo[a]anthracene; benzo[k]fluoranthene (B[k]Fl), benzo[b]fluoranthene (B[b]Fl), (B[a]Py), benzo[a]pyrene; (B[ghi]P), benzo[ghi]perylene; (dB[α,h]An), dibenzo[α,h]anthracene; (I[1,2,3-cd]Py), indeno[1,2,3-cd]pyrene.

Table 2. PAHs concentrations from coffee samples

	Concentrations (µg/kg)			
	Green coffee bean	Roasted coffee bean	Instant coffee granules	Coffee without caffeine
B[a]An	0.017	0.742	0.473	0.014
B[k]Fl	0.002	0.085	0.495	0.010
B[b]Fl	0.001	0.219	0.104	0.028
B[a]Py	ND	0.293	0.857	0.119
B[ghi]P	LOQ	LOQ	LOQ	LOQ
dB[α,h]An	ND	0.040	0.045	0.011
I[1,2,3-cd]Py	0.003	0.113	0.142	0.014

ND- not detected; LOQ- below quantification limit

Benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and indeno[1,2,3-cd]pyrene were found in the most of the samples. Their contents are at µg/Kg level. Benzo[ghi]perylene were found under the quantification limit in all samples.

The least contaminated sample was the green coffee bean, with a mean content of 0.023 µg/Kg and the most contaminated sample was instant coffee granules, with a mean content of 2.116 µg/Kg.

Benzo[a]pyrene and dibenzo[α,h]anthracene were not detected in the green coffee beans. So, the possibility of contamination by environmental pollution, storage etc. is eliminated. But this PAH was found in the coffee without caffeine, in roasted and soluble coffee. Its presence can be explained by the processing of the coffee (important to produce marketable coffee), due probably to the roasting of the coffee. Roasting process is fundamental to obtain a coffee of a good quality, but is harmless to human health. This hypothesis is supported by the fact that B[a]P contamination of coffee is due to the kind of roasting process utilized (Badolato et al., 2006). The values obtained for B[a]Py concentrations were from 0.119 to 0.857 µg/Kg for roasted coffee samples. These values are comparable with those obtained by Badolato and others in ground roasted coffee (0.47-12.5 µg/kg) (Badolato et al., 2006). Also, B[a]Py levels measured in the studied types of coffee samples are lower than those measured in roasted coffee, coffee brews, or dried coffee brew by other authors (Garcia-Falcon et al. 2005; Kayali-Sayadi et al.,1999). Bishnoi and others measured the total PAH content (16.47-18.24 µg/L) in coffee samples and it can be observed that the total PAH content in our studied coffee samples is lower than that (Bishnoi et al., 2005).

The proposed method was used to determine nine OCPs in coffee sample and the representative chromatogram obtained are shown in Fig. 2, respectively the typical chromatograms of standards are shown in Fig. 3.

The levels of organochlorine pesticides detected in coffee samples are summarized in Table 3. The table shows that the OCP residue detected in all samples was lindane and the highest concentration was detected for pesticide aldrin 0.007 mg/Kg (this pesticide was detected in only one sample of coffee).

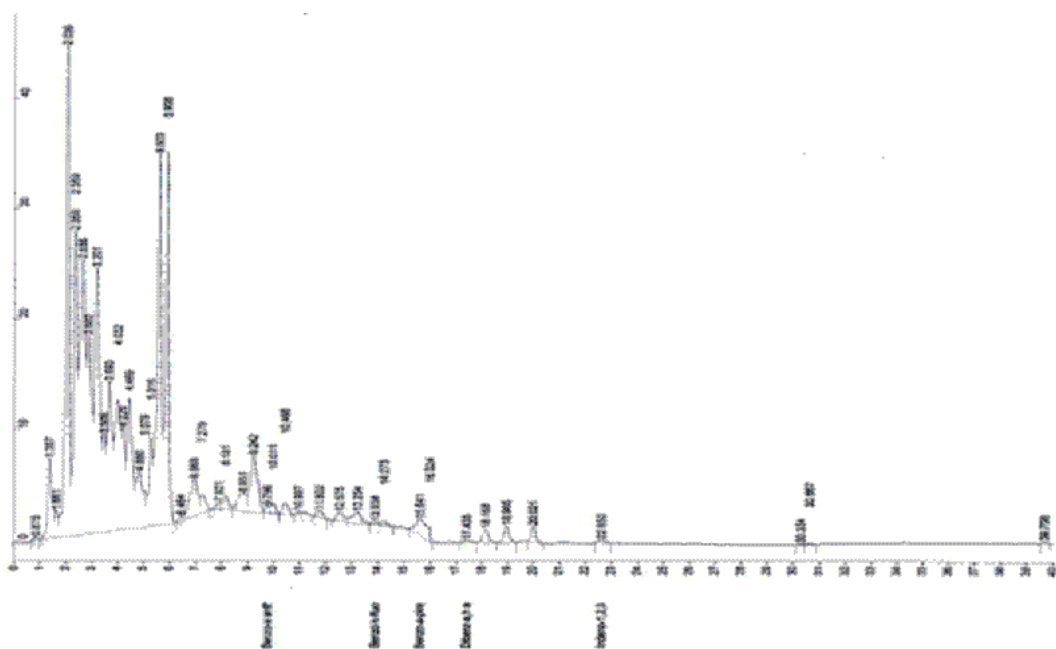


Fig.1. Representative HPLC chromatogram for coffee without caffeine samples

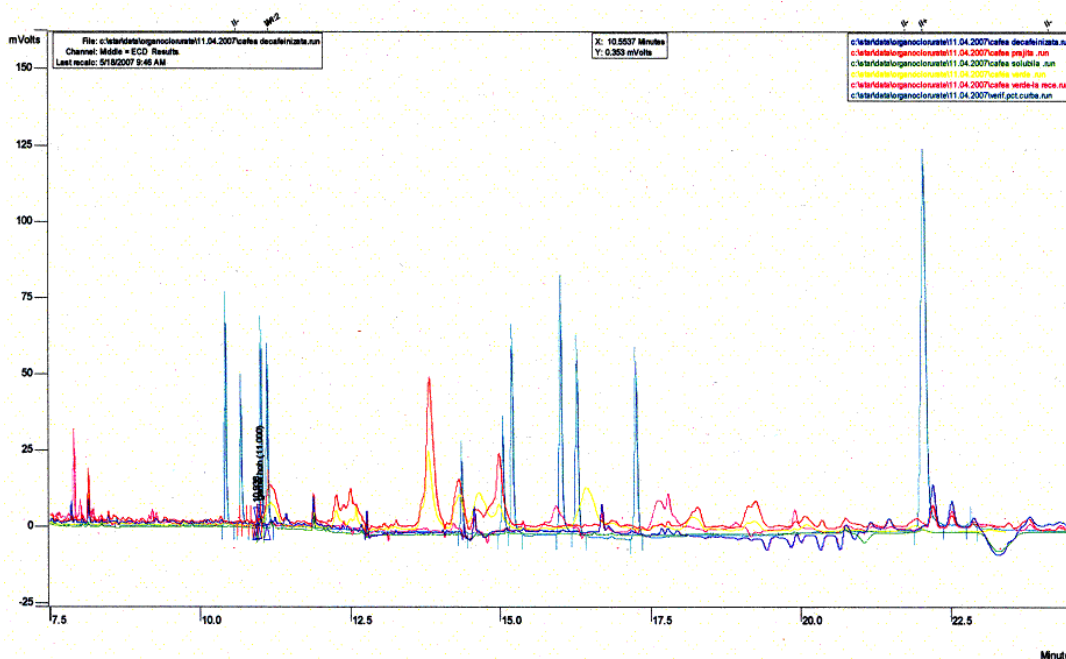


Fig.2. Representative GC-ECD chromatogram for coffee samples

Heptachlor was detected in 2 samples and HCB in one sample. DDT and its metabolites (which degrade very slowly under environmental conditions) were not detected in all studied samples.

Green bean coffee is a material rich in nutrients that promotes the growth of microorganisms (Avallone et al., 2001). Bacteria isolated from defective green bean coffee with traditional

enrichment techniques were able to grow on and to degrade DDT in liquid media (Barragan-Huerta et al., 2007). So, its possible that in coffee beans DDT and its metabolites to be degraded by bacteria. Also, DDT and its metabolites were not detected because of the restricted use in agricultural activity.

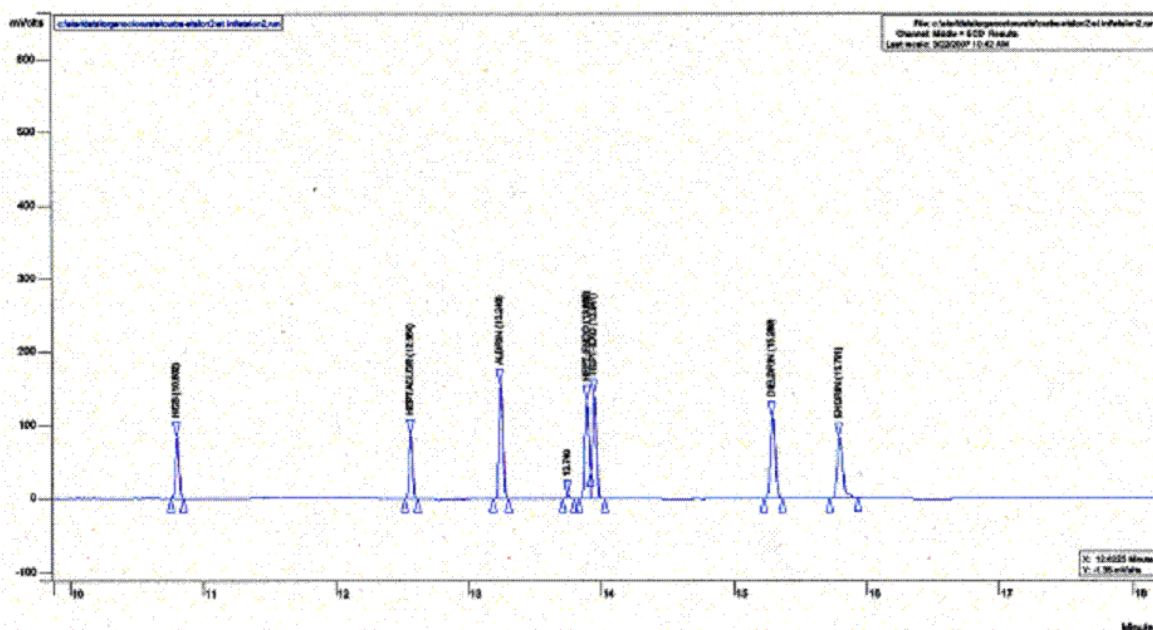


Fig.3. The chromatograms of organochlorine pesticides standards

Table 3. The levels of organochlorine pesticides in coffee samples

Pesticides	Concentration (mg/Kg product)			
	Green coffee bean	Roasted coffee bean	Instant coffee granules	Coffee without caffeine
HCB	ND	0.002	ND	ND
lindane	0.0014	0.001	0.004	0.001
heptachlor	0.011	ND	ND	0.004
DDT	ND	ND	ND	ND
DDD	ND	ND	ND	ND
DDE	ND	ND	ND	ND
aldrin	ND	0.007	ND	ND
dieldrin	ND	ND	ND	ND
endrin	ND	ND	ND	ND

The low residual levels of pesticides in coffee at concentrations between 0.001 and 0.007 mg/Kg indicate a situation without toxicological risks for the consumer of coffee. However, the problem of human impact connected to use of these compounds cannot be ignored.

4. Conclusions

HPLC and GC-ECD are ideal techniques for analytical quality control and research in the food and beverage industry. Detection and quantification limits for the PAHs in the coffee samples (green coffee bean, roasted coffee bean, instant coffee granules and coffee without caffeine, all being registered to the same producer) were found to be satisfactory and much lower than the restrictions given in proposals of EU Directive.

Benzo[a]pyrene is the most studied and measured PAH and serves as an indicator of the total PAHs content.

In the green coffee beans, no Benzo[a]pyrene was found. But Benzo[a]pyrene was found in the roasted, the soluble and coffee without caffeine. Its presence can be explained by the processing of the coffee, due probably to the roasting of the coffee. Some processes as drying of seeds, roasting and processing are potential ways to contaminate food with Benzopyrene. In order to minimize health risk as well as for enforcement activities, monitoring of polycyclic aromatic hydrocarbons and organochlorine pesticide residues is increasingly important and essential.

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AN INTEGRATED ASSESSMENT OF THE SUITABILITY OF DOMESTIC SOLAR STILL AS A VIABLE SAFE WATER TECHNOLOGY FOR INDIA

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Abstract

Improving access to safe drinking water can result in multi-dimensional impacts on people's livelihood. This has been aptly reflected in the Millennium Development Goals (MDG) as one of the major objectives. Despite the availability of diverse and complex set of technologies for water purification, pragmatic and cost-effective use of the same is impeding the use of available sources of water. Hence, in country like India simple low-energy technologies such as solar still are likely to succeed. Solar stills would suffice the basic minimum drinking water requirements of man. Solar stills use sunlight, to kill or inactivate many, if not all, of the pathogens found in water. This paper provides an integrated assessment of the suitability of domestic solar still as a viable safe water technology for India. Also an attempt has been made to critically assess the operational feasibility and costs incurred for using this technology in rural India.

Keywords: Solar stills, integrated assessment, technologies, impacts

1. Introduction

Water is fundamental for life, health and productive livelihood. According to the World Resources Institute report 1992-1993, many developing countries, where 80% of the population lives in the rural areas, their fresh water supplies can be far lower (< 55 L) per capita than in urban centers (Government of Karnataka, 2001; World Resources Institute, 1993). In India, 40 liters per capita is considered as an adequate supply per capita per day was the target to be achieved in rural areas as compared to 150-200 liters per capita is considered for urban domestic purposes (Park, 2007). Improving access to safe drinking water can result in multi-dimensional impacts on people's livelihood. Such as improvements in health and hygiene, rural and urban livelihoods, children's attendance at school, psychological well being and social interaction. An estimated 1.3 billion people globally lack access to clean potable water. Depending upon the season, children in the villages often had to stay dirty (Lamphe, 2007). A minimum of 3-4 L per person per day drinking water is required by an individual depending upon the geographical variations

(Ponnuraj, 2006). Possibly water should be accessible within 500 meters (Mann and Williamson, 1979).

Currently, one in 15 people live in areas with inadequate fresh water supplies. Using United Nations' minimum population projections and data on renewable fresh water supplies, it is estimated that one in three people world-wide will be living under these conditions by the year 2025 (Ayoub and Alward, 1996). India ranks 133rd among 180 in water availability and 120th among 122 in water quality (The Hindu, 2003).

With increase in population and pollution there came centralized treatment units to treat the source water to each household, which lead to the municipal facilities in towns and cities. Assuming it would suffice the physiological needs of man by providing treated water pertaining to the local region. Experience shows that current system cannot always afford the operating and maintenance costs. For example, the capacity of the sewage water treatment plants in Bangalore, Karnataka is 718 million liters per day, but the treatment plants at 12 locations are treating only 350 million liters per day of sewage generated in the core area daily. Centralized treatment

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may be a one of good option in cities but may not be suitable in villages because of sparsely populated area, where decentralized technologies are more likely to succeed.

There are various technologies which cater to the different needs for users. The available decentralized technologies such as Reverse Osmosis (RO), Electrodialysis (ED), Ion-Exchange (IE), Mechanical Filters (MF) etc. are made easily available in the market, but they are energy intensive, require operational and maintenance (O&M), needs a skilled labour etc. Most of these technologies would tend to fail due to the lack of institutional support to sustain O&M. Hence, in country like India, simple low-energy technologies are likely to succeed. One of such technologies to treat water is solar still. Solar stills would suffice the basic minimum drinking water of man. Solar stills use sunlight, which can be used to kill or inactivate many, if not all, of the pathogens found in water. This paper provides an integrated assessment of the suitability of domestic solar still as a viable safe water technology for India.

2. Current water status in India

With the declared objectives of providing at least the basic amenities, there has been a tremendous development in India in the agriculture and industrial sector, with concomitant pressure on the fresh water resources.

The waste generated by anthropogenic activities has not only polluted the environment as a whole, but had a particular detrimental effect on the quality of aquatio-envision too. Leachates from compost pits, animal refuse of garbage dumping grounds nutrient enriched return irrigation flows seepage from septic tanks, seepage from sewage etc. has adversely affected the ground water quality in several parts of India. Thirteen states in India (Fawell et al., 2006) have been identified as endemic to fluorosis due to abundance in natural occurring fluoride bearing minerals (Fig. 1, Table 1). In some villages of Rajasthan and Gujarat, the fluoride level has been recorded up to 11.0 mg/L. It has been estimated that the total population consuming drinking-water containing elevated levels of fluoride is over 66 million in India alone (Fawell et al., 2006).

Though iron content in drinking water may affect the human system as a simple dietary overload, the long run prolonged accumulation of iron in the body may result in homochromatosis, where tissues are damaged.

Iron content (Yellow color) in some districts of Rajasthan, Uttar Pradesh (U.P) and Bihar has found to have above the permissible level of 1.0 mg/L (IS 10500, 1991). In some districts of Assam (Barpota, Darrang, Kamrup, Sonipni) and Orissa (Balasore, Cuttack, Puri) ground water have high iron content ranging from 1 to 10 mg/L (Red color) as shown in the Fig 2.

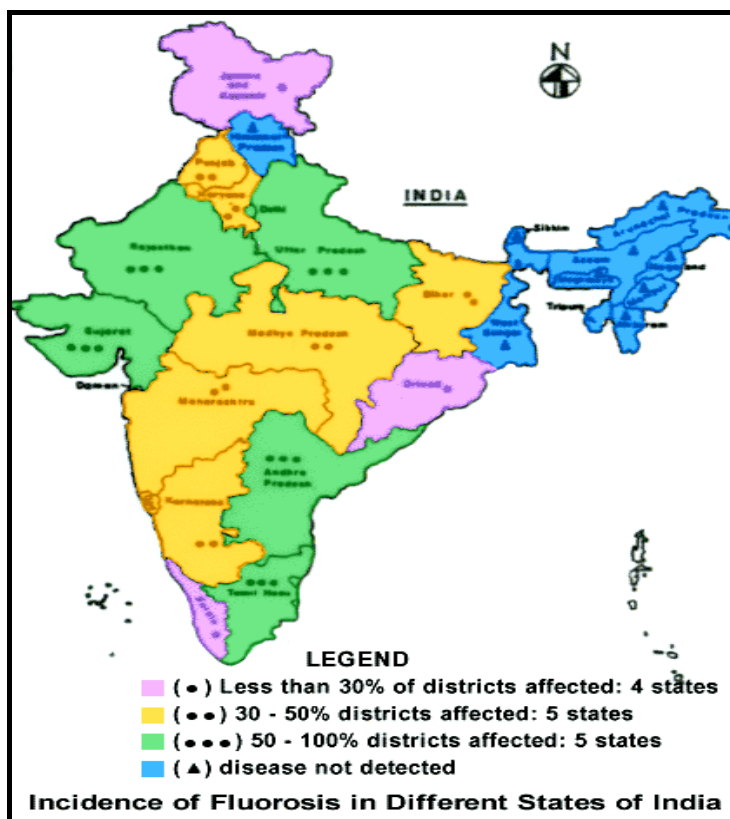


Fig 1. Map of India showing endemic states fluorosis (www.medvarsity.com)

Table 1. Fluoride concentrations reported in groundwaters of India (Fawell et al., 2006)

Regions/State	Fluoride concentration (mg/L)	Maximum severity of fluorosis observed
North-West India	0.4-19	Severe
Central India	0.2-10	Moderate
South India	0.2-20	Severe
Deccan Province	0.4-8	Moderate

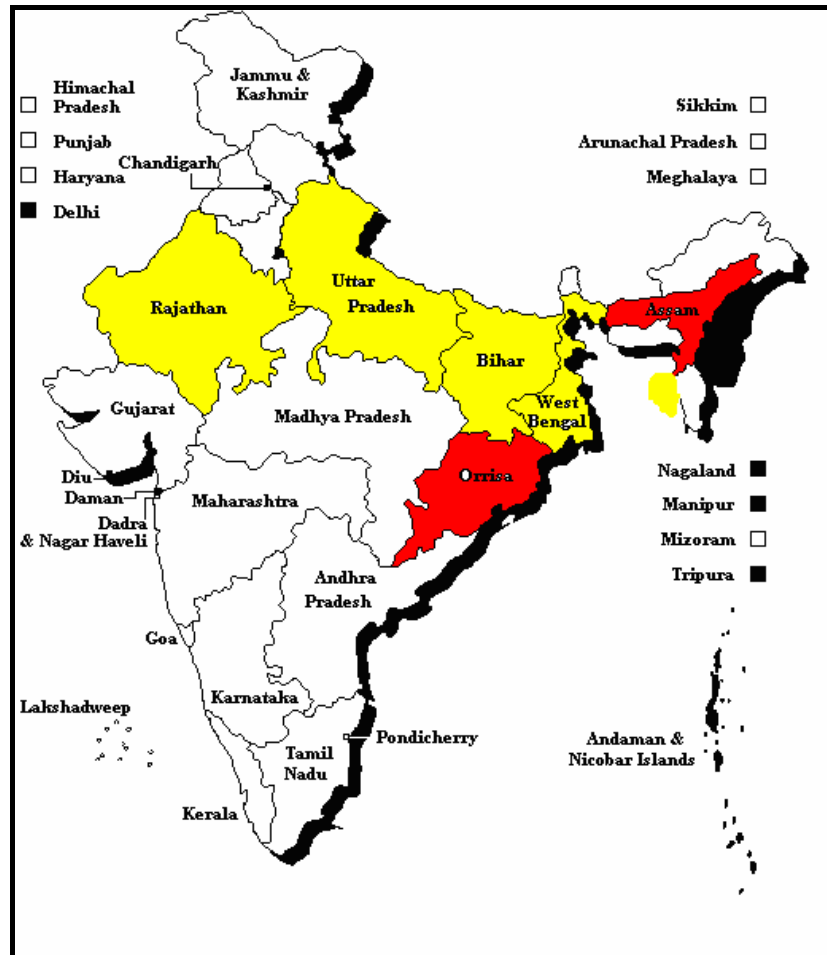


Fig. 2. Map of India showing endemic state of Iron content

Arsenic contamination of groundwater and sufferings of the people of West Bengal are well documented (Mandal et al., 1996). The present situation in West Bengal is that about 5 million people in 978 villages of 67 blocks from 9 districts including the southern part of Kolkota (Fig 3), are drinking contaminated water containing arsenic above the permissible limit of 0.05 mg/L and around 300 000 people are suspected to be suffering from arsenical skin lesions.

India has about 53 000 habitants with salinity greater than 1500 mg/L, most being remote and arid areas with saline water.

Statistics emphasis atleast 40% of the world's population lives without drinking water and roughly 80 000 habitations across the planet have no source of

safe water. Of the 575 000 Indian villages, about 162 000 face problems of brackish or contaminated water and scarcity of fresh water. Fig 4 shows the places suffering from salinity lie in high radiation zones from 5.4 to 6.4 kWh/m² (annual average).

Even the annual average temperature of the country is sufficient to operate the solar stills (Fig. 5). This makes the use of solar desalination systems in these areas even more practical and sustainable.

There are about 575,000 villages in the country, about 227,000 have been classified as problem villages because either there is no water source available at less than 1.6 km distance, at less than 15m depth and 100 m elevation difference or the water is chemically and or biologically contaminated. The population of Indian villages ranges between 100 and 10,000.

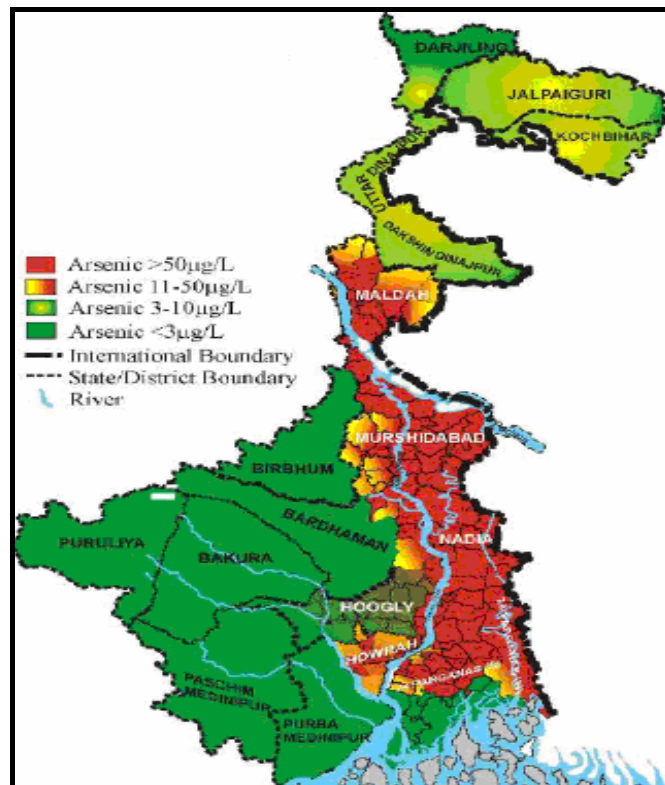


Fig. 3. Arsenic ground water Arsenic contamination status in West Bengal –India upto 2005

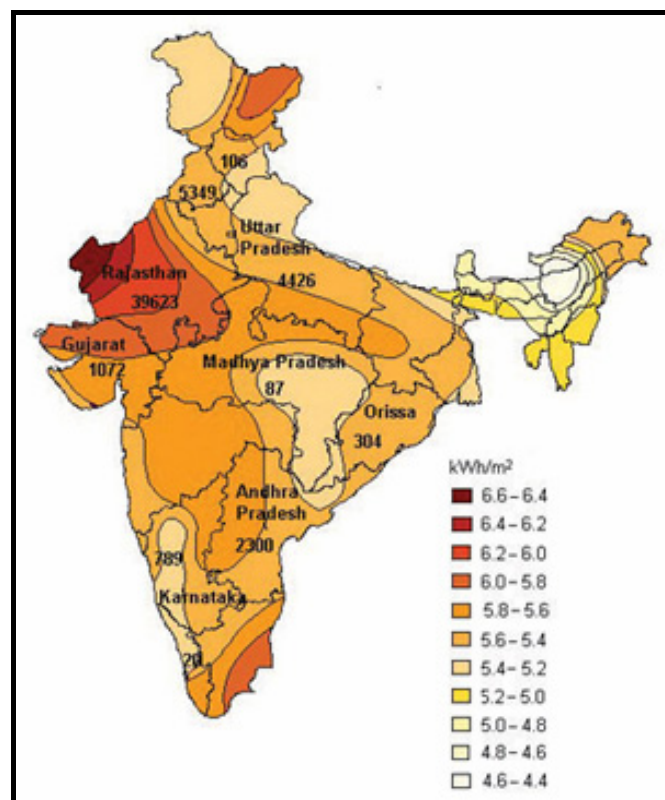


Fig. 4. Number of Habitants in India with salinity more than 1500 mg/L
Maps of India 2007, (<http://www.infobase.co.in>)

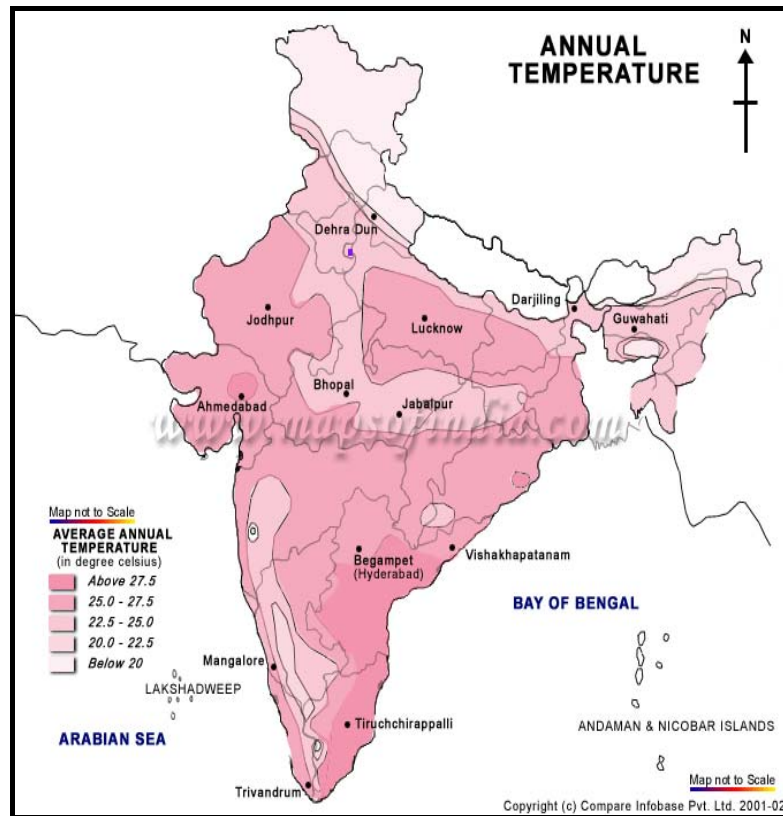


Fig. 5. Average Annual Temperature of India
 Maps of India 2007 (<http://www.infobase.co.in>)

In many areas, the water table falls during the summer, and at times the wells and tanks run dry. Agriculture being the majority activity in Indian villages, there is great water requirement during summer. About 325,000 km² of the country (9.73% of the total area) is arid, characterized by dry climate, isolation, low population, and lack of fresh water; there may be abundance of brackish water or sea water (coastal areas) (Gomkale, 1988).

Globally, industrial water use is approximately 200 km³/year or twice the actual domestic consumption. An additional 225 km³/year is used by power stations as cooling water, and 40 km³/year is taken up for livestock. Annual internal renewable water resources in India is about 1850 km³ (18%) and about 380 km³ annual withdrawals (Water Resources Institute, 1992-93).

The high water availability figure, however, includes some poor quality water caused by heavy industrial contamination and atmospheric acid rain pollution (Ayoub and Alward, 1996). The annual population growth rate of Indian population is around 1.44% (2004 estimate) (Sahu, 2007). The current population of India is 1,095 billion (July 2006 estimate) and 1,147 billion project population for 1 March 2008 (Census, 2001, Sawaal, 2008) and population density of India is about 324 person per sq km.

Fig 6 depicts the population of India (2001) at different scale. With increase in population and diminishing forests, inflation in standard of living has

led to inventions of new technology to cope with the present standard of living. As environmental issues continue to gain world-wide attention, the world is becoming increasingly aware of shortage of fresh water. It is projected that the Indian population may be around 1.6 billion by 2050. As a result, gross per capita water availability will decline from approximately 1820 m³/ year in 2001 to as low as 1600 m³/year and ~1140 m³/ year in 2017 and 2050 (Thacker, 2008).

Total water requirement of the country has been assessed to 1450 km³/ year. This is significantly more than the current estimate utilizable water resource potential (1122 km³/ year) through conventional development strategies. Therefore, when compared to with the availability of ~500 km³ year at present, the water availability around 2050 needs to be almost trebled (Gupta and Desphande, 2004).

This problem is exacerbated by population growth in many developing countries, such as India in this paper, with projections anticipating significant continued growth.

From the above all discussion it has become to have permanent technology which would provide clean water for various purposes.

Conversion of saline water to potable water has been the major response undertaken by water-poor countries to provide their populations with, at least, the essential daily basic requirements (Ayoub and Alward, 1996).

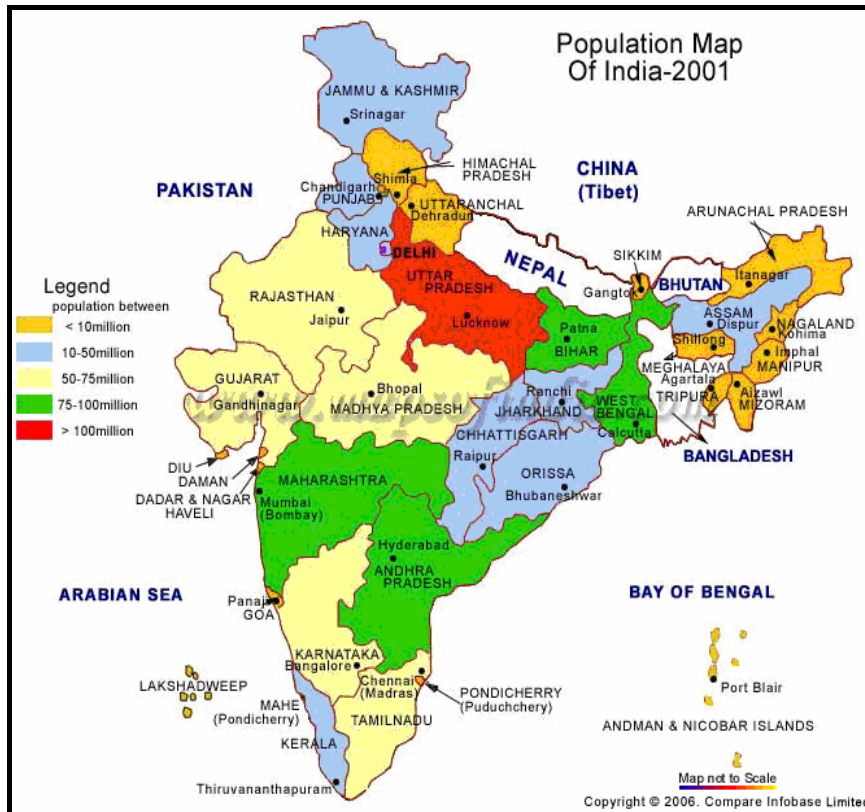


Fig. 6. Map of India showing the population of India -2001
 Maps of India 2007 (<http://www.infobase.co.in>)

3. An overview of current decentralized/household technologies

There are various technologies available to treat brackish or sea water to produce fresh water as an alternative to water supplies. These can be classified into three main categories: membrane technologies, chemical methods, and distillation.

There are about 575,500 villages in India out of which 227,000 have been classified as problem villages because of no water source and/or contaminated water. Some of the factors needing careful examination are: the socio-economic circumstances of the community; the possibilities of adopting new technologies for treatment of contaminated or brackish water, cost of transporting the water to the village even if centralized system is implemented to serve the population of Indian villages ranges between 100 and 10,000 (Gomkale 1988). India has about 96,000 villages still to be electrified.

About 20,000 villages are isolated and situated in arid, semi-arid or coastal areas of the country, which cannot be electrified by conventional grid extension (Sastry, 2003).

In spite of their poor education they show a good capacity to learn the routine operation of new methods but they lack interest in good maintenance over long periods (Gomkale, 1988).

The above said technologies (Table 2) require power supply for treating and supplying water at large scale, medium and small level. This would be one of the major disadvantages of the advanced technologies in rural areas. The following passages discuss about the intangible impacts or cons of the alternative technologies.

The *Reverse osmosis* would reject constituents as small as 0.0001 μ m. There are different modules used in membrane field such as tubular, hollow fiber and spiral wound. These modules need periodic cleaning due to plugging using chemicals and generally expensive. Selection of membrane modules is important because polyamide and TFC membranes are sensitive to chemicals. Membrane fouling is an important consideration in the design and operation of membrane systems as it affects pretreatment needs, cleaning requirements, operating conditions, cost, and performance.

Regular chemical cleaning of the membrane elements (about once a month) is necessary to restore the membrane flux. In *Electrodialysis* process water has to be retained for about 10 to 20 days in a single stack or stage. Membranes are needed to be continuously washed. Problems associated with the electro dialysis process for wastewater renovation include chemical precipitation of salts with low solubility on the membrane surface and clogging of the membrane by the residual colloidal organic matter in wastewater.

Table 2. Pros and Cons of various technologies (* Younos and Tulou, 2005; ** Metcalf and Eddy, 2003)

<i>Technologies</i>	<i>Pros</i>	<i>Cons</i>
Membrane Technologies* • Reverse osmosis	<ol style="list-style-type: none"> 1. Can remove dissolved constituents 2. Can disinfect treated water 3. Can remove organic compounds 4. Can remove natural organic matter and inorganic matter 5. Reduces labor requirements; can be automated easily 6. Smaller space requirements; membrane equipment requires 50 to 80 percent less space than conventional plants 	<ol style="list-style-type: none"> 1. Works best on ground water or low solids surface water or pretreated wastewater effluent 2. Lack of reliable low-cost method of monitoring performance 3. May require residuals handling and disposal of concentrate 4. Expensive compared to conventional treatment 5. Require replacement of membranes about every 3 to 5 years 6. Scale formation can be a serious problem. Scale-forming potential difficult to predict without field testing 7. Flux rate gradually declines over time. Recovery rate may be considerably less than 100 percent 8. Lack of a reliable low cost- method of monitoring performances 9. Rejects particles as small as 0.0001µm.
• Electrodialysis	<ol style="list-style-type: none"> 1. Adaptable to various operation parameters 2. Require little labor and the maintenance cost is low 	<ol style="list-style-type: none"> 1. Treatment cost is directly related to TDS concentration in feed water 2. Best suited upto 4000 mg/L TDS 3. Short design life 4. Membrane cleaning (backwashing or chemical treatment), high membrane replacement cost, low resistance to chlorine, and lack of resistance to fouling.
Chemical methods* ** • Ion Exchange	<ol style="list-style-type: none"> 1. Feasible for removal and recovery of metals 	<ol style="list-style-type: none"> 1. Extensive pre-treatment is required 2. Concerns about life of ion-exchange resins 3. Complex regeneration system required
Distillation * ** • Solar distillation	<ol style="list-style-type: none"> 1. Low energy cost 2. Low material, maintenance and equipment cost 3. Ultra-pure water 	<ol style="list-style-type: none"> 1. Requires large amount of land and direct sunlight 2. Low productivities 3. Scaling and corrosion (medium and large scale and material used) 4. Disposal of concentrated waste

Since villagers are not educated, they take longer time to adapt to new developments. Disposal of the concentrated waste streams produced by the membrane represents the major problem that must be dealt with in their applications.

The concentrate will contain hardness, heavy metals, high-molecular-weight-organics, microorganisms, and often hydrogen sulfide gas.

Around 3643 g/m³ concentration of the concentrated waste stream will remaining if 90 percent of recovery and rejection is considered to produce 4000 m³/d of water for industrial cooling operation. This figure would depicts how large volume of the waste stream that must be treated (Metcalf and Eddy, 2003).

Ion exchange process uses resins; the stability of resins will be an important for the long-term performance. In turn these resins selectivity is based

on operating and wastewater conditions such as pH, temperature, other ionic species, and chemical background. For example, higher concentration of influent total suspended solids (TSS) can plug the ion-exchange beds, causing high headlosses and inefficient operation. To date, ion-exchange has limited application because of the extensive pretreatment required, concerns about the life of the ion-exchange resins, and the complex regeneration system required (Metcalf and Eddy, 2003).

There are various house hold **mechanical filters** (spun cellulose) used in our day today life. There are various sizes used to connect the cold water lines (Tap) for treating small quantities of water. There are various problems associated with mechanical filters such as bacterial contaminations, rotten egg smell, bad taste, clogging of the filter etc., on prolong use. These do not remove nitrate, bacteria,

or heavy metals. It requires regular maintenance such as cleaning and replacement.

Iron filters remove iron and manganese that cause staining of clothes and plumbing fixtures. Iron removal from the water supply can involve complex choices. Careful planning is needed when iron removal equipment is used in conjunction with other water treatment equipment. The type of iron removal equipment chosen depends on the type and quantity of iron in the water, the characteristics of the water supply, other water treatment equipment in use, and the user's requirements for cost, ease of use, and maintenance.

Neutralizers, passing the water through granular calcite (marble, calcium carbonate, or lime) are the most common method of home treatment. Neutralizers using soda or sodium compounds increase the sodium content of water which may be a health concern. Using calcite to neutralize water increases calcium, which increases water hardness. These factors must be considered in the treatment choice. All systems require routine maintenance to replenish the chemical used to neutralize the water. There are various models of Aquaguard available which uses little or no power input, but has its own limitations. It can treat specific kind of contamination. Some models need back flushing, in other terms little maintenance. However, it is important to keep in mind that no single water treatment device treats all problems, and that all devices have limitations. As many of villages do not have access to electricity, cost of device would be high and maintenance which would set back people using these kinds of models.

Thus if these non-electrified places have to be provided with drinking water by small-capacity desalination plants powered by renewable energy sources, solar energy will have to be adopted in most cases. The most of the technologies are expensive and uneconomical for small quantity of freshwater (Gomkale, 1988).

With any increase in population, economic development and global warming create an imbalance worldwide between supply and demand of fresh water. The task of providing adequate supplies of fresh water may indeed become the most serious problem facing the world on the onset of this new century (Naim and Abd El Kawi, 2002). The Bangalore city (India) lets 700 million litres of untreated sewage into three valleys everyday, contaminating groundwater and wells around these valleys of Bangalore, Karnataka, India (Pooja, 2007). The current systems cannot cope with the load. Even as the 50-year-old sewage network struggles with the growing load, it is no surprise that the 14 sewage treatment plants that together have the capacity to treat 718 million litres of sewage a day receive just about half that capacity is the present scenario of Bangalore, India. Many areas in the Bangalore city have no collection system at all (Hindu Newspaper, 2007).

With the reality of climate change very imminent relatively small climatic changes can cause large water resource problems, particularly in arid and semi-arid regions such as northwest of India. This will have impact on agriculture, drinking water and on generation of hydro-electric power. The various studies conducted by scientist at IIT Delhi have shown that the surface air temperatures in India are going up at the rate of 0.4°C per hundred years, particularly during the post-monsoon and winter season. They also warn that India will experience a decline in summer rainfall by the 2050s. Apart from monsoon rains, India uses perennial rivers, which originates and depend on glacial melt-water in the Hindukush and Himalayan ranges. Since the melting season coincides with the summer monsoon season, any intensification of the monsoon is likely to contribute to rising of snowline, reducing the capacity of these natural reservoirs, and increasing the risk of flash floods during the wet season. Deltas will be threatened by flooding, erosion and salt intrusion. Water-borne diseases like malaria may penetrate elevation above 1800m and 10% more states may become breeding ground for malaria vector. India has already started witnessing this by the last epidemics of chikungunya and dengue (Thacker, 2008). In India, water-borne diseases alone are said to claim 73 million work days every year. The world faces challenges if we are to deal effectively with the biggest challenge faced by humankind. Hence there is immediate demand to reduce carbon dioxide emissions drastically by moving to renewable technologies as soon as possible. The various sectors such as industrial, domestic etc. use fuel (oil, coal etc) for the production of energy and this would lead to global warming.

4. Solar stills overview

Solar energy can be used to evaporate water from the brine solution for household or community water supplies by constructing sealed units covered with glass known as solar stills. Solar distillation exhibits considerable economic advantage over other present technologies for treatment and recovery of water because of its use of free energy and its insignificant operating costs. Distillation with solar energy is a most favourable process for small compact water desalting at geographical locations where there is considerable solar radiation. Another advantage is its simplicity (no moving parts) as it requires low operation and maintenance. Solar stills are highly reliable, as they would be located in isolated communities without immediate access to technical assistance. Solar stills can easily provide us with the necessary daily amount of drinking water for the water scarce and drought areas like Africa, Asian countries etc.

To date commercial development of simple, reliable, and inexpensive desalting units has been very limited due to high engineering and manufacturing costs (Ayoub and Alward, 1996). India

has good climatic conditions and abundant solar energy is available, it is worthwhile developing and implementing solar stills. Solar distillation will provide with potable/distilled water virtually from any type of dirty input water such as sea, bore, effluent, urine, radioactive, arsenic contaminated, brackish etc. (Ward, 2003).

The technology for converting sea and brackish water to potable water is well established. The first written description of desalination is traced to the Old Testament (Bible) (Vetus, M.Dc. XXVIII), in Exodus (22-25) (about 1500 BC). So Moses brought the sons of Israel from the Red Sea and they went to the desert of Sour. And they marched three days in the wilderness and they found no water to drink. And then they arrived to Merara and they could not drink from the water of Merara, because they were bitter, therefore he gave to the place the name Bitterness. And the people murmured against Moses. Saying: What shall we drink? and Moses cried unto the Lord. And the Lord showed him a wood and he put it into the water and the water became sweet. It is conceivable that the "wood" mentioned above had ion-exchange properties (Delyannis, 2003).

Aristotle (384-322) first described the production of drinking water by distillation of seawater undertaken by Greek sailors in the fourth century BC (Popkin, 1968; Ayoub and Alward, 1996). The water cycle is a huge solar energy open distillation plant in a perpetual operational cycle. For the seawater he writes salt water when it turns into vapor becomes sweet, and the vapor does not form salt water when it condenses again. This is known by experiment. Until medieval times no important ideas or applications of desalination by solar energy existed, but during this period, solar energy was used to fire alembics in order to concentrate dilute alcoholic solutions or herbal extracts for medical applications, and also to produce wine and various perfume oils.

The stills or alembics were discovered in Alexandria, Egypt, during the Hellenistic period (4 B.C.-1 B.C). Cleopatra the Wise, a Greek alchemist, developed many distillers. The head of the pot was called ambix, which in Greek means the "head of the still", but this word was applied very often to the whole still (Delyannis, 2003).

In the first century A.D., the Romans are reported to have filtered sea water through a clay soil to obtain drinking water (Ayoub and Alward, 1996). The Arabs who overtook science and especially alchemy about the 7th century, named the distillers Al-Ambiq, from which came the name alembic (Delyannis, 2003). Della Porta (1589) used wide earthen pots, as shown in the Fig. 7, exposed to the intense heat of solar rays to evaporate water and collect the condensate into vases placed underneath (Nebbia and Mennozi, 1966; Tiwari et al., 2003). In 1589 he issued the second edition comprising 20 volumes. In the volume on distillation Della Porta mentions seven methods of desalination, but the most important reference is in the 19th volume where he describes a solar distillation apparatus that converted brackish water into fresh water. He also

describes, in the second chapter of volume 20, a method to obtain fresh water from the air (nowadays called the humidification–dehumidification method) (Delyannis, 2003).

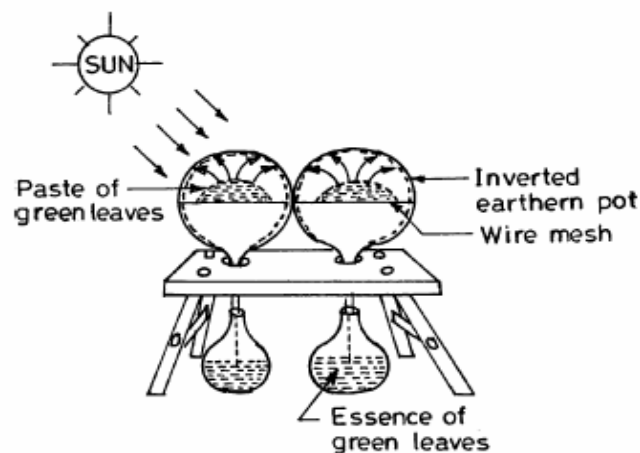


Fig. 7. The Della Porta solar distillation apparatus, as presented in his book "Magiae Naturalis" (Nebbia and Nebbia-Menozi, 1966)

This basic process continued in use on shipboard well into the late 16 century (Popkin, 1968; Ayoub and Alward, 1996; Tiwari et al., 2003). Mouchot the well-known French scientist who experimented with solar energy during 1860's, mentions in one of his numerous books that during medieval times Arab alchemists carried out experiments with polished Damascus concave mirrors to focus solar radiation onto glass vessels containing salt water in order to produce fresh water. He also reports on his own experimental work with solar energy to distill alcohol and about a metal mirror having a linear focus with a boiler located along the focal line.

5. Solar still modern application

The first known patent for a desalination process involving steam distillation was granted in England in 1869. In 1870 the first American patent on solar distillation was granted to Wheeler and Evans, (1870). The patent, based on experimental work, was very detailed. Almost everything known to us about the basic operation of the solar stills and the corresponding corrosion problems was described in that patent.

The report stated as follows: this invention is based upon well known physical laws. The inventors described the greenhouse effect, analyzed in detail the cover condensation and re-evaporation, discussed the dark surface absorption and the possibility of corrosion problems. High operating temperatures were claimed as well as means of rotating the still in order to follow the solar incident radiation (Wheeler and Evans, 1870). Two years later, in 1872, an engineer from Sweden, Carlos Wilson, designed and built the first large solar distillation plant, in Las

Salinas, Chile. The plant was constructed to provide fresh water to the workers and their families of a saltpeter mine and a nearby silver mine. They used the saltpeter mine effluents, of very high salinity (140 g/kg or 140,000 ppm), as feed water to the stills. The plant was constructed of wood and timber framework covered with one sheet of glass. It consisted of 64 bays having a total surface area of 4450 m² and a total land surface area of 7896 m². It produced 22.70 m³ of fresh water per day (Fig. 8). The plant was in operation for about 40 years until the mines were exhausted (Delyannis, 2003).

Land-based desalination plants, in the other hand, came into use only in the early 1900s and were encouraged by the evolution of the petroleum industry, particularly in water-poor countries of the Arabian Gulf (Popkin, 1968; Ayoub and Alward, 1996). According to the technical brief report, UK, mass production occurred for the first time during the second world War (1939-1945) when 200,000 inflatable plastic stills were made to be kept in life crafts for the US Navy. However, it was not until the mid-1950s that the use of large land-based desalination plants, particularly those using multistage flash (MSF) distillations, began to appear economically feasible for non-industrial purposes. This spurred intensive research and development into a variety of desalination processes. By the mid-1960s, desalination was still some-what of a novelty for community water supply, and much of the work in this field remained experimental, improving on earlier designs of plants which failed to meet expectations (Ayoub and Alward, 1996).

Between the years 1965 and 1970 solar distillation plants were constructed on four Greek Islands to provide small communities with fresh water (Delyannis and Delyannis, 1983; Delyannis, 2003). The design of the stills was done at the Technical University of Athens (Fig 9). They used seawater as feed and were covered with single glass. Their capacity ranged from 2044 to 8640 m³/day. The installation in the island of Patmos was the largest solar distillation plant ever built. These solar stills were of the asymmetric glass covered greenhouse-type with aluminum frames.

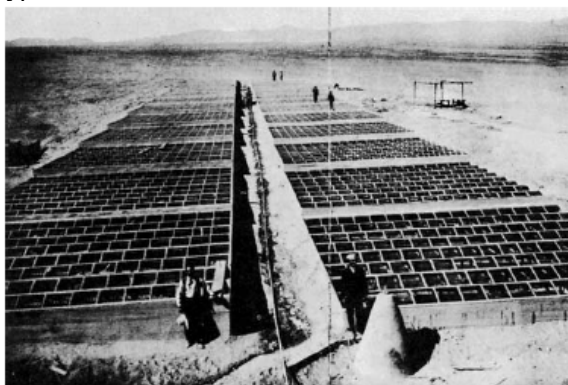


Fig. 8. The world-wide first large-scale solar distillation plant at Las Salinas, Chile

In three more Greek Islands the Church World Service of New York erected three solar distillation plants. These plastic covered stills (tedlar) with capacities of 2886, 388 and 377 m³/day met the summer fresh water needs of the Young Men's Christian Association (YMCA).

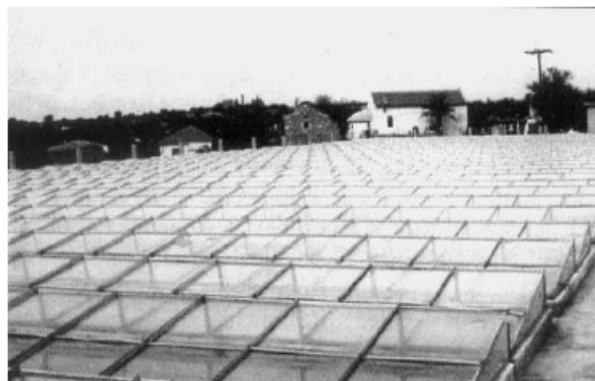


Fig. 9. The island of Symi (Greece) solar distillation plant

Edlin designed the stills which were tested by the OSW in Daytona Beach, FL. The first plant was an inflated, plastic cover design, while the other two were plastic V-shape configuration.

Solar distillation plants were also constructed on the Island of Porto Santo, Madeira, Portugal and in India for which no detailed information exists. Today most of these plants are not operational (Delyannis, 2003).

Renewable energy is the alternative solution to the decreasing reserves of fossil fuels. Total worldwide renewable energy desalination installations amount to capacities less than 1% of that of conventional fossil fuel desalination plants. This is due mainly to the high capital and maintenance costs required by renewable energy, making these desalination plants noncompetitive with conventional fossil fuel desalination plants. Fig 10 shows the estimation by World Energy Council (WEC, 1994) of the increasing general use of renewable energies.

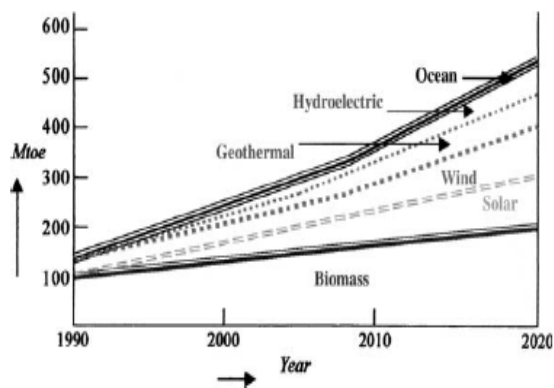


Fig. 10. The World Energy Council (WEC) estimation of renewable energies utilization increase up to year 2020.

The utilization of the sun's energy solar energy is the oldest energy source ever used. The Sun was adored, in many ancient civilizations, as powerful God (Delyannis, 2003).

6. Relevance of small-scale domestic solar still for India

Small desalting units in rural arid and semi-arid areas may provide individual households and communities with sources of clean drinking water otherwise unavailable. These units can be used as alternative where other water supply systems are not available. Solar distillation units are simple to operate, as there are no moving parts, high reliability, as they would be located in isolated communities without immediate access to technical assistance. Solar stills are economical because of cost-free energy and reduced operating costs. To date commercial development is of simple, reliable, and inexpensive solar stills has been very limited due to increased amortization cost, sometimes high engineering and manufacturing cost depend directly upon the location and local conditions. Nevertheless, there is continued interest in developing desalting equipment suitable in developing countries like India and Egypt where solar energy is abundantly found using renewable energy (Ayoub and Alward, 1996; Buros, 1991; Delyannis and Delyannis, 1983).

Several attempts have been made to develop high efficient solar stills. Which involve sophisticated designs, increased capital cost and operate more efficiently at relatively higher temperatures than the conventional solar still would do. These attempts were restricted to laboratory demonstration units and never reached a scale-up to commercial sizes (Delyannis and Delyannis, 1983).

Solar stills is a simple technology which will not only provide distilled water or drinking water for various end use, it even act as a good disinfectant for polluted water. It uses solar radiation to destroy pathogenic micro-organisms which cause water borne diseases. Sunlight is used for treating the contaminated water through two synergetic mechanisms: Radiation in the spectrum of UV-A (Wavelength 320-400 nm) and raises above 50°C, disinfection process is three times faster.

Indians are exposed to multitudes of natural and man-made calamities and their vulnerability to disasters has been exceedingly high due to high density of population. The number of people exposed to such disasters is increasing year after year for want of preparedness. The experience of Tsunami in the east coast, the earthquake at Kashmir and Gujarat taught us that micro level community based preparedness is very important in reducing the adverse impact. In many emergencies, only contaminated surface water (standing water, streams or rivers) is initial available. Water may contain pathogens, which are transmitted from faeces to mouth. The greatest risk associated with polluted water is the spread of diarrhea, dysentery, cholera,

and infectious hepatitis (hepatitis A). Solar stills are useful in such places to provide clean and safe drinking water. As solar still is well-proven and familiar techniques, combined with efforts to improve protection against pollution, is often a sound solution. It acts through heating, the second through the effect of the natural UV radiation and the third through a mixture of both thermal and UV effects. Solar disinfection is included in the technologies reviewed by World Health Organization (WHO) for household water treatment and storage. Turbid water more than 30 NTU is not suitable for solar disinfection. The promoters of SODIS suggest the use of thin PET plastic bottles. The half of the bottle furthest from the sun should be painted with black paint to improve the heat gain from the absorption of thermal radiation, and the bottle can be laid on a dark roof to further increase the potential temperature rise in water. In order to make people aware of solar stills and usability during such emergencies various tools can be used such as social marketing one of them (Ponnuraj, 2006).

Solar energy is clean, pollution free and renewable source of energy. Development of this source of energy requires accurate detailed long term knowledge of the potential latitudes of 40°N and 40°S is generally known as the solar belt and this region is supposed to be with an abundant solar radiation. Karnataka (South India) being located between 11° 40' N and 18° 27'N has a geographic position that favors the harvesting and development of solar energy. Karnataka receives global solar radiation in the range of 3.8 – 6.4 kWh/ m². From the data it may be concluded that coastal parts of Karnataka with the higher global solar radiation and these regions are ideally suited for harvesting solar energy (Ramachandra and Shruthi, 2007).

The discussion of the paper may be extended to more precise way taking Karnataka state (India) as an example. The paper will further discuss the water pollution, need and necessities of solar energy technology in Karnataka. Karnataka is the eight largest states in India with 191,791 km², with 52 million population with mean population density of 275/ km² (Census, 2001) out of which 28 % population is in Urban, with summer: March to May (18°C to 40°C), winter: Oct to Dec (14°C to 32°C), South-West Monsoon: June to August and North-East Monsoon: October to December with minimum 500mm to 4000 mm rainfall ever year. There are many river basins such as Krishna River, Godavari River etc.

In Karnataka, 37% of habitations have found to have ground water contaminated. Habitations in Bagalkot, Bangalore Urban, Bijapur, Chamarajnagar, Chitradurga, Haveri, Mandya, Tumkur, Bellary, Davanagere, Kodagu, Kolar, Raichur and Koppal districts have serious groundwater quality problems, ranging from 50 to 79 per cent of habitations. More specifically, excess fluoride in groundwater is a major problem in 14 districts, ranging from 10 to 67 per cent of total habitations in each district.

Similarly, excess brackishness in 13 districts (10 to 27 per cent of habitations), excess nitrate in 8 districts (10 to 51 per cent of habitations) and excess iron in 12 districts (10 to 63 per cent of habitations) have adversely affected drinking water quality (Table 5). Nitrate levels in Banshankari premises (Bangalore) are as high as 300 mg/L (against the permissible limit is 45mg/L) in some places because of sewage contamination of groundwater (Hindu 24 February 2007).

Surface water contamination is yet another environmental problem in Karnataka as water has been polluted at certain pockets of some rivers and other water bodies. For instance, water in the river Bhadra is turbid and contaminated at the point of effluent discharge by the Mysore Paper Mills and Vishweshvaraiiah Iron and Steel Limited.

Similarly, in Kabini and Cauvery rivers water is polluted around townships situated on the banks (Deccan Herald, 24 February 2001).

Table 3. Status of water quality by habitations in Karnataka state – 2002

Districts	No. of Habitations affected by				Total No. of Habitations affected	% of affected habitations	Total No. of Habitations
	Excess Fluoride	Brackishness	Excess Nitrate	Excess Iron			
Bagalkote	135	158	33	88	414	65.30	624
Bangalore (U)	262	224	0	318	804	62.57	1285
Bangalore (R)	406	148	411	189	1154	34	3394
Belgaum	134	159	1	419	713	47.34	1506
Bellary	499	91	38	26	644	55.14	1168
Bidar	37	56	123	1	217	26.72	812
Bijapur	200	241	19	113	573	61.75	928
C.R.Nagar	34	27	425	173	659	79.40	830
Chikkmagalore	51	77	136	524	788	23.41	3366
Chitradurga	519	345	126	87	1077	78.67	1369
D.Kannada	2	4	0	294	300	9.56	3137
Davangere	358	156	288	1	803	74.08	1084
Dharwad	49	115	1	74	239	48.38	494
Gadag	127	42	0	0	169	48.38	494
Hassan	159	181	39	323	702	18.00	3900
Haveri	77	113	130	198	518	82.22	630
Kodagu	3	0	6	306	315	54.97	573
Kolar	509	319	1005	109	1942	51.90	3742
Koppal	477	50	0	4	531	74.89	709
Mandya	158	518	51	684	1411	75.33	1873
Mysore	105	434	121	288	948	49.02	1934
Raichur	322	195	129	51	697	57.18	1219
Shimoga	89	87	2	362	540	12.21	4424
Tumkur	658	585	976	1490	3709	67.63	5484
Udupi	11	2	1	218	232	4.11	5640
Uttara Kannada	24	74	13	145	256	6.56	3901
Total	5838	4460	4077	6633	21008	37.06	56683

Source: Govt of Karnataka 2002, Rural Development and Engineering Department

Additionally, mining activities too affect surface water quality, for instance in intensive mining areas of Bellary district water has been reported to contain neutral pH, high turbidity and suspended solids . 72 villages in and around Bangalore water sources are contaminated with e-coli form bacteria (Times of India 17 February 2007). All these evidences indicate that the quality of surface water is deteriorating in the state. As observed from the above discussion environmental pressures are rising on drinking water sources, both ground and surface, and also in the distribution system. Problems of depletion and deterioration of quantity and quality respectively result either in sub-optimal or nonfunctioning of drinking water supply systems, ultimately crippling the process of providing adequate safe drinking water to people (Government of Karnataka 2002).

The adequate solar radiation and need for relatively small quantities of fresh drinking water in Karnataka, solar distillation may have excellent possibilities in such situation.

Remarkably, many regions of the world present this situation, including developing countries where in many cases energy cost are high, labor costs are low, and populations are not highly concentrated (Bloemer et al., 1965). In Karnataka more than 90 per cent of habitations especially rural out of 56682 rural areas, depend upon ground water and are facing major risks of depletion of the source.

Out of 56682 rural habitants (Government of Karnataka, 2001), over 35 per cent of the rural habitations are yet to be covered with adequate drinking water supply.

The problem of inadequate drinking water supply is more acute in drought, where more than 30 per cent rural habitations lack access to adequate water supply (Table 3).

The drought regions are the yellow shaded regions (except Kolar) and few parts of light blue shaded regions (Dharwad, Bangalore Urban, Chitradurga) from the Fig. 11. From Fig. 12 it results that these regions have relatively higher density of populations compared to adequate water regions. For the drought regions the solar technologies would mean more viable, as adequate solar radiation may be available and needs less maintenance. This can be justified by the following discussion as follows:

A survey by the Directorate of Economics and Statistics (Government of Karnataka, 2002) evidenced that majority of habitants had below 55 liters per capita per day (lpcd) of water supply (Table 4), an indication of lacunae in engineering plan, capacity installation and satisfaction derived by people. The department of mines and geology (DMG) while studying fluctuations and depletion in ground water has concluded that the level of ground

water has depleted up to 7m in several districts (Table 5).

Many rural habitations in Karnataka are facing health problems due to inadequate water use and fecal oral transmission. For instance, people in few villages of Jagalur taluk in Davanagere district reported skin diseases after they stopped bathing due to shortage of water. Gastroenteritis (GE) is the major diseases with nearly 24 thousands of incidences and about 200 deaths in 2001 and 20,524 cases of GE in 2006. It should be noted that viral hepatitis is increasing rapidly in the state from 1714 cases in 1997 to 5438 in 2001. Apart from health effects, inadequate water supply increases hardship on women and children, compelling them to spend more time and energy in collecting water.

India received solar energy equivalent to more than 5000 trillion kWh/ year, which is far, pre than its total annual energy consumption. The daily average global radiation is around 5 kWh/m² day with the sunshine hours ranging between 2300 and 3200 per year.

Table 4. Status of rural water supply in Karnataka (Government of Karnataka, 2002)

District	No. of Inabitants with lpcd < 55 lpcd			
	No.	% to total	55 lpcd and above	Total
Bangalore (R)	956	30.09	2221	3177
Belgaum	995	64.44	549	1544
Bellary	590	57.28	440	1030
Bidar	211	23.29	695	906
Bijapur	524	52.04	483	1007
Bagalkot	333	46.77	379	712
Chikkamagalore	705	19.79	2857	3526
Chitradurga	504	33.14	1017	1521
Davanagere	391	31.94	833	1224
Dakshina Kannada	1470	47.88	1600	3070
Udupi	1402	41.38	1986	3388
Dharward	245	54.69	203	448
Haveri	339	48.85	355	694
Gadag	128	34.04	248	376
Gulbarga	1208	62.59	722	1930
Hassan	1923	44.53	2395	4318
Kodagu	452	82.94	93	545
Kolar	705	18.29	3149	3854
Mandya	705	18.29	3149	3854
Mysore	540	26.77	1477	2017
Chamarajnagara	509	75.18	168	677
Raichur	529	37.7	874	1403
Koppal	265	33.42	528	793
Shimoga	1068	23.39	3498	4566
Tumkur	1918	37.33	3220	5138
Uttara Kannada	1298	22.74	4411	5709
Bangalore(U)	701	64.79	381	1082
Total	20495		36187	56682
% to total no of villages	36.16		63.84	100

Table 5. Actual level of drinking water supply in rural areas (Puttaswamaiah, 2005)

Bore-well with hand pumps	91.7% of 470 rural habitations had less than 55 lpcd
Mini water supply schemes	Out of 646 schemes surveyed 91.48% reported less than 55 lpcd
Piped water supply schemes	86.07% of 977 rural habitations had adequate water supply less than 55 lpcd

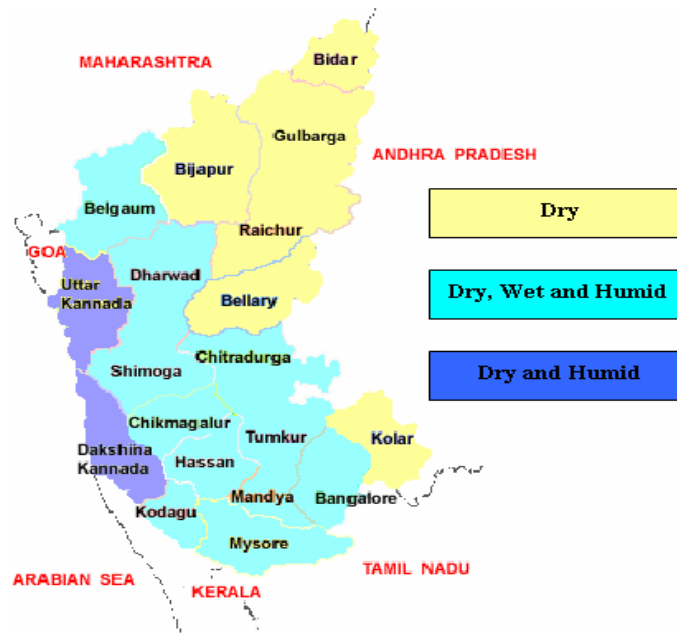


Fig. 11. Climatic variations in Karnataka (adapted: upon Government. of Karnataka, 2001)

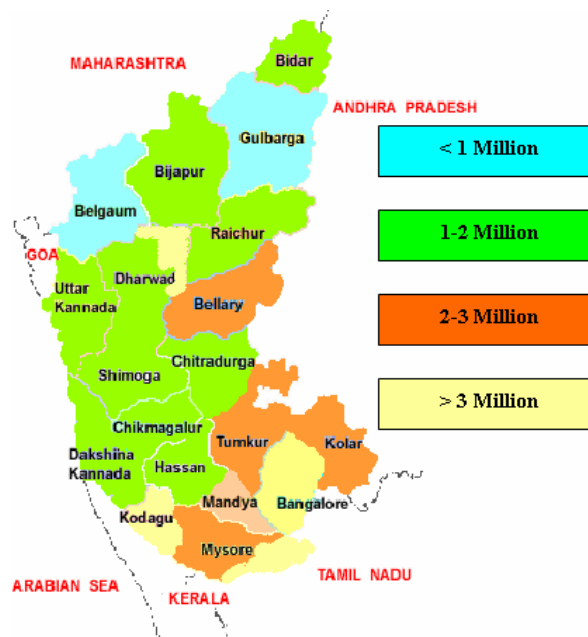


Fig. 12. Human settlement density in Karnataka (adapted: upon Government. of Karnataka, 2001)

Karnataka receives daily solar radiation in the range of 5.1–6.4kWh/m² during summer, 3.5–5.3kWh/m² during monsoon and 3.8–5.9kWh/m² during winter. The potential analysis reveals that maximum global solar radiation is in districts such as Uttara Kannada, Dakshina Kannada, etc. The study identifies that coastal parts of Karnataka with higher global solar radiation are ideally suited for harvesting solar energy.

Global solar radiation in Uttara Kannada during summer, monsoon and winter is 6.31, 4.16 and 5.48kWh/m², respectively. Similarly, Dakshina Kannada has 6.16, 3.89 and 5.21kWh/m² during summer, monsoon and winter, while Mandya district

has minimum global solar radiation of 5.41, 3.45 and 3.73 kWh/m² during summer, monsoon and winter, respectively. The results were implemented in GIS to obtain maps showing district wise variation of global solar radiation. Fig. 13 shows the district-wise variation of global solar radiation during summer, Fig. 14 during monsoon and Fig. 15 during winter (Ramachandra and Shruthi, 2007). If one is keen in using solar stills, some of the few important parameters need to be considered such as area required per house, area availability, adequacy of insolation. Let us consider Bagalkot district (Northern Karnataka) which is located off the Raichur-Belgaum state highway as shown in the Fig.16.

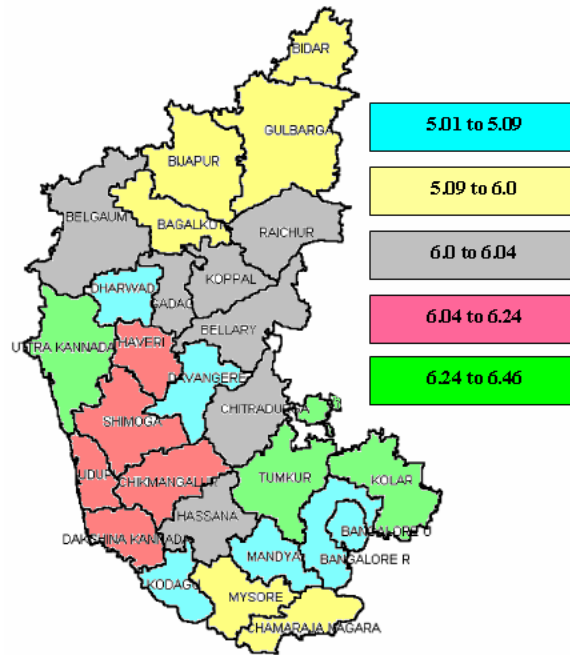


Fig. 13. Global solar radiations during summer

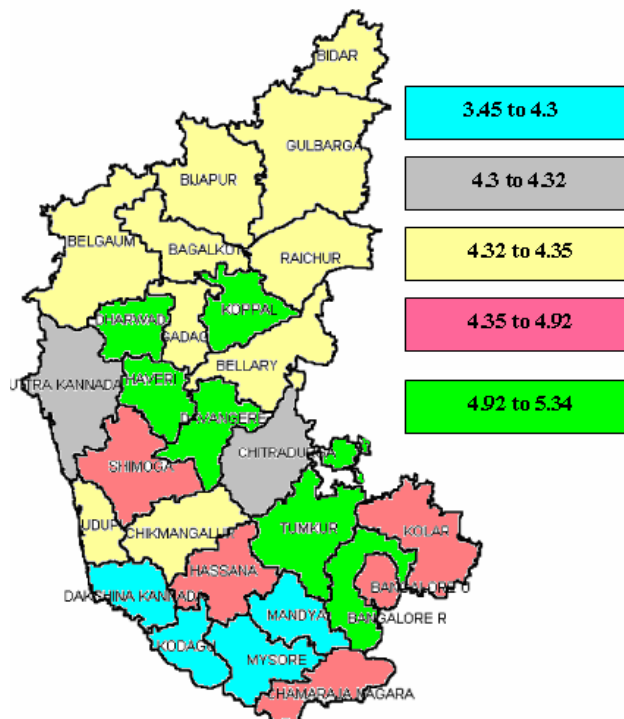


Fig. 14. Global solar radiations during monsoon

The Bagalkot district is spread over 6593 Sq. km. of an area, with 1.65 Million populations, 251 per Sq. km. of populations' density. It is positioned at 16°12'N, 75°45'E, the climate is warm and dry (41° C to 28° C) through out the year and rainfall (489 mm) is scarce (Census, 2001).

The following solar stills are considered for the analysis of selection of solar stills:

Single sloped solar still (left) consists of two units with and without perforated black plate (act as

energy storage) were designed and constructed to maintain the comparison under the same weather conditions (Fig 17). The area of each solar still is 0.25 m² and 3.2 L/ m²/ day and 2.8 L/m² /day were the respective productivity for 500 – 1400 W/m² (Nafey et al. 2001). The high output single unit solar still of 0.5 m² which would give 9 L/m²/day at 35° C ambient temperature or approximately 1000 W/m² of insolation (Ward 2003).

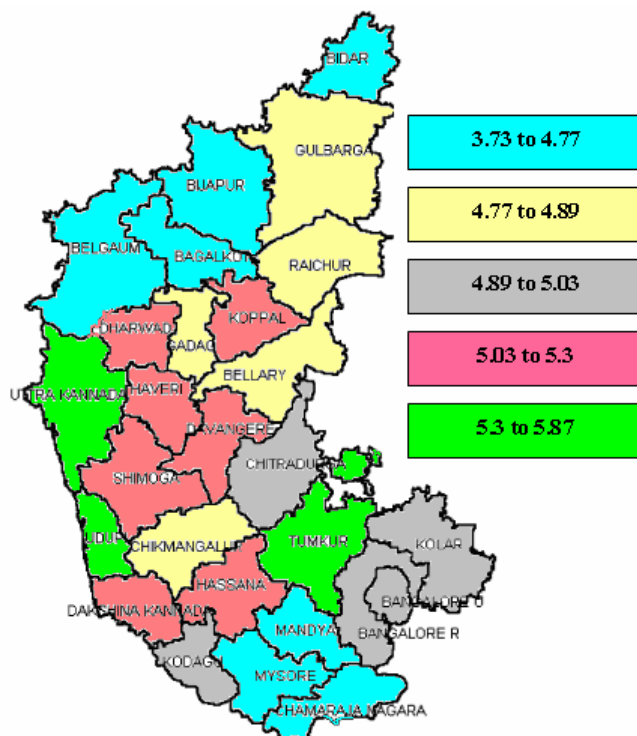


Fig. 15. Global Solar radiations during winter (Ramachandra and Shruthi, 2007) (Fig 13, 14 & 15)

7. An integrated assessment into suitability of various solar stills for India

Solar distillation (Bloemer et al., 1965), if a basin still is used, has a number of economic characteristics that are different from the other sea water conversion processes:

1. Unit construction cost is not affected appreciably by still size.
2. Power requirement are negligible.
3. The still is constructed on-site using unskilled or semi-skilled labor.

4. Operation and maintenance can be handled by people with little technical training.
5. Materials of construction are durable and readily available.
6. The still design is essentially modular; capacity of an existing still can be increased by any desired increment with practically no cost penalty.

Considering household size (per household) 6, the number solar still(s) required is/are:

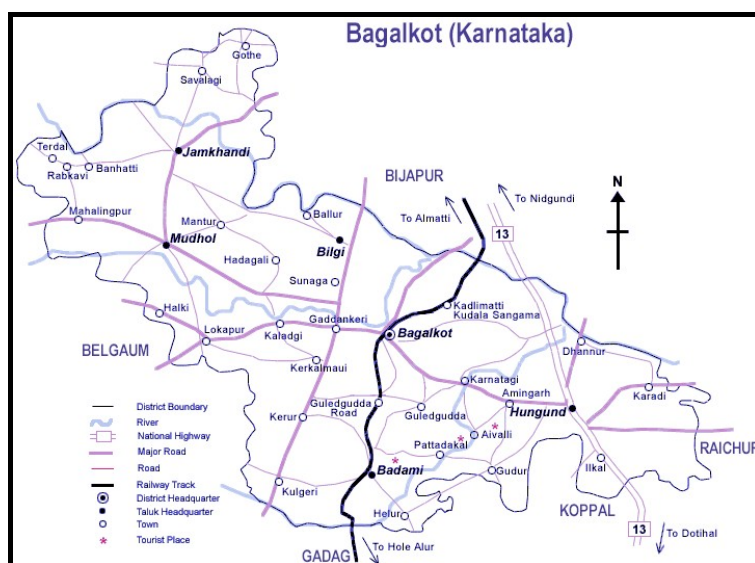


Fig. 16. Map of Bagalkot district (Northern Karnataka) (<http://bagalkot.nic.in>)

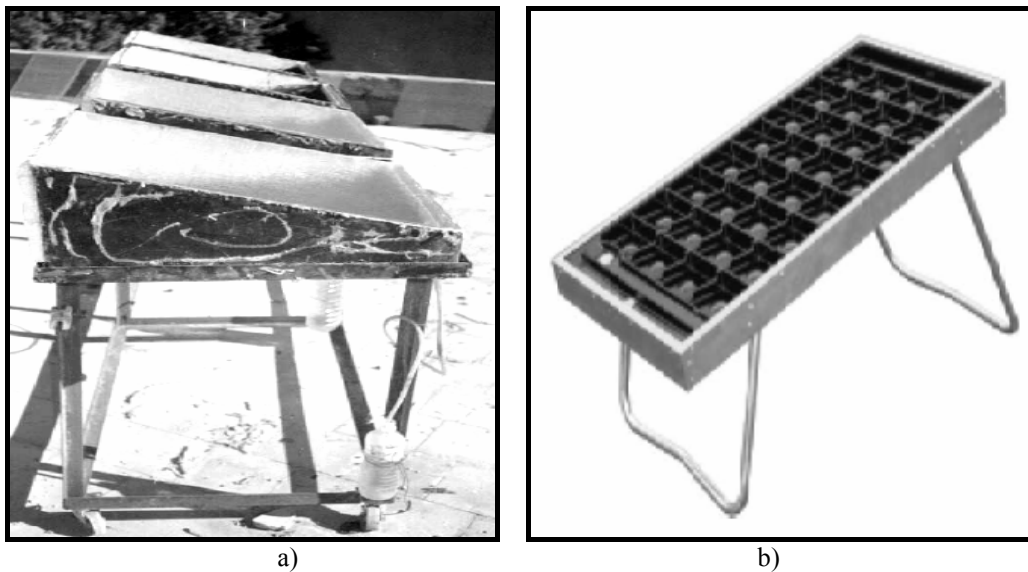


Fig. 17. Single slope solar still (a) and High output single unit solar water purifier (b)

- Assuming the consumption of water per person is 3 L/day for drinking purposes. For a household size of 6, approximately 18 L/day for drinking purposes is needed. The selection of which type of solar still will depend upon the area available, for the singled slope solar still (left) of 0.25 m^2 whose productivity is $3.2 \text{ L/m}^2/\text{day}$. The number of solar stills required would be 6 stills. If one chooses the high output solar still unit (right) then two units would suffice. The above analysis can be used to extrapolate the study for any other regions also.

- The cost of the singled solar still would be 3000 (Indian Rupees) or 74 US \$ (1 US Dollar = 40.00 Approx Indian Rupee (INR, Nov 2007)). The common configurations are V and L shapes. They are simple from the maintenance view and low construction cost. On the other hand, the advantages of having solar purifier are it is rugged, lightweight, portable and suitable for remote outback or Third World countries (Ward 2003). Other sophisticated solar still such as solar purifiers (Fig. 17) have been constructed, but the gain of increasing the productivity is canceled by the complexity of the unit (Nafey et al. 2001).

The above explanations can be justified as follows; when the purifier is operated in the static mode the dissolved solids in the water continuously flow through the purifier, then solids which were in solution are deposited on the surface on each tray and further exposure to the sun ultimately produces a colored hardened deposit that is undesirable. In order to remove these deposits dilute acids such as citric acid or oxalic acid need to be used, which be additional cost apart from labor cost. This means skilled labour is needed to maintain the solar purifier. Where has the singled sloped solar still would require minimum maintenance such as cleaning once in two days using simple brush.

- For common man time is equivalent to money. Having easy accessible to safe drinking water will reduce poverty. According to Asian Water Watch 2015 report (2006) safe water supplies immediately improves people's health and save them time, which they can use to study, or improve their livelihoods, so they can earn more, eat nutritiously, and enjoy more healthy lives (Paelmo, 2006). The above explanation can be justified with subsequent discussion.

Poverty Alleviation

Studies conducted by the Asian Development Bank (ADB, 2003) and Water Aid India (2005) on the impact of their projects on the communities in different parts of the Asia region found that multiple benefits were the norm, including many that had not been anticipated or invested in these benefits, which affected many aspects of life (UN-HABITAT 2006), included (Fig 18):

Time saved, along with reduced fatigue from not having to collect water from, on average, 6 kilometers away: this was often the benefit most valued by the community. The saving was usually directly translated into productive activities, especially women. For example, the education of women is severely affected as they have to devote much time in procuring water from long distances. The literacy rate for women in Rajasthan is the lowest in India 1.7 %, as compared to 87.8 % in Kerala (Census, 2001).

Health benefits, including lower medical expenditure and the reduction of the long-term debilitating effects of diseases such as endemic dysentery and worm infestations.

In India, water-borne diseases alone are said to claim 73 million work days every year. The cost in terms of medical treatment and lost production is around US\$600 million per year.

Improved **income opportunities** from home-based livelihood activities that used the new water supplies, such as vegetable and live-stock production, brick and pot making, and operating food stalls.

Multiplier effects throughout the local economy from increased incomes and new enterprises based on improved water supplies.

Local organizations set up to build and run water supplies were often the basis for wider social mobilization, and led to the empowerment of women and greater social cohesion.

Savings and credit groups led to the development of wider access to credit among the communities and improved financial management skills. In urban areas, poor households also saved on the cost of water, as they had to pay informal providers high process.

The new skills, organizations and social cohesion, along with increased economic momentum, had impacts on the wider **political and social system**, including at times influencing government policies and bringing about more balanced representation.

The above explanations can be justified by the following example, ease availability of water in Makueni district, Eastern Kenya has made life much easier as they used to travel for 3 hours carrying 20 litre of jerry can on their back in search of water along with group of people because of wild animals in their region.

Women in village worked out a timetable with their husband where they would go on alternate days to fetch water. They could now grow varieties of crops and vegetables. The diet has changed and they could save some money (Kshs* 300) after selling vegetables at the market (Lampe, 2007).



Fig. 18. Benefits of water for poverty alleviation

8. Conclusion

It can be concluded from the above the discussion that there is alarming need of solar distillation for community/ domestic levels to curb the existing problems to certain extent. Desalination may be advantageous for villages which are more than 20-25 km away from fresh water source from where a pipeline would have to be laid down. As seen above the situation in India is grim with its inherent problems of affordability and adaptation of cost intensive modern technologies. Thus the above technology has all the potential to be one of the cost-effective and pragmatic solutions to the water problems of rural areas in developing countries.

Operationalizing this technology on a pilot basis to ascertain the affectiveness and receptive factors would enable it to be adopted on a large scale basis.

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INFRASTRUCTURE DEVELOPMENT OF QUALITY CONTROL FOR ENVIRONMENTAL FACTORS LABORATORY IN ORDER TO ESTIMATE, CHARACTERIZE AND RECOVERY RENEWABLE AND RECYCLE RESOURCES, USING CHEMICAL AND BIOCHEMICAL PROCESSES *MEDRES LAB, Research Grant no. 94 /2007 (PNCDI II)*

The aim of the project is infrastructure development and capacity extension of an analysis and control of environmental factors laboratory in order to estimate, characterize and upgrade renewable and recycled resources, the first regional laboratory specialized in the recovery of this resources using chemical and biochemical processes.

The data provided by the Romanian Accreditation Association (www.renar.ro) shows a deficiency at national level of a specialized laboratory equipped for complex biochemical modifications of these types of resources taking into account environmental protection.

This project has two major objectives:

- **Upgrading** the Environmental Quality Control Laboratory, part of the Faculty of Chemical Engineering and Environmental Protection, which in the 8 years of activity had realized numerous partnerships with different universities, economic agents, research institutes and non-governmental organizations. Using all the available means, the laboratory ensure the logistics for environment components (water, air, soil) quality control, aside with information and education for specialized staff.

- **Development** of new possibilities to evaluate renewable and recycled resources. The uses of the new directions are in agreement with the current researches, the requirements of the industry and the actual European trends. Currently, the renewable and recycled resources are used as rough material for chemical and energetic supplies and the tendency is to substitute conventional initial materials. Based on this information, the recycling of the secondary products can fulfill the sustainable development conditions, becoming the centre of a close functional system compatible with the environment. In the same time, the laboratory will make use of the present knowledge in upgrading secondary products and the development of new processing methods of different resources or special rough materials used for obtaining biopolymers, biofuels, proteins and natural regulators substances. The preservation of environment will be assured by special attentions to recycling, closing the circuits and the following of the duration of life function the use of the products. All these problems will open new possibilities for collaboration and to strengthen relationship with industry and research institutes, founding the premise for competitive approach in different domains and also for technological transfers. The laboratory endowment will anticipate the equipment acquisition necessary to enlarge the offered services and will contribute to testing and certification of special products obtained by biotechnological processes. The project will carry on **four activities**: equipment acquisitions, materials, soft and calculation technologies, applicative and pre-competitive (testing, verifications, measurements, analysis) research activities, dissemination and project management activities. The project will accomplish training activities, audit and certification ISO 17025 of the laboratory and the initialization of the proceeding of RENAR accreditation.

The **general objective** is represented by the **development of the material base for research in the field of sustainable and incorporate management of resources.**

The **specific objectives** are:

- **Development of existing infrastructure** of the Environmental Factors Quality Controls Regional Laboratory, through acquirement of performing equipments in order to reinforce the public private partnership in the region.

- **Accomplish of material base** necessary to build a new research direction of renewable and recycled resources, using the already existing structure.

- **Development of research capacities** in order to participate as work packages or European programs (such as FP 7) coordinators.

- **Disseminations of relevant results** for the national and international scientific communities, governmental organizations specialized in renewable resources management (Agriculture and Forestry Departments, Environment Protection Agencies, local and regional authorities) and civil society.

Implementation of MEDRES laboratory will lead to the following **estimative results**:

- Development of C-D activities and approach of new domains/sub domains of scientific researches, in agreement with the European trends in renewable and recycled resources.
- The quality increase and diversification of the educational act, upgrading of faculties laboratories for practical applications.
- Better accessibility of Romanian research in European programs C-D (there is a partnership proposal in FP 7 - BIOAROMATICS)
- Extensive and new research services for industrial units, especially for measurements, testing, trials and certifications.

Regarding the **stipulated benefits**, taking into account the present tendencies and personnel experiences, it is highly possible that in the next period new opportunities will be develop for resources diversification and increase the treatment possibilities using biorefinery technologies. In this way, renewable and recycled resources are use to obtain chemical products with/or energetic value. These activities in the north east development area will be **correlated with future programs**, having in mind the good use of agricultural areas, supplementation of the forestry zone necessary for providing additional renewable resources. "Gheorghe Asachi" Technical University will have an important role in the excellence centre SUSTENPOL INNOVATION (SUSTINOV) from Piatra Neamt, used to promote the concept of sustainable development. Beside the excellence centre, this laboratory proposed in this project will allow the **promotions of new technologies and activities**, having a positive role in setting up **new working positions** in this area with a high rate of unemployment. The approach of new research programs using the created C-D base will permit the increase of the research capacities of the personnel with the involvement of young researchers (PhD students and postdoctoral researches). The possible risks of this project are related with the difficulties in finding partners and the implementation of developed technologies and products. These risks can be preventive and diminish by the involvement of TECHNOLOGICAL PLATFORM FOR FOREST BASED SECTOR -FTP and the existing excellence centre.

The **estimate profit** is the integration of excellence centers in international CD networks, as well as the expansion of the possible applications in the various regions of Romania. The implementation of this project will allow the access to CDI infrastructure, necessary to obtain new products within the "green chemistry" concept. The created infrastructure will permit specialized and certified services for the business medium and the possibilities of financial support for PhD and postdoctoral fellowships. **Potentials beneficiary** are partners universities thanks to their integration in a CD network regarding the Resources Management, specialized organizations from MEDRES laboratory geographical area, members of national and international networks related with Resources Management, Romanian civil society, researches, PhD students.

For more information on the **Medres Lab Project**, please visit http://medres_lab.cs.tuiasi.ro and contact iwolf@ch.tuiasi.ro

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INVESTIGATIONS ON THE POSSIBILITY OF NATURAL HEMP FIBERS USE FOR Zn(II) IONS REMOVAL FROM WASTEWATERS

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Abstract

Natural hemp fibers have been evaluated for Zn (II) ions sorption from diluted aqueous solutions. In order to establish the optimum conditions, the effect of initial pH of solution, hemp dose, Zn (II) concentration, temperature and contact time of phases on the Zn (II) sorption by natural hemp has been studied. To model the Zn (II) sorption at three different temperatures the Langmuir and Freundlich isotherms have been used. The Langmuir maximum sorption capacities were determined as being of 0.2545, 0.3238 and 0.3754 mmol/g at 5°C, 20°C and 50°C, respectively. In order to evaluate the thermodynamic feasibility of the Zn (II) sorption process, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated on the basis of Langmuir constants. The constants of the pseudo first sorption rate, k' , determined by means of Lagergren equation is $6.678 \times 10^{-3} \text{ min}^{-1}$. The results of this study suggest that the natural hemp can be efficiently used in the removal of Zn (II) ions from wastewaters with low content of the tested cation.

Key words: hemp fibers, isotherm, sorption, wastewaters

1. Introduction

With the current interest in environmental pollution, removal and/ or recovery of heavy metal ions from effluents is important in eliminating one of the major causes of water pollution. Among the other heavy metals, zinc is an essential mineral for all aerobic and anaerobic organisms. However, it has been proven that large amounts of zinc (II) can seriously affect the health of environment because of its toxicity (Gavrilescu, 2004).

Sorption has been evolved into one of the most effective methods for the removal and recovery of heavy metals from industrial and municipal effluents. The use of sorbents based on expensive synthetic polymers involves some major disadvantages among the fact that their manufacturing in itself is environmental – malign is of crucial importance.

Natural materials or waste products from industrial or agricultural activities can be used as

alternative sorbents since they are inexpensive, abundant in nature, require little processing and can be disposed in a sustainable matter if is necessary (Bailey et al. 1999).

Among these materials peat, wood, tree bark, fibers of flax, cotton or jute, sand, sawdust, bauxite, bentonite clay, steel plant slag and fly ash can be numbered (Gene-Fuhrman et al., 2007; Hamadi et al., 2001; Khazali et al., 2007; Pehlivan et al., 2006; Sharma et al., 2007, Tofan et al., 2008).

Hemp is another commonly available unconventional material that can be efficiently used in natural and modified forms for removal of Cr (III), Cu (II), Ag(I), Cd(II), Pb(II) ions from polluted waters (Paduraru, 2002; Tofan, 1999; Tofan, 2000; Tofan et al., 2001a; Tofan et al., 2001b; Tofan, 2004).

In this work the sorption and kinetic properties of natural hemp fibers in batch retention of zinc (II) ions from aqueous solutions have been assessed.

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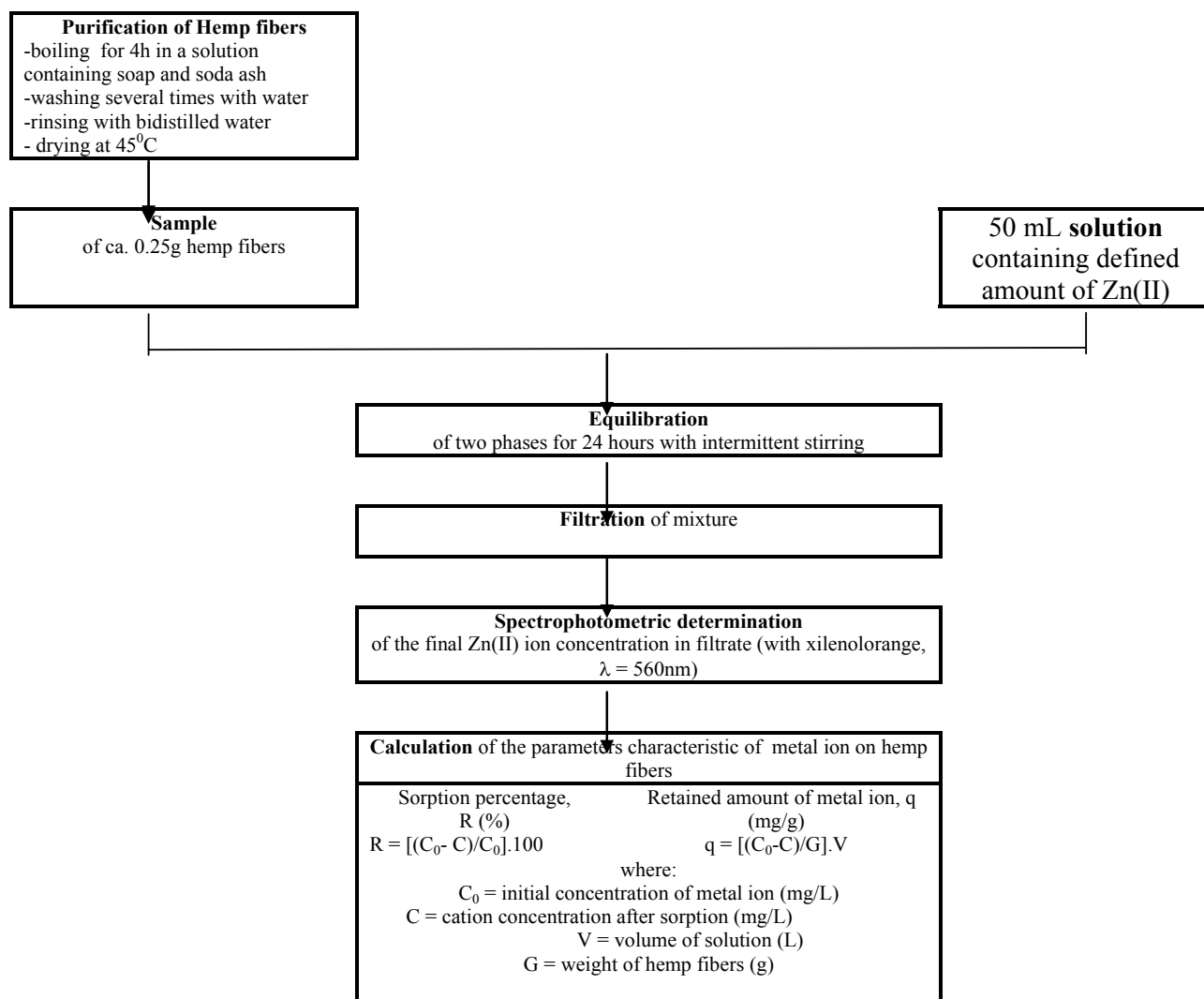


Fig.1. A schematic representation of the batch sorption procedure carried out in this study

The choice of hemp as a sorbent of study is based on its remarkable fundamental features: low cost, availability, high mechanical strength and porosity, hydrophilic character, fast sorption, tolerance to biological structures, easiness in functionalization, possibility of being used as fibers and filters.

2. Experimental

2.1. Materials and reagents

Hemp fibers were purified by boiling for 4h in a solution containing soap and soda ash, followed by washing several times with water, rinsing with doubly distilled water, drying in an oven at 45⁰C.

Stock solution of 1mg Zn (II)/ mL was prepared by dissolution of 1.0652 g ZnSO₄·7H₂O and dilution to 250mL. Subsequently this solution was standardized gravimetrically. Working solutions were prepared by the requisite dilution of the stock solution.

2.2. Sorption Procedure

The sorption study of Zn (II) ions on natural hemp has been carried out in batch conditions, according to the procedure presented in Figure 1.

2.3. Apparatus

Absorbance measurements were performed on a S104D–WPA Linton Cambridge spectrophotometer. The solution pH has been measured with an M – 64 Radiometer pH – meter.

3. Results and discussion

The hemp fiber is a cellulosic natural plant fiber having the chemical composition recorded in Table 1. Fig. 2 shows the structure of the hemp fibers under study.

The idea of this unconventional natural cellulosic material use for the batch retention of zinc (II) ions is based on the presence of some potential

chelating groups (hydroxyl, carbonyl, methoxy) in the structure of the cellulose and lignine structure.

Table 1. Chemical composition of hemp

Cellulose (%)	74-75	Ash (%)	0.82
Hemicellulose (%)	18.4-15.4	Xylans (%)	3.0- 7.0
Lignin (%)	3.7	Proteins (%)	0.5 – 1
Waxes (%)	4.04	Pectins (%)	4.0 – 8.0

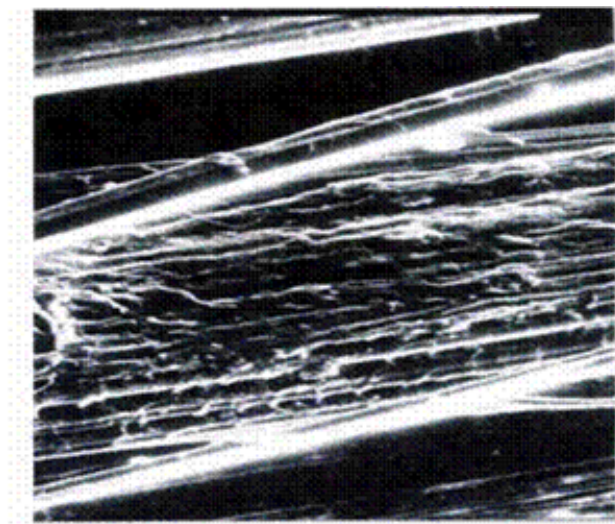


Fig. 2. Electronic micrograph of hemp fibers

In order to establish the optimum conditions of sorption, the effects of pH, adsorbent dose, metal concentration, temperature and contact time on the Zn (II) retention by natural hemp have been studied.

3.1. Effect of initial pH

The effect of solution acidity on Zn (II) sorption by untreated hemp was studied in the initial pH range of 2 – 5 and is shown in Fig. 3. In this pH range no Zn(OH)₂ precipitation takes place. According to the speciation data from literature, on solutions at pH 2-5, the studied metal exists in its double positively charged form (Zn²⁺) (Ferguson, 1990).

As can be seen from Fig. 3, the smallest amount of retained Zn(II)(2.064mg/g) was found at pH=2 (reached by acidification with H₂SO₄ solution). Then the sorption increases with pH increasing. The highest Zn(II) retained amount (4.75mg/g) is reaching at initial pH=5 from unbuffered solutions. For this reason, the subsequent dependences have been studied from solutions of pH=5 obtained by the simple dilutions of initial solutions.

The pH dependence in the Zn(II)–natural hemp batch sorption system might be due to the dissociation of superficial functional groups, resulting in negative charges at the active sites on the hemp surface that would allow Zn²⁺ ion to be chemisorbed.

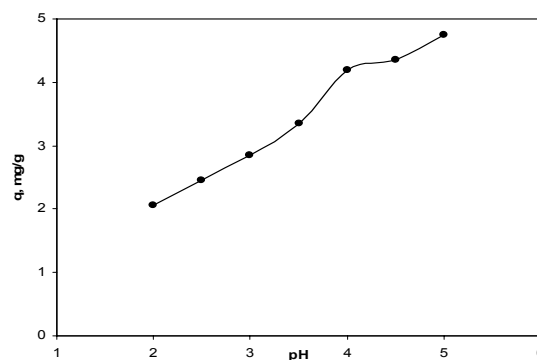


Fig. 3. Influence of initial pH on Zn (II) – natural hemp batch sorption system ($C_0 = 40\text{mg/L}$; 0.25 g of hemp; contact time = 24 hours)

3.2. Effect of hemp dose

The influence of hemp dose has been investigated from solutions of initial concentration equal to 80 mg/L. The resulting dependence is given in Fig. 4.

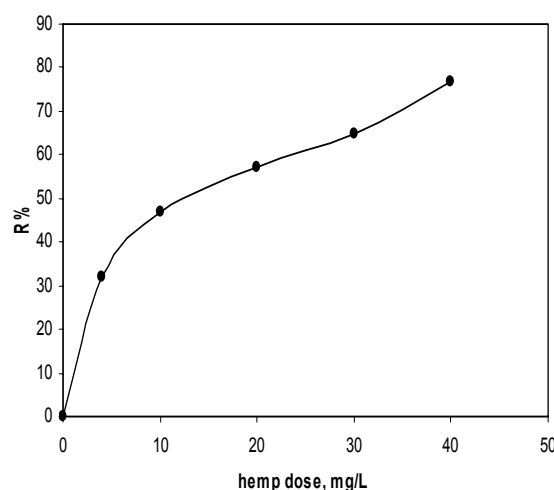


Fig. 4. Percentage of Zn(II) retention as function of hemp dose (pH = 5, $C_0 = 80\text{mg/L}$, time contact = 24h)

As follows from Fig.4, the values of the sorption percentage increased with increasing hemp dose. This trend is in good agreement with higher number of available sites of the natural hemp for zinc(II) binding. At the maximal dose of 40 mg hemp/L, the percentage of Zn (II) retention reached a value of 80 %.

3.3. Effect of initial Zn(II) concentration

The amount of Zn (II) retained on the hemp fibers (q) increased with increasing Zn(II) concentration in initial solution (Table 2).

On the other hand, the Zn (II) amount increasing results in the decrease of the sorption percentage, R% (Table 2).

The enhancement of the metal uptake on higher Zn (II) initial concentration might be due to the high values of initial number of Zn (II) mmoles /

limited number of available binding sites ratio. The access of Zn (II) ions is hindered probably by the occupation of the total active sites on the hemp. As a consequence, the percentages of Zn (II) retention decreased. This trend leads to the conclusion that the natural hemp can be efficiently used in the removal of Zn (II) ions from wastewaters with low contents of the tested cation.

Table 2. The effect of initial Zn(II) concentration on its sorption by natural hemp

C_0 (mg/L)	q_e (mg/g)	R , %
20	2.85	75.2
40	5.25	70.1
60	7.25	64.2
80	8.56	60.0
100	9.25	55.1
120	10.3	49.2
160	11.75	41.5
180	12.0	34.8

3.4. Sorption modeling

To describe the equilibrium distribution of Zn (II) ions between the hemp phase and the aqueous solution phase, two different sorption models, Langmuir and Freundlich have been used.

Langmuir Isotherm

The most widely used isotherm equation for modelling of the sorption equilibrium data is the Langmuir two parameters equation (Langmuir 1916) (Eq. 1):

$$Q = \frac{q_0 \cdot K_L \cdot C}{1 + K_L \cdot C} \quad (1)$$

where q is the amount of cation sorbed per unit of sorbent at equilibrium (mmol/g); C is the equilibrium concentration of cation remaining in the solution (mmol/L) and q_0 and K_L are the Langmuir constants related to the sorption capacity and energy of sorption, respectively.

The Langmuir isotherms for Zn (II) cation sorption on the fibrous sorbent under study at three different temperatures are shown in Fig.5.

The validity of the Langmuir equation assumes that the uptake of Zn (II) ions on hemp occurs via formation of a monolayer coverage of the sorbate at the outer surface of the sorbent without any interaction between the sorbed ions.

The Langmuir equation can be linearized as follows:

$$\frac{1}{q} = \frac{1}{q_0} + \frac{1}{K_L \cdot C} \quad (2)$$

The linear form can be used for the linearization of experimental data by plotting $1/q$ against $1/C$.

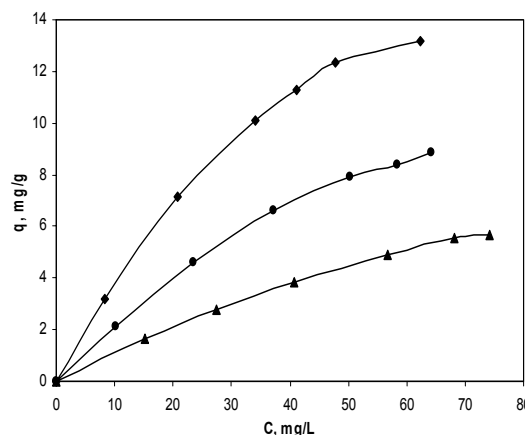


Fig.5. Langmuir isotherms for Zn(II) retention on natural hemp at different temperatures($t= 4^{\circ}\text{C}$ (\blacktriangle); $t= 50^{\circ}\text{C}$ (\blacklozenge); $t= 20^{\circ}\text{C}$ (\circ); hemp dose= 0.25g; pH=5)

The Langmuir constants can be evaluated from the slope and the intercept of linear equation. Table 3 characterized the Zn (II) sorption on hemp fibers at three different temperatures by means of Langmuir constants

Table 3. Description of Zn (II) sorption on hemp by means of Langmuir constants

T, K	q_0		K_L (L/mol)
	mmol Zn(II)/g hemp	mg Zn(II)/g hemp	
277	0.2545	16.54	474
293	0.3238	21.047	734.05
323	0.3754	24.401	1351.7

It is significant from Table 3 that the hemp is a reasonable sorbent for Zn (II) removal from aqueous solutions. The low values for the maximum capacity of sorption, q_0 (maximum amount of sorbed ion required to give a complete monolayer on a surface) are in good agreement with literature data reporting the retention of Cr(III), Cu(II), Ag(I) and Cd(II) ions on natural hemp (Paduraru, 2002; Tofan, 2000).

In this context, our attention has been focused on the improvement of hemp sorption capacity by physical and chemical treatment (Tofan, 1999; Tofan et al., 2001a; Tofan et al., 2001b; Tofan, 2004).

K_L is a measurement of relative sorption affinity being the Langmuir constant related to the energy of sorption. Its high values recorded in Table 3 involve strong bonds between sorbed Zn (II) ions and hemp.

Freundlich isotherm

The Freundlich isotherm is represented by Eq. (3) (Gupta et al., 2006):

$$\lg q = \lg K_F + (1/n) \lg C \quad (3)$$

where q is the amount of cation sorbed per unit gram of sorbent at equilibrium; C is the cation

concentration left in solution at equilibrium; K_F (sorption capacity) and n (sorption intensity) are the Freundlich constants. If the sorption is favorable, then the ratios $1/n < 1$ or $n > 1$, means that the forces within the surface layer are repulsive.

The plots of Equation (3) for the sorption of the tested cation on fibrous hemp at three different temperatures are given in Fig.6.

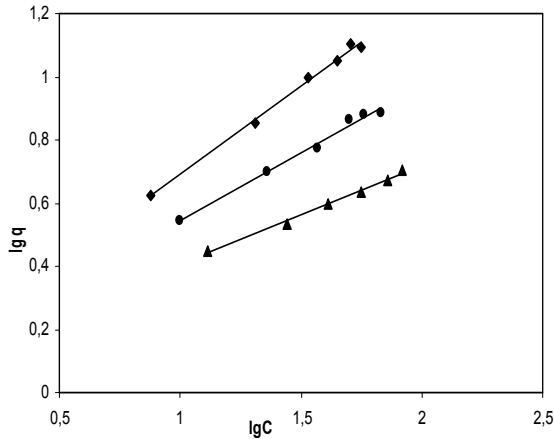


Fig. 6. Freundlich plots for sorption of Zn(II) ions by hemp fibers ($t= 4^{\circ}\text{C}$ (▲); $t= 50^{\circ}\text{C}$ (◆); $t= 20^{\circ}\text{C}$ (●); hemp dose= 0.25g; pH=5)

The linear plots in Fig. 6 point out that the Zn (II) – natural hemp sorption system may be modeled by means of the Freundlich isotherm, too. Table 4 records the K_F and n values derived from the slope and the intercept of the linear Freundlich plots recorded in Fig.6.

Table 4. Freundlich constants characteristic to the Zn (II) retention on hemp fibers at different temperatures

T, K	n	K_F
323	1.78	1.34
293	2.33	1.30
277	3.13	1.23

As follows from Table 4, the values of $n > 1$ indicated that the sorption capacity is only slightly suppressed at lower equilibrium concentrations. Saturated fibrous hemp with sorbed Zn(II) ions was no evident by this isotherm; thus infinite coverage is predicted mathematically, indicating multilayer sorption on the surface (Tsai et al., 2005).

3.5. Goodness of models fit

To compare the Langmuir and Freundlich isotherm models, the experimental data have been statistically processed by linear regression. The regression equations of $y = ax + b$ type and the obtained values of the correlation coefficient, R^2 , are given in Table 5. Obviously, it can be seen that the obtained data fit better to the Langmuir model than the Freundlich model (higher values for R^2).

3.6. Effect of temperature and thermodynamic parameters

The temperature has a favorable effect within the batch sorption systems under study (Figures 5 and 6). Both Langmuir and Freundlich constants increase with increasing temperatures, showing that the capacity of sorption and sorption intensity are enhanced at higher temperatures. In order to evaluate the thermodynamic feasibility of the Zn (II) sorption process on hemp, the thermodynamic parameters, free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) have been calculated. On the basis of the values of Langmuir constants, K_L , at different temperatures, the following equations have been used (Hasany et al. 2002):

$$\Delta G = RT \ln K_L \quad (4)$$

$$\ln K_L = \text{constant} = -\Delta G/RT \quad (5)$$

$$\Delta S = (\Delta H - \Delta G)/T \quad (6)$$

where R is the gas constant and T is the absolute temperature.

The values obtained by equations (4-6) application are recorded in Table 6.

At all working temperatures, the ΔG values are negative, showing the spontaneous nature and the feasibility of Zn (II) sorption on hemp fibers. The positive values of ΔH indicate that the Zn (II) sorption on hemp is an endothermic process, favored by temperature increasing. For ΔS a positive value has been obtained, suggesting an increased randomness at the interface of hemp – solution and affinity of the natural hemp for Zn (II) ions.

3.7. Effect of contact time of phases

Fig. 7 illustrates the influence of contact time on the Zn (II) retention from solutions with initial concentration of 80 $\mu\text{g}/\text{mL}$ and initial pH = 5 by natural hemp. It can be seen from Fig. 7 that the Zn(II) amounts retained on hemp increase with contact time of phases increasing. Usually, the kinetic data are treated with the aid of Lagergren equation (7):

$$\lg(q_e - q_t) = \lg q_e - k' t / 2.303 \quad (7)$$

where:

q_e and q_t are the amounts of Zn(II)(mg/g) sorbed at equilibrium and at any time(t), respectively and k' is the constant rate of sorption (min^{-1}).

The kinetic parameters derived from the linear Lagergren plot of $\lg(q_e - q_t)$ against t are listed in Table 7. The data from Table 7 point out that the Zn(II) sorption process on hemp is of pseudo – first order with respect to the concentration.

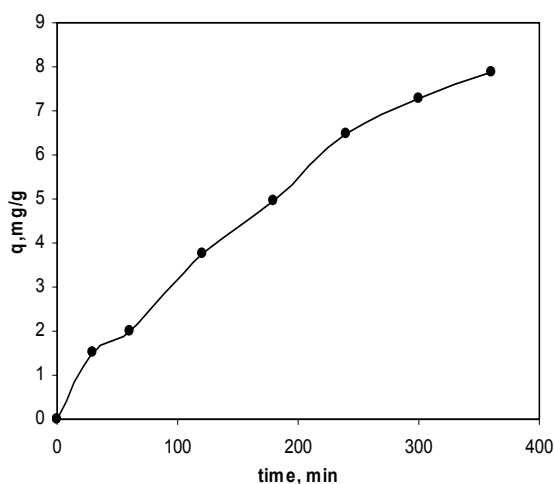
Table 5. Statistical analysis

T, K	Langmuir isotherm		Freundlich isotherm	
	Linear regression equation	R ²	Linear regression equation	R ²
323	y = 3.9281x + 8.2659	0.9988	y = 0.5611x + 0.1283	0.9945
293	y = 3.0876x + 4.2063	0.9973	y = 0.429x + 0.1147	0.9891
277	y = 2.6634x + 1.9705	0.9976	y = 0.3125x + 0.0933	0.9925

Table 6. Thermodynamic characterization of the sorption process of Zn (II) on natural hemp

T, K	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (J/mol.K)
278	- 14.183		112
293	- 16.066	16.98	112
323	- 19.350		112

The results obtained in this study are significant for future development of the natural hemp into beneficial material for environmental applications.

**Fig. 7.** The effect of contact time of phases on the Zn(II) – natural hemp batch sorption system (hemp dose=0.25g; pH=5)**Table 7.** Kinetic description of the Zn(II) sorption process by means of Lagergren equation

t, min	lg (q _e - q _t)	Linear regression equation	R ²
30	0.82	y = -0.0029x + 0.9423 q _e = 8,56 k' = 6,678x10 ⁻³ min ⁻¹	0.9963
60	0.75		
120	0.59		
180	0.44		
240	0.26		
300	0.085		
360	-0.052		

4. Conclusions

Natural hemp exhibits reasonable sorption properties with potential applicability in removal/recovery of Zn (II) ions from wastewaters. In the studied initial pH range of 2-5 the sorption increases with pH increasing. The highest Zn (II) retained

amount (4.75mg/g) is reaching at initial pH=5 from unbuffered solutions. The values of the sorption percentage increase with increasing hemp dose.

The amount of Zn(II) retained on the hemp fibers increase with increasing Zn(II) concentration in initial solution, but the sorption percentages decrease.

The Langmuir and Freundlich isotherms were used to model the sorption equilibrium. The results indicated that the Langmuir model has a better correlation with the experimental data than the Freundlich model. The values obtained for the thermodynamic parameters point out the spontaneous and endothermic nature of the Zn (II) sorption process, favoured by temperature increasing.

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ENVIRONMENTAL ASSESSMENT LABORATORY

The Environmental Assessment Laboratory was founded in 2006, within a project financed by the INFRA TECH Program, administrated by the Ministry of Education and Research.

The laboratory operates as a part of Tehnopolis Science and Technology Park Iasi – a consortium having our Technical University “Gh. Asachi “ of Iasi as partner.

The laboratory is staffed by some members of the Environmental Engineering and Management Department of the Faculty of Chemical Engineering and Environmental Protection (Technical University “Gh. Asachi “of Iasi).

With a rich expertise in environmental engineering and management, the staff is especially competent in:

- Environmental monitoring
 - Specialized in complex environmental analysis such as the identification and quantification of organic pollutants (VOC, POPs, pesticides, PCBs etc.) from air, water and soil;
- Environmental impact assessment;
- Risk assessment
- Environmental consulting (Environmental permitting, Quality management certification for ISO 14.001, Emission reduction plan for VOC; Solvent management plan);

The research activity of the group members is illustrated by:

- More than 100 scientific articles, published in well-known national and international (ISI);
- More than 45 national and international patents;
- Books published in Romania (publishers accredited by CNCSIS) and abroad;
- PhD thesis approaching new and original topics in environmental engineering and management;
- Centers of excellence in research
- International collaborations (within programs such as PHARE, EcoLinks, or financed by German Ministry for Education and Research, Swiss Science Foundation, Swedish Institute Stockholm etc)

During the last decade of activity, the members of the laboratory have participated in more than 200 research contracts with the industry, on different activities:

- Environmental permitting;
- Integrated pollution prevention and control;
- Technical Inspection Certificates for VOC (according to H.G. 568/2001), being one of the six accredited laboratories in the country);
- VOC emission reduction schemes (H.G. 699/2003)
- Other projects concerning the cleaning or depollution of different industrial effluents and streams.

Facilities and Equipments

The laboratory is being organized according to the requirements of the Quality management system ISO /IEC 17025:2000 “General requirements regarding the competence of the testing and calibration laboratories”.

The main equipments used in the laboratory, fully compliant with international standard methods, are:

- High resolution GC-MS with hyperbolic quadrupole mass analyzer (Agilent)
- Thermal desorber (Markes International)
- High precision analytical balances
- Ovens, automatic pipettes etc

In addition to the classical GC-MS/FID methods, our laboratory is especially interested in using the analytical thermal desorption methods for the measurement of trace level volatile and semi-volatile organic chemicals (VOCs and SVOCs). It is the technique of choice for air monitoring (indoor, outdoor, workplace, automobile interior, breath, etc.) and is an invaluable tool for the analysis of soil, polymers, packaging materials, foods, flavors, cosmetics, tobacco, building materials, pharmaceuticals, and consumer products. Indeed, virtually any sample containing volatile organic compounds can be analyzed using some variation of this technique.

In this context, we are opened for collaboration with scientific institutions in the areas covered by our laboratory.

Cezar Catrinescu

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REMOVAL OF ACID RED 398 DYE FROM AQUEOUS SOLUTIONS BY COAGULATION/FLOCCULATION PROCESS

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Abstract

The removal of Acid Red 398 (AR398) dye from dye-containing solution using coagulation/flocculation process with polyaluminum chloride (PAC) and Alum was investigated. The effect of different parameters involving pH, dosage of coagulant, initial dye concentration, and bentonite as a natural coagulant aid was examined. According to the obtained results, the optimum pH, at which the maximum removal occurred, was about 4 and 5 for PAC and Alum, respectively. However, PAC performed efficient in a broader pH range. In the case of PAC, the best removal efficiency was about 80% for the dosage of 100-120 mg/l, while, it was about 60% for 140-160 mg/l of Alum. With the increase of initial dye concentration in the range of 25-250 mg/l, the removal efficiency for both coagulants increased at first (from 25-100 mg/L) and then declined. Bentonite, as a coagulant aid, slightly enhanced the removal efficiency. By adding 20 mg/l of bentonite, the efficiency increased by 15% and 9% for Alum and PAC, respectively.

Keywords: Acid Red 398, Coagulation/Flocculation, Dye Removal

1. Introduction

Dyes are widely used in many industries such as textile, rubber, paper, plastic, cosmetic etc. Among them, textile ranks first in usage of dyes (Saiful Azhar et al., 2005). Presently, more than 10,000 of different commercial dyes and pigments are available (Eren and Acar, 2006; Ozer et al., 2006), and more than 7×10^5 tons per year are produced world wide (Crini, 2006; Saiful Azhar et al., 2005). Two percent of dyes that are produced are discharged directly in aqueous effluents (Crini, 2006). These colored compounds are not only aesthetically displeasing, but they also impede light penetration, retard photosynthetic activity and inhibit the growth of biota. Some dyes are also toxic and carcinogenic (Eren and Acar, 2006). Presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Crini, 2006). Therefore it is necessary to eliminate dyes from wastewater before it is discharged.

Since dye compounds are specifically designed to be recalcitrant with poor biodegradability, they are very stable and difficult to degrade by conventional aerobic biological treatments, such as activated sludge process. Thus, they are usually treated by physico-chemical processes (Ozer et al., 2006; Shi et al., 2007).

Coagulation/flocculation is one of the most popular unit operations in water and wastewater treatment trains. Also it is one of the most effective chemical treatment methods for dye removal from industrial wastewaters (Gao et al., 2007; Golob et al., 2005).

In this work, the removal efficiency of Acid Red 398 dye was investigated using PAC and Alum as coagulants.

The study focused on the effect of different parameters such as pH, coagulant dosage, initial dye concentration and bentonite (as a coagulant aid) on the dye removal efficiency.

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2. Materials and methods

In this study, commercial grades of PAC (30% w/w Al₂O₃) and Alum (17% w/w Al₂O₃) were used. All experiments were performed at laboratory scale. Synthetic wastewater was prepared by dissolving Acid red 398 (AR398, trade name: Erionyl Red BL), which was provided by Ciba Company. This dye is widely used in textile industries in Iran. Stock dye solutions of 1000 mg/l were prepared and then diluted using deionized water to obtain desired concentrations. pH of the synthetic wastewater was adjusted with H₂SO₄ and NaOH solutions. Bentonite was sieved by 75 µm sieve. The particles under 75 µm were used in further experiments.

The effects of various parameters were determined by jar test procedure. A period of 2 min was allowed for the rapid mixing of the dye containing solutions at 200 rpm followed by a 10 min period of slow mixing at 30 rpm. Then, the solutions were allowed to settle for 45 min. After settling, samples for measurement of dye concentration were withdrawn using a pipette from a height of 2-3 cm below the surface in each jar. The maximum absorbance (λ_{max}) of the dye with the background of deionized water was 504 nm, which was determined according to scanning pattern performed on HACH spectrophotometer DR/4000. Percentage of dye removal was calculated by Eq. (1):

$$\text{dye removal (\%)} = \frac{C_r - C_t}{C_r} \times 100 \quad (1)$$

where, C_r and C_t are the dye concentration in raw and treated solutions, respectively.

3. Results and discussion

3.1. Effect of pH on the removal of AR398 dye

pH plays an important role in coagulation/flocculation process using inorganic coagulants. Charge on hydrolysis products and precipitation of metal hydroxides are both controlled by pH variations. Thus, pH must be controlled to establish optimum conditions for coagulation (Li and Gregory, 1991). To study the effect of pH on AR398 dye removal efficiency, dosages of PAC and Alum were kept constant at 100 mg/L, while varying pH of the samples using H₂SO₄ and NaOH. Dye concentration was 100 mg/l for all solutions during the experiment.

As shown in Fig. 1, removal of AR398 dye was absolutely dependent on the pH variations. The optimum pH, at which the maximum removal occurred, was about 4 and 5 for PAC and Alum, respectively. However, PAC was effective in a broader pH range relative to Alum. In the other words, the performance of Alum was more sensitive to the pH variations. This is in consistent with the findings reported by some other researchers. (Jiang, 2001; Ye et al., 2007).

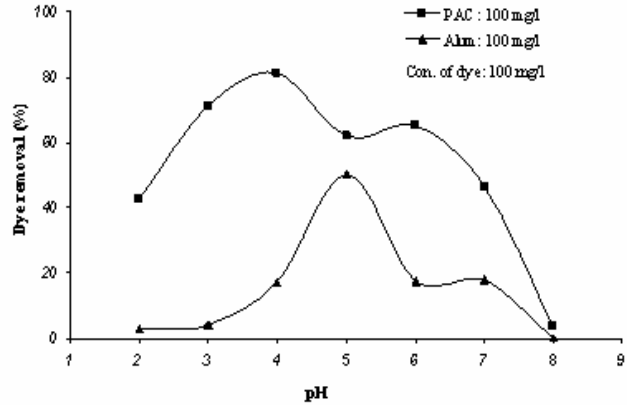


Fig. 1. Effect of pH on the removal of AR398 dye with PAC and Alum

3.2. Effect of the coagulants concentration

In this step, to study the effect of coagulant dosage on dye removal efficiency, different amounts of PAC and Alum were dosed into the dye-containing solutions. Dye concentration was kept constant at 100 mg/l and pH was adjusted to 4 and 5 (optimum pH) for PAC and Alum, respectively. The variations of the dye removal with coagulants dosage are shown in Figure 2.

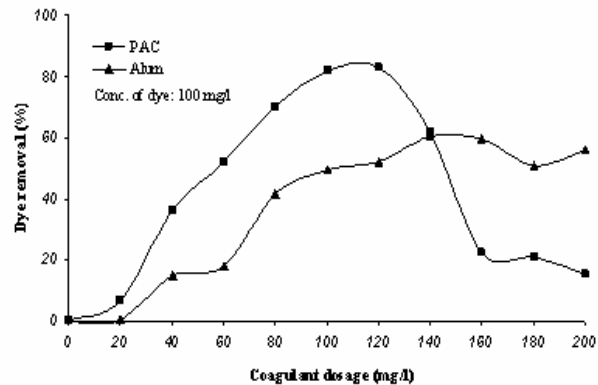


Fig. 2. Effect of coagulant dosage on the removal efficiency of AR398 dye, pH: 4 for PAC; 5 for Alum

According to the results, with the increase of the coagulants dosage, the removal efficiencies increased at first (from 0 to 120 mg/L) for both of the coagulants. However, the efficiencies were much higher for PAC. For the dosages more than 120 mg/l, the curve relatively approached plateau for Alum, while, for PAC, the efficiency decreased rapidly which was probably due to re-stabilization phenomenon.

3.3. Effect of initial dye concentration

This step was performed to determine the influence of initial dye concentration on dye removal efficiency, using a constant coagulant dosage (100

mg/L for PAC, and 140 mg/L for Alum, the dosages which led to the maximum dye removal).

In addition, the variations of the amount of the removed dye per unit mass of coagulant (Q), versus the initial dye concentration are presented. The results are illustrated in Fig. 3.

For PAC, with the increase of initial dye concentration from 25 mg/L to 100 mg/L, the removal efficiency increased dramatically from 14% to about 81%. While, for dye concentrations more than 100 mg/L, the efficiency decreased and reached to about 37% for the dye concentration of 250 mg/L. The highest value of Q was 1.3 mg dye/ mg PAC for the dye concentration of 200 mg/L. (Fig. 3(a)).

In the case of Alum, the curves relatively showed similar changing trends. However the values of the removal efficiency and the Q were superior for PAC. The largest value of the Q (0.7 mg dye/ mg Alum) was observed for initial dye concentration of 200 mg/l, while the highest removal efficiency was 60% for dye concentration of 100 mg/L (Fig. 3b).

Little data was found in literature to compare the influence of dye concentration on coagulation efficiency. According to the data of Klimiuk group, at the optimum coagulant (polyaluminum chloride)

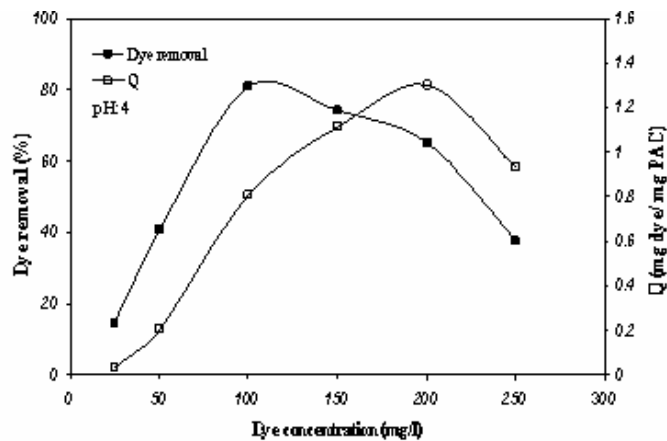
dosage, the removal degree (the amount of the removed dye per unit mass of Al) was associated with the initial concentration of the selected dyes, and the smallest removal degree was obtained for smallest concentrations of the dyes (Klimiuk et al., 1999).

This result is in consistent with the results obtained for PAC and Alum in this study, which showed the smallest values of Q for dye concentrations of 25 and 50 mg/L.

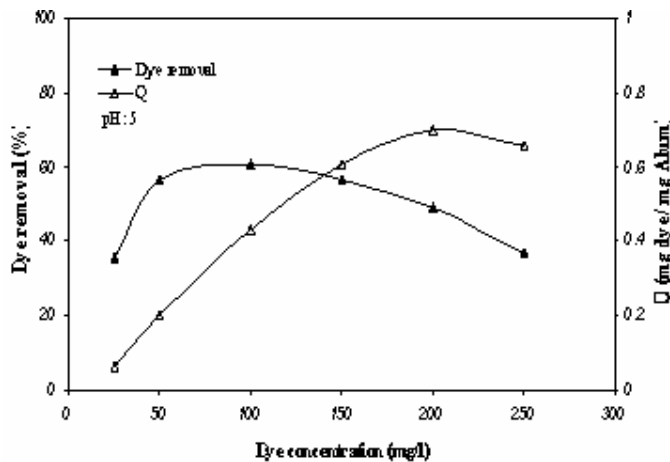
3.4. Effect of addition of bentonite as a coagulant aid

Coagulant aids such as activated silica, clay and polyelectrolytes are used in coagulation/flocculation process, usually to obtain higher efficiency, to reduce the amount of required coagulant, and to form stronger and more settleable flocs (AWWA, 2003).

In this step, the effect of bentonite as a natural coagulant aid on AR398 dye removal efficiency was investigated. The experiments were conducted under two selected dosage levels for both coagulants (60 mg/L and 80 mg/L), with different concentrations of the coagulant aid. The results are shown in Fig. 4.



a)



b)

Fig. 3. Effect of initial dye concentration on dye removal efficiency and Q for: (a) PAC, (b) Alum

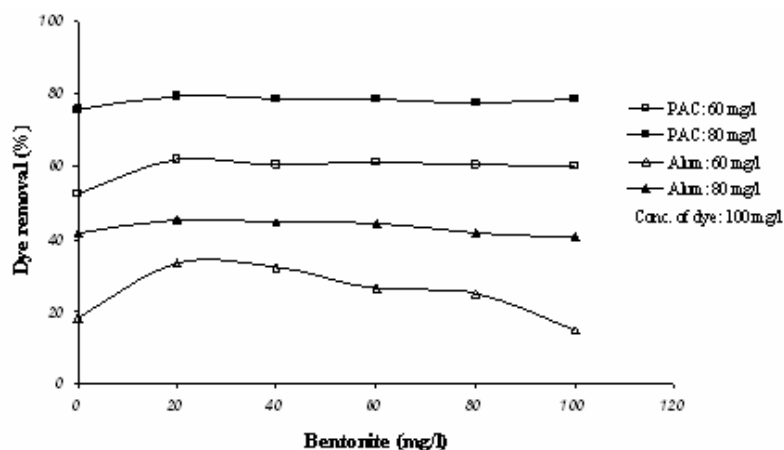


Fig. 4. Effect of bentonite on AR398 dye removal efficiency, pH: 4 for PAC; 5 for Alum

By adding bentonite to the coagulation/flocculation process, the dye removal efficiencies increased slightly. When the coagulants concentration was 60 mg/L, with the aid of 20 mg/l of bentonite, the removal efficiency increased from 18% to about 33% for Alum, and from 52% to 61% for PAC. No significant change was observed when the coagulants concentration was 80 mg/L.

According to the reports of other researchers, in some cases coagulant aids positively affected on dye removal and in some others, they acted reversely and reduced the removal efficiency. For example, Nabi Bidhendi group reported that Polyelectrolyte did not have any positive effect on dye removal with Alum and $MgCl_2$ (Nabi Bidhendi et al., 2007). Also, Joo group found that with Alum alone, dye removal efficiency was 20% or less, while it increased to 99% with the aim of 150 mg/l of a synthetic polymer (Joo et al, 2007).

4. Conclusions

In this study, the following conclusions were drawn:

- Removal of AR398 dye was absolutely pH dependent. The maximum removal efficiency occurred when the pH was about 4 and 5, for PAC and Alum, respectively.
- PAC performed more efficient than Alum and removed the dye with higher efficiencies. However, for the dosages more than 120 mg/l, a removal reduction or re-stabilization phenomenon was happened for PAC.
- With the increase of initial dye concentration (in the range of 25 to 250 mg/L), both coagulants showed similar changing trends, however, the values of the removal efficiency and the Q were higher for PAC.
- By adding bentonite as a coagulant aid, the removal efficiency of AR398 dye increased slightly. For the coagulants concentration of 60 mg/l, by adding 20 mg/l bentonite, the removal efficiency

increased by 15% and 9% for Alum and PAC, respectively.

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INTERDISCIPLINARY TRAINING AND RESEARCH PLATFORM

HIGH PERFORMANCE MULTIFUNCTIONAL POLYMERIC MATERIALS FOR MEDICINE, PHARMACY, MICROELECTRONICS, ENERGY/INFORMATION STORAGE, ENVIRONMENTAL PROTECTION

The Platform aims to develop **training and interdisciplinary research in high-performance multifunctional polymeric materials**. The nucleus of the Platform is based on the **Center of Excellence POLYMERS**, officially accredited by CNCIS (7.06.2003), center acting within the “Gh. Asachi” Technical University of Iasi.

The Platform will be *integrated in national/European networks* and will ensure the *training and improvement of human resources through high education and research*, will *enhance the research performance and the visibility* of Romania, will contribute to *Romanian high education and research integration in European Education Area and European Research Area*, to the *development of the knowledge-based society* and will increase the *socio-economic impact of research*.

To ensure the success of the Project, a set of **specific objectives** has been defined:

- *New educational programmes*, oriented towards *European priorities*, able to ensure highly qualified human resources and to integrate them into the knowledge-based modern society
- *New contents, forms and methods of training*, specific for the development of education and research in multifunctional polymeric materials and in agreement with *Lisbon Agenda* and with *Bologna Process*, as well as with *Romanian priorities*
- Elaboration and implementation of *interdisciplinary programmes of training (master, doctoral, post-doc)*
- *Consolidation of excellence in research* in the field of high performance multifunctional materials by promoting interdisciplinary programmes and by attracting the most talented graduates – from Romania and abroad – for PhD and post-doc studies
- *Extension and consolidation of the research infrastructure (hard equipment)* of the Platform, to improve the training and research process, in order to *increase Platform competitiveness in accessing national (CNCIS, CEEX, PNCDI 2) and international (FP7, NATO, NSF etc.) programmes* and the efficiency in answering the requirements of the regional, national and European economic areas
- *Strengthening the scientific cooperation* with academic and economic partners at national and European level
- *Promoting the exchange of information and communication* between the academic and socio-economic environments, to consolidate the knowledge-based society and to accelerate the integration of Romania into the European Union.

The Project will develop **(i) education activities** through **(i-a) master studies** (two directions are proposed – **Biomaterials** – addressed to graduates of chemistry, chemical engineering, medical bioengineering, biology, medicine, pharmacy – and **Multifunctional Materials for**

Advanced Technologies, addressed to graduates of chemistry, chemical engineering, medical bioengineering, physics, electronics and electrical engineering, civil engineering, environment protection; *both master programmes will be in Romanian and/or English*), **(i-b) doctoral studies** with a pronounced interdisciplinary character and implemented within the “*co-tutelle*” system, **(i-c) post-doc studies** (financed from other programmes), and **(ii) research activities** developed within five programmes, i.e., **(ii-a) Biomaterials. Polymer-drug Systems with Controlled and Targeted Release** (polymer-drug conjugates, diffusional systems, drug inclusion in polymeric micro- or nanoparticles), **(ii-b) Smart Multifunctional Polymeric Materials** (molecular imprinting, diagnostics and bioseparation, nanocapsules and nanostructured membranes *via* core-shell particles, smart hydrogels and nanostructured gels, biomimetic polymeric networks, nanofabrication), **(ii-c) Motile Molecular Systems** (hybrid and organic polymers for biology, microelectronics, nanorobotics and energy/information storage), **(ii-d) Liquid Crystal Hetero-organic and Organic Compounds** (liquid crystals for displays, opto-electronic devices, ferro-electric liquid crystals), **(ii-e) Molecular Modeling and Artificial Intelligence** (conformational analysis and simulation of properties, neuronal networks, fuzzy systems).

All planned activities and actions are based on a **deep analysis of the tendencies in the interdisciplinary education and research**, on the **requirements of the national and European market**.

Most of Platform budget is dedicated to the serious improving of the **research infrastructure (hard equipments)**. *Additional funding and expertise* will be obtained through the facilities offered by the “Gh. Asachi” Technical University of Iasi, the infrastructure and human resources of the POLYMER Centre of Excellence, through the facilities offered by the *traditional national and European partners of the Platform*. **Platform sustainability** will be ensured by different funding attracting activities – **training of specialists from SMSs, consulting activities, national and international grants**, the **RENAR accredited laboratories**, the **Technology Transfer Center** and the **Innovation Relay Centre** established within the Platform, the *specific activities* to be performed within the **Science and Technology Park** in Iasi.

The benefits of the Platform will cover the whole high education and research environment in Iasi and in the North-Eastern Region of Romania and all Platform partners – both academic and economic.

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EFFECT OF VANADIUM REPLACEMENT BY ZIRCONIUM ON THE ELECTROCHEMICAL BEHAVIOR OF Ti6Al4V ALLOY IN RINGER'S SOLUTION

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Abstract

The electrochemical behaviour of Ti6Al4V and Ti6Al4Zr alloys has been evaluated in Ringer's solution at 25°C. The effect of the substitution of vanadium in Ti6Al4V alloy has been specifically addressed. The evaluation of the corrosion resistance was carried out through the analysis of the open circuit potential variation with time, potentiodynamic polarization curves, and electrochemical impedance spectroscopy (EIS) tests. Very low current densities were obtained (order of nA/cm²) from the polarization curves and EIS, indicating a typical passive behaviour for both investigated alloys. The EIS results exhibited capacitive behaviour (large corrosion resistance) with phase angle close to -80° and high impedance values (order of 10⁵ Ω cm²) at low and medium frequencies, which are indicative of the formation of a highly stable film on these alloys in Ringer's solution. In conclusion, the electrochemical behaviour of Ti6Al4V is not affected on substituting vanadium with zirconium.

Key words: current corrosion, impedance, polarization, Titanium alloys

1. Introduction

Commercial titanium and titanium alloys are used on a large scale in medical applications as implants to restore lost functions or replace organs functioning below acceptable levels, due to their advantages as compared with other similar materials: chemical inertia, low densities, toxicity absence and higher biocompatibility (Assis et al., 2006; Eriksson et al., 2007; Kim et al., 2007; Mantani and Tajima, 2006; Newman et al., 1988; Taddei et al., 2004).

The physical metallurgy of titanium shows that it undergoes an allotropic transformation at about 885°C, changing from a close-packed hexagonal (c.p.h.) crystal structure (i.e. alpha phase) to a body-centred cubic (b.c.c.) crystal structure (i.e. beta phase). Alloying elements are known to either lower or raise the transformation temperature. Depending on their microstructure, titanium alloys fall into five categories: alpha, near-alpha, alpha-beta, near-beta or beta. Each of these denotes the general type of microstructure present after heat treatment and

processing (Boyer and Gall, 1985; Collings, 1984; Donachie, 1988). Substitutional alloying elements play an important role in controlling the microstructure and properties of titanium alloys.

Vanadium and niobium are beta amorphous with b.c.c. titanium (Boyer and Gall, 1985). Zirconium is one that is unique in that it is isomorphous with both the alpha and beta phases of titanium (Donachie, 1988). Beta isomorphous elements are preferred since they do not form intermetallic compounds. The aluminium continues to fulfil its role as a useful alpha phase stabilizer, and thus, maintain the improved mechanical properties over pure titanium.

Ever since the pioneer metal alloys have been used as biomaterials, lack of biocompatibility has been extensively reported and research on improved materials with appropriate mechanical behaviour and adequate biocompatibility was developed. The Ti6Al4V alloy was the first titanium alloy registered as implant material in the ASTM standards (F-136-84). Further studies have indicated that vanadium,

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used to stabilize the beta-phase, produces harmful oxides for the human body (Hallab et al., 2005; Okazaki et al., 1998). The toxicity of vanadium pushed forward the search for materials to replace Ti6Al4V.

Ti, Nb, Zr, Pd and Ta are low cytotoxic elements (Okazaki et al., 1998). The Ti6Al7Nb alloy was developed using the alloying element niobium to replace vanadium in the Ti6Al4V alloy. It has been suggested by Khan et al., (1996) that Ti6Al7Nb alloy can be a better alternative to Ti6Al4V alloy because of its corrosion resistance and resistance to loss of mechanical properties with changes in pH in simulated body fluid environment.

Electrochemical behaviour of the implant materials in physiological medium is necessary to access the nature of the passive film formed and its role in biocompatibility.

Electrochemical behavior of the pure titanium and several (alpha + beta) titanium alloys in Ringer's solution was the subject of a number of prior investigations (Gonzalez and Mirza Rosca, 1999; Kuphasuk et al., 2001; Mirza Rosca et al., 2008; Popa et al., 2004).

In the present study, the electrochemical and corrosion behaviour of Ti6Al4V alloy has been compared with that of Ti6Al4Zr alloy in which vanadium was replaced with zirconium.

2. Materials and methods

2.1. Materials and sample preparation

The Ti6Al4V and Ti6Al4Zr alloys used in present investigation were acquired in form of a rod from National Institute of Research & Development for Non-ferrous and Rare Metals, Bucharest, Romania. The both alloys were submitted to a semi-quantitative chemical analysis by plasma optical emission spectrometry technique and its results are given in Table 1.

The testing medium was an aerated Ringer's solution whose composition is: NaCl – 8.6 g/L, KCl – 0.3 g/L, CaCl₂ – 0.48 g/L.

The pH was measured with a multiparameter analyzer CONSORT 831C. The pH of this reference solution was 6.1.

The titanium samples were cut into 1 cm² size and brass nut was attached to each experiments using conductive paint to ensure electrical conductivity. The assembly was then embedded into an epoxy resin disk. Then the samples were ground with SiC abrasive paper up to 1000 grit, final polishing was done with 1 µm alumina suspension.

The samples were degreased with ethyl alcohol followed by ultrasonic cleaning with deionised water and dried under a hot air stream.

2.2. Microstructure characterisation

The structural studies were performed with an optical microscope, Olympus PME 3-ADL. The microstructures were revealed by etching in 10%HF + 5%HNO₃ solution for 3-5 s at 25°C.

2.3. Potentiodynamic polarization studies

For all the electrochemical tests, experiments were performed using an aerated Ringer's solution maintained at 25 ± 1°C as an electrolyte. The assembled specimen was placed in a glass corrosion cell, which was filled with freshly prepared electrolyte (within 24 hours). A saturated calomel electrode (SCE) was used as the reference electrode and a platinum coil as the counter electrode.

The measurements were performed with a Princeton Applied Research potentiostat (Model 263 A) controlled by a personal computer and a dedicate software (PowerCorr, Princeton Applied Research).

For each specimen, 24 hours of open circuit potential, E_{OC}, measurement was performed initially followed by the linear polarization measurement. Linear polarization was conducted from E_{OC} -150 mV to E_{OC} + 150 mV at a scanning rate of 0.2 mV/s, to identify the *b_a* (Tafel slopes for the partial anodic processes) and *b_c* (Tafel slopes for the partial cathodic processes), the *i_{corr}* (corrosion current density) and the ZCP (zero current potential). It was then followed by the general polarization tests from -600 mV to 1200 mV at a scanning rate of 0.5 mV/s for evaluating the stability of passivation. From the obtained anodic polarization curves, *i_{pass}* (passivation current density) was determined.

2.4. Electrochemical Impedance Spectroscopy studies (EIS)

The electrochemical impedance spectroscopy (EIS) was performed 24 hours after immersion in aerated solutions at the open circuit potential using a Princeton Applied Research potentiostat (Model 263 A) connected with a Princeton Applied Research 5210 lock-in amplifier.

The spectra were recorded in the 10⁻² Hz to 10⁵ Hz frequency range. The applied alternating potential signal had amplitude of 10 mV.

Table 1. Alloys composition determined by plasma optical emission spectrometry technique

Element	Al	V	Zr	Fe	O ₂	N ₂	C	Ti
Ti6Al4V Weight %	5.88	3.91	-	0.021	0.175	0.0153	0.048	balance
Ti6Al4Zr Weight %	6.01	-	4.05	0.032	0.198	0.0184	0.065	balance

Data acquisition and analysis were performed with a personal computer. The spectra were interpreted using the ZSimpWin program. Impedance data were represented in both complex impedance diagram (Nyquist plot) and Bode amplitude and phase angle plots. In the Nyquist graph, the imaginary component of the impedance is plotted as a function of the real component, whereas the Bode representation shows the logarithm of the impedance modulus (Z_{mod}) and phase angle as a function of the logarithm of the frequency. The advantage of the Bode plot is that the data for all measured frequencies are shown and that a wide range of impedance values can be displayed.

Surface morphology after the electrochemical treatments of the samples was studied with a research electronic microscope of Tesla BS 300 type.

3. Results and discussion

3.1. Microstructural characterization

Surfaces of the three alloys exposed at electrochemical testing were characterized from the structural point of view. Both the samples exhibit a biphasic (α - β) microstructure, but with different morphology. The Ti6Al4V alloy has a Widmanstätten-type structure that consists of α -phase lamellae. The optical images from Fig. 1A show basket weave morphology of α -phase regardless of chemical compositions of titanium alloy. The Ti6Al4Zr alloy has an isotropic structure.

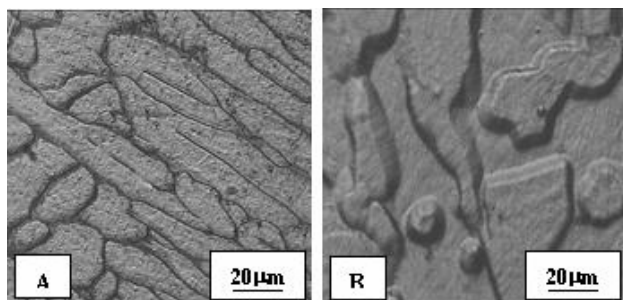


Fig. 1. Micrographs for: (A) Ti6Al4V and (B) Ti6Al4Zr alloys

3.2. Potentiodynamic polarization studies

Fig. 2 shows the E_{OC} curves for both stationary samples immersed in Ringer's solution at 25°C. The potential pattern with respect to time was similar for both alloys. Initially, the potential of the two titanium based alloys presents approximately the same value: -511 mV for Ti6Al4V and -521 mV for Ti6Al4Zr.

During the first moments of immersion, an abrupt E_{OC} displacement towards positive potentials was noticed in Fig. 2. This initial increase seems to be related to the formation and thickening of the oxide film on the metallic surface, improving its corrosion protection ability (Kedici et al., 1998). Afterwards,

the E_{OC} increases slowly suggesting the growth of the film onto the metallic surface. However, Ti6Al4Zr alloy showed nobler potential than Ti6Al4V alloy.

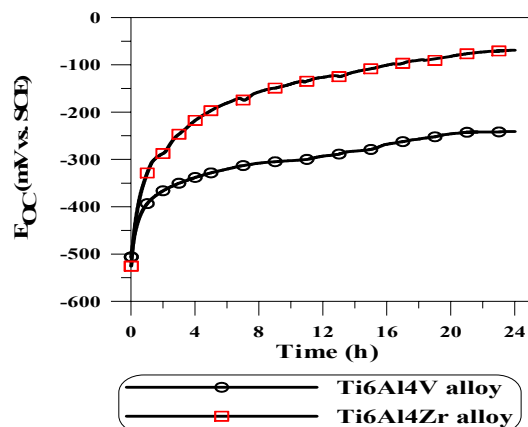


Fig. 2. Variation of open circuit potential (E_{OC}) with time for Ti6Al4V and Ti6Al4Zr alloys in Ringer's type solution

Standard techniques were used to extract zero current potential (ZCP) and corrosion current density (i_{corr}) values from the potentiodynamic polarization plots. The Tafel slopes (b_a and b_c) were determined by fitting the theoretical polarisation curve to the experimental polarisation curve plotted in a range of ± 150 mV vs. E_{OC} . The two Tafel slopes intercept at the point of the coordinates (ZCP, i_{corr}). In most of the aerated neutral solutions the corrosion rate is controlled by the oxygen diffusion at the surface of the electrode when $b_c \gg b_a$. This supposition is confirmed by the values presented in the Table 2. The corrosion current density (i_{corr}) is representative for the degradation degree of the alloy. The average values b_a , b_c , ZCP and i_{corr} from polarization curves determined by the PowerCorr program are presented in Table 2. The very low i_{corr} values obtained for both tested titanium alloys are typical of passive materials.

The corrosion current densities for both alloys were of the same order of magnitude (nA/cm^2): 210 nA/cm^2 for Ti6Al4V alloy and 195 nA/cm^2 for Ti6Al4Zr alloy.

Fig. 3 compares typical potentiodynamic curves in a semi-logarithmic version between -600 mV and +1200 mV of the titanium alloys tested in Ringer's solution aerated at 25°C after being immersed for 24 hours.

The nature of the potentiodynamic polarization curves indicated that Ti6Al4V and Ti6Al4Zr alloys have been passivated immediately after the immersion in the Ringer's solution; both materials translated directly from the "Tafel region" into a stable passive state, without exhibiting a common active-passive transition.

For the potentials above approximately 100 mV up to approximately 300 mV both anodic curves indicates behaviour typical of activation polarization showing a well defined linear range, suggesting conformity to the Tafel's Law.

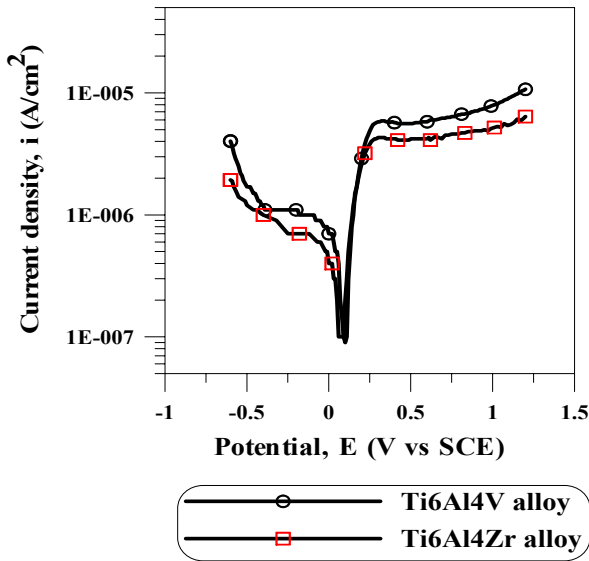


Fig. 3. The potentiodynamic polarisation curves for titanium alloys after 24 hours of immersion in Ringer's type solution

From 300 mV the curves show a passive behaviour. Passive current density (i_{pass}) was also determined from the potentiodynamic anodic diagram of each specimen in Ringer's solution. Passive current densities (i_{pass}) are obtained around the middle of the passive range and are listed in Table 2.

The passive current densities (i_{pass}) for both alloy samples are higher than corrosion current densities (i_{corr}) and suggest that the protective Ti oxide film can be more defective (Lavos-Valereto et al., 2004; Assis et al., 2006; Cremasco et al., 2008). From the polarization curves it was found that both alloys are maintained in their passive state at 1.2 V potential too. No breakdown was observed for Ti6Al4V and Ti6Al4Zr alloys.

No significant differences were found in ZCP, i_{corr} or i_{pass} for both the samples. The results indicate that the polarization curves behaviour of the Ti6Al4Zr alloy resembles that of the Ti6Al4V alloy. Ti6Al4Zr alloy had a good corrosion resistance within the potential range used in this study.

Fig. 4 shows the SEM image of Ti6Al4V alloy after the electrochemical treatments. After electrochemical treatments salt depositions were formed on the surface of the alloy.

The Ringer's solution contains calcium ion, which generally precipitates on titanium alloys surface.

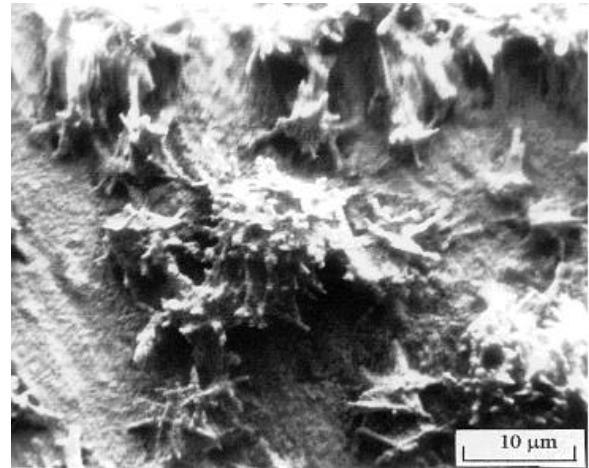


Fig. 4. The salts depositions on the surfaces of the Ti6Al4V alloy

3.3. Electrochemical impedance spectroscopy (EIS) studies

The corrosion resistance can also be estimated by means of the impedance method known as Electrochemical Impedance Spectroscopy (EIS). This technique requires minimal invasive procedures, neither the oxidation nor the reduction was forced to take place in the open circuit mode.

Fig. 5 showed the EIS data, in the form of Nyquist plot, of Ti6Al4V and Ti6Al4Zr alloys at open circuit potential, after 24 hours of immersion in Ringer's solution.

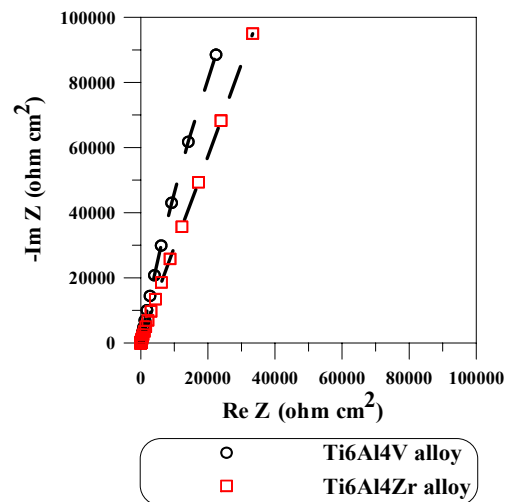


Fig. 5. Nyquist plots of Ti6Al4V and Ti6Al4Zr alloys at open circuit potential, after 24 hours immersion in Ringer's solution

Table 2. The main parameters of corrosion process after 24 h of immersion in Ringer's type solution

Alloy	ZCP (mV)	$b_a(mV dec.^{-1})$	$b_c(mV dec.^{-1})$	$i_{corr}(nA cm^{-2})$	$i_{pass}(\mu A cm^{-2})$
Ti6Al4V	88	85	∞	210	6.1
Ti6Al4Zr	96	82	∞	195	4.8

Both diagrams show a capacitive arc. The capacitive arc may be related with the dielectric properties of the formed film on the electrode surface at the open circuit potential but it may be also related to the electric double-layer capacitance at the electrode/solution interface, which includes a metal-film interface followed by a film-solution interface.

In the Fig. 6 for titanium alloys the EIS spectra are shown in Bode plots of the logarithm of impedance magnitude and of the phase angle as a function of the frequency's logarithm.

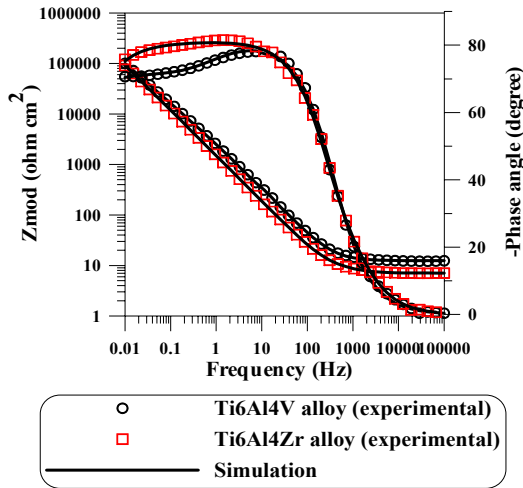


Fig. 6. Bode plots of tested materials recorded at open circuit potential after immersion for 24 hours in Ringer's type solution

A capacitive behaviour, typical of passive materials is indicated from medium to low frequencies range by phase angle approaching -80° , suggesting that a stable film is formed on both tested alloys in the electrolyte used. The large phase angle peak could be indicative of the interaction of at least two time constants.

For the interpretation of the electrochemical behaviour of a system from EIS spectra, an appropriate physical model of the electrochemical reactions occurring on the electrodes is necessary. The electrochemical cell may be representing by an equivalent circuit (EC).

The impedance results were interpreted using the ZSimpWin software. After testing a number of different electrical circuit models in the analysis of the impedance spectra obtained at the open circuit potential, it was found that the whole set of data for both the samples could be satisfactorily fitted with the EC given in Fig. 7. This is based on the consideration of a two-layer model for the surface film. The results of the analysis are shown in Table 3.

In Fig. 6 the experimental data are shown by the symbols and the simulated data, which are generated using the equivalent circuit depicted in Fig. 7, are shown as the solid lines.

The Ringer solution contains calcium ion, which generally precipitates on titanium surface form a layer. The high-frequency parameters R_1 and Q_1

represent the properties of the reactions at the outer precipitate layer/solution interface. The symbol Q signifies the possibility of a non-ideal capacitance (CPE, constant phase element). The impedance of the CPE is given by (Raistrick et al., 1987):

$$Q = Z_{CPE} = \frac{1}{C(j\omega)^n} \quad (1)$$

where for $n = 1$, the Q element reduces to a capacitor with a capacitance C and, for $n = 0$, to a simple resistor. The parameter R_2 coupled with Q_2 describes the processes at the inner barrier layer at the electrolyte/passive film interface.

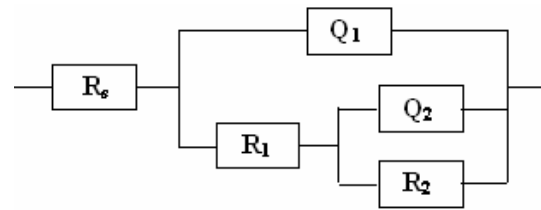


Fig. 7. Equivalent circuit (EC) used in the generation of simulated data

The EIS results exhibited capacitive behaviour (high corrosion resistance) with phase angle close to -80° and large impedance values (order of $10^5 \Omega \text{ cm}^2$) at medium and low frequencies, which are indicative of the formation of a stable film on these materials in the Ringer's solution.

The same value for R_s , equals 35Ω , was observed for both specimens after 24 hours of immersion and was not inserted in Table 3.

Polarization resistance (R_p) is represented by the sum of the resistance of the inner and outer layer, $R_1 + R_2$. A high R_p value is an indication of the working electrode strongly resisting change from its equilibrium state and corresponds to a low rate of titanium ion release. From the Stern-Geary equation (Stern and Geary, 1957):

$$i_{corr} = \frac{b_a b_c}{2.3 R_p (b_a + b_c)} = \frac{B}{R_p} \quad (2)$$

where: b_a and b_c are the Tafel slopes for the partial anodic and cathodic processes, respectively and B is a constant:

$$B = \frac{b_a b_c}{2.3(b_a + b_c)} \quad (3)$$

The polarization resistance of the alloys after 24 hours of immersion is large indicating a sufficient stability of titanium alloys in Ringer's solution. The corrosion currents for both titanium alloys were of the same order of magnitude (nA/cm^2) and are in agreement with the polarization data.

Table 3. The main parameters of the proposed equivalent circuit obtained for both studied samples

Alloy	R_1 ($\Omega \text{ cm}^2$)	n_1	Q_1 ($S \text{ s}^n \text{ cm}^{-2}$)	R_2 ($\Omega \text{ cm}^2$)	n_2	Q_2 ($S \text{ s}^n \text{ cm}^{-2}$)	i_{corr} ($\mu A \text{ cm}^{-2}$)
Ti6Al4V	$1.1 \cdot 10^3$	0.75	$2.6 \cdot 10^{-5}$	$2.1 \cdot 10^5$	0.87	$4.6 \cdot 10^{-5}$	175
Ti6Al4Zr	$1.7 \cdot 10^3$	0.76	$2.2 \cdot 10^{-5}$	$2.3 \cdot 10^5$	0.88	$2.7 \cdot 10^{-5}$	161

The exponents of the Q_1 , n_1 , are equals a value in between 0.75 and 0.76 while the exponents of the Q_2 , n_2 , are equals a value in between 0.87 and 0.88. This indicates that Q_2 corresponds to a capacitance of the inner layer while, Q_1 is a consequence of frequency dispersion of the outer layer (Tkalec, 2001).

Results indicate that the electrochemical behaviour of the Ti6Al4Zr alloy examined resembles that of the Ti6Al4V.

4. Conclusions

The electrochemical techniques used in this investigation led to the following conclusions:

a) Ti6Al4V and Ti6Al4Zr alloys exhibited stable passive polarization behaviour. Very low corrosion current densities were obtained for both titanium alloys tested in Ringer's solution. The passivation behaviour of Ti6Al4Zr was comparable with that of Ti6Al4V.

b) The EIS spectra results indicated that the film formed on the titanium materials is composed of a bi-layered consisting of an inner barrier layer associated to high impedance and responsible for corrosion protection and an outer precipitate layer.

c) Both electrochemical techniques show that Ti6Al4Zr alloy exhibits corrosion behaviour in Ringer's solution similar to Ti6Al4V alloy in the as-received condition. The electrochemical and corrosion behaviour of Ti6Al4V is not affected on substituting vanadium with zirconium.

Note

This paper is especially dedicated to Professor Neculai Aelenei on his 70th anniversary.

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STUDIES ON EQUIPMENT CORROSION IN CATALYTIC REFORMATION OF C₁ - C₅ FRACTION

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Abstract

Observations and data regarding the intense corrosion and deposit phenomena of the carbon steel tube bundle of the heat exchanger are presented. The bundle ensures the cooling of the light fraction C₁ - C₅ from the top of the distillation column which carries out the removal of pentane and smaller derivatives into the RC equipment. Chemical and mineralogical analyses confirm the aggressive action of the fluids flowing through the exchanger. Tests have been done in order to replace the carbon steel with austenitic stainless steel into the manufacturing process of the tube bundle. The corrosion behaviour of the selected metallic materials in recycled cooling water and technological fluids was monitored.

Key words: austenitic stainless steel, corrosion, heat exchanger, tube bundle

1. Introduction

The metallic parts of the carbon steel equipment and also the heat exchanger from the top of the distillation column ensuring the removal of C₁ - C₅ fraction into the RC equipment are intensively affected by the corrosion and deposit phenomena. Subsequently the heat exchange process slows down and the functional time of the equipment decrease, together with lower safety in the operational process of the equipment. Another considered disadvantage could be the less purified technological fluid (C₁ - C₅ fraction). In order to solve the inconvenient the equipments should be manufactured from highly anticorrosive resistance materials like less alloyed steels and austenitic stainless steel (Chesa et al., 1984; Fontana and Greene, 1986; Trușculescu and Ieremia, 1983). The last one is characterized by good resistance to corrosion in aggressive environments containing hydrogen and H₂S. The surface is also characterized by less roughness and more glossy,

where the depositions do not belong, involving easier cleaning methods and longer periods of time between maintenance procedures compared to the carbon steel. The costs involved present high differences, while the maintenance of austenitic stainless steel equipment is cheap and the carbon steel equipment permanent maintenance is expensive. For short periods of time the carbon steel is cheaper, while for longer times the stainless steel present obvious advantages, the costs expense liquidation is achieved in time (Chawla and Gupta, 1993).

2. Experimental setup

The heat exchanger S₁, under monitoring for three years, ensures the cooling of the C₁ - C₅ fraction collected from the top of the column which condense the light hydrocarbons after passing through air condenser A₁ (Fig. 1). The composing elements of the heat exchanger S₁ are manufactured from carbon steel, the chemical composition being presented in Table 1.

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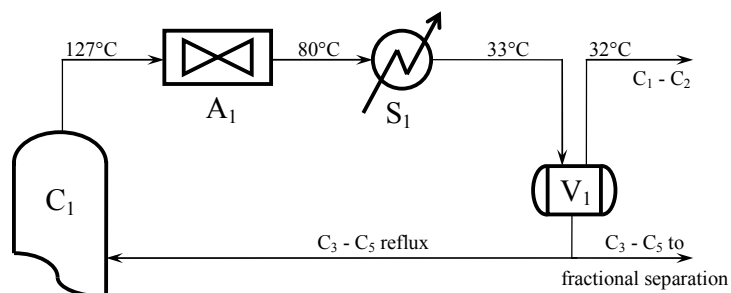


Fig. 1. The heat exchanger place, S_1 , into the technological flux of the reforming catalytic equipment

Table 1. Chemical composition of the construction material

Heat exchanger constructive parts	Material	Concentration, %				
		C	Si	Mn	S	P
Tube bundle $\phi 20 \times 2$	OLT35K	0.13	0.27	0.66	0.025	0.026
Tube sheet	K460.2b	0.17	0.37	1.22	0.015	0.016
Shell, Plenum	K41-2b	0.11	0.20	0.62	0.041	0.014
Baffle	OL37-2K	0.13	0.34	0.60	0.030	0.032

Table 2. Chemical composition of the deposit samples from the heat exchanger

Deposition sample place	Composition, %			
	Iron oxides (Fe_2O_3)	Ca and Mg salts ($CaCO_3$)	Phosphates (PO_4^{3-})	other components
Plenum	85.7 - 87.3	4.3 - 5.2	1.12 - 1.23	0.08 S; traces: Cu, Ni
Baffle, tube bundle	78.0 - 84.2	1.85 - 2.17	traces	0.3 Cr; 0.8 Zn; 0.032 S; traces: Ni, Cu, K
Tube sheet	84.9 - 86.5	2.91 - 3.18	traces	1.0 Zn; 0.5 Cr; 0.44 Na; 0.14 K; 0.12 Cu; 0.046S

During the monitoring period, the cooling water presented the following general characteristics: pH = 7.2 - 8.0; total hardness 326 - 493 mg $CaCO_3/L$; alkalinity "m" 157 - 318 mg $CaCO_3/L$; chlorides 80 - 120 mg/L; organic substances 20 - 68 mg/L and iron content 0.6 - 5.7 mg/L, indicating high probability to form large quantities of deposits.

The cooling tower water flows through the pipes of the fascicle, while the $C_1 - C_5$ fraction and H_2 (desorbed from reformed gasoline) with H_2S traces (< 1 ppm S_T) and chlorides (0.1 - 0.2 ppm) flow into the intertubular space. Deposition processes occur on tube bundle, tube sheets and baffles containing organic and inorganic substrates and promote local corrosion processes. Carbon steel getting in contact with sulphuric acid traces and the hydrochloric acid from hydrocarbons present into the inner tubular space is affected by corrosion processes and deposit formation. The phenomenon described above is not encountered in the case of austenitic stainless steel equipment. Salt deposits and microbiologic colonies are usually formed on the warm surfaces of the heat exchange, while the iron oxides resulted from the corrosion attack are supporting their accumulation and adhesion.

Microbiologic colonies are giving birth through their metabolic activity to corrosion effects due to their electrochemical activity with the metal but also due to the direct chemical attack of the metabolites

formed (H_2S , SO_2 , NH_3 , NO_2 , CO_2 etc.), which present highly aggressive behaviour against metals.

Visual inspections over the tube bundle and the inner tubular space show after three years use mud deposits, corrosion products, while some of the pipes are totally or partially closed (Fig. 2).

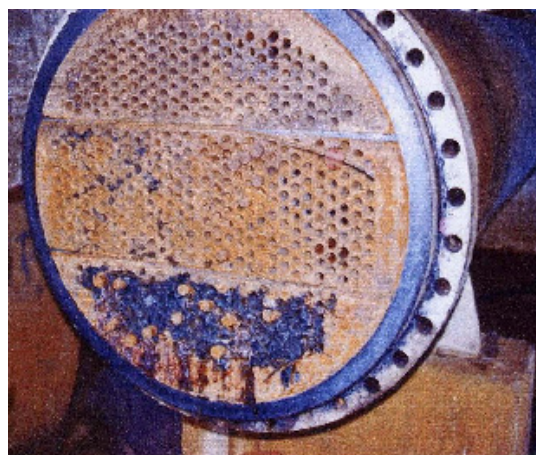


Fig. 2. Deposits on carbon steel tube sheet

At the upper part of the tube sheet, into the warm area, the main deposit is formed from biological mud.

Into the central part, between the baffles where the temperature is lower, the quantity of

biological mud decreases, while on the lower part of system and the technological fluid is evacuated, almost no mud is present but dark brown, iron oxides layers are noticed and also highly frequent clogged pipes.

The carbon steel plenum present grey-yellow- brown deposits and dark brown- black corrosion tubercle with 5 - 10 mm diameter scattered on the walls of the plenum. The corrosion tubercles are usually associated with corrosion plates measuring 10 - 20 mm in diameter.

The laboratory corrosion tests were performed using cooling water from the cooling tower and aqueous solutions resulting from washing the technological GPL (liquid petroleum gas) fluid with corrected pH. Other tests were done by placing samples in the operational heat exchanger.

3. Results and discussion

The surface of the walls in the plenum, the tube sheet and the tube bundle present accentuated local corrosion forms, after the deposit have been removed with water under pressure (plague). Deposit samples have been dried (contain 20 - 29% water) at 105°C and the results of the analysis are presented. (Table 2).

The tubercles skeleton is thin, probably mostly consisting of ferro-ferric oxides, was a black soft-spongy deposit formed from hydrated ferric oxides and metal sulphides (Herro and Port, 1993). The sulphates are reduced to sulphurous acid by the action of the bacteria present in water, and subsequently their action against iron is leading to black ferrous sulphur. Onto the sulphur layer hydrated iron oxides layers are deposited, which are also including other impurities from water. Iron oxides can be considered in this case as the "germs" of subsequent appearance and accumulation of various deposits.

The wet deposits sampled from tube bundle and tube sheet have been submitted to further biological analysis. The results show high biological loads of this mud: total number of mezophile bacteria

W1.4541	50 / 1200	0.0008	0.00088
		0.0009	0.0010
		0.0025	0.0028
		0.0032	0.0036
W1.4571	50 / 1200	0.0007	0.00077
		0.0008	0.00088
		0.0012	0.0013
		0.0021	0.0023

The visual inspection of the surface of the carbon steel samples OLT35K emphasized soft deposits in a thin layer, scattered allocated, under which corrosion spots occurred, while the austenitic stainless steel samples present no deposits, and the general aspect was not changed.

Real condition tests were done in the plant by assembling samples on board into the industrial system on the tubular heat exchanger S₁. The results

the shell, where the cooling water enters into the (which are developing at about 37°C) is 21·10⁹ UFC/cm³; total coliform 240·10⁹/100 cm³; fecal coliformi 1609·10⁹/100 cm³ and fecal streptococcus 542000/cm³.

Anticorrosive substances are added into the cooling water (inhibitors, bactericide, antifouling etc. (Apostolescu et al., 1999; Apostolescu et al., 2001; Constatinescu, 1976; Patton, 1995). Their efficiency is not high enough to prevent and reduce, considering the normal working parameters, the corrosion and deposition processes, which are strongly altering the heat exchange equipment.

In order to ensure optimal and safe functionality of the heat exchanger S₁, under the given conditions, the replacement of the carbon steel with austenitic stainless steel was proposed. Two sets of tests were run considering the corrosion behaviour of the materials into the fluids flowing through the heat exchanger. The values of the corrosion rate, P (mm/an) were determined by gravimetric method (Constatinescu, 1976).

The first set of laboratory tests were performed on the cooling water from the cooling tower, using metallic samples (25×40×1.5 mm) manufactured from carbon steel OLT35K and austenitic stainless steel W1.4541 (10TiNiCr180) and W1.4571 (10TiMoNiCr175) properly prepared (Constatinescu, 1976). Tests were run in laboratory facility in closed system, samples being totally emerged into water. Fluid volume/ metallic surface ratio were 15 mL/cm². The experimental results are presented in Table 3.

Table 3. Laboratory corrosion speeds of the metallic samples in cooling water from the cooling tower basin

Materials	Immersion time, days / hours	Corrosion speed	
		K _g , g/m ² h	P, mm/an
OLT35K	50 / 1200	0.066	0.073
		0.067	0.074
		0.072	0.080
		0.086	0.096

are indicative of corrosion speeds greater than those determined in laboratory for carbon steel, namely 0.16 to 0.19 mm/year and 0.0042 to 0.0050 mm/year for austenitic stainless steel.

The second set of tests was conducted in aqueous solutions resulting from washing the technological GPL (liquid petroleum gas) fluid, taken out of the ebb vessel V₁. The GPL fluid was washed with hot water to extract the corrosive agents contained; a solution with pH = 6.8 resulted. In order to increase the corrosivity of the solution, a part was treated by adding sodium hydroxide up to pH = 9.0, and into the other acid was added to reach pH = 3.5.

With these three aqueous solutions, laboratory tests have been conducted at 50°C for 480 hours. The results are presented in Table 4. Austenitic stainless steel present also in these aqueous solutions corrosion speed values with two orders size smaller

than the carbon steel, and the tested samples surface do not present signs of corrosion or deposits.

All these calls for austenitic stainless steel heat exchanger manufacturing of the tubular fascicle S₁.

Table 4. Corrosion rates for the carbon and austenitic stainless steel samples in aqueous solution extracted from GPL

Working conditions	Material	Corrosion rate	
		K _g ⁻² , g/m ² h	P, mm/an
Aqueous solution with pH corrected at 9.0	OLT35	0.0770	0.0850
	W1.4541	0.0019	0.0021
	W1.4571	0.0009	0.0010
Aqueous solution with pH corrected at 6.8	OLT35	0.0920	0.1020
	W1.4541	0.0022	0.0024
	W1.4571	0.0013	0.0014
Aqueous solution with pH corrected at 3.5	OLT35	2.8900	3.2100
	W1.4541	0.0056	0.0062
	W1.4571	0.0031	0.0034

Table 5. Heat exchangers costs*

	The name of the items of expenditure	Value, EUR	
		carbon steel	austenitic stainless steel
1.	Materials value	2970	14600
2.	Supply costs (10% from 1)	297	1460
3.	Labour value	974	1100
4.	Overhead cost (135% from 3)	1315	1485
5.	Price cost (1 + 2 + 3 + 4)	5556	18645
6.	Profit (8% from 5)	444	1492
7.	Total value (5 + 6)	6000	20137

*ensure the cooling of the C₁ - C₅ fraction from the top of the column into the RC equipment

Besides testing the corrosion behaviours of the two metallic materials, the costs were summarized, both for manufacturing the tubular fascicle with W1.4571 austenitic stainless steel and carbon steel (Table 5). Additional costs were calculated for the maintenance during 3 years run of the carbon steel heat exchanger (Table 6).

Although the stainless steel tube bundle is 3.35 times more expensive than carbon steel, the maintenance costs of the carbon steel heat exchanger over 3 years overstep significantly the cost of the stainless steel equipment. Thus, the recovery of manufacturing and mounting costs of the austenitic stainless steel exchanger is made in only 7 to 8 months of operation.

4. Conclusions

During 3 years monitoring of the heat exchanger whose tube bundle is carbon steel OLT35K, it was noticed that the two fluids, C₁ - C₅ fraction circulating intertubular and the cooling water

generate intense corrosion and deposit phenomena, which requires large expenses for equipment maintenance.

Table 6. Expenses for by the heat exchanger from the top of the C₁ - C₅ removal column

Make-up costs	Value, EUR
Fascicle cleaning and pipe cancelling (every 7 - 8 months)	
a. Pipes and plenum disassembling, cleaning, washing, closing broken pipes, pressure tests, plenum closure, pipes connection.	8150
b. Stop / start installation, production losses	16300
Technical solution study	1630
Tubular carbon steel fascicle replacement (every 36 months)	
a. Pipes and plenum disassembling, old tube bundle disassemble, new tube bundle assembling, pressure tests, plenum closure, pipes connection.	13580
b. Stop / start installation, production losses	16300
TOTAL EXPENSES	
4 stops every 7 - 8 months for fascicle cleaning and pipe cancelling: 4 × (8150 + 16300)	97800
1 stop every 36 months for fascicle replacement	29880
Technical solution study	1630
Full costs for 36 months operation (carbon steel)	129310

Chemical and microbiological analyses carried out on deposition taken in the heat exchanger confirm the aggressiveness of the two fluids.

The corrosion reaction rate of austenitic stainless steel, in both fluids are up to two orders of magnitude smaller compared with the carbon steel case, arguing their use in manufacturing of the tubular fascicle.

Construction costs for the tube bundle austenitic stainless steel equipment could be recovered in 7 to 8 months of operation.

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STUDIES REGARDING SURFACE WATER TREATMENT USING A MICROFILTRATION-ULTRAFILTRATION PILOT PLANT

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Abstract

In this paper the results of surface water treatment process for drinking purpose are presented, using the microfiltration-ultrafiltration process. The experimental studies were carried out using a microfiltration-ultrafiltration pilot plant and raw water from Bega River, Timisoara as feed. To assess process performance, the water quality, *e.g.*, turbidity, total coliforms and hardness parameters were determined for two different operating regimes subjected to filtration time. A good efficiency of turbidity removal was achieved, the residual values being situated below the maximum allowable value admitted by drinking water regulation. The presence of total coliforms in treated water imposed the necessity of a final disinfection step, after applying microfiltration-ultrafiltration process.

Keywords: surface water, pilot plant, microfiltration, ultrafiltration

1. Introduction

Water resources are becoming increasingly scarce in many areas of the world due to development, and increased demand (Pearce, 2008).

In the present, at European level, the drinking water treatment technology requires new and innovative processes, based on the raw water quality and flows.

Among innovative technology, microfiltration-ultrafiltration process have been remarked, because no chemical agents are used, constant producing of treated water with high quality and simple automation of process (Ghayeni et al., 1996; Readon et al., 2005).

While membrane separation process have been widely used to recover valuable products from complex mixtures, only recently have membrane technologies emerged as viable for drinking water production and for wastewater treatment (Musteret and Teodosiu, 2007; Taniguchi et al., 2003).

Ultrafiltration process applied to water treatment has become a more attractive technology worldwide to produce drinking water (Sheng-ji et al,

2007). Ultrafiltration process uses a finely porous membrane to separate water and microsolutes from macromolecular and colloids (with diameters between 0.001 and 0.1 μ m). Microfiltration process refers to filtration process that use porous membranes to separate suspended particles with diameters between 0.1 to 10 μ m. Thus, microfiltration membranes fall between ultrafiltration membranes and conventional filters (Baker et al., 2004).

Ultrafiltration (UF) and microfiltration (MF) process are theoretically the best pre-treatment upstream reverse osmosis, removing from the feed water most of the potential elements responsible of desalinating membranes fouling such as particles, turbidity, bacteria and large molecular weight organic matters (Bonnelye et al., 2008).

Membrane technologies were used in many applications of water treatment. (Durman et al., 2001; Gille and Czolkoss, 2005; Jarusutthirak and Amy, 2001; Lipp et al., 1998; Panglisch et al., 1997; Panglisch et al., 1998; Podaru et al., 2008; Reissman and Uhl, 2006; Sayed et al., 2007).

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In Timisoara City, 66 % of water for drinking use is originated from surface water. The actual drinking water treatment plant uses the classical technology consisted of coagulation, decantation, filtration and disinfection.

The present study was carried out for surface water treatment plant, from Timisoara City, using the microfiltration and ultrafiltration process. To evaluate the process performance, influent (raw water) and effluent (permeate) quality, expressed by turbidity, total coliforms and total hardness was determined.

2. Experimental

2.1. Pilot plant

Fig.1 presents the technological scheme of a microfiltration-ultrafiltration pilot plant (microfiltration-ultrafiltration module, SCED-06-006, PIASA firm, Engineering and Trading S.A., Spain), used for the treatment of surface water, from Bega River, Timisoara. In Fig. 2 it is shown the image of microfiltration-ultrafiltration pilot plant.

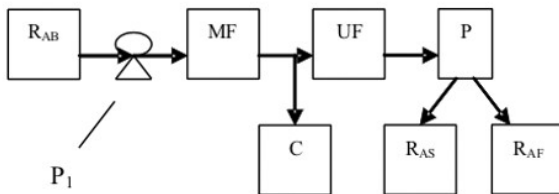


Fig.1. Technological scheme of microfiltration-ultrafiltration pilot plant



Fig.2. The image of microfiltration-ultrafiltration pilot plant

Pilot plant was provided with a principal screen (PLC) that offers access to all running processes and operated in automatic and continuous regime. Two different operation situations subjected

to filtration process duration until membrane cleaning, *i.e.*, $T_1 = 30$ minutes, $T_2 = 90$ minutes were used. In addition, the aspects related to membrane fouling were followed.

Raw water passed through microfilter (MF – spiraled cartridge filter CA-0804-04 model, 50 microns) with a 200 L/h flow, and then passed through a tangential ultrafiltration membrane (UF - TRIHIGH Hallow Fiber type, CLN4000So model (30-50 Kdalton). The feed flow was achieved with P1 pump (PRINZE pump, CK 50 III 220/380 V model, with 600 L/h capacity)

A permeate (P) and a concentrate (C) results as a product of pilot plant. Part of permeate, P (filtered water) was accumulated in washing water tank (R_{AS}), fitted with a float bowl, and the rest was stored in filtered water tank (R_{AF}).

Filtration operation was controlled by a security system that controls the differential pressure between the inlet and outlet of the ultrafiltration module. The objective of this operation is to avoid the membrane fouling by colloid accumulation on its surface, and was operating in automatic mode, at different range time. Membrane cleaning consisted of three steps *e.g.* air drainage, pressurization (air, with 1 bar pressure) and backwashing (with filtered water).

2.2. Analytical methods

To assess the process efficiency, analyses of influent (raw water, AB) and effluent (permeate, P) were carried out. Turbidity (T) (HATCH 2100 N Turbidimeter, Made in Germany), total coliforms (CT) (SR 3001-91), respective total hardness (SR 3026-76) parameters were analyzed.

3. Results and discussions

3.1. Operating conditions

3.1.1. Membrane cleaning after 30 minutes of filtration process operation

Turbidity is a principal physical characteristic of water and an expression of the optical property that causes light to be scattered and absorbed by particles and molecules rather than transmitted in straight lines through a water sample. It is caused by suspended matter or impurities that interfere with the clarity of the water (EPA Guidance, 1999). Minimum, average and maximum values for 104 numbers of turbidity determinations for raw water (T_{AB}) and permeate (T_P), respective removal efficiency (E_T) are presented in Table 1.

Table 1. T_{AB} and T_P values, respective E_T (membrane cleaning after 30 minutes of filtration process operation)

Value	T_{AB} [NTU]	T_P [NTU]	E_T [%]
Minimum	3.55	0.10	67.48
Average	8.68	0.51	93.64
Maximum	19.30	2.14	98.00

In Fig. 3 it is shown the evolution of T_{AB} , T_P parameters, respective E_T during operating microfiltration-ultrafiltration process.

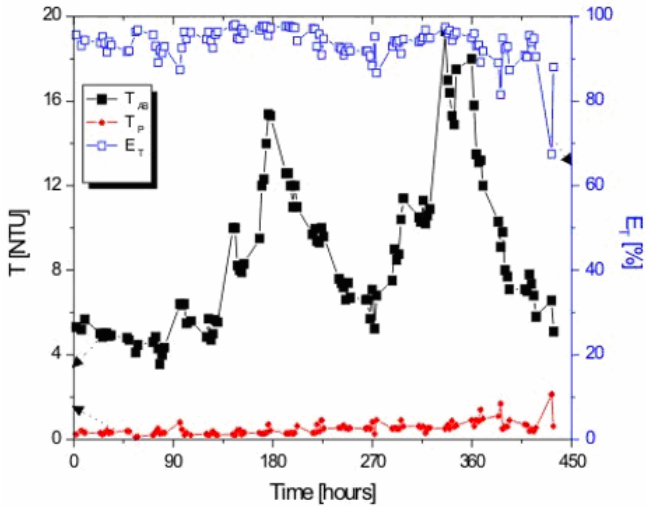


Fig.3. The evolution of T_{AB} , T_P and E_T during microfiltration-ultrafiltration process with membrane cleaning after 30 minutes of filtration process operation

It can be noticed that the T_P values varied between 0.10 and 2.14 NTU, which are below maximum allowable value required by drinking water regulation, of 5 NTU (Law 311, 2004). Good efficiency of turbidity removal was achieved, ranged between 67.48 and 89.00 %.

The presence of total coliform bacteria in water within the distribution system (but not in water leaving the treatment plant) indicates that the distribution system may be vulnerable to contamination or may simply be experiencing bacterial re-growth (Health Canada, 2006). Minimum, average and maximum values for 13 numbers of total coliforms determinations for raw water (CT_{AB}) and permeate (CT_P), respective the removal efficiency (E_{CT}) are presented in Table 2.

Table 2. CT_{AB} , CT_P , respective E_{CT} values (membrane cleaning after 30 minutes of filtration process operation)

Value	CT_{AB} [no./100cmc]	CT_P [no./100cmc]	E_{CT} [%]
Minimum	3480.00	130.00	53.76
Average	27278.46	2100.92	89.87
Maximum	91800.00	16090.00	99.63

The dynamics of the parameters, CT_{AB} , CT_P respective E_{CT} , during operating microfiltration-ultrafiltration process, is shown in Fig. 4.

Even if the good efficiency for CT removal was achieved (53.76 and 99.63 %), however the presence of CT in effluent (3480.00 ÷ 91800.00 no./100 cmc), no Romanian regulation requirements were met. In addition, the total hardness parameter was checked. The values of total hardness for raw

water (influent) and permeate (effluent) were similarly and ranged from 4.40 to 5.20 German hardness degree.

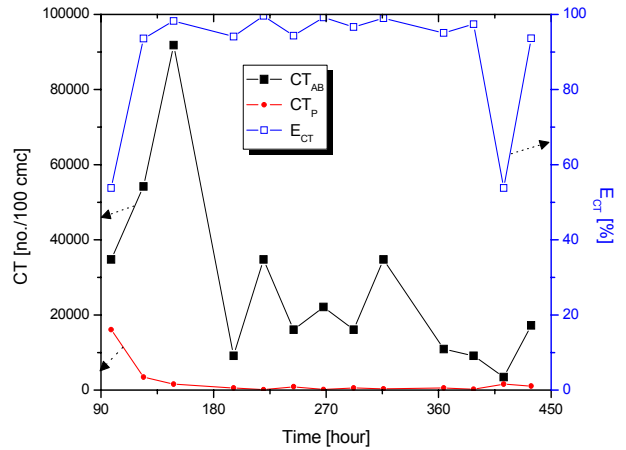


Fig.4. The dynamics of CT_{AB} , CT_P and E_{CT} during microfiltration-ultrafiltration process (membrane cleaning after 30 minutes of filtration process operation).

These results demonstrate that the microfiltration-ultrafiltration process application did not affected the water hardness, desired aspect, because of drinking water regulation requirements (minimum 5 German hardness degree).

3.1.2. Membrane cleaning after 90 minutes of filtration process operation

Table 3 gathered the minimum, average and maximum values of a number of 54 determination for T_{AB} , T_P , respective E_T .

Table 3. T_{AB} , T_P , respective E_T values (membrane cleaning after 90 minutes of filtration process operation)

Value	T_{AB} [NTU]	T_P [NTU]	E_T [%]
Minimum	3.00	0.53	57.80
Average	6.42	1.20	80.76
Maximum	16.20	3.70	87.25

In Fig.5 shows the evolution of T_{AB} , T_P parameters, respective E_T during operating microfiltration-ultrafiltration process.

From Fig.5, could be observed that T_P values ranged between 0.53 and 3.70 NTU, also below maximum allowable value of 5 NTU. Under these working conditions, E_T ranged between 57.80 and 87.25 %.

The minimum, average and maximum values for 5 determinations of total coliforms - CT_{AB} , CT_P , and E_{CT} are presented in Table 4.

In Fig. 6 it is shown the variation of CT_{AB} , CT_P and E_{CT} parameters during operating microfiltration-ultrafiltration process.

Under these operation condition, CT ranged between 542.00 and 3480.00 no./100 cmc, and the removal efficiency between 35.79 and 95.03 %.

Regarding water hardness, no reduction was achieved.

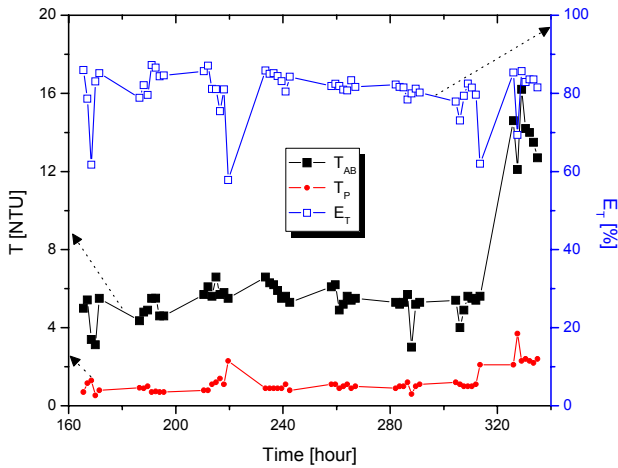


Fig.5 The evolution of T_{AB} , T_P parameters, respective E_T (membrane cleaning after 90 minutes of filtration process operation)

Table 4. CT_{AB} , CT_P , respective E_{CT} values (membrane cleaning after 90 minutes of filtration process operation)

Value	CT_{AB} [nr./100cmc]	CT_P [nr./100cmc]	E_{CT} [%]
Minimum	5420.00	542.00	35.79
Average	7612.00	1751.80	71.67
Maximum	10900.00	3480.00	95.03

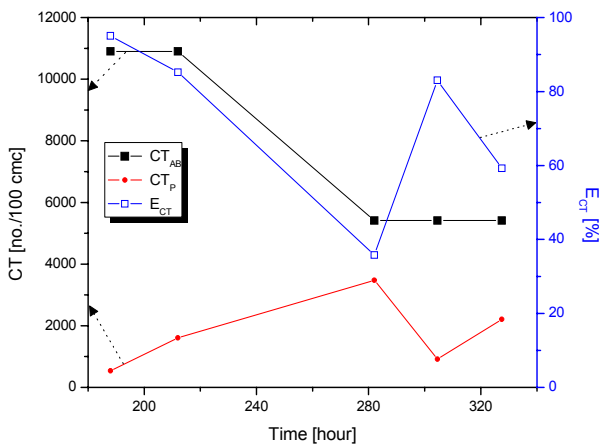


Fig. 6. Variation of CT_{AB} , CT_P , E_{CT} during microfiltration-ultrafiltration process (membrane cleaning after 90 minutes of filtration process operation)

6. Conclusions

The studies were performed on a microfiltration-ultrafiltration pilot plant in order to test the performance during the treatment of surface water for drinking purposes, from Bega River, Timisoara, Romania.

By applying the microfiltration-ultrafiltration process, a good physical-chemical quality of drinking water results, in agreement with Romanian Drinking

Water Regulation (Law 311, 2004). Therefore, a good removal efficiency of turbidity was achieved.

For the filtration process where the duration until membrane cleaning can be $T_1=30$ minutes, E_T ranged between 67.48 and 89.00 %, while it can reach 57.80 and 87.25 %, when the duration until membrane cleaning becomes $T_2=90$ minutes.

The results regarding total hardness of the water shown that, by applying microfiltration-ultrafiltration process, the values of this parameter were almost unchanged.

The requirements of drinking water regulation subjected to the microbiological quality were not achieved, although good removal efficiency was obtained. Total coliforms removal efficiency ranged between 53.76 and 99.63 %, for operating time of 30 minutes of microfiltration-ultrafiltration process, respective between 35.79 and 95.03 %, for operating time of 90 minutes.

For both operating regimes no membrane fouling occurred significantly.

Based on these results, it can be concluded that the water quality can meet the imposed request from the physical-chemical point of view by using microfiltration-ultrafiltration pilot plant for surface water treatment for drinking water proposal, but the total coliforms presence in the pilot plant effluent imposes to insert a final disinfection step.

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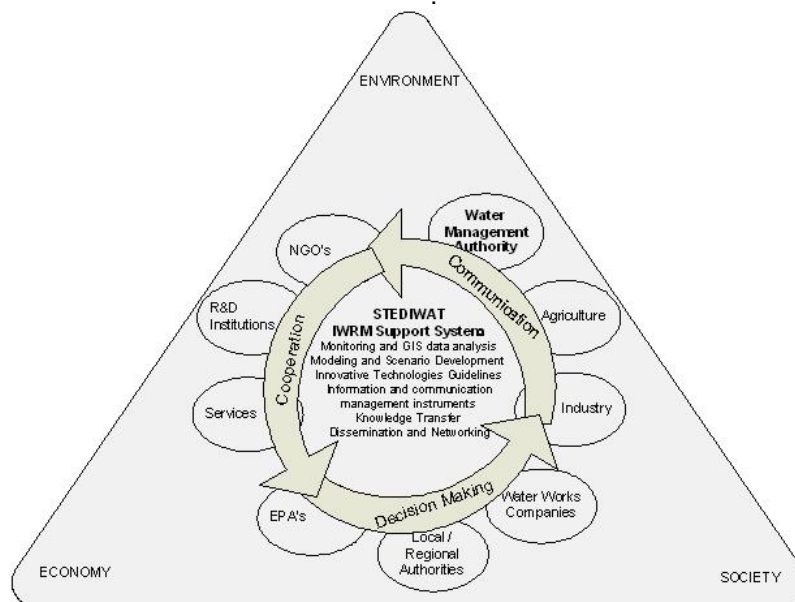
TECHNICAL AND DECISION MAKING SUPPORT SYSTEM FOR SUSTAINABLE WATER MANAGEMENT *STEDIWAT*

Research Grant 32125/2008, PNCDI II (National Programme for Research, development and Innovation II), Duration: 2008 – 2011

Project objectives

1. Development of technical innovative support related to monitoring, modeling and prediction tools to be used for integrated and sustainable water resources management at basin level;
2. Development of the capacity of collaboration, knowledge transfer and communication between universities and local/regional water authorities, industries and other stakeholders in the studied basins (Prut, Banat, Arges-Vedea, Olt) with impacts on local and regional sustainable development;
3. Completion of the research infrastructures of the participating universities and facilitation of further research cooperation at national and international scale;

- *integrated* issues related to the water cycle, supply, treatment, use and reuse at the level of stakeholders considering their interaction at the level of four basins in Romania (Prut, Banat, Arges-Vedea, Olt); development of an original and complex support system based on multidisciplinary research and novel technical achievements: online monitoring with wireless sensor networks, usage of GIS techniques, data analysis and modeling, scenario development, considering sustainable development components, innovative technologies for wastewater treatment and reuse, information and communication management instruments;



Integrated concept of water resources management within the STEDIWAT Project

4. Development of capacities and competitiveness of Romanian researchers at international scale, as well as of the national partnerships contributing to environmental sustainability (protection and conservation of water resources);
5. Dissemination of relevant results of the project at the level of scientific community, and also at the level of stakeholders dealing with water resources management.

Project description/activities

The activities of the STEDIWAT Project rely on a **multidisciplinary and integrated approach** that focuses on:

- *integrated* issues related to the water cycle, supply, treatment, use and reuse at the level of stakeholders considering their interaction at the level of four basins in Romania (Prut, Banat, Arges-Vedea, Olt);

- development of a complex support system that will facilitate **decision-making interaction and adaptive management** at the level of the stakeholder but also on the level of the system as a whole (management of complexity of decision contexts specific to IWRM).
- it facilitates of knowledge transfer, training, communication, dissemination and collaboration between the scientific groups, decision makers and other stakeholders, considering also the actual “water demand and supply” pressures and behaviors of different stakeholders involved.

Project director:

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MANAGEMENT OF WASTE IN RURAL AREAS OF GORJ COUNTY, ROMANIA

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Abstract

On the top of the ecological priority list in Romania, waste management is on the third place following the problems regarding the surface and underground water pollution, as well as that of the atmosphere. The clean-up of the landscape represents an issue largely discussed in Romania. The paper presents the advantages of waste management for the landscape, which includes: waste gathering and transfer, waste selection, waste biological treatment and the storage.

Some analyses of the constituent components of the soil are presented, in order to assess the possibility to use the compost obtained from waste household within a composting station in agricultural sector of the district of Gorj. The experimental data demonstrated the possibility of using the compost as a fertilizer on the agricultural fields.

By applying good management and treatment practices of the household wastes, one may achieve long-term economic objectives such as: the improvement of public health as well as the protection of the natural resources by diminishing the soil, water and air contamination.

Key words: compost, management, rural, waste

1. Introduction

The household and the municipal waste, as well as waste on the outskirts of forests, orchards and pastures or worse, in lakes or rivers, represent a real hazard for the future of the society by influencing the quality of the environment and its natural evolution.

The cleaning of landscape represents a problem discussed at present in Romania, unlike the situation of the West European landscape, where it represents no longer an issue.

The measures and methods imposed step by step as well as their chronological order are materialized and exposed in a clear way in an integrated concept of waste management.

The most important developing directions within the waste management are presented as follows (Apostol et al., 2006; Bold and Mărăcineanu, 2003; Jones et al., 2005; Păunescu et al., 2002):

- the valorization, separate gathering and ecological removal in a secure way of the dangerous wastes;

- the coordination and ordering of cleaning measures (for example: selecting the proper legal forms for the functioning of the waste management; finding some suitable private third parties for taking care of operations like waste evacuation and cleaning measures side by side with the local community, the upholding and coordination of commercialization measures and safely keeping the component in the valuable materials);
- the control of the cleaning up service (through the elaboration of some balance sheets regarding the quantity of the materials, as well as the examination of the fundamental costs for an eventual continuation or variation, or improvement of the waste management objectives);
- the information and counseling of the waste generating companies in order to minimize the waste production as well as to encourage the valorization measures;

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- to conceive and issue some legal stipulations (resolutions, norms and regulations of the district council) considered as the most important legal base for waste removal with the possibility of influencing the citizen's behavior towards a reduction of waste production mentality (by regulating the wastes cleaning, the obligation to have proper waste recipients).

The concept of waste integrated management may be useful within the authorization of some treatment and removal waste equipments, for proving the understanding of waste management priorities, for prevention of waste formation before valorization and ecological removal.

The necessity of some waste storage within a global concept together with the due measures for the limitation of production and valorization in a credible manner for the population is evident.

In conformity with the fundamental norms in the process of waste removal, one has to start from the premise of a high level environmental protection.

The paper presents an analysis of the household waste management on the Romanian landscape.

2. Experimental

2.1. Gathering and waste transfer

The gathering of the domestic wastes represents a great present day issue because their volume increases with the increase in the population and of its welfare; the increase of these factors generate hazards and risk of environmental deterioration.

The variety of the wastes composition makes the process of aerobic and anaerobic degradation faster and more difficult to follow, provoking in the case of a delayed and unsanitary gathering the pollution of the air and water.

Previous to the collection operation of the domestic wastes – process performed by specialized units – there is another phase that may be considered as a 'pre-collection' realized by the tenants or the service personnel from the public locals, stores or institutions.

The transfer refers to the moving of the wastes from the first collecting vehicle to a secondary one, bigger and more efficient.

While the systems of waste management have a collection structure, not all the systems have the transfer one.

2.2. Waste selection

The European policy in the environmental field stipulates that the waste selection has to be made in one unique fraction, as much as possible at the source. This operation has to be followed by the waste gathering and separate elimination, where their nature is known. This is an important aspect both from the ecological point of view as well as from the

sanitary and security one. The separate collection and selection of the domestic wastes may be realized also by the population in the process of their generation. But to achieve this, the population has to be made aware by the gravity of the problem linked to the waste management and the related issues of problem posed to the environment and population by the wastes.

There is selection in the district of Gorj. This selection is carried out taking into account some aspects: dimensional; from density point of view; optical; magnetic; manual.

2.3. Waste biological treatment

The elimination, the waste biological treatment respectively, relies on the decomposition of the organic substances from the wastes under the action of the microorganisms (Ahn et al., 2004; Boullagiu et al., 2004; Chae et al., 2004; Lissens et al., 2004; Mahmoud et al., 2004).

The decomposition is realized by two procedures:

- the transformation in compost through air feeding;
- the transformation in biogas through tight closing that leads to a reduction of the initial content of organic substances.

By the biological treatment are realized both the valorization and the residues removal. By the process of obliteration the wastes are converted in a non-polluting product with a high nourishing value for plants and a very good supplement for the soil physical and chemical state. The waste conversion in used compost in agriculture is known in practice from about 7-8 decades, mostly after the populated centers met with an important development.

Although until now there have been realized many researches and processing procedures, the problem of obliteration remains still actual and continues to be studied, both independent and together with other methods of waste valorization (Celis-Garcia et al., 2004; Dohanyos et al., 2004; Mahmoud et al., 2004).

Basically the compost preparation technology has two fundamental phases:

- the mechanical preparation;
- the actual obliteration.

Table 1 presents the compost composition from the composting station from the district of Gorj.

The samples for the determination of the utilization possibility in agriculture of the mud were taken from the soil surface, from 2 agro-chemically homogeneous plots, of 1 hectare each, the sampling depth being 0-20 cm, in 1 kg plastic bags, separately labeled. The soil sampling was done with the help of the Mole type agro-chemical probes.

The soil samples were passed through solution with the help of the mineralizer by oxidation with concentrated H₂SO₄ and 50% perhydrol, then the samples are analyzed by flame atomic absorption spectrometry by using a flame system AA Spectrometer novA®300.

Table 1. Average composition of compost probe from the domestic wastes prepared in the compost station or formed in the baluster for controlled storing

<i>Characteristics</i>	<i>The average composition of the compost%</i>	
	<i>Composting station</i>	<i>Storing baluster</i>
Water	35.98	34.14
pH	7.4	7.62
Dried substances		
Total organic material	45.38	41.50
Carbon	17.22	12.78
Nitrogen	0.77	1.35
Carbon/Nitrogen	18.78	9.47
Main elements		
Phosphorus Pentoxide (P ₂ O ₅)	0.85	0.75
Potassium (K ₂ O)	0.78	0.64
Soda (Na ₂ O)	0.89	0.62
Lime (CaO)	6.67	9.80
Magnesium (MgO)	0.94	1.86
Iron (Fe)	5.54	6.45
Sulphur (S)	0.75	1.09
Chlorides (Cl)	0.66	0.90
Oligoelements (substances necessary for the microorganisms nourishment)		
Magnesium (Mg)	0.0452	0.0689
Copper (Cu)	0.0669	0.0929
Zinc (Zn)	0.0803	0.1519
Boron (B)	0.0017	0.0017

Table 2. Characterization of the soil samples - first sampling point

<i>Parameters</i>	<i>Unit</i>	<i>Source values</i>										<i>Normal Values</i>	<i>Limit Alert Values Sensitive use</i>
		01	02	03	04	05	06	07	08	09	10		
pH at 20°C	pH unit	8.32	7.93	8.11	8.00	8.20	8.08	7.30	8.15	8.5	7.46	-	-
Humidity	%	3.37	3.19	3.89	3.11	3.69	3.65	3.65	3.65	3.75	3.72	-	-
N-total	mg/kgSU	58.56	60.59	63.62	64.95	60.14	58.41	65.35	62.95	63.7	60.39	-	-
NO ₃ -N	mg/kgSU	41.68	42.59	44.42	46.35	44.34	44.51	47.65	47.46	43.7	44.19	-	-
NH ₄ -N	mg/kgSU	16.88	18.0	19.20	18.6	15.8	13.9	17.7	15.49	20	16.2	-	-
P ₂ O ₅	mg/kgSU	3.814	4.181	4.47	2.62	3.09	1.42	1.38	3.32	3.90	1.14	-	-
MgO	mg/kgSU	10.779	11.40	11.52	11.77	13.03	10.96	11.12	13.68	14.61	11.64	-	-
CaO	mg/kgSU	17.411	14.921	15.068	16.49	14.75	12.77	12.615	12.31	22.82	21.66	-	-
K ₂ O	mg/kgSU	4.973	3.841	4.513	4.123	4.899	3.764	4.640	4.733	3.49	4.42	-	-
Cd	mg/kgSU	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1	3
Cu	mg/kgSU	17.2	20.02	16.76	16.23	14.19	16.68	18.92	17.21	15.30	18.76	20	100
Ni	mg/kgSU	27.21	25.66	24.59	23.7	22.51	23.54	25.38	23.19	28.8	27.95	20	75
Pb	mg/kgSU	15.06	14.12	14.95	13.41	12.33	14.54	13.38	14.15	14.17	14.77	20	50
Zn	mg/kgSU	36.32	36.47	32.08	29.5	25.8	25.82	29.33	26.50	25.19	30.29	100	300
Cr	mg/kgSU	32.04	33.2	37.55	37.22	31.3	37.42	31.85	31.66	30.3	34.11	30	100
Mn	mg/kgSU	374.48	378.35	403.5	416	363.9	376.8	413.17	426.8	467.7	439.1	900	1500
Hg	mg/kgSU	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	1	<0.1	<0.1	<0.1	0.1	1

SU – dried substance

Table 3. Characterization of the soil samples from the second sampling point

Parameters	Unit	L1 01	L2 02	L3 03	L4 04	L5 05	L6 06	L7 07	L8 08	L9 09	L10 10	Normal Values	Limits Alert Values
pH at 20°C		8.39	8.29	8.01	8.30	8.27	7.57	7.68	8.36	7.66	8.09	-	-
Humidity	%	3.75	3.74	3.11	3.60	3.66	3.58	3.35	3.41	3.63	3.50	-	-
N total	mg/kgSU	52.43	45.47	49.1	52.92	45.18	48.06	46.54	49.89	49.76	48.67	-	-
N-NO ₃	mg/kgSU	41.74	36.86	39.60	42.12	37.25	37.7	39.07	38.12	38.59	37.17	-	-
N-NH ₄	mg/kg SU	10.69	8.61	9.5	10.80	7.93	10.36	7.47	11.77	11.17	11.5	-	-
P ₂ O ₅	mg/kgSU	3.446	2.673	3.504	3.085	2.205	1.661	1.420	1.836	1.664	1.304	-	-
MgO	mg/kgSU	19.838	13.519	17.82	11.41	15.308	20.5	14.925	19.05	12.062	10.7	-	-
CaO	mg/kgSU	30.225	21.272	19.517	19.464	18.70	21.385	25.121	28.818	17.445	23	-	-
K ₂ O	mg/kgSU	3.927	4.05	3.667	3.678	3.689	3.777	4.033	3.578	4.241	4.329	-	-
Cd	mg/kgSU	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	1	3
Cu	mg/kgSU	18.91	11.48	18.78	13.69	22.68	23.03	22.03	14.92	14.68	16.81	20	100
Ni	mg/kgSU	16.41	16.20	29.37	19.07	26.87	32.13	34.5	30.94	18.41	27.02	20	75
Pb	mg/kgSU	21.88	20.97	15.16	25.64	17.96	24.21	22.92	24.03	22.40	18.33	20	50
Zn	mg/kgSU	49.58	45.34	43.39	46.89	43.71	46.61	43.40	39.27	31.34	48.12	100	300
Cr	mg/kgSU	36.69	28.51	31.92	32.34	32.62	27.1	37.34	32.05	31.05	30.11	30	100
Mn	mg/kgSU	412.72	402.69	362.53	418.96	451.12	405.82	373.54	433.16	387.53	405.78	900	1500
Hg	mg/kgSU	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.1	1

2.4. Waste storage

Until now, both on national as well as on the global level there is the practice of the residue evacuation in the so-called 'garbage dumps'. They are formed either in natural depressions or are the result of field hosing or construction quarries. Due to the fact that the number of the garbage dumps is getting smaller and the distance to reach them is great, the waste transportation expenses are considerable.

The waste storage may be (Apostol et al., 2006; Căpățină et al., 2006):

- simple;
- controlled.

The storehouse represents a location for the final elimination of the wastes through storage on the ground or in the underground, including:

- internal spaces for the waste storage, that is storehouses where a waste producer performs its own waste elimination (the producing site);
- a permanent arranged surface (that is, for a period of over a year) for the temporary storage of the wastes, but exclusively;
- installations where the wastes are unloaded to allow their preparation for a later transportation for the recuperation, treatment and final elimination somewhere else;
- the waste storage before its valorization or treatment for a period smaller than 3 years, as a general rule, or the storage before the elimination for a period smaller than one year.

3. Results and discussion

3.1. The possibility of using the compost as a fertilizer

For the first sampling point (Table 2), the results of the samples indicate the fact that the soil has a neutral to weak alkaline pH (7.3 - 8.5), a relatively constant humidity (3.11 - 3.89%), and the heavy metals content is under the alert limit.

The analytical results of the heavy metals in the medium soil samples lead to the following conclusions:

- cadmium and mercury are not detectable;
- nickel with concentrations of 22.5-28.8 ppm (1 mg/kg = 1 ppm) exceeds the normal values for the soil (20 ppm), but is still under the alert limit (75 ppm);
- total chromium with concentrations from 30 to 37.5 ppm exceeds the normal value of 30 ppm, but is still under the alert limit (100 ppm).

The lead, zinc, copper, manganese concentrations are under the normal limits.

In Table 3 there are presented the analytical results for the second sampling point. The results of the samples indicate the fact that the soil has a weak alkaline pH (7.57-8.4), a relatively constant humidity (3.11 -3.75%); and the heavy metals content is under the alert limit. The heavy metals concentration is not significantly different as compared to other areas:

- cadmium and mercury are not detectable;
- copper is present in a concentration between 11.48 and 23.03 ppm. Three of the medium

samples have concentrations that exceed the normal value of 20 ppm but are much below the alert limits (100 ppm).

- nickel, with concentrations from 16.2 to 34.5 ppm, often exceeds the normal value (20 ppm), but remains under the alert limit (75 ppm);
- total chromium, with concentrations between 27.1 and 37.34 ppm, for all samples, is much under the alert limit (100 ppm);
- the zinc and manganese concentrations are below normal limits.

This study made in order to establish the possibility of using the compost as a fertilizer was followed by a study based on a questionnaire for people attitude examination about environmental problems especially waste problems.

3.2. Study regarding the attitude of the population over the problematic of solid wastes in the countryside

This questionnaire was made for the examination of the individual's attitude, with the residence in the countryside, over the problem of the environment pollution with solid wastes and the lack of a waste management system. The study used a sample of 21 persons that live in the countryside. The researchers tried to understand as much as possible the way each person conceived the problem.

In the following we will present some graphics that reflect the answers of the persons interviewed regarding the issue. The age of those interviewed ranged from 18 to 58 years, the last one being the age of the retiring persons. Regarding the occupation, they qualify in the following categories: pupil, housekeeper, manager, unemployed, retired person, civil servant, worker, professor, engineer, economist, foreman, technician, electrician etc. Regarding their level of study qualification, the respondents range from those with medium studies (vocational education, high school), primary studies (7 and 8 grades) and higher studies (faculty).

Regarding the question (1): „On a scale from 1 to 10, appreciate the importance of the environment protection for the territory arrangement in comparison with other socio-economic sectors?” the answer is given in Fig. 1

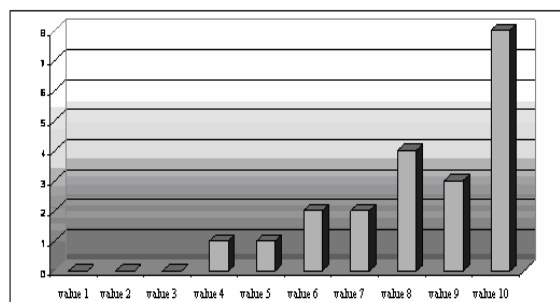


Fig. 1. Graphic representation for question No. 1

Question (2): „How do you appreciate the quality of the environment in the countryside?” has the answer graphically represented in Fig. 2.

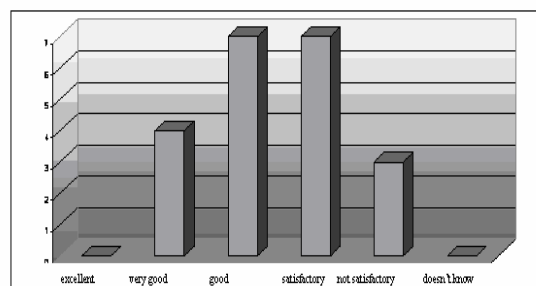


Fig. 2. Graphic representation for question No. 2

The answers given to this question are mostly positive, in the sense that the administrative territory of the commune was not covered with wastes and the condition of the environment is still favorable.

Question (3): „Which is the most serious environment problem from the countryside?” Through this question the research followed the knowledge of the most serious present day problem for the commune and if it is perceived at its real value for the protection of the environment (Fig. 3).

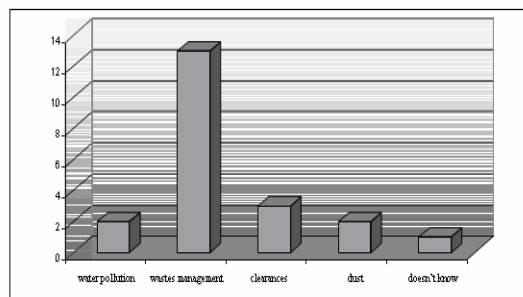


Fig. 3. Graphic representation for question No. 3

Question (4): „How do you appreciate the countryside people behavior confronted with the environment problems?” is answered in Fig. 4.

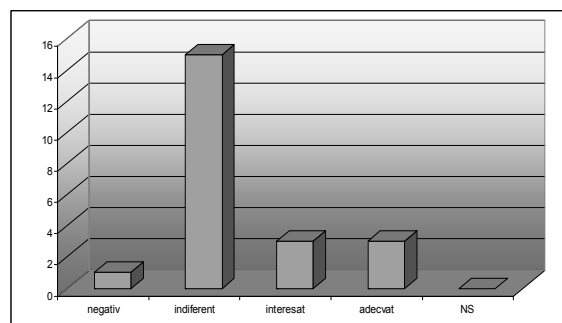


Fig. 4. Graphic representation for question No. 4

Question (5): „How do you consider that the countryside problems should be solved?” The

answers show that this particular problem of the waste management should be confronted together by the local communities with the local people involvement (Fig. 5).

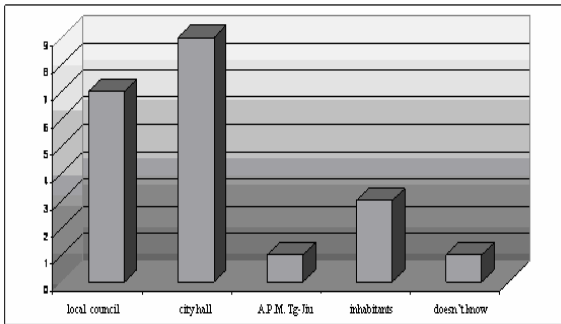


Fig. 5. Graphic representation for question No. 5

Question (6): „How do you appreciate the outcome of the measures undertaken by the parties involved in resolving the environment problems?” Contrary to our expectations, the answers given by the questioned reflects indifference for this problem (Fig. 6).

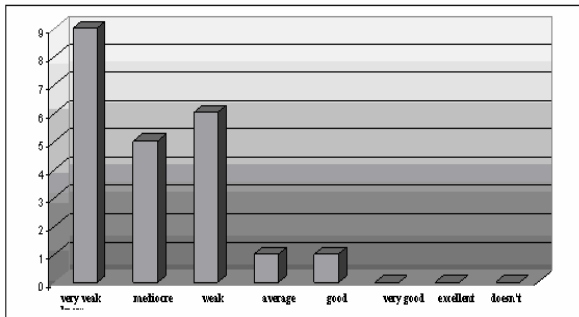


Fig. 6. Graphic representation for question No. 6

Question (7): „What do you understand by waste management?” has the answer presented in Fig. 7.

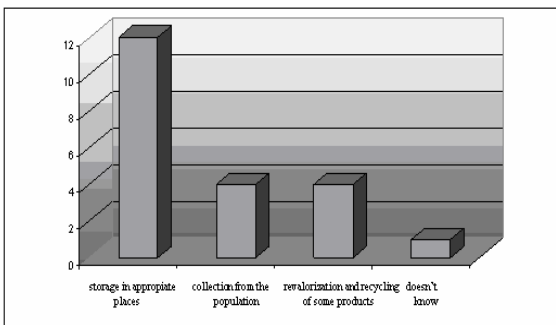


Fig. 7. Graphic representation for question No. 7

Question: „Would you orientate yourself for the acquisition of some 'ecologic products', given the conditions that they would have higher prices than the conventional ones?” is answered in Fig. 8.

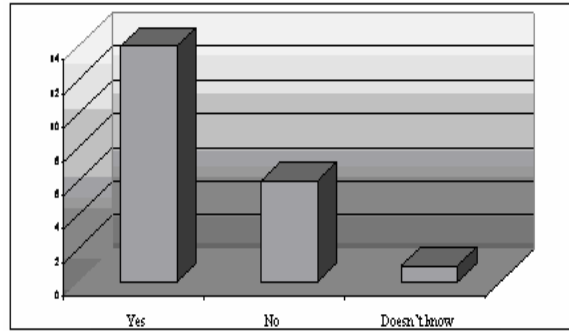


Fig. 8. Graphic representation for question No. 8

For the question (9): „If a tax would be perceived for collecting domestic wastes within the commune would you agree with it?” the answer is given in Fig. 9.

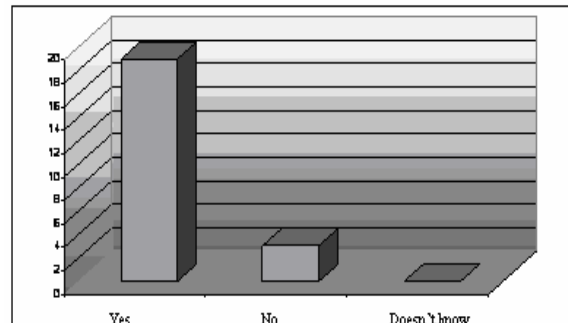


Fig. 9. Graphic representation for question No. 9

Question (10): „Do you believe that development of your children personality requires the cultivation of an attitude regarding the protection of the environment?” has the answer represented in Fig. 10.

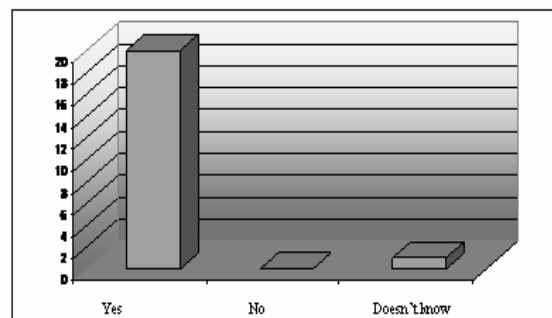


Fig. 10. Graphic representation for question No. 10

4. Conclusions

The compost improves the physicochemical characteristics of the soils and the requirements of using it as a fertilizer on the agricultural fields.

Because of the light alkaline pH and its chemical features, the soil from the district of Gorj allows the application of the compost with the condition that it has to be in a finished state (ripped)

and with the condition of respecting the doses of applied mud and calculated on the surface unity.

The measures and methods are materialized and exposed in a clear way through an integrated concept of waste management in the countryside:

- implementing real measures for cleaning;
- coordination and ordering of cleaning measures;
- informing and counseling the waste producers in order to minimize the quantity of wastes generated as well as encouraging the valorization measures;
- imaging and issuing of some legal stipulations, considered as the most important legal basis for the waste removal, with the possibility of influencing the citizen's behavior towards a reduction of waste production mentality.

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EUROPEAN Ph.D. IN SCIENCE FOR CONSERVATION

EU Project -05-MEST-CT2005-020559, EPISCON

To promote the synergy between the cultural heritage field, natural sciences and engineering, the European Community's Marie Curie programme is funding the EPISCON - European Ph.D. in Science for Conservation. The goal of the project is to form and develop the first generation of "true" conservation scientists in Europe, a goal to be attained by providing education, training, and research opportunities in the field of science for conservation of cultural heritage to young researchers.

EPISCON started in September 2006 and makes an original contribution to national and Community policies, as well as to the already existing knowledge in the field. Recent years, the number of national and European institutions and bodies of various types supporting the development of conservation-restoration projects significantly increased, as well as the number of organisations and bodies that carry out conservation-restoration projects.

16 three-year fellowships have been offered by ten EPISCON partners' host institutions within the European Community - internationally distinguished European academic and conservation centres working in the field of cultural heritage preservation and research:

University of Bologna, Italy (UNIBO) - coordinator
School of Conservation (SoC), Denmark
Eotvos Lorand University (ELTE), Hungary
Aristotle University of Thessaloniki (AUTH), Greece
Universidad de Oviedo (UNIOVI), Spain
"Alexandru Ioan Cuza" University of Iasi (UAIC), Romania
University of Perugia (UNIPG), Italy
Instituut Collectie Nederland (ICN), The Netherlands
Hungarian National Museum (HNM), Hungary
Istituto Conservazione e Valorizzazione Beni Culturali (ICVBC), Italy

Four other centers are associated to the host institutions within the project:

Istituto Centrale per il Restauro (ICR), Italy
Institute of Atmospheric Sciences and Climate (ISAC), National Research Council (CNR), Italy
"Petru Poni" Institute of Macromolecular Chemistry (IPPMC), Romania
Opificio delle Pietre Dure (OPD), Italy.

The fellowships include funding of an intensive six month training at the University of Bologna - Ravenna Campus (Italy) in all aspects and levels of the conservation of cultural heritage, followed by a two and a half years research to be performed at one of the host institutions. These activities are finalized with the defence of a thesis to be recognised by the participating countries.

The 16 selected fellows are coming from all over the world, their home countries being Romania, Italy, Czech Republic, Ecuador, Japan, Canada, Denmark, Hungary, Spain, Poland, France and Greece. They graduated in different fields, i.e. chemical engineering/technology, geology, mechanical engineering, environmental management and science, physics, natural sciences, material science or civil engineering.

The training received by the young researchers will not only give them the opportunity of developing new skills in a particular form(s) of analysis, but also provide exposure to a multidisciplinary way of thinking and problem solving. These skills are essential for building a long-term research career in both conservation and scientific community.

The holistic multidisciplinary educational approach the PhD curriculum is based on, and the establishment of a common language among themselves and with the other professionals involved in conservation will allow newly trained conservation scientists to better work and share knowledge within an integrated conservation system.

Ana-Bogdana Simionescu
University of Oviedo
Oviedo, Spain





IMPLEMENTING A SEA POLLUTION AND SAFETY MANAGEMENT SYSTEM IN THE NAVIGATION COMPANIES

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Abstract

The paper presents the main causes of the sea accidents and disasters, which call for the implementation of a sea pollution and safety management system (SMS) in the navigation companies, for certification purposes, in compliance with the International Management Code for the safe vessel operation and pollution prevention (ISM). For this purpose the objectives of the ISM codes are presented and which are to be found in the implemented Management System.

From the main causes of the safety deficiencies in vessel operation, by applying the cause-effect method, it was found necessary to implement a sea pollution and safety management system in the navigation companies able to provide more safety in ship operation, an implementation in the absence of which the international traffic would no longer be possible.

Thus the basic SMS implementation stages have been established taking into account the related international legislation.

Key words: conventions for sea pollution prevention, ISM code, sea pollution and safety prevention, SMS implementation

1. Introduction

The world economic growth reported in the last decades has been accompanied by an increase in the foreign trade and implicitly in the world sea trade. At the same time, the evolution of the world and European sea transport has been marked by more acute exigencies as regards safety, quality and sea-going vessels pollution prevention, the major cause being the large number of accidents and related high casualties along with heavy sea pollution (Bătrâna, 2004).

The maritime transport is an ample and complex economic activity both as amount of cargoes shipped annually and as material value. Its complexity also comes from its particular environmental conditions where it takes place – seas and oceans – which call for special safety measures (Bauchet, 1992).

The causes of sea accidents and their effects are constantly investigated by international organizations and institutions having authority in regulation, statistics, and insurance along with sports associations. They are investigated, classified and the conclusions are further turned into rules

norms or international conventions for the purpose of reducing or eliminating similar accidents in the future (Voicu et al., 2000). Therefore, international organizations such as UNO, EC and specialized agencies such as IMO (International Maritime Organization), ILO (International Labour Organization) have elaborated a significant number of conventions, regulations, rules, norms, international standards that contain essential criteria for the sea safety and sea pollution prevention.

Due to the IMO member governments having accepted the constant modifications to the rules and conventions referring to ship safety at sea and sea and air pollution prevention, their evolution is constant. Thus the IMO OILPOL 1954 convention was first modified in 1969, and in 1973 a much sever convention was adopted, “the Convention for Prevention of Sea Pollution by Ships”. The latter’s ratification was initially slow, but a number of accidents that occurred in the period 1976-1977, determined the call for the Conference on Oil tankers safety and Pollution Prevention in 1978, the Convention of 1973 being amended under the form known today as MARPOL 73/78 (MARPOL73/78, 1997).

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In 1967-1977, a series of accidents of some oil tankers have result in new modifications to the SOLAS Conventions (International Convention for the Safety of Life at Sea) adopted in 1974 and MARPOL (Convention for the Prevention of Pollution from Ships). SOLAS, the most important convention, has been repeatedly modified as a response to major disasters (SOLAS, 1974).

In 1989 IMO adopted the International Convention for Saving (SALVAGE, 89) and the International Convention on Oil Pollution Preparedness and Cooperation (OPRC, 1990), for the purpose of introducing a global system of response to the major oil discharges (International Convention on Oil Pollution Preparedness and Cooperation, 1995).

The navigation disasters resulting in casualties and severe contamination of the marine environment made it that in 1993 the IMO General Assembly elaborate and adopt the International Code of Safety Management (ISM, 1993). This is integral part of the International Convention SOLAS and it became compulsory for all vessels over 500 GRT (Gross Tons), since July 1, 2002. The ISM Code was elaborated to make from safety a major priority in the shipping companies' management (ISM, 2002).

Navigation accidents have had a considerably strong impact on the national economies, on companies and civil society as a whole. That why all over the worlds the new norms and regulations have had a major impact on the management of both navigation and shipping companies.

Within this world-wide strive for a safety and unpolluted marine transport with the slogan "Safer Shipping and Cleaner Oceans" a large number of programs are focused on two fundamental objectives: maritime safety and sea pollution protection.

The concern for achieving these two objectives covers international organizations, governments, navigation companies, ship owners, crews. It can be assessed that these objectives are the objectives of a World Management of Sea Safety Assurance.

The paper intends to present the main causes of a poor safety in ship operation and the need for implementing the Safety Management System and sea pollution prevention in the navigation companies.

2. Case-study

2.1. Applying the cause-effect method to establish the main causes resulting in poor safety at sea

Elimination or reducing naval accidents is only possible if there is full knowledge of their causes. Statistics reveal that the most frequent causes resulting in naval accidents are: complex technology, improper operation and maintenance of equipment, fittings, featuring old service life, improper spare parts, ships' age, the company itself, the management and last but not least the human factor.

An item on which all studies on naval accident coincide is that most of them are based on human error. The human element is a multidimensional

complex source which affects sea safety and sea environment protection. It is involved in the entire range of human activities performed by the ship crew, the on-shore management, regulating organisms, recognized organizations, shipyards and other relevant institutions, being necessary the cooperation of these factors for an efficient and safety orientation of the human element.

The proportion of the human error influence is variable but, in general, it is very high. Thus, a study carried out by the Institute of Shipping Economics of Bremen, Germany revealed that 75% of the accidents have been caused by two factors: the too heavy work the crew had to performed, especially in the harbour, and their unsuitable training (Alexiu and Alexiu., 2002).

An analysis carried out by United Kingdom Protection & Indemnity Club, shows that 60% of the accidents are caused by human error. The human error is also responsible for 50% in the case of pollution, 65% in case of staff injury, and 90% in case of collisions. The supervising by the Advisory Committee on Pollution of the Sea of numerous cases of oil discharges in the Great Britain waters in 1990, has found out that the human error is the cause of 66% of the cases (MEPC, 1999).

The Australian Ministry of Transports and Communications reported in 1992 that approx. 75% of the accidents investigated were caused by human errors. A report published by the American Bureau of Shipping Marine Service in 1994 revealed that, statistically 65% of the major damages reported are due to human operating errors, out of which 27% are due to uncertain practices (IMO, 1994). Although percentages may vary, all studies on the subject show that most maritime accidents take place due to an error which might have been avoided.

Consequently, any attempt to reduce accidents at sea should focus on the elimination of the human error, the human factor being considered almost unanimously to be the cause of 80% of the naval accidents (Branch, 1996). An evaluation of the possible causes resulting in poor safety is made by the cause-effect method (Ishikawa diagram). Evaluation is based on the data from the literature and the main causes of maritime accidents are investigated. Major causes can be thus revealed along with sub-caused which effect is poor safety in ship operation.

In conformity with the statistic data published, the rate of accidents which further led to marine disasters is as follows: complex technology 5%, improper equipment operation /handling 8%, old equipment 3%, ship aging 4%, human error 80%. Taking into account the percentages, the cause-effect diagram (Fig. 1) highlights the major causes which are based on human factor.

The diagram highlights that the major causes for human factor error are: no plans for emergency situations, no planned actions, lack of information, lack of standards, unclear instructions, no proper knowledge and experience and, last but not least, no motivation.

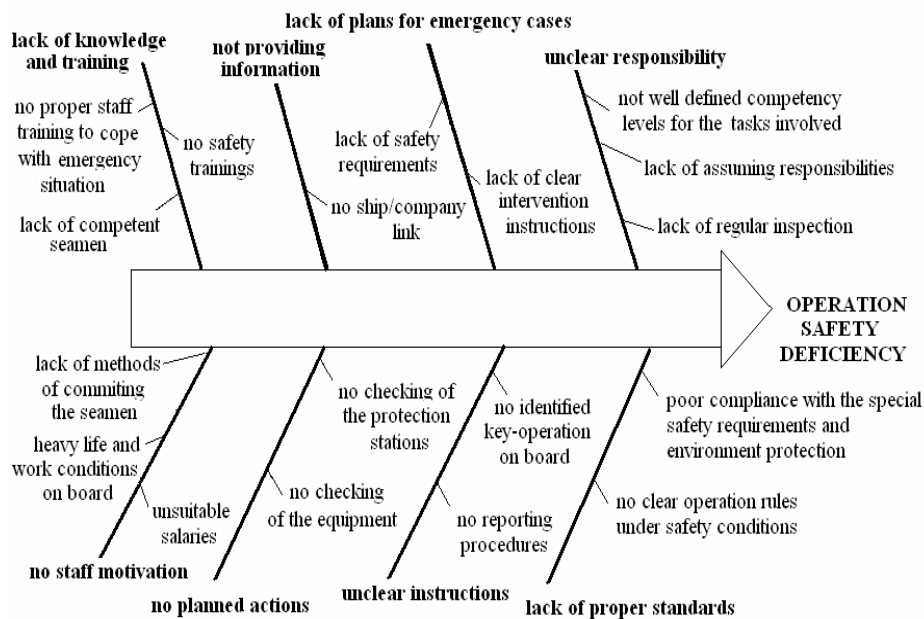


Fig.1. The cause-effect diagram (sursa : original)

All such causes can be eliminated and human errors avoided or reduced by implementing a Safety Management System.

Management and human resources is the key for success in a company nowadays. Maintaining a navigation company in the sea traffic implies to accept the idea that improving sea safety depends on the human factor.

2.2. Necessity of implementing a Safety Management System in the navigation companies

The new requirements and rules of the international maritime organisations bring in front of the navigation companies a number of problems such as (Iordanoia, 2003):

- Pollution protection and prevention of the environment and especially the marine environment;
- Safer marine operation procedures;
- Methods of response to emergency situations, identified or likely to occur;
- Development of integrated management systems of quality -environment – safety;
- Training of the onboard staff so as to be able to work safely on board, to know and observe the international norms and rules on safety and environment protection.

Taking into account all this, as well as the causes affecting safety at sea, the ISM code require each navigation company to implement and maintain its own Safety Management System (SMS). Thus, this becomes not only the condition to take part in the international traffic but also a compulsory condition to insure the ship (starting with July 1998).

The Safety Management System, which as a result of the evolutions in the international maritime world, becomes compulsory for the entire world sea fleet, stands for the national dimension of the ISM code, this being the most important dimension, the system efficiency and results depend on.

The ISM code is considered by the literature as the norm document having the heaviest impact on the world commercial fleet. It is an international standard for the operation and management of ship safety and pollution prevention (ISM, 2005).

The main objective of this code has been the increase in ship safety and keeps the marine environment uncontaminated. The ISM code is a unitary set of rules and requirements applicable to both ships and navigation/shipping companies, starting from the pre-requisite that the most important modality of preventing maritime accidents and sea pollution by ships is to design, manufacture, equip and maintain vessels and further having them operated by properly trained crew, in compliance with the international conventions and standards about maritime safety and prevention of marine pollution (ISM, 2005).

Applying the ISM code is expected to encourage the development of a true culture for shipping safety. The success factors for developing such a safety culture may include confidence, values and conviction. The motivation of the Safety Management System is to keep ship in the international maritime traffic under safety and environment protection conditions, reducing the number of accidents, damages and disasters. Its general objectives are the ship safety, life and work conditions on board and prevention of the

contamination of the sea where the ship is operating (Iordanoaia, 2006).

A model of Safety Management System is given in Fig. 2. The Safety Management System makes specific provisions for suitable steps likely to ensure that the company, due to its organisation capabilities, be able to cope any time with the dangers, accidents and emergency situations which might occur.

3. Results and discussion

Highlighting the main causes and sub-causes that affect ship operation safety at sea revealed the need for implementing a Safety Management System in each shipping company.

The SMS proposed model (Fig. 2) provides for the major stages of its implementation for the purpose of obtaining the safety management Certificate for each ship and the Certificate of conformity of the shipping company.

They are the proof that both the ship and the company meet the requirements of the ISM code issued in 1993.

The stages provided are: evaluation of the existing state of the company in terms of ISM code, establishing a Safety Management System implementation program, and the certification audit as per ISM code.

The company objectives with respect to safety management and pollution prevention as defined by ISM code are to be found in the company's SMS (ISM, 1993).

They are the followings: assuring safe practices in ship operation and a danger-free working environment, establishing safety measures against the identified risks, permanent improving of the on shore and on board staff competences as regards the safety management, including staff training for emergency cases.

In order to achieve these objectives, the shipping company establishes whether it applies and maintains a safety and marine pollution prevention policy. This policy shows how objectives are out into practice at all organization levels on shore and onboard equally.

To guarantee safety operation of each vessel and to make the proper link between shipping company and the staff on board, the company appoint one or more persons on-shore which have direct access to the highest management level. Among their responsibilities is the surveying the ship operation, pollution safety and prevention, assign the suitable resources and their related support on shore.

A good safety and pollution prevention management both off- and on- shore implies that the operational responsibility is the ship captain's but the overall responsibility asks for a deeper commitment of the on-shore management.

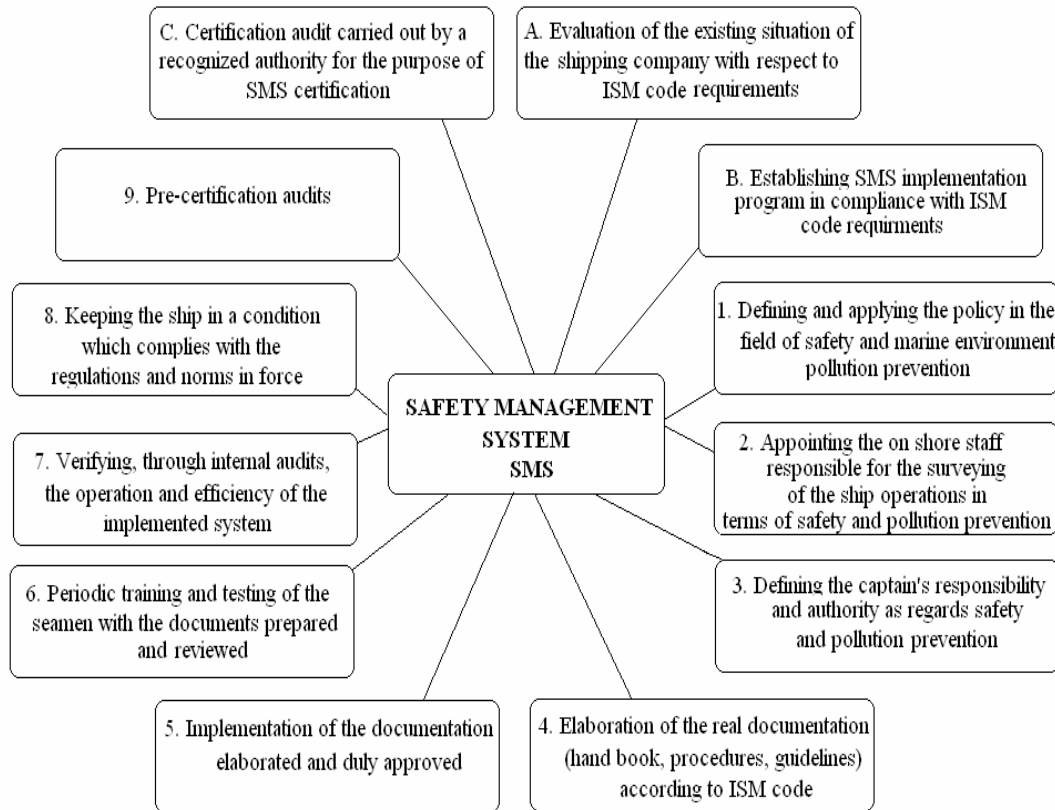


Fig.2. Safety Management System

The company clearly defines the captain's responsibility as regards: implementing the policy, motivating the crew, making up the orders and guidelines very clear, checking the compliance with the specific exigencies, analysing the safety Management system and informing about lack of compliance with the on-shore management. Within the system the supreme authority belongs to the ship's captain since it is up to him to take decisions on safety and pollution prevention.

Within the System, the company establishes a set of procedures for: training the staff for the system implementation, making the schedules and instructions for the major operations on board, identify and describe the emergency situations and measures to take, identify the equipment and installations whose sudden damage may create dangerous situations. The system provides for specific measures to increase reliability of such equipment.

The procedures included in the Safety Management System must ensure that potentially dangerous accidents are reported to the company, as they are investigated so as to improve ship safety and pollution prevention (Willingale, 1998).

The company performs internal audits to check if the activities related to safety and pollution prevention are in compliance with the implemented system, making periodical evaluations of its efficiency.

The safety management certificate is issued to a ship after the initial verification of the compliance with the ISM code requirements. This includes verification if the company conformity document is applicable to the specific type of ship and the implemented system is in accordance with the ISM code and is properly applied (ANR, 2005).

4. Conclusions

The cause-effect analysis as regards the causes and sub causes that determine the human errors accompanied by accidents and marine disasters resulting in casualties and sea contamination has shown that such causes may be eliminated by introducing a SMS in the shipping companies.

The safety Management system means a structured and documented unit which enables the implementation of the company policy of safety and marine pollution prevention. It should ensure that compulsory rules and regulations are strictly observed, along with the applicable codes, standards recommended by the organization, administration, classification societies and marine organizations.

The fundamental condition of a good safety management is the highest commitment. In the issues of safety and pollution prevention the final result is

determined by the commitment, competence, attitude and motivation of individuals at all levels.

The Safety Management System provides for adequate measures so as to ensure that the company organization is able to face, any time, the accident dangers and emergency situations its ship may found itself into.

Implementation of such a system is a condition to maintain each ship in the international traffic circuit.

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SOFT COMPUTING HYBRID CONFIGURATIONS APPLIED IN CHEMISTRY

IDEI PROGRAMME PNCDI II, Research Grant ID_592, Contract no. 59/2007

This project targets the use of Artificial Intelligence Techniques (neural networks, genetic algorithms, classifiers, fuzzy systems), combined in hybrid heuristic configurations, for modeling and optimization of chemical processes. The synthesis of new materials, based on ferrocene, with liquid crystal properties is considered as a case study. The problems attempted to solve are the subject of complex interdisciplinary research, requiring advanced knowledge in both chemistry and computer science.

The project objectives are organized on two parallel plans, which correspond to the domains of computer science and chemistry. Applying the methods of Artificial Intelligence (AI) to modeling and optimization of chemical systems represents the bridge between the two fields and defines the inter-disciplinary character of our proposal.

Mainly, the scientific goals of the project are:

1) Advanced research oriented toward the elaboration and improvement of techniques based on AI instruments, with a special emphasis on hybrid soft computing techniques that provide computational efficiency and large-spectrum applicability.

2) Synthesis and characterization of ferrocene based new materials with liquid crystal properties.

3) Modeling and optimization of the parameters associated to ferrocene-based materials, making use of soft computing techniques.

Meanwhile, specific goals of the research program *Idei* are as follows:

1) Obtaining scientific achievements at the international level as the result of complex research based on real novelties ("ideas"). Solving the scientific objectives will lead to acquiring advanced knowledge, contributing to generating new scientific and technical knowledge, development and strengthening of those

research directions of scientific and technological top fields, in particular soft computing. The need for "excellency" as the quality level of the Romanian research, in agreement with the international standards, will create the true conditions for the participation in the European programs.

2) Development of the human resource, as a premise for constituting and consolidating of a working team suitable for interdisciplinary research, with both experienced and young researchers and engineers working effectively in AI and chemical synthesis of materials. Promoting young people, preparing them for research, stimulating them adequately to remain to work in research, and supporting them for the highest standards in the field, including Ph.D. degrees, signify important aspects involved within the project.

Starting from the continuous evolution of the life quality, which implies the need for new and higher characteristics of the materials, devices and real systems, the scientific research has to cope with current and future difficult problems. According to the estimated results of the project, the scientific impact of the project will be mainly evaluated by the number and quality of the published papers, related to the scientific level of the chosen journals (their ISI ranking), the quality of the edited monographs, and the scientific level of the Ph.D. theses accomplished within this project.

The social impact is associated to the fact that the project integrates young post-docs, Ph.D. and master students that can develop their talents in research and software product development. Organizing exploratory workshops and research documentation stages in Romania and abroad will represent useful opportunities for the young researchers and for the orientation of their future activity.

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GROUNDWATER CONTAMINATION FROM WASTE STORAGE WORKS

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Abstract

Groundwater is an important source of drinking water, especially for rural population. In the last years, bacteria, nitrate, organic chemicals and other pollutants existing in groundwater have increased public concern about the quality of groundwater. Groundwater provides about 22% of all freshwater withdrawals; 37% of agricultural use (mostly for irrigation); 37% of the public water supply withdrawals; 51% of all drinking water for the total population and 99% of drinking water for the rural population; 46% of domestic and commercial use; 24% of industrial and mining use. The most severe groundwater quality depreciation appeared in the rural built-up area, where the lack of minimum public facilities allows liquid waste to reach directly or indirectly into the groundwater. The paper analyzes the soil and groundwater behaviour in the presence of three of the most significant sources of groundwater contamination due to waste storage works: sewer lines, septic tanks and landfills.

Keywords: groundwater contamination, landfills, sewer lines, septic tanks, waste storage works

1. Introduction

The elevation of underground water threatens the stability and the correct exploitation of many buildings due to the influence of the pollutants into the foundation soil. Groundwater usually contains high concentrations of natural dissolved materials that affect the ground composition.

Most groundwater originates from rainfall that has entered the ground. About one-fourth of the quantity of precipitation infiltrates the soil and recharges local aquifers and the sediments that store and transport groundwater.

Shallow, permeable water table aquifers are the most susceptible to contamination, due to specific site characteristics as: distance from the contamination source to the aquifer, residence time of the water in the unsaturated area, presence of clay and organic matter in the unsaturated area, potential of a particular contaminant to decompose, amount of precipitation that affects recharge, evaporation that

decreases the amount of water that moves downward to the aquifer.

The main factors influencing the transport of the pollutants in the ground are: the underground water level, the quantity of pollutants, their type, and soil bedding (Bedient et al., 1999).

The groundwater measurement consists in: measurements of the water level depending on the level fluctuation amplitude, temperature measurements in specific drillings, experimental pumping to determine the properties of the hydrogeological layer, and periodical sampling to determine the water physico-chemical characteristics (Rotaru et al., 2001).

2. Case study

Taking Romania as a case study, this research focuses on the groundwater contamination due to waste storage.

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From the point of view of pollutants, there are four types of soils (Tobolcea, 2007): (i) soils that allow pollutants accumulation; (ii) soils that allow pollutants migration; (iii) soils polluted due to natural sources; (iv) soils polluted due to human activities.

In the first case, even if the tests were performed at distance from the sewage system (100m), pollutant concentrations in the underground water are as high as in the sewage system.

In the second case, an example from Romania consists of lead traces migrated from the Roman Pipe Factory and founded in Siret Plateau, in northeaster of Roman City.

Groundwater contamination can be both natural- and human-induced. Groundwater commonly contains one or more naturally-induced chemicals, leached from soil by percolating water.

In the third case, the soil pollution was analyzed within the framework of some water drain projects realized in Iasi area, Romania, and by the mediation of some boreholes drilled in Iasi City. The presence of sulphur in weak, medium and hard soil layers was observed in the analyzed area, with great concentrations in areas like: S.C. Moldomobila S.A., S.C. Lactis S.A. and Nicolina Hospital. The values for different sulphur compounds are there up to 1200 mg/l, very high in comparison with the limits cleared up by national regulations (NTPA 002/2005) that allow maximum values of 1,0 mg/l sulphides and 600 mg/l sulphates in urban sewage systems.

The deep drillings realized by the National Hydrogeological Network in Romania investigate unknown areas from deep groundwater layers analyzing the behaviour of groundwater under natural conditions.

In the fourth case, it is obvious that groundwater pollution levels vary widely by location and depend on local industry and agriculture. In Romania, only desultory groundwater-quality measurements are available. These measurements reveal that groundwater is highly polluted in some areas, especially with nitrates, phosphates, pesticides, heavy metals and organic pollutants, the concentrations exceeding the admissible concentration limits specified by STAS 1342-9: Siret corridor on the downstream Roman-upstream Adjud stretch; Bistrita corridor downstream of Piatra Neamt; Trotus corridor on the downstream Onești - upstream Adjud stretch; Sitna depression - downstream of Botosani; Bahlui corridor downstream of Podu Iloaiei; Prut corridor downstream of Ungheni; eastern Covurlui Plain; lower Siret Plain; the eastern half of southern Dobrogea; lower Danube Plain; northern Baragan Plain; Ialomita corridor on the Urziceni-Tandarei corridor; piedmountaneous Ploiesti Plain; mountain and under-mountain depression areas drained by Olt-Ciuc, Brasov, Fagaras and Cibin; Crasna corridor; middle area of the Banat Plain; Mures corridor on the Reghin – Ludus stretch; Tarnava Mare corridor downstream of Sighisoara as well as Somes lower plain.

Contaminants enter groundwater from more than 30 different sources related to human activities. Some of these sources are: inadequate irrigation systems generating increased piezometric levels in Bailesti, Romanati and Baragan plains (2-15 m) and southern Dobrogea (3-10 m); excessive catchment of water generating decreases of the piezometric level of groundwater in Bucharest – "Fratesi Layers" (20–50 m); mining area drying generating in Rovinari over 80 m decreases of the piezometric level; products used in agriculture such as fertilizers (NH₄, NO₂, NO₃, phosphates) or pesticides in factories as AZOMURES Targu Mures, ARCHIM Arad, DOLJCHIM Craiova, OLTCHIM Ramnicu Valcea, AZOCHIM Roznov; products resulting from industrial processes contaminating areas around large industrial platforms such as Victoria, Fagaras, Codlea, Tohanu Vechi, Zarnesti, Bod, Isalnita, Craiova; oil products and phenol compounds due to Petrobrazi, Astra and Petrotel Ploiesti refineries; domestic products contaminating areas around important cities like Pitesti, Oradea, Bucharest, Cluj, Suceava; sewage.

Some man-made activities influence the water quality: landfill solid waste disposal, liquid waste disposal basins, septic waste infiltration systems, gasoline service stations, underground storage tanks, many industrial activities, urban storm-water infiltration (Fitts, 2002).

The common sources of human-induced groundwater contamination are: waste disposals, agricultural activities, and saline water intrusion.

Waste disposal can be made by: septic systems, landfills, waste-injection wells, and direct application of stabilized wastes to the land (Sharma and Lewis, 1994).

The most important sources of groundwater contamination in Romania are associated with the storage of liquid and solid wastes caused by (i) sewer lines, (ii) septic systems and the country's many legal and illegal (iii) waste landfills with an inadequate protection against pollutant leakage.

The organic substances resulting from waste disposal frequently existing in groundwater are: trichloroethylene (TCE), chloroform, benzene, pentachlorophenol, tetrachloroethylene (PCE), creosote, phenolic compounds, 1,1,1-trichloroethane, toluene, xylene (Fetter, 1999).

In Romania, 3% of rural citizens are connected to sewage system, 11% have individual (septic) system, 15% have access to central drinking water system.

2.1. Sewer lines

In Romania approximately 20% of population uses storm water systems combined with sanitary sewer systems and 46% of population uses separate systems, especially in urban areas. When leaking sewer lines are located underground below the biologically active layer, the sewage can enter groundwater directly.

Sewer leaks can occur from tree root invasion, soil slippage, seismic activity, loss of foundation due to washout, flooding and sewage back up, among other events.

In Romania, the loss of foundation due to washout is among the top dangers for a foundation. Underground rivers move the soil under the building and put stress on the foundation. The amount of water in the soil is also a damaging factor. In an area where heavy rainfall is followed by a dry season, such as in much of the northeast of Romania, the amount of water in the soil varies. As moisture evaporates, the soil contracts; as moisture seeps into the soil, it will expand.

2.2. Septic systems

Where no sewer system exists, such as in rural areas, to store and process wastes are used septic systems. But approximately one-third of existing septic systems contaminate aquifers because improper operation.

The typical sources of waste water entering a septic system are: toilets (approximately 38%), laundry (25%), baths (22%) and sinks (15%). These systems are sources of bacteria, viruses, nitrate, phosphorus, chloride and organic substances.

Making a septic system, the important factors for environment are: the quality of water receiver, the chemical characteristics of the groundwater, the materials used for pipes and work quality.

Contamination of water from septic systems occurs under various conditions: poor placement of septic leach fields, bad percolation system, high density placement of tanks, and construction or maintenance practices. Additionally, there are soil properties, subsurface geology, climate and vegetation which may affect the quality and quantity of waste water (Fig.1).



Fig. 1. Contaminated groundwater from septic systems

Septic systems must be located below the building and where the water will not come to surface or cause slope instability. The steep slopes cause

effluent to surface. Large areas in Moldavia region, Romania, are steeper than 20%, being subjected to natural landslides. These soils represent thin deposits of loess, a fine-grain wind deposited sandy, silty, clayey soil with a low dry density, which has clay cementation that makes it strong and stable when dry. However, this soil is highly compressible due to its low density and unstable when wet. It becomes wet naturally resulting in landslides when moisture contents are higher than 18%. Buildings may also cause the soil to become wet or saturated resulting in large settlements under applied loads and loss of bearing capacity.

Septic systems are ones of the largest sources of pollution. A septic system consists of a septic tank (a container made of concrete, fibre-glass, or polyethylene), a distribution box, and a drain field. Wastewater flows into the tank, where it is held for a time to allow suspended solids to separate out. The heavier solids sink to the bottom of the tank and are partially decomposed by microbes forming a layer of sludge. The lighter materials (grease, oil, fat, digested solids or small food particles), float on the surface to form a layer of scum. The partially clarified wastewater between the layers of scum and sludge flows to the distribution box, which distributes it through the drain field (a network of perforated pipes laid in gravel-filled beds). Wastewater flows out of the pipes, through the gravel, and into the surrounding soil (Zheng and Bennett, 2002).

The leach field must have a certain separation from the water table to prevent contamination. Likewise layers of impermeable soil must be a certain depth below the leach field.

2.3. Landfills

Landfills represent an important threat to groundwater contamination. A landfill is a site for the disposal of waste materials by burial, the oldest form and the most common method of waste treatment.

Some hazardous waste materials are deposited in landfills and underlying groundwater may become contaminated. Most household waste is buried in landfills. Wastes deposited at industrial landfills include traces of metals, acids, volatile organic compounds and pesticides, which may cause local contamination.

3. Results and discussion

Among geological risks, the groundwater pollution is an induced one. The risk evaluation and management involves four stages (Bocanegra et al., 2003; Vrba and Zaporozec, 1994): (i) prediction, (ii) prevention, (iii) monitoring, and (iv) mitigation, as follows:

(i) The prediction of the future behaviour of the system means diagnosis of the current situation measuring the most important parameters: water resources, stream discharge, aquifer recharge, area affected by waste disposal, volume of urban waste

produced, total population lacking sanitary services, untreated waste, polluting industries, fertilisers and pesticides used.

(ii) Monitoring determinates the main parameters in a given time to measure groundwater quality (Scharp et al., 1997): unsaturated thickness, area affected by waste disposal, chemical and bacteriological pollution, heavy metals in water and sediment, persons affected by hydric diseases.

(iii, iv) Prevention works with mitigation. These stages are planned and executed to avoid the contamination risk. Mitigation consists of actions taken to attenuate or eliminate alteration processes or the contamination of groundwater. Mitigation measures during design phase and afterwards are: materials chosen according to soil aggressiveness, proper work execution, and sewers monitoring during performing (El-Kadi, 1995).

In order to work properly, a septic system must accomplish some parameters.

Soil permeability must ensure proper treatment of system effluent (Rotaru and Raileanu, 2004). The water carrying capacity of the soil must be measured before the design of the septic system using a percolation test.

In general, groundwater flow is slow and depends on the permeability of the subsurface materials and on the hydraulic gradient. Soils with percolation rates slower than 20 min/cm make the septic systems unsuitable. Soils with rapid percolation rate (high permeability) are incapable to absorb effluent from the leach field. As result, alternative systems may be design.

Many environmental factors (rainfall, soil moisture, temperature, pH, organic material in the soil) influence the movement of contaminants from the septic system through the soil to groundwater.

There are two important conditions to be kept: minimum horizontal setback distances from buildings and drinking water wells, and minimum vertical setback distances from impermeable soil layers and water table.

The geotechnical features of the foundation soil presenting wastewater assume the possibility of groundwater and foundation ground pollution (Rotaru and Raileanu, 2004).

The analysis developed in Iasi area, Romania, at 2.00 m deep is presented in Table 1. Iasi City, in northeastern of Romania, is the second city of the country, with more then 350,000 inhabitants.

Iasi soils are commonly plastic clay at 2.00 m deep without foundation ground pollution, with a clay fraction between 61% and 82% and with geotechnical features as in Table 2. Drained loamy soils are proper for septic systems.

Soil characteristics and topography must be taken into account in designing the septic system, especially the drain field, located in relatively flat areas to ensure uniform effluent flow. The lower the soil permeability, the larger the drain field required. The infiltration capacity of the soil is reduced when the soil is already compacted and dry. The knowledge of the groundwater influences to the foundation soil allows the comparison of the initial properties of the foundation soil with those after its pollution.

Proper maintenance of septic system is important to prevent contamination: annually inspection to verify the internal structures and to monitor the scum level; wastewater from basement pumps and the surface runoff from roofs must not be discharged into the system; pumping out every two to five years depending on the tank size, wastewater volume, and types of solids entering the system, because the concentration of solids entering the drain field can reduce soil permeability and cause the drain field to fail. Trees should not be planted over the drain field because the roots can enter the perforated piping.

Remedial methods include: excavation and offsite removal, excavation and onsite treatment, groundwater "pump and treat", bioremediation, in-situ treatment (Rotaru, 2004).

For landfills the environmental protection should focus on: contaminated water, control water from precipitation entering into the landfill body, prevent groundwater entering into landfill waste, prevent lateral dissipation of the medium, gas control, stability insurance, hazards minimization, relation with local landscape (Nicholson et al., 1983).

Table 1. Geotechnical features in Iasi area, Romania, at 2.00m deep, for soils presenting wastewater

<i>Geotechnical features</i>	<i>Symbol</i>	<i>U.M.</i>	<i>Value</i>	<i>Observation</i>
Moisture content	w	%	33.70	
Plasticity Index	I_P	%	32.04	high plasticity
Consistency Index	I_C		0.62	
Natural unit weight	γ_{med}	g/cm ³	1.83	
Porosity	p	%	49.84	
Void ratio	e	%	1.02	
Degree of saturation	S_R		1.89	saturated
Oedometric modulus	M_{2-3}	daN/cm ²	83.29	
Specific settlement	ε_z	cm/m	4.57	very compressive
Angle of internal friction	\emptyset	degree	18	
Cohesion	c		0.4	

Table 2. Geotechnical features in Iasi area, Romania, at 2.00m deep, for soils without pollution

<i>Geotechnical features</i>	<i>Symbol</i>	<i>U.M.</i>	<i>Value</i>
Natural unit weight	γ_{med}	g/cm ³	1.67 – 1.69
Dry unit weight	γ_d	g/cm ³	1.23 – 1.35
Porosity	p	%	53.1 – 55.6
Degree of saturation	S_R		0.701 – 0.984

4. Conclusions

In many regions of Romania the groundwater quality is in critical condition. As a result of environmental pollution, 7 million hectares of agricultural land are affected by erosion, especially in the southern part of the country. For this reason, within the water quality management policy, measures to prevent the quality degradation of the water resources should be a priority (Miller and Scalf, 1974).

If groundwater contamination is identified on a site, and if contaminant concentrations are found above regulatory limits, remedial activities or feasibility studies must be done just to keep a site in compliance. Such activities vary with the contaminant, medium contaminated, and surrounding environmental factors.

Assessment of the groundwater contamination is difficult. Groundwater moves very slowly, and it may be years after remedial actions are taken before improvements in water quality are obtained. For this reason, the enhancement of the quality of the groundwater requires a long-term commitment.

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NEW APPLICATIONS OF ARTIFICIAL INTELLIGENCE TOOLS IN MODELING AND DETERMINING CERTAIN PHYSICAL-CHEMICAL CHARACTERISTICS

Idei Programe PNCDI-II, Project ID _600 (Contract no. 64/1.10.2007)

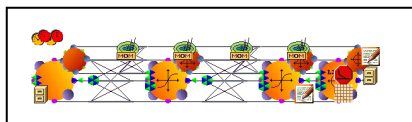
Significant efforts have been noticed at international level these latest years, to reduce the number of experimental determinations, which has also become a more frequent requirement in the study of physical, chemical and biological processes. This trend is particularly supported by the economic advantages that may result from it, like, for instance, less time-consuming and less expensive experimental research. The use of artificial intelligence tools in modelling and determining certain physical-chemical characteristics helps the achievement of this desideratum.

To support the above considerations, the overall objective of the grant proposition is the assessment of the applicability of various artificial intelligence tools like: neuronal networks and genetic algorithms in modeling and determining certain physical-chemical characteristics, while one of the specific objectives of the project would be aimed at discovering new applications for artificial intelligence tools in the study of the characteristics of real systems by means of proper models. Also, it tries to contribute to the establishment of new mathematical models, by means of modern and topical methods, namely – neuronal networks and genetic algorithms. The new calculus concept – neuronal calculus – that led to concrete achievements also known as artificial neuronal networks (in short neuronal networks) distinguishes itself through its applicability to very different fields.

The calculus based on neuronal networks is one of the artificial intelligence areas with the fastest development due to the ability of neuronal networks to memorize different types of relations. Neuronal networks proved able to estimate any continuous non-linear function, which means that they may be applied to non-linear system modelling.

The project theme has a multi-disciplinary nature, as it combines experimental abilities with high performance computational methods, thus providing useful tools to chemical engineering and also observing the preoccupations of the researchers at international level.

The project theme is an applicative and fundamental research area based on the synergy of pluri-disciplinary approach in physics, chemistry and mathematics.



It has a multi-disciplinary nature and it is compliant with the national society computerization policy, by the transfer and implementation of the most recent information technologies in chemical engineering, aimed at obtaining high performance solutions for new technologies and products.

The scientific importance of the theme replies on the two directions of application of the artificial intelligence tools we approached: 1. – modeling and especially determination of certain physical-chemical characteristics like: excess refraction index, excess molar volume and excess superficial stress of binary fluid systems and 2. – prediction of the thermal stability of certain organic compounds based on their molecular structure.

The design of materials having certain compulsory biological, chemical and physical characteristics requires the modeling of significant interactions between the basic structural units for characteristic prediction, as well as the efficient localization of viable structures that could help achieve the wanted synthesis performance. This area of molecular design is a way to combine neuronal networks and genetic algorithms. Neuronal networks model the non-linear structure-characteristics correlations more accurately and more easily as compared to other conventional approaches and that is why they are used to solve the direct problem. The opposite problem concerning molecular design is also solved by means of neuronal networks optimized with genetic algorithms, based on the fact that, wishing to obtain certain macroscopic characteristics, molecular structures are built that could provide such characteristics. Both research directions shall contribute to the achievement of the project desideratum, namely the reduction of the number of experimental determinations required for the establishment of certain physical-chemical characteristics with implications on time and money saving.

For more information on the PN-II-ID _600 project please visit the project site at:
<http://www.ch.tuiasi.ro/cercetare/PNCDI/glisa/en/ind ex.html>

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MODELLING CHLORINE DECAY IN DRINKING WATER MAINS

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Abstract

Drinking water treatment plays an important role in maintaining public health. Chlorine is the most often disinfectant used for microbiological protection of water. Required residual chlorine concentration must be in treated water when it leaves treatment plant, to comply with the regulations. The chlorine residual must be 0.5 mg/L at the entrance into the distribution system and 0.25 mg/l at consumers, according to the law. Any less and there is no guarantee that the water has adequate quality. The major problem that occurs as water flows between treatment plant and the consumer is water quality deterioration because of decreasing of residual chlorine concentration, especially for long residence times. This can be lead to high microbiological concentration in water downstream and it is necessary additional treatment with chlorine. This study presents a theoretical model based on dispersion equation, which was validated with experimental measurements in drinking water mains that supply Ramnicu-Valcea town, Romania.

Key words: drinking water treatment, disinfection, chlorine decay, dispersion equation

1. Introduction

Disinfection is the last safety barrier on the way to render sanitary quality to drinking water. Chlorine is the most used disinfectant for this purpose, providing high degree of sanitation at a relatively low cost. The major drawback is formation of disinfection by-products because of chlorine reaction with natural organic matter from water. Destruction of harmful microorganisms by chlorine is mainly related to contact time, concentration of chlorine and water quality. Successful chlorination requires that amount of chlorine added corresponds with chlorine demand tests to achieve disinfection and oxidation. A little more amount of chlorine than is required is added, to be sure that is sufficient. This will lead to free chlorine residual that can be measured. However, chlorine must not be added in amounts that are wasteful and create unnecessarily operational costs. There are many researches to predict chlorine demand, (Chen and Jensen, 2001; Haas et al., 2002; Yu and Cheng, 2003).

A number of researches have been developed to modeling chlorine decay in drinking

water distribution system: (Islam et al. ,1997), (Clark and Sivaganesan, 2002; Ucak and Ozdemir, 2004; Leeuwen et al, 2004; Jivan, 2005). A review of several models for predicting the decay of disinfectants and the formation of disinfecting by-products have been presented by Clark et al. (2001). These models are mostly based on first-order decay, second order decay, power-law decay (nth order) and exponential decay assumption or reacting balance equation. Some authors divided the chlorine decay into two phases: an initial consumption phase and a slower second phase.

In this paper it is used dispersion equation to model chlorine decay, with a first-order decay term for chlorine consumption with different values along the pipe, correlated with flowrate. A customized program was developed in FlexPDE for numerically integration of equation. The results were compared with experimental data from mains that supply Ramnicu - Valcea town.

The water distribution system for Ramnicu – Valcea area is composed of: 1) raw water pipe (8574 m length and 1200 mm diameter) that brings water from Bradisor Artificial Lake on Lotru river to

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hydroelectric power plant Valea lui Stan (Stan's Valley); 3) Drinking Water Treatment Plant (DWTP) located in Valea lui Stan village; 3) treated water distribution pipe to Ramnicu - Valcea (1200 mm diameter, 12 mm thickness and 36 615 m length, made of carbon steel).

Water flows by gravity in distribution systems, because of the difference of ground elevation (DWTP - 350.5 m, Ramnicu-Valcea - 312 m), leading to great energy savings. However, the system includes 3 pumping stations for increasing water supplying pressure. DWTP supplies water in 6 municipalities in Ramnicu Valcea area. Average production is 1600 l/s. Water is treated initially in mixing tank with addition of chemicals (aluminum sulphate, polymers, chlorine and lime) and after that with sedimentation, filtration, final chlorination and storage. There are 2 storage tanks in DWTP, each of 975 m³, laying out under the filters. After years of work, in distribution pipe occurred deposits of 15...25mm height. In 2004 the distribution pipe was cleaned using COLBACH patented technology, initially used in oil industry, based on helicoidally brushes on a cylinder.

2. Mathematical model

Theoretical study of chlorine decay considers dispersion and consumption of chlorine in water. General unsteady dispersion equation of chlorine in water is:

$$\begin{aligned} \frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial x}(\bar{u}\bar{C}) + \frac{\partial}{\partial y}(\bar{v}\bar{C}) + \frac{\partial}{\partial z}(\bar{w}\bar{C}) = \\ \frac{\partial}{\partial x}\left(\varepsilon_x \frac{\partial \bar{C}}{\partial x}\right) + \frac{\partial}{\partial y}\left(\varepsilon_y \frac{\partial \bar{C}}{\partial y}\right) + \frac{\partial}{\partial z}\left(\varepsilon_z \frac{\partial \bar{C}}{\partial z}\right) + \\ + D_m \left(\frac{\partial^2 \bar{C}}{\partial x^2} + \frac{\partial^2 \bar{C}}{\partial y^2} + \frac{\partial^2 \bar{C}}{\partial z^2} \right) \\ + S(x, y, z, t) \end{aligned} \quad (1)$$

where S(x,y,z,t) is the source or consumption of chlorine.

The following assumptions are made in order to simplify this equation:

- unidirectional flow on Ox axis direction, v = w = 0
- there is molecular diffusion on longitudinal axis direction Ox and it is negligible on the others axis
- axial symmetric flow
- dispersion on transversal direction and longitudinal direction have the same intensity, so that

$$\frac{\partial C}{\partial x} \approx \frac{\partial C}{\partial y}, \text{ but } \frac{\partial C}{\partial z} = 0$$

The dispersion equation becomes

$$\begin{aligned} \frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial x}(\bar{u}\bar{C}) = \frac{\partial}{\partial x}\left(\varepsilon_x \frac{\partial \bar{C}}{\partial x}\right) + \frac{\partial}{\partial y}\left(\varepsilon_y \frac{\partial \bar{C}}{\partial y}\right) \\ + D_m \frac{\partial^2 \bar{C}}{\partial x^2} + S(x, y, z, t) \end{aligned} \quad (2)$$

This equation should be numerically integrated for determining chlorine concentration variation along longitudinal axis of the pipe. In order to simplify it, additional hypotheses are considered:

- a) permanent flow regime; thus, axial component of velocity, u, is constant along the pipe
- b) transversal and vertical dispersion are negligible against axial dispersion
- c) molecular diffusion effect is negligible against turbulent dispersion

Eq. (2) becomes

$$\frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial x}(\bar{u}\bar{C}) = \frac{\partial}{\partial x}\left(\varepsilon_x \frac{\partial \bar{C}}{\partial x}\right) + S(x, y, z, t) \quad (3)$$

The last right term of equation takes into account chlorine concentration decay because of consumption reactions. It is considered first-order decay term for chlorine consumption

$$\frac{\partial \bar{C}}{\partial t} + \frac{\partial}{\partial x}(\bar{u}\bar{C}) = \frac{\partial}{\partial x}\left(\varepsilon_x \frac{\partial \bar{C}}{\partial x}\right) - kC \quad (4)$$

3. Numerically integration

For numerically integration of Eq. (4) a customized program was written using FlexPDE software (version 2.21b), (Robescu et al., 2004). Distribution pipe is presented in fig. 1: AB = 1.2 m (diameter of the pipe), BD = 5846 m (distance between Water Treatment Plant of Valea lui Stan and Brezoi), DF = 20500 m (distance between Brezoi and Pausa) and FH = 19800 m (distance between Pausa and Ramnicu Valcea). Because the ratio length/diameter is too big and therefore is very difficult to compute and visualize results, the distribution pipe is divided in sections of 300 m or 350 m length. Final results for chlorine distribution in previous section are used as initial conditions for the next section.

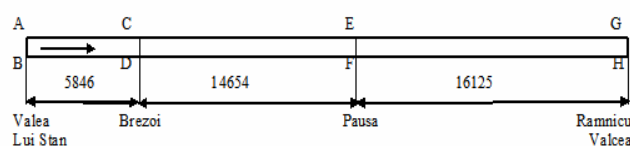


Fig.1 Distribution pipe

The boundaries conditions for a certain section (Fig.2) are Dirichlet for MP (value of residual

chlorine concentration at pipe inlet) and Neumann for MN and PQ (flux of chlorine is zero).

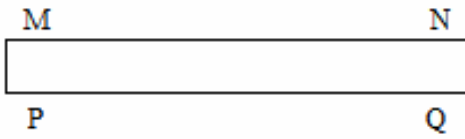


Fig.2 Boundaries conditions for a certain longitudinal part of the pipe, 300 or 350 m length

The constants in equation are considered $D_m = 0.01 \text{ m}^2/\text{s}$ and $\epsilon_x = \epsilon_y = 0.01 \text{ m}^2/\text{ngth} / \text{s}$. For decay rate there are different values in the literature. Clark et al (2001) indicate $k = 0.55 \text{ d}^{-1} = 0.63 \cdot 10^{-5} \text{ s}^{-1}$, resulting from the measurements realized for Cherry Hill/Brushy Plains and Barsan (2005) presents a summary of decay rates found in the literature noticed that the range is $0.1 - 0.5 \text{ h}^{-1} = (2.77 - 13.88) 10^{-5} \text{ s}^{-1}$. In this paper different values for decay rate is taking into account: $k = 2 \cdot 10^{-5} \text{ s}^{-1}$ in the first section (Drink Water Treatment Plant – Brezoi), $k = 25 \cdot 10^{-5} \text{ s}^{-1}$ in the second section (Brezoi – Pausa) and $k = 5 \cdot 10^{-5} \text{ s}^{-1}$ in the third section (Pausa – Ramnicu Valcea). These different values for rate of flow are considered because of the flowrate variations between DWTP and Ramnicu Valcea: $u = 0.65 \text{ m/s}$ for the first section, $u = 0.64 \text{ m/s}$ for the second section and $u = 0.52 \text{ m/s}$ for the third section.

These values result from the measurements, which were done between July 4th 2005 and July 22nd 2005, regarding flowrates and pressures in water mains. The main reason for rate of flow decreasing is the decreasing of flowrate due to supplying with water of Brezoi (15 L/s) and Pausa (130 L/s).

Initial chlorine concentration, at the exit from Drinking Water Treatment Plant is considered 1.14 mg/L, taking into account of a medium value from those resulting from measurements.

Figs. 3 and 4 presented results for chlorine distribution in pipe, 300 m upstream Brezoi, respectively Pausa. Theoretical results from FlexPDE are processed in Matlab R2007, for a better view of chlorine distribution for entire length of the pipe, and are presented in Fig.5.

One can observe that the residual chlorine concentrations are in the limits imposed by regulations for Brezoi and Pausa (Fig. 3), but for Ramnicu Valcea and the village close to it, Bujoreni (25.464 km), are below of these limits. Thus, an additional chlorination has to do in Pausa so that the chlorine residual in Ramnicu Valcea to be above limits imposed by regulations.

4. Experimental research

The simulation results were validated with real-experimental data. Experimental measurements had in view chlorine residual concentration in water in some important points: at the exit of Drinking Water Treatment Plant Valea lui Stan, at 5846 m from DWTP where is the bifurcation for water supply of Brezoi, at 20500 m from DWTP where is the bifurcation for water supply of Pausa and at 36615 m from DWTP where is the water supply for Ramnicu Valcea city. The measurements were done in August and September 2005. The experimental results are presented in Fig. 6, together with numerical results.

The residual chlorine concentration at the exit of water treatment plant during experiments is in the range 1 - 1.25 mg/L. This concentration decrease along the distribution pipe, but for Brezoi and Pausa is above the regulation limit. The situation is different for Ramnicu Valcea where the residual chlorine concentration is in the range 0.05 - 0.3 mg/l, below the regulation limits.

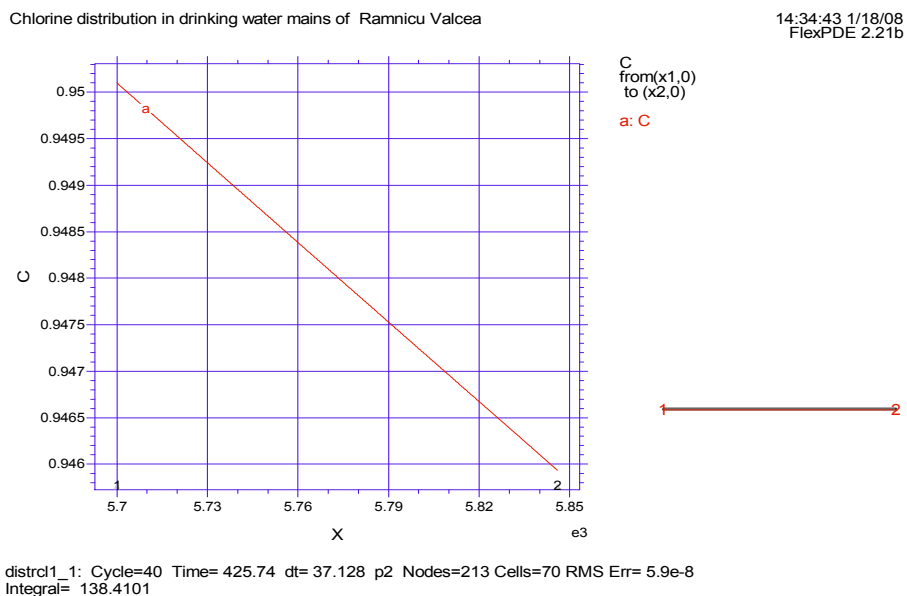
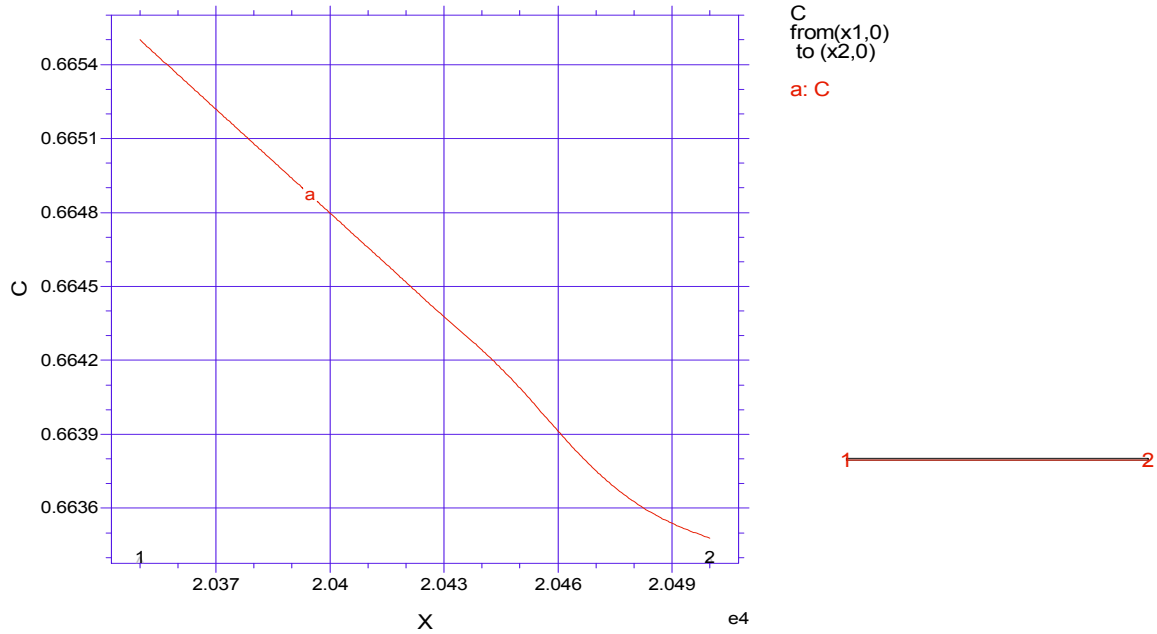


Fig.3. Chlorine distribution in pipe, 300 m upstream Brezoi

Chlorine distribution in drinking water mains of Ramnicu Valcea

15:38:11 1/18/08
FlexPDE 2.21b



distrc1_1: Cycle=25 Time= 240.00 dt= 12.718 p2 Nodes=219 Cells=72 RMS Err= 5.7e-7
Integral= 99.66584

Fig.4. Chlorine distribution in pipe, 300 m upstream Pausa

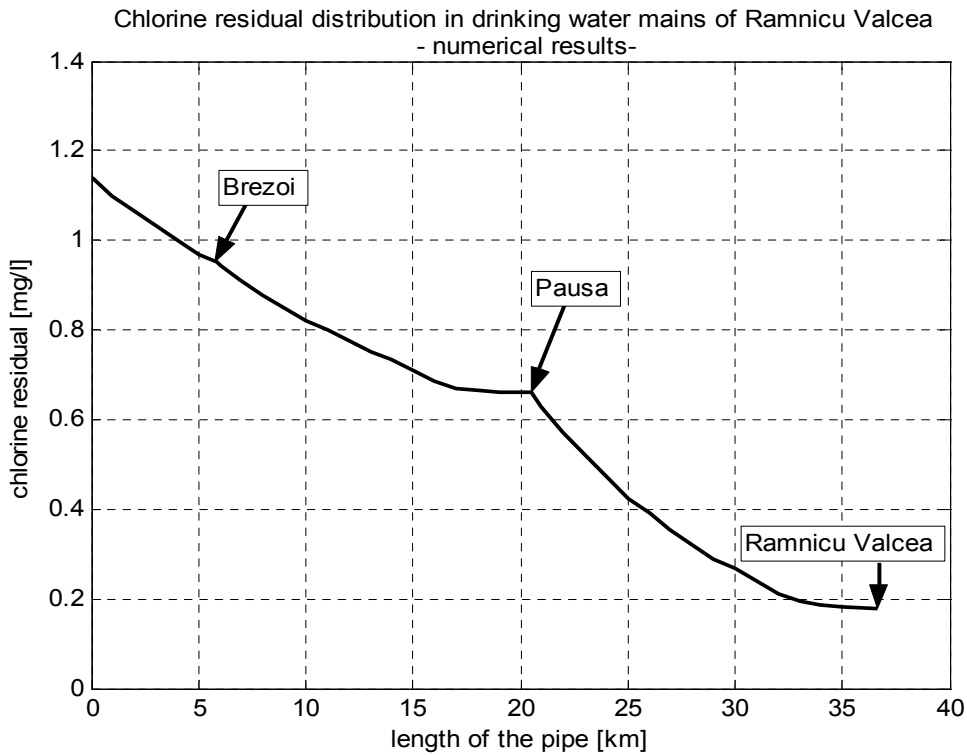


Fig. 5. Theoretical results for chlorine residual distribution in drinking water mains of Ramnicu Valcea area

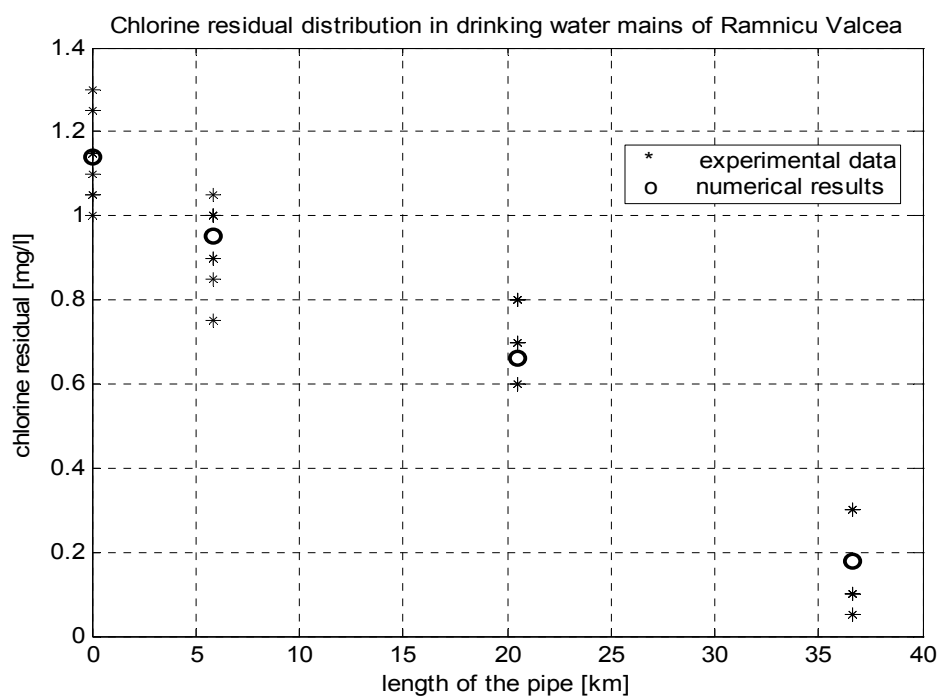


Fig. 6. Experimental and theoretical results for chlorine concentration in drinking water mains

Theoretical results are close to experimental ones. Differences may result because the mathematical model doesn't take into account different aspects related to biochemical reactions that occurs in the pipe and which are difficult to model.

5. Conclusions

Mathematical model presented in the paper predicts pretty well chlorine concentration in water mains and can be used. Initial data introduced in the program can be easily modified taking into account a given situation and the results are immediately obtained. Thus, the points where additional chlorination is needed are identified.

Abbreviations and notations

C - chlorine concentration in water [mg/L];
 x, y, z - coordinates (x – distance along the pipe) [m];
 t - time [s];
 u, v, w - average flow velocity components [m/s];
 $\varepsilon_x, \varepsilon_y, \varepsilon_z$ - longitudinal, transversal, respectively vertical dispersion coefficients [m^2/s];
 D_m diffusion constant [m^2/s];
 k - first – order reaction rate decay coefficient [s^{-1}].

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SORT IT: Recovered Paper Sorting with Innovative Technologies

Project summary:

Number: 21188; Call identifier: FP7-ENV-2007-1

Activity code most relevant topic: ENV.2007.3.1.3.2 – New Technologies for Waste Sorting.

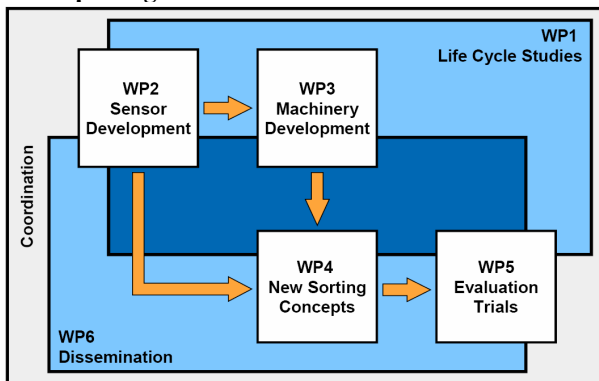
Startig date: 1st May 2008; Duration: 36 months

Project concept aims the development of new sensors and automatic identification units that will be integrated into the sorting processes in order to provide optimal separation of unwanted materials as well as characterisation of the final output from recovered paper sorting.

Project main objectives:

- to enable sustainable and cost effective paper recovery at higher than 95% yield of all recyclable paper and board grades;
- to provide tailor made recovered paper for the best possible re-use in paper & board products.

Work packages:



SORT IT includes the research and development on improved separation of unwanted materials by providing a breakthrough in sensor sorting technology for recovered paper from various collection systems. Combined image analysis, colour measurement and near-infrared sensor units will enable secure identification of materials and paper converting. Chemometrics will allow detailed characterization of the sorted raw materials and provide the information on the optimal future utilization. State-of-the-art sorting equipment as well as new and improved solutions will be assessed for establishing the highest possible sorting efficiency. The impacts of sorting will be evaluated in a complete Life Cycle study, including assessment of the environmental, economic and social impacts. The dissemination and communication plan includes conventional dissemination activities, introducing of new findings on the market and production of foreground for the development of the European environmental policy.

Project main targets:

- *Improve the recovery of used paper and increasing the collection rate:*

- analyzing European collection systems in terms of quantitative, qualitative and cost potentials, considering typical social and geographic conditions of EU member states;

- identifying collection systems with great acceptance and high separation ration;

- providing optimized sorting technologies.

- *Develop technological processes for optimum use of recovered paper:*

- optimum sorting technologies for recovered paper to produce significant increase in yield and a further improved purity of recovered paper;

- dry separation of non-paper components from recovered paper to allow their optimum use as secondary raw material or fuel;

- *Lowering the environmental impacts in recovered paper processing and papermaking related processes:*

- evaluating the influence of recovered paper sorting systems on the specific energy demand of secondary fiber production in order to identify solutions for decreasing the specific energy demand;

- dry sorting and improved quantities and controlled quality of recovered paper in order to reduce resource use in transportation, stock preparation, papermaking and further processing.

Participating institutions:

- Papiertechnische Stiftung (DE), *Coordinator*
- Centre Technique de l'Industrie des Papiers, Cartons et Celluloses (FR)
- STFI-Packforsk AB (SE), *Leader WP1*
- Universitatea Tehnica "Gheorghe Asachi" Iasi (RO), *Leader WP6*
- Instituto Tecnológico del Embalaje Transporte y Logística (ES)
- Bumaga BV (NL), *Leader WP4*
- Bollegraaf Recycling Machinery (NL), *Leader WP3*
- EVK DI Kerschhaggl GmbH (AT), *Leader WP2*
- Rauch Recycling Dienstleistungen GmbH (AT)
- Vrancart S.A. Adjud (RO)
- GREGOIRE SA (FR)
- Norske Skog (NO), *Leader WP5*
- RTT Systemtechnik GmbH (DE)
- Papeles y Cartones de Europa S.A. (ES)

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MIGRATION AND FATE OF PERSISTENT ORGANIC POLLUTANTS IN THE ATMOSPHERE - A MODELLING APPROACH

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Abstract

Considering that the fate and behaviour of contaminants within the environment is an extremely complex issue, this paper analyzes the development of predictive models which can contribute to the understanding of the release of a contaminant. Different types of models concerning the atmospheric transport of POPs are examined, taking into consideration that these models can be used to simulate the behaviour of contaminants. A successful simulation, in which there is satisfactory agreement between observations and results derived from the models, suggests that a solid theoretical understanding of how chemicals move, react, and distribute among media is sufficient to explain their behaviour in real-world situations.

Keywords: intermedia transport; long range transport potential; multimedia models; multiple compartment models

1. Introduction

The occurrence, sources, transport and fate of xenobiotic chemicals into the environment and resulting effects are major issues that give rise to concerns at local, national, regional and global scales (Rieger et al., 2002; Baun et al., 2006). Synthetic organic chemicals are discharged into the environment through various processes which may possibly include: release during the production process, at some point in use (e.g. pesticides), or accidental emissions during combustion processes (e.g. dioxins).

Persistent organic pollutants are a group of chemical compounds with different origins but common characteristics: semi-volatility, lipophilicity, bioaccumulation and great persistence in the environment (Betianu and Gavrilescu, 2006; Gavrilescu, 2005; Jones and de Voogt, 1999; Bennett et al., 1999). They persist in the environment for a long time, being also able of long-range transport (Beyer et al., 2000), bioaccumulate in the food chain and human and animal tissue, biomagnifying in food chains, and to have potential significant impacts on human health and the environment being toxic to humans and/or wildlife. As a consequence of these

characteristics, POPs are found and measured in all environmental media, far from source regions, even in isolated areas with no usage or direct emissions of these compounds (Pacyna et al., 1995; Koziol and Pudykiewicz, 2001; Breivik et al., 2004; Gavrilescu, 2005).

Assessment of environmental pollution can be achieved by means of monitoring and modeling (linear and nonlinear regression, chemometric analysis, neural networks and artificial intelligence), which can identify which variables are likely to exert an influence on the seasonality of ambient POPs monitoring data, thereby providing indications as to the dominant processes and the reliability of emission inventories (Prevedouros et al., 2004).

2. Persistent organic pollutants in the atmosphere

The emergence and subsequent behaviour of POPs in the atmosphere proved to be processes, as once in the environment and based on their semivolatile character (P_v between 10^{-4} and 10^{-11} atm at 25 °C), owing to their ability to associate with atmospheric particles or distributed between these two phases as well (Aceves and Grimalt, 1993; Kaupp and McLachlan, 1999).

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Therefore, a complex interaction between the environmental compartments in relation with POPs transport and fate occurs, where the atmosphere is the main actor (Fig.1). Many researches revealed that the atmosphere is the main transport media for the global distribution of POPs in the environment, only days to weeks being necessary for an air bundle to mix completely in the northern hemisphere, while the transport times of ocean currents can be measured in years and decades (Finlayson-Pitts et al., 1999; Prevedouros et al., 2004). The scale of atmospheric transport of POPs depends on the meteorological conditions, POPs physical/chemical properties, removal processes which include photochemically driven reaction and physical depositional mechanism (Foreman et al., 2000). The transfer of chemicals from land surface to atmosphere consists of two steps (Beyer, 2000; Toose et al., 2004; Gavrilesu, 2005):

- change from liquid or solid state to vapors;
- subsequent dispersion by turbulent mixing.

Because several physico-chemical properties governing the environmental fate of POPs are temperature dependent, POPs atmospheric transport should be seen as *single-hop* pathways (a compound is emitted to the atmosphere, transported and deposited to earth's surface and never returns to atmosphere) or *multi-hop* pathways (a compound re-enters the atmosphere after initial deposition to the earth's surface, it can travel long distances via subsequent multiple atmospheric hops; also the so-called *grasshopper effect*) (Fernandez and Grimalt, 2003) (Fig. 2). This can occur passing through volatilizations from the earth's surface under high temperatures driven out by soil moisture, or sudden exposure of ocean water to the atmosphere after being covered by ice, or by resuspension of dust or snow by winds. Also, the transfer from low to high latitudes

takes place in successive condensation/volatilization steps (*the grasshopper effect*).

This way a mass transfer occurs between air and terrestrial surfaces according to seasonal temperature changes at mid-latitudes, when these compounds are exchanged (Fernandez and Grimalt, 2003) (Fig. 2). As a result of this phenomenon, POPs can undertake several cycles of deposition and re-emission (the so named *grasshopper* or *multi-hop* transport) before reaching their final destination (Hansen et al., 2004). Also, the transport of gas phase contaminants from the warm regions of the planet, that is tropical or temperate source areas, to colder, higher latitude regions can be predicted by the theory of the *global distillation effect* (Blais, 2005).

3. Modelling atmospheric transport of persistent organic pollutants

3.1. Premises for modelling the transport and fate of persistent organic pollutants

Modelling as the application of fundamental knowledge or experience to simulate or describe the performance of a real system to achieve certain goals has long been an integral component in organizing, synthesizing, and rationalizing observations of and measurements from real systems and in understanding their causes and effects (Barber et al., 2004; Gavrilesu, 2005).

Environmental studies have to be multidisciplinary, dealing with a wide range of pollutants undergoing complex biotic and abiotic processes in the soil, surface water, groundwater, ocean water, and atmospheric compartments of the ecosphere (Table 1).

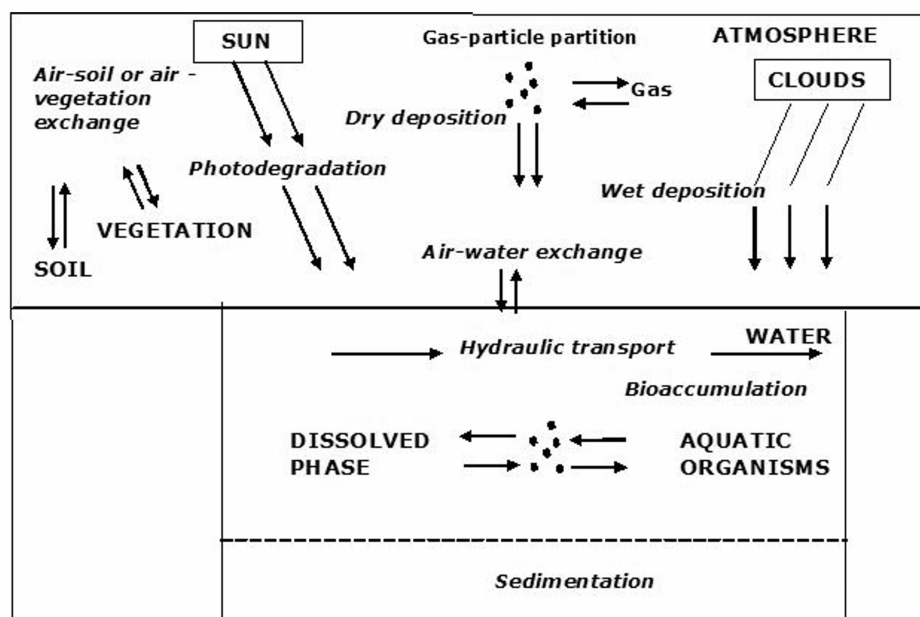


Fig. 1. Environmental processes occurring during long-range atmospheric transport of POPs (adapted upon Fernandez and Grimalt, 2003)

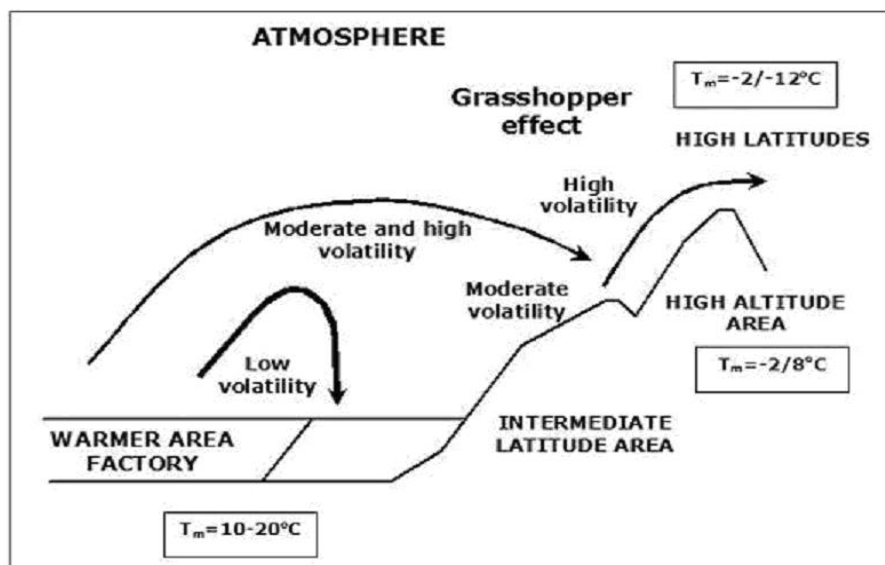


Fig. 2. Representation of the *global distillation effect* through the grasshopper mechanism (T_m – the mean air temperature in each region) (adapted upon Fernandez and Grimalt, 2003)

Table 1. Application of mathematical modelling for environmental processes (Nirmala Khandan N., 2002)

<i>Environmental component</i>	<i>Issues/Concerns</i>	<i>Use of models in</i>
Atmosphere	Hazardous air pollutants; air emissions; toxic releases; acid rain; smog; CFCs; particulates; health concerns; global warming.	Concentration profiles; exposure; design and analysis of control processes and equipment; evaluation of management actions; environmental impact assessment of new projects; compliance with regulations.
Surface water	Wastewater treatment plant discharges; industrial discharges; agricultural/urban runoff; storm water discharges; potable water source; food chain.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes and equipment; wasteload allocations; evaluation of management actions; environmental impact assessment of new projects; compliance with regulations.
Groundwater	Leaking underground storage tanks; leachates from landfills and agriculture; injection; potable water source.	Fate and transport of pollutants; design and analysis of remedial actions; drawdowns; compliance with regulations.
Subsurface	Land application of solid and hazardous wastes; spills; leachates from landfills; contamination of potable aquifers.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes; evaluation of management actions.
Ocean	Sludge disposal; spills outfalls; food chain.	Fate and transport of pollutants; concentration plumes; design and analysis of control processes; evaluation of management actions.

The difficulty at some stage in modelling process is to identify which models are the best appropriate to address a variety of tasks, how they should be tested and applied, and how their accuracy can be assessed (Sabjic and Peijnenburg, 2001).

Since atmosphere is the environmental component in which mass flows occur most rapidly on a global scale, mobility is generally reflected in volatility. Also, the release of a particular chemical depends to a large extent on its persistence.

These aspects lead to various model types for the fate and migration of persistent organic pollutants, by taking into account the temporal and spatial scales (Fig. 3).

Local scale air pollution models assess the impact of emissions to the atmosphere on ground level concentrations in the surrounding area of the emission source, which could be industrial stack discharges, fugitive emissions from factories, diffuse emissions from other areas such as landfill sites, and traffic emissions from roads, but they could be applied to predict concentrations in air over a wider scale. Two broad categories of local scale air pollution models are applied in the evaluation of local air pollution:

- *Eulerian* (plume and puff) models;
- *Lagrangian* particle dispersion models;
- *Gaussian* (plume and puff) models.

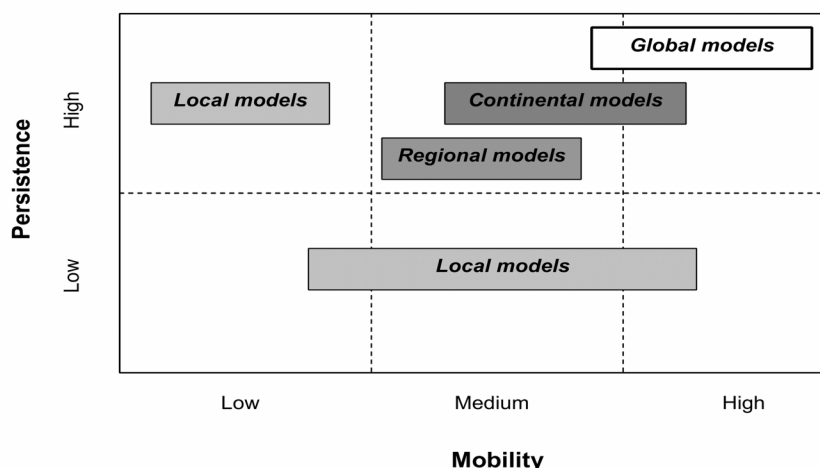


Fig. 3. Model categories depending on spatial scale determined by POPs persistence and mobility (adapted upon EEA, 2007)

Multimedia models have been developed to estimate fate and behaviour of a chemical in the environment on a large (regional or global) scale. Their particular application refers to assessing and managing the risks that persistent organic pollutants induce in the environment, even because of their potential for long range transport.

Currently, *multimedia box models and models based on atmospheric dispersion* are used to investigate the global behaviour of POPs.

Box models are simpler to construct and use, but they have only low spatial and temporal resolution. Several box models have been in use to understand the behaviour of persistent non-polar substances in the multimedia environment (Wania and Dugani, 2003; Wania et al., 2006). Models composed of meridionally connected boxes have been used to study long-range transport in two dimensions (Mackay et al., 1992; Wania and Mackay, 1995; van Jaarsveld et al., 1997).

Dispersion models have high resolution but also require high computational effort (van Jaarsveld et al., 1997).

In recent years, models have been used to simulate the observed behaviour of contaminants in a real situation and to address the following miscellaneous tasks (Scheringer et al., 2000; Frohn et al., 2002; Geels et al., 2004; Prevedouros et al., 2004):

- comparison of relative fates of different chemicals;
- identification of important fate processes;
- estimation of overall persistence and residence times;
- estimation of potential for Long Range Transport (LRT);
- estimation of environmental concentrations and exposures;
- determination of bioaccumulation in organisms and food webs;
- evaluation of likely recovery times of contaminated environments;
- checking the consistency of monitoring data;

- screening and prioritizing chemicals;
- in general, as a decision support tool documenting the sources and nature of contamination and feasible remedial strategies.

A successful simulation, in which there is satisfactory agreement between observations and model results, suggests that the degree of theoretical understanding of the way chemicals partition, move and react is sufficient to explain the observed behaviour in that environment. Some aspects are to be considered during modelling process, as is highlighted in Table 2 (Woodfine et al., 2001; Galiuulin et al., 2002; Macleod and Mackay, 2004).

3.2. POPs modelling framework

In order to get quantitative information on major sources, environmental concentrations, transport pathways and routes of exposure to humans and wildlife, several issues need to be investigated, such as:

- emission sources;
- global distribution;
- degradation processes;
- potential for long-range transport.

These properties are difficult to be evaluated in an accurate way, so that models were developed, based on measurements of the dispersion, toxicity, bioaccumulation or persistence, by analyzing samples taken from certain environmental areas (Mackay and MacLeod, 2002).

Other attributes cannot be measured directly, particularly fluxes such as evaporation rates, persistence and distance traveled (Totten et al., 2006).

3.3. Models

3.3.1. General structure

Models are able to evaluate the fate of compounds in the environment, for a wide range of chemicals and environments.

Table 2. Some important characteristics for modelling process

<i>Characteristic</i>	<i>Relevance</i>
<i>Transparency</i>	The assumptions and methodologies used for emission estimation should be clearly explained to facilitate replication and assessment of the data by users of the reported information.
<i>Consistency</i>	Emission data should be internally consistent in all their elements with data from other research. Emission data are consistent if the same methodologies are used for all stages and if consistent data sets are used to estimate emissions. Emission data using different methodologies for different years can be considered to be consistent if they have been recalculated in a transparent manner.
<i>Comparability</i>	Estimates of emissions reported by different researchers should be comparable.
<i>Completeness</i>	A certain emission report covers, at least all sources, as well as all compounds, as well as other existing relevant source categories that are specific.
<i>Accuracy</i>	A relative measure of the exactness of an emission estimate. Estimates should be accurate in the sense that they are systematically neither over nor under true emissions, as far as can be judged, and that uncertainties are reduced as far as practicable.

They can calculate transfers rates and quantities of different compounds between air, soil, water and living organisms, evaluate expected concentrations or relative proportions between environmental components and estimate persistence and potential for long range transport (Beyer et al., 2000; Scheringer et al., 2004).

A chemical released to the atmosphere can experience dry and wet deposition: it could be deposited onto the vegetation, soil and surface water. The transport processes between different environmental compartments are illustrated in Fig. 4.

In this situation, pollutant fate and transport can be assessed by means of multimedia models, which offer an attractive alternative for assessing the potential for multimedia impact of chemical pollutants (Taboas, 1993; Eisenberg et al., 1998).

These models can evaluate the exchange characteristics of a chemical based on its physical chemical properties and total air, water and soil concentrations.

So, the distribution of the compound at defined, probably unsteady-state, conditions is described.

Because it is difficult to achieve the steady-state concentrations, for comparison, the fugacity in each medium is calculated from the other medium, assuming steady-state conditions (Shafi et al., 2006). Some information are required as input data, such as:

- chemical properties;
- environmental properties;
- concentrations.

The model outputs can be:

- all input data;
- chemical amounts in each medium;
- residence times in each medium;
- fugacity of each medium for the user-specified concentrations;
- fugacities at steady-state;
- intermedia transport and loss rates;
- concentrations in all subcompartments;
- a summary diagram.

The general structure of a model is presented in Fig. 5.

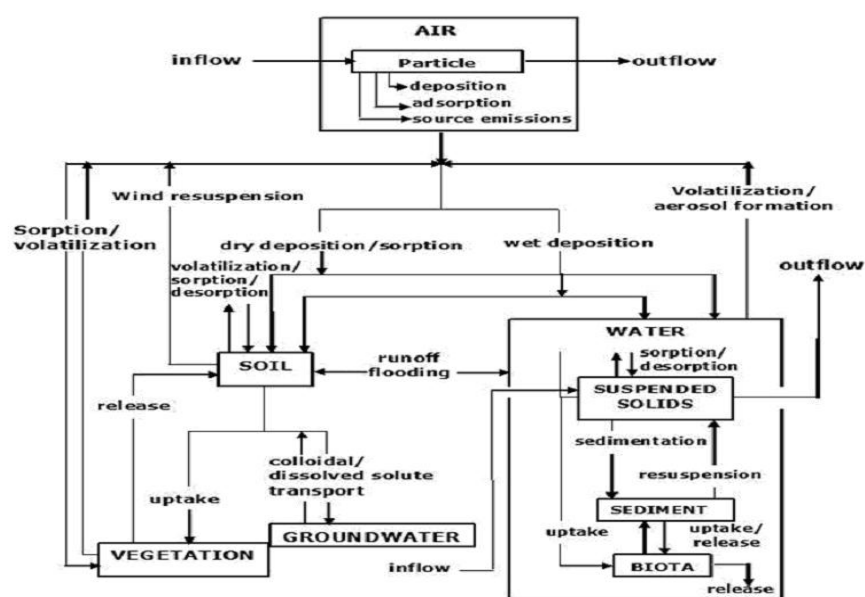


Fig. 4. Schematic representation of the transport processes between the environmental compartments (taken from Cohen and Cooter, 2002)

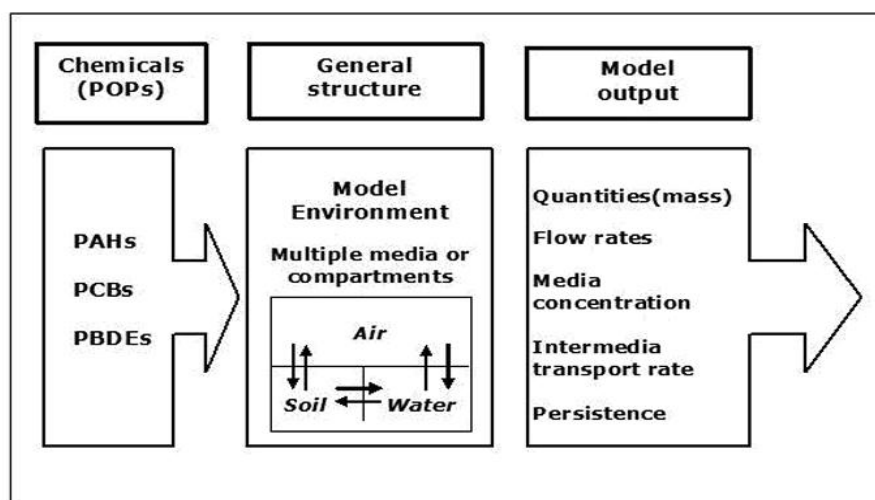


Fig. 5. The general structure of a model for intercompartmental transfer of chemicals in the environment

3.3.2. Model categories

A large and growing volume of literature exists on multimedia models.

Although these models can range greatly in complexity and can be elaborated in various ways, it is preferable to use the simplest model that can generate the desired result (Mackay and MacLeod, 2002).

Abbot et al. (2005) described two types of models for the atmosphere:

- *air quality models*, which include: *local air pollution models, photochemical models, acid deposition and eutrophication models*;
- *multimedia models*, ranging from *simple screening models to highly complex simulation models*.

External and internal exposure models

Mathematical models are being used to simulate actions in the exposure-response field, and to support quantitative predictions of risks to human health (Rosenbaum et al., 2007). The importance of contaminants to species, populations, and their ecosystems partly has been evaluated by measuring contaminant levels in air, water, and soil, and assumed effects in organisms.

Multimedia models of environmental fate and transport are mathematical tools that describe the entry, movement and distribution of chemicals within the environment, which includes both abiotic and biotic media, along with intermedia transport processes leading to chemical mass exchange among the various media (Cohen and Cooter, 2002; Shafi et al., 2006; Rosenbaum et al., 2007).

In the case of POPs, high trophic level organisms are vulnerable to accumulating high concentrations of POPs, but considerable variation exists among species (Kannan et al., 1995)

Integrated human and ecological risk assessment must be sufficiently flexible to be

applicable to a wide range of circumstances and target species, as a series of host factors have been demonstrated to affect bioavailability, fate, and effects of contaminants (Gavrilesu, 2006). Using external and internal exposure models from better understood species may be the most effective approach in many cases, but attention should be given to the ecological circumstances for the species or case in question.

Multimedia models

Four basically types of multimedia modelling approaches are relevant, such as (Paterson et al., 1994; McDonald and Gelston, 1998; Armitage et al., 2007):

- *integrated spatial multimedia models*, that describe chemical transport and fate in all the pertinent media *via* spatial models with interactions among media specified by well-posed boundary conditions and where the set of medium-specific transport equations are solved simultaneously;
- *linked spatial single-medium models*, which consist of serially-linked single-medium transport models (i.e., for air, water, soil and other media of interest) that first solve for concentrations in a given specific medium. Calculated intermedia fluxes (e.g., due to dry deposition) are then used as pseudo-source inputs to solve for contaminant concentrations in other adjoining media;
- *compartmental ("well-mixed" media) models*, being simpler and easy to execute relative to linked model systems and requiring fewer parameters. Literature makes a distinction between compartmental and fugacity-type multimedia models (Mackay and MacLeod, 2002);
- *integrated spatial-multimedia compartmental models (ISMCM)*, include both "well-mixed" and spatial compartments tightly integrated through well-posed intermedia physical boundary conditions.

Multimedia models (MMMs) have been set up for regions, nations, continents and even the global

system. These can be referred to as models of *real* systems. Another family of models consists of the *evaluative* models in which the environment is imaginary i.e. it does not correspond to a particular area (Mackay and MacLeod, 2002). These models do not explicitly attend to the likelihood of chemicals being transported from source regions and deposited to a specific target ecosystem, but they are required to estimate the relative contribution of different sources to the contaminant load present in a particular ecosystem (MacLeod and Mackay, 2004).

Multimedia models have often been limited to oversimplifications of the environmental processes governing the transport of chemicals, mainly because of the large uncertainty on the physical and chemical properties of substances, which discourage any refined computing exercise. Multimedia models require input data related to the properties and behaviour of the chemical under consideration, the environment into which it is released and the means of release (Margini et al., 2004). Some specific necessary inputs data are as follows:

- *meteorological data* (wind speed, direction, air temperature, depth of mixing layer);
- *hydrological data* - annual (or other time period) rainfall, runoff, infiltration, ground water recharge, surface water depth, sediment loads;
- *soil properties* – bulk density, porosity, water content, erosion rates and root zone depth.

Assessing concentrations of POPs in the atmosphere and their environmental fate relies also on modelling. Several groups, using various methods over the past two decades, have attempted numerical modelling of long-range atmospheric transport of persistent organic pollutants. Several approaches have been used such as: *generic box models based on the fugacity concept* (Mackay and Wania, 1995; Wania and Mackay, 1999) and *dynamic transport models* (Margini et al., 2004).

Multimedia mass balances

Multimedia are relatively simple mathematical descriptions of fate and transport of chemicals in the natural environment, which can provide a qualitative and quantitative understanding of the environmental behaviour of persistent organic pollutants, likely to be found in more than one environmental phase or medium (Margini et al., 2004; Foster et al., 2006).

Typically, a multi-media mass balance model separates the environment into a number of boxes or compartments of defined, well-mixed and homogeneous volume, with respect to both environmental characteristics and chemical contamination, then linked by a variety of inter-compartmental transfer processes (Shamsudeheen and Lammel, 2003; Wania et al., 2006). The model then calculates how a chemical is distributed within that simplified system. The distribution, and thus the concentration that is established in each medium, is influenced both by the chemical's intrinsic properties

and emission patterns and the characteristics of the environment into which it is released.

Multimedia models have variable numbers and types of compartments ranging from one or two, but more than a hundred could be connected. Several investigators suggest that the minimum number of compartments for a model aimed at estimating an overall persistence should be *three*, namely *air, water and soil* (Muller-Herold et al., 1997; Bennet et al., 1999; Margini et al., 2004).

The approach of Webster et al., (1998) is based on a model which additionally includes a sedimentation compartment. In the model proposed by Scheringer (1996), the basic three-compartment block is multiplied to additionally provide the possibility to assess a spatial range parameter.

The models could also integrate information on multiple and interacting processes of partitioning, transport and transformation into a comprehensive yet readily comprehensible picture of a chemical's fate in the environment (Hollander et al., 2007). A very clear description of the compartmental mass balance for multimedia models development was presented by Mackay et al., (2001) and Wania and Mackay (1999). Such models tend to include multiple environmental compartments, have a low spatial resolution, and involve simplifying assumptions of equilibrium and steady state (Mackay and MacLeod, 2002).

The single compartmental mass balance

Mackay et al., (2001) have considered first a single compartment as shown in Fig. 6, so that it was possible to set out the input and output processes such as:

- discharge or emission;
- convective inflow in air or water (and the corresponding convective outflow);
- diffusion to and from neighboring compartments;
- chemical species generation from other chemicals and degrading reactions.

According to the mass balance principles, the total rate of chemical input minus the total rate of output must equalize the rate of the chemical mass change in the given volume (Gavrilescu et al., 2005). Mathematically this can be expressed by Eq. (1):

$$\frac{dm}{dt} = \frac{d(VC)}{dt} = \text{input rate} - \text{output rate} \quad (1)$$

where $m[\text{kg}]$ is mass in the compartment, $V[\text{m}^3]$ - compartment volume, $C[\text{kg}/\text{m}^3]$ - concentration of chemicals.

Based on input and output fluxes from Fig. 5, Eq. (1) can be written in mathematical form as follows (Eq. 2) (Mackay et al., 2001):

$$\frac{dm}{dt} = T_{IN} + E + F_{IN} + S - (T_{OUT}) + F_{OUT} + R \quad (2)$$

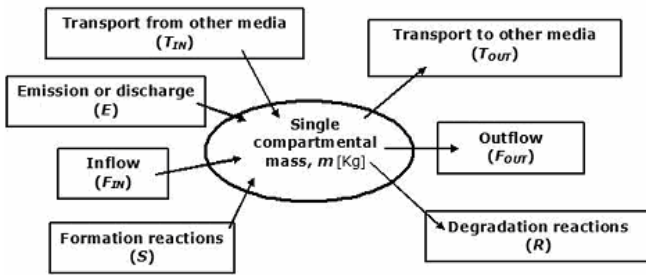


Fig. 6. Mass balance for single compartmental model (adapted upon Mackay et al., 2001)

If the following expressions for some terms in Eq. (2) are considered (Eqs. 3), then Eq. (2) can be written as (Eq. 4):

$$\begin{aligned} T_{OUT} &= VCk_T \\ F_{OUT} &= VCk_F \\ R &= VCk_R \end{aligned} \quad (3)$$

$$\frac{dVC}{dt} = T_{IN} + E + F_{IN} + S - VC(k_T + k_F + k_R) \quad (4)$$

An important quantity to be considered is the persistence of the chemical, which can be expressed as the residence time of the chemical in the box. It can be the best calculated at steady-state (Eq. 5) (Mackay et al., 2001):

$$\frac{dm}{dt} = \frac{dVC}{dt} = 0 \quad (5)$$

Thus the chemical concentration will be determined with (Eq. 6), while the residence time with Eq. (7):

$$C = \frac{T_{IN} + E + F_{IN} + S}{V(k_T + k_F + k_R)} \quad (6)$$

$$Residence\ time = \frac{Inventory}{Output\ rate} = \frac{m}{VC(k_T + k_F + k_R)} = \frac{1}{(k_T + k_F + k_R)} \quad (7)$$

Under unsteady-state, or dynamic conditions, a characteristic time (the average time that the chemical spends in the single compartment or box, as a first indication of persistence) can be calculated similarly as the mass divided by the output rate, as well as a residence time attributable to reaction and other loss processes (Mackay et al., 2001; Hollander et al., 2007).

Multiple compartments models

If the model consists of two connected boxes as in Fig. 7, the same approach can be applied to each box, as well as to the combination of the two boxes, i.e. the system as a whole (Mackay et al., 2001).

The individual residence times, for each compartment, can be calculated with Eqs. (8, 9):

$$\tau_1 = \frac{m_1}{F_{OUT_1} + R_1 + T_{12}} + \frac{1}{k_{F_1} + k_{R_1} + k_{12}} \quad (8)$$

$$\tau_2 = \frac{m_2}{F_{OUT_2} + R_2 + T_{21}} + \frac{1}{k_{F_2} + k_{R_2} + k_{21}} \quad (9)$$

while the residence time for the whole system with Eq. (10):

$$\tau_0 = \frac{(m_1 + m_2)}{F_{OUT_1} + F_{OUT_2} + R_1 + R_2} \quad (10)$$

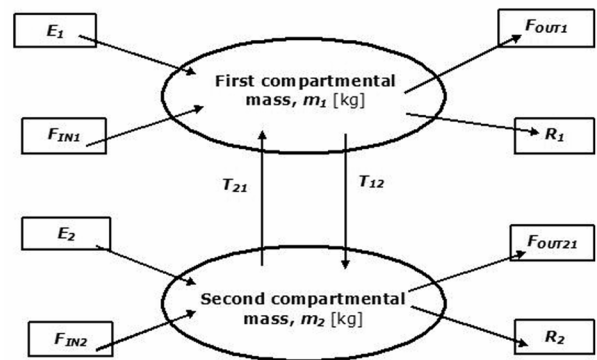


Fig. 7. Individual and overall media residence time of a chemical pollutant in a steady state multiple compartment system (E₁- emissions or discharge in the first compartment; F_{IN1}- inflow in the first compartment; E₂- emissions or discharge in the second compartment; F_{IN2}- inflow in the second compartment; F_{OUT1}- outflow from the first compartment; R₁- rate of degradation reactions in the first compartment; R₂- rate of degradation reactions in the second compartment; T₁₂- transport from the first to the second compartment; T₂₁- transport from the second to the first compartment) (adapted upon Mackay et al., 2001)

The overall residence time attributable only to reactions can be derived from Eq. (11):

$$\tau_{OR} = \frac{m_1 + m_2}{R_1 + R_2} = \frac{m_1 + m_2}{m_1 k_{R_1} + m_2 k_{R_2}} = \frac{m_1 + m_2}{f_1 k_{R_1} + f_2 k_{R_2}} \quad (11)$$

By following the same procedure, other compartments can be added, assuming that they are in chemical equilibrium with an existing compartment. Examples are aerosol particles added to the air, or suspended solids and biota to water (Mackay and MacLeod, 2002).

The overall persistence in a multimedia system including *n* compartments results by using the residence time in the system without considering advective losses (Eq. 12) (Mackay et al., 2001; Hollander et al., 2007):

$$\tau_{OR} = \frac{m_{total}}{R_{total}} = \frac{m_{total}}{m_1 k_{R_1} + m_2 k_{R_2} + \dots + m_i k_{R_i} + \dots + m_n k_{R_n}} = \frac{1}{\sum_{i=1}^n (f_i k_{R_i})} \quad (12)$$

where $f_i = m_i / m_{tot} =$ mass fraction in compartment i and R_{total} is the total rate of reaction.

The number of mass balance equations is given by the number of independent compartments (those that are not at equilibrium). If the concentrations differ significantly between two locations, they could be treated as separate compartments.

Connected multimedia models for evaluation of long-range transport

The global environment is treated as a series of connected multimedia environments of various configuration (e.g. circular), where the spatial distribution of concentrations can be calculated and expressed as a distance within which most of the chemicals are located (Mackay et al., 2001; Hollander et al., 2007). The description of LRT can be also made by using a Lagrangian system applied to a volume of air (or water) containing chemical as it is transported. This case is illustrated in Fig. 8, where long-range transport calculations in Lagrangian coordinate considers that the changing concentrations in a segment of the atmosphere is followed as it travels over soil (Mackay et al., 2001). The mass balance equations for this system are as bellow. The fraction retained is given by (Eq. 13):

$$S = \frac{k_{RS}}{(k_{RS} + k_D S)} \quad (13)$$

where $k_D S$ is the net deposition.

Characteristic travel distance (CTD) can be expressed with (Eq. 14):

$$CTD = \frac{U}{(k_{RS} + k_D S)} \quad (14)$$

If the residence time in air is given by Eq. (15), CTD could be determined using Eq. (16):

$$\tau_A = \frac{1}{(k_{RS} + k_D S)} \quad (15)$$

$$CTD = \tau_0 U f_A \quad (16)$$

where:

τ_0 - overall residence time; f_A - fraction of the chemical in air;

so that the residence time in air results as (Eq. 17):

$$\tau_A = \tau_0 f_A \quad (17)$$

Hybrid multimedia compartmental models

An integrated hybrid spatial-compartmental modelling approach was presented by Cohen and Cooter (2002) for analyzing the dynamic distribution of chemicals in the multimedia environment, which may consist of both uniform (air, water, suspended solids, vegetation, biota, suspended solids, and atmospheric aerosols) and nonuniform (soil and sediment) environmental compartments.

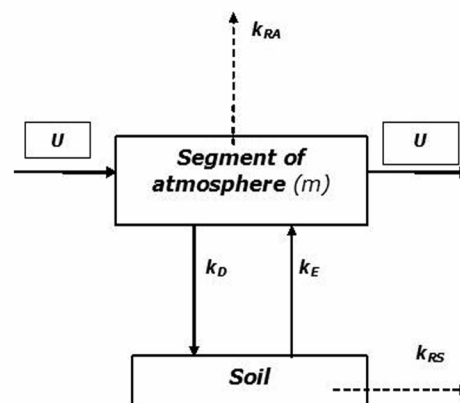


Fig. 8. Scheme for long-range transport in Lagrangian coordinates, between air and soil (U - velocity; k_{RA} - reaction constant rate in air; k_D - deposition rate constant; k_E - evaporation rate constant; k_{RS} - reaction rate constant in soil) (adapted upon Mackay et al., 2001)

The resulted information includes temporal chemical concentration profiles in various media, mass distribution, and intermedia chemical mass fluxes.

The interactive system of model equations for the uniform compartments (ordinary differential equations) and nonuniform compartments (1D partial differential equations) must be solved simultaneously to ensure conservation of mass (Cohen and Cooter, 2002).

Fugacity-based modelling

The fugacity concept can be applied to a model unit world to gain valuable information about a chemical's behaviour in the natural environment (Abbott et al., 2005). This information can be of significant value in designing a chemical with desired environmental characteristics, managing environmental emissions, ranking chemicals, and environmental policy-making (Mackay and Fraser, 2000; Gavrilescu, 2006).

This kind of models is also based on the intercompartmental approach. A basic configuration of the unit world proposed by Mackay and MacLeold, (2002) consists of the water, soil, air, and sediment compartments. Compartmental fugacity-type models express the driving forces for diffusional interfacial mass transfer (among compartments) in terms of fugacity (or chemical potential) instead of concentration driving forces (Berding et al., 2000; Mackay and MacLeold, 2002).

The fugacity concept can be applied at various levels of complexity by including more detailed compartments in the unit world, inter- and intraphase transport and reactive processes, emissions etc. (Mackay and Fraser, 2000; Berding et al., 2000):

- *Level I model* is based on a closed system mass balance of a defined quantity of chemical, without reaction, as it partitions at equilibrium between compartments. They consider the steady state in a closed system. The equilibrium distribution of a fixed quantity of conserved chemical occurs in a closed environment at equilibrium, with no degrading reactions, no advective processes, and no intermedia transport processes (no wet deposition, or sedimentation).

Level I models cannot be used to calculate persistence and LRTP because they don't take degradation into account, and rely on mass balancing by equilibrium partitioning alone.

- *Level II model* is a steady-state open system description of chemical fate at equilibrium with constant chemical emission rate. It includes reaction and advection as loss processes. It can describe a situation in which a chemical is continuously discharged at a constant rate, achieving equilibrium condition at the steady-state, at which the input and output rates are equal. Degrading reactions and advective processes are the loss or output processes treated. Intermedia transport processes (no wet deposition, or sedimentation) are not quantified. They are the simplest models to calculate persistence and LRTP (EEA, 2007).

- *Level III model* is a steady-state description of the fate of a chemical between a number of well-mixed compartments, which are not at equilibrium. This level thus includes intermedia mass transport expressions. Similar to the Level II model, the chemical is continuously discharged at a constant rate and steady state condition is achieved, when input and output rates are equal.

The loss processes are degrading reactions and advection. Unlike the Level II model, equilibrium between media is not assumed and, in general, each medium is at a different fugacity. These models include the rates of intermedia transport. Mass balance conditions are applied to each environmental compartment (EEA, 2007).

Rates of intermedia transport are calculated using information on mass transfer coefficients, areas, deposition and resuspension rates, diffusion rates, and soil runoff rates. In this situation, it is necessary to define inputs to each medium separately, whereas in Level II only the total input rate was requested (Berding et al., 2000).

- *Level IV model* is an unsteady-state version of Level III. The obtained information refers to the influence of mode of emission on P_{ov} and LRTP, as well as to the time course of response of contaminant inventory by compartment to any time varying conditions (EEA, 2007). In addition to the four levels of sophistication of multimedia models referred to above, models may also be classed according to how

they reflect the environmental properties. Removal rates and rates of intermedia transport between environmental compartments are used to define a time dependent description of mass distribution. This makes assessment of transient effects possible, such as seasonal variations in emissions and/or climate and soil conditions. A general multimedia environmental fate model is presented by Cahill et al. (2003) for simulating the fate of up to four interconverting chemical species. It is an extension of the existing equilibrium criterion (EQC) fugacity model, which is limited to single-species assessments.

It is suggested that multispecies chemical assessments are warranted when a degradation product of a released chemical is either more toxic or more persistent than the parent chemical or where there is cycling between species, as occurs with association, disassociation, or ionization. The model is illustratively applied to three chemicals, namely chlorpyrifos, pentachlorophenol, and perfluorooctane sulfonate, for which multispecies assessments are advisable (Berding et al., 2000; Baker et al., 2000).

3.4. Particular models for POPs transport and fate

Different models are applied in order to estimate atmospheric travel distance of POPs (Mackay et al., 1992; van de Meent, 1993; Scheringer, 1996; Brandes et al., 1996; Scheringer, 1997; Bennett et al., 1998; Wania, 1998; van de Meent et al., 2000; Wania et al., 2000; Beyer et al., 2000), and those are presented in Table 3.

Several of the models listed in Table 3 are highly complex models requiring substantial computing resources to operate, with typical run times extending to several hours or even days.

3.4.1. DEHM-POP Model

DEHM-POP is developed based on the Danish Eulerian Hemispheric Model (DEHM) as a 3-D Eulerian dynamical atmospheric transport model.

DEHM was originally developed to study the atmospheric transport of sulphur into the Arctic (Christensen, 1997). DEHM has also been expanded to study the atmospheric transport of lead (Christensen, 1999), CO₂ (Geels et al., 2004) and a chemical scheme with 60 components (Frohn et al., 2002); it has been validated for these compounds (Hansen et al., 2004).

The DEHM-POP model is coupled with a weather prediction model, such as MM5v2 (Fig. 9). The model is based on the continuity equation (Eq. 18):

$$\frac{\partial q}{\partial t} = -\left(u \frac{\partial q}{\partial x} + v \frac{\partial q}{\partial y} + \sigma \frac{\partial q}{\partial \sigma}\right) + K_x \frac{\partial^2 q}{\partial x^2} + K_y \frac{\partial^2 q}{\partial y^2} + \frac{\partial}{\partial \sigma} \left(K_\sigma \frac{\partial^2 q}{\partial \sigma^2} \right) + P(t, x, y, \sigma, q) - Q(t, x, y, \sigma, q) \quad (18)$$

Table 3. Models applied to evaluate and predict the persistent organic pollutants persistence and long range transport (Mackay et al., 2001; EEA, 2007)

<i>Model</i>	<i>Reference</i>	<i>Description</i>
BENNX	Bennett et al., 1998; Bennett et al., 1999	<i>Persistence and long-range transport models</i>
CalTox	McKone, 1993	<i>Level III evaluative model developed in California, includes exposure.</i>
ChemCAN	Mackay et al., 19991	<i>A level III regional model with a database of Canadian regional environments, which can represent 24 Canadian regions, providing information on average concentrations in air, fresh surface water, soils, vegetation, fish and marine coastal water.</i>
ChemFrance	Devillers et al., 1995	<i>A level III regional model applied for 12 regions of France and France itself, for generic chemical fate. Assessment, giving information on steady state concentrations in air, water, soil and vegetation.</i>
ChemRange and SCHE	Scheringer, 1996; Scheringer, 1997	<i>Circular multi-box model for calculating persistence and long-range transport. ChemRange is an evaluative, one-dimensional steady-state (level III) model.</i>
ChemRange-CliMoChem	Scheringer et al., 2000; Scheringer et al., 2004	<i>Combines ChemRange model with a two-dimensional model with different temperatures, land/water ratios and vegetation types in different latitudinal zones.</i>
CoZMo-POP	Wania et al., 2006	<i>Regional model specifically for large drainage basins or costal environments, providing information on average concentrations in air, fresh surface water, soils, vegetation, fish and marine coastal water; it's level IV model, including up to 19 compartments, incorporating the forest, soils and fresh water bodies of the drainage basin, and a variable number of sequentially arranged marine water units</i>
DEHM-POP	Christensen, 1997	<i>A 3-D dynamical atmospheric transport model developed to describe the long-range transport. It has a horizontal resolution of 150 km x 150 km and 20 unevenly distributed vertical layers in terrain-following sigma-coordinates extending to about 18 km height.</i>
ELPOS	Beyer and Matthies, 2001	<i>A level II or III modified EUSES/SimpleBox to calculate overall persistence and characteristic travel distance, CTD in air and water (Environmental Long-Range Transport and Persistence of Organic Substances)</i>
EQC	Mackay et al., 1996	<i>Level I, II and III calculations in a single model, fixed environment, evaluative - especially for chemical to chemical comparison; it provides steady state concentrations in air, water, sediment and soil.</i>
EVN-BETR and UK-MODEL	Prevedouros et al., 2004	<i>Calculates steady and non-steady state (dynamic) mass balances of chemical contaminants from inputs describing the environmental characteristics of Europe, the physicochemical properties of the chemical of interest, and contaminant emission rates; the focus is on describing pollutant fate and transport, including transfer, transport and cycling in and between air, vegetation, soil, surface water, sediments and coastal water.</i>
G-Ciems	Suzuki et al., 2004	<i>Grid-Catchment Integrated Environmental Modeling System, is a geo-referenced multimedia and river environmental fate model system for region-scale environment; it is as an expansion of Mackay-type multimedia fate model to multi-box compartments with geo-referenced geographical resolution on GIS software and calculates multimedia environmental concentration on specified geographical environmental area.</i>
GloboPOP	Wania and Mackay, 1993; Wania et al., Wania and Mackay, 1999	<i>A zonal averaged global multimedia fate and transport model formulated in fugacity notation.</i>
HELD	Held, 2001	<i>3D version of the SCHE model</i>
HYSPLIT 4	Draxler and Rolph, 2003	<i>Hybrid Single Particle Lagrangian Integrated Trajectory atmospheric transport model by taking into account weather patterns and the chemical characteristics of the pollutant affecting atmospheric destruction and deposition; the source-to-receptor relationship can be represented; it can be applied on any scale; .</i>
MEDIA	Koziol and Pudykiewicz, 2001	<i><u>M</u>ulticompartment <u>E</u>nvironmental <u>D</u>iagnosis and <u>A</u>ssessment, a three dimensional, global scale multicompartment environmental transport model including atmosphere, soil, cryosphere and ocean compartments</i>
PENX	Pennington and Ralston, 1999; Pennington, 2001	<i>PEN1: Steady-state concentration based model, has been used by the EPA PEN2: Heuristic-based approach</i>

POPCYCLING-Baltic	Pacyna et al., 2003	A regional multimedia fate and transport model formulated in fugacity notation. Its aim is to describe the long-term, large-scale fate of persistent organic pollutants in the drainage basin and water body of the Baltic Sea
SimpleBox	van de Meent, 1993	A nested multi-media fate model of the "Mackay type" Level III regional model: the environment is modelled as consisting of a set of well-mixed, homogeneous compartments (air, two water compartments, sediments, three soil compartments and two vegetation compartments) in regional, continental and global scales
TAPL3	Beyer et al., 2000; Webster et al., 1998	Transport and persistence Level III model with user-defined environment, fixed emissions; evaluation of long range transport and persistence for chemical to chemical comparison. Lack of advection means that it is unsuitable for absolute assessments. Provides information on steady state concentrations in air, water, sediment and soil, persistence and characteristic travel distances.
VDMX	Van de Meent, 1993; Brandes et al., 1996	Persistence and LRT models based on SimpleBox
WANIA	Wania, 1998	Three compartment (air, water, soil) Level III fugacity model
WANX	Wania, 1998	WAN1: Includes global scale advective loss processes WAN2: Does not include advectons

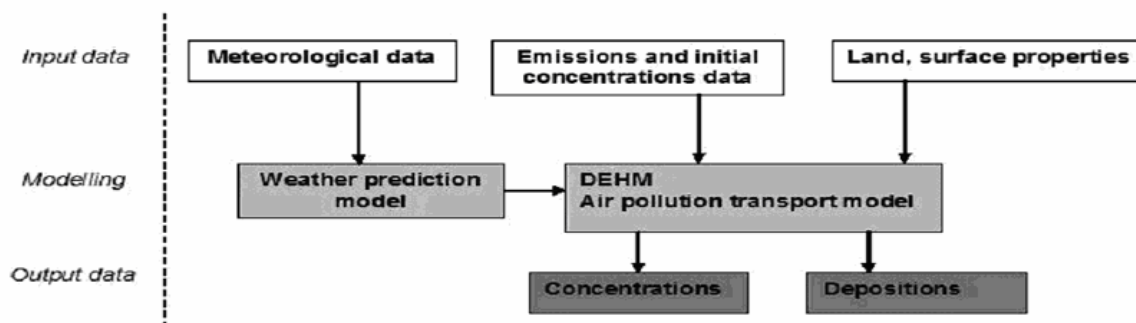


Fig. 9. Tiers of DEHM model (Hansen et al., 2004)

where q is the mixing ratio of the modeled compound, t is time, x , y , and z are the horizontal and vertical coordinates, u and v are the components of the horizontal wind field and w is the generalized vertical velocity, K_x , K_y , and K_z are the horizontal and vertical diffusion coefficients, and P and Q are sources and sinks.

Time integration of the continuity equation is done by splitting it into five sub-models, which are then solved successively in each time step.

The first sub-model is the three-dimensional advection, sub-models two to four are diffusion in the three dimensions and the fifth sub-model is sources and sinks including the special air-surface exchange processes for POPs (Hansen et al., 2004; Hansen et al., 2006). The time step is calculated using a Courant-Friedrich-Levy stability criterion on the basis of the horizontal and vertical wind fields and the horizontal boundary conditions are non-periodic (Frohn et al., 2002). The boundary conditions are free at the top of the domain (Christensen, 1997), and are given by the air-surface exchange fluxes at the ground. The model was used by Hansen et al. (2004) to study the atmospheric transport and environmental fate of the α -HCH for the years 1991–1998. Wet

deposition of α -HCH is calculated in DEHM-POP using a simple parameterization based on a scavenging coefficient formulation (Christensen, 1997), while the reaction with OH radicals is assumed to be the most important transformation of α -HCH in the atmosphere. A first order degradation rate is calculated in the model using an estimated mean residence time in the atmosphere due to reactions with OH radicals of $k_{\text{air}} = 1/(118 \text{ days})$.

The model include also equations for the change in α -HCH concentration in soil, C_s , with time, input and flux out of the soil due to evaporation of water, the air-soil gas exchange flux, the excess run-through, α -HCH biodegradation in soil.

Meteorological data and emissions, initial concentrations in the three media are used as input to the model simulations, high spatiotemporal resolution being also developed to address these issues (Hansen et al., 2006).

3.4.2. ChemRange-CliMoChem Models

The long-range transport of persistent organic pollutants (POPs) could be investigated with two multimedia box models of the global system mainly developed by Scheringer et al. (2004):

ChemRange - an evaluative, one-dimensional steady-state (level III) model, and CliMoChem - a two-dimensional model for different temperatures, land/water ratios and vegetation types in different latitudinal zones (Scheringer et al., 2000), (Fig. 10).

Modelling was applied for different case studies (Scheringer et al., 2004; Abbott et al., 2005), which aimed to obtain information on:

- (i) the effect of atmospheric aerosol particles on the long-range transport of POPs;
- (ii) the effect of oceanic deposition on the long-range transport of different PCB congeners;
- (iii) the global fractionation of different PCB congeners.

Formation or transformation of various POPs, such as DDE from DDT can be modeled, under the influences of varying environmental conditions on the physico-chemical properties and the degradation rate constants of POPs (Scheringer et al., 2004).

3.4.3. General Circulation ECHAM Model

Three dimensional atmosphere global general circulation model types (ECHAM3, ECHAM4 and ECHAM5, which differ through the horizontal resolution), were used by to study the long-range transport of POPs, and their fate in the multimedia environment (Lohmann et al., 1993; Lorenz et al., 1996).

The models comprise a fully developed atmospheric compartment, soil with a 'bucket model' hydrology, two-dimensional vegetation surface and a mixed layer ocean. The process of volatilization plays an important role in the increase of concentration of pesticides in the atmosphere away from the exploitation area. The physico-chemical properties relevant to pesticide volatilization from the soil surface are molecular mass, vapour pressure, solubility in water, adsorption and half-life values.

The model incorporates atmosphere, soil, vegetation and ocean compartments (Fig. 11). Transports only occur in the atmosphere. Soil, vegetation and the ocean mixed layer are represented as two-dimensional compartments. The parameters used to describe the intra- and inter-compartmental processes of mass exchange and conversion are listed

in Table 4 (Semeena and Lammel, 2003; Shamsudheem, 2005).

The global multicompartamental fate and long-range transport of two persistent semivolatile organic pollutants, DDT and γ -HCH were studied on a time scale of 10 years (Shamsudheem, 2005).

The scenarios were selected such as to address questions on:

- the environmental fate for the same substance but changing over time, as a function of geographic regions of entry, or
- function of mode of entry and for two substances under the same application scenario.

Semeena et al. (2005) applied the global multicompartamental model which is based on a 3-D atmospheric general circulation model (ECHAM5) coupled to 2-D soil, vegetation and sea surface mixed layer reservoirs to simulate the atmospheric transports and total environmental fate of DDT and γ -HCH.

- The global environment is predicted to be contaminated by the substances within about 2 years.

The model is based on an atmosphere general circulation model (AGCM) which had been shown to be well suited to represent the large scale atmospheric dynamics and, the hydrological and aerosol cycle, ECHAM. By addition of 2-D ground compartments, a multicompartamental model is complemented.

3.4.4. EMEP/MSCE POPs Model

A three-dimensional Eulerian transport model ASIMD (**AS**ymmetric **I**mproved **Mo**del) used for calculations of the long-range transport of persistent organic pollutants was developed in EMEP/MSCE (Munthe and Palm, 2003).

A simplified scheme of the EMEP/MSCE POPs model (Fig. 12) indicates that it is a multi-compartmental Eulerian-type advection scheme model with spatial resolution 150×150 and 50×50 km. It includes atmosphere, soil, sea water and vegetation. The model is able to assess the redistribution of POPs between these media and estimate concentration levels in them. Obviously, many uncertainties remain of concern, such as: emission rates, degradation rates and the role of sediments.

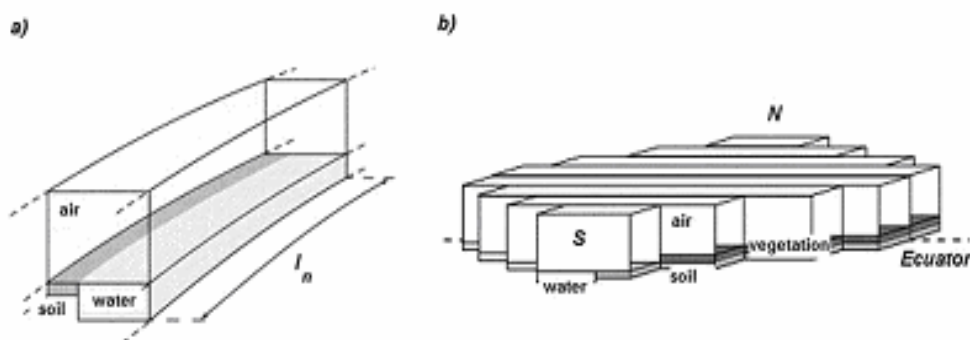


Fig. 10. Geometry of the multimedia box models ChemRange (a) and CliMoChem (b)

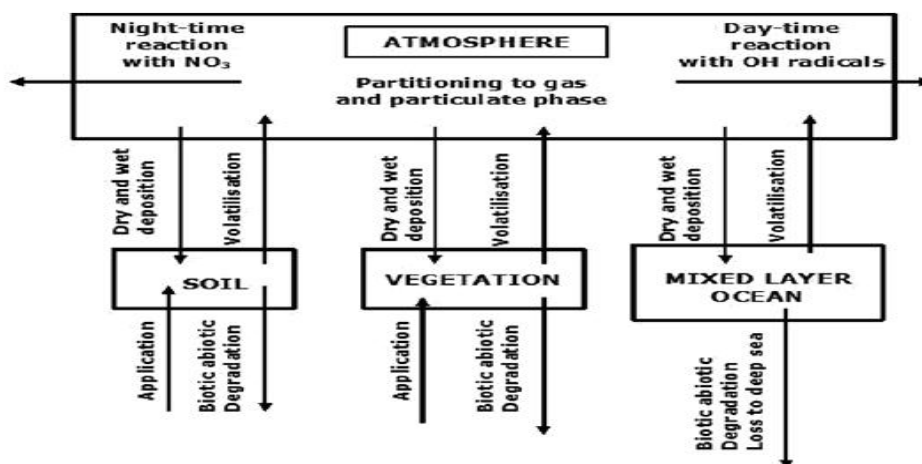


Fig. 11. Multicompartmental approach, processes involved in substance cycling (Shamsudheen, 2005)

Table 4. Intra- and intercompartmental mass exchange and conversion processes (Semeena and Lammel, 2003)

Process	Process description	Parameter representation
Partitioning between gas-phase and atmospheric particulate matter, θ	Assumed to be determined by absorption into organic matter, empirically based on the octanol-air partition coefficient (Finizio et al., 1997), K_{oa} ⁽¹⁾ prescribed spatially and temporally variable aerosol concentration	Diagnostic
Chemical degradation in the atmosphere	Reaction with hydroxyl radical, similar in the gaseous and particulate-bound state; prescribed spatially and temporally variable oxidant concentration (Roelofs et al., 1997)	Prognostic
Degradation in soil, vegetation and in ocean	Overall first-order rates, assumed to double per 10 K temperature increase ⁽²⁾	Prognostic
Partitioning in soils	Phase equilibrium in 3-phase soil system, temperature dependent, soil hydrology represented by bucket model (Roekner et al., 1996)	Diagnostic
Volatilisation from soils	Loss of gaseous substance from the soil pore space using an empirically derived rate from pesticide application studies	Prognostic
Volatilisation from vegetation	Loss of gaseous substance from plant surfaces using an empirically derived rate from pesticide application studies	Prognostic
Flux of trace substances from the ocean to the atmosphere	Two-film model (Wania et al., 2000), temperature dependent	Prognostic
Atmospheric dry deposition	Fixed deposition velocities “vdep” for gaseous molecules ⁽³⁾ and according to the particle mass (Slinn, 1982) median diameter for particulate-bound molecules	Prognostic
Atmospheric wet deposition	In-cloud and below-cloud scavenging from stratiform and convective clouds according to water solubility (gaseous molecule) and wet-scavenging coefficient, ϵ ⁽⁴⁾ (particulate-bound molecule)	Prognostic

⁽¹⁾ $c_{gas}/(c_{gas}+c_{particulate})=\theta=[1/(K_p c_{TSP})+1]^{-1}$; $\log K_p=0.55 * \log K_{oa}-8.23$; particulate mater concentration $c_{TSP}(cm^{-3})$, gas-particle equilibrium constant; K_p , temperature dependence of θ assumed to be similar to polycyclic aromatic hydrocarbons;

⁽²⁾ $k_{soil}=k_{vegetation}$; in the case of γ -HCH the contribution of the hydration reaction to the degradation in ocean water is accounted for, too;

⁽³⁾ dry deposition velocities are 1.4 and 1.38 $cm\ s^{-1}$ over land and 0.08 and 1.38 $cm\ s^{-1}$ over sea for DDT and γ -HCH, respectively;

⁽⁴⁾ $\epsilon=1.0$ and 0.1 for in-cloud and below-cloud scavenging, respectively.

3.4.5. CoZMo-POP Model

The Coastal Zone Model for Persistent Organic Pollutants (CoZMo-POP) is a non-steady state multimedia mass balance model which can describe the long term fate of persistent organic pollutants (POPs) in a coastal environment or the drainage basin of large lakes (Wania et al., 2006).

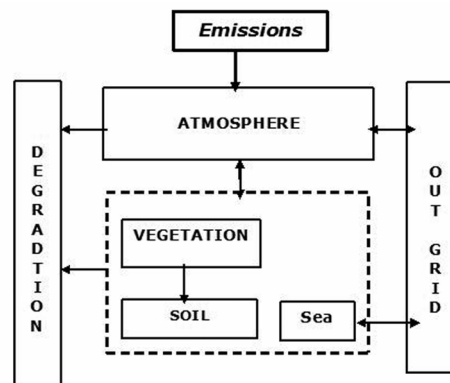


Fig. 12. Simplified scheme of the EMEP/MSCE POPs model (adapted upon Munthe and Palm, 2003)

The main focus is on quantifying the relative importance of the riverine and atmospheric pathway for delivering POPs to the aquatic ecosystem as well as to distinguish the fraction of the riverine load which is atmospherically derived vs. being emitted directly to the soils, plants and rivers of a drainage basin. The aim of the model is to describe the rates of release (and the seasonal change of this release) of POPs from the main terrestrial storage media, i.e. soil and vegetation, into the two transport media delivering POPs to the aquatic environment, i.e. atmosphere and fresh water, considering two processes (Wania et al., 2000; Wania et al., 2006):

- the two-directional exchange, or cycling, of POPs between the atmosphere and aquatic and terrestrial surfaces;
- the uni-directional run-off of chemical from soil to fresh water and further to the marine system.

Also, degradation and deposition in the atmosphere, and degradation, net sedimentation to fresh water sediments, and volatilization in the fresh water system are considered.

The model is driven by historical emission estimates and the inflow of contaminated air and water across the model boundaries. The default assumption is that all emission occurs into the atmosphere. CoZMo-POP may consist of eight boxes or compartments: atmosphere (A), forest canopy (F), forest soil (B), agricultural soil (E), fresh water (W), fresh water sediment (S), coastal water (C), and coastal sediment (L), but up to 19 compartments can be assumed within CoZMo-POP 2 model, which takes into account seasonably variable wind speeds, temperatures, canopy developments and OH radical concentrations, and allows for the definition of time-variant emission scenarios (Wania et al., 2006).

3.4.6. BETR North America Model

The Berkeley-Trent North American contaminant fate model (BETR North America) was applied by some researchers to model intermedia transfer processes (Betts, 2001; Woodfine et al., 2001; MacLeod et al., 2001; Dahl, 2002). Twenty-four ecological regions are considered in BETR model for evaluation of the North American environment, where the fate of environmental contaminants is described using a seven-compartment fugacity model including a vertically segmented atmosphere, vegetation, soil, freshwater, freshwater sediments and coastal water (MacLeod and Mackay, 2004). Contaminants can be transported between adjacent regions of the model in the atmosphere and in flowing rivers and near-shore ocean currents.

Contaminant fluxes between all regions and environmental compartments are constant at steady state, such that emissions are balanced by removal processes for the entire continental environment (MacLeod and Mackay, 2004). The emission rate used as input to the BETR North America model represents primary emissions only (Toose et al., 2004). Revolatilization of chemical from the terrestrial and aquatic surfaces is calculated by the

mass balance equations in the model. A transfer efficiency (TE) was calculated as a percentage from the steady-state solution with Eq (19) (MacLeod and Mackay, 2004):

$$TE = \frac{\text{rate of contaminant flux to the target ecosystem (kg/year)} \times 100}{\text{emission rate in the source region (kg/year)}} \quad (19)$$

The BETR North America model uses first-order kinetics to describe all transport processes. If a competing degrading reaction with half-time t_R is introduced in the atmosphere in all regions of the model, the fraction of chemical that survives to deposit to the Lakes (F), relative to a perfectly persistent chemical will be (Eq. 20):

$$F = \frac{t_R}{t_R + t_A} \quad (20)$$

where t_A is the time or half-life to the transport and deposition process that represents the atmospheric residence time between emission and deposition, while t_R is a competing degrading reaction half-time.

The model allowed for identification of combinations of physico-chemical properties that favour efficient transport and deposition to the Great Lakes, and estimated the time-scale required. Also, it was found that for an ecosystem to become contaminated from distant sources of chemicals two processes must occur: (i) transport from the source region and (ii) deposition to the target ecosystem. Efficient transport and deposition to specific ecosystems is only possible for chemicals with certain combinations of partitioning properties and sufficient environmental persistence to survive the journey (MacLeod and Mackay, 2004).

A regionally segmented multimedia fate model for the European continent has been developed to provide fate and behaviour information for POP compounds on a continental scale, built on the regionally segmented BETR North America model structure. The European continent is described by a $5^\circ \times 5^\circ$ grid, leading to 50 regions together with 4 perimeter boxes representing regions buffering the European environment¹¹. Each zone comprises seven compartments including: (i) upper and lower atmosphere, (ii) soil, (iii) vegetation, (iv) fresh water and sediment and (v) coastal water. Inter-regions flows of air and water are described, exploiting information originating from GIS databases and other georeferenced data.

3.4.6. POPCYCLING-Baltic Model

The POPCYCLING-Baltic model is a MFTM that aims to distinguish and quantify the environmental pathways of selected persistent organic pollutants (POPs) in the Baltic Sea environment, which are inaccessible to measurements (Wania et al., 2000; Pacyna et al., 2003; Wania et al., 2001) (Fig. 13).

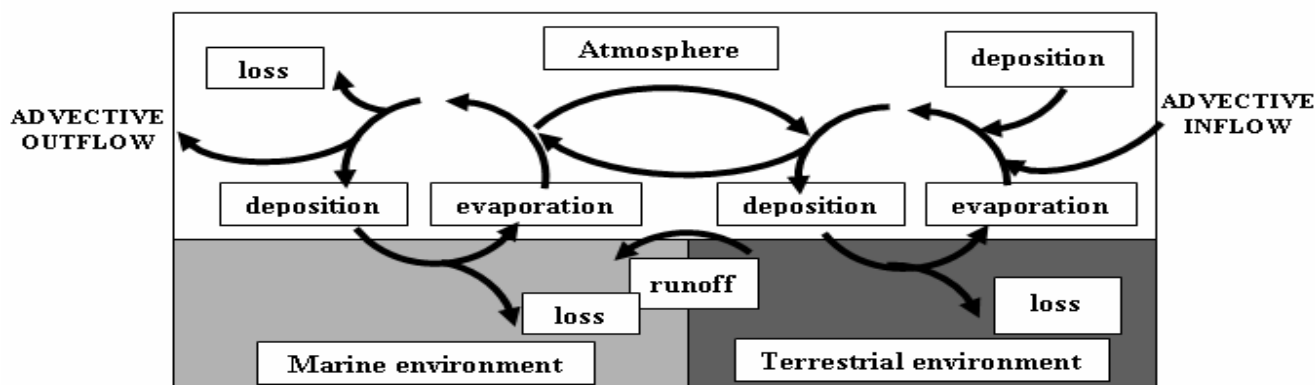


Fig. 13. Representation of POPCYCLING model of POPs migration from the terrestrial environment to the marine environment via atmosphere and rivers (adapted upon Wania et al., 2000)

In particular, it aims to estimate the fractions of the POPs currently present in various parts of that environment, which are derived from (i) recent releases within the drainage basin, (ii) past emissions in the drainage basin and (iii) contaminated air masses being advected into the area (Wania and Mackay, 1999)

Within the model region, a main focus is on the relative importance of the riverine and atmospheric pathway for delivering POPs to the marine ecosystem of the Baltic Sea. The model was developed as part of the POPCYCLING-Baltic project funded by the European Union, a detailed description of the project has been provided by Wania and McLachlan, (2001). It traces its origin to the QWASI model (Mackay et al., 1983) as well as the generic model (Mackay et al., 1992).

The focus of the model evaluation was on the absolute concentration levels, on the spatial and temporal concentration patterns in various media and biota, and on atmospheric depositional in the Baltic Sea fluxes to the drainage basin (Fig. 13).

4. Concluding remarks

The application of modelling to estimate the environmental fate of chemicals at local and global scales proved to be a very valuable tool because of the impossibility to measure the chemical concentrations in various environmental media and locations.

Atmosphere can be considered the most favorable environmental component for a rapid mass flow of persistent organic pollutants, with a great potential to transport them over long distances.

A large number of models are now available for predicting environmental concentrations of chemicals in single or multiple environmental media. Because a wide range of factors determines the fate of chemicals in the environment, especially persistence and mobility, they have to be included as input data in the model. For this reason, models range from highly

complex spatially and temporally resolved models capable of predicting small scale variations in chemical concentrations in one or more environmental media, to simpler screening tools that predict concentrations averaged over wider spatial and temporal domains.

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EARTH OIL EXTRACTION – MAJOR ENVIRONMENTAL POLLUTION SOURCE

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Abstract

The work presents the negative environmental impact produced by an extraction of crude oil activity. To highlight and quantify the negative effects on the environment produced from such activity, the experimental part has been focused on evidence of samples of soil, water from groundwater aquifers and surface, and the air emissions. The values of quality indicators are presented in graphs and tables, highlighting an activity with all major impact on the environment.

Keywords: Crude oil extraction, groundwater aquifers, emission, ecological rehabilitation, ecological reconstruction

1. Introduction

For several years, the present productive system and especially the oil extraction activities have an important weight in the generation of polluting products and their negative impact on the environment have been in the process of evaluation.

There is an international consensus as to the need to modify industrial processes in order to decrease the generation of toxic effluents and/or effluents of a polluting character, to increase the recycling of waste, to improve efficiency in transformation and, in all cases, to seek sustainable development for the middle and long term (Dreher et al., 1997; Gupta et al., 2004; Gavrilesco, 2006; Russel, 2006).

Also, these impose actions to respect and preserve the environment while helping to reclaim places that have already been polluted (DAS, 2005; Danielopol et al., 1997; Gavrilesco and Nicu, 2005).

The work presents all sources of pollution and quantifies their effects on the quality of the environment, generated by activities in the extraction of oil deposits – Suplacul de Barcau. Potential sources of pollution of soil, surface water and groundwater, the atmosphere were identified on the examined site, as a result of past and present activities or near it.

The results led to the establishment of measures aimed to minimize the impact of analyzed activity on the environment.

2. Case study – crude oil extraction area

The oil exploitations are located in a large area with low hills (up to 400 m) and in the corridor of meadow of Barcau River, which frequently leads to flooding. The relief is relatively plan, with numerous "Craters" that have accumulated rich in salt lakes. The analyzed site: *Crude oil extraction area – The group of earth oil deposits of Suplacul de Barcau* is situated in Bihor county, and covers an area of 3786 m², including a 225 extraction wells.

The oil deposits of Suplacul de Barcau are exploited through thermal processes such as underground combustion and steam injection cycle. These methods ensure that the degree of oil recovery keeping is from approx. 12% in the primary operation until approx. 50% through these processes. Along with crude oil, are bringing to the surface also significant amounts of gas fuel, with the main ingredients: dioxide and carbon monoxide.

The following types of sources of pollution in the environment results from the flow of technology for the exploitation of oil deposits:

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- permanent sources
- sources with non-permanent and local actions
- accidental sources
- sources in case of major damage due to natural causes.

From the category of permanent risk sources, they can mentioned the gas emission through eruptive craters, which leads to atmosphere pollution with combustion gases, and also to soil pollution, their aspects being of sloppy volcanoes.

Among the reasons causing these phenomena, the followings have been identified:

- technical failure by applying heat methods (corrosion of the column, destroying the ring of cement as a result of the process of cementing);
- gas flow from the oil deposit through blowholes affected by the process of combustion in the operating area;
- the formation of preferential flow paths way of both the gas injection (air) and combustion (carbon oxides and cracking compounds).

Environmental factors that affect the extraction process are: soil; water (both surface and groundwater) and air. For this reason, experimental determinations were based on sampling and analysis of actual indicators of quality of these environmental factors.

2.1. Soil investigations

For quantitative evaluation of soil pollution, have been executed a number of 10 drillings at various depths, up to max. 0.5 m depth, in areas adjacent to oil wells, on an area of 1000 m².

The following analytical methods were used:

- for THP (total petroleum hydrocarbons)– SR/ISO TR 11046/1997;
- pH – instrumental method;

The values of the two determined indicators from the 10 points (drillings) (mg/kg dry soil), and witness sample are found in Table 1. Reporting in this case will be made to the industrial soil.

2.2. Underground water investigation

To identify groundwater pollution, groundwater samples have been taken from 5 different locations (existing wells in inhabited areas in the vicinity of the site), which are monitored frequently.

The indicators of quality and methods of analysis used are:

- pH –SR ISO 10523/1997 –electrochemical method;
- Petroleum products – SR 7877-2/1995;
- Chlorides – STAS 8663/1970;
- Phosphates – SR-EN 1189/2000;
- Nitrates – SR ISO 7890-2/2000;
- Nitrites – STAS 12754/1989;
- Ammonium nitrogen– SR ISO 7150-1/2001.

The samples were taken according to standard SR EN 25667-12/2002 and SR ISO 5667-11/2000.

Preservation of evidence was made by acidification and cold storage. Results of tests for the samples from the 6 wells, compared with norms are found in Table 3.

Table 1. The characteristics of soil samples taken from the site

No.	Drilling	Depth (m)	pH	Extractives substances in petroleum ether [mg/kg dry soil]
1.	F1	0.2	7.75	20884.30
2.		0.5	7.70	4362.10
3.	F2	0.2	8.15	3129.85
4.		0.5	7.95	112154.90
5.	F3	0.2	7.45	3054.35
6.		0.5	7.60	3400.60
7.	F4	0.2	6.45	24327.50
8.		0.5	6.55	28087.90
9.	F5	0.2	7.5	22706.0
10.		0.5	7.4	21279.6
11.	F6	0.2	8.0	5039.45
12.		0.5	8.05	3400.00
13.	F7	0.2	5.9	3045.70
14.		0.5	5.95	2215.50
15.	F8	0.2	2.88	4113.50
16.		0.5	2.52	5927.10
17.	F9	0.2	6.3	2965.85
18.		0.5	6.4	28198.20
19.	F10	0.2	7.85	2074.10
20.		0.5	7.75	3199.00
21.	Witness sample	0.3	6.0	185.00
22.		0.5	6.05	140.00

Table 2. The reference values according MAPPM Order no. 756/1997

Element	Normal concentration	Alert concentration [mg/kg dry soil]		Intervention concentration [mg/kg dry soil]	
		Soil for sensitive use	Soil for less sensitive use (industrial)	Soil for sensitive use	Soil for less sensitive use (industrial)
THP	<100	200	1000	500	2000

Due to the lack of regulations on the quality of groundwater, the results of the analysis were compared with values of the maximum allowable in accordance with:

- Law no. 458/2002 on the quality of drinking water, amended by Law no. 311/2004;
- STAS 1342/1998 - drinking water;
- Dutch List

2.3. Surface water investigations

To identify the pollution of surface water on site, samples have been taken from the exhausting water channel after the cleaning station, and before discharging in Barcău River.

The methods of analysis are those specified for groundwater. Results are presented and compared

with HGR no. 352/2005 (NTPA 001) and presented in the Tabel 4.

The samples were taken according to standard SR EN 25667-1, 2/2002 and SR ISO 5667-11/2000. On the analyzed site, a number of 3 baskets of harmful exhaust gas (of combustion) and a battery of boilers for steam are running.

The emission indicators of air quality were determined with an automatic analyzer. They are: dust and combustion gases: CO, SO₂, NO, NO₂.

The used methods are:

- For dust – SR ISO 9096/2005 –gravimetric method;
- For CO, SO_x expressed as SO₂, NO_x expressed as NO₂ – automatic instrumental method – SR ISO 10396/2001.

Table 3. Characteristics of water from groundwater aquifer, taken from the established samples, compared to in force norms

No.	Analyzed Parameter	Sample symbol / Internal code / Registered value / CMA								
		F1	F2	F3	F4	F5	F6	Permissible limits STAS 1342/91	Law no. 458/2002 and 311/2004	Dutch list
1.	pH	7.53	7.77	7.59	7.54	7.40	7.19	6.5-7.4; max. 8.5	6.5-9.5	-
2.	Petroleum products [mg/L]	0.2	0.5	0.45	0.6	0.35	0.70	-	-	0.42
3.	Chlorides [mg/L]	151	83	32	87	94	230	250 max. 400	-	-
4.	Phosphates [mg/L]	0.30	3.90	0.70	1.10	1.00	0.79	0.1 max. 0.5	-	-
5.	Nitrates [mg/L]	128.8	116.1	101.8	105.0	62.10	204	45	-	-
6.	Nitrites [mg/L]	0.03	0.03	0.17	0.04	0.04	0.25	0 - max. 0.3	-	-
7.	Ammoniacal nitrogen [mg/L]	2.28	2.55	3.09	2.74	2.93	1.65	0 - max. 0.5	0.35	-

Table 4. Characteristics of surface water samples, compared with the in force norms

Nr. crt.	Analyzed Parameter	Sample symbol / Internal code / Registered value / CMA		
		Channel P1-P5	Testing method	Permissible limits HGR 352/2005
1.	pH	7.30	SR ISO 10523/1997	6,5-8,5
2.	Petroleum products [mg/L]	1.00	SR 7877-2/1995	5,00
3.	Chlorides [mg/L]	67.00	STAS 8663/1970	500
4.	Phosphates [mg/L]	5.4 (din care fosfor = 1.76)	SR-EN 1189/2000	Fosfor = 1,00
5.	Nitrates [mg/L]	27.30	SR ISO 7890-2/2000	25
6.	Nitrites [mg/L]	0.05	STAS 12754/1989	1,00
7.	Ammoniacal nitrogen [mg/L]	2.15	SR ISO 7150-1/2001	2,00

2.4. Air – emission investigations

Samples were taken for dust, on the filter with constant mass. Equipment used were taken portable gas and dust, analytical balance, Testo 350XL analyzer, analyzer automatically Sick-MAIHAK model 3006, UV-VIS Spectrophotometer.

The values of the indicators measured in the emissions from 4 fixed emission sources, are found in Table 5.

- Phosphates – CMA exceeded 7 times up to 39 times;
- Nitrates - CMA exceeded by 1.38 times to 2.86 times;
- Ammoniacal nitrogen –CMA exceeded by 3.38 times to 6.18 times.

3. Results and Discussion

3.1. Soil pollution

Comparing the values of analyzed indicators with the reference values according MAPPM Order no 756/1997, we can conclude the following: pollution is reported with HTP soil, being located in the area of shallow soil, up to 0.5 meters deep. All the samples analyzed exceeded the admissible concentration both the alert and intervention concentration, for the soil with industrial use (Fig. 1). Massive pollution of the soil with petroleum products in the area of crude oil extraction highlights a long-term pollution (past and present activities).

It requires as remedial measures, the ecological rehabilitation of the fields, and decontamination of contaminated soil and ecological reconstruction of affected areas.

3.2. Underground water quality indicators

Analyzing the data in Table 3, it is found that exceeded the CMA values was registered for the following indicators:

Table 5. Concentrations of quality indicators determined in the fixed sources of emissions, compared to in force norms

Section / process	Source	Pollutant / measure unit	Registered value [mg/m ³]	CMA according to MAPP M Order no. 462/1993
Park no.	Dispersion	Dust	36.70	50
		CO	25000	-
		NO _x (NO ₂)	2814	500
		SO _x (SO ₂)	394	500
Park no.	Dispersion	Dust	26.70	50
		CO	4671.5	-
		NO _x (NO ₂)	11.33	500
		SO _x (SO ₂)	55.17	500
Park no.	Dispersion	Dust	17.30	50
		CO	10298.06	-
		NO _x (NO ₂)	35.49	500
		SO _x (SO ₂)	717.81	500
Battery	Dispersion	Dust	15.9	5*
		CO	5.20	100*
		NO _x (NO ₂)	119.6	350*
		SO _x (SO ₂)	12.2	35*

* - values according to MAPP M Order nr. 756/1997

The "petroleum products" is not limited in the Romanian norms, but his values are very high. In Fig. 2 the concentrations of the indicator "petroleum products" are provided, comparative to the limits allowed by the Dutch list, the only regulation that can be taken into account.

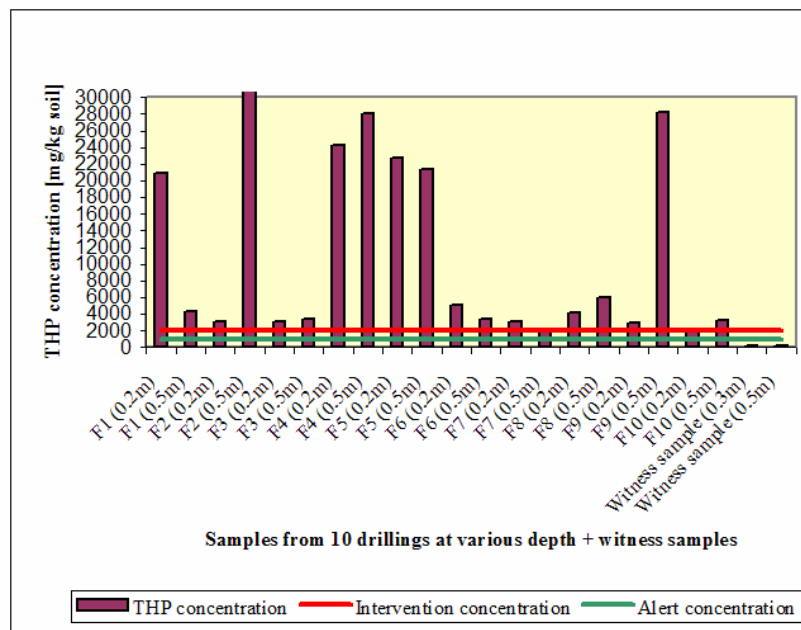


Fig. 3.1. THP concentration level in soil compared with the in force norms

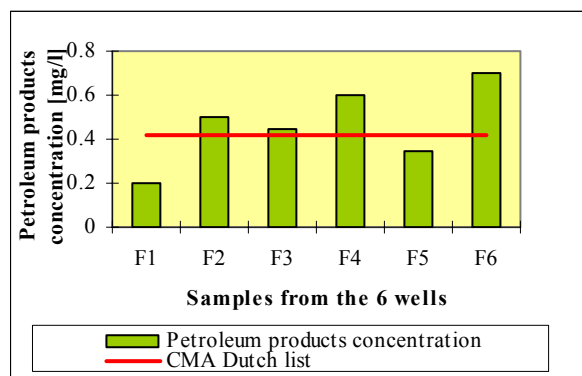


Fig. 2. Petroleum products concentration for the 6 monitored drillings

Therefore, water from groundwater aquifers in the vicinity of the site is not recommended for drinking purposes.

High concentrations of indicators: phosphate, nitrogen and ammoniacal nitrogen are not caused by the oil extraction activities; they can be imported from other sources of pollution in the area (e.g. the use of chemical fertilizers in agriculture).

The "petroleum products" present levels of impermissible concentration in the aquifer layer.

3.3. Surface water quality indicators

Fig. 3 shows that the following indicators overshoot the maximum allowed concentration:

- Phosphates – CMA exceeded with 76%;
- Ammoniacal nitrogen – CMA exceeded with 7.5%.

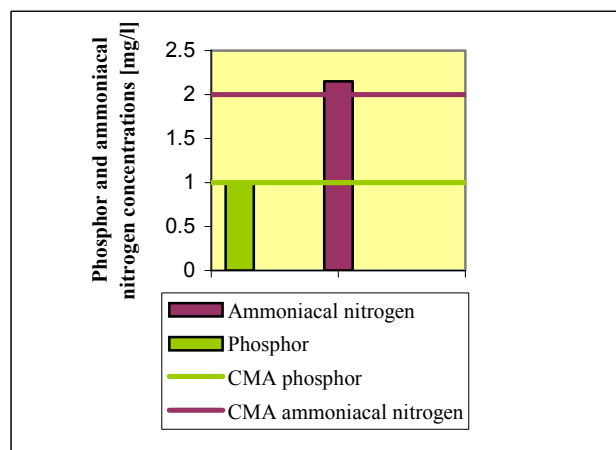


Fig. 3. Phosphorous and ammoniacal nitrogen concentrations of in surface water

Therefore, technological waste waters are properly treated, the identified type of contamination being unspecified for oil extraction activity.

3.4. Emissions

MAPP Order no. 462/1993 establishes the limits for the emission directed in the atmosphere, emissions resulted from the technological process and combustion plants. The graphical representation of indicators that exceed the CMA, in Fig. 4 evidences the following:

- The average concentration of NO_x is 2814 mg/m³ exceeds 5.6 times the norm under the CMA;
- The average concentration of 717.81 mg/m³ SO_x exceeds 1.4 times the CMA under the same regulation.

Emissions of CO are not limited, and the concentrations recorded shows higher values. Also, dust discharged from the battery of boilers exceed the CMA under Order MAPP No. 756/1997.

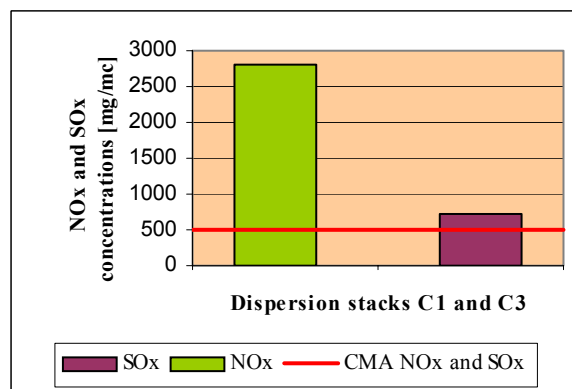


Fig. 4. NO_x and SO_x concentrations in emissions from fixed sources

4. Conclusions

Experimental researches and determination made on the crude oil extraction site – Suplacul de Barcau, show a significant environmental impact exerted by this activity.

Negative effect is exercised on all environmental factors (water, soil, and air), but the most affected are the soil and groundwater aquifers, which leads to impossibility to use this water as potable water.

Measures to be taken for removing these effects are:

- Ecological rehabilitation of the oil extraction area;
- Decontamination of polluted soil;
- Ecological Reconstruction of the affected land;
- Permanent monitoring of groundwater aquifers and stopping the phenomenon of pollution it.

From research made on site, in the area of the modern well, ecological rehabilitated, it is found that the phenomenon of soil pollution can be controlled and reduced

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*** SR-ISO 7890-2/2000
*** STAS 12754/1989
*** SR / ISO 7150-1/2001
*** SR-EN 25667-1,2/2002
*** SR-ISO 5667-11/2000
*** SR / ISO 7150-1/2001
*** SR / ISO 9096/2005
*** SR / ISO 10396/2001



IDENTIFICATION, COMMUNICATION AND MANAGEMENT OF RISKS RELATING TO DRINKING WATER POLLUTION IN BIHOR COUNTY

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Abstract

At global level, the microbiological quality of water is a matter of concern, since diarrhoea represents the second cause of mortality. In addition, nitrates represent a significant problem and their high concentration - above the accepted limits - in drinking water is frequently encountered in Romania. Water samples have been analyzed in accordance with the methodology recommended by The Public Health Institute Bucharest. 78.15% of the water samples evaluated during the interval 2004-2007 proved that they do not fit the quality norms. The frequency of the samples which do not meet the minimal requirements of the specific norms indicates an increasing tendency. The layered analysis of data has established ascending trajectories, inverse correlations and acceptable levels of association for both the out-of-norms microbiological samples and the physical-chemical. Despite the fact that the pollution of the drinking water supplied by public distributing stations has become more intense, the frequency of acute water-related diarrhoeal illnesses and of infantile methemoglobinemia is often underestimated.

Key words: acute diarrhea, chemical pollution, microbiological pollution, , cyanotic infantile methemoglobinemia.

1. Introduction

Drinking water is an essential environmental constituent, with a major impact upon the quality of life and the health state of the population. There are speculations that associate the modern civilization with the rediscovery of hygiene, rather than with the industrial revolution.

Drinking water is intended to be ingested by humans: the phrase "drinking water" refers to any type of water, either treated or in a natural state, which is used for drinking, cooking or any other domestic purposes, regardless of its origin or whether it is supplied by distribution stations, provided in water tanks or stored in bottles or other containers; the words "drinking water" also refer to other types of water, used as material by the food industry (Law 458, 2002).

Drinking water must be healthy and clean, meeting the following demands: it should not contain microorganisms, parasites or substances that might represent a potential hazard for human health and it must meet the minimal requirements stipulated in

Law 458 (2002), concerning the quality parameters of potable water (microbiological, chemical and indicators).

Water pollution refers to a change in the natural qualities of water as a result of its contamination with external elements, to an extent that makes it unsuitable for use and ingestion; it can be the consequence of natural phenomena, but most frequently it appears as a result of human activity. The specific pollutants that can have negative effects upon the health state of the population (injury, disease or death) represent risk factors and can be grouped in the following categories: microbiological pollutants (bacteria, viruses, parasites) and chemical pollutants (toxic chemical substances). They can be identified and their level of toxicity and particular effects can also be established (Manescu et al., 1996; Popa, 2001).

Recent statistics indicate that the infectious hydric pathology has marked an ascending trend, and is chiefly the result of polluted water ingestion. The infectious diseases caused by water intake continue to make around 25 000 victims in the whole world every

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day. Though water ingestion is the main cause of infectious diseases, people can also be contaminated while washing, bathing or inhaling water vapors (<http://www.greenagenda.org/eco-aqua/potabil.htm>, 2008).

The microbiological quality of water is decreasing in many countries. The bacterial diarrhoea, which can be caused both by water ingestion and the absence of water (when the norms of individual hygiene are not observed), continue to represent a threat for public health, even in developed countries. At global level, diarrhoea occupies the second place among mortality causes, after the cardiovascular diseases, and studies conducted in many countries conclude that the incidence of this disease is highly underestimated. Its recent evolution is disturbing, since 2 million children die every year due to water-related diarrhoeal illnesses, and the annual number of people becoming ill with such diseases is of about 900.000.000 (<http://www.greenagenda.org/eco-aqua/potabil.htm>, 2008; Ionut, 2004).

Part of the toxic chemical substances that can be transmitted through water ingestion have their origin in nature, but their large majority result from the pollution of aquifers (<http://www.greenagenda.org/eco-aqua/potabil.htm>, 2008). Nowadays, at both the global and the local level, pollution accidents in punctual and non-punctual sources represent a frequent cause of chemical contamination of water, with possible acute or chronic consequences upon the health of the population living in the contaminated area. The water-related illnesses, especially the ones associated with the ingestion of contaminated water, continue to represent a problem of public health; more and more studies emphasize the connection between the chemical pollution of potable water and the creation of favorable circumstances for maladies such as cancer, congenital malformations, endocrine disruptions, acute and chronic intoxications (<http://www.ara.ro/apa%20curata>).

Nitrates, which are toxic chemical elements that indicate an older pollution, can represent a major problem since their concentration in water, above the accepted limits, is frequently encountered in our country. Nitrites, resulting from the reduction of nitrates either before consumption or in the lumen of the digestive tract, cause cyanotic infant methemoglobinemia, which affects people at very young ages, and sometimes even at adulthood. Our country presents a high incidence of methemoglobinemia, with a significant mortality, this illness being much underestimated, given the difficulty of diagnosing it. Nitrates may be found in human or animal excrements, but their presence in water can also be associated with the large-scale use of fertilizing substances in agriculture (<http://www.greenagenda.org/eco-aqua/potabil.htm>, 2008; Ionut, 2004; Laza and Ionut, 2001; Popa, 2001).

In Romania, a certain percentage of water sources should not be used, but people's ignorance or the absence of alternatives determines the use of water from inadequate wells and springs.

The aim of this study is to evaluate the quality of the potable water supplied by public distributing stations (central systems and public wells) in Bihor County between 2004 and 2007, and to analyze the effects of pollution on people's health.

2. Materials and method

The probe sampling has been done in accordance with the methodology recommended by The Public Health Institute, Bucharest, the samples being periodically collected from the water treatment plant, from along the water-supply network and from the consumers' taps.

The interpretation of results has been achieved by means of their correlation with the sanitary regulations (Table 1), while data analysis has been completed with the help EPIINFO6 and EXCEL statistical programs. The control of drinking water quality has been continually and permanently carried out in the laboratories of the water plant and in the Public Health Authority laboratory of Bihor County.

Table 1. The quality parameters of drinking water (extract from Law number 458, 2002 - Appendix 1)

<i>Parameter / Units</i>		<i>Accepted value</i>
<i>Microbiological parameters</i>	Escherichia coli (E. Coli)/100 mL	0
	Enterococci (Faecal streptococci)/100 L	0
<i>Chemical parameters</i>	Ammonium (mg/L)	0.50
	Nitrates (mg/L)	50
	Nitrites (mg/L)	0.50

3. Results and discussions

During the period of research, 4254 water samples were drawn; of this total, 2218 proved inadequate, the microbiologically inadequate ones being predominant (64.9% from the total of inadequate samples and 33.9% from the total of gathered samples) (Fig. 1).

The annual evolution of the relative frequency of the total inadequate samples marked a clear upward trend between 2004 and 2006 (increasing with 73.97%); when attention is focused upon the last year, and a comparison is made with 2006, a decrease in the percentage of the inadequate samples can be observed, though this percentage continues to present values that are superior to the first two years of research (Figs. 2, 3). The percentage of physical-chemical inadequate samples presented a growing tendency during the first three years of the period under investigation (showing an increase with 30.26%), but a decrease with 29.46% can be observed in the last interval that was evaluated.

Since only one hydric epidemic was registered during the period under investigation, in 2006, the study proceeded to the research of acute infectious diarrhea cases, recorded during the period mentioned above.

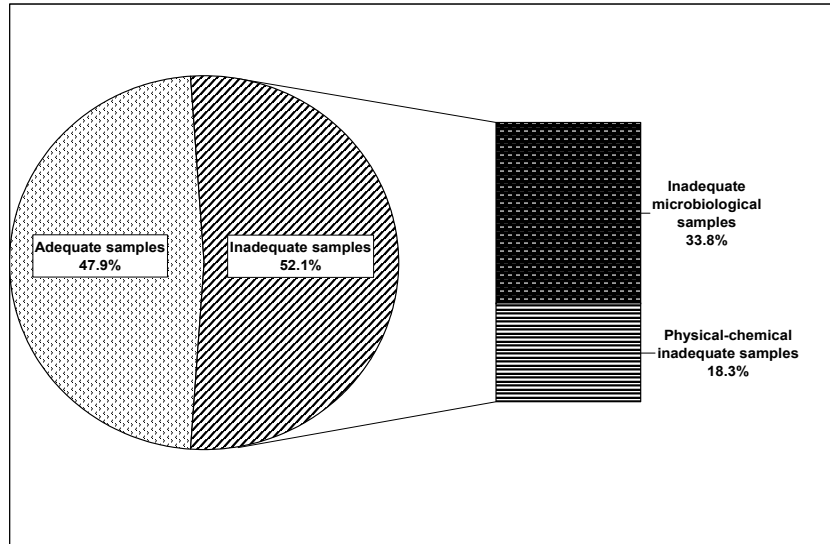


Fig. 1. The relative frequency of samples

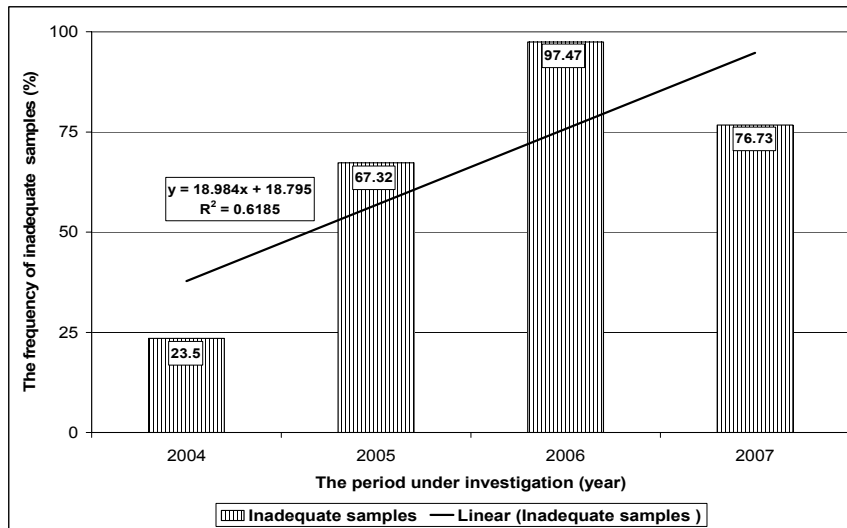


Fig.2. The annual evolution of the relative frequency of the inadequate samples

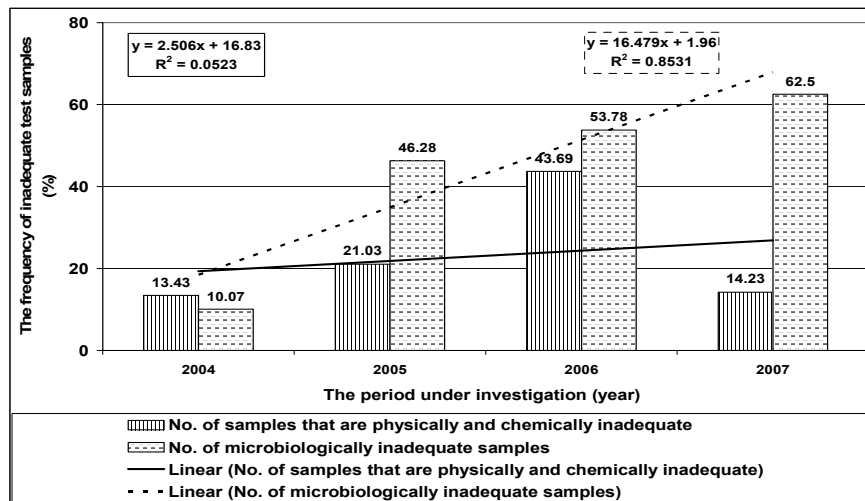


Fig. 3. The annual evolution of the relative frequency of the inadequate sample types

Between 2004 and 2007, a number of 13,682 cases of acute diarrhea have been recorded, this illness being the most frequent among health problems caused by the ingestion of microbiologically contaminated water (3,717 in 2004; 2,911 in 2005; 3,724 in 2006 and 3,330 in 2007).

The regression and correlation analysis indicates an inverse correlation and a moderate association level ($r = -0.659$) between the number of persons taken ill by the ingestion of contaminated water and the number of microbiologically inadequate samples (Fig. 4).

The determination coefficient $R^2 = 0.4351$ suggests the fact that the variation in the number of acute diarrhea cases can be explained, in proportion of 43.51%, through the linear relationship which exists between this coefficient and the number of the microbiologically polluted test samples, while the rest of 56.49% corresponds to an unexplained or residual variability (disease caused by contaminated food, direct contact with ill persons or an unreal number of persons who were taken ill). During the period of investigation, a number of 4 cases of cyanotic infantile methemoglobinemia, caused by ingestion of water coming from public wells, have been registered.

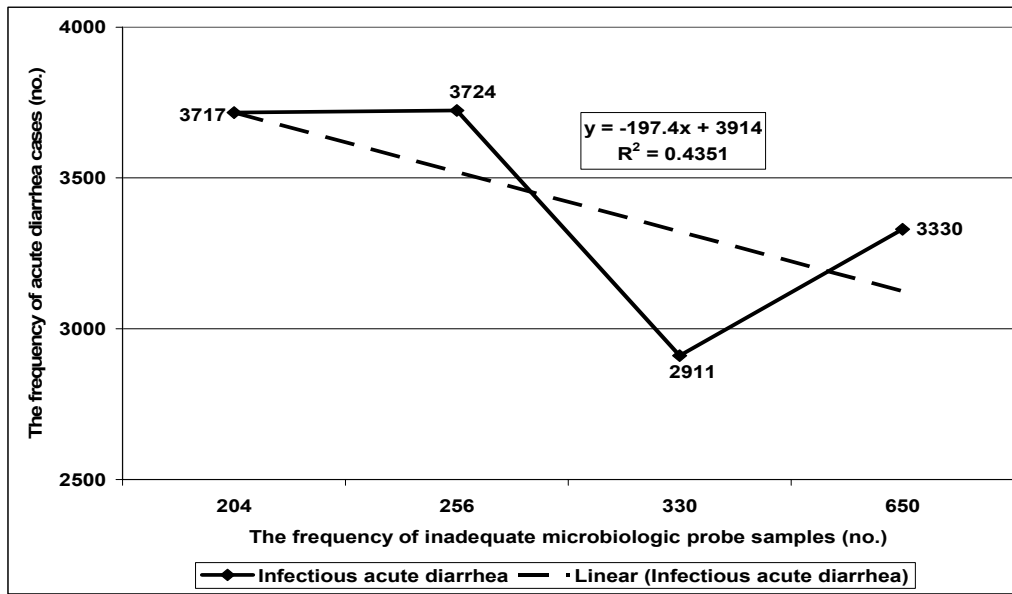


Fig. 4. The evolution of the acute diarrhea in relation with the frequency of microbiologically contaminated samples

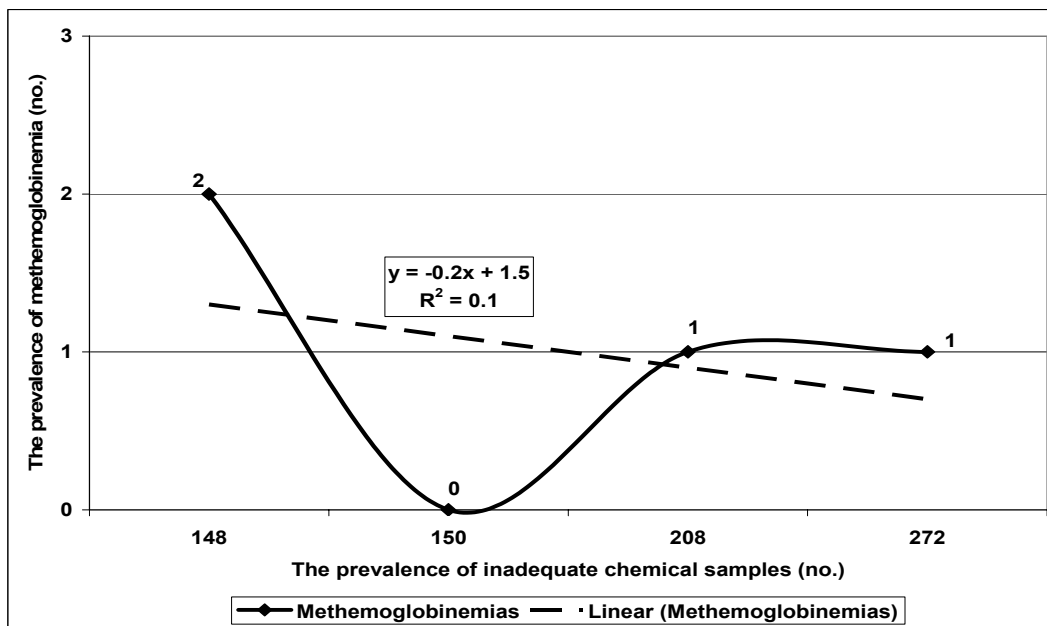


Fig. 5. The evolution of infantile cyanotic methemoglobinemia in relation with the frequency of samples inadequate from the physical-chemical point of view

The regression and correlation analysis indicates an inverse correlation and an acceptable association level ($r = -0.316$) between the number of patients taken ill and the number of samples that are inadequate from the physical and chemical point of view (Fig. 5).

The determination coefficient $R^2 = 0.1$ indicates the fact that the variation in the cyanotic infant methemoglobinemia occurrence rate can be explained, in proportion of 1%, by the linear relation that exists between this factor and the number of the chemically polluted samples, while the remaining 99% corresponds to an unexplained or residual variability (disease caused by the ingestion of polluted water coming from other sources or an inaccurate number of persons taken ill).

The negative correlation coefficients might suggest the fact that the intensification of microbiological and chemical pollution of water sources could have determined the decrease in the number of both acute diarrhea cases and cyanotic infantile methemoglobinemia, which is a very unlikely situation. This particular aspect and the high residual variations indicate the fact that there is no linear correspondence between the number of the above-mentioned illnesses and the prevalence of inadequate samples.

The control of potable water supply systems indicates a series of deficiencies: the inadequate quality of water at source (which presents a high quantity of ammonium and nitrites), the inefficient maintenance of water-intake works and of purifying plants, the empirical procedure used for water purification, outdated and inadequate, or even unavailable disinfection equipments, the intermittent distribution of water, the absence of sanitary protection areas or the inadequate hygienic maintenance of these areas, the existence of disintegrated, outworn or undersized water supply networks, the disregard for the hygienic and sanitary norms concerning the maintenance of water tanks.

4. Conclusions

With regards to the quality of the potable water provided to consumers in Bihor County between 2004 and 2007, the following can be concluded:

1. The chemical and microbiological pollution of water has been constant and intensive, an improvement - from the physical and chemical point of view - being observed in the last year of the period focused upon;

2. There are no linear relations between the number of inadequate samples and the number of people taken ill as a result of the ingestion of polluted water (acute diarrheas or cyanotic infantile methemoglobinemia). Accountable for such results is either the underestimation of the number of cases of the two diseases mentioned above (this situation may be the result of an absence of information on the one

hand, and of the absence of reports concerning the actual number of diseases caused by water ingestion on the other hand) or the replacement of the drinkable water that is supplied by public distributing stations with bottled water – still or carbonated mineral water, or different other beverages.

3. The absence of eco-technology in rivers and water catching protection areas, which continuously causes the pollution of water resources.

4. The technologic equipments available in water plants are incompatible with the water quality complex, while the difficulties related to the running of water plants and to the supply of quality water is accentuated by over-production, the absence of current or capital repairs or by the need to replace equipments.

5. Among the most important situations accountable for the contamination of potable water with nitrates, the inadequate agricultural activities and the absence of hygienic conditions can be mentioned. Despite the attempts to replace some elements of the distribution system, the recurrent interventions continue to contribute substantially to the decrease in the quality of water that is supplied to consumers in Bihor county.

Since regulations referring to water quality are often ignored, the resulting drawbacks should be identified and coercive measures should be put into practice as soon as possible, in order to obtain drinking water of a better quality. If necessary the distribution of water should be restricted or even ceased.

For the time being, since it is impossible to ameliorate the properties of underground water, before it is introduced into the system of potable water distribution, the only solution for the improvement of potable water quality is its dilution with the water produced in already existing water plants.

Current legislation stipulates the necessity to provide consumers with adequate and updated information concerning the quality of potable water. Accurate information with regards to the quality of water will probably increase people's awareness with respect to the importance and the role of water for human health.

In this context, the *risk management* and implicitly the assurance of water biostability while it is being transported, stored or distributed, requires the following:

- The production of a type of water that can maintain its initial quality at consumers' taps, without being transformed by the condition of the external or the internal distribution system;
- The proper maintenance of water distribution systems, in order to preserve the quality of water, which requires a standing water pressure, the detection and reduction of water losses, the control of the process of sedimentation and corrosion of materials that are used in water distribution systems,

and the use of new materials (PE, thermoplastic resins, composite materials);

- The building of data bases that facilitate the identification of optimal solutions for the problems that might appear in the system;

- The information of population with regards to hygienic measures, which are necessary for the prevention of hydric pathology.

The increased exigency of consumers with reference to potable water, alongside the rise of prices, accentuates the problem of water quality.

The main objectives related to the supply of drinking water in Bihor County refer to:

- ✓ The surveillance of European standards concerning the quality of water, the assimilation of a the quality management system and the availability of adequate water treatment technologies;

- ✓ The reduction of operation costs, by updating the techniques of exploitations and by implementing the principles of efficient management;

- ✓ Minimizing specific consumption (of electric energy and reactive substances) through the use of new technologies, the building of a functional pipe systems, and the provision of automatic and common equipment systems;

- ✓ The permanent supply of all consumers with water, the reduction of water losses, and the increase of potable water production.

A more efficient coordination between institutions that are responsible for the quality of water is imperative in order to create the context for a more complex research activity and a scientific approach to the improvement and upgrading of water distribution networks and water plants in Bihor county.

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ENVIRONMENTAL ENGINEERING EDUCATION IN IRAN: NEEDS, PROBLEMS AND SOLUTIONS

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Abstract

Since public concerns about the environmental issues have increased, several universities all over the world have been establishing environmental engineering programs. Environmental engineering programs in Iran at graduate level have been developed since 1990. At the present time, there are ten universities are presenting environmental engineering programs at graduate levels. The environmental engineering education systems of almost all Iran universities are quite traditional. As the environmental engineering problems have become very diverse and complex, it is necessary to define the new scope of environmental engineering, especially in developing countries, to cope with environmental problems and sustainable development concerns. Therefore, the Environmental Engineering programs of Iran Universities must be modified in the near future. For example several courses such as "Green Chemistry", "Energy Management", "Environmental Law", "Environmental Economics" and "Environmental Ethics and Philosophy", "Environmental Sociology" and "Sustainable development" are suggested to add to the curriculum of the all environmental engineering programs in Iran. The aim of this paper is to explain the present situation and challenges of environmental engineering education in Iran.

Keywords: environmental engineering, education, curriculum, course development, Iran

1. Introduction

"Engineering" may be defined as the application, under constraints of scientific principles to the planning, design, construction and operation of structure, equipment and system for benefit of society (Sincero and Sincero, 1996). Environmental Engineering is defined as "that branch of engineering that is concerned with protecting environment from the potentially deleterious effects of human activity, protecting human populations from the effects of adverse environmental factors and improving environmental quality and for human health and well-being" (Peavy et al., 1985).

Environmental engineering, which was traditionally a sub-set of civil engineering focusing on water sanitation, has mushroomed to include all aspects of human and terrestrial environment water and wastewater management, air quality, solid and hazardous waste management noise and light pollution, and radioactive waste management

(Bishop, 2000). So, environmental engineering covers a broad spectrum of environmentally related activities.

Nowadays, environmental issues affect almost all commercial and industrial sectors, and are a central concern for the public, governments, and even international relations. The main environmental issues of the present age are safe drinking water, wastewater processing, solid and hazardous waste disposal, outdoor and indoor air pollution, ecological risk management, and pollution prevention through better, safer products or improved process design. (EVEN, 2003).

Since public concerns about the environment issues have increased, several universities have been establishing environmental engineering course in both developed and developing countries. Environmental engineering education program of developed country have changed over the past several decays. For example in US this program passed three following steps: First step (Before 1950): mainly focus on

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engineering practice, using uniform design codes and traditional design procedures; Second step: more scientific based approach, in which a fundamental understanding of natural phenomena was emphasized; Third Step: More holistic approach to understanding environmental processes and design of environmental systems (Bishop, 2000).

On the other hand the environmental engineering education program of the most universities of developing countries is quite traditional. It is necessary for these universities to modify their curricula. The main aim of this paper is to explain the present situation and challenges of environmental engineering education in Iran.

2. A brief history of higher education in Iran

The history of the establishment of academic universities in Iran dates back to 1851 with the establishment of “Darolfonoon”, aimed at training and teaching Iranian experts in many fields of science and technology. It was in 1928 that Iran's first university (The University of Tehran) was proposed by an Iranian physicist, Mahmoud Hessaby which was built in 1934. The main purpose of the establishment of the University was to disseminate advanced knowledge in relation to the sciences, technology, literature and philosophy (Higher Education, 2006; Higher education in Iran, 2006). The first university of Iran (University of Tehran) started its activity by establishment of the following six faculties (History, 2006): 1) Theology, 2) Natural science and Mathematics, 3) Literature, Philosophy and Educational Sciences, 4) Medicine and its various branches, 5) Law, Political Science and Economics, 6) Engineering. In 1934 only 40 students were

admitted to the engineering faculties of the University of Tehran in the fields of civil engineering, mechanical engineering, mining engineering and electrical engineering fields (History of UT, 2006).

Since the Islamic Revolution of 1979 in Iran, the educational system of the country has gone under qualitative and quantitative changes. The two Ministries responsible for higher education in Iran are the Ministry of Science, Research and Technology (MSRT) and Ministry of Health and Medical Education (MHME). Presently, 54 universities and institutes of higher education and 42 medical schools are active under the MSRT and MHME, respectively. In addition, Islamic Azad University; as the first private university in Iran, is presently active in over 110 cities in Iran with more than half a million students (Education System, 2006; Higher Education, 2006; Higher Education in Iran, 2006).

3. An overall review on environmental education programs in Iran

Nowadays, environmental issues affect almost all commercial and industrial sectors, and are a central concern for the public, governments, and even international relations. There are several Universities in Iran that are presenting different programs related to Environmental Science and Engineering. Different Faculties, Schools and Departments are currently offering Associate Diploma, BSc, MSc. and PhD degrees in various subjects related to environment, which are shown in Table 1.

In this paper the mainly focus is put on the environmental engineering programs that are offering by Engineering Departments.

Table 1. Environmental educational programs in Iran*

<i>Name of Department/ Schools/ Faculties</i>	<i>Offered Degree</i>	<i>Authorized by</i>	<i>Main Universities</i>
Department of Civil Engineering	MSc and PhD in Environmental Engineering	MSRT	Sharif University of Technology, Amirkabir University of Technology, Tarbiat Modares University, Iran University of Science and Technology, Khaje Nasir University of Technology, The University of Shiraz, Isfahan University of Technology
Faculty of Environment	MSc and PhD in Environmental Engineering, MSc in Environmental planning and Management, Msc in Environmental design	MSRT	The University of Tehran
Department of Chemical Engineering	MSc and PhD in Environmental Engineering	MSRT	Sharif University of Technology
Faculty of environmental resources	BSc and MSc in Environmental Science	MSRT	The University of Tehran, Tarbiat Modares University, Isfahan University of Technology
School of Public health	Associate Diploma, BSc, MSc and PhD in Environmental health	MHME	Tehran University of Medical Sciences, Isfahan University of Medical Sciences, Iran University of Medical Sciences

MSRT = Ministry of Science, Research and Technology (Iran)

MHME =Ministry of Health and Medical Education (Iran)

* Non-governmental Universities (Islamic Azad Universities) are not included in this list

There is no BS level of Environmental Engineering in Iran now. Environmental engineering program at graduate level have been developed since 1990 in Iran. At that time only two universities (The University of Shiraz and Tarbiat Modares University) offered MSc of environmental engineering in Iran and only a few students admitted in these programs. For example in 1990 only three students were accepted as Master students of Environmental Engineering at Tarbiat Modares University. At that time the entrance exam for MSc of environmental engineering was separated from other fields of civil engineering and admitted students had different backgrounds such as civil engineering, chemical engineering and irrigation engineering.

Presently, there are ten universities in Iran (except non-governmental Universities) that are presenting environmental engineering courses at the graduate levels which are accepting more than 90 master students per year (Table 2).

Table 2. Number of student admitted for MSc degree of Environmental engineering in 2007*

No.	University	Department / Faculty	No. of student admitted
1	Sharif University of Technology	Civil Engineering	11
2	Amirkabir University of Technology	Civil and Environmental Engineering	10
3	Tarbiat Modares University	Civil Engineering	8
4	Iran University of Science and Technology	Civil Engineering	8
5	Khaje Nasir University of Technology	Civil Engineering	10
6	Shiraz University	Civil Engineering	5
7	The University of Tehran	Faculty of Environment	20
8	Tarbiat Moalem University	Civil Engineering	10
9	Mazandaran university	Civil Engineering	6
10	Ferdowsi University (Mashhad)	Civil Engineering	6
Total			94

*Adopted from Guideline MSc (2007), Ministry of Science, Research and Technology.

At present the admittance exam of environmental engineering is the same as other fields of civil engineering and therefore more than 90 percent of admitted students have civil engineering background.

Among ten above-mentioned Universities, two of them (Tarbiat Modares University and The University of Tehran) have PhD program of Environmental Engineering in Iran. Therefore, only a few of master students are accepting for PhD program.

The number of Universities in Iran offering Ms and PhD of environmental engineering is not acceptable in compared with the Universities of developed countries. For example there are approximately 140 Universities in North America offering MSc. and PhD (Bishop, 2000).

As an example of environmental engineering education in Iran, the curriculum of the department of civil and environmental engineering at Amirkabir University of Technology (AUT) for Master program is explained hereafter.

4. Environmental engineering education in the Department of Civil and Environmental Engineering, Amirkabir University of Technology (AUT)

Civil and Environmental Engineering (CEE) Faculty of AUT established MSc degree of environmental engineering in 2003. At the same time, the name of the "Department of Civil Engineering" was changed to the "Department of Civil and Environmental Engineering (CEE)". The main objectives of the environmental engineering program at AUT are to provide environmental engineering education for the students who have different backgrounds (Civil engineering, Chemical engineering, Mechanical engineering and so on) at the graduate level.

The MSc educational program of Environmental Engineering including all fields and the courses (including main and elective courses), offered by the CEE Department of AUT, is shown in Fig. 1. According to this program, students can select their fields of study after the 2nd semester. After that, the students will choose at least three elective courses with the approval of their supervisors.

Full-time master students of Environmental Engineering will normally be expected to finish their degree in 2 or 2.5 years (4 or 5 semester) by completion of a minimum of 30 credit units, and a thesis (6 credit units).

There are not big differences between MSc curricula of environmental Engineering in AUT and other Universities in Iran. Some Universities such as Sharif University of Technology replaced the "Advanced Mathematics" course by "Environmental Planning and Management" course for their MSc Program. In addition, there is a difference on elective courses offering by each department that are mainly depends on the professional fields of academic staff.

5. Challenges of environmental education in Iran

Nowadays, the environmental engineering problems have become very diverse and complex. For this reason, it is necessary to define the new scope of environmental engineering to cope with environmental problems and sustainable development concerns, especially in developing countries.

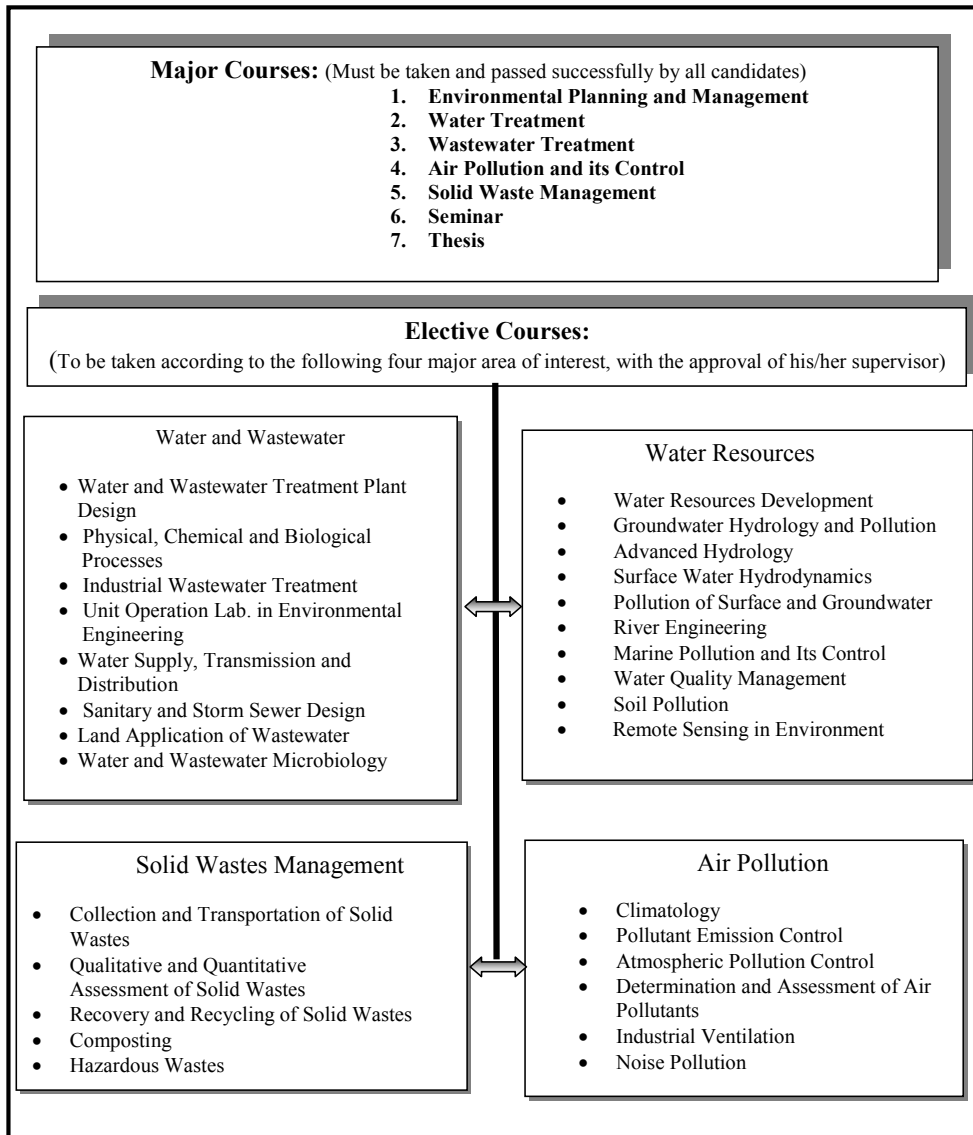


Fig. 1. MSc educational program of Environmental Engineering in Department of Civil and environmental Engineering (Alavi Moghaddam et al., 2004; Curriculum Book, 2003)

On the other hand “the complex nature of the environmental problems of the present age implies the necessity for collaboration among engineers, social and natural scientists, economists” (Mino, 2000). Unfortunately, integration of the engineering curricula with social, cultural and economic sciences is not started in any fields of Engineering in Iran. So it is crucial for all Universities in Iran (especially environmental engineering fields) to modify their curricula to achieve the main sustainable development goals.

It is no doubt that the traditional program of environmental engineering cannot cope with the complex nature of the present environmental problems of developing countries. The Environmental Engineering departments of Iran’s Universities should modify their curriculum by adding several new and multidisciplinary courses in the near future. Several courses such as “Green Chemistry”, “Energy Management”, “Environmental Laws”,

“Environmental Economics” and ‘Environmental Ethics and Philosophy”, “ Environmental Sociology” and “Sustainable development” are suggested to add to the curriculum of the all environmental engineering program as elective courses in Iran. By adding these courses, all other engineering students (both undergraduate and graduate levels) can have this chance to take part in these interdisciplinary courses. It is not so easy to introduce these lectures in graduate program of Environmental engineering in Iran mainly due to lack of academic staff in these multidisciplinary fields.

The Universities should promote their activities toward sustainable development. One of the main fields that can promote a society toward sustainable development is “environmental engineering”. According to the article 65 of 4th development plan of Iran (2005-2009), government is urged to prepare regulation regarding sustainable development path for all ministries, universities, and

other organization. It will be a good chance for universities to enhance their activity for establishment of different related fields e.g. environmental engineering and science. The government is encouraging these activities in universities by introducing some University as "Green University". For example based on AUT activities toward sustainable development, it was approved for this university to be "Green University" in 2003 by Iran Ministry of Science, Research and Technology as well as Department of Environment. Therefore, AUT as one of the main technical universities in Iran has chosen the strategy "pioneer of Sustainable Development in Iran" for the next decade (Alavi Moghadam et al., 2004; Alavi Moghadam et al., 2005)

Environmental Engineering education in Iran is at the beginning of way and there are a lot of obstacles for promoting these fields of study. The main obstacles are summarized as:

- 1) The budget limitation for establishment of environmental engineering programs in Iran's Universities.
- 2) Lack of academic staff in different new field of environmental engineering.
- 3) Lack of professional jobs for environmental engineering graduates due to weak legislation for environmental protection.
- 4) Lack of long- term planning for environmental engineering education program in Iran
- 5) Lack of International collaboration among the universities of Iran and developed countries
- 6) Difficulties in official procedure of establishment of new fields in Iran's Universities.
- 7) Lack of professional organization to audit and evaluate the environmental engineering programs in Iran.

6. Conclusions

Environmental engineering program at graduate level have been developed since 1990 in Iran. At the present time, there are ten universities in Iran that are presenting environmental engineering program at the graduate levels. The numbers of graduated students of this field are dramatically increased within past few years. The environmental engineering education system of almost all universities in Iran is quite traditional and it should be modified in the near future according to the public needs and concerns.

It is necessary to define the new scope of environmental engineering to cope with environmental problems and sustainable development concerns, especially in developing countries. Several courses such as "Green Chemistry", "Energy Management", "Environmental Laws", "Environmental Economics" and "Environmental Ethics and Philosophy", "Environmental Sociology" and "Sustainable development" are suggested to add to the curriculum of the all environmental engineering

program as elective courses in Iran. Environmental Engineering education in Iran is at the beginning of way and there are a lot of obstacles for promoting these fields of study. The main obstacles are 1) The budget limitation for establishment of environmental Engineering programs 2) Lack of academic staff 3) Lack of professional jobs for environmental engineers 4) Lack of long- term planning for environmental engineering program in Iran. 5) Lack of International collaboration 6) Difficulties in official procedure of establishment of new fields and 7) Lack of professional organization to audit and evaluate the environmental engineering programs.

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THE GORGON METHOD AS A TOOL IN SUSTAINABLE BEHAVIOR AND DEVELOPMENT

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Abstract

The paper proposes a solution for life quality improvement by changing the individual's mentality and creating a sustainable behavior. The solution consists of the development of a psycho-behavioral pattern starting from the Gorgon experiences. The latter are hurtful experiences in the individual's life the effect of which is a complete or partial emotional components blockage. The hindrance of these components performance affects the individual's behavior, placing him or her in a state of shock which he or she can hardly outrun. The research in this paper approaches the high potential fundamental research at the border between environmental psychology and sustainable development. The creation of a sustainable behavior is a dynamic and complex process, consisting of the loop: problem – problem solving – solution finding – validation. The Gorgon method represents a starting point in raising an individual's sustainable behavior. It implies a body of knowledge, a "core", a sum of specific values and the deliberately use of some searching innovative opportunities techniques. The main objective of the paper is the accomplishment of a multidisciplinary research that can evidence the complex relationship between the environment's components, the quality and the sustainability of human health and of the socio-economical systems, considering the three interconnected sustainable development components: economy, society, and environment. The expected results of the Gorgon method development consist of deep changes in the individual's mentality, which will be directed toward sustainable development and life quality improvement.

Key words: sustainable behavior, education for sustainable development, Gorgon method, psychological behavioral pattern

1. Introduction

Harmful experiences can result in a total or partial blockage of emotional components. The hindrance of these components' operation has effects upon the behavior of the individual, who falls in a state of perplexity he or she can hardly overcome. The above description defines what we have dubbed the *Gorgon Hypothesis*. We call such events *Gorgon-type Experiences* (Ioan, 1995), as they describe the behavior of the Gorgon's miserable victims who were petrified by the mythological monster's eyes. Legend has it that valiant Perseus has defeated Medusa by putting before her eyes his polished shield which reflected her image and thus she went petrified by her own stare allowing Perseus to behead her. Thinking of a modern Perseus, we try to go deeper into such experiences that are crucial to many people and to control them in order to create a sustainable behavior.

The paper aims at developing a method based on the Gorgon Hypothesis that intends to shape the individual's behavior. In the Gorgon Hypothesis, this behavior corresponds to a social passiveness (paralysis) similar to the petrified state induced by Medusa's eyes. Modern days Medusa epitomizes the traumatizing environment that has blocked the individuals' attitude in a passive (petrified) state that defines an unsustainable behavior.

Ecological problems such as environmental pollution and its consequences represent this traumatizing environment. The mechanisms that generate mental trauma derive from the consequences of global warming, desertification, water shortage, climatic anomalies (hurricanes, flooding, el Niño, etc.) which erode the life quality and determine high levels of insecurity.

The Gorgon Method aims at shaping the individual's behavior by triggering an active state

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with active attitudes towards nature, environment and other individuals (society). Such a state defines a sustainable mentality that generates the sustainable behavior.

2. The Gorgon Hypothesis

In the first instance, the emotional path of an individual subjected to a Gorgon Experience is to accept the situation and to place in the foreground of his/her existence a tough truth, that by that moment he or she had thought that it existed somewhere very far away and possibly affecting the others. Much more frightening is the abrupt and totally unexpected revelation that this tough truth was from the very beginning here with him or her, and it even didn't hide. During such crucial experiences an affective sensitivity sharpening superposes to the deepening of the self-consciousness which can either evolve to a more or less severe inner disruption, or (on the contrary) to the identification and putting into action of some poorly rendered valuable creative resources. This succession characterizes any Gorgon-type experience.

In the process of self-awareness, an acute emotional affectivity can be added after this kind of experiences, which can evolve either to an interior more or less serious or, on the contrary to find out and to use some of the less used creative resources, as a sequence of any Gorgon type experiences. When it was tried to define the essence to approach the theme, it started from the idea that every individual, beside his ethnic origins, educational level, status or social standing etc. has a set of fundamental needs. More or less this means survival, a certain quality of life and it represents the "selfish" part of each one of us. There are two ways of satisfying these needs: the "hard" way, when the individual is satisfying his/her needs by any necessary way (without carrying of anything) and the "smooth" way, when the individual is aware that he or she is a part of the community and there are other people who must be taken into consideration (an image that the individual will have in a mirror), namely their perspective and their future generations, as a result of applying the Gorgon method.

The individual's way of acting is determined by the attitude towards the environment (the world he/she lives in). This is why it is firstly essential to define those fundamental needs of an individual that lead to an unsustainable development of humankind. They constitute what we call the matrix which is present in each individual and which has to be stimulated to "grow" just like as dough in order to go beyond the stage of immediate satisfaction.

Another aspect of the human reality is the care for future generations. (McKeown, 2004) Unfortunately, this concern is very short-ranged, since individuals care only for their offspring with whom they can interact during their life. Those in the far future (three or four generations away) already represent some abstract entities which say nothing to us. This represents another unsustainable element of

the matrix that must be changed with the help of the Gorgon method.

Once the matrix has been defined, the corresponding skills/attitudes/capabilities/behaviors that can be educated in a sustainable manner can be found and transferability can be achieved. Transferability means that they don't have to stick to some particular/specific elements, since in the previous step only the fundamental elements that belong to any individual, regardless of his/her origin, etc. were identified (Ioan et al., 2005).

The expected result of the Gorgon method should represent profound changes in the individual's mentality, which will be oriented towards a sustainable development. Need is the mental expression of the energy of innate and acquired necessities of the human being. The development of individual needs derives inevitably from the interrelations exchange of the individual with the natural and social environment. Needs are oriented towards the necessity for shelter, clothing, food, safety, culture, etc. Need tends to develop in harmony and balance with the civilized structures of satisfaction means. Generally, need expresses the necessity of organisms and organs to utilize what is necessary for their good operation. They must be analyzed in their relation with satisfaction, recurrence, interests, and requirements of preservation, all of them included in their structure.

3. The Gorgon Method

According to Maslow's motivational theory, the hierarchical organization of human needs is based on two laws (Maslow, 1972) (Fig. 1):

A need is less likely to occur when it is continuously and more intensely satisfied.

A need emerges as a motivation only when stronger needs of a lower level had been previously satisfied.

Fundamental needs are satisfied in a cyclical continuous manner; other ones have an occasional character (i.e., to be esteemed, to obtain self-achievement), and another category have a circumstantial character.

From this short presentation, it results that the **fundamental needs matrix** (Table 1) should include needs that envisage:

A. Need for physical and mental health

B. Need to learn

C. Need for security

The need to live a better life is satisfied in the matrix by the economic, intellectual, and emotional **immediate interests**.

The emphasis falls on transferability, namely on the capability of the fundamental needs matrix defined above to adapt to future's context accordingly to the specific of present-time.

Transferability is the property by means of which representative significant specific elements which define the fundamental needs

matrix become educable, perfectible and applicable to any population (Ioan et al., 2005).

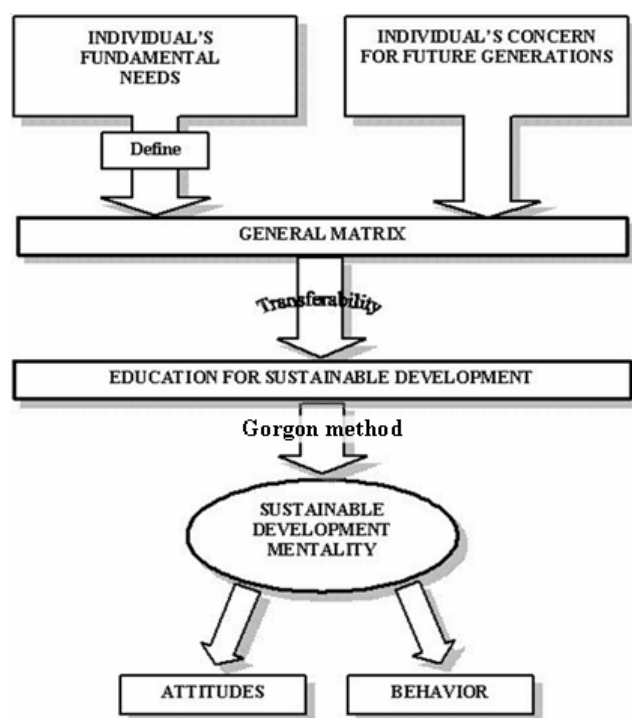


Fig. 1. Flowchart of education for sustainable development in the Gorgon Method context

When designing an education for sustainable development program in the context of the Gorgon Method, attention must be paid to *un-transferable* elements (Ioan, 2003), such as:

- *ethnic/national specific;*
- *mentalities related to a specific geographic/regional area;*
- *specific civilization, religion and culture elements;*
- *specific civic attitude and awareness.*

Poverty aspects must be addressed very carefully since it is useless to try to educate in the spirit of sustainable development an individual or a group living at the limit of subsistence, by teaching them on how to buy expensive ecological products whereas un-ecological ones are cheaper and they represent the difference between survival and starvation (Soubbotina, 2000). These extreme cases must be tackled in a special manner. This remark defines the transferability limits of this guide, which addresses to nations with a minimum living standard in terms of acceptability (Ioan et al., 2005).

The Gorgon method aims at changing the passive, still or socially-petrified behavior of the individual, into a sustainable one. The main objective is to study the evolution of a psychological behavior triggered by Gorgon experiences and to start the process of creating a sustainable behavior.

The secondary objectives of the method are:

- to identify the causes of the individual's lack of attitude towards the environment;
- to examine the issue from different points of view;
- to select the most adequate analysis methods;
- to verify the solutions efficiency and to define the rationale of the chosen solution;
- to study the case from a pedagogical point of view.

Table 1. The fundamental needs matrix and the skills than can be educated in the Gorgon Method context

<i>Matrix of fundamental needs</i>	<i>Skills/attitudes to educate for sustainable development</i>
Physical and mental health	<ul style="list-style-type: none"> • Responsibility • Communication • Awareness • Forecast • Planning • Aspiration for a better life • Concern for other people • Concern for nature
– Food and water	
– Warmth	
– Sex and care for future generations	
– Clothing	
Need to learn	
Need for security	
– Shelter	
– Job	
– Family	
– Independence of movement	
– Leisure	

The Gorgon Method is designed to provide practical solutions for the development of a sustainable behavior in the present socio-economical context in order to improve the quality of life (Macoveanu, 2005).

Considering the interdisciplinary character of this approach, the importance for the implied domains arises from the fact that the Gorgon Method tackles a new perspective, a new view and a new approach. The estimated impact of the method implies three aspects: the change of the behavioral paradigm, the development of a mechanism which can set free the elements of a sustainable behavior, and a last aspect which representing the sustainable development of the individual.

The beneficial change (total or partial) of the individual through the implementing of the Gorgon Method has as an immediate effect the change of view, the awakening of the society, the awareness of the public, having consequences on the cultural heritage or on the socio-economical environment.

The method requires a close cooperation between the specialists of different areas, thus assuring the interdisciplinary between environmental sciences, pedagogy, and psychology. Pedagogy supports the educational activities; psychology pays attention to the human behavior as a structure of the motivation that determines it.

Sustainable behavior, integrated in the sustainable development and consequence of the

sustainable mentality, can be developed through the Gorgon Method.

In order to shape a sustainable behavior, the purpose of the research consists in the development of the Gorgon method, based upon the Gorgon Hypothesis and starting from Gorgon experiences. The steps in the research are:

1. the study and description of the Gorgon Hypothesis, as a solution in shaping a sustainable behavior;
2. the study of the modalities to develop a psychological behavior pattern based upon the Gorgon experiences;
3. construction and development of the Gorgon Method;
4. validation of the Gorgon Method.

The general hypothesis of the Gorgon Method asserts that the shaping of a sustainable behavior is a dynamic and complex process involving the loop: problem – problem solving – solution development – verification.

The Gorgon Method implies a general knowledge, a “core”, a sum of specific values and the deliberately use of innovative opportunity searching techniques.

In the methodological repertory of the research procedures one can enumerate: questionnaires, case studies, quasi pedagogic experiment, comparisons with other psycho-pedagogic procedures, curricular documents analysis.

4. Conclusions

The Gorgon Hypothesis represents a starting point in the shaping process of a sustainable behavior and an opportunity for life standard improvement. The fundamental needs matrix, which signifies a certain quality of life, becomes by means of the Gorgon Method (as a consequence of the educable skills), a foundation and a possibility for a higher standard of life, assuring a sustainable behavior of the individual in relation with the society and the environment.

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ESTABLISHING THE ACCEPTABLE RISK LEVEL IN OCCUPATIONAL ACCIDENTS AND DISEASES BASED ON A FORMAL ANALYSIS

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Abstract

The occupational safety is that state of the working system where there is no possibility that occupational accidents and diseases should occur.

Considering the specific features of the component elements there are no such full safe working systems for men because there is always a hazard of occupational accidents and diseases.

Generally speaking, all the component parts of the system, together with the relations built among them have been conceived, designed and produced so that there is no possible occurrence of occupational accidents and /or diseases; nevertheless, the carrying out of the working process shall wear out these component parts. In addition, no matter how well the performer may be selected, his behavior cannot be taken into consideration because it depends on the variables of his momentary state of mind.

Key words: acceptable risk level, cost, formal analysis

1. Introduction

Each real system displays a wider or narrower deviation from the ideal state of occupational safety. This deviation shall be in the long run in relation to the status and evolution of the component elements of the system.

Consequently, the optimum shaping of the occupational safety in a working system involves the following targets: a permanent awareness of the deviation magnitude; establishing the maximum accepted deviation from the ideal state; correcting the magnitude of the deviation and bringing it to the maximum accepted limit by preventive and protective measures.

Establishing the magnitude of the deviation means an evaluation of the occupational health and safety risk i.e. establishing the real amplitude of this status.

If the overall costs of the occupational safety (made up of the following elements: costs involved

by the risk study reports and by the safety gears – a priori costs – and costs related to the results of occupational accidents and diseases – a posteriori costs) are taken into consideration, an „economically” reasonable value can be established, by considering the previously evaluated levels of the residual occupational lack of safety and the investment costs and the costs related to the efforts made to rehabilitate the working system that has been damaged.

2. Experimental establishing the background for the occupational risk

Starting from the idea that there are no absolutely safe working systems, it has to be established the extent to which the occupational safety of the system is acceptable, considering the possible occurrence of occupational accident and diseases.

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In order to be able to adopt a decision, it is necessary to get a means to express occupational safety, which should meet two conditions:

The highest possible level of impartiality;

It should allow comparison among different status of the some system, as well as among different working systems.

These two conditions can be observed when an iterative correlation is identified, irrespective of the specific parameters of real situations, between a quantitative or qualitative dimension and the extent to which there is no probability of occupational diseases or accidents.

As the absolute quantitative indicators basically provide a more impartial expression compared to the relative quantitative ones and to the qualitative indicators, the ideal situation is to establish a quantitative dimension („level of occupational risk”) that can be expressed by the same value for all the systems that provide the same safety level. During practice, there has to be considered a minimum occupational risk, i.e., a level of this risk distinct from zero, but sufficiently low to consider the working system as safe, and a maximum limit of occupational risk that should be equal to such a low level of occupational safety so that the operation of the system is no longer allowed.

Consequently, in order to establish these limits it is necessary to find a means to quantify the occupational risk and the levels of occupational risks. This operation gives two problems:

- the manner used to establish the coordinates of the occupational risk (the pair between seriousness probability);
- what coordinates for the occupational risk are to be selected in order to part the acceptable areas from the unacceptable ones.

According to the literature on occupational health and safety (Kaplan and Garrik, 1981; Moraru and Băbuș, 2000; Vasilescu, 2008), risk is the combination between the probability of occurrence and seriousness of a possible injury or health damage during a hazardous situation and shows the frequency and seriousness of possible consequences which may come up during a working process.

In order to describe risk in relation to seriousness and probability, IEC 812 defines a “curve of acceptability” (Fig. 1) which is a decreasing exponential that allows a division between the acceptable risk and the unacceptable risk. In compliance with this idea, the risk of occurrence for an event E_1 , with serious consequences but low frequency, situated under the curve of acceptability, is considered as acceptable, while the risk posed by the event E_2 , with less serious consequences, but with a higher probability of occurrence, located above the curve, is considered as unacceptable.

Consequently, the occupational risk can be expressed as:

$$R_{\text{occupational}} = f(P_{G_{\text{max}}}, G_{\text{max}}) \quad (1)$$

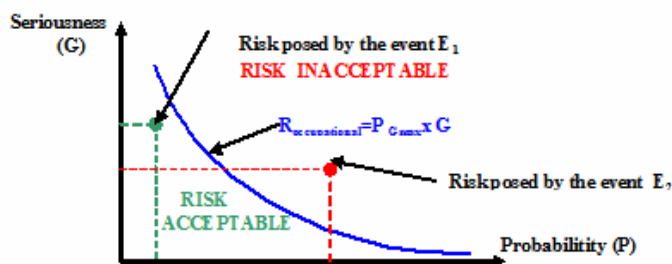


Fig.1. Risk acceptability curve

where:

$R_{\text{occupational}}$ = occupational risk related to hazards for occupational accidents and diseases;

$P_{G_{\text{max}}}$ = probability of occurrence for risk of occupational accidents and diseases;

G_{max} = seriousness of the maximum envisaged consequence due to the occurrence of the occupational risk.

The values on the ordinate of the curve are symbolically, but they can be individualized as values expressed in financial losses (money) or human and material damages expressed from a quantitative point of view etc.

The study of the risk acceptability curve gives the relative nature of „acceptability”; consequently, it can be noticed that the unwanted events with a „high seriousness but with a very low probability of occurrence” are accepted the same as the unwanted events with „low seriousness but high probability of occurrence”, because the values of the former situate under the curve.

A risk study can answer to several questions:

- *What might go wrong?*
- *What can happen?*
- *How often does it happen?*
- *What might the results be?*
- *What can be done so as to avoid?*

As an evaluation assigns real values to hazards on occupational diseases and accidents, it is possible to establish a risk level for the working process which relates to a certain activity; this risk level can be subsequently compared to the acceptable occupational risk but for grounding a decision, it is necessary to define „acceptable”.

Whether the acceptable occupational risk represents a level of risk admitted by a social agreement based on the experience gathered, on occupational safety for a certain type of activity, this notion shall have to comply with the results and benefits.

The mechanism regarding the material and human efforts necessary for providing occupational health and safety depends on the ratio between acceptable and unacceptable and the accuracy for establishing this ratio gives the success of the implemented measures.

As a result, the experts in occupational health and safety work to improve and multiply the

methods used to evaluate the occupational risk and to classify the criteria that establish the acceptable occupational risk.

Until now, there have appeared two trends regarding the efforts to establish the acceptability of the occupational risk:

- a - Taking into consideration the cost of human life;
- b - By comparisons to other occupational risks that have already been accepted or which cannot be avoided.

Things get more complicated if the factors that influence the level of acceptance (costs, level of influence, safety level, usefulness etc.) are taken into consideration, because these factors have a strong subjective character.

Practice hasn't imposed unanimously recognized models regarding the establishment of the acceptable occupational risk. This operation remains the responsibility of the factor that takes the management decision.

Estimation, evaluation and control of the occupational risk represent prerequisites for grounding and for a continual support of the decision that has been previously taken on occupational safety in a working system; envisaging unwanted events is being determined by the occupational risk and is expressed by the ratio between the possible occurrence of occupational diseases and accidents (which displays a random character) and the total amount of available resources with the view to providing a suitable occupational safety.

3. Results and discussion

3.1. Graphical presentation of the risk for occupational accidents and diseases

For the case of a working system (Desroches, 1995; Matei et al., 1996), the acceptable risk is an indicator used to evaluate the level of occupational safety; it represents the results of a decision implemented objectively, by comparing to the known and agreed risks of occupational accidents and diseases. Several domains use the notion of admissible risk or limit risk.

Establishing the acceptable risk means a compromise between the issues agreed by the responsible body from an economic point of view when this one takes a priori in consideration the occurrence of occupational accidents and diseases risk (together with the occupational safety measures that should be implemented) and the expenses that shall have to be recovered a posteriori whether the occupational risk has been ignored, considering the following elements (Drăghici, 2007).

- The cost related to the removal of human and material damages;
- The cost involved by the unavailability of the system;
- The impact in the mass - media.

- By taking into consideration the fact that overall costs involved by the occupational safety cover the following elements:
- The costs of the risk studies and of the safety devices (a priori cost).

The costs related to the consequences of occupational diseases and accidents (a priori cost), it is possible to determine an „economically”, reasonable value, with the consideration of the residual occupational levels of unsafeness that have previously evaluated and of the investment costs and the costs related to the efforts made to rehabilitate the working system after the accident.

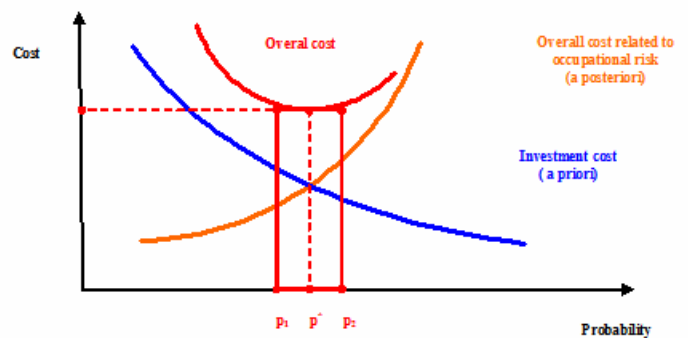


Fig. 2. Principle presentation of the acceptable (C_0 – minimum cost; p^* - optimal probability; $[p_1 p_2]$ - acceptable occupational risk level)

Fig. 2 shows the principle for the presentation of the jeans used to establish the economic optimum, by comparing the probability for the occurrence of unwanted events (such as the case of occupational accidents and diseases) to the accepted level of occupational unsafeness.

3.2. Establishing the acceptable level of occupational risk, starting from the criterion of the cost price

It shall be formally analyzed the function related to the cost price which is being established in relation to the probable occurrence of occupational accidents and diseases; this represents the manner used to establish this function for the condition of minimum (Drăghici, 2007).

The overall cost price C (shown in Fig. 3) is made of the a priori cost related to investment cost C_1 and the a posteriori cost related to the (occupational and technologic) risk, so that:

$$C = C_1 + C_2 \tag{2}$$

$$C_1 = C_{1const} + C(p) = C_{1const} + C_1/p \tag{3}$$

$$C_2 = C_{2const} + C_2 p \tag{4}$$

$$C = C_{1const} + C_{2const} + C_1/p + C_2 p \tag{5}$$

$$C = C_3 + C_1/p + C_2 p \tag{6}$$

where C_1 , C_2 and C_3 are constant values.

Establishing the acceptable occupational risk level in relation to the economic optimum, means to provide a balance between the increment of the risk related expenses concomitant to the diminution of the

investment costs, so that the cost price should not increase a lot above the minimum price.

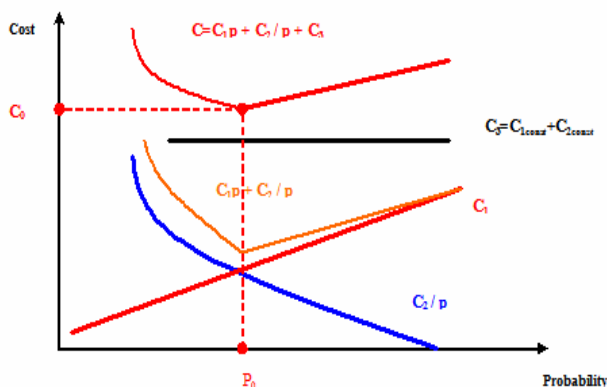


Fig. 3. Graphic presentation of the structure of the overall cost price C

Establishing the acceptable occupational risk level in relation to the economic optimum and the optimal probability regarding the occurrence of an unwanted event (such as occupational accidents and diseases) is performed by deriving the cost function C from the evaluation variable p:

$$dC/dp=0 \Rightarrow C_2-C_1/p_2=0 \quad (7)$$

$$p_0=(C_2/C_1)^{1/2} \quad (8)$$

Equation (8) is introduced in equation (5), by taking into consideration only the costs that depend on probability. Consequently, the following equations are obtained:

$$C_0=C_2p_0+C_1/p_0 \quad (9)$$

$$C_0=2(C_1 C_2)^{1/2} \quad (10)$$

Whether Δ deviation of the cost price against the minimum price is considered then it is possible to establish the range inside which the variation of probabilities (with the related risk levels) don't influence with more than Δ the minimum calculated cost price (C_0).

An analytical equation of the aspects mentioned above shall take the following form:

$$C_0(1+\Delta)=C_1/p+C_2p \quad (11)$$

By replacing the value of C_0 from (10) in (11), the equation obtained is:

$$2(1+\Delta)(C_1 C_2)^{1/2}=C_1/p+C_2p \quad (12)$$

If the terms of the equation are arranged in accordance with p, the result is:

$$p^2-2p(1+\Delta)(C_1 C_2)^{1/2}+C_1/C_2=0 \quad (13)$$

The equation has the following results:

$$p_1=(1+\Delta)p_0-[(2+\Delta)\Delta]^{1/2}p_0 \quad (14)$$

$$p_2=(1+\Delta)p_0+[(2+\Delta)\Delta]^{1/2}p_0 \quad (15)$$

Subsequently, it is possible to determine the values of p_1 and p_2 , based on the results gained above, as well the range between these roots which corresponds to the acceptable risk level, when the variations of the probabilities regarding the occurrence of unwanted events don't influence the minimum cost price with more than Δ .

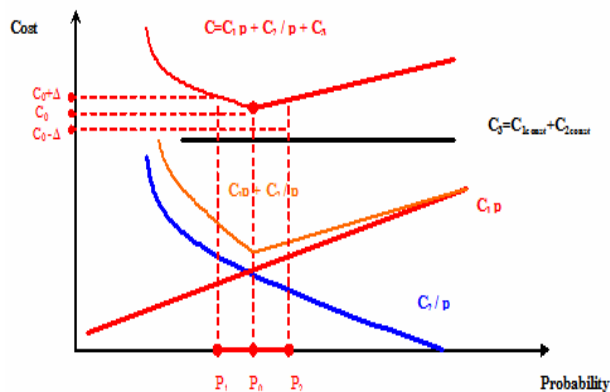


Fig. 4. Graphical presentation of the acceptable occupational risk level

For example, if a deviation of 5 % from the minimum cost price is admitted ($\Delta = 0,05$) the values of p_1 and p_2 shall be the following ones:

$$p_1=(1+0,05)p_0-(0,1025)^{1/2}p_0=0,7p_0 \quad (16)$$

$$p_2=(1+0,05)p_0+(0,1025)^{1/2}p_0=1,4p_0 \quad (17)$$

It has to be underlined the fact that a variation of 5 % of the cost price against the minimum value gives a rather large range for the optimum domain of the occupational risk level. This allows a comprehensive consideration of the main and secondary occupational accidents and diseases risk factors so as to carrying on the activity in optimum economic conditions, with an acceptable level of occupational safety.

Establishing the acceptable risk level is a compromise between the aspects to which the responsible entity (organization, body, legal entities) agrees to take risk from an economic point of view, whether this entity has considered, a priori, the possible occurrence of risks (together with the safety measures that should be applied) and the expenses that should be recovered a posteriori whether risk has been ignored, by taking into consideration the following elements:

- costs involved with the removing of material and human damages;
- costs generated by the unavailability of the system;
- impact in the media.

4. Conclusions

Evaluating the occupational safety means to determine (measure) the extent to which the working systems deviate from the ideal state when there is no possibility for the occurrence of occupational accidents and diseases.

Evaluation of occupational accidents and diseases represents an indirect means to assess the occupational safety by assigning values to the indicator called "risk level for occupational accidents and diseases".

The general management of any activity requires an analysis and evaluation of the

occupational risk since working process always involves the occupational safety policy.

Establishing the acceptable occupational risk level against an economic optimum value requires a balance between the augmentation of expenses related to occupational accidents and diseases risks at the same time with the diminution of expenses for investments so that the cost prices should reach a reasonable amount.

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QUANTIFICATION OF ENVIRONMENTAL IMPACT AND RISK INDUCED BY INDUSTRIAL ACTIVITIES ON GROUND WATER QUALITY: CASE STUDY CORDUN - ROMAN AREA, ROMANIA

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Abstract

The question of whether environmental assessment has achieved its goal of helping to reach better decisions has continually engaged the attention of academics, policy makers and environmental impact assessment practitioners. Answering this question requires several different groups working together and/or in sequence, and examining the effectiveness of environmental impact and risk assessment. *EIA* has tended to focus on the identification of impacts associated with planned activities or projects, whereas *ERA* involves a rigorous analysis of those impacts: the calculation of the probability, and magnitude of effects. The integrated method described herein for environmental impact and risk assessment has the advantages that it is very easy to be used by non environmental experts: it calculates the impacts and risks, correlated with measured concentrations of quality indicators for environmental component, considered representative in assessment process; it is not a subjective method because several mathematical steps are applied. Also, the lack of experience of evaluator doesn't influence the results of assessment process, and it will reflect in a very objective way the real situation. The purpose of this work was to propose a new method for integrated environmental impact and risk assessment and apply it on a case study in order to make the right decision concerning the quality of ground water from evaluated area. Thus, groundwater from ten drillings was sampled and analyzed over the period 1995-2006 (exception years 1997, 1998 and 1999). From each drilling over the period 1995-2006, eight quality indicators considered representative for evaluated situation were analyzed. The results showed that, in period 1995 – 2006, the ground water quality was highly negative influenced by industrial activities developed on studied area. The maximum value for impact and risk induced in ground water is in 1995 year, when the industrial activities from this area were working at maximum capacity. Thus, it is absolutely necessary to apply the measures for remediation to improve the quality of ground water and control the pollution, considering the fact that the ground water quality needs to be at optimum parameters, required by national legislation.

Keywords: ground water, quality indicators, impact and risk assessment, pollution control

1. Impact and risk assessment

Risk assessment has been suggested as a tool to help manage ecological problems. Ecological risk assessment is usually defined as the process that evaluates the likelihood that adverse ecological effects are occurring, or may occur, as a result of exposure to one or more stressors. Risk assessment has been used extensively to link environmental stressors and their ecological consequences. The risks associated with chemical exposure are the typical

concern. Quantifying the risk of various chemicals to human health is a logical outgrowth of risk assessment as applied in the insurance industry and other fields. Over the past 20 years, a body of procedures and tools has been used for environmental risk assessment for human health. Risk assessment applied to ecological problems is more recent, but has also focused primarily on chemicals, with animals used as surrogates for *ecological health*. Adapting the risk paradigm from assessing insurance risks to assessing human health risks to assessing ecological

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risks has not been simple (Lackey, 1994). Even so, it is still unclear whether ecological risk assessment will actually improve decision making and ultimately protect ecological resources. In spite of the difficulties of defining problems in complex ecological policy questions, the use of risk assessment to help solve ecological problems is widely supported. Risk assessment could be a valuable tool and should be used extensively in solving ecological problems. Risk assessment has historically been separated from management. Such separation requires that scientists play clearly defined roles as technical experts, not policy advocates; these distinctions are blurred when scientists advocate political positions.

In the last few years, a new, very broad and far from simple art has sprung up within the wide field of risk analysis, *comparative risk analysis*. Applied to environmental risks, it is intended to be an instrument of governmental environmental prioritization, policy making, and policy implementation. Once environmental risks are assessed and ranked, the consideration of additional factors such as the feasibility of risk reduction; the benefits of risk reduction; public risk perception; special risks to subgroups or ecosystems; and political, economic, and social factors, is needed to develop a prioritization of the same risks for attention and, finally, to develop policy options leading to legislation, regulation, or other types of risk abatement possibilities. It is important to note that a ranking according to risk is not synonymous with a ranking according to priority. The entire span of the environmental *comparative risk analysis* (CRA) process consists of the following two major stages, as is the case with other forms of risk analysis:

1. Comparative risk assessment (CRASS), in which the risks associated with specific environmental issues or problems are assessed and compared, usually by being ranked against each other
2. Comparative risk management (CRM), in which there are three stages:
 - a. Risk reduction prioritization
 - b. Risk reduction policy option development
 - c. Implementation of risk reduction policy options, including monitoring of the results.

Carrying out this full process requires several different groups working together and/or in sequence. Thus, *comparative risk studies are very labor intensive*. The question of whether environmental assessment has achieved its goal of helping to reach better decisions has continually engaged the attention of academics, policy makers and environmental impact assessment practitioners (Sandham and Pretorius, 2007). One approach to answering this question is by examining the effectiveness of environmental impact assessment, where effectiveness refers to whether something works as intended and meets the purpose(s) for which it is designed. The newly established Environmental Impact Assessment system (EIA) consisted of the following main steps (Sandham and Pretorius, 2007):

- pre-application consultation;

- plan of study for scoping;
- scoping report (including public involvement);
- plan of study for EIA;
- Environmental Impact Report (EIR) (including public involvement);
- authority review;
- record of decision (including conditions of approval).

One of the purposes of Environmental Impact Assessment (EIA) is in advance to identify and evaluate the important environmental consequences of proposed projects. As a concept of EIA, the impact should be documented and predicted as well in advance as possible (Morris and Therivel, 2004). EIA is also a process that provides information about the proposal to decision makers (Ridgway, 2005). Both of these targets benefit if decent EIA methodology is used to present and organize the high number of variables that an assessment process may produce. It is especially important to understand how distinctly the separate variables have impact on the environment, depending on their nature as either natural or human-induced, extensive or small-scale, cumulative or non-cumulative, local and national planning or generally essential or inessential. The early emphasis on natural environmental consequences of capital projects has since been enlarged to encompass not only the ecological, but also the social, health, and economic effects of projects, policies, programs, plans, technologies or activities. There are many tools and techniques that have been developed for use in impact assessment processes, including scoping, checklists, matrices, qualitative and quantitative models, literature reviews, and decision-support systems (Macoveanu, 2005; Robu, 2005; Sandham and Pretorius, 2007). While impact assessment processes have become more technically complicated, it is recognized that approaches including simpler applications of available tools and techniques are also appropriate (Kuitunen et.al., 2007).

The purpose of this work was to propose a new method for integrated environmental impact and risk assessment and apply it on a case study in order to make the right decision concerning the quality of ground water from evaluated area. Thus, groundwater from ten drillings was sampled and analyzed over the period 1995-2006 (exception years 1997, 1998 and 1999). Eight quality indicators considered representative for evaluated situation were analyzed from each drilling, over the period 1995-2006, and, based on these experimental data, the integrated environmental impact and risk assessment was applied.

2. Site characterization

The iron and steel industry is highly intensive in both materials and energy consumption. Important subject for action in response to environmental

concerns are generally considered to relate to controlling of air emissions and managing of solid wastes. Wastewaters discharge from coke oven plants is of significant higher relevance than discharges from the water circuits at blast furnaces, basic-oxygen steel making, and continuous casting plants. Contaminated leakages from the solid wastes disposal sites cause great environmental problems, both, in the near future (short term) and long term. The polluted leakages are formed due to the interactions of solid, liquid and gaseous phases. Over time, both, the wastes and the leakages can considerable change the quality of environmental components, especially soil and groundwater, because the wastes deposits are heterogeneous and dangerous for environment. Different chemical interaction fronts that serve as geochemical barriers accumulate certain types of toxic compounds and move inside the landfills. When the geochemical barriers are damaged, the outflow location suddenly releases the contaminants, accumulated over years.

The evaluated area Cordun-Roman, Romania has an industrial site used for wastes deposit, and represents a potential source of pollution especially for soil, ground and surface water, and it is located in Moldova river bed, on left side with 4-5 m above everglade. This area (4.79 ha) is situated 3 km far of company, where the industrial activities take place, and it is surrounded by residential areas, run off water and pastures. The investigations regarding the quality of soil and vegetation from industrial site, including residential areas, showed that there are 2 kind of pollution: soil acidification from industrial site and heavy metals contamination. It has to be mentioned that the measured concentrations of heavy metals from soil samples didn't reach the maximal allowed concentrations, according to Romanian legislation.

The technical characteristics of industrial site used for wastes deposit are the followings:

- Capacity of deposit is 114168 m³;
- It can assure minimum 10 years for sludge depositing;
- The area is surrounded by residential area;

- The stockyard has 2 compartments surnamed "cells", used to deposit slag (cell no.1), and sludge, including other different residues (cell no.2).
- The dig made from argyles soil closes the stockyard on 0.6 km length and its high is 4.5 m (0.3 m is underground).

There have been analyzed ten ground water samples from ten drillings, over the period 1995-2006, in order to control the leakages and prevent the ground water pollution (fig.1). The hydro-geologically properties of ground water from evaluated area depend on the layer impermeability, and from hydro geological point of view tow factors are very important: the altimetry position of aquifer and the permeability of soil layers from evaluated site. To control the ground water quality in this area, ten drillings were used (F1 to F10), situated at 4 – 10 m deep (Fig.1):

- Drilling F₁ – 10 m deep, situated off site (upstream) in North-East side;
- Drilling F₂ – 4 m deep, situated on site, in oily scoria cell;
- Drilling F₃ – 5 m deep, situated off site (downstream) in North-West side;
- Drilling F₄ – 8 m deep, situated off site (upstream of cell no. 2), in East side;
- Drilling F₅ – 4 m deep, situated on site of cell no. 2;
- Drilling F₆ – 4 m deep, situated on site, central part of cell no. 2;
- Drilling F₇ – 4 m deep, situated off site, in West side;
- Drilling F₈ – 4 m deep, situated on site, in oily scoria cell;
- Drilling F₉ – 5 m deep, situated on site, cell no. 2;
- Drilling F₁₀ – 4 m deep, situated off site, in South-West side.

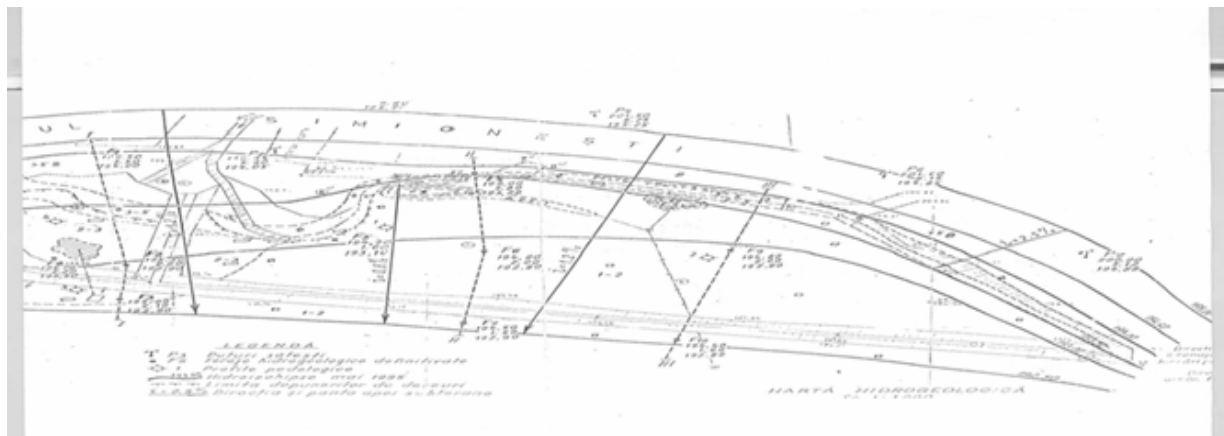


Fig.1. The map of drillings F1 to F10

3. Ground water quality evaluation

3.1. Sampling and analyses

To evaluate the quality of ground water, various samples were taken from ten drillings, on site and off site. Eight quality indicators (CCO-Cr, NO₃⁻, NO₂⁻, SO₄⁻, Fe²⁺, Pb²⁺, Cu²⁺, Ni²⁺) have been analyzed by standardized methods, according to national legislation, over the period 1995-2006 (exception years 1997, 1998, 1999).

3.2. Results

The results of physical-chemical analysis of ground water samples from evaluated area, over the period 1995 – 2006 (exception years 1997, 1998, 1999) are shown in Table 1.

It can be observed that the evaluated site, especially the ground water is significantly polluted due to the presence of various pollutants such as organic compounds, nitrate, nitrite and heavy metals.

Table 1. Measured concentrations of quality indicators considered in evaluation process

Drilling	Year MAC*	Quality indicators Measured concentrations (mg/dm ³)							
		CCOCr	NO ₃ ⁻	NO ₂ ⁻	SO ₄ ²⁻	Fe ²⁺	Pb ²⁺	Cu ²⁺	Ni ²⁺
		5	50	0.5	250	0.20	0.01	0.1	0.02
F1	1995	6.32	40	0.0007	37.8	7.6	-	-	-
	1996	22.12	32	0.0018	63.35	1.2	0.05	0.05	0.009
	2000		27.4	0.008	69.25	0.151	-	-	-
	2001	6.68	20.46	0.010	53.5	0.24	-	-	-
	2002	14.42	20.15	0.017	59.5	0.28	-	-	-
	2003	9.61	23.63	0.040	78.6	2.11	3.0	0.7	0.55
	2004	4.0	62.67	0.045	154	0.63	1.0	0.4	0.01
	2005	9.41	198.07	0.03	79.25	1.51	0.026	0.03	0.00
2006	54.1	214.5	0.74	176.5	0.14	0.062	0.009	0.02	
F2	1995	15.8	20	0.07	78.6	4.8	0.76	0.056	0.01
	1996	42.64	0	0.07	134.5	1.2	0.05	0.185	0.009
	2000	17.75	22.8	0.06	150	3.62	-	-	-
	2001	11.84	19.8	0.036	82.5	1.77	-	-	-
	2002	25.77	15.85	0.024	86	1.46	-	-	-
	2003	29.60	18.81	0.055	102.5	1.51	2.0	0.5	0.32
	2004	11.20	17.17	0.60	120.5	0.545	1.0	0.2	0.01
	2005	13.97	82.07	0.315	79	0.165	0.050	0.01	0.00
2006	67.79	41.7	0.925	220	0.111	0.092	0.014	0.01	
F3	1995	9.48	38	0.0004	55.1	1.6	-	-	-
	1996	20.2	23	0.0018	83	1.2	0.05	0.07	0.08
	2000	3.02	24.25	0.003	91	2.125	-	-	-
	2001	8.47	16.92	0.012	70.25	2.41	-	-	-
	2002	8.49	12.07	0.014	93.75	3.35	-	-	-
	2003	10.35	16.88	0.042	119.5	3.59	2.0	0.5	0.32
	2004	7.94	22.07	0.137	99.25	0.89	1.5	0.2	0.02
	2005	9.01	71.64	0.10	86	0.74	0.083	0.01	0.00
2006	67.44	116.82	0.22	246	0.09	0.029	0.006	0.008	
F4	1995	11.37	11	0.0004	25.1	0.8	-	-	-
	2000	1.58	3.62	0	30.12	0.73	-	-	-
	2001	4.36	2.93	0	40.75	0.15	-	-	-
	2002	6.48	6.12	0.013	58.5	1.18	-	-	-
	2003	3.82	2.54	0.011	43.35	0.40	1.0	0.3	0.15
	2004	7.30	58.7	0.055	53.5	0.23	0.5	0.1	-
	2005	7.87	195	0.012	60.5	0.62	0.11	0.01	0.00
	2006	83.14	104.02	0.156	185.75	0.14	0.0035	0.011	0.008
F5	1995	20.9	0	0.18	93.4	80	0.80	0.04	0.009
	1996	72.7	5	0.0018	1315.24	3.2	0.0575	0.085	0.009
	2000	4.08	6	0	405.5	2.3	-	-	-
	2001	14.37	14.1	0.027	1152	3.38	-	-	-

	2002	13.18	26.32	0.046	1722.5	15.31	-	-	-
	2003	12.77	19.34	0.023	749	13.29	0.5	0.3	0.15
	2004	12.29	27.17	0.042	295.5	4.85	-	-	-
	2005	20.74	54.57	0.072	723.75	5.23	0.17	0.02	0.00
	2006	103.64	30.95	0.176	2230	0.33	0.034	0.015	0.017
F6	1995	15.8	12.4	0.07	87.6	1.24	0.48	0.32	0.009
	2000	5.13	11.55	0.04	117.5	1.52	-	-	-
	2001	9.61	10.25	0.02	277.5	1.17	-	-	-
	2002	11.71	8.55	0.016	430	5.91	-	-	-
	2003	9.47	20.21	0.019	402.5	13.79	2.0	0.3	0.15
	2004	9.17	4.92	0.072	310	6.40	0.8	0.1	-
	2005	26.29	37.26	0.07	787.5	3.67	0.13	0.01	0.00
	2006	65.96	37.2	0.323	1592.5	0.20	0.154	0.012	0.012
	1995	13.9	1	0.07	148.9	11.2	-	-	-
F7	1996	12.6	18	0.07	264.5	2.4	0.065	0.070	0.009
	2000	4.17	8.4	0.039	204.25	1.36	-	-	-
	2001	9.67	9.2	0.012	240.5	1.17	-	-	-
	2002	14.49	9.8	0.010	546.5	2.97	-	-	-
	2003	12.62	15.55	0.013	359.75	9.05	1.0	0.1	0.1
	2004	7.54	30.82	0.514	213	2.01	1.0	0.3	0.02
	2005	15.17	95.09	0.36	480	0.76	0.19	0.01	0.00
	2006	70.57	10.85	0.87	1192.5	0.21	0.059	0.019	0.007
	1995	17.7	39.2	0.037	72.8	1.2	0.36	0.08	0.009
F8	2000	4.03	17.5	0.030	48.75	2.02	-	-	-
	2001	9.35	19.00	0.053	232	3.45	-	-	-
	2002	11.92	14.57	0.032	82.75	5.07	-	-	-
	2003	11.75	18.88	0.018	145.5	6.47	1.0	0.1	0.1
	2004	8.43	59.35	0.549	129.75	1.89	-	0.1	-
	2005	7.47	43.32	0.612	110.5	0.30	0.19	0.02	0.00
	2006	66.63	86.42	0.775	212.5	0.19	0.0085	0.014	0.005
	1995	6.3	17.8	0.037	53.9	2.4	0.28	0.06	0.008
F9	2000	3.31	13.6	0.1	153.75	2.72	-	-	-
	2001	8.04	13.37	0.0075	93.5	1.78	-	-	-
	2002	25.09	13	0.0047	130	1.94	-	-	-
	2003	9.03	18.47	0.024	218.5	2.51	1.0	0.1	0.1
	2004	7.80	18.12	0.108	200	0.71	-	0.1	0.01
	2005	6.50	66.62	0.075	273	0.36	0.27	0.00	0.00
	2006	64.89	81.12	0.246	517.5	0.22	0.008	0.016	0.006
	1995	11.4	0	0.0018	195	0.42	-	-	-
F10	2000	0.625	5.375	0.073	171.5	0.85	-	-	-
	2001	5.192	5.85	0.001	150	1.45	-	-	-
	2002	6.057	6.1	0.001	406.5	1.10	-	-	-
	2003	7.737	14.94	0.026	328.5	3.75	0.5	0.1	0.1
	2004	4.817	50.47	0.078	142	1.577	0.3	-	-
	2005	15.307	43.07	0.052	499.75	2.665	0.29	0.02	0.00
	2006	67.012	227.7	0.042	1470	0.225	0.137	0.022	0.007

*maximum admissible concentrations concordant to Law no. 458/2002, modified by Law no.311/2004.

Thus, the quality indicators analyzed had values for measured concentrations higher than maximum admissible concentrations:

- Organic compounds analyzed by CCO-Cr indicator had over the period 1995-2006 measured concentrations higher than maximum admissible concentration almost in all drillings. The maximum analyzed value was 103.64 mg/L (in 2006) from samples from drilling F5 and 83.14 mg/L (in 2006) from samples from drilling F4.

- The ground water contamination with nitrate was higher in 2005 in drilling F1 (measured concentration of NO_3^- was 198.07 mg/L and 214.5 mg/L), drilling F3 (measured concentration of NO_3^- was 71.64 mg/L and 116.82 mg/L), drilling F4 (measured concentration of NO_3^- was 195 mg/L in 2005 and 104.02 mg/L in 2006), and drilling F10 (measured concentration of NO_3^- was 227.7 mg/L in 2006).

- The quality of ground water was also highly negative influenced by the presence of nitrites, and

the most influenced areas are from drilling F2 (measured concentrations 0.6 mg/L in 2004 and 0.925 mg/L in 2006) and drilling F8 (measured concentration 0.612 mg/L in 2005 and 0.775 mg/L in 2006).

4. Integrated environmental impact and risk assessment

4.1. Method description

The integrated method to evaluate the environmental impact and risk used herein is a combination between two methods: global pollution index and matrix of significance scale (Gavrilescu 2003, Macoveanu, 2005; Robu, 2005; Robu and Macoveanu, 2005a,b). An algorithm developed as software designed as **SAB** was applied to automatically quantify the environmental impacts and risks that arise from an evaluated activity, considering the measured concentration, levels of quality indicators (Robu, 2005; Robu et al., 2005a,b, 2007, 2008).

This new method for environmental impact and risk assessment (**EIRA**) was applied considering only the *ground water* in the assessment process. The evaluation of environmental impacts was done using a matrix in order to calculate the significance of environmental component, potentially affected by the industrial activities. The significance parameter can take values between 0 and 1; value 1 represents the most significant environmental component (in this case the ground water). These values are assigned by the evaluator (Table 2). For the evaluated situation, the rest of environmental components such as surface water, air and soil were not considered in evaluation process (Table 3).

The impact on environmental component (*EI*) directly depends on measured concentration of pollutants, and it is expressed as the ratio between significance units (*IU*) and quality of environmental component (*EQ*), defined as follows (Eq. 1):

$$EI = \frac{IU}{EQ} \tag{1}$$

The parameter *quality of environmental component (EQ)* is defined as follows (Eq.2):

$$EQ = \frac{MAC}{MC} \tag{2}$$

where:

MAC – maximum allowed concentration of quality indicators;

MC – measured concentration of quality indicators.

After the calculation of significance units, the next step was to calculate the quality of environmental component defined above. If the quality parameter of environmental component longs for zero, it results that the environmental quality is very poor (this means that the measured concentration of pollutant is very high); if *EQ* value is close to 1, or higher than 1, then the quality of environmental component is very good (Goyal and Deshpande, 2001).

The impact on *ground water (EI_{gw})* is given by Eqs. 3, 4:

$$EI_{gw} = \frac{\sum_{i=1}^n EI_{(gw)_i}}{n} \tag{3}$$

EI_{(gw)_i} – environmental impact on ground water, considering quality indicator *i*;

i – quality indicators (e.g. COD-Cr, BOD etc.);

n – number of quality indicators considered in evaluation process.

$$EI_{(gw)_i} = \frac{IU_{gw}}{EQ_{(gw)_i}} \tag{4}$$

EQ_{(gw)_i} – quality of *ground water*, considering the quality indicator *i*;

IU_{gw} – significance units obtained by *ground water*.

Table 2. The calculation of *significance units* for environmental components

<i>Environmental component</i>	<i>Surface water (l)</i>	<i>Ground water (m)</i>	<i>Soil (n)</i>	<i>Air (o)</i>
Surface water (l)	0.001	(l/m)	(l/n)	(l/o)
Ground water (m)	0.85	(m/m)	(m/l)	(m/o)
Soil (n)	0.001	(n/m)	(n/n)	(n/o)
Air (o)	0.001	(o/m)	(o/n)	(o/o)

l – significance value for surface water, m – significance value for ground water, n – significance value for soil, o – significance value for air

Table 3. Significance units obtained by solving the matrix from Table 2

<i>Environmental component</i>	<i>Normalized weights (NW)</i>	<i>Significance units (IU = NWx1000)</i>
Surface water	0.001	1.173
Ground water	0.997	996.48
Soil	0.001	1.173
Air	0.001	1.173

This way the impacts for environmental component ground water considered the most representative for the evaluated situation were calculated. The next step was to quantify the risks that arise, in the view of the results for environmental impacts. The risks are calculated as follows (Eq.5):

$$ER_j = EI_j \cdot P_j \quad (5)$$

ER_j – environmental risk for environmental component j ;

EI_j – environmental impact on environmental component j ;

P_j – probability of impact occurrence on environmental component j .

The probability of impact occurrence was calculated using the same matrix as described above (Table 2) to calculate the significance units. The evaluator has to assign values for probability between 0 and 1 (Table 4), concordant to probability description, detailed in Table 5 (Pearce, 1999).

Table 4. Probability units for environmental components

Environmental component	Probability units (P)
Surface water	0.001
Ground water	0.65
Soil	0.001
Air	0.001

Considering the fact that the measured concentrations of main pollutants analyzed in samples from ground water are higher than the maximum admissible concentrations (MAC), and the pollution will probably occur in most circumstances, 0.65 probability units were accorded.

Table 5. Description of probability

Probability	Probability units	Description
Almost certain	0.91-1.0	Is expected to occur in most circumstances (99%)
Likely	0.61-0.9	Will probably occur in most circumstances (90%)
Possible	0.31-0.6	Might occur at some times (50%)
Unlikely	0.05-0.3	Could occur at some times (10%)
Rare	<0.05	May occur only in exceptional circumstances (1%)

Table 6. The quantification of parameter *environmental component quality* Q (ground water) and environmental impact and risk (IM, RM) for each quality indicator analyzed over the period 1995-2006 in ten drillings (example drilling F1)

Indicator	1995					IM 1995 =	8015.00
	MAC*	Cm**	Q	IM	RM		
COD-Cr, mgO ₂ /L	5.00	6.32	0.79	1259.55	1253.77	RM ₁₉₉₅ =	7978.21
NO ₃ ⁻ , mg/L	50.00	40.00	1.25	797.19	793.52		
NO ₂ ⁻ , mg/L	0.50	0.0007	714.29	1.40	1.39		
SO ₄ ²⁻ , mg/L	250.00	37.80	6.61	150.67	149.98		
Fe, mg/L	0.20	7.60	0.03	37866.35	37692.39		

4.2. Results

According to integrated method for environmental impact and risk assessment, the first step is to assign the significance of each environmental component for evaluated situation.

This parameter significance have values between 0 and 1, and value 1 value 1 represents the most significant environmental component (in this case the ground water). So that, the value 0.85 was assigned as significance for ground water, and the probability for a negative event (impact) to occur was considered *likely* (0.61-0.9) that will probably occur in most corcumstances (90% of situations).

Quantification of impact and risk induced on ground water quality was automatically done (Table 6). The results of automatically quantification for those ten drillings are presented in Figs. 2 – 11.

It has to be emphasized that if the impact and risk have very high values, then the impact induced by the considered activities in the environment is great and the environmental risks are at an unacceptable level.

High values for environmental impacts and risks underlay the presence of pollutants in environment in very high concentrations, because impact directly depends on the measured concentration of pollutants.

Taking into account the impact classification from method of global pollution index (Rojanschi et.al., 1997; Robu et.al., 2005, 2007, 2008; Robu and Macoveanu, 2005 a, b), a classification of impacts and risks is proposed (Table 7).

Pb, mg/L	0.01	0.000	0.00	0.00	0.00		
Cu, mg/L	0.10	0.00	0.00	0.00	0.00		
Ni, mg/L	0.02	0.00	0.00	0.00	0.00		
1996							
Indicator	MAC*	Cm**	Q	IM	RM	IM 1996 =	2151.30
COD-Cr, mgO ₂ /L	5.00	22.12	0.23	4408.44	4388.19		
NO ₃ ⁻ , mg/L	50.00	32.00	1.56	637.75	634.82	RM₁₉₉₆ =	2141.40
NO ₂ ⁻ , mg/L	0.50	0.0018	277.78	3.59	3.57		
SO ₄ ⁻² , mg/L	250.00	63.35	3.95	252.51	251.35		
Fe, mg/L	0.20	1.20	0.17	5978.90	5951.43		
Pb, mg/L	0.01	0.050	0.20	4982.42	4959.52		
Cu, mg/L	0.10	0.0500	2.00	498.24	495.95		
Ni, mg/L	0.02	0.0090	2.22	448.42	446.36		
2000							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2000 =	397.60
COD-Cr, mgO ₂ /L	5.00	0.00	0.00	0.00	0.00		
NO ₃ ⁻ , mg/L	50.00	27.40	1.82	546.07	543.56	RM₂₀₀₀ =	395.77
NO ₂ ⁻ , mg/L	0.50	0.0080	62.50	15.94	15.87		
SO ₄ ⁻² , mg/L	250.00	69.25	3.61	276.03	274.76		
Fe, mg/L	0.20	0.15	1.32	752.34	748.89		
Pb, mg/L	0.01	0.000	0.00	0.00	0.00		
Cu, mg/L	0.10	0.0000	0.00	0.00	0.00		
Ni, mg/L	0.02	0.0000	0.00	0.00	0.00		
2001							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2001 =	633.60
COD-Cr, mgO ₂ /L	5.00	6.68	0.75	1331.30	1325.19		
NO ₃ ⁻ , mg/L	50.00	20.46	2.44	407.76	405.89	RM₂₀₀₁ =	630.69
NO ₂ ⁻ , mg/L	0.50	0.0100	50.00	19.93	19.84		
SO ₄ ⁻² , mg/L	250.00	53.50	4.67	213.25	212.27		
Fe, mg/L	0.20	0.24	0.83	1195.78	1190.29		
Pb, mg/L	0.01	0.000	0.00	0.00	0.00		
Cu, mg/L	0.10	0.0000	0.00	0.00	0.00		
Ni, mg/L	0.02	0.0000	0.00	0.00	0.00		
2002							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2002 =	988.30
COD-Cr, mgO ₂ /L	5.00	14.42	0.35	2873.86	2860.65		
NO ₃ ⁻ , mg/L	50.00	20.15	2.48	401.58	399.74	RM₂₀₀₂ =	983.77
NO ₂ ⁻ , mg/L	0.50	0.0170	29.41	33.88	33.72		
SO ₄ ⁻² , mg/L	250.00	59.50	4.20	237.16	236.07		
Fe, mg/L	0.20	0.28	0.71	1395.08	1388.67		
Pb, mg/L	0.01	0.000	0.00	0.00	0.00		
Cu, mg/L	0.10	0.0000	0.00	0.00	0.00		
Ni, mg/L	0.02	0.0000	0.00	0.00	0.00		
2003							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2003 =	43327.00
COD-Cr, mgO ₂ /L	5.00	9.61	0.52	1915.24	1906.44		

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NO ₃ ⁻ ,mg/L	50.00	23.63	2.12	470.94	468.77	RM ₂₀₀₃ =	43127.90
NO ₂ ⁻ , mg/L	0.50	0.0400	12.50	79.72	79.35		
SO ₄ ⁻² , mg/L	250.00	78.60	3.18	313.29	311.85		
Fe, mg/L	0.20	2.11	0.09	10512.90	10464.60		
Pb, mg/L	0.01	3.000	0.00	298944.90	297571.49		
Cu, mg/L	0.10	0.7000	0.14	6975.38	6943.33		
Ni, mg/L	0.02	0.5500	0.04	27403.28	27277.39		
2004							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2004 =	13752.60
COD-Cr, mgO ₂ /L	5.00	4.00	1.25	797.19	793.52	RM ₂₀₀₄ =	13689.45
NO ₃ ⁻ ,mg/L	50.00	62.67	0.80	1248.99	1243.25		
NO ₂ ⁻ , mg/L	0.50	0.0450	11.11	89.68	89.27		
SO ₄ ⁻² , mg/L	250.00	154.00	1.62	613.83	611.01		
Fe, mg/L	0.20	0.63	0.32	3138.92	3124.50		
Pb, mg/L	0.01	1.000	0.01	99648.30	99190.50		
Cu, mg/L	0.10	0.4000	0.25	3985.93	3967.62		
Ni, mg/L	0.02	0.0100	2.00	498.24	495.95		
2005							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2005 =	2373.10
COD-Cr, mgO ₂ /L	5.00	9.41	0.53	1875.38	1866.77	RM ₂₀₀₅ =	2362.21
NO ₃ ⁻ ,mg/L	50.00	198.07	0.25	3947.47	3929.33		
NO ₂ ⁻ , mg/L	0.50	0.0300	16.67	59.79	59.51		
SO ₄ ⁻² , mg/L	250.00	79.25	3.15	315.89	314.43		
Fe, mg/L	0.20	1.51	0.13	7523.45	7488.88		
Pb, mg/L	0.01	0.026	0.38	2590.86	2578.95		
Cu, mg/L	0.10	0.0300	3.33	298.94	297.57		
Ni, mg/L	0.02	0.0000	0.00	0.00	0.00		
2006							
Indicator	MAC*	Cm**	Q	IM	RM	IM 2006 =	3149.60
COD-Cr, mgO ₂ /L	5.00	54.10	0.09	10781.95	10732.41	RM ₂₀₀₆ =	3135.16
NO ₃ ⁻ ,mg/L	50.00	214.50	0.23	4274.91	4255.27		
NO ₂ ⁻ , mg/L	0.50	0.7400	0.68	1474.79	1468.02		
SO ₄ ⁻² , mg/L	250.00	176.50	1.42	703.52	700.28		
Fe, mg/L	0.20	0.14	1.43	697.54	694.33		
Pb, mg/L	0.01	0.062	0.16	6178.19	6149.81		
Cu, mg/L	0.10	0.0090	11.11	89.68	89.27		
Ni, mg/L	0.02	0.0200	1.00	996.48	991.90		

*maximum admissible concentrations concordant to national legislation, ** measured concentration

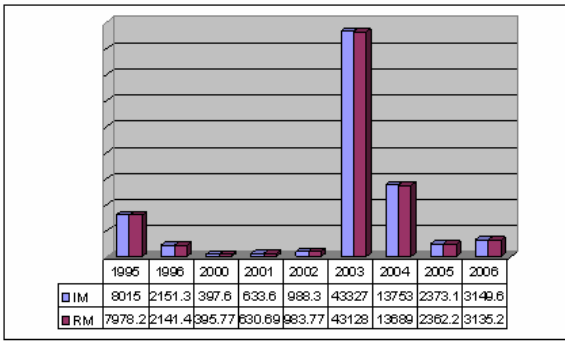


Fig.2. Impact and risk induced on ground water quality, period 1995-2006, drilling F1

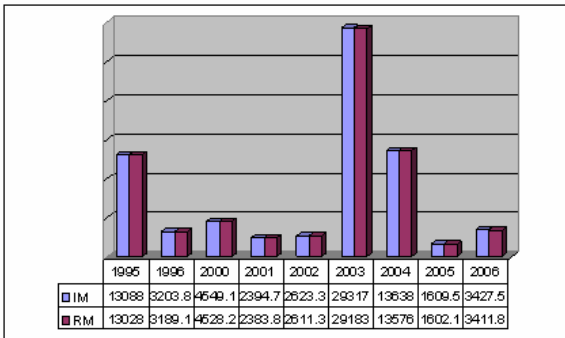


Fig. 3. Impact and risk induced on ground water quality, period 1995-2006, drilling F2

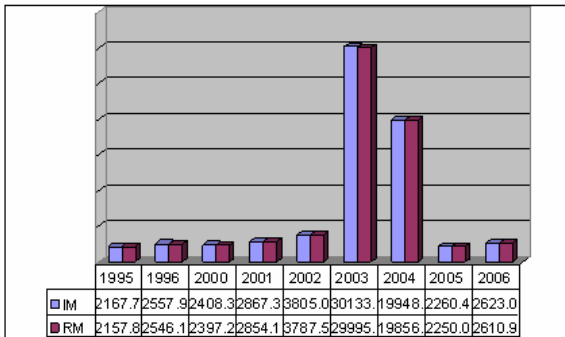


Fig. 4. Impact and risk induced on ground water quality, period 1995-2006, drilling F3

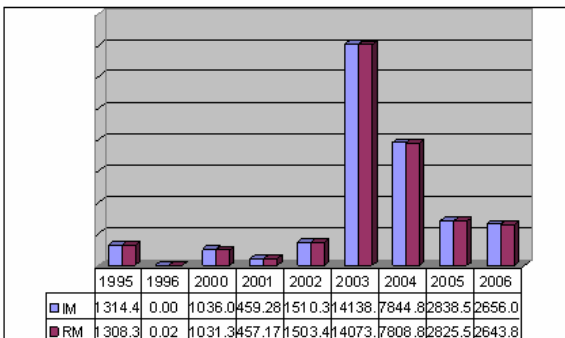


Fig. 5. Impact and risk induced on ground water quality, period 1995-2006, drilling F4

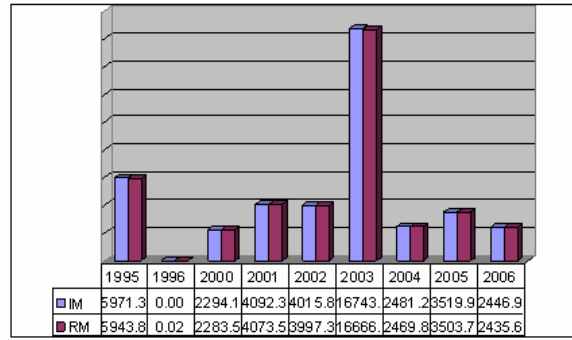


Fig. 6. Impact and risk induced on ground water quality, period 1995-2006, drilling F5

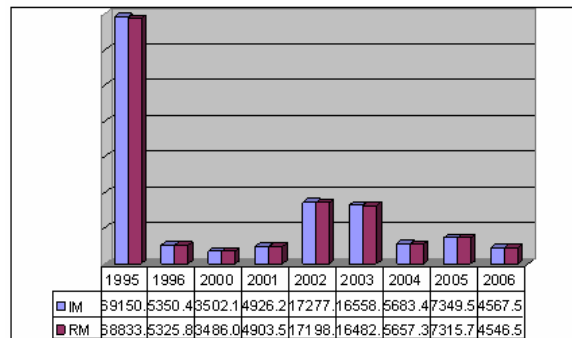


Fig. 7. Impact and risk induced on ground water quality, period 1995-2006, drilling F6

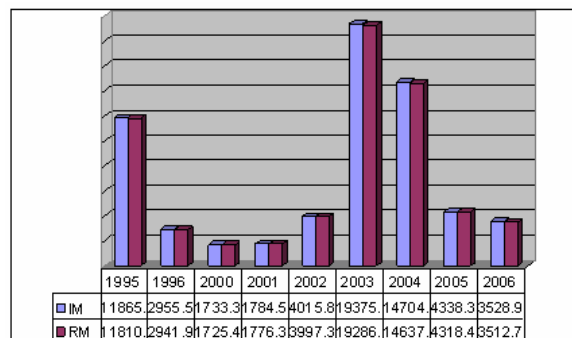


Fig. 8. Impact and risk induced on ground water quality, period 1995-2006, drilling F7

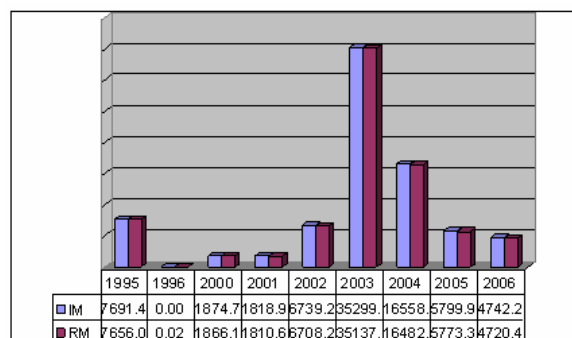


Fig. 9. Impact and risk induced on ground water quality, period 1995-2006, drilling F8

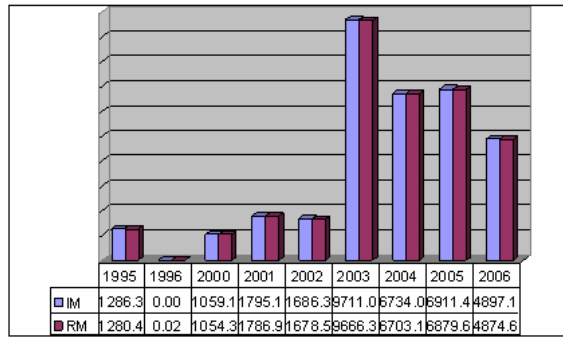


Fig. 10. Impact and risk induced on ground water quality, period 1995-2006, drilling F9

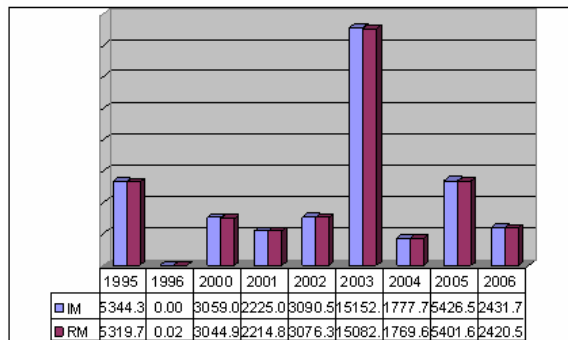


Fig. 11. Impact and risk induced on ground water quality, period 1995-2006, drilling F10

In Fig. 12 the comparison of environmental impact induced on ground water quality, years 2006, 2003 and 1995 is shown.

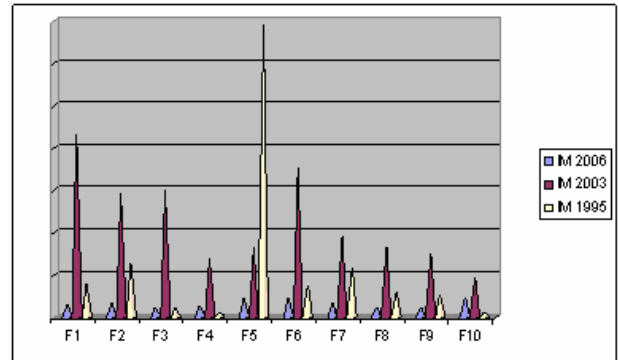


Fig.12. Comparison of environmental impact induced on ground water quality: years 2006, 2003 and 1995

It can be observed that the most negative impact induced in ground water was in 1995 and 2003, years when the industrial activities took place on site at maximum capacity of installations, thus, pollution control and monitoring actions should be applied on this site in order to prevent the aquifer and surface water pollution.

Table 7. Classification of environmental impact and risk

Impact Scale	Impact description	Risk Scale	Risk description
<100	Natural environment, not affected by industrial/human activities	<100	Negligible/insignificant risks
100-350	Environment modified by industrial activities within admissible limits	100-200	Minor risks, monitoring actions are required
350-500	Environment modified by industrial activities causing discomfort conditions	200-350	Moderate risk at an acceptable level, monitoring and prevention actions are required
500-700	Environment modified by industrial activities causing distress to life forms	350-700	Moderate risks at an unacceptable level, control and prevention measures are needed
700-1000	Environment modified by industrial activities, dangerous for life forms	700-1000	Major risks, remediation, control and prevention measures are needed
>1000	Degraded environment, not proper for life forms	>1000	Catastrophic risks, all activities should be stopped

6. Conclusions

The purpose of this work was to propose a new method for integrated environmental impact and risk assessment and apply it on a case study in order to make the right decision concerning the quality of ground water from evaluated area. Thus, groundwater from ten drillings was sampled and analyzed over the period 1995-2006 (exception years 1997, 1998 and 1999). From each drilling, over the period 1995-2006 eight quality indicators considered representative for evaluated situation were analyzed, and, based on

these experimental data, the integrated environmental impact and risk assessment was applied.

Regarding the experimental results, it can be concluded that the evaluated site, especially the ground water is significantly polluted due to the presence of various pollutants such as organic compounds, nitrate, nitrite and heavy metals. Thus, the quality indicators analyzed had values for measured concentrations higher than maximum admissible concentrations:

- Organic compounds analyzed by CCO-Cr indicator had over the period 1995-2006 measured concentrations higher than maximum admissible

concentration almost in all drillings. The maximum analyzed value was 103.64 mg/L (in 2006) from samples from drilling F5 and 83.14 mg/L (in 2006) from samples from drilling F4.

- The ground water contamination with nitrate was higher in 2005 in drilling F1 (measured concentration of NO_3^- was 198.07 mg/L and 214.5 mg/L), drilling F3 (measured concentration of NO_3^- was 71.64 mg/L and 116.82 mg/L), drilling F4 (measured concentration of NO_3^- was 195 mg/L in 2005 and 104.02 mg/L in 2006), and drilling F10 (measured concentration of NO_3^- was 227.7 mg/L in 2006).

The quality of ground water was highly negative influenced by the presence of nitrites, and the most influenced areas are from drilling F2 (measured concentrations 0.6 mg/L in 2004 and 0.925 mg/L in 2006) and drilling F8 (measured concentration 0.612 mg/L in 2005 and 0.775 mg/L in 2006).

The new integrated method applied herein for environmental impact and risk assessment has the advantages that it is very easy to be used by non environmental experts: it calculates the impacts and risks, correlated with measured concentrations of quality indicators for environmental component, considered representative in assessment process; it is not a subjective method because several mathematical steps are applied. Also, the lack of experience of evaluator doesn't influence the results of assessment process, and it will reflect in a very objective way the real situation. The results showed that in period 1995 – 2006 the ground water quality was highly negative influenced by industrial activities developed on studied area. The maximum value for impact and risk induced in ground water from evaluated site is in 1995 year, when the industrial activities from this area were working at maximum capacity. Thus, it is absolutely necessary to apply the measures for remediation, to improve the quality of ground water and control the pollution, considering the fact that the ground water quality needs to be at optimum parameters, required by national legislation.

Acknowledgements

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DETERMINATION OF MAJOR AND MINOR ELEMENTS IN MILK THROUGH ICP-AES

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Abstract

Milk products are a very important human nutrient since their consumption has increased in recent years. Good quality measurements are essential to control and maintain milk products and processes quality, both in manufacturing, trade and in research. The presence of toxic elements in powdered and liquid milk may create significant health problems for people. The aim of this paper was to determine the content of major and minor elements in different milk samples, sold in major supermarket chains in Romania. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was used for the quantitative determination of elements in this matrix. Analyses were performed after the chemical mineralization of the samples with nitrogen acid. Detection limits ranged from 0.4 to 7.03 ng/g.

Key words: milk, ICP-AES, major and minor elements

1. Introduction

Good quality measurements are essential to control and maintain products and processes quality, both in manufacturing, trade and in research. Milk products are a very important human nutrient since their consumption has increased in recent years. These products are also a good source of calcium and their bioavailability is high.

Many dangerous elements or compounds, such as metals and metalloids, accumulate along the food chain. Furthermore their concentrations in the environment grow with the increase of urban, agricultural, and industrial emissions. The almost ubiquitous presence of some metal pollutants, especially Cd and Pb, facilitates their entry into the food chain and thus increases the possibility of them having toxic effects on humans and animals. Although heavy metals have industrial uses, their potential toxicity for people and animals is the object of several studies. For some elements the effects are accumulative and it is necessary to control their level in consumed food.

So, measurements of minor and trace metal contents, comprising Al, Pb, Cd, Cr, Cu, Fe, Mg, Mo,

Mn, Ni, P, Sb, Si, Sn, Zn, Ti is also very helpful in assessment of quality of milk during its manufacturing treatment and production.

For carrying out these determinations were used different techniques: flame atomic absorption spectrometry (Kondyli et Prusisz, 2007; Pohl et al., 2007), capillary zone electrophoresis (Suarez-Luque et al., 2007), inductively coupled argon plasma emission spectroscopy (Park, 2000), differential pulse anodic stripping voltammetric technique (Tripathi et al., 1999), inductively coupled plasma optical emission spectrometry (Kira and Maihara, 2007), flow injection spectrometric methods (Nogueira Rita de Araujo et al., 1998), atomic fluorescence spectrometry (Cava-Montesinos et al., 2004) and stripping potentiometry (Munoz and Palmero, 2004).

Many reports indicate the presence of heavy metals in milk, and often it is needed to assess the levels of heavy metals in food. Lead, cadmium and mercury residues in milk are of particular concern because milk is largely consumed by infants and children (Caggiano et al., 2005; Licata et al., 2004; Tajkarimi et al., 2008; Zheng et al., 2007), and the determination of these heavy metals levels in milk is

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particularly attended by international organizations (Codex Alimentarius Commission, 2003).

The objective of this study was to determinate the Al, Pb, Cd, Cr, Cu, Fe, Mg, Mo, Mn, Ni, P, Sb, Si, Sn, Zn, Ti in milk samples by inductively coupled plasma atomic emission spectrometry (ICP-AES). This technique performs the simultaneous-sequential determination in a large number of elements from environmental and biological samples, being advantageous from the viewpoint of the short time and the low limit of detection.

2. Experimental

2.1 Reagents and solutions

All reagents used were of analytical reagent grade (Merck). Deionised water was used for the preparation of all solutions.

The working standard solutions were prepared by diluting the stock solutions (1000 mg/l) in 10% hydrochloric acid. All working standard solutions were stored in polypropylene bottles.

The nitric acid (65%) and hydrogen peroxide solutions used were of ultrapure grade, purchased from Merck.

All glassware was initially washed with detergent and water, and then the glassware was rinsed several times with deionized water and dried.

2.2. Sample preparation

Powder milk and cow milk (fresh and pasteurized from different producers) were the samples analyzed in this study and they were purchased in local markets in the city of Constanta, Romania.

A known volume of milk (25 mL) was evaporated to near dryness, wet-ashed and taken up in 10 ml of 0.25% HNO₃.

2.3. Sample analysis

A Spectroflame P (Spectro Company, Germany) ICP-AES instrument was used. After scanning a blank, a standard solution and a sample solution in the programmed wavelength range, the background correction wavelengths were selected manually at appropriate background positions for each analyte peak. Instrument configuration and general experimental conditions are summarized in Table 1. For each sample three determinations were performed and average results were reported. Detection limits of the elements studied in milk samples (Table 2) were determined from the standard addition curves of each element in different samples. It was based on the usual definition as the concentration of the analyte yielding a signal equivalent to three times the standard deviation of the blank signal. The detection limits of the method are

good and permit the determination of the elements in milk at background concentrations.

Table 1. ICP-AES operating conditions

<i>Operating conditions</i>	
RF frequency	27.12 Hz
RF power	2.5 Kw
Outer gas flow rate	Ar 17 L/min
Intermediate gas flow rate	Ar 1 L/min
Carrier gas flow rate	Ar 1 L/min
Observation height	18 mm above work coil
Plasma's temperature	8000-9000 K

Table 2. Detection limits for ICP-AES method

<i>Element</i>	<i>Detection limit (ng/g)</i>	<i>Element</i>	<i>Detection limit (ng/g)</i>
Al	1.02	Mn	1.87
Pb	7.03	Ni	1.03
Cd	0.63	P	0.4
Cr	1.87	Sb	6.5
Cu	0.90	Si	1.0
Fe	0.5	Sn	5
Mg	2.27	Zn	4
Mo	1.16	Ti	2

3. Results and discussion

The results of the mineral analysis of milk samples are given in table 3 and 4. The P content of powder milk was lower than the value reported by Park (Park, 2000) and the concentrations of fresh cow milk samples were comparable with those encountered in goat milk samples (Kondyli et al., 2007). This mineral plays an essential role in the human organism and it is well known that milk and dairy products are good dietary sources of P and their contributions to the total P daily intake have been reported to be 30–45% (Cashman, 2003).

The concentration levels of Mg in fresh cow milk observed in this study are higher than those observed in raw goat milk: 151-167 ppm (Kondyli et al., 2007). Also, the concentration levels of Mg in commercial milk samples observed in this study were higher than those observed in commercial milk samples from Spain: 126 ppm (Suarez-Luque et al., 2007).

Table 3. P and Mg contents of milk samples collected from local markets

<i>Element</i>	<i>Concentration (ppm)</i>				
	<i>powder milk</i>	<i>fresh cow milk</i>	<i>pasteurized milk</i>		
			<i>Brenac</i>	<i>La Dorna</i>	<i>Diami</i>
P	3933.00	1608.00	2736.00	914.00	922.00
Mg	919.80	214.00	344.00	139.21	155.24

As far as trace minerals are concerned, there were no indications of abnormal levels of Cr, Cu, Fe, Zn, Al, B, Mn, Mo, Ni, Sb, Sn and Ti in the milk samples collected from local markets.

The level of iron in fresh cow milk is slightly higher than the report of Park (Park, 2000)

where the average Fe concentration in fluid goat milk was 0.55 mg/L. The mean Fe content (ppm) of the pasteurized milk samples in this study was 4.64 mg/l, which is significantly lower than that of powdered milk (Table 4).

Table 4. Mineral contents of milk samples collected from local markets

Element	Concentration (ppm)				
	powder milk	fresh cow milk	pasteurized milk		
			Brenac	La Dorna	Diami
Cr	0.18	0.04	0.10	0.04	0.06
Cu	0.54	0.17	0.10	0.08	0.16
Fe	21.73	0.72	11.84	1.30	0.80
Zn	3.24	0.98	1.54	0.52	0.48
Al	1.90	1.18	4.16	4.14	1.22
B	0.10	0.04	0.04	0.04	0.04
Mn	0.29	0.08	0.09	0.04	0.07
Mo	0.18	0.04	0.04	0.04	0.04
Ni	0.18	0.04	0.04	0.04	0.05
Si	0.49	0.44	1.08	0.66	0.52
Sb	0.45	0.10	0.10	0.10	0.10
Sn	0.45	0.10	0.10	0.10	0.10
Ti	0.19	0.04	0.04	0.04	0.04

The mean Zn concentration in the analyzed fresh cow milk samples (0.98 ppm) was lower than those reported in raw bovine milk (0.29-4.96 ppm) (Licata et al., 2004). The mean Zn concentration in powdered milk is 3.24 ppm and the Zn concentrations in the commercial cow milk samples are in range 0.48-1.54 ppm. These concentrations were lower than those determined in powdered and commercial goat milk (32.10 ppm, respectively 3.10 ppm) (Park, 2000).

Cu levels are in the line with those reported by other authors (Kira et al., 2007; Kondyli et al., 2007; Tripathi et al., 1999). The low concentrations of Cu could be due to Zn contained in food that interferes with the copper absorption system, explaining the presence of low levels of this metal in milk (Doull's, 2000).

The range obtained for aluminium in this study was (1.18 - 4.16 ppm). These values are higher than those reported in other research papers (Ikem et al., 2002). There is concern because of the possibility of increased amounts of aluminium being deposited in the brain and the resulting risk of brain dysfunction (Walker, 2000) and aluminium is now being implicated as interfering with a variety of cellular and metabolic processes (American Academy of Pediatrics, 1998).

The trace minerals contents of the commercial cow milk products in this study generally were lower than the content of powdered milk.

The concentrations of "toxic" metals (Cd and Pb) in milk samples are reported in Table 5. The lowest levels were those of Cd (0.001-0.005 ppb). This study demonstrates that, in milk from Romania, there are highest concentrations only of lead among "toxic" metals. From a more detailed analysis of the results obtained, it appears that milk samples show a range of Pb (0.04-0.16 ppb) higher than those

reported in literature (Caggiano et al., 2005; Tajkarimi et al., 2008) and lower than those reported by Licata (Licata et al., 2004).

Table 5. Cd and Pb (toxic metals) contents of milk samples collected from local markets

Element	Concentration (ppb)				
	powder milk	fresh cow milk	pasteurized milk		
			Brenac	La Dorna	Diami
Cd	0.001	0.004	0.005	0.004	0.003
Pb	0.16	0.12	0.04	0.11	0.04

However, it is of particular interest to note the presence of Pb in all samples studied were not in dangerous concentrations. If the maximum limits of lead for milk and secondary milk products were taken as 0.05 ppm each, the total exposure in the European diet (European diet provides maximum potential for weekly intake of lead through food) would be 4.631 g of lead per kg body weight (GEMS/food regional diets, 2003).

The results obtained show how this metal is ever more frequently found in milk samples, not only in regions with great industrial activity. The presence of Pb in milk samples could be due to various factors: transhumance along roads and/or motorways, fodder contamination, climatic factors, such as winds, and the use of pesticide compounds. One of the most important sources of lead contamination in milk is water, especially in more contaminated areas (Codex Alimentarius Commission, 2003); so, water testing should be one of the important topics for future study. Therefore, it is necessary to monitor this metal over time to better clarify its presence in milk.

At present, the CE Regulation no. 2001/466 (CE Regulation, 2001) establishes a limit for Pb in milk (MRL= 0.02 mg/kg w.w.). Therefore, the Pb concentrations below MRLs found in powdered, fresh and pasteurized milk samples from local markets indicate that the milks products are safe for the consumers. As regards Cd, its presence at low concentrations in milk samples shows that there are no toxicological risks in Romania.

4. Conclusions

The dry ashing procedure has proved to be precise and accurate sample preparation procedure for multi-element determination of Cr, Cu, Fe, Zn, Al, B, Mn, Mo, Ni, Sb, Sn and Ti in the powdered, fresh and pasteurized milk samples.

The results of this study showed that the studied cow milk samples generally, contained sufficient quantity of trace elements, a fact which has a great impact on its nutritional quality. The trace minerals contents of the commercial cow milk products in this study generally were lower than the content of powdered milk

The mean concentrations of the macroelement P in fresh cow milk samples were similar to those reported in the literature and the mean concentrations of the macroelement Mg in fresh and

commercial cow milk samples were higher than those reported in the literature.

Further studies are necessary to evaluate the contents of “essential” and “toxic” heavy metals on a greater number of milk samples from various producers in Romania and to confirm the absence of possible toxicological risks.

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EQUATIONS FOR ALLUVIAL SOIL STORAGE COEFFICIENTS

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Abstract

The paper defines the average and local soil storage coefficients, for a soil with relatively shallow water table. By means of an adequate law for the suction distribution on soils level and certain parametrical models for the moisture retention curve of soil, the analytical equations for these storage coefficients were determined. Theoretical results are to be applied for a case study and on the basis of a pertinent analysis, and some recommendations were made for the practical use of formulae proposed for the storage coefficients.

Keywords: analytical equations, mathematical model, soil, storage coefficients

1. Introduction

The soil storage coefficients are mainly used within the mathematical modeling of the draining of a soil profile. In text-books (Kabat, 1998) there is defined an unique storage coefficient, μ , by means of the ratio between the change in soil moisture storage of the profile, ΔW , [L], and the corresponding change in water table depth, ΔZ , [L]. Anyway, after a more thorough analysis it can be seen that the significance and/or the value of coefficient μ are depending on the next factors: a) the original water table depth compared to the land's area, Z^* ; b) the sense of depth change ΔZ ($\Delta Z > 0$ – decrease; $\Delta Z < 0$ – increase); c) the nature of change nature ΔZ (finite or infinitesimal).

In the process of assessing the μ coefficient the next simplifying assumptions are accepted: 1) the whole soil profile is located in the capillary fringe's area; 2) hydrodynamic balance (constant hydrodynamic load upon the whole soil profile) – this, in both conditions: in initial condition (water table at depth Z^*), and, as well, in the final condition (water table stabilized at depth $Z^* + \Delta Z$).

For a water tables finite descent ΔZ , has been defined *the soil storage coefficient*, $\bar{\mu}$, average on depth $[Z^*, Z^* + \Delta Z]$, by mean of next equation:

$$\bar{\mu} = \frac{\Delta W_{1-2}}{\Delta Z} = \frac{\text{the decrease of soil water reserve on domain } [Z_1 = 0, Z_2 = Z^* + \Delta Z]}{\text{the decrease of water table's level}} \quad (1)$$

For an infinitesimal decrease of water table ΔZ , can be defined *the local soil storage coefficient* corresponding to depth Z^* , $\mu^* = \mu(Z^*)$, by means of the next limit (Eq. 2):

$$\mu^* = \lim_{\Delta Z \rightarrow 0} \frac{\Delta W_{1-2}}{\Delta Z} \quad (2)$$

Between the two storage coefficients, $\bar{\mu}$ and μ^* , the next integral equation can be defined (Eq. 3):

$$\bar{\mu} = \frac{1}{\Delta Z} \int_{Z^*}^{Z^* + \Delta Z} \mu^*(\zeta) d\zeta \quad (3)$$

In this paper the authors proposed a procedure to determine the analytical equations (on basis of distribution law for piezometric height (suction) and

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parametric models for the constitutive equation suction-humidity) for a direct and highly accurate assessment of storage coefficients, $\bar{\mu}$ and μ^* .

2. The mathematical model

Currently, the constitutive equation of suction-humidity for a soil horizon, considered to be a porous, homogenous and unsaturated medium, has the form (4):

$$S_w = S_w(\psi) \text{ or } \theta_w = \theta_w(\psi) \tag{4}$$

where:

S_w = the saturation degree (saturation);

ψ = the piezometric height (for $\psi \leq 0$, $|\psi|$ represents the vacuum-metrical height or the suction), [L].

In usual parametrical models, the constitutive equation (4) can be expressed with the notion of effective saturation degree, S_w^e , defined as follows (Diersch, 2002) (Eq. 5):

$$S_w^e = \frac{S_w - S_w^r}{S_w^s - S_w^r} = \frac{\theta_w - \theta_w^r}{\theta_w^s - \theta_w^r}, \tag{5}$$

where:

S_w^s is the degree of maximal saturation ($S_w^s = 1$); S_w^r - the degree of residual saturation;

θ_w - the volumetric humidity ($\theta_w = eS_w$, where e is the voids factor); θ_w^s is the maximal humidity ($\theta_w^s = e$) and θ_w^r - the residual humidity.

The way of which the effective saturation degree S_w^e depends on water's piezometric height within soil's pores, ψ , is given by means of empirical equations, depending on the type of parametrical.

For example:

a) for the *van Genuchten-Mualem* model,

$$S_w^e(\psi) = \begin{cases} \left[1 + (A|\psi - \psi_a|)^n\right]^{-m}, & \text{for } \psi < \psi_a \\ 1, & \text{for } \psi \geq \psi_a \end{cases} \tag{6a}$$

where m and n , are exponents and A , $[L^{-n}]$, the model's coefficient, and ψ_a , [L] – the piezometric height of air within soil;

b) for the exponential model (proposed by authors),

$$S_w^e(\psi) = \begin{cases} Ee^{\alpha(\psi - \psi_a)}, & \text{for } \psi < \psi_a \\ 1, & \text{for } \psi \geq \psi_a \end{cases}, \tag{6b}$$

where α , $[L^{-1}]$, is the sorptive number, and E , [-], the model's coefficient (in the classic exponential model, $E=1$).

If the humidity θ_w , will be taken from Eq. (5), the next expression for the constitutive will result (Eq. 7):

$$\theta_w(\psi) = \begin{cases} \theta_w^r + S_w^e(\psi)(\theta_w^s - \theta_w^r), & \text{for } \psi < \psi_a \\ \theta_w^s, & \text{for } \psi \geq \psi_a \end{cases} \tag{7}$$

When water table is at depth Z^* under soil's level, the piezometric height's distribution, in conditions of hydrodynamic balance (assumption 2°), is given by the law (8):

$$\psi = Z - Z^* + \psi_a \tag{8}$$

therefore Eqs. (9) will result.

$$\psi - \psi_a = \begin{cases} Z - Z^* \leq 0, & \text{for } Z \in [0, Z^*] \\ Z - Z^* \geq 0, & \text{for } Z \geq Z^* \end{cases} \tag{9}$$

$$|\psi - \psi_a| = \begin{cases} Z^* - Z, & \text{for } Z \in [0, Z^*] \\ Z - Z^*, & \text{for } Z \geq Z^* \end{cases}$$

If Eqs. ((6) and (9) are considered in Eq. (7), the humidity distribution laws upon soil's profile will result (Eqs. 10):

a) for the *van Genuchten-Mualem* model (Eq. 10a):

$$\theta_w(Z) = \begin{cases} \theta_w^r + \frac{\theta_w^s - \theta_w^r}{\left[1 + A^n (Z^* - Z)^n\right]^m}, & \text{for } Z \in [0, Z^*] \\ \theta_w^s, & \text{for } Z \geq Z^* \end{cases} \tag{10a}$$

b) for the *exponential* model (Eq. 10b):

$$\theta_w(Z) = \begin{cases} \theta_w^r + (\theta_w^s - \theta_w^r) Ee^{\alpha(Z - Z^*)}, & \text{for } Z \in [0, Z^*] \\ \theta_w^s, & \text{for } Z \geq Z^* \end{cases} \tag{10b}$$

The water reserve stored upon soil's profile between depths Z_1 and Z_2 , with $0 \leq Z_1 < Z_2$, can be assessed with Eq. (11):

$$W_{1-2} = \int_{Z_1}^{Z_2} \theta_w(Z) dZ. \tag{11}$$

In the initial situation (when water table is at depth Z^*), the humidity distribution upon soil's profile on depth $[Z_1 = 0, Z_2 = Z^* + \Delta Z]$ is given by Eqs. (10). Hence, the stored water reserve, given by Eq. (11), is expressed by Eqs.(12):

a) for the *van Genuchten-Mualem* model (Eq. 12a)

$$W_{1,2}^0 = \theta_w^r Z^* + \theta_w^s \Delta Z + (\theta_w^s - \theta_w^r) \int_0^{Z^*} \left[1 + (A(Z^* - Z))^n \right]^{-m} dZ \quad (12a)$$

b) for the *exponential* model (Eq. 12b)

$$\begin{aligned} W_{1,2}^0 &= \theta_w^r Z^* + \theta_w^s \Delta Z + (\theta_w^s - \theta_w^r) E \int_0^{Z^*} e^{\alpha(Z-Z^*)} dZ = \\ &= \theta_w^r Z^* + \theta_w^s \Delta Z + \frac{E}{\alpha} (\theta_w^s - \theta_w^r) (1 - e^{-\alpha Z^*}). \end{aligned} \quad (12b)$$

In the final situation (when water table is at depth $Z^* + \Delta Z$), it results from Eq. (8):

$$\psi - \psi_a = Z - (Z^* + \Delta Z) \leq 0, \text{ for } Z \in [0, Z^* + \Delta Z] \quad (13)$$

Therefore, humidity distribution upon soil's profile, on the depth $[Z_1 = 0, Z_2 = Z^* + \Delta Z]$ is expressed by Eqs. (14):

a) for the *van Genuchten-Mualem* model (Eq. 14a):

$$\theta_w(Z) = \theta_w^r + \frac{\theta_w^s - \theta_w^r}{\left[1 + (A(Z^* + \Delta Z - Z))^n \right]^m}, \text{ for } Z \in [0, Z^* + \Delta Z] \quad (14a)$$

b) for the *exponential* model (Eq. 14b):

$$\theta_w(Z) = \theta_w^r + (\theta_w^s - \theta_w^r) E e^{\alpha(Z-Z^*-\Delta Z)}, \text{ for } Z \in [0, Z^* + \Delta Z] \quad (14b)$$

Therefore, in the final situation, from Eq. (11) it results the following stored water reserve on the depth $[Z^*, Z^* + \Delta Z]$ (Eqs. 15):

a) for the *van Genuchten-Mualem* model (Eq. 15a):

$$W_{1,2}^F = \theta_w^r (Z^* + \Delta Z) + (\theta_w^s - \theta_w^r) \int_0^{Z^* + \Delta Z} \left[1 + (A(Z^* + \Delta Z - Z))^n \right]^{-m} dZ \quad (15a)$$

b) for the *exponential* model (Eq. 15b):

$$W_{1,2}^F = \theta_w^r (Z^* + \Delta Z) + \frac{E}{\alpha} (\theta_w^s - \theta_w^r) \left[1 - e^{-\alpha(Z^* + \Delta Z)} \right] \quad (15b)$$

Taking into account Eqs. (12) and (15), the basic equation (1) for the **average storage coefficient** becomes (16):

$$\bar{\mu} = \frac{W_{1,2}^0 - W_{1,2}^F}{\Delta Z} \quad (16)$$

In case of the *van Genuchten-Mualem* model, generally, the integrals within 12th and 15th equations can be determined only by means of numerical methods; thus the average storage coefficient $\bar{\mu}$ will be determined too by means of numerical methods. However, in the case of the exponential model, when using for $W_{1,2}^0$ and $W_{1,2}^F$ and the analytical equations (12-b) and (15-b), the following equation for the $\bar{\mu}$ coefficient results (Eq. 17):

$$\bar{\mu} = (\theta_w^s - \theta_w^r) \left[1 - \frac{E}{\alpha \Delta Z} e^{-\alpha Z^*} (1 - e^{-\alpha \Delta Z}) \right]. \quad (17)$$

In a similar way, the basic equation (2) for the **local storage coefficient** μ^* , becomes (18):

$$\mu^* = \lim_{\Delta Z \rightarrow 0} \frac{W_{1,2}^0 - W_{1,2}^F}{\Delta Z}. \quad (18)$$

If equations (12) and (15) are incorporated within equation (18), and if the rules for differential and integral calculation are applied, algebraic equations for μ^* coefficient will result (Eqs. 19):

a) for the *van Genuchten-Mualem* model (Eq. 19a):

$$\mu^* = (\theta_w^s - \theta_w^r) \left\{ 1 - \left[1 + (A \cdot Z^*)^n \right]^{-m} \right\} \quad (19a)$$

b) for the *exponential* model (Eq. 19b):

$$\mu^* = (\theta_w^s - \theta_w^r) (1 - E e^{-\alpha Z^*}). \quad (19b)$$

Eq. (19-b) can also be obtained directly, applying the *L'Hospital* rules to the limit given below (Eq. 19c):

$$\mu^* = \lim_{\Delta Z \rightarrow 0} (\theta_w^s - \theta_w^r) \left[1 - \frac{E}{\alpha \Delta Z} e^{-\alpha Z^*} (1 - e^{-\alpha \Delta Z}) \right] \quad (19c)$$

In case of the Genuchten-Mualem model, generally, for the m and n exponents, from the 6th law, it can be seen that: $m \notin \mathbf{Z}$ and $(m+1)/n \notin \mathbf{Z}$, where \mathbf{Z} is the integer set.

Therefore the binomial integrals within Eqs. 12, 15 and 3 do not satisfy the precise analytical integration conditions deduced by Tchebyshev; hence, all these integrals are to be solved numerically.

In the particular case when the trapeze formula and, respectively, the rectangle formula are applied, formal approximate analytical equations will result from Eq. (3) for the storage coefficient $\bar{\mu}$ (Eqs. 20a and b):

$$\bar{\mu} \cong \frac{1}{2} [\mu^*(Z_1) + \mu^*(Z_2)] = (\theta_w^s - \theta_w^r) \left\{ 2 - \left[1 + (AZ^*)^n \right]^{-m} - \left[1 + A^n \left(Z^* + \Delta Z \right)^n \right]^{-m} \right\} \tag{20a}$$

and

$$\bar{\mu} \cong \mu^* \left(Z^* + \frac{\Delta Z}{2} \right) = (\theta_w^s - \theta_w^r) \left\{ 1 - \left[1 + A^n \left(Z^* + \frac{\Delta Z}{2} \right)^n \right]^{-m} \right\} \tag{20b}$$

3. The numerical application

In order to test the proposed mathematical model the next basic data were considered:

- The nature of soil horizon: clay, featuring the next physical and hydric parameters: porosity, $n = 0.33643$ (or voids factor, $e = 0.507$); volumetric humidity, [expressed in m^3 water / m^3 solid phase], residual, $\theta_w^r = 0.18252$; maximal volumetric humidity,

$$\theta_w^s = e = 0.507; \text{ air piezometric height, } \psi_a = 0.$$

- The constitutive equation (4): given (Table 1 – columns 2 and 3) by the next pairs of values:

$$(\psi, \theta_w)_i = (\psi_i, \theta_{wi}), \text{ with } i=1,2,\dots, N_{date}=10. \tag{21}$$

At the initial moment the water table level is at the depth $Z^*=50$ cm, and at final moment the level descends with an amount $\Delta Z=70$ cm.

The next calculation stages have been carried:

- By means of a proprietary software, **funcția_genuchten.m**, using the input data (21), the A coefficient can be computed and the power exponents n, m for law (6a) result:

$$\begin{aligned} A &= 3.163067198535394e-4 \\ n &= 0.538301890103307 \\ m &= 0.999999999999965 \end{aligned} \tag{22}$$

- By means of a proprietary software, **funcția_exponent.m**, with input data (21), the E coefficient and the α exponent for law (6b) can be computed:

$$E=0.964379348962526, \alpha=0.001128727262118. \tag{23}$$

- Incorporating in Eq. (6a) the values of A, n and m computed by (22) and the values from (21) for ψ_i – in equation (7), the values for humidity θ_w result approximated with Genuchten-Mualem model (Table 1 – column 4):

$$\theta_{wi}^{G-M}, \text{ with } i=1,2,\dots, N_{date}=10. \tag{24}$$

Incorporating in Eq. (6b) the values of E and α given by (23) and the values from (21) for ψ_i – in Eq. (7), the values of humidity θ_w are obtained, approximated with the exponential model (Table 1 – column 5) (Eq. 25):

$$\theta_{wi}^{Exp}, \text{ with } i=1,2,\dots, N_{date}=10. \tag{25}$$

The relative errors corresponding to the approximation with the two models - Genuchten-Mualem, ε_i^{G-M} , and exponential, ε_i^{Exp} - evaluated, respectively, with equations (26):

$$\varepsilon_i^{G-M} = 100 \frac{\theta_{wi}^{G-M} - \theta_{wi}}{\theta_{wi}}, i=1,2,\dots, N_{date}=10, \quad [\%]$$

and

$$\varepsilon_i^{Exp} = 100 \frac{\theta_{wi}^{Exp} - \theta_{wi}}{\theta_{wi}}, \text{ with } i=1,2,\dots, N_{date}=10, \quad [\%]$$

centralized in Table 1- columns 6 and 7.

- After assessment of data within Table 1 – columns 6 and 7, it can be seen that the maximal relative error, in the module (absolute value), introduced by the Genuchten-Mualem model, is much inferior to the one corresponding to the exponential model,

$$\left| \varepsilon_9^{G-M} \right| = 0.2019 \ll \left| \varepsilon_{10}^{Exp} \right| = 1.2503.$$

For this reason the results obtained with the Genuchten-Mualem model has been considered as reference results.

- Also the depths are computed (Eq. 27):

$$\begin{aligned} Z_1 &= Z^* = 50 \text{ cm, } Z_2 = Z^* + \Delta Z = 120 \text{ cm,} \\ Z_{med} &= (Z_1 + Z_2) / 2 = 85 \text{ cm.} \end{aligned} \tag{27}$$

Table 1. Experimental and theoretical values (the Genuchten-Mualem and exponential models) for the suction-humidity curve

<i>i</i>	1	2	3	4	5	6	7	8	9	10
ψ_i [cm]	-120	-100	-80	-70	-50	-40	-30	-20	-10	-2
θ_{wi} , [-]	0.4590	0.4630	0.4680	0.4700	0.4760	0.4790	0.4830	0.4870	0.4920	0.5010
θ_{wi}^{G-M} , [-]	0.4594	0.4633	0.4676	0.4700	0.4756	0.4788	0.4825	0.4870	0.4930	0.5010
θ_{wi}^{Exp} , [-]	0.4558	0.4620	0.4684	0.4717	0.4783	0.4816	0.4850	0.4885	0.4919	0.4947
\mathcal{E}_i^{G-M} [%]	0.0889	0.0556	-0.0839	0.0060	-0.0925	-0.0399	-0.0934	0.0099	0.2019	-0.0081
\mathcal{E}_i^{Exp} [%]	-0.6966	-0.2069	0.0905	0.3551	0.4770	0.5485	0.4189	0.2992	-0.0143	-1.2503

Table 2. Values for the average and local storage coefficients

Nr. Crt	Parameter	The Genuchten-Mualem model			The exponential model		
		Equation	Value	Error [%]	Equation	Value	Error [%]
1	W_{1-2}^0	(12a)	59.7913380636225	0.0000	(12b)	59.8287760899752	0.0626
2	W_{1-2}^F	(15a)	56.977067476729	0.0000	(15b)	57.0209851251355	0.0771
3	$\bar{\mu}$	(16), (3)	0.04020386552705	0.0000	(16), (17)	0.0401112994977	-0.2302
4	$\mu^*(Z^*)$	(19a)	0.03144031900876	0.0000	(19b)	0.02872926395388	-8.6229
5	$\mu^*(Z^*+\Delta Z)$	(19a)	0.0475919176681	0.0000	(19b)	0.05119749328637	-15.5629
6	$\mu^*\left(Z^* + \frac{\Delta Z}{2}\right)$	(19a)	0.04053627817868	0.0000	(19b)	0.04018525416554	-0.8660
7	$\bar{\mu}$	(20a)	0.03951611833843	-1.7106	-		
8	$\bar{\mu}$	(20b)	0.04053627817868	0.8268	-		

By analyzing data from Table 2, the next issues could be highlighted:

1° The assessment of the average storage coefficient $\bar{\mu}$ with Eq. (17) leads to relative errors, in module, inferior to 0.25%;

2° The assessment of the local storage coefficient μ^* , with equation 19-b), in extreme positions of water table (Z^* and $Z^*+\Delta Z$), leads to non-acceptable relative errors;

3° The assessment of the $\bar{\mu}$ storage coefficient with the approximate Eqs. (20) may lead to relative errors, in module, exceeding 1%.

4. Original contributions and conclusions

On basis of obtained results the next contributions and conclusions can be highlighted:

1. A rigorous definition of the average and local storage coefficients.

2. For the suction-humidity soil constitutive equation has been presented and implemented an original enhanced exponential model.

3. The authors are recommending the assessment of the average storage coefficient $\bar{\mu}$ by means of Eq. (17) deducted on basis of an enhanced exponential model of suction-humidity constitutive equation.

4. The authors are recommending the assessment of the local storage coefficient μ^* by means of the Eq. (19a) – deducted on basis of the Genuchten - Mualem model of suction-humidity constitutive equation.

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OVERVIEW OF *EX SITU* DECONTAMINATION TECHNIQUES FOR SOIL CLEANUP

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Abstract

The paper is a short review on the soil decontamination applying *ex-situ* techniques. Some sources and pathways of soil contamination are discussed. It was revealed that available techniques for soil decontamination can be divided in two parts, depending on where the action have place: *in-situ* or *ex-situ*. Also, depending on the nature of the process, these techniques can be biological, physical-chemical and thermal. In order to decontaminate soils properly, the primary contaminants (hydrocarbons such as petroleum residues, solvents, pesticides, herbicides, wood preservatives, heavy metals, munitions, which result from different industries and agricultural activities) have to be detected and analyzed.

The main features of *ex-situ* soil decontamination are reviewed and also status of each technology, advantages, disadvantages, limitations, and contaminants treated, are included.

Keywords: contaminant, *ex-situ*, remediation, soil

1. Introduction

The soil is a very unique part of the natural and agricultural aspects of the terrestrial ecosystem given its role in the growth of plants and the degradation and recycling of dead biomass. It is heterogeneous in nature and often comprises mineral and organic solids, aqueous and gaseous components (Alloway, 1995; Edwards and Stinner, 1988; Hyman and Dupont, 2001).

The mineral component of soils often consists of weathering product of rock parent materials and secondary minerals such as phyllosilicates, or clay minerals oxides of Fe, Al, and Mn and sometimes carbonates such as CaCO₃. Living organisms (mesofauna and microorganisms), dead plants and colloidal humus formed by the action of microorganisms on plant litter make up the organic matter component of the soil. These solid components are usually clustered together in the form of aggregates, thus creating a system of interconnected pores (voids) of various sizes filled with either water

or air (Alloway, 1995; Gavrilescu, 2006; Gavrilescu et al., 2008).

The resulting soil-water-air environment is very complex. This is because different soil fractions and constituents give rise to different reactions when anthropogenic chemicals are introduced. In many cases, contaminants become bonded, especially to clay and or organic materials and are hence unavailable to present future risks (Schacht and Ajibo, 2002). In other situations however, the anthropogenic chemicals may remain un-bonded, or could be remobilized by changes in soil acidity or redox potential and becomes far more able to create risk (Gavrilescu, 2006, Mirsal, 2008).

Many pesticides have been converted to 'bound residues' in soil (Alexander, 1999; Dankwardt and Hock, 2001). Most of the complexes formed is with the organic or humus fraction of the soils, and probably usually involves the formation of covalent bonds between the compound and the humic material. The complexes are assumed to be formed either by an attachment of the compound to reactive sites on the surfaces of the organic colloids or by incorporation of

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the compound into the structure of the humic or fulvic acids that are being formed microbiologically (Stevenson, 1976; Worsztynowicz et al., 2008).

The goal of a remediation effort is to limit the extent of contamination at a hazardous waste site, to prevent further deterioration of the environment and to prevent exposure by humans and other life forms to hazardous chemicals. The remedies at a given site vary depending on the properties of the chemicals found at the site, the t

ypes of soils, and the depth of contamination, and natural processes that may occur at the site (Mirsal, 2008). The criteria for selecting remediation technologies or treatments are (Cheremisinoff, 1998; Gavrilesku, 2006; Lodolo et al., 2001; Rao et al., 2002; Vik et al., 2001):

- Short-term and long-term effectiveness at meeting the remediation goals
- Reduction in the volume of contaminants most effectively
- Reduction in the toxicity of contaminants
- Cost effectiveness.

Other factors affect the choice of remedies-for example, land disposal of hazardous materials is restricted under present environmental regulations. Because a variety of remedies can often control contamination at hazardous waste sites, selecting the appropriate technology or technologies can be a challenge.

The following categories of remedies are listed in order from least disruptive, intensive and expensive to most disruptive, intensive and expensive (EPA, 2008; GFG, 2002; Hyman and Dupont, 2001; Pare, 2006):

1) **Do nothing.** If the environmental assessment indicates that humans and the environment are not at risk, then no remediation activity is required. "Do nothing" may be deemed the appropriate action for small-scale spills on sites where human and animal exposure is not likely.

2) **Institutional Controls (IC)** - institutional controls are legal or institutional mechanisms that limit access to or use of property, or warn of a hazard. An IC can be imposed by the property owner, such as use restrictions contained in a deed or by a government, such as a zoning restriction. At contaminated sites, institutional controls are used to prohibit access to the contaminated areas. Examples of institutional controls include fencing off a contaminated site or prohibiting the construction of wells near polluted aquifers.

3) **Monitored Natural Attenuation** - In some cases nature promotes cleanup of contamination. Some contaminants may be broken down into safe elements via sunlight (known as photolysis), natural bioremediation, and chemical reactions (such as hydrolysis). Contaminants can also "stick" (or sorb) to soil or other solid particles, limiting the mobility of contaminants in the soil.

4) **Containment of Contaminants** - The risk of environmental contamination can be reduced by

limiting the ways that humans, wildlife or the environment can come in contact with the contaminants. Methods include capping of soils with clean material, creating physical barriers, and stabilizing or solidifying contaminants in place. Containment of contaminated groundwater is more difficult and may involve elaborate and often expensive pumping and treatment systems.

5) **Destruction of contaminant** - Destroying the contaminants may remove the risk posed by contaminants if the by-products are not toxic. Treatments can be in situ (in place) or ex situ (after excavation of the soil or pumping of the ground water from the aquifer). Technologies include phytoremediation, bioremediation, Fenton's Reagent and ozonization.

6) **Removal** - In some cases, the best option may be to physically remove the contaminated soil and move it to a permitted Treatment, Storage and Disposal Facility (TSDF). This is especially true with soils that are contaminated with both chemicals and radioactivity. In other cases, it is possible to remove the contaminant from the soil using such technologies as surfactant washing, soil washing or thermal desorption. Contaminants in groundwater can be removed using pump-and-treat technologies involving methods such as activated carbon or ion exchange.

The soil is a structure that is stratified. The upper layer is the unsaturated zone (or infiltrating zone), below which we have the saturated zone. There are many characteristics of the soil that influence the transport of contaminants, such as: density, porosity, humidity and permeability. This phenomenon is also influenced by some properties of the contaminants, such as vapor pressure and chemical nature (Norris, 1994). After identifying the type of soil and the nature of the contaminants, a suitable remediation technique must be chosen, and the effectiveness of the decontamination process evaluated (Castelo-Grande and Barbosa, 2003; Hyman and Dupont, 2001).

The existing methods for soil decontamination may be divided in: "in situ" techniques, "ex situ" techniques, and the confining/isolation of the contaminated area, which is a temporary solution. These methods can be further divided in biological and non-biological methods. The non-biological methods are subdivided in physical-chemical methods, thermal methods and others methods (e.g., supercritical extraction and electrokinetic) (Castelo-Grande et al., 2003). In Tables 1 and 2 some of the existing decontamination techniques are summarized, and some of their advantages and disadvantages are given (FRTR, 2000; Hyman and Dupont, 2001).

2. *Ex-situ* biological treatment

One of the main advantages of ex-situ bioremediation is that it requires less time than the in-situ treatment. Another advantage is the certainty of the control treatment due to the ability to uniformly screen, homogenize and mix the soil.

Table 1. Advantages and disadvantages of some biological technologies used in soil remediation (Castelo-Grande et al., 2003).

<i>Technology</i>	<i>Advantages</i>	<i>Disadvantages</i>
Landfarming	-Relative simple design and implementation; -Short treatment times (six months to two years under optimal conditions).	-Reductions of concentration greater than 95% and concentrations lower than 0.1 ppm are difficult to achieve; -The required area is high; -Dust and vapor generation during landfarming aeration may cause some air quality problems.
Bioventing	-Uses readily available equipment, easy to install; - Creates minimal disturbance to the treatment site; -May not require costly off gas treatment; -Easily combinable with other technologies (e.g., air sparging, groundwater extraction).	-The high concentrations may be toxic for microorganisms; -Not applicable for certain site conditions (e.g., low soil permeability); -Sometimes requires nutrients and air injection wells; -Only treats unsaturated zones of soils, and needs other methods to treat saturated zones of soils and groundwater.
Natural attenuation	-The generation of less remediation waste, and less impact on the environment; -Ease to use when combined with other technologies; -No equipment down time.	-The public may not perceive the effectiveness of the process correctly; -Site characterization can be more costly and complex; - Due to monitoring, active remediation may be more economical; -The potential exists for continued migration.
Phytoremediation	-Is much less expensive than conventional options.	-Is a technology that is seasonal; - Only applicable to low profundity.
Biosparging	-Readily available equipment; -Cost competitive; -Requires no removal, treatment, storage or discharge of groundwater.	-Some interactions among complex chemical, and physical and biological processes are not well understood; -Potential for inducing migration of constituents.
Bio – Rehabilitation in-situ	-Degradation of material dissolved in infiltrated and saturated zone; -Equipment easily available.	-The hole can be obstructed by biomass or precipitation; -Continuous monitoring and maintenance.

Table 2. Advantages and disadvantages of some non-biological technologies used in soil remediation (Castelo-Grande et al., 2003)

<i>Technology</i>	<i>Advantages</i>	<i>Disadvantages</i>
Vitrification (Thermal)	-Ex situ vitrification is a well developed technology; -The mobility of contaminants is reduced/eliminated; -The vitrified mass resists leaching for geologic periods of time.	-The process requires intensive energy and high temperatures up to near 2000 K; -Water in soil affects operation and increases the total costs of the process; -Off gases must be collected and treated before release; -In situ vitrification is in pilot scale development.
Incineration (Thermal)	-Contaminant toxicity, as well as volume reduction is addressed by this technology. This is specially true for organic contaminants; -Widely used and available commercially.	-Metals are not destroyed and end up in the flue gases or in the ashes; -Community resistance to incineration is often present; -Certain types of soils such as clay soils or soils containing rocks may need screening.
Soil Washing (Physical-Chemical)	-Reduces the volume of contaminant, therefore, further treatment or disposal is less problematic; -Commercially available.	-Contaminant toxicity is unchanged, although volume is reduced; -Less effective when soil contains a high percentage of silt and clay; -Costs associated with the disposal of

		the subsequent waste streams must be considered.
Soil Vapour Extraction (physicalchemical)	- Proven performance, readily available equipment, easy to install; - Minimal disturbance to site operations; - Short treatment times (6-48 months).	-Concentration reductions greater than 90% are difficult to achieve; -Effectiveness decreases when applied to sites with low permeability; -Only treats the unsaturated zone; -May require costly treatment for atmospheric discharge of the extracted vapor.
Electrokinetic (others)	-In situ technology that has small impact on environment (soil removal is not required). -Metals are actually removed from soil unlike stabilization, which leaves the metals in the soil.	-Alkaline soils reduce the effectiveness of the process; -Requires soil moisture.

These factors have made this one of the most commonly used treatment technologies (EPA, 1993b; Mirsal, 2008). However, *ex-situ* bioremediation involves the excavation and the treatment of the contaminated soil somewhere else, which makes it less cost-effective (Donlon and Bauder, 2008; Pare, 2006; Schacht and Ajibo, 2002). *Ex-situ* treatment technology is further divided into slurry-phase bioremediation and solid-phase bioremediation.

2.1. Slurry-phase Bioremediation

Slurry-Phase bioremediation, also known as bioreactors, is a controlled treatment that involves the excavation of the contaminated soil, mixing it with

water and placing it in a bioreactor. Fig. 1 shows a typical bioreactor system (FRTR, 2000).

As shown in the figure, the process requires the processing of the soil to provide a low viscosity. This processing involves the separation of stones and rubbles from the contaminated soil. Next, the soil is mixed with a predetermined water amount to form the slurry. The concentration of water added depends on the concentration of pollutants, the rate of biodegradation, and the physical nature of the soil (EPA, 2003; Hyman and Dupont, 2001).

When this process is done the soil is removed and dried up using pressure filters, vacuum filters or centrifuges. The next procedure is the disposition of the soil and further treatment of the resulting fluids.

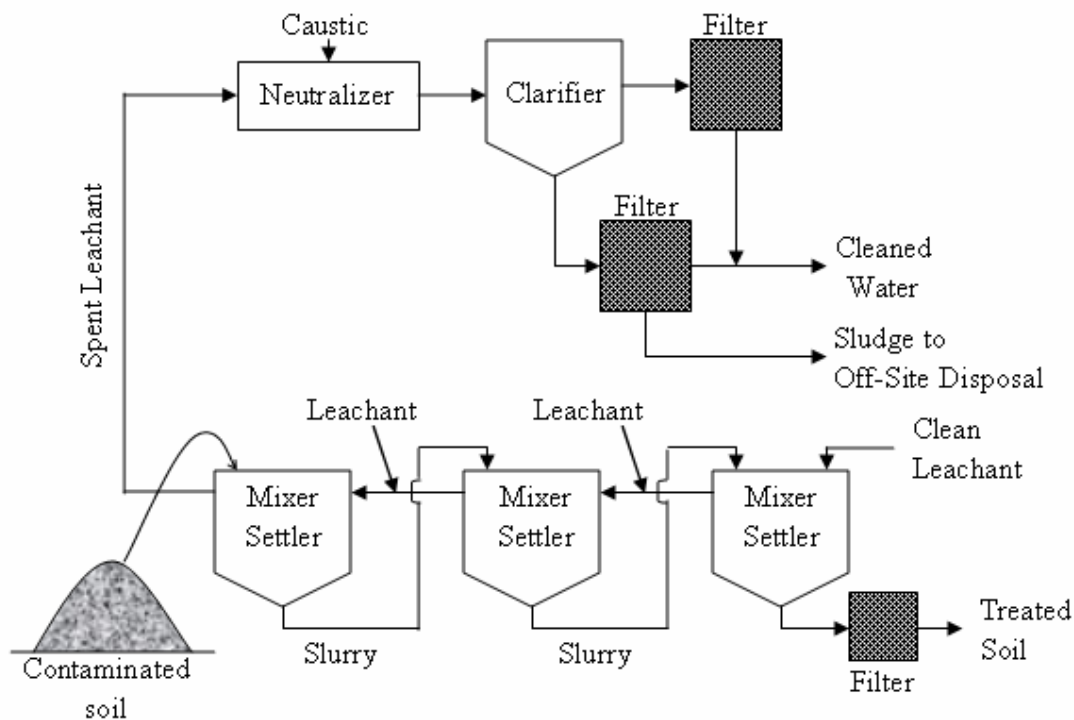


Fig. 1. Bioreactor system (FRTR, 2000)

2.2. Solid-phase bioremediation

Solid-Phase bioremediation is an ex-situ technology in which the contaminated soil is excavated and placed into piles. Bacterial growth is stimulated through a network of pipes that are distributed throughout the piles (Hyman and Dupont, 2001). By pulling air through the pipes the necessary ventilation is provided for microbial respiration.

Moisture is introduced by spraying the soil with water. Solid-phase systems require a large amount of space, and cleanups require more time to complete than with slurry-phase processes (EPA, 2001). Some solid-phase treatment processes include land farming, soil biopiles, and composting.

2.2.1. Landfarming

Landfarming, also known as land treatment, is a bioremediation technique that involves the excavation of the contaminated soil and spreading it on a thin surface. Biodegradation of pollutants is stimulated aerobically by tilling or plowing the soil. Nutrients and minerals are also added to promote the growth of the indigenous species. Fig. 2 is a schematic representation of the landfarming system.

According to The United States Environmental Protection Agency (EPA) report on underground storage tanks (EPA, 2003), before the remediation takes place the site must be prepared by clearing and grading the soil, by installing leachate collection and treatment systems, and also building vapor treatment facilities.

Also, the report states that if a contaminated soil is less than three feet then there is no need for excavation.

As it can be seen in the figure, while soil moisture is controlled by periodically sprinkling soil with water, building barriers or terraces around the contaminated soil controls erosion.

Sprinkling with water also minimizes the dust created while tilling the soil to promote aeration (Rubinos et al., (2007).

2.2.2. Soil biopiles

Soil biopiles, also known as biocells, is a biodegradation technique used for the remediation of excavated soil contaminated with petroleum contents. This technology involves the accumulation of contaminated soil into piles and the stimulation of microbial activity either aerobically or by the addition of nutrients, minerals or moisture. A typical height of biopiles is between three and ten feet.

Biopiles are in a way similar to landfarms due to the fact that this technology also uses oxygen as a way to stimulate bacterial growth. However, while tilling or plowing aerates land farms, biopiles are aerated by forcing air to move by injection through perforated piping placed throughout the pile (EPA, 2003). A schematic of this technology can be seen in Fig. 3. As it can be seen in the figure, the contaminated soil is piled up to a depth of a few feet and then the piping, which provides aeration, is laid down. The next load of contaminated soil is then added. This process continues until the desired pile height is achieved. The soil is usually mixed with a bulking agent (straws) to improve aeration and therefore enhance the growth of the microbial population.

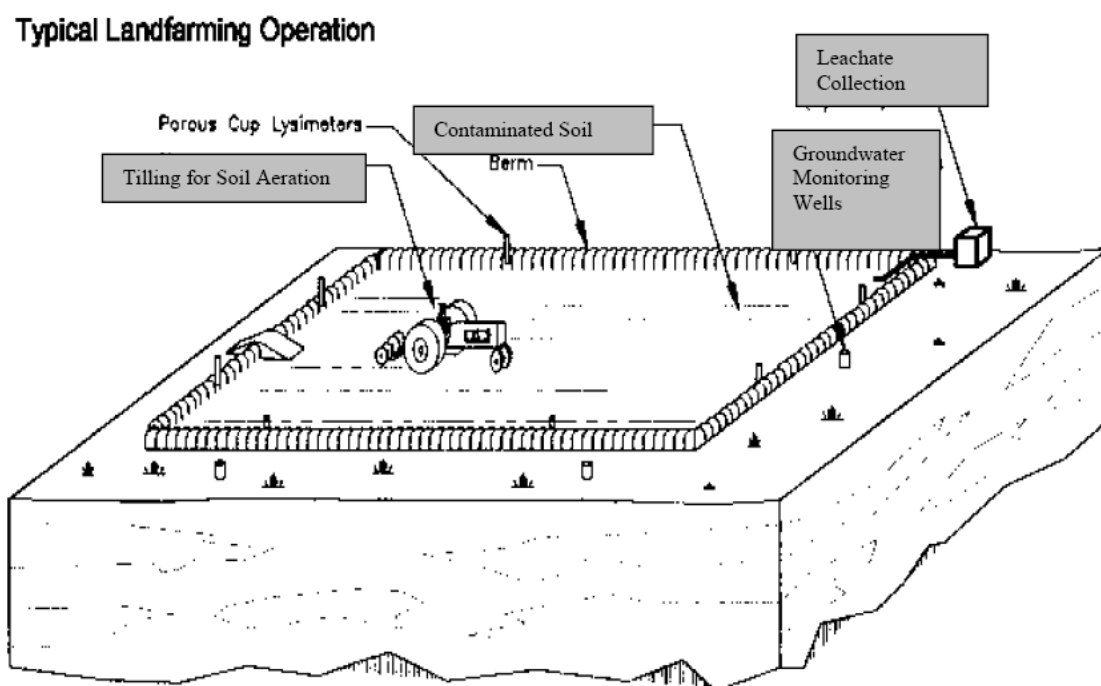


Fig. 2. Landfarming (FRTR, 2000)

Since air is also injected into the soil there is the possibility for evaporation or volatilization of contaminants. To counter this problem, the system also includes the monitoring and containment of soil vapors.

2.2.3. Composting

Composting involves mixing the contaminated soil with a bulking agent such as straw, hay, or corncobs to make it easier to deliver the optimum levels of air and water to the microorganisms. The most common designs are static pile composting, mechanically agitated composting, and window composting.

In static pile composting the contaminated soil is placed into piles and aerated with blowers or vacuum pumps. Mechanically agitated composting involves the placement of the contaminated soil in treatment vessels where it is mixed to achieve aeration. In window composting, the soil is placed in long piles known as windows and periodically mixed by tractors (Cunningham, 2000).

As stated before, the contaminated soil is mixed with a bulking agent or compost to enhance bacterial growth. A typical ratio of soil to compost is 75% contaminated soil to 25% compost. This ratio is changeable depending on the soil type, contaminants level and characteristics. After mixing, the soil is covered to protect it from erosion and to maintain the proper moisture and temperature necessary for bacterial growth.

Compost remediation is known to have faster cleanup results since cleanup can be estimated in terms of weeks instead of months.

2.3. Factors affecting biodegradation

A. Soil water

Water present in soil affects not only the moisture available to microorganisms, but also the soil aeration status, the nature and amount of soluble, osmotic pressure and the pH. Water activity in the soil is measured in terms of potential (matrix and osmotic). Matrix potential is the capability of water to adsorb to solid surfaces. This potential is usually negative because it reduces the free energy of water. Osmotic potential in the other hand is related to solubility. Since water is a universal solvent, the presence of solute in the soil tend to also reduce the free energy of water and create another negative potential (Subhas and Irvine, 1998).

The sum of osmotic and matrix potentials describe the water availability, and as a result will define how much energy must a microorganism spend to obtain water. Microbial activity is known to have maximum reaction rates at water potentials of -0.01Mpa (megapascals); however, these rates tend to decrease if the soil becomes either waterlogged (near zero Mpa) or drier, at negative water potentials. Fig. 4 shows the relation between water potential and bacterial reaction rates.

B. Redox Potential

Bacteria obtain their energy from oxidation and reduction of compounds present in the soil by removing electrons from these compounds in order to obtain the energy available during the oxidation process.

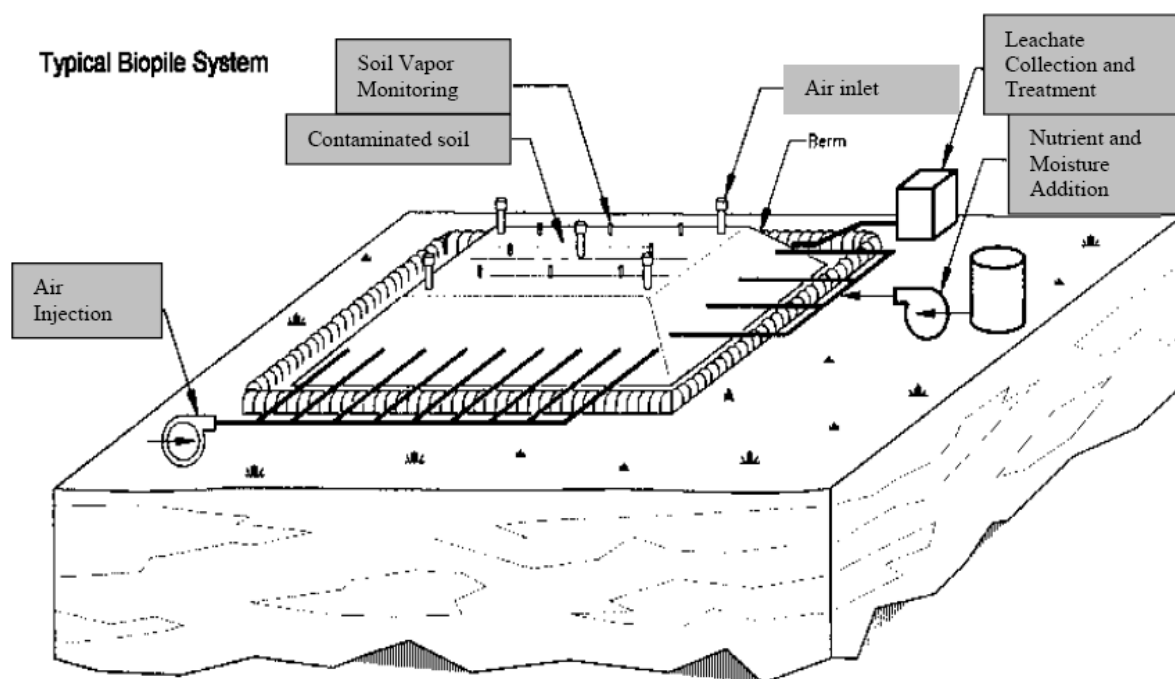


Fig. 3. Biopile system (FRTR, 2000)

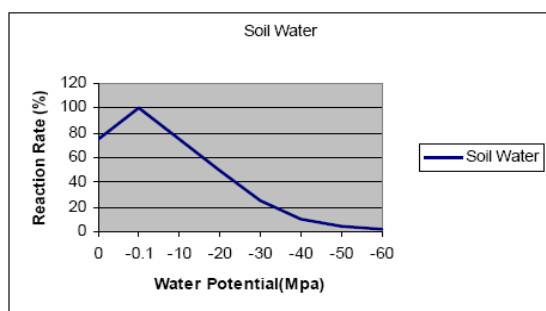


Fig. 4. Relation between water potential and bacterial reaction rates (Subhas and Irvine, 1998)

This process depends largely on a compound that can accept electrons. When talking about aerobic degradation the final electron acceptor is oxygen.

C. Soil pH

Soil pH values are somewhat related to the size of the organisms present and the multiplicity of enzymes at the microbial level (Schacht and Ajibo, 2002). Bacteria tend to have optimum pH between 6.5 and 7.5, which equals the intracellular pH. The biodegradation of a compound is dependent on specific enzymes, which are secreted by the organisms. These enzymes are largely pH dependent (Singh et al, 2003; Hyman and Dupont, 2001).

D. Soil temperature

Temperature is one of the major factors affecting the biodegradation of a toxic compound. It not only affects the rates of biochemical reactions in the organisms, but also the soil moisture, and redox potential. All microbial activities are dependent upon the laws of thermodynamics. At too high temperatures there is a denaturing of the proteins and the cell membrane permeability. It is generally known that metabolism tends to slow down at low temperatures; however, psychrophiles, bacteria which grow in cold temperatures, are capable of degrading contaminants due to osmotic regulations and cytoplasm constituents that prevent the bacteria's cell interior from freezing. Fig. 5 shows the bacterial response to temperature variations.

3. Ex-situ physical/chemical treatment

Available *ex-situ* physical/chemical treatment technologies include (EPA, 1993a ; FRTR, 2000 ; Gavrilescu, 2006):

- chemical reduction/oxidation
- dehalogenation
- soil washing
- fluid vapor extraction
- stabilization/solidification
- solvent extraction

3.1. Chemical reduction/oxidation

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to

nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert. Redox reactions involve the transfer of electrons from one compound to another (Wang and Li, 2007). Specifically, one reactant is oxidized (loses electrons) and one is reduced (gains electrons) (FRTR, 2000; Pare, 2006).

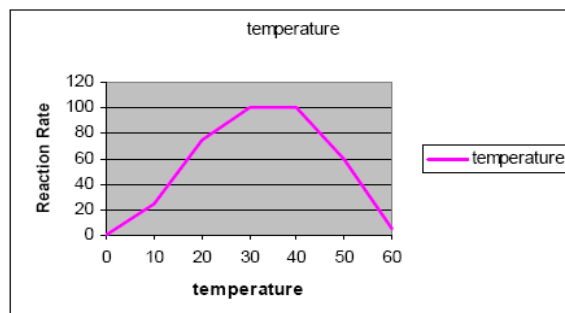


Fig. 5. Temperature vs. chemical reactions (Subhas and Irvine, 1998)

Chemical oxidation reactions involve the transfer of electrons and the breaking of chemical bonds. Oxidants are generally non-specific and will react with the targeted contaminants and with the soil organic content (Pare, 2006). The oxidizing agents most commonly used for treatment of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical redox is a full-scale, well-established technology used for disinfection of drinking water and wastewater, and it is a common treatment for cyanide wastes (Fig. 6.). Enhanced systems are now being used more frequently to treat contaminants in soils (EPA, 1991). The target contaminant group for chemical redox is inorganics. The technology can be used but may be less effective against nonhalogenated VOCs and SVOCs, fuel hydrocarbons, and pesticides (Mayer et al., 1990).

Factors that may limit the applicability and effectiveness of the process include:

- incomplete oxidation or formation of intermediate contaminants may occur depending upon the contaminants and oxidizing agents used.
- the process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required.
- oil and grease in the media should be minimized to optimize process efficiency.

3.2.1. Dehalogenation (base - catalyzed decomposition (BCD))

The dehalogenation [base -catalyzed decomposition (BCD)] process was developed by EPA's Risk Reduction Engineering Laboratory (RREL), in cooperation with the National Facilities Engineering Services Center (NFESC) to remediate soils and sediments contaminated with chlorinated organic compounds, especially PCBs, dioxins, and furans.

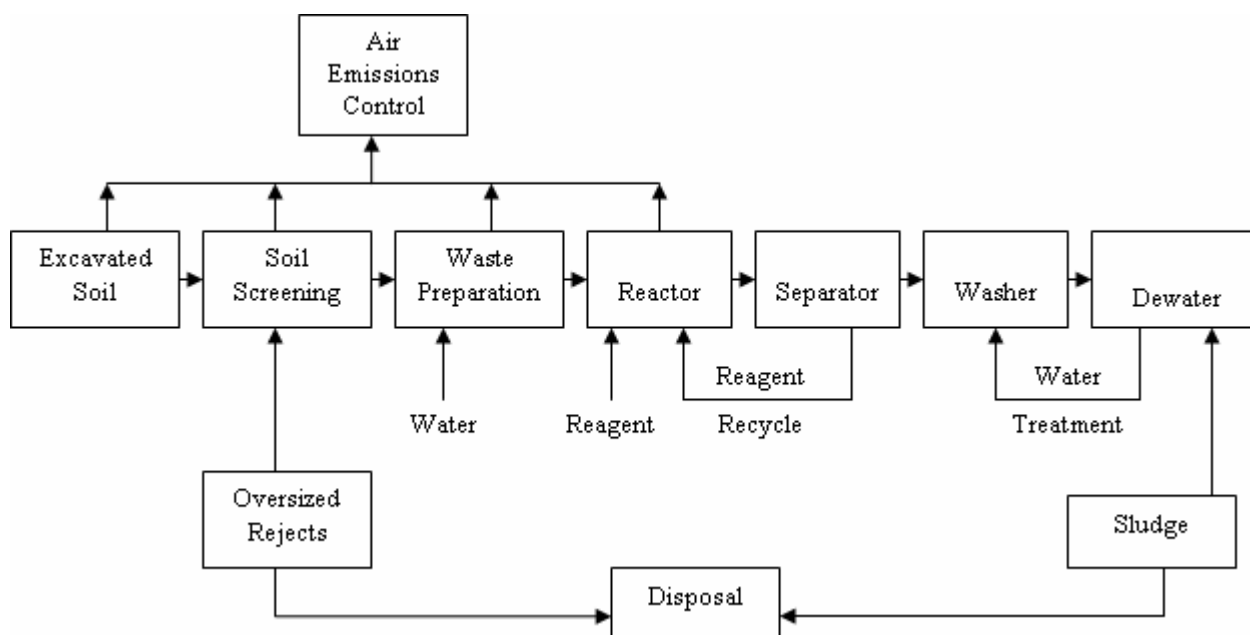


Fig. 6. Schematic representation of Chemical Reduction/oxidation process (<http://www.frtr.gov/matrix2/section4/D01-4-16.gif>)

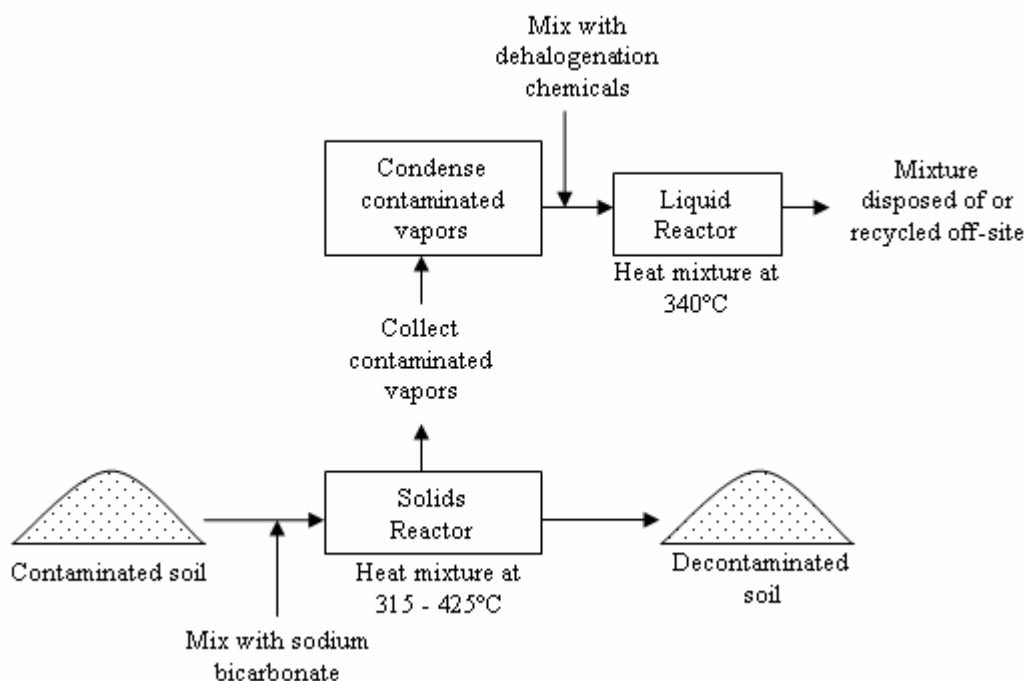


Fig. 7. Dehalogenation (base – catalyzed decomposition (BCD)) process

Contaminated soil is screened, processed with a crusher and pug mill, and mixed with sodium bicarbonate. The mixture is heated to above 330°C in a rotary reactor to decompose and partially volatilize the contaminants, as it is shown in Fig. 7 (EPA, 1992).

The contaminant is partially decomposed rather than being transferred to another medium. Whereas alkaline polyethylene glycol (APEG)

residuals contain chlorine and hydroxyl groups, which make them water – soluble and slightly toxic, the BCD process produces primarily biphenyl and low-boiling point olefins, which are not water – soluble and are much less toxic, and sodium chloride (Donald et al., 2007).

The target contaminant groups for dehalogenation (BCD) are halogenated SVOCs and pesticides. The technology can be also used to treat

halogenated VOCs but will generally be more expensive than other alternative technologies.

The applicability and effectiveness of the process can be limited by high clay and moisture content will increase treatment costs.

3.2.2. Dehalogenation

Dehalogenation is a full-scale technology in which an alkaline polyethylene glycol (APEG) reagent is used to dehalogenate halogenated aromatic compounds in a batch reactor (Fig. 8) (FRTR, 2000). Potassium polyethylene glycol (KPEG) is the most common APEG reagent. Contaminated soils and the reagent are mixed and heated in a treatment vessel. In the APEG process, the reaction causes the polyethylene glycol to replace halogen molecules and render the compound nonhazardous or less toxic (EPA, 1990). For example, the reaction between chlorinated organics and KPEG causes replacement of a chlorine molecule and results in a reduction in toxicity. Dehalogenation (APEG/KPEG) is generally considered a standalone technology; however, it can be used in combination with other technologies. Treatment of the wastewater generated by the process may include chemical oxidation, biodegradation, carbon adsorption, or precipitation (Soesilo and Wilson, 1997).

The metal hydroxide that has been most widely used for this reagent preparation is potassium hydroxide (KOH) in conjunction with polyethylene glycol (PEG) (typically, average molecular weight of 400) to form a polymeric alkoxide referred to as KPEG.

Sodium hydroxide has also been used in the past, however, and most likely will find increasing use in the future because of patent applications that have been filed for modification to this technology. This new approach will expand the technology's applicability and efficacy and should reduce chemical costs by facilitating the use of less costly sodium hydroxide.

A variation of this reagent is the use of potassium hydroxide or sodium hydroxide/tetraethylene glycol, referred to as ATEG, that is more effective on halogenated aliphatic compounds. In some KPEG reagent formulations, dimethyl sulfoxide (DMSO) is added to enhance reaction rate kinetics, presumably by improving rates of extraction of the haloaromatic contaminants.

Previously developed dehalogenation reagents involved dispersion of metallic sodium in oil or the use of highly reactive organosodium compounds. The reactivity of metallic sodium and these other reagents with water presented a serious limitation to treating many waste matrices; therefore, these other reagents are not discussed here and are not considered APEG processes. The reagent (APEG) dehalogenates the pollutant to form a glycolether and/or a hydroxylated compound and an alkali metal salt, which are water-soluble byproducts.

The target contaminant groups for glycolate dehalogenation are halogenated SVOCs and pesticides. The technology can be used but may be less effective against selected halogenated VOCs. APEG dehalogenation is one of the few processes available other than incineration that has been successfully field tested in treating PCBs. The technology is amenable to small-scale applications.

Factors that may limit the applicability and effectiveness of the process include:

- the technology is generally not cost-effective for large waste volumes.
- media water content above 20% requires excessive reagent volume.
- concentrations of chlorinated organics greater than 5% require large volumes of reagent.

The concentrations of PCBs that have been treated are reported to be as high as 45,000 ppm.

Concentrations were reduced to less than 2 ppm per individual PCB congener. PCDDs and PCDFs have been treated to nondetectable levels at part per trillion sensitivity.

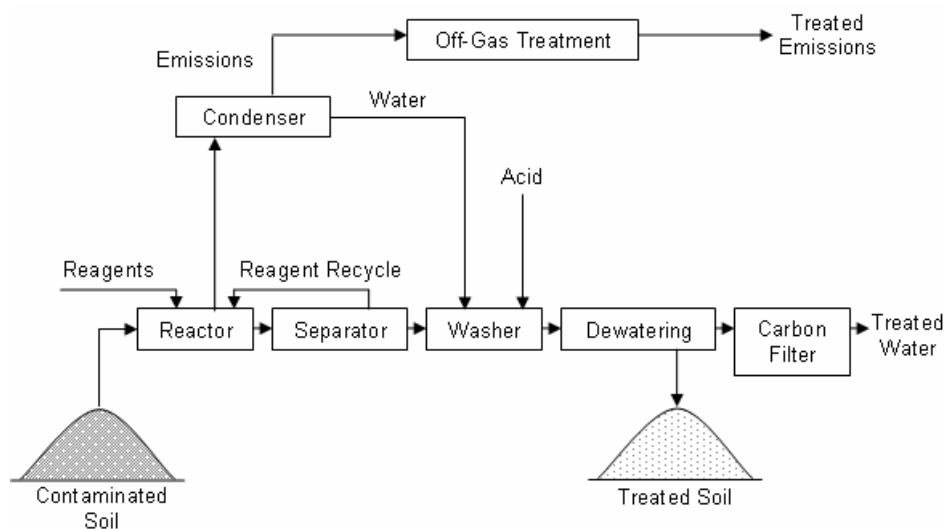


Fig. 8. Dehalogenation (glycolate) process

The process has successfully destroyed PCDDs and PCDFs contained in contaminated pentachlorophenol oil. For a contaminated activated carbon matrix, direct treatment was less effective, and the reduction of PCDDs/PCDFs to concentrations less than 1 ppb was better achieved by first extracting the carbon matrix with a solvent and then treating the extract.

3.3. Soil washing

Soil washing is a water-based process for scrubbing soils *ex situ* to remove contaminants. The process, Figure 9, removes contaminants from soils in one of two ways:

- By dissolving or suspending them in the wash solution (which is later treated by conventional wastewater treatment methods).
- By concentrating them into a smaller volume of soil through particle size separation, gravity separation, and attrition scrubbing (similar to those techniques used in sand and gravel operations) (Raghavan et al., 1989).

Soil washing systems incorporating most of the removal techniques offer the greatest promise for application to soils contaminated with a wide variety of heavy metal, radionuclides, and organic contaminants.

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion.

Washing processes that separate the fine (small) clay and silt particles from the coarser sand and gravel soil particles, effectively separate and concentrate the contaminants into a smaller volume of soil that can be further treated or disposed off. Gravity separation is effective for removing high or

low specific gravity particles such as heavy metal-containing compounds (lead, radium oxide, etc.). Attrition scrubbing removes adherent contaminant films from coarser particles. The clean, larger fraction can be returned to the site for continued use (EPA, 1992).

The target contaminant groups for soil washing are SVOCs, fuels, and inorganics. The technology can be used on selected VOCs and pesticides. The technology offers the potential for recovery of metals and can clean a wide range of organic and inorganic contaminants from coarse-grained soils. Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000; Raghavan et al., 1989):

- fine soil particles (e.g., silt, clays) may require the addition of a polymer to remove them from the washing fluid.
- complex waste mixtures (e.g., metals with organics) make formulating washing fluid difficult.
- high humic content in soil may require pretreatment.
- the aqueous stream will require treatment

Soil washing is most commonly used in combination with the following technologies: bioremediation, incineration, and solidification/stabilization. Depending on the process used, the washing agent and soil fines are residuals that require further treatment. When contaminated fines have been separated, coarse-grain soil can usually be returned clean to the site.

3.4. Ex-situ soil vapor extraction (SVE)

Ex situ soil vapor extraction (SVE), Fig. 10, is a full-scale technology in which soil is excavated and placed over a network of aboveground piping to which a vacuum is applied to encourage volatilization of organics (Hyman and Dupont, 2001).

The process includes a system for handling off-gases.

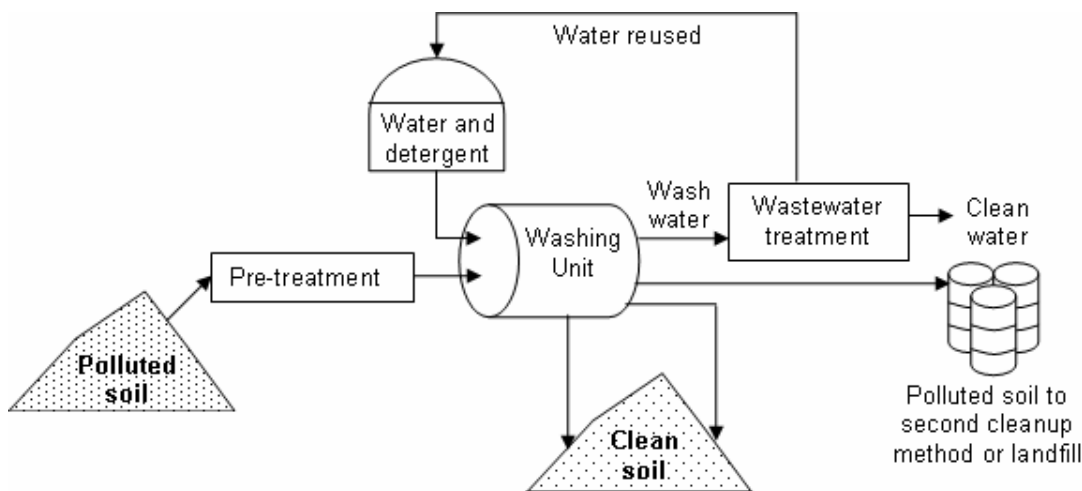


Fig. 9. Soil washing system

Advantages over its in situ counterpart include that the excavation process forms an increased number of passageways, shallow groundwater no longer limits the process, leachate collection is possible, and treatment is more uniform and easily monitored (EPA, 1990).

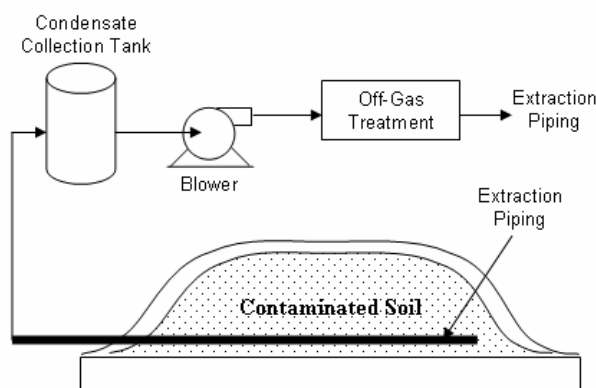


Fig. 10. Ex-situ soil vapor extraction (SVE) system

The target contaminant group for ex situ SVE is VOCs. The following factors may limit the applicability and effectiveness of the process (FRTR, 2000):

- air emissions may occur during excavation and materials handling, possibly requiring treatment.
- high humic content or compact soil inhibits volatilization.
- as a result of air emission treatment, SVE may require treating residual liquid and spent activated carbon, increasing the project cost.
- a large amount of space is required (Raghavan et al., 1989).

An advantage of the technology over its in situ counterpart is the increased number of passageways formed by the excavation process; however, as an ex situ remedy, the excavation associated with SVE poses a potential health and safety risk to site workers through skin contact and air emissions (James and Kovalick, 2001; Hyman and Dupont, 2001). Personal protective equipment, at a level commensurate with the contaminants involved, is normally required during excavation operations. The time required to remediate a site using ex situ SVE is highly dependent upon the specific soil and chemical properties of the contaminated media.

3.5. Solidification/stabilization

As for in situ solidification/stabilization (S/S), ex situ S/S contaminants are physically bound or enclosed within a stabilized mass (solidification), or chemical reactions are induced between the stabilizing agent and contaminants to reduce their mobility (stabilization) (Bricka et al., 1988). Ex situ

S/S, however, typically requires disposal of the resultant materials (Fig. 11).

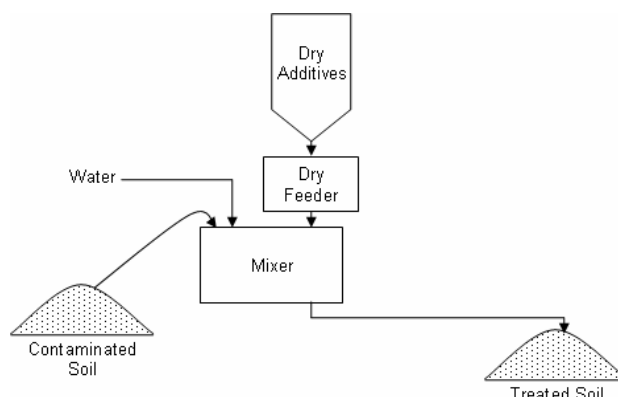


Fig. 11. Ex-situ solidification/stabilization

The target contaminant group for ex situ S/S is inorganics, including radionuclides. The technology has limited effectiveness against SVOCs and pesticides; however, systems designed to be more effective against organic contaminants are being developed and tested (Swarnalatha et al., 2006).

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- Environmental conditions may affect the long-term immobilization of contaminants.
- Some processes result in a significant increase in volume (up to double the original volume).
- Certain wastes are incompatible with different processes. Treatability studies are generally required.
- VOCs are generally not immobilized.
- Long-term effectiveness has not been demonstrated for many contaminant/process combinations (Raghavan et al., 1989).

Depending upon the original contaminants and the chemical reactions that take place in the ex situ S/S process, the resultant stabilized mass may have to be handled as a hazardous waste. For certain types of radioactive waste, the stabilized product must be capable of meeting stringent waste form requirements for disposal (e.g., Class B or Class C low level materials) (EPA, 1993a).

3.6. Solvent extraction

Solvent extraction does not destroy wastes but is a means of separating hazardous contaminants from soils, sludges and sediments, thereby reducing the volume of the hazardous waste that must be treated. The technology uses an organic chemical as a solvent and differs from soil washing, which generally uses water or water with wash-improving additives (Raghavan et al., 1988). Commercial scale units are in operation; they vary in regard to the solvent employed, type of equipment used, and mode of operation.

Solvent extraction is commonly used in combination with other technologies, such as solidification/stabilization, incineration, or soil washing, depending upon site-specific conditions. It also can be used as a standalone technology in some instances. Organically bound metals can be extracted along with the target organic contaminants, thereby creating residuals with special handling requirements. Traces of solvent may remain within the treated soil matrix, so the toxicity of the solvent is an important consideration. The treated media are usually returned to the site after having met Best Demonstrated Available Technology (BDAT) and other standards.

Solvent extraction has been shown to be effective in treating sediments, sludges and soils containing primarily organic contaminants such as PCBs, VOCs, halogenated solvents, and petroleum wastes. The technology is generally not used for extracting inorganics (i.e., acids, bases, salts, or heavy metals). Inorganics usually do not have a detrimental effect on the extraction of the organic components, and sometimes metals that pass through the process experience a beneficial effect by changing the chemical compound to a less toxic or leachable form. The process has been shown to be applicable for the separation of the organic contaminants in paint wastes, synthetic rubber process wastes, coal tar wastes, drilling muds, wood – treating wastes, separation sludges, pesticide/insecticide wastes, and petroleum refinery oily wastes (EPA, 1990).

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- organically bound metals can be extracted along with the target organic pollutants, which restrict handling of the residuals.
- the presence of detergents and emulsifiers can unfavorably influence the extraction performance.
- traces of solvent may remain in the treated solids; the toxicity of the solvent is an important consideration.
- solvent extraction is generally least effective on very high molecular weight organic and very hydrophilic substances.

- some soil types and moisture content levels will adversely impact process performance.

4. Ex-situ thermal treatment

Ex situ thermal treatment generally involves the destruction or removal of contaminants through exposure to high temperature in treatment cells, combustion chambers, or other means used to contain the contaminated media during the remediation process (http://www.clu-in.org/techfocus/default.focus/sec/Thermal_Treatment:_Ex_Situ/cat/Overview/). It includes:

- hot gas decontamination
- incineration
- open burn/open detonation
- pyrolysis
- thermal desorption
- Ex-situ Vitrification

4.1. Hot gas decontamination

The process involves raising the temperature of the contaminated equipment or material to 260°C for a specified period of time. The gas effluent from the material is treated in an afterburner system to destroy all volatilized contaminants (Fig. 13). The method eliminates a waste that currently is stockpiled and requires disposal as a hazardous material. This method will permit reuse or disposal of scrap as nonhazardous material (Topfer, 1995).

Consideration is being given to applying the hot gases to explosives – contaminated underground piping in situ. Hot gas decontamination can also be used for decontamination of explosives – contaminated masonry or metallic structures.

The method involves sealing and insulating the structures, heating with hot gas stream to 260°C for a prescribed period of time, volatilizing the explosive contaminants, and destroying them in an afterburner. Operating conditions are site – specific. Contaminants are completely destroyed (Hyman and Dupont, 2001; Raghavan et al., 1989).

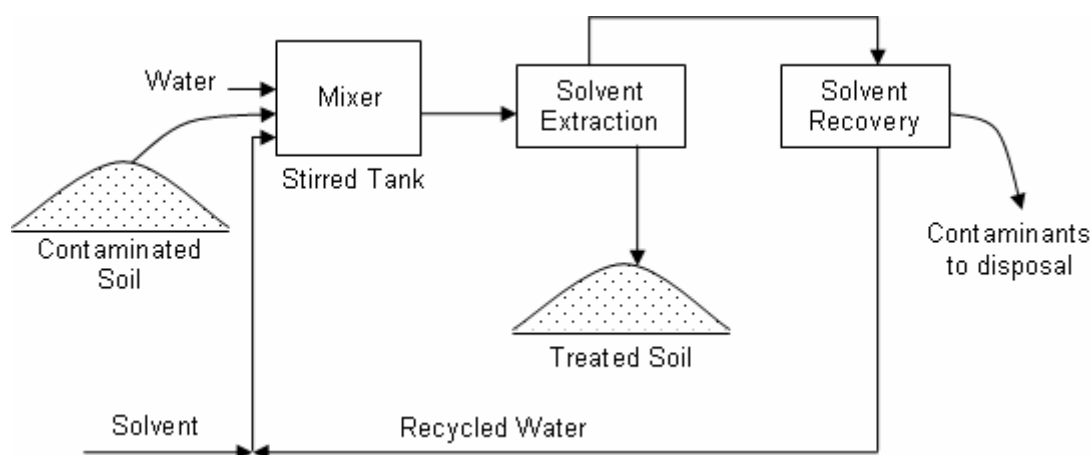


Fig. 12. Solvent extraction process

The method is applicable for process equipment requiring decontamination for reuse. It is also applicable for explosive items, such as mines and shells, being demilitarized (after removal of explosives) or scrap material contaminated with explosives.

The method can also be used for buildings or structures associated with ammunition plants, arsenals, and depots involved in the manufacture, processing, loading, and storage of pyrotechnics, explosives, and propellants.

The following factors may limit the applicability and effectiveness of the process:

- the costs of this method are higher than open burning.
- flash chamber design must take into consideration possible explosions from improperly demilitarized mines or shells.
- the rate at which equipment or material can be decontaminated is slower than that for open burning.

4.2. Incineration

High temperatures, 870 to 1,200°C, are used to volatilize and combust (in the presence of oxygen) halogenated and other refractory organics in hazardous wastes. The destruction and removal

efficiency (DRE) for properly operated incinerators exceeds the 99.99% requirement for hazardous waste and can be operated to meet the 99.9999% requirement for PCBs and dioxins (EPA, 1987).

Commercial incinerator designs are rotary kilns, equipped with an afterburner, a quench, and an air pollution control system, Figure 14. The rotary kiln is a refractory-lined, slightly-inclined, rotating cylinder that serves as a combustion chamber and operates at temperatures up to 980°C. An experimental unit, the circulating fluidized bed (CFB), uses high-velocity air to circulate and suspend the waste particles in a combustion loop and operates at temperatures up to 870°C. Another experimental unit, the infrared unit uses electrical resistance heating elements or indirect – fired radiant U-tubes to heat material passing through the chamber on a conveyor belt and operates at temperatures up to 870°C (Soesilo and Wilson 1997).

Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (HCl, NO_x, and SO_x). Baghouses, venturi scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases. Limestone or caustic solution added to the combustor loop removes acid gases in the CFB.

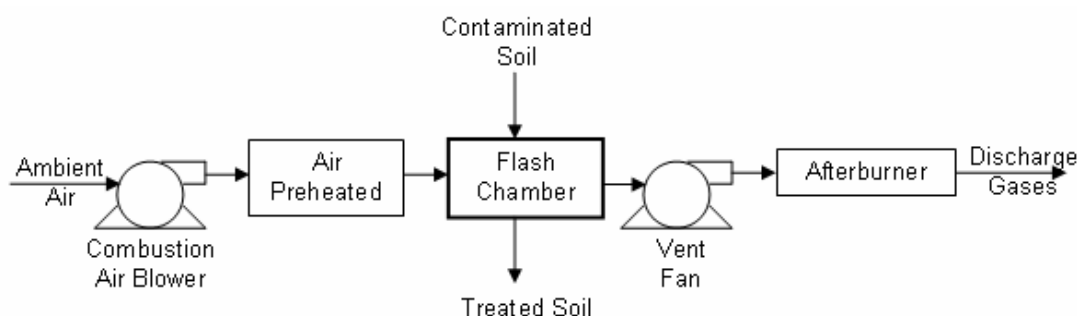


Fig. 13. Hot gas decontamination

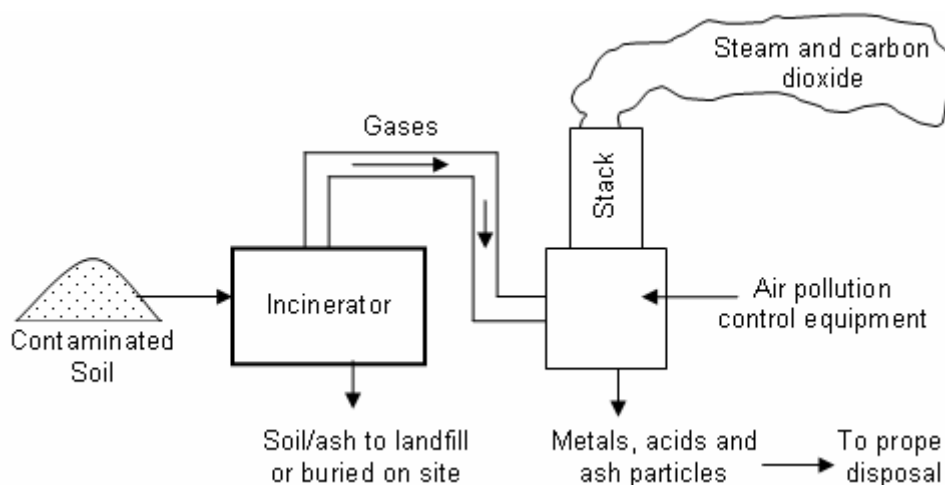


Fig. 14. Incineration process

Incineration is used to remediate soils contaminated with explosives and hazardous wastes, particularly chlorinated hydrocarbons, PCBs, and dioxins. Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- only one off-site incinerator is permitted to burn pcbs and dioxins.
- there are specific feed size and materials handling requirements that can impact applicability or cost at specific sites.
- heavy metals can produce a bottom ash that requires stabilization.
- volatile heavy metals, including lead, cadmium, mercury, and arsenic, leave the combustion unit with the flue gases and require the installation of gas cleaning systems for removal.
- metals can react with other elements in the feed stream, such as chlorine or sulfur, forming more volatile and toxic compounds than the original species. such compounds are likely to be short-lived reaction intermediates that can be destroyed in a caustic quench.
- sodium and potassium form low melting point ashes that can attack the brick lining and form a sticky particulate that fouls gas ducts.

If an off-site incinerator is used, the potential risk of transporting the hazardous waste through the community must be considered.

4.3. Open burn (OB) and open detonation (OD)

Open burn (OB) and open detonation (OD), operations are conducted to destroy unserviceable, unstable, or unusable munitions and explosive materials. In OB operations, explosives or munitions are destroyed by self-sustained combustion, which is ignited by an external source, such as flame, heat, or a detonation wave (that does not result in a detonation). In OD operations, Fig. 15, detonatable explosives and munitions are destroyed by a detonation, which is initiated by the detonation of a disposal charge (Teer et al., 1993).

OB/OD operations can destroy many types of explosives, pyrotechnics, and propellants. OB areas must be able to withstand accidental detonation of any or all explosives being destroyed, unless the operating OB technicians recognize that the characteristics of the materials involved are such that orderly burning without detonation can be ensured. Personnel with this type of knowledge must be consulted before any attempt is made at OB disposal, especially if primary explosives are present in any quantity.

OB and OD can be initiated either by electric or burning ignition systems. In general, electric systems are preferable because they provide better control over the timing of the initiation. In an electric system, electric current heats a bridge wire, which ignites a primary explosive or pyrotechnic, which, in turn, ignites or detonates the material slated to be burned or detonated. If necessary, safety fuses, which

consist of propellants wrapped in plastic weather stripping, are used to initiate the burn or detonation (USAMC, 1985).

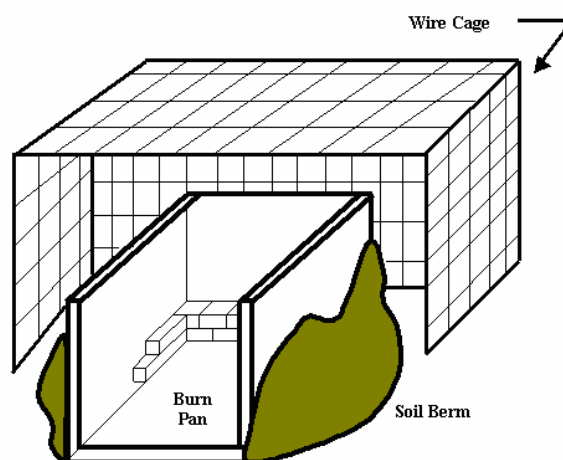


Fig. 15. Open burn (OB) and open detonation (OD)

OB/OD can be used to destroy unserviceable, unstable, or unusable munitions and explosive materials. The applicability and effectiveness of the process could be limited by:

- minimum distance requirements for safety purposes mean substantial space is required.
- ob/od operations emissions are difficult to capture for treatment and may not be permitted in areas with emissions limitations.
- ob/od operations require that prevailing winds carry sparks, flame, smoke, and toxic fumes away from neighboring facilities. ob/od operations are never conducted during sand, snow, or electrical storms strong enough to produce static electricity, which might cause premature detonation.
- in addition, with growing ob/od restriction, dod's ability to treat energetic wastes is diminishing and energetic disposal may be eliminated.

4.4. Pyrolysis

Pyrolysis is formally defined as chemical decomposition induced in organic materials by heat in the absence of oxygen. In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen (Soesilo and Wilson 1997). Because some oxygen will be present in any pyrolytic system, nominal oxidation will occur. If volatile or semivolatile materials are present in the waste, thermal desorption will also occur, Fig. 16.

Pyrolysis transforms hazardous organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed carbon and ash. Pyrolysis of organic materials produce combustible gases, including carbon monoxide, hydrogen and methane and other

hydrocarbons. If the offgases are cooled, liquids condense producing an oil/tar residue and contaminated water. Pyrolysis typically occurs under pressure and at operating temperatures above 430°C. The pyrolysis gases require further treatment. The off-gases may be treated in a secondary combustion chamber, flared, and partially condensed. Particulate removal equipment such as fabric filters or wet scrubbers are also required.

Pyrolysis is an emerging technology. Although the basic concepts of the process have been validated, the performance data for an emerging technology have not been evaluated according to methods approved by EPA and adhering to EPA quality assurance/quality control standards (EPA, 1992).

The target contaminant groups for pyrolysis are SVOCs and pesticides. The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote-contaminated soils, hydrocarbon contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint waste. Pyrolysis systems may be applicable to a number of organic materials that "crack" or undergo a chemical decomposition in the presence of heat.

Pyrolysis has shown promise in treating organic contaminants in soils and oily sludges. Chemical contaminants for which treatment data exist include PCBs, dioxins, PAHs, and many other organics. Pyrolysis is not effective in either destroying or physically separating inorganics from the contaminated medium. Volatile metals may be removed as a result of the higher temperatures associated with the process but are similarly not destroyed.

The limitative factors for the applicability and effectiveness of the process include (FRTR, 2000):

- there are specific feed size and materials handling requirements that impact applicability or cost at specific sites.

- the technology requires drying of the soil to achieve a low soil moisture content (<1%).
- highly abrasive feed can potentially damage the processor unit.
- high moisture content increases treatment costs.
- treated media containing heavy metals may require stabilization.

4.5.1. High temperature thermal desorption (HTTD)

High temperature thermal desorption (HTTD) is a full – scale technology (Fig. 17), in which wastes are heated to 560°C to volatilize water and organic contaminants. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system. HTTD systems are physical separation processes and are not designed to destroy organics. Bed temperatures and typical residence times will cause selected contaminants to volatilize but not be oxidized (Anderson, 1993).

HTTD is frequently used in combination with incineration, solidification/stabilization, or dechlorination, depending upon site – specific conditions. The technology has proven it can produce a final contaminant concentration level below 5 mg/kg for the target contaminants identified (Khan et al., 2004).

The target contaminants are SVOCs, PAHs, PCBs, and pesticides; however, HTTD systems have varying degrees of effectiveness against the full spectrum of organic contaminants. VOCs and fuels also may be treated, but treatment may be less cost - effective. Volatile metals may be removed by HTTD systems. The presence of chlorine can affect the volatilization of some metals, such as lead. The process is applicable for the separation of organics from refinery wastes, coal tar wastes, wood-treating wastes, creosote – contaminated soils, hydrocarbon-contaminated soils, mixed (radioactive and hazardous) wastes, synthetic rubber processing wastes, and paint wastes.

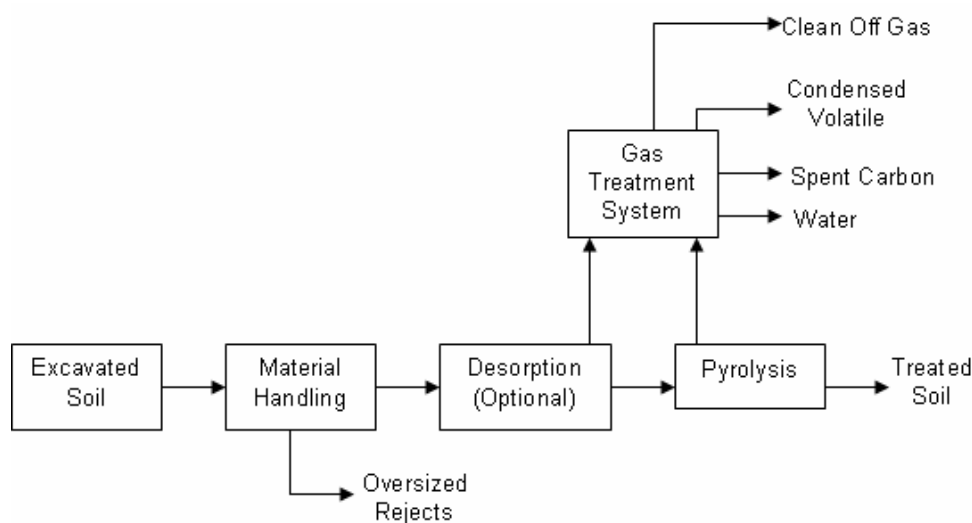


Fig. 16. Pyrolysis

The applicability and effectiveness of the process include could be limited by the following factors (FRTR, 2000; Johnson et al., 1987):

- feed particle size greater than 2 inches can impact applicability or cost at specific sites.
- dewatering may be necessary to reduce the amount of energy required to heat the soil.
- highly abrasive feed can potentially damage the processor unit.
- clay and silty soils and high humic content soils increase reaction time as a result of binding of contaminants

4.5.2. *Low temperature thermal desorption (LTTD)*

Low temperature thermal desorption (LTTD) systems are physical separation processes and are not designed to destroy organics. Wastes are heated to between 90 and 320°C to volatilize water and organic contaminants, Fig. 18. A carrier gas or vacuum system transports volatilized water and organics to the gas treatment system.

The bed temperatures and residence times designed into these systems will volatilize selected contaminants but will typically not oxidize them. LTTD is a full-scale technology that has been proven successful for remediating petroleum hydrocarbon contamination in all types of soil.

Contaminant destruction efficiencies in the afterburners of these units are greater than 95%. The same equipment could probably meet stricter requirements with minor modifications, if necessary. Decontaminated soil retains its physical properties and ability to support biological activity (Lighty et al., 1987).

Two common thermal desorption designs are the rotary dryer and thermal screw. Rotary dryers are horizontal cylinders that can be indirect - or direct fired.

The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot oil or steam circulates through the auger to indirectly heat the medium.

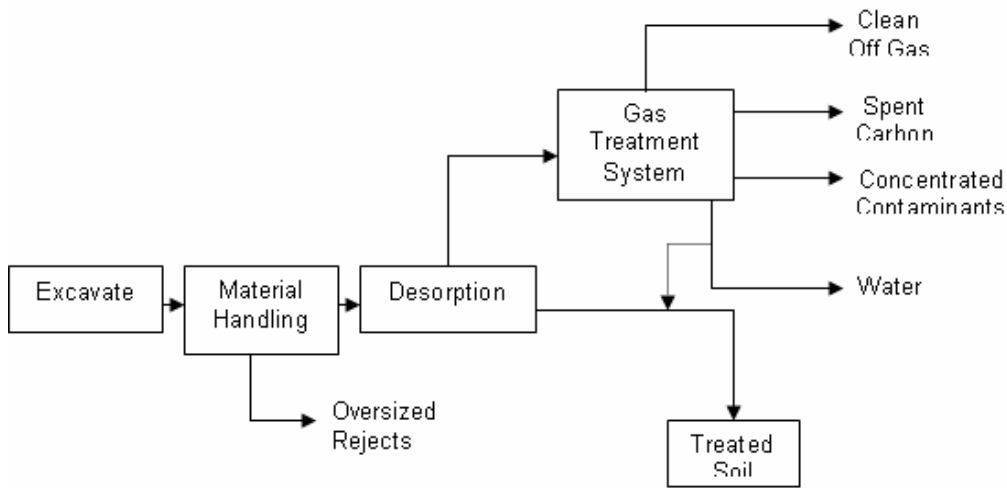


Fig. 17. High temperature thermal desorption (HTTD)

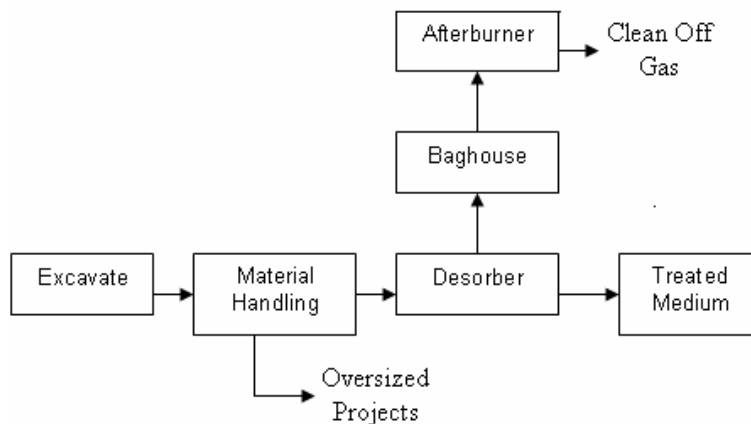


Fig. 18. Low temperature thermal desorption

All thermal desorption systems require treatment of the off-gas to remove particulates and contaminants. Particulates are removed by conventional particulate removal equipment, such as wet scrubbers or fabric filters. Contaminants are removed through condensation followed by carbon adsorption, or they are destroyed in a secondary combustion chamber or a catalytic oxidizer. Most of these units are transportable (EPA, 1994).

The target contaminant groups for LTDD systems are nonhalogenated VOCs and fuels. The technology can be used to treat SVOCs at reduced effectiveness. Factors that may limit the applicability and effectiveness of the process include:

- there are specific feed size and materials handling requirements that can impact applicability or cost at specific sites.
- dewatering may be necessary to achieve acceptable soil moisture content levels.
- highly abrasive feed potentially can damage the processor unit.
- heavy metals in the feed may produce a treated solid residue that requires stabilization.

All *ex-situ* soil thermal treatment systems employ similar feed systems consisting of a screening device to separate and remove materials greater than 5 centimeters, a belt conveyor to move the screened soil from the screen to the first thermal treatment chamber, and a weight belt to measure soil mass. Occasionally, augers are used rather than belt conveyors, but either type of system requires daily maintenance and is subject to failures that shut the system down. Soil conveyors in large systems seem more prone to failure than those in smaller systems. Size reduction equipment can be incorporated into the feed system, but its installation is usually avoided to minimize shutdown as a result of equipment failure.

Soil storage piles and feed equipment are generally covered as protection from rain to minimize soil moisture content and material handling problems. Soils and sediments with water contents greater than 20 to 25% may require the installation of a dryer in the feed system to reduce the energy cost to heat the soil.

Some volatilization of contaminants occurs in the dryer, and the gases are routed to a thermal treatment chamber.

4.6. Ex-situ vitrification

Ex-situ vitrification is designed to encapsulate inorganic contaminants, rather than reduce contaminant concentrations. Destruction of the organic contaminants present in the treated media, however, does occur because of temperatures achieved in the process (Fig. 19)(DOE, 1993).

Ex-situ vitrification is effective in reducing the mobility of the contaminated wastes within the media. The vitrified mass has high strength and resistance to leaching. The strength properties of material vitrified by different systems can vary widely. Systems in which the vitrified mass is quench-cooled may produce a more easily fractured mass than systems in which the mass is allowed to air cool. Systems in which fluxing agents are used will also have different strength properties. The composition of the soil that is vitrified may also affect the strength properties of the vitrified material.

Ex-situ vitrification is normally considered a standalone technology; however, its potential for use in treating the solid residuals from other technologies, such as incinerator ash, is receiving increasing attention (Circeo, 1991).

Ex-situ vitrification is applicable to the full range of contaminant groups, but inorganics is the target contaminant group. Metals, radionuclides, etc. are encapsulated in the vitrified mass, resisting leaching for geologic time periods.

Factors that may limit the applicability and effectiveness of the process include (FRTR, 2000):

- organic off-gases need to be controlled. some volatile heavy metal and radioactive contaminants may volatilize and require treatment in the off-gas system.
- use or disposal of the resultant vitrified slag is required.

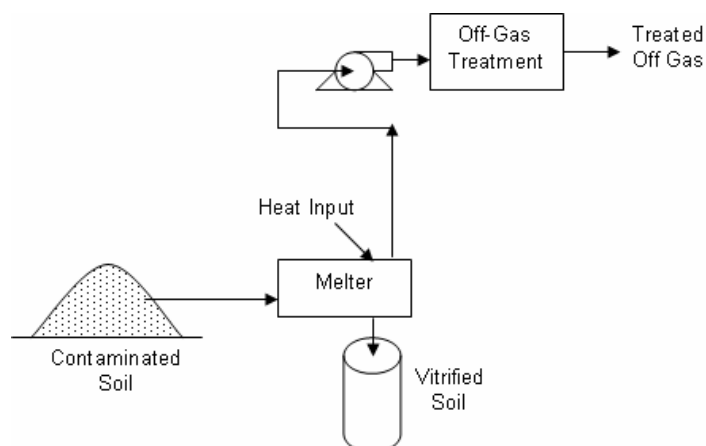


Fig. 19. Ex- situ vitrification

5. Excavation, retrieval, and off-site disposal

Contaminated material is removed and transported to permitted off-site treatment and/or disposal facilities. Some pretreatment of the contaminated media usually is required in order to meet land disposal restrictions (Church, 1981).

Excavation and off-site disposal is applicable to the complete range of contaminant groups with no particular target group. Although excavation and off-site disposal alleviates the contaminant problem at the site, it does not treat the contaminants.

Limiting factors that may limit the applicability and effectiveness of the process include:

- generation of fugitive emissions may be a problem during operations.
- the distance from the contaminated site to the nearest disposal facility will affect cost.
- depth and composition of the media requiring excavation must be considered.
- transportation of the soil through populated areas may affect community acceptability.
- disposal options for certain waste (e.g., mixed waste or transuranic waste) may be limited (EPA, 1991).

6. Conclusions

The main advantage of ex situ treatment is that it generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment because of the ability to homogenize, screen, and continuously mix the soil. However, ex situ treatment requires excavation of soils, leading to increased costs and engineering for equipment, possible permitting, and material handling/worker exposure considerations.

Bioremediation techniques are destruction or transformation techniques directed toward stimulating the microorganisms to grow and use the contaminants as a food and energy source by creating a favorable environment for the microorganisms. Generally, this means providing some combination of oxygen, nutrients, and moisture, and controlling the temperature and pH. Sometimes, microorganisms adapted for degradation of the specific contaminants are applied to enhance the process.

Biological processes are typically easily implemented at low cost. Contaminants can be destroyed or transformed, and little to no residual treatment is required; however, the process requires more time and difficult to determine whether contaminants have been destroyed. Biological treatment of PAHs leaves less degradable PAHs (cPAHs) behind. These higher molecular cPAHs are classified as carcinogens. Also, an increase in chlorine concentration leads to a decrease in biodegradability. Some compounds, however, may be broken down into more toxic by-products during the bioremediation process.

An advantage over the in situ applications is that in ex situ applications, these byproducts are contained in the treatment unit until nonhazardous end-products are produced. Although not all organic compounds are amenable to biodegradation, bioremediation techniques have been successfully used to remediate soils, sludges, and groundwater contaminated by petroleum hydrocarbons, solvents, pesticides, wood preservatives, and other organic chemicals. Bioremediation is not generally applicable for treatment of inorganic contaminants.

Physical/chemical treatment uses the physical properties of the contaminants or the contaminated medium to destroy, separate, or contain the contamination. Chemical reduction/oxidation and dehalogenation (BCD or glycolate) are destruction technologies. Soil washing, SVE, and solvent extraction are separation techniques, and stabilization/solidification is an immobilization technique.

Physical/chemical treatment is typically cost effective and can be completed in short time periods (in comparison with biological treatment). Equipment is readily available and is not engineering or energy-intensive. Treatment residuals from separation techniques will require treatment or disposal, which will add to the total project costs and may require permits.

Thermal treatments offer quick cleanup times but are typically the most costly treatment group. This difference, however, is less in ex situ applications than in in situ applications.

Thermal processes use heat to increase the volatility (separation); burn, decompose, or detonate (destruction); or melt (immobilization) the contaminants.

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STUDIES ON THE INFLUENCE OF IRRIGATION ON A CALCIC CHERNOZEM IN THE EASTERN REGION OF ROMANIA

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Abstract

The Romanian strategy in the field of irrigations for the years of 2008-2011 consists of the modernization of the existing works covering about 3.1 mil. ha, while for the years of 2011-2025 the irrigation of additional area of 0.9 mil. ha is expected. In the climate conditions of Romania, the irrigation has a complementary character over the precipitations. Because of this reason, a correct regime of irrigations needs a very good correlation between watering and precipitations in order to achieve both a favorable moisture regime for the growing plants and for the quality protection of soil. Using uncontrolled watering regime or inadequate quality of water, leads in many situations to inappropriate processes for soil evolution. A study regarding the modifications of the soil quality as result of the irrigations was carried out in the district of Bacău, in the East of Romania and its results are presented in this paper. The research objectives were focused on a Calcic Chernozem (FAO-UNESCO) in three areas with different watering conditions and consisted of: analyses regarding the evolutions of porosity and hydro-physical parameters; analyses regarding the dynamic of soil salinity; analyses regarding the dynamic of heavy metals in mobile form; analyses regarding dynamic of nitrogen in the soil; analyses regarding the biologic activity of the soil. The research method consisted in soil sampling at pre-established time periods, their laboratory studying, data processing and interpretation. The conclusions of this study bring new contributions to the development of management for irrigated lands in Romania.

Key words: calcic chernozem, heavy metals, hydro-physical parameters, irrigation, mobile form; soil salinity; nitrogen in soil, biologic activity of the soil.

1. Introduction

Romania covers a total area of 23,839,139 ha, of which the greatest percentage (61.84%) is agricultural land, followed by forests and other surfaces covered with forestry vegetation (28.28%). Other types of land represents 9.88% of the whole surface of the country (water surfaces, ponds, yards, buildings, communications ways and unproductive land).

The surface of the plough land is 63.9 of the whole agricultural land; the rest is covered by pastures (about 22.82%), hay production land (about 10.28%) vineyards (1.52%) and orchards (1.48%).

In 2007, the total area with irrigation was about 3,200,000 ha. The functional status of the irrigation works is rather poor; some of them missing the working equipment, some other have badly

maintained parts, some other missing the necessary exploitation and maintaining funds. In fact, during the years of 2000 - 2007 the irrigated area varied between 45,719 and 754,498 ha (Table 1).

For the years of 2008 – 2011, the Romanian strategy in the field of irrigations takes into account the modernization of the existing works covering about 3.1 mil. ha, and for the years of 2011 – 2025 in the irrigation of an additional area of 0.9 mil. ha.

The irrigations have a complementary character over the precipitations in the climate condition of Romania so that, a correct regime of irrigations needs a very good correlation between watering and precipitations in order to achieve both a favorable moisture regime for the growing plants and for the quality protection of the soil (Gorontiwari and Smout, 2005; Stătescu, 2003).

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Uncontrolled watering regimes or inadequate quality of water lead in many situations to the soil degradation as result of the following processes (Acosta-Martinez et al., 2006; Bedano and Cantu, 2006; De Nys et al., 2005; Feyereisen et al., 2007; Guganesharajah et al., 2007; Krishnamoorth et al., 2007; Niklinsca et al., 2006; Salazar et al., 2005; Tafaldar J.C., Gharu A., 2006; Vlek et al., 2007; Wöhling and Schmitz, 2007; Wöhling and Mailhol, 2007):

- a) *soil clogging*, due to clay and organic particles from irrigation water, sometimes accompanied by an out of measure increase of nitrogen compounds;
- b) *soil salinization*, manifested by the increase of soluble salts over a the critical value;
- c) *soil alkalization*, caused by the saturation of the absorbing complex with Na⁺ ions and the increase of carbonates and alkaline bicarbonates;
- d) *soil acidification* caused by the use of acid waters or by the neutralization of some easy solving salts;
- e) *decrease of soil fertility*, as result of the microelements growth within the soil (Zn, Cu, Al) under a mobile form, in organic acids, amino acids, and other toxic compounds resulted from the decay of organic mater, kalium and iron range wash and of the soil structure degradation;
- f) *excess of humidity*, which is causing the lack of oxygen into the soil which is necessary both for the respiration of plants' roots and the intensification of chemical and biochemical anaerobic processes;

g) *soil infection with pathogenic germs*, can appear if waters with a high biologic load are used for irrigations.

This study investigates the modifications of the soil quality as result of the irrigations in several areas of the district of Bacau, in the East of Romania based on a comparative analysis of physical proprieties.

2. Materials and Methods

The researches were carried on in three areas: P.I. – farming with irrigations and organic fertilization, P.II. – farming with irrigations and chemical fertilization, P.III. – farming without irrigations but organic fertilization. A brief description of soils within the research areas are presented in Tables 2, 3 and 4.

The comparative analyze of physical proprieties of the soils within the three areas (Table 5) shows that soils are not compressed and have an average permeability. So the irrigations can be applied without restrictions for this soil. In Table 5, the abbreviations have the following significance: TP - total porosity; K_s - saturated hydraulic conductivity; FC - field capacity; WCO - wilting coefficient; AP - aeration porosity; WHC - water holding capacity; MWC - maximum water holding capacity.

The research method consisted in sampling soil, irrigation water and sedimentation dusts from these areas at precise time ranges, their laboratory analyze, and the data processing and interpretation.

Table 1. The effectively irrigated area (at least one watering) between 2000 and 2007

Area	Year						
	2000	2001	2002	2004	2005	2006	2007
ha	85,000	216,100	327,900	569,100	45,719	96,224	754,498
%	100	254	286	670	54	113	888

Table 2. P.I.- Cambic cernozem (The Romanian Taxonomy System), Calcic Chernozem (FAO-UNESCO)

Specification	Soil horizon					
	Ap	Am	AB	Bv ₁	Bv ₂	Cca
Depth (cm)	0-30	31-44	45-60	61-104	105-134	135-150
Sand (%)	44.3	44.5	-	46.3	-	50.0
Dust (%)	28.1	27.2	-	25.8	-	29.0
Clay (%)	27.6	28.3	-	27.9	-	21.0
Apparent density (g/cm ³)	1.35	1.38	1.41	1.39	-	-
Humus (%)	2.6	2.1	1.5	-	-	-
pH in water	5.45	6.35	6.85	7.20	7.35	8.25
Ability for cationic exchange (me/100 g sol)	19.5	18.7	19.6	-	-	-
Natrium saturation degree (%)	74.3	86.1	96.9	-	-	-
Nitrogen total (%)	0.125	-	-	-	-	-
Phosphorus (ppm)	54	-	-	-	-	-
Kalium (ppm)	110	-	-	-	-	-
Carbonates (%)	-	-	-	-	-	13.2

Table 3. P.II - Cambic Chernozem (The Romanian Taxonomy System) Calcic Chernozem (FAO-UNESCO)

Specification	Soil Horizon						
	Ap	Am	AB	Bv ₁	Bv ₂	Cca ₁	Cca ₂
Depth (cm)	0-25	26-43	44-55	56-75	76-110	111-130	131-150
Sand (%)	45.1	43.9	46.3	51.8	45.0	51,8	75.1
Dust (%)	27.2	30.6	29.1	26.9	33.4	30,6	15.7
Clay (%)	27.7	25.5	24.2	21.3	21.6	17,6	9.2
Apparent density (g/cm ³)	1.32	1.42	1.44	1.27	-	1,29	-
Humus (%)	2.9	2.8	1.9	1.3	1.3	-	-
pH in water	6.7	6.65	6.70	6.75	8.05	8,15	8.20
Ability for cationic exchange (me/100 g sol)	23.6	23.4	-	-	-	-	-
Causticity saturation degree (%)	96.6	96.1	-	-	-	-	-
Nitrogen total (%)	0.16	0.12	0.12	0.12	0.10	-	-
Phosphorus (ppm)	83	6	13	13	10	-	-
Kalium (ppm)	215	95	95	95	75	-	-
Carbonates (%)	-	-	-	-	5.5	9,6	6.0

Table 4. P.III - Cambic Chernozem (The Romanian Taxonomy System), Calcic Chernozem (FAO-UNESCO)

Specification	Soil Horizon					
	Ap	Am	AB	Bv ₁	Bv ₂	Cca
Depth (cm)	0-20	21-35	36-50	51-80	81-120	121-140
Sand (%)	43.7	41.1	-	45.0	45.3	45.3
Dust (%)	27.2	28.5	-	25.4	29.2	30.2
Clay (%)	26.7	30.4	-	29.6	25.5	24.5
Apparent density (g/cm ³)	1.33	1.43	1.44	-	-	-
Humus (%)	2.3	1.5	1.0	-	-	-
pH in water	6.5	6.85	7.0	7.20	7.2	8.65
Ability for cationic exchange (me/100 g sol)	20.7	20.1	-	-	-	-
Causticity saturation degree (%)	91.6	90.2	-	-	-	-
Nitrogen total (%)	0.12	0.09	-	-	-	-
Phosphorus (ppm)	2.6	1.4	-	-	-	-
Kalium (ppm)	29.2	10.0	-	-	-	-
Carbonates (%)	-	-	-	-	-	15.8

Table 5. Physical proprieties of the soils within the three areas

Area	Physical proprieties						
	TP (%)	K _s (mm/h)	FC (%)	WCO (%)	AP (%)	WHC (%)	MWC (%)
P.I	48.9	3.5	22.95	9.82	10.37	13.13	35.43
P.II	51.48	7.02	22.51	7.38	24.04	15.13	39.30
P.III	48.52	3.3	22.91	9.54	16.67	13.37	34.91

3. Results and discussions

3.1. Evolution of porosity and hydro-physical characteristics

Since the shape of the suction curve is a reasonable and precise base for analyzing the porosity and the hydro-physical characteristics of soil, its variation under the irrigation influence was studied. The suction curves, for the three areas have been experimentally determined at two distinctive moments: at the beginning of the research interval and at its end (after 2.5 years).

The main observations resulted from the shape modification of suction curve were:

- a) the total porosity of the soil have dropped with 2.43% to 4% (of the volume) in the

irrigated areas and with 2.5% in the un-irrigated area;

- b) at the irrigated soils the pore percentage with a diameter of 10 – 0.2 μm dropped significantly and the pores percentage with a diameter smaller than 0.2 μm grew;
- c) at the area without irrigations the pore percentage with a diameter of 30 – 10 μm dropped, this explaining the reduction of total porosity;
- d) the dynamic of different porosity compounds in the tree areas is presented in Table 6;
- e) due to salts and colloidal substances in the irrigation water, the average pores (manly those having a diameter of 10 – 0.2 μm) have clogged up by physical adoption processes, what lead to the decrease of utile water capacity of the soil (Table 7).

Table 6. Soil porosity modification

Area	Porosity (% v)								
	>50-10 μm			10-0,2 μm			< 0,2 μm		
	Initial	Final	Dif.	Initial	Final	Dif.	Initial	Final	Dif.
P.I	17.45	16.52	-0.93	21.50	17.50	-4.00	11.00	13.50	+2.50
P.II	28.50	20.00	-1.50	20.50	13.00	-7.50	9.50	14.50	+5.00
P.III	17.50	15.00	-2.50	20.00	20.00	0.00	1.50	11.50	0.00

Table 7. Modification of hydro-physical coefficients

Area	Hydro-physical coefficients (% v)								
	FC			WCO			WHC		
	Initial	Final	Dif.	Initial	Final	Dif.	Initial	Final	Dif.
P.I	32.5	31.0	-1.5	11.0	13.5	+2.5	21.5	17.5	-4.0
P.II	30.0	27.5	-2.5	9.5	14.5	+5.0	20.5	13.0	-7.5
P.III	31.5	31.5	0.0	11.5	11.5	0.0	20.0	20.0	0.0

3.2. Soil salinity dynamics

The researches focused on revealing distribution of the total soluble salts content (TSSC) and the results are presented in Figs. 1, 2, and 3.

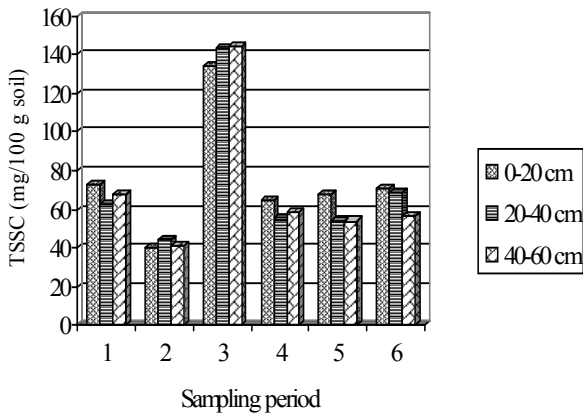


Fig. 1. TSSC evolution in the P.I area

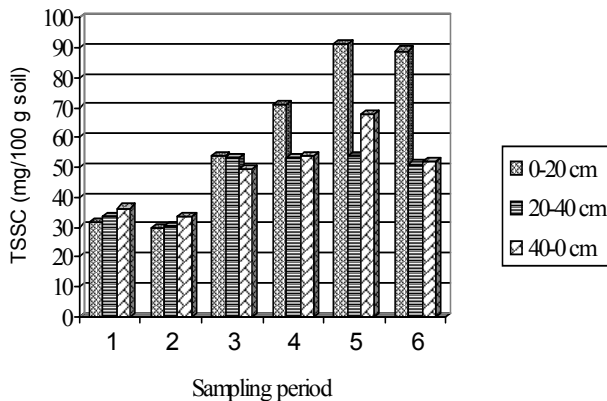


Fig. 2. TSSC evolution in the P.II area

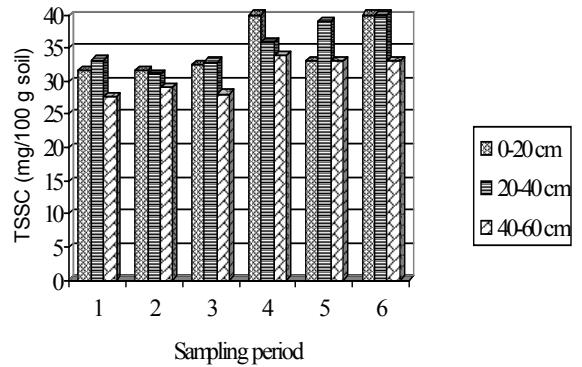


Fig. 3. TSSC evolution in the P.III area

Analyzing these results, the following aspects are revealed:

- a) within P.I area, where small amounts of irrigation water with 0.25 – 0.38 g/l fix residuum were used, the TCSS dynamics was especially influenced by the climatic regime and the quantity of irrigation water; the amount of salts added into the soil by the irrigation water varied between 5.612 g/m² and 9.147 g/m²;
- b) within P.II area, where grater amounts of irrigation water with 0.21 – 0.32 g/L fix residuum were used, high quantities of salts were added into the 0 – 20 cm soil layer without modifying the salinity class; the quantity of salts brought into the soil by the irrigation water was between 7.742 g/m² and 13.890 g/m²;
- c) within P.III area, with no irrigation, the variation of TCSS, for the analyzed period, was insignificant comparing to irrigated areas;
- d) the quality of irrigation water were appropriate, the maximal admissible limit of the fix residuum, under the Romanian climate conditions, being 1.2 g/L.

3.3. Dynamics of heavy metals in mobile form

Within the studied area, the heavy metals sources for the soil are represented by the irrigation water and the silting dusts. Considering one metal, Zn, a very important microelement for the growth and development of plants the conclusions are:

- a) the Zn quantities brought into the soil by the irrigation water varied between 1.9 mg/m²
- b) and 15 mg/m² in the P.I area, and respectively 2.8 mg/m² and 4.6 mg/m² in P.II area;
- c) the Zn quantities fell on the soil with the silting particles varied between 7.70 mg/m² and 40.47 mg/m² in the P.I. area and respectively between 0.47 mg/m² and 40.47 mg/m² in the P.II. and P.III area.

The dynamics of Zn in the three studied areas are presented in Figs. 4, 5 and 6.

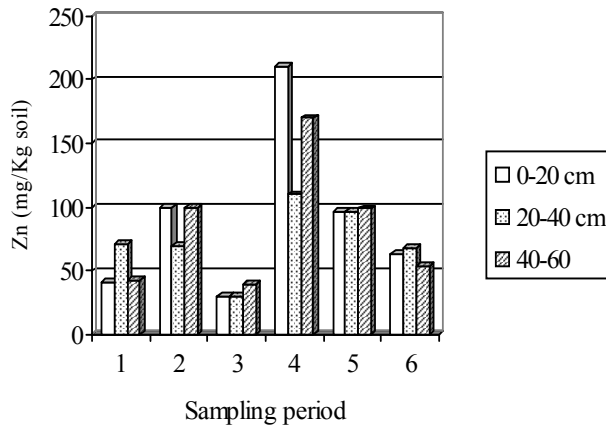


Fig. 4. The dynamics of Zn in the soil cross section of P.I area

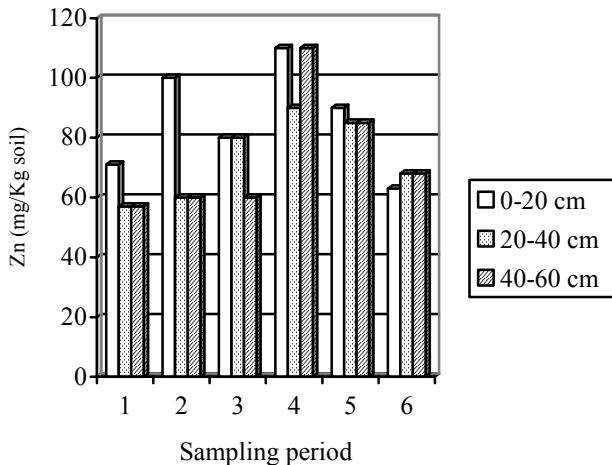


Fig. 5. The dynamics of Zn in the soil cross section of P.II area

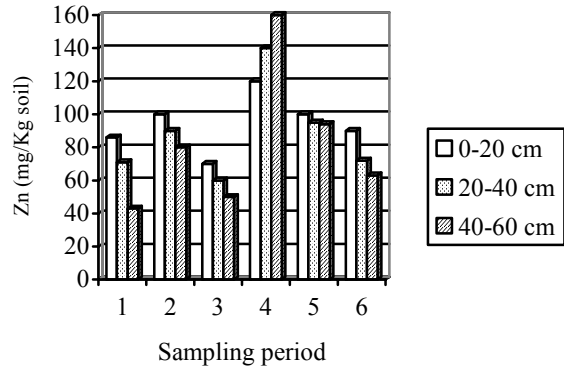


Fig. 6. The dynamics of Zn in the soil cross section of P.III area

3.4. Studies regarding the nitrogen activity in the soil

Starting from the fact that the mineralization of organic matter is a process influenced by the water content in the soil, an equation has been established stating that quantity of nitrogen in the soil in the 0-20 cm layer is growing in logarithm way while the humidity grow. So for the three experimental areas analyzing the results regarding the nitrogen content in the soil and the weather recordings (precipitations and temperatures) and also taking into account the distributed irrigation ratios, Eq. (1) results:

$$N = 0.269 (1 - e^{-0.053Iu}) \quad (1)$$

where: N is the total nitrogen in the soil at 0-20 cm layer (%), and Iu – humidity index, calculated with Eq. (2):

$$Iu = \frac{P + I}{10 + t} \quad (2)$$

where: P- average annual precipitations (mm), I – irrigation ratio (mm), t – annual average temperature (°C).

The supplementary water by irrigations is generating a smaller mineralization of the organic matter, a humus accumulation is generating into the soil accompanied by an increase of the amount of total nitrogen.

3.5. Studies regarding the biological activity in the soil

When analyzing the soil quality the biological aspect should not be neglected. Studying the results, as regard to CO₂ quantity in the soil, and the total number of germs (TNG), as seen in Table 8, the following conclusions are revealed:

- (a) the very small quantities of CO₂ show a weak biological activity in the soil, in all of the studied areas;

Table 8. Biological analyzes

Sample Nr.	Season	P.I		P.II		P.III	
		CO ₂ (%)	TNG (germ/g)	CO ₂ (%)	TNG (germ/g)	CO ₂ (%)	TNG (germ/g)
1	Spring	0.036	298,500	0.0202	260,400	0.0194	200,000
2	Summer	0.0162	56,640	0.0168	185,600	0.0220	264,380
3	Autumn	0.0326	182,400	0.0298	328,500	0.0210	226,100
4	Spring	0.0216	255,080	0.0320	258,500	0.0180	224,240
5	Summer	0.0128	248,000	0.0158	105,500	0.0188	283,200
6	Autumn	0.0176	233,200	0.0264	247,500	0.0062	167,000

b) in the P.III area, where a bio agriculture is practiced, a higher level of CO₂ concentration is revealed during summer as comparing with spring and autumn;

c) in the P.I and P.II areas a decrease of CO₂ concentration is revealed during summer, comparing with spring and summer, due to a mobilization by irrigation of the chemical substances spread on the soil, this inhibiting the microbes activity;

d) comparing the value of CO₂ concentration with the microbes number (TNG) into the soil, a very good direct relation can be seen between these two elements.

4. Conclusions

Irrigation is a common technical method for supplementing the water necessary into the soil and mitigating the drafts consequence. For the next period of time, dominated by climate changes, the Romanian strategy in this field, has as purpose the modernization of the existing irrigation works for the existing 3.1 mil ha, and after 2011 the construction of new irrigation systems of 0.9 mil ha.

The sustainable management for irrigated soils cannot be done without a constant monitoring of qualities and a scientific prognosis of their evolution. In the presented context, the experimental researches are very useful, showing both the processes determining both the modification of soil quality and their intensity. Based on these pieces of information, the best technical solutions for a sustainable use and conservation of the soil can be established.

The incorrect use of irrigations, with low quality water, can cause the start of unfavorable processes for soil evolution. Among these, the most frequently meet at the Romanian soils are: silting, salinity, alkalinity, acidification, decrease of fertility, excess of humidity, infestation with pathogenic germs.

It is very useful to find the starting moment of these processes, in order to stop them, since is easily to prevent the soil decay then to apply curative measures. For this purpose the modernization of soil quality monitoring system is necessary; it can be done by a combination of intelligent sensors, programs for data processing and internet technology.

List of acronyms

Am – humus enriched horizon;
Ap – plowing horizon;
AB – transitional horizon;
Bv – cambic horizon;
Cca – horizon of carbonate accumulation.

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ENVIRONMENTAL ISSUES FROM AN ECONOMIC PERSPECTIVE

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Abstract

The paper discusses some aspects concerning environmental issues considered from an economic perspective, since economic globalization as well as ecological globalization follows new ways of conditioning each other. In the past the most important thing was the impact of the environmental protection pressure - soil deterioration, water system, the atmosphere and the forests - upon economical perspectives. In the recent past years the society had to face the quick growth of the economical interdependency among nations, but also the environmental interdependency among them is being accelerated. Economy and environmental issues interfere more and more with each other - on a local, regional, national and global level - forming a network of cause and effect. The harsh cycles operate at a national and regional level. The deterioration in the arid areas make million of people go over the national borders. Some consideration on water resource scarcity and agriculture and environmental impacts are made from economic perspective. It was highlighted that economic premises and principles play a major role in the shaping of environmental policy.

Key words: environment, globalization, economic perspective.

1. Introduction

In recent decades, growing awareness of environmental issues and their relationship to the economy has seen the emergence three main policy goals in natural resource management: efficiency, equity and sustainability, as parts of sustainable development (Fig. 1) (Turpie, 2008).

An ecological economics view of sustainability is inevitably based in systems thinking (Capra 2002; Costanza et al. 1997; Costanza 2001).

Sustainable development can be defined as development that meets the needs of the present without compromising the ability of future generations to meet their own needs. This requires balancing the demand for natural resources with the protection of ecosystems that also contribute goods and services necessary for economic growth (Greiner and Semmler, 2008; Tănăsie, 1992; .

Certainly, not only does the environmental pollution strongly affect the current generation, but the environmental degradation affects future

generations as well. As for the dependence on natural resources, technical progress has led to a more efficient use of technologies so that emissions of some pollutants have been reduced considerably.

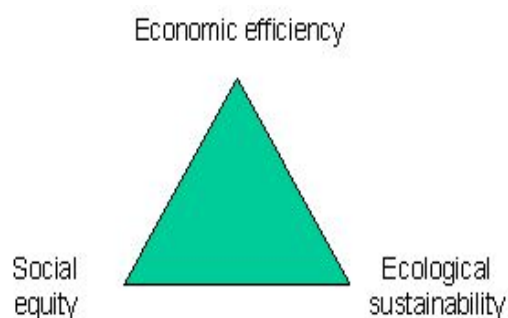


Fig. 1. The three goals of resource management

From an economist point of view, pollution becomes a problem only when it introduces externalities that distort the allocation of resources.

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Distortion occurs when those who cause pollution do not bear its costs but instead impose them on society (Greiner and Semmler, 2008; Raynauld, 2008).

Economic premises and principles play a major role in the shaping of environmental policy. Instruments of environmental policy are traditionally assessed on the basis of efficiency criteria, such as optimal social welfare, Pareto efficiency and cost-effectiveness (van den Bergh et al., 2007).

The European Union defines a Community strategy to integrate environmental issues into economic policy using various instruments such as market mechanisms, Member States' annual reports and the Broad Economic Policy Guidelines (<http://europa.eu/scadplus/leg/en/lvb/l28018.htm>).

2. Development and environmental protection

Even at the beginning of the deterioration of the environment, its protection has worried the developed countries. These have started in the latest years to enterprise certain ecologically efficient actions, the phenomenon spreading afterwards in the developing countries as well.

Numerous areas unpopulated before become now active from an economical point of view, for example by increasing the number of farmers. A population which does not own land looks for living resources in these regions.

Developing countries possess little resources for ecological objectives, but what they have or get from the developed countries is not sufficient to solve at least the development issues. It must be observed that the economic inequality between the developed countries and the developing countries becomes in the same time an ecological inequality among them. Between the North and the South it exists a fundamental difference regarding the environment deterioration. Introducing the causality issue, it becomes evident that in the developing countries the main cause is poverty. In the industrial countries the cause is the growing consumption and the way of living based on mass production, by using a lot of energy and by exploiting the natural resources on a large scale (Tietenberg, 1996).

In the last 20 years, the global awareness of the humanity regarding the problems of the environment has evolved rapidly - especially emphasizing aspects such as: reducing the ozone layer, devastation of equatorial forests, deterioration of water quality, global warming of the planet. The more developed knowledge and the acquired experience about the environment issue during this period have led to a reconsideration of the role and responsibility of the leaders as well as of the economic entities.

Especially in the developed countries, in the last two - three decades, as far as this topic is concerned, some fundamental changes have been introduced, such as:

- extension of settlement regarding environment protection at a central and local level;
- the growth of the environment protection cost, both for the public sector as for the private one. The resources used by both sectors for the pollution control have increased and the government entities, as well as the productive ones, are searching for more efficient ways of conforming the existent settlements;
- the financial - national and international - institutions have also become aware of the environment problems. The attentive pressure and supervision exerted by these institutions stimulate the authorities but also the business companies to pay more attention to environment problems;
- as a result of the United Nations Conference about the environment, held at Rio de Janeiro, the governments and corporations from all over the world have started to pay more attention to lasting development.

3. Environmental context initiatives and events

Deterioration of environment quality state has direct and long term consequences from an economic, social and ecological point of view. The natural capital resources are consumed in a rhythm which surpasses their regenerative capacity and, at the same time, they suffer the devastating action of certain activities.

In this context, it can be pointed out that even UNO has been called to initiate, organize and support co-operation within the environment domain by forming a system of international co-operation in order to protect the environment which takes action in the following main directions:

- elaboration of principles and programmes for international co-operation regarding the environment issues;
- creating the legal international structure for this co-operation;
- acquiring funds and making use of them to protect the environment especially in the developing countries.

A very important action and with positive effects for international co-operation in this field was the United Nations Conference for Environment (Stockholm, June 5 - 16, 1972). The Conference has adopted the Declaration about the environment which comprises 26 principles regarding the countries' rights and obligations referring to environment protection, the ways and means of international co-operation development in this domain. It has also been adopted a Plan of actions which contains 109 action suggestions at international level to protect the environment. After the Stockholm Conference, in the same year, the General Reunion of UNO has created its own subsidiary organism to co-ordinate the international co-operation - the United Nations Environment Programme (UNEP) with its headquarters in Nairobi (Kenya).

The UNO system takes action to support bilateral and regional co-operation; since the main role to protect the environment belongs to each and every country, the international co-operation is only a complementary factor. At national level there are in most countries national agencies for the environment protection and administration of natural resources. The UNO system helps to strengthen these agencies and through them environment protection projects are being carried out in various countries, especially in the developing ones. UNO also supports the specific regional pre-occupation for trans-frontier ecological areas, existing for instance over 200 distinct biogeographic areas in the world.

At present, as well, the debates within UNO plead for UNEP strengthening. UNEP is the environment programmes and projects' catalyst and coordinator in the whole UNO system. Thus, it has been proposed that UNEP should concentrate its activities in the following directions (Lămătic and Bostan, 2000; Tanasie, 1992):

- development, experimentation and support of practical methods applications and specific projects for ecological evaluations at national level;
- extension of international agreements to other domains such as the chemical products and dangerous waste products;
- extension of the regional programme regarding seas;
- development of similar programmes for the international river basins;
- identification of technical assistance requirements and training courses for the administration and environment protection and for the co-ordination in this sense of the international agencies;
- guidance of the international agenda towards environment scientific research and technological development;
- global ecological evaluation and international media report regarding the environment state, in this case global risks should be evaluated. The creation of a "Programme for global risks' evaluation" has been proposed, which is to be a co-operation mechanism between the existent organizations and organisms.

4. Environmental goods valuation: the *Total Economic Value*

Environmental accounting becomes the paradigm of the conservation and preservation of such capital by the same standards of an enterprise patrimony. Environmental values are supported and reinforced in their informative content by the economic evaluation in confront of other values present in decisional process (Demian, 2000; Plottu and Plottu, 2007). Environmental goods valuation can be a prerequisite in order to control and contain the damages caused by man to the environment (Bishop and Woodward, 1995; Costanza et al., 1997).

In economy, the expression "environmental values" means essentially two relationships, which

are not at the basis of the decisions concerning the environmental politics broadly speaking. None of these two meanings has to be confused with that of the economic value.

In the *Millennium Ecosystem Assessment* (MEA, 2005) economic valuation is stated as a powerful tool for placing ecosystems on the agenda of conservation and development decision-makers. In fact the three main domains are recognized as critical to choose and implement successful policies: the biophysical information about the ecosystem status and process, the socioeconomic information about the context in which and for which the decision will be made and the information about the values, norms and interests of key stakeholders shaping and affected by decisions. Within the MEA the Total Economic Value (TEV) is confirmed as the most widely used framework to identify and quantify the contribution of ecosystem services to human well being.

When the notion of value is connected to the notion of TEV it refers to the social context overlapping the ecosystem, taking into account the relations between the socio-economic system and the natural systems, with all the involved complex dynamics and feedbacks. Assessing the TEV could be a useful tool for policymakers: determining the total flux of benefits that ecosystems generate and assessing the effects of specific projects or policies, can support a better management of the territory. TEV is composed by use values, option values and non-use components. There is neither in the literature a single standard categorization nor terminology. Often *Total Value* is reported as the sum of use value and non-use values or passive values (Perman et al., 2003; Tietenberg, 1996) (Fig. 1).

Use values can be direct when goods and services are exchanged on the market that thus reveals their value. Use values are indirect refer to the life support services role of the natural environment, which are 'indirectly used'. Non-use values include: existence values, where the benefit results from knowledge that goods and service exist and will continue to exist, independently of any actual or prospective use by the individual; and bequest value, where the benefit is in ensuring that future generations will be able to inherit the same goods and services of the present generation. Beyond a purely typological distinction between use, option and non-use values, these different environmental values are not treated differently within the concept of Total Economic Value. When expressed in monetary terms from individual preferences, these values are incorporated into a sole approach reasoning in terms of utility (Plottu and Plottu, 2007).

5. An economic perspective on water and the environment

As economies expand globally, the strain on the earth's natural resources becomes increasingly apparent, and perhaps one of the most pertinent issues facing us today is that of water scarcity.

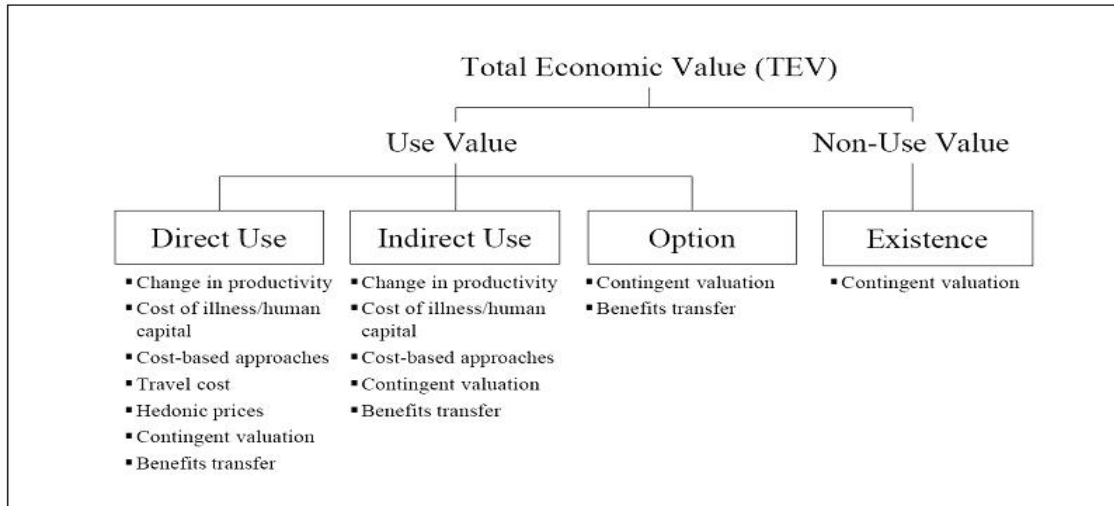


Fig. 1. Components of *Total Economic Value* (TEV)

The demand for water now surpasses supply over much of the Earth's surface (Tietenberg, 1996; Turpie, 2008). Water is a finite natural resource, essential for the sustenance of life on earth. Agenda 21, a major outcome of the United Nations Conference on Environment and Development (UNCED), popularly referred to as the Earth Summit, held in Rio de Janeiro, Brazil, in June 1992, states that effectively integrated management of water resources is important to all socio-economic sectors relying on water. Rational allocation prevents conflict and enhances the social development of local communities, as well as economic planning and productivity (<http://www.unu.edu/unupress/unupbooks/uu18ce/uu18ce02.htm>).

The value of aquatic ecosystems is less readily understood. Aquatic ecosystems offer a range of goods, services and attributes that generate value and contribute to human welfare. The concept of ecosystem goods and services, popularized in the ecological-economics literature, stems from the perception of ecosystems as natural capital which contributes to economic production (Turpie, 2008).

As economies expand globally, the strain on the earth's natural resources becomes increasingly apparent, and perhaps one of the most pertinent issues facing us today is that of water scarcity. The value of water is most readily appreciated as a direct input to economic production. Water is an essential input to all sectors that contribute to the overall economic output of the economy, although the productivity of water differs enormously from sector to sector (Perry et al., 1997).

Economists see water as a scarce resource because it is generally non-substitutable, there is an increasing overall demand for water, water use is intensifying, and there are limits to its use. Moreover, the provision of freshwater to end-users is itself an activity requiring resource-input. Despite this position, fresh water is still commonly treated as an

almost free resource. The consequence of this is inefficient use and potential over-use problems. But in reality water is a valuable resource requiring greater efficiency in usage, re-usage and proper economic pricing (Perry et al., 1997; Turner and Dubourg, 2006).

Economics is the study of the allocation of scarce means (total resources, man-made and natural) towards the satisfaction of the maximum number of human ends (wants and needs) as is feasible with prevailing technology and knowledge (Turner and Dubourg, 2006).

Integrated water resources management (IWRM) is based on the four 1992 Dublin principles (Lant, 2004):

- I) Fresh water is a finite and vulnerable resource, essential to sustain life, development and the environment;
- II) Water development and management should be based on a participatory approach, involving users, planners and policy-makers at all levels.
- III) Women play a central part in the provision, management and safeguarding of water.
- IV) Water has an economic value in all its competing uses and should be recognized as an economic good.

Principle IV is central to an ecological-economic approach to sustainability (Fig. 3) (GWP, 2000; Lant, 2004).

The market value of water is only a portion of the economic value of water, to which must also be added the non-market values to human capital and ecosystem service values if the total ecological economic value of water is to be identified. "On the cost side, the fixed and variable cost of manufactured capital used to deliver water is the supply cost, but in order to find the total economic cost, the opportunity cost of allocating the water itself to its next best use, and any economic externalities (positive or negative) associated with this allocation must be added" (Lant, 2004).

VALUES OF WATER				COSTS OF WATER				
Ecological Economic Value	Ecosystem Service Value			Diminishment of Ecosystem Services		Ecological Economic Cost		
	Non-Market Value to Human Capital			Economic Externalities				
	Economic Value	Net Benefits from Indirect Use		Opportunity Cost of Water				Economic Cost
		Net Benefits from Return Flows		Capital Charges	Supply Cost			
	Market Value	Value to Users of Water		Operation and Maintenance				

Fig. 3. Comparison of market, economic, and ecological-economic values and costs of water

The highest and best ecological-economic use of water is the use with the greatest net value as shown in Fig. 3. This use often differs from current uses of water. Consequently, IWRM has been touted as an evolving framework for applying the concept of sustainability to the practice of water resources management.

6. Agriculture and the environment: an economic perspective

There are many dozens of different economic perspectives on environmental issues affecting and affected by agriculture. Agricultural production has harmed environmental quality primarily because of inadequately designed policies and natural resource projects (Zilberman et al., 1999).

Agriculture places a serious burden on the environment in the process of providing humanity with food and fibres. It is the largest consumer of water and the main source of nitrate pollution of groundwater and surface water, as well as the principal source of ammonia pollution (Bruinsma, 2003). It is a major contributor to the phosphate pollution of waterways and to the release of the powerful greenhouse gases (GHGs) methane and nitrous oxide into the atmosphere (IPCC, 2001; OECD, 2001).

The main agro-environmental problems fall into two groups. First, there are those that are global in scale such as, for example, the increase in atmospheric concentrations of the GHGs carbon dioxide (CO₂) through deforestation, and nitrous oxide (N₂O) arising from crop production (Houghton et al., 1995; Mosier and Kroeze, 1998). The second group of problems is found in discrete locations of the major continents and most countries, but at present has no substantive impact at the global level (Zilberman et al., 1999).

Public attention tends to focus on the more visible signs of agriculture's impact on the environment, whereas it seems likely that the non-

visible or less obvious impacts of air pollution cause the greatest economic costs (Pretty et al., 2001).

Agriculture affects air quality and the atmosphere in four main ways: particulate matter and GHGs from land clearance by fire (mainly rangeland and forest) and the burning of rice residues; methane from rice and livestock production; nitrous oxide from fertilizers and manure; and ammonia from manure.

Agriculture now contributes about 30 percent of total global anthropogenic emissions of GHGs, although large seasonal and annual variations make a precise assessment difficult (Bouwman, 2001). More attention is now being given to methane (CH₄) and nitrous oxide (N₂O), since agriculture is responsible for half or more of total global anthropogenic emissions of these GHGs (Table 1). In recent decades the most important environmental issues concerning land have been land cover change, particularly deforestation, and land use intensification, especially its impact on land degradation.

Agricultural and environmental policies, markets, farm management practices, structural change, technological developments and socio-cultural preferences are the main driving forces that interact – and sometimes give conflicting signals – in determining agriculture environmental performance. The appropriate integration of agricultural and environmental policies can bring multiple benefits, by ensuring that policy goals are reached at least cost and that the burdens which agricultural policies can impose on the environment are fully accounted for.

There is now widespread interest in the use of economic instruments to complement regulatory instruments for environmental management. These include taxes on farm inputs which are sources of pollution, on farm emissions, or taxing farmers for their failure to meet required levels of environmental quality. An approach being tried in several countries is the use of input taxes to reduce the use of agricultural chemicals.

Table 1. Agriculture's contribution to global greenhouse gas and other emissions (Bruinsma, 2003)

<i>Gas</i>	<i>Carbon dioxide</i>	<i>Methane</i>	<i>Nitrous oxide</i>	<i>Nitric oxides</i>	<i>Ammonia</i>
Main effects	Climate change	Climate change	Climate change	Acidification	Acidification Eutrophication
Agricultural source (estimated % contribution to global emissions)	Land use change, especially deforestation	Ruminants (15)	Livestock (including manure applied to farmland) (17)	Biomass burning (3)	Livestock (including manure applied to farmland) (44)
		Rice production (11)	Mineral fertilizers (8)	Manure and Mineral fertilizers (2)	Mineral fertilizers (17)
		Biomass burning (7)	Biomass burning (3)		Biomass burning (11)
Agricultural emissions as % of total anthropogenic sources	15	49	66	27	93

7. Concluding remarks

Economic policies must recognize that environmental protection is a condition, and a prerequisite, for long-term economic growth. Experience shows that economic instruments, if designed and implemented properly, often in combination with other environmental policy instruments, can contribute to achieving economic benefits.

At the present time, economic policy is essentially concerned with economic stability and the functioning of markets.

For a great many environmental groups and services, there is no market or it is incomplete and these missing markets give rise to economic inefficiency. Consequently, the best strategy for integrating the environment into economic policy must be to create or improve the functioning of markets for environmental goods.

Finally, it must point out that the international co-operation strengthening to the advantage of the environment protection requires a more substantial support from the part of the multilateral financial institutions (The World Bank, The International Monetary Fund and the regional development banks), which should have a major influence upon the economic development in the world, being thus necessary to contribute in a higher degree to environment - development relation.

Growth typically enables societies to provide their members with a cleaner, healthier environment as it allows them to invest in cleaner technologies and products. Accordingly, the issue is how improvements in living standards can be accompanied by the safeguarding and improvement of the quality of the environment. As part of achieving the Lisbon European Council's goal of making the Community the world's most competitive and dynamic knowledge-based economy, capable of sustainable economic growth it is essential to change the actual approach to environmental policy.

Policy makers should acknowledge that market forces are implicated in many environmental problems and should seek to use them in order to achieve environmental policy aims.

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QUALITY ANALYSIS OF THE SOILS IN THE CORDUN METALLURGICAL PLATFORM AREA

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Abstract

The present article deals with the study of the quality of the soils in the Cordun area – the waste dump. This refers to the characteristics of the analyzed location site (geomorphological, geological considerations, the pedological and agrochemical characterization of the soils in the area outside the plant), but also to the establishment of the pollution rate in the location site (experimental data, results and debates). The conclusion of the present article is that the analyzed area presents a potentially significant pollution rate in the area outside the plant and significant in the area inside the plant's yard.

Keywords: levigation, clay iluviation, eluviation, gleization, leaching (percolation)

1. Characteristics of the analyzed site

1.1. Geomorphological considerations

Fluvial geomorphological forms, which resulted as a consequence of the action of the active factors, but also because of the structure and the rock, form together a microregion of confluence. From the morphostructural point of view, it is part of the province of the East-European platform, where different grounds are formed such as structural plains - plateaux, structural plains and cuestas, (Andone et al., 1992). Morphogentically, the ground has taken the present configuration in the quaternary, under the influence of the negative tectonic movements and the climatic oscillations, which caused the alternation of the glacial and interglacial phases.

The studied area is included from the geomorphological point of view in Moldavian Plateau, more precisely in the subunity known under the name of Moldova – Siret Chute. This subunity is delimited at the West by the hill Piemountain area, and in the East by Barlad Plateau.

In the studied area, the Chute includes two different relief forms, namely the terminal Sector of the Moldova inter-river – Siret, with altitudes higher

than 200 m on the balance line which links Sabaoani - Traian – Cordun villages and a flat relief of Moldova's and Siret's major streambeds.

Here and there, the steps of the cliffs situated at relative altitudes from 20 m to 115 m, can be distinguished in the area on the left side/slope. Their morphological elements are hardly perceptible, because of the areolar erosion phenomenon and the coluvio- proluvial glaciais. In fact, the terminal sector of Moldova- Siret inter-river is a unification of the terraces of the two rivers, their deposits being covered by an alluvial layer.

1.2. The geology of the region

The terraces in this area were formed in Quaternary as a consequence to the alluviations in the interglacial phases, in other words, these terraces correspond to some sedimentation stages, respectively glacial stages (Oncescu, 1959). A difference between the geological age and the morphological age can be made. The Roman area was formed from two morphological units (Oancea, 1959).

- the Sub-Carpathian neogenen unitaty – composed mostly of aquitanian deposits (argillaceous with salt), burdigalians (sandstones, sandstones

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alternated with marls) and tortonian (marls and sandstones).

- the Moldavian Platform unity – composed of Bessarabian subdeposits (sands interlayered by marls, limous sandstones and two-three eolitic lime levels) combined with paleozoic, mezozoic and neozoic formations. The quaternary is formed of fluvial and slope deposits.

The territory of the Cordun village is situated in the South-Western part of the Moldavian Platform. This area is an alluvial plain of young age, being composed mostly of medium gravel interlayered with chads/shingles, subordinated to the argillaceous and argillo-dusty sands, their thickness beyond of maximum 3-5 m.

1.3. Pedological and agrochemical characterization of the soils from the area outside the metallurgical platform

The geographical disposition of the village of Cordun plays an essential role in what concerns the general physical geographical setting of formation of zonal soils; the presence of Moldova and Siret rivers, some of the most important hydrographic drainages in the Eastern part of Romania, have conditioned the formation of intrazonal soils.

Pedogenic processes through which soils in the area were formed are levigation, clay iluviation, eluviation, gleization, pseudogleization (Lupascu et al., 1998):

- levigation as a pedogenic process represents the shifting on the profile of the soil or out of it, through the infiltration water, of some soil constituents;
- clay iluviation is the pedogenic process characterized by the mechanical translocation of clay from a superior horizon to an inferior horizon; thus such a clay iluvial or argilic horizon, rich in clay thanks to the above horizon, is formed;
- eluviation is represented the shifting on the profile by water, in suspension or in solution, of some components of the soil material, usually from a superior horizon to an inferior one;
- gleization as a process of pedogenesis or alteration means the reduction of the ferric iron with the marbling of the material mass in a mainly anaerobe environment, temporary or permanent, in a weak draining determined by the presence of water;
- pseudogleization means the marbling process of the soil material as a consequence of the oxidation and reduction process in the soil in aerobiosis and anaerobiosis conditions, due to storage and stagnation of water from precipitations in the soil profile on to an impermeable or low-impermeable horizon;

In the area, the following soil types can be found:

- Cambic chernozem (no humus cumulation)
- Clay iluvial chernozem (profound distribution of the humus according to the profile)

- Brown luvic soil (reduced distribution of the humus)

- Brown eumezobasic soil (reduced distribution of the humus)

- Alluvial protosoil

- Alluvial soil

- Anthropogenic protosoil is a type of soil formed on the materials deposited through human activities; the deposited materials have different chemical and physical characters.

The soils situated in the Moldavian alluvial plain have been permanently under the influence of flooding and lateral erosion processes exercised on the banks. Nowadays, through the embanking of the bank of Moldova, important areas covered with alluvial soils and anthropogenic protosoils have been drawn from under the influence of these processes.

Out of the analysis of the types of soil regarding the reserve of humus in the studied area – we can observe a low weight of soils with a high content of humus and thus it results for this territory the soils' lower capacity to retain pollutant elements.

Soils permeability is a characteristic of soils dependent on soils' texture on the control section and the total porosity. The data presented in the surveys made for the analyzed area demonstrates the fact that 24.25 % of the territory has an accelerated permeability, insuring an intense percolation of the soils and thus a levigation possibility of the pollutant products towards depth (OSPA Neamt, 1996).

Percolation as a process means the depth penetration of the descending water current obtained from precipitations or other sources. In the analyzed area, 49.21 % of the territory has a low or very low permeability and on these surfaces percolation is produced more slowly, thus producing a bigger stagnation of the pollutant elements on the soil area (OSPA Neamt, 1996).

Quality soil classes of the studied area (the waste dump) shows the following situation:

- low quality areas : they include areas or soils affected by limitations or strong degradation processes (gleization, flooding and edaphic volume), which represents the 4th soil class;

- very low quality areas : not advisable to use for arable land; non-improving limitations, or improving limitations (gleization, pollution, flooding rate, surface humidity excess), which represent the 5th soil class;

2. Soil pollution evaluation in the metallurgical platform area

2.1. The analysis of the health status of the soil in the platform area – global pollution index method

This method assumes the implementation of several stages of synthetic appreciations based on quality indicators that may reflect the general status of one of the analyzed environmental factors and then indicate them through a graphical method.

Soil quality framing at a given time is done with a bonity scale, by giving some grades to express the nearness or the remoteness from the ideal status (Table1). The bonity scale uses grades from 1 to 10. The natural status unaffected by human activity is represented by 10, and 1 is the grade representing an irreversible status and extremely serious of deterioration of the analyzed environmental factor.

2.2. Experimental data

2.2.1. Samples

In order to determine soil characteristics at the surface and in depth (5 and 30 cm), a manual sampling device was used, which has been cleaned after every assay. Soil logs have been performed on the basis of influential areas analysis and they may have been influenced by the activity in the area.

For the site surface characterization it has been gathered a number of (15x2) samples from the site [S₁ – East T sect., S₂ – M (N) sect.– billet store, S₃ – residue oils separator, S₄ – Combustible bank, S₅ – FMT sect.– in the back, the water tower, S₆ – etching – T sect. , S₇ – neutralization station – etching, S₈ – North HTS, S₉ – the oxygen plant (in the front), S₁₀ – CHP – dam, S₁₁ – main gate 1, S₁₂ –hammer shop (in the front) – cooling tower, S₁₃ – 30 m South from the exist hammer shop, S₁₄ –S shop– turboblowers pump, S₁₅ – brisk shop], (2x2) samples outside the sitei [S₁₆ – in front of the unit – near the eating-hall, S₁₇ – arable land at 100 m behind the unit], but in the near vicinity (neighbouring) and a sample considered as etalon (at the same depth) on the Roman–Iasi highway 5 km from the analyzed unit.

2.2.2. Analytical techniques for soil

As a result of the current activities there was a need for some determinations concerning: waste of heat, pH, the total amount of extractable substances, organic carbon, gas and vapours, iron, chrome, lead, nickel and cadmium ions content.

a. Substances extractable in petroleum ether

Tapped soil samples were analyzed from the point of view of the total content of substances extractable in ether, using the petroleum ether extraction method according to STAS 7587 -96.

Soil samples were dried, pestle milled and passed through a 2 mm coarse sieve. Approximately 10 g of sieved soil, weighed analytically, were contacted under agitations with 50 ml of petroleum ether. After approximately 20 minute of extraction the suspension is being filtered on to 1g of anhydrous sodium sulphate. The extract is collected in a tared crucible, and then introduced in the drying system for the evaporation of the solvent (40°C maximum). When the evaporation residue gets to a constant point, the extract quantity is determined.

b. Organic carbon

The establishment of the content of the soil analyzed in organic matter, absorbed gas and vapours was made through the treating of the samples with potassium dichromate, at heat in the presnce of sulphuric acid, the dichromate excess being titrated in Mohr salt solution in the presence of ferronine as an indicator (yellow –red green turn).

c. Contents of chrome, lead, zinc, nickel si cadmium ions

2 g of soil dried in air and pestle milled are introduced in a Berzelius glass on to which we add approx. 5 ml concentrated azotic acid and it's covered with a watch glass. It is mineralized on sand bath, at the blockout, until the residue turns completely white.

If the residue is not completely mineralized after the vaporization of the nitric acid, we should add 2 cm³ of perchloric acid and the mineralization continues (according also to SR ISO 11047/1999). The distruction of the organic component of the soil occurs. The residue is being re-treated with nitric acid 4% solution, easily heated to facilitate solving. After cooling it is filtred on low prorsity filter paper in a graded bottle at 25 cm³. The bottle is properly washed in distilled water and it is filled in at the sign. The content of chrome, lead, nickel and cadmium ions is determined using atomic absorption spectrophotometriy according to the graduation curves for each and every studied ion (a Perkin Elmer atomic absorption spectrophotometer and for calibration it has been preferred the use of salts of nitric or sulphate studied ions).

Table 1. Evaluation scale for environmental component soil (Robu et al., 2005)

Evaluation grades	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)	Ni (mg/kg)	Cd (mg/kg)	C _r ^{total} (mg/kg)	TOC (%)	Extractable compounds (mg/kg)
10	0-100	0-100	0-100	0-50	0-1	0-30	<3	<100
9	100-150	100-250	100-250	50-200	1-5	30-150	3 -3.2	100-500
8	150-250	250-550	250-550	200-350	5-7	150-300	3.2 -3.4	500-1000
7	250-500	550-750	550-750	350-500	7-10	300-600	3.4 -3.6	1000-2000
6	500-550	750-800	750-800	500-750	10-15	600-750	3.6-3.8	2000-3750
5	550-600	800-850	800-850	750-800	15-20	750-800	3.8-4.0	3750-5000
4	600-650	850-900	850-900	800-850	20-25	800-850	4.0-4.5	5000-6250
3	650-700	900-950	900-950	850-900	25-40	850-900	4.5-7	6250-7500
2	700-800	950-1000	950-1000	900-1000	40-50	900-1000	7-10	7500-10000
1	>800	>1000	>1000	>1000	>50	>1000	>10	>10000

2.3. Results and discussions

The results of the analyses are presented in Tables 2-9.

Note: The determining of the substances extractable in petrolium ether may cumulate other organic substances besides petrolium hydrocarbons.

According to MAPPM Order no. 756/1997 (MO, 1997), the analyzed site is characterized as being a soil:

- with less sensible usage (for intra-plant soil);
- with sensitive usage (for outside plant area usage).

From the examining of the experimental data, the following items resulted:

- in many of the points inside the the unity (6 points) the intervention point is outlevelled for the substances extractable in petrolium ether; the same thing can be told about the alert values (it is outlevelled at 42.86% of the number of the soil samples).

Table 2. The results of the physical-chemical analyses of the soil samples (5 cm depth of sampling)

Soil sample	The depth sampling 5 cm				
	Organic carbon (%)	Extractable compounds (mg/kg)			
		Normal values	Alert values	MAC*	Measured values
S ₁	4.31	<100	1000	2000	3720
S ₂	3.58	<100	1000	2000	940
S ₃	3.45	<100	1000	2000	3380
S ₄	4.28	<100	1000	2000	27480
S ₅	4.10	<100	1000	2000	2880
S ₆	3.82	<100	1000	2000	9330
S ₇	4.54	<100	1000	2000	670
S ₈	4.45	<100	1000	2000	720
S ₉	3.58	<100	1000	2000	110
S ₁₀	4.26	<100	1000	2000	840
S ₁₁	6.40	<100	1000	2000	250
S ₁₂	3.76	<100	1000	2000	100
S ₁₃	4.52	<100	1000	2000	140
S ₁₄	4.69	<100	1000	2000	660
S ₁₅	7.59	<100	1000	2000	700
S ₁₆	4.29	<100	200	500	2080
S ₁₇	2.62	<100	200	500	140
Etalon	2.44	<100	200	500	180

* MAC – Maximal allowed concentration

Table 3. The results of the physical-chemical analyses of the soil samples (30 cm depth of sampling)

Soil sample	The depth of sampling 30 cm				
	Organic carbon (%)	Extractable compounds (mg/kg)			
		Normal values	Alert values	MAC	Measured values
S ₁	2.82	<100	1000	2000	2830
S ₂	3.52	<100	1000	2000	600
S ₃	3.60	<100	1000	2000	11730
S ₄	2.87	<100	1000	2000	15090
S ₅	3.08	<100	1000	2000	3140
S ₆	3.28	<100	1000	2000	5012
S ₇	4.00	<100	1000	2000	1870
S ₈	3.95	<100	1000	2000	950
S ₉	4.32	<100	1000	2000	280
S ₁₀	4.50	<100	1000	2000	330
S ₁₁	5.96	<100	1000	2000	380
S ₁₂	3.71	<100	1000	2000	2540
S ₁₃	4.52	<100	1000	2000	440
S ₁₄	3.52	<100	1000	2000	780
S ₁₅	7.47	<100	1000	2000	337
S ₁₆	3.86	<100	200	500	1050
S ₁₇	3.00	<100	200	500	160
Etalon	2.38	<100	200	500	195

Table 4. The content of total chromium from soil samples

Soil sample	Total Cr (mg/kg)				
	Normal values	Alert values	MAC	Masured values at 5 cm	Masured values at 30 cm
S ₁	30	300	600	28.12	23.18
S ₂	30	300	600	181.01	49.12
S ₃	30	300	600	30.10	27.12
S ₄	30	300	600	56.78	86.10
S ₅	30	300	600	79.92	58.42
S ₆	30	300	600	26.10	23.16
S ₇	30	300	600	61.66	58.12
S ₈	30	300	600	21.28	20.12
S ₉	30	300	600	75.01	76.25
S ₁₀	30	300	600	69.12	51.05
S ₁₁	30	300	600	20.13	20.08
S ₁₂	30	300	600	18.71	17.02
S ₁₃	30	300	600	21.08	21.00
S ₁₄	30	300	600	42.61	31.11
S ₁₅	30	300	600	27.11	23.42
S ₁₆	30	100	300	21.13	15.08
S ₁₇	30	100	300	17.92	16.12
Etalon	30	100	300	17.89	17.51

Table 5. The content of lead from soil samples

Soil sample	Total Pb (mg/kg)				
	Normal values	Alert values	MAC	Masured values at 5 cm	Masured values at 30 cm
S ₁	20	250	1000	14.11	10.50
S ₂	20	250	1000	49.15	47.20
S ₃	20	250	1000	16.21	20.12
S ₄	20	250	1000	53.81	68.12
S ₅	20	250	1000	41.75	90.05
S ₆	20	250	1000	18.11	17.65
S ₇	20	250	1000	32.12	30.08
S ₈	20	250	1000	18.61	20.40
S ₉	20	250	1000	22.62	30.76
S ₁₀	20	250	1000	13.08	14.11
S ₁₁	20	250	1000	10.62	11.14
S ₁₂	20	250	1000	13.10	14.44
S ₁₃	20	250	1000	5.86	6.03
S ₁₄	20	250	1000	8.33	9.12
S ₁₅	20	250	1000	5.56	5.58
S ₁₆	20	50	100	4.81	4.86
S ₁₇	20	50	100	5.12	6.14
Etalon	20	50	100	1.36	1.88

- the organic carbon content is an indicator which allows the appreciation of the pollution level of a soil. The organic carbon percentage found indicates a soil between easily (1-3 % Corganic) and strongly polluted (>4 % Corganic) (Manescu, et al., 1994). We can observe the presence in eleven prelevation points of some values of the organic carbon content bigger than 4 %, which indicates the presence in these areas of a strongly polluted soil (42.85 %).
- the alert values for the chrome ions of 300 mg/kg dry soil (MAC 600 mg/kg) is not outlevelled, the maximum value found being that of 181,01 mg/kg (S₂) at 5 cm and , respectively, 86,10 mg/kg at 30 cm (S₄) – these values outlevel the normal values of 30 mg/kg.
- for the zinc ions, the alert values of 700 mg/kg dry soil (MAC : 1500 mg/kg) is not outlevelled; three of the values (5cm) outlevel the normal value of 100 mg/kg.
- lead ions outlevel the normal value of 20 mg/kg in seven prelevation points (at 30 cm) – S₂, S₃, S₄, S₅ si S₇, S₈, S₉, but without attaining the alert and MAC.
- copper ions outlevel the normal value of 20 mg/kg in seven prelevation points (at 5 cm) – S₁, S₂, S₃, S₄, S₅, S₆ si S₉, but without attaining the alert and MAC.

Table 6. The content of zinc from soil samples

Soil sample	Zn (mg/kg)				
	Normal values	Alert values	MAC	Masured values at 5 cm	Masured values at 30 cm
S ₁	100	700	1500	47.52	41.26
S ₂	100	700	1500	71.10	68.12
S ₃	100	700	1500	49.81	44.15
S ₄	100	700	1500	131.07	126.12
S ₅	100	700	1500	110.32	91.16
S ₆	100	700	1500	44.10	44.07
S ₇	100	700	1500	88.10	56.08
S ₈	100	700	1500	113.54	99.55
S ₉	100	700	1500	98.44	56.71
S ₁₀	100	700	1500	43.21	25.61
S ₁₁	100	700	1500	49.33	38.77
S ₁₂	100	700	1500	35.14	30.19
S ₁₃	100	700	1500	29.44	28.77
S ₁₄	100	700	1500	98.66	65.87
S ₁₅	100	700	1500	22.13	21.88
S ₁₆	100	300	600	17.65	16.57
S ₁₇	100	300	600	12.66	12.22
Etalon	100	300	600	7.21	6.54

Table 7. The content of copper from soil samples

Soil sample	Cu (mg/kg)				
	Normal values	Alert values	MAC	Masured values at 5 cm	Masured values at 30 cm
S ₁	20	250	500	22.51	16.52
S ₂	20	250	500	82.13	36.12
S ₃	20	250	500	24.10	18.12
S ₄	20	250	500	91.12	65.10
S ₅	20	250	500	69.65	77.10
S ₆	20	250	500	21.95	20.55
S ₇	20	250	500	10.61	9.12
S ₈	20	250	500	15.64	15.36
S ₉	20	250	500	38.60	21.12
S ₁₀	20	250	500	11.56	5.62
S ₁₁	20	250	500	8.12	5.61
S ₁₂	20	250	500	15.11	13.20
S ₁₃	20	250	500	7.12	7.08
S ₁₄	20	250	500	18.99	12.11
S ₁₅	20	250	500	5.65	5.91
S ₁₆	20	100	200	11.82	13.65
S ₁₇	20	100	200	10.10	8.30
Etalon	20	100	200	8.12	8.31

- nickel ions outlevel the normal value (20 mg/kg) in fourteen prelevation points (both at a depth of 5 cm and 30 cm) : S₁, S₂, S₃, S₄, S₅, S₆, S₇, S₈, S₉, S₁₀, S₁₁, S₁₂, S₁₃ și S₁₄ ; none of the values doesn't attain the intervention or alert values.
- regarding the cadmium content : all the seventeen determined values outlevel the normal value (1 mg/kg s.u.), and three of the values outlevel the alert values level (S₃ – at 30 cm, S₁₀ – at 5 cm and at 30 cm, S₁₄ - at 5 cm); moreover, in the outside plant area the cadmium content is close to the alert values.
- the evaluation level for the soil has been calculated in basis of the measured values in total organic carbon, substances extractable in

petroleum ether and heavy metals (Cu, Zn, Pb, Cr^{total}, Ni, Cd).

Thus the following values have been obtained:

- total organic carbon– plant area: 5.15; outside plant area: 7
- substances extractable in petroleum ether - plant area: 6.85; outside plant area: 7.75
- Cr^{total} – plant area: 8.93; outside plant area: 10
- Pb – plant area: 10; outside plant area: 10
- Zn – plant area: 9.85; outside plant area: 10
- Cu – plant area: 10; outside plant area: 10
- Ni – plant area: 9.75; outside plant area: 10
- Cd – plant area: 8.49; outside plant area: 9

Table 8. The content of nickel from soil samples

Soil sample	Ni (mg/kg)				
	Normal values	Alert values	MAC	Measured values at 5 cm	Measured values at 30 cm
S ₁	20	200	500	23.77	24.86
S ₂	20	200	500	146.23	53.13
S ₃	20	200	500	26.41	29.89
S ₄	20	200	500	58.11	56.09
S ₅	20	200	500	51.81	45.72
S ₆	20	200	500	30.54	27.12
S ₇	20	200	500	25.16	22.36
S ₈	20	200	500	41.13	63.33
S ₉	20	200	500	30.12	41.12
S ₁₀	20	200	500	31.41	71.45
S ₁₁	20	200	500	37.33	31.22
S ₁₂	20	200	500	36.11	28.71
S ₁₃	20	200	500	25.33	21.33
S ₁₄	20	200	500	22.12	22.08
S ₁₅	20	200	500	19.87	16.45
S ₁₆	20	75	150	17.55	15.44
S ₁₇	20	75	150	16.32	15.11
Etalon	20	75	150	14.33	13.45

Table 9. The content of cadmium from soil samples

Soil sample	Cd (mg/kg)				
	Normal values	Alert values	MAC	Measured values at 5 cm	Measured values at 30 cm
S ₁	1	5	10	1.56	1.28
S ₂	1	5	10	9.71	2.68
S ₃	1	5	10	11.12	5.69
S ₄	1	5	10	10.11	14.12
S ₅	1	5	10	1.96	1.41
S ₆	1	5	10	1.99	1.54
S ₇	1	5	10	1.65	1.42
S ₈	1	5	10	3.77	3.12
S ₉	1	5	10	4.12	3.71
S ₁₀	1	5	10	5.82	5.11
S ₁₁	1	5	10	1.91	1.20
S ₁₂	1	5	10	2.71	2.50
S ₁₃	1	5	10	4.32	4.20
S ₁₄	1	5	10	5.12	4.32
S ₁₅	1	5	10	3.75	3.01
S ₁₆	1	3	5	2.89	2.56
S ₁₇	1	3	5	2.75	2.50
Etalon	1	3	5	0.98	0.96

▪ Soil evaluation level is of 8.91 (plant area: 8.62; in outside plant area: 9.21)

In order to connect the points resulted from the attachment of the values expressing the real status, a geometrical figure - a circle results (Fig. 1), with a surface smaller, included in the regular geometrical figure of the initial status.

The indicator of the global pollution status of the environment, *I_{pg}* results from the ratio between the surface representing the ideal status *S_i* and the surface representing the real status *S_r* (Fig. 1).

$$S_{ideal} = \Pi \cdot r^2 = \Pi \cdot 10^2 = 314$$

$$S_{real} = \Pi \cdot 8.91^2 = 249.27$$

$$I_{pg} = \frac{314}{249.27} = 1.25$$

When there are no modifications of the environmental factors, thus no pollution, this indicator is equal to 1. Graphically speaking, the geometrical figure, illustrating the environmental real status is superposed on the figure illustrating the ideal status. When there are modifications in the quality of the environmental factors, *I_{pg}* is bigger and bigger supra-unitary values as the surface of the real circle are reduced.

In order to analyze the values obtained for the global pollution indicator, a scale from 1 to 6 has been proposed, as follows:

$I = 1$ – natural environment unaffected by human activity;

$1 < I < 2$ – environment affected by human activity in admissible limits;

$2 < I < 3$ – environment affected by human activity, causing discomfort status to life forms;

$3 < I < 4$ – environment affected by human activity, causing troubles to life forms

$4 < I < 6$ – environment greatly affected by human activity, dangerous to life forms;

I above 6 – degraded environment, improper to life forms

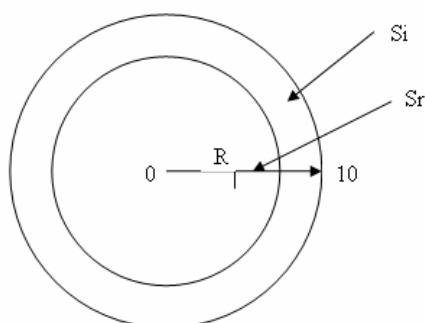


Fig. 1. Graphic representation for I_{pg} evaluation

For the studied case the following results were obtained:

$1 < I_{pg} < 2$ – environment affected by human activity, causing discomfort to all life forms;

4. Conclusions

Plant area soil may be considered in some areas as significantly polluted. The main contaminants of the plant area soil are the organic carbon content (considering the substances extractable in petroleum ether) and the cadmium content.

Outside the plant area soil presents a pollution rate potentially significant: mostly polluted is the area in front of gate 1, in front of the eating-hall (S_{16}), the reduction measures of the pollution and degradation

tendence of the area soil must mainly regard the waste management, water discharges from the site and the fall-out and solid particles emission through the dispersion funnels or chimneys of the unity.

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WASTEWATER CHARACTERISTICS IN TEXTILE FINISHING MILLS

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Abstract

The aim of this paper was to accurately analyze the sources of water pollution and loading concentrations in textile finishing mills. A process data collection was performed and integrated with a characterization of the process effluents in terms of treatability and reusability. In order to evaluate properly the wastewater loading, an analysis course was set. The samples have been gathered for two months; instantaneous samples (PI) were drawn from the wastewater, as well as from the painting baths, at the time of the overflow. Based on several daily average values, a general average (PG) has obtained. The experimental data were statistically analyzed and the average values of the investigated parameters for each collecting point corresponding to the sectors of the finishing section were assessed..

Key words: analysis, dye, maximum admissible limit, pollutant, wastewater

1. Introduction

Textile industry is a very diverse sector in terms of raw materials, processes, products and equipment and has very complicated industrial chain. The textile finishing covers the bleaching, dyeing, printing and stiffening of textile products in the various processing stages (fibre, yarn, fabric, knits, finished items). The purpose of finishing is in every instance the improvement of the serviceability and adaptation of the products to meet the ever-changing demands of fashion and function.

The impacts on the environment by textile industry have been recognized for some time, both in terms of the discharge of pollutants and of the consumption of water and energy (Lacasse and Baumann, 2006). Finishing processes can be categorized into purely mechanical and wet processes. The liquid phase for the latter type is primarily water, and - to a lesser extent - solvents and liquefied ammonia gas. Another important medium is steam. To achieve the desired effects, a range of chemicals, dyes and chemical auxiliaries are used.

Environmental problems of the textile industry are mainly caused by discharges of wastewater. The textile sector has a high water

demand. Its biggest impact on the environment is related to primary water consumption (80–100 m³/ton of finished textile) and waste water discharge (115–175 kg of COD/ton of finished textile, a large range of organic chemicals, low biodegradability, colour, salinity). Therefore, reuse of the effluents represents an economical and ecological challenge for the overall sector (Li Rosi et al., 2007). Textile processing employs a variety of chemicals, depending on the nature of the raw material and product (Aslam et al., 2004). The effluents resulting from these processes differ greatly in composition, due to differences in processes, used fabrics and machinery (Bisschops and Spanjers, 2003).

Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems.

Major pollutants in textile wastewaters are high suspended solids, chemical oxygen demand, heat, colour, acidity, and other soluble substances (Venceslau et al., 1999; World Bank, 2007).

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This paper assesses the characteristics of wastewaters and the average values of the analyzed parameters for each collecting point in the in the finishing mill from a textile factory in Romania.

2. Case study

The technological diagram for wastewater discharging sections from a textile company that processes cotton and cotton-like fabrics was presented together with the wastewater quality parameters, resulted from instantaneous, as well as general samples (Fig. 1) (Savin and Butnaru, 2009). This sector consists of 12 active sections, each of them being provided with monitoring collecting lines, through which the water flows towards the pretreatment plant.

Analysis was carried out for two months and the preliminary conclusions drawn on the basis of the experimental data allowed for a comparison between the concentration of the polluting loading corresponding to some sectors of the Finishing mill and the maximum admissible limits of the analyzed parameters according to NTPA 002/2005 (GD, 2005; Nisteanu et al., 1997; Zaharia, 2008)

The examination of wastewater characteristics is based on the data grouped in Tables 1-6, corresponding to the sections in the finishing sector where the maximum allowable values were exceeded, as well as Tables 7-12, by taking into account the maximum admissible values of the analyzed parameters, according to NTPA 002/2005 (GD, 2005). Some values for Maximum Allowable Concentration are presented in Table 13 (GD, 2005).

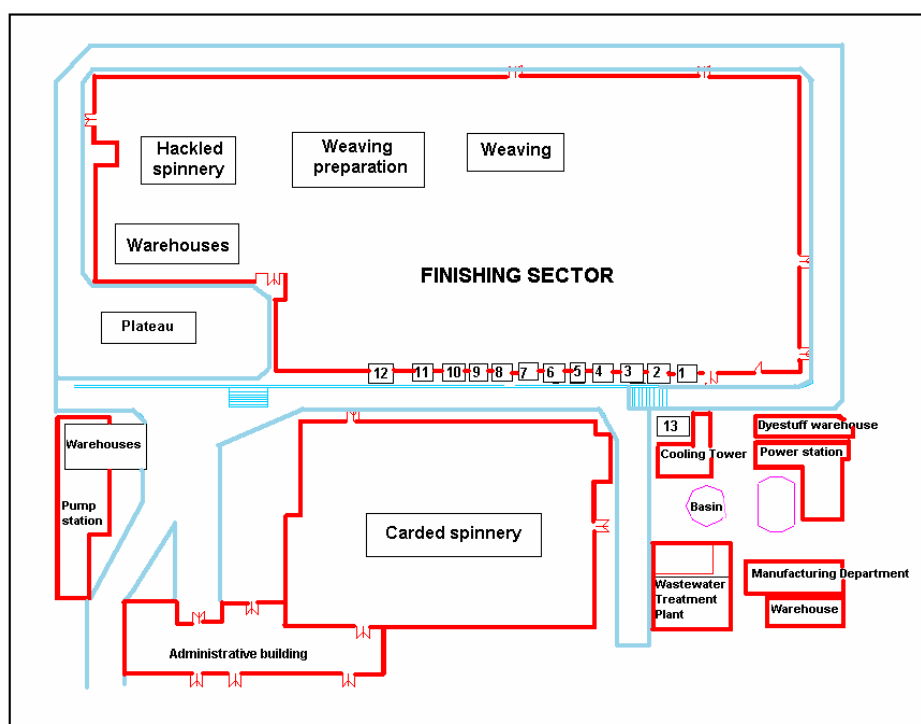


Fig.1. Scheme with the locations of the industrial wastewater sampling points (1. Burning Sector; 2. CH Station; 3. Bleaching Station; 4. Mercerization Section; 5. Thermofixing section, 6. Chemicals Warehouse, 7. Dyestuff Warehouse; 8. Dyeing Sector; 9. Dyeing Gauge; 10. Printing Sector; 11. Printing Warehouse; 12. Dressing Sector, 13. Wastewater Treatment Plant)
(Note: The samples have been drawn upstream the entrance to the sections)

Table 1. Wastewater characteristics for Section 1, corresponding to Burning Sector (instantaneous samples, PI)

Date	pH	NO_3^- mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residue mg/L	BOD ₅ mgO ₂ /L
14-07	5.2	3	158	169	1749	1.6	7.11	3	992	-
16-07	6.5	1.7	105	64	1512	2.8	3	0.08	4535	675
24-06	5.9	5.3	425	132	2995	1.1	7.9	0.32	3275	800
28-07	5.0	0.025	936	118	3784	2.1	5.7	2.5	6000	-
30-07	5.5	2.1	248	66.8	3106	1.1	3.62	1.2	4400	925
15-08	5.0	2.9	725	180	7802	2.3	6.75	1.75	6920	-
Average	5.51	2.5	432.8	121.6	3491.3	1.83	5.676	1.475	4353.6	800

Table 2. Wastewater characteristics for Section 3, corresponding to Bleaching Sector (PI)

Date	pH	NO ₃ ⁻ mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residual mg/L	BOD ₅ mgO ₂ /L
14-07	10.5	6.1	219	100	1865	-	15.3	6.1	4231	-
16-07	9.3	2.2	135	2200	966	-	2.5	0.2	4785	-
25-07	12.3	6.3	88	80	2960	0.0	5.0	0.36	6222	326
26-07	12.5	5.2	938	830	1261	2.7	6.9	0.4	6000	-
28-07	11	6.1	617	600	6200	8.1	9.1	2.85	6000	-
29-07	12.3	7.1	106	60	2820	9.62	9.16	0.24	7694	100
30-07	13.0	5.1	120	120	3441	5.52	7.9	1.1	9600	188
01-08	12.4	6.0	85	140	1995	6.7	8.1	0.36	8195	122
average	11.6	5.54	288.5	516	2688.5	5.44	8.0	1.45	6590.9	184

Table 3. Wastewater characteristics for Section 4, corresponding to Mercerizing Sector (PI)

Date	pH	NO ₃ ⁻ mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residual mg/L	BOD ₅ mgO ₂ /L
16-07	10.5	3.3	56	128	2142	3.6	8.7	0.16	3474	-
25-07	11.6	6.4	125	160	3160	0.0	5.6	12.8	3345	500
28-07	7.0	9.4	137	175	6556	0.92	2.150	0.025	3600	520
29-07	12.3	4.1	56	40	1820	0.32	7.62	0.56	3594	100
30-07	11.0	10	147	64	1991	-	8.5	2.8	5600	80
01-08	12.4	4.4	110	150	1060	1.7	18.6	0.32	3650	-
average	10.8	9.4	105.2	119.5	2788.2	1.31	8.53	2.773	3877.2	300

Table 4. Wastewater characteristics for Section 8, corresponding to Dyeing Sector

Date	pH	NO ₃ ⁻ mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residue mg/L	BOD ₅ mgO ₂ /L
16-07	10.7	8	344	104	3836	-	33.3	1.28	1046	195
24-07	6.3	3.7	72	48	258	0.8	0.48	0.08	548	70
25-07	8.3	6.2	956	141	1185	1.3	11.5	0.92	184	300
26-07	8.05	6.04	147	-	1907.6	-	14.31	0.9	1600	-
28-07	6.5	4.7	820	386	5443	0.8	14.29	-	6800	-
29-07	8.0	8.3	534	601	920	3.3	9.9	0.96	836	140
30-07	8.0	7.4	500	139	860	1.6	14.33	0.89	4400	155
01-08	8.6	4.1	623	100	853	1.9	16.5	1.32	717	-
average	8.06	6.06	499.4	213.2	1907.8	1.62	14.34	0.91	2016	170

Table 5. Wastewater characteristics for Section 9, corresponding to Dyeing Gauge Sector (PI)

Date	pH	NO ₃ ⁻ mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residue	BOD ₅ mgO ₂ /L
28-07	6.5	4.9	325	230	7561	5.9	18.4	0.21	2000	410
30-07	6.5	4.7	-	70	2800	6.2	18.8	0.19	2400	230
01-08	12.1	4.8	175	150	458	-	18.6	0.2	2135	-
average	8.36	4.8	250	150	3606.3	6.05	18.6	0.2	2178.3	320

Table 6. Wastewater characteristics for Section 12, corresponding to Dressing Sector (PI)

Date	pH	NO ₃ ⁻ mg/L	TSS mg/L	Chlorides mg/L	COD mgO ₂ /L	H ₂ S mg/L	NH ₄ ⁺ mg/L	NO ₂ mg/L	Fixed Residue mg/L	BOD ₅ mgO ₂ /L
14-07	7	1.6	140	40	1369	9.6	5.06	1.0	610	180
25-07	7.3	3.6	544	80	825	7.6	14.8	2.2	66	60
26-07	7.11	-	135	-	1905	-	9.93	1.6	400	-
average	7.15	2.6	273	60	1097	8.6	9.93	1.6	358.6	120

Table 7. Sample drawn from the course corresponding to the Burnt Sector (Section 1)

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>TSS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/L</i>	<i>H₂S</i> <i>mg/L</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	5.0	0.025	105	64	1512	1.1	3	0.08	992	675
max.	6.5	5.3	936	180	3784	2.8	7.9	3	6000	925
Average(PG)	5.62	2.5	374.4	121.6	2629.2	1.83	5.4	1.475	3840.4	800

Table 8. Sample drawn from the course corresponding to Section 3

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>MTS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/L</i>	<i>H₂S</i> <i>mg/L</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	9.3	2.2	85	60	966	0.0	2.5	0.2	4231	122
max.	13	7.1	938	2200	6200	9.62	15.3	6.1	9600	326
average	11.6	5.54	288.5	516	2688.5	5.44	8	1.45	6590.9	184

Table 9. Sample drawn from the course corresponding to the Mercerized sector (Section 4)

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>TSS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/L</i>	<i>H₂S</i> <i>(mg/L)</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	7.0	3.3	56	40	1820	0.0	2.15	0.025	3345	80
max.	12.4	10	147	175	6556	3.6	18.6	12.8	5600	520
Average (PG)	10.8	9.4	105.2	119.5	2788.2	1.31	8.53	2.773	3877.2	300

Table 10. Sample drawn from the course corresponding to the Section 8

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>TSS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/L</i>	<i>H₂S</i> <i>mg/L</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	6.3	3.7	72	48	258	0.8	0.48	0.08	184	70
max.	10.7	8.3	820	601	5443	3.3	33.3	1.28	6800	300
average	8.06	6.06	499.4	213.2	1907.8	1.62	14.34	0.91	2016	170

Table 11. Sample drawn from the course corresponding to the Dyeing Sector (Section 9)

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>TSS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/D</i>	<i>H₂S</i> <i>mg/L</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	6.5	4.8	175	70	458	5.9	18.6	0.2	2000	230
max.	12.1	4.8	325	230	7561	6.2	18.6	0.2	2400	410
Average (PG)	8.36	4.8	250	150	3606.3	6.05	18.6	0.2	2178.3	320

Table 12. Sample drawn from the course corresponding to Section 12

<i>Value</i>	<i>pH</i>	<i>NO₃⁻</i> <i>mg/L</i>	<i>TSS</i> <i>mg/L</i>	<i>Chlorides</i> <i>mg/L</i>	<i>COD</i> <i>mgO₂/L</i>	<i>H₂S</i> <i>mg/L</i>	<i>NH₄⁺</i> <i>mg/L</i>	<i>NO₂</i> <i>mg/L</i>	<i>Fixed Residue</i> <i>mg/L</i>	<i>BOD₅</i> <i>mgO₂/L</i>
min.	7	1.6	135	40	825	7.6	5.06	1.0	66	60
max.	7.3	3.6	544	80	1369	9.6	14.8	2.2	610	180
Average (PG)	7.15	2.6	273	60	1097	8.6	9.93	1.6	358.6	60

Table 13. Maximum Allowable Concentrations (MAC) values according to NTPA 002/2005 (GD, 2005)

No.	Quality indicator	Units	MAC	Analysis method
1.	Temperature, T	⁰ C	40	-
2.	pH	pH units	6.5-8.5	SR ISO 10523-97
3.	Suspended solids (TSS)	mg/L	350	STAS 6953-81
4.	BOD ₅	mg O ₂ /L	300	STAS 6560-82
5.	COD (as CCO-Cr)	mg O ₂ /L	500	SR ISO 6060/96
6.	Nitrogen (as [NH ₄ ⁺])	mg/L	30	STAS 8683-70
7.	Total phosphorus (as P)	mg/L	5.0	STAS 10064-75
8.	Total cyanides (CN)	mg/L	1.0	SR ISO 6703/1-98
9.	Sulphides and Hydrogen Sulphide (S ₂ ⁻)	mg/L	1.0	SR ISO 10530-97
10.	Sulphites (SO ₃ ²⁻)	mg/L	2	STAS 7661-89
11.	Sulphates (SO ₄ ²⁻)	mg/L	600	STAS 8601-70
12.	Phenols (C ₆ H ₅ OH)	mg/L	30	STAS 7167-92
13.	Substances extractable with organic solvents	mg/L	30	SR 7587-96
14.	Biodegradable synthetic detergents	mg/L	25	SR ISO 7875/1.2-96
15.	Lead (Pb ²⁺)	mg/L	0.5	STAS 8637-79
16.	Cadmium (Cd ²⁺)	mg/L	0.3	SR ISO 5961/93
17.	Total Chromium (Cr ³⁺)+(Cr ⁶⁺)	mg/L	1.5	SR ISO 9174-98
18.	Hexavalent Chromium (Cr ⁶⁺)	mg/L	0.2	STAS 7884-91
19.	Copper (Cu ²⁺)	mg/L	0.2	STAS 7795-80
20.	Nickel (Ni ²⁺)	mg/L	1.0	STAS 7987-67
21.	Zinc (Zn ²⁺)	mg/L	1.0	STAS 8314-87
22.	Total Manganese (Mn)	mg/L	2.0	SR ISO 6333-96
23.	Free residual chloride (Cl ₂)	mg/L	0.5	STAS 6364-78

3. Effluents characterization

Characterization of textile process effluent streams is very important to develop strategies for water treatment and reuse. To optimize treatment and reuse possibilities, textile industry waste streams should be in principle considered separately. When the characteristics of the separate streams are known, it can be decided which streams may be combined to improve treatability and increase reuse options (EWA, 2005; Le Rosi et al., 2007).

Data from Tables 1-12 lead to the following outcomes:

- in **Section 1**, corresponding to the **Burning** sector, the analyzed parameters which exceed the maximum admissible values given in Table 13 are pH, TSS, COD, H₂S, BOD₅;

- in **Section 3**, corresponding to the **Bleaching** sector, the analyzed parameters which exceed the maximum admissible values in Table 13 are pH, COD, H₂S;

- in **Section 4**, corresponding to the **Mercerized** sector, the analyzed parameters which exceed the maximum admissible values in Table 13 are pH, COD, H₂S;

- in **Section 8**, corresponding to the **Dyeing** sector, the analyzed parameters which exceed the maximum admissible values in Table 13 are TSS, COD, H₂S;

- in **Section 9**, corresponding to the **Printing** sector, the following analyzed parameters exceed the maximum admissible values given in Table 13: COD, H₂S, BOD₅;

- in **Section 12**, corresponding to the **Dressing** sector, the analyzed parameters which exceed the maximum admissible values in Table 13 are: COD, H₂S.

These characteristics are dependent on the main activity developed in each sector. A comparison of the textile effluent and the standard for discharge of textile wastewater into receiving waters shows that the wastewaters have to be treated in order to meet the acceptable range of the effluent discharge standards.

If untreated wastewater would be discharged in aquatic environment, some effects could take place, for example:

- Effect of BOD: depletes dissolved oxygen from streams, lakes and oceans; may cause death of aerobic organisms (fish kills etc.); increases anaerobic properties of water
- Effect of TSS: increases turbidity (less light - reduced photosynthesis, causes fish's gills to get plugged up); increases silting (reduces lifetime of lakes, changes benthic ecology)
- Effect of pH: organisms are very susceptible to acids and bases

4. Consideration on water conservation and pollution prevention in textile finishing mills

The value of water resources is universally recognized and water shortage is increasing in many companies. The need to preserve this resource is the driving force behind the identification and exploitation of non-conventional water sources. For industry, in particular textile production, wastewater reclamation appears a technically feasible solution (Bergenthal, 1984; Li Rosi et al., 2007).

Under these concerns a variety of wastewater recycle/reuse technologies have been developed during time to allow these mills to reduce the volume of wastewater and the amount of pollutants discharged.

With most of these technologies, specific technical and economic factors affect their application at a given mill, and thus each application must be considered under its own mill-specific conditions.

The first step in a pollution prevention strategy for water is a thorough audit and characterization of wastewater from textile operations. A program of maintenance, inspection, and evaluation of production practices should be established. Significant reductions in water use can be made by implementing the following: minimizing leaks and spills, maintaining production equipment properly, identifying unnecessary washing of both fabric and equipment, training employees on the importance of water conservation.

5. Conclusions

The results can be used as starting points in order to design the sewage network and to ensure its protection in case of the joint effect of some toxic and corrosive pollutant agents. Certain pollutants in textile wastewater are more important to target for pollution prevention. The organic load (COD as CCO-Cr) is exceeded in all analyzed sectors: Burnt, Bleaching, Mercerized, Dyeing, Printing, Dressing.

Wastewater in Bleaching, Mercerized and Printing sectors requires separate treatment, which can decrease the concentration of polluting agents.

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Book Review

NANOMATERIALS
An Introduction to Synthesis, Properties and Application

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The book focuses on the special phenomena related to nanomaterials and attempt to provide explanations which avoid – as far as possible any highly theoretical and quantum mechanical description. The difficulties with nanomaterials arise from the fact that, in contrast to conventional materials, a profound knowledge of materials science is not sufficient.

The book includes 11 chapters and a subject index. The authors give initially two definitions for nanomaterials. The first - and broadest - definition states that nanomaterials are those materials where the size of the individual building blocks are less than 100 nm, at least in one dimension. This definition is well suited for many research proposals, where nanomaterials have a high priority. The second definition is much more restrictive, and states that nanomaterials have properties which depend inherently on the small grain size and, as nanomaterials are usually quite expressive, such a restrictive definition makes more sense. The main difference between nanotechnology and conventional technologies is that the “bottom-up” approach is preferred in nanotechnology, whereas conventional technologies usually use the “top-up” approach. The difference between these two approaches can be explained simply by using an example of powder production, where the chemical synthesis represents the bottom-up approach, while the crushing and milling of chunks represents the equivalent top-down process.

Chapter 1 is an introductory part, which refers to nanomaterials and nanocomposites, elementary consequences of small particle size, surface of nanoparticles, thermal phenomena, diffusion scaling law.

Chapter 2, “Surfaces in Nanomaterials” presents some general consideration in nanomaterials, where the surface forms a sharp interface between a

particle and its surrounding atmosphere, or between a precipitated phase and the current phase. These are free surface in the case of particulate materials, or grain boundaries in bulk material. Nanomaterials have large surfaces, a fact which can be demonstrated by using spherical particles as examples.

The origin of surface energy is explained by a mode which assumes that particles are produced by breaking a large solid piece of material into smaller parts. In order to achieve this, it is necessary to cut the bonds between the neighboring atoms.

Chapter 3, “Phase Transformation of Nanoparticles” focuses on thermodynamics of nanoparticles, heat capacity, phase transformations and coagulation, structures of nanoparticles, nanoparticle melting, structural fluctuations.

The simplest possible description is used, neglecting any influential factors required for an exact description of equilibria. Phase transformations are connected with changes in physical properties, and in most case it is the density of the material that is changing. Within the context of phase transformations of small particles, the majority of extensive studies have been conducted with respect to the melting of metal particles. Phase transformation might be caused by the temperature flash that occurs during the coagulation of two particles.

In the case of zirconia for example, the temperature of phase transformation was found to decrease with decreasing particle size, which led to the fact that tetragonal phase – a high temperature phase – is in fact found at room temperature. Additionally, in the case of particles with size less than 5 nm the cubic phase is quite often found. This phenomenon is not restricted to compounds with comparably simple structures; rather, it is also found in the case of more complex structures with typical examples being ferroelectric or antiferroelectric compounds. At high temperature, these compounds

are cubic, however, by reducing the temperature a transformation occurs to the tetragonal perovskite structure, which is ferroelectric below the Curie point. The continuous transition from one phase to another (distorted) phase, in combination with an increase in the lattice parameter with decreasing particle size appears to be general, and was even observed for high-temperature superconductors.

Although until now those considerations that have been made were purely thermodynamic in nature, nanoparticles are so small that thermal fluctuations are in fact observed. Typical examples of those phenomena are superparamagnetism and its analogue, superferroelectricity, and electron microscopy studies on the melting of small metal nanoparticles have provided information on similar phenomena.

By determining the relative amounts of solid and melted particles as a function of the particle size, it is possible to calculate phase diagrams where two-phase regions caused by fluctuations are indicated.

Chapter 4, "Gas-Phase Synthesis of Nanoparticles" includes some fundamental considerations, inert gas condensation process, physical and chemical vapor synthesis processes, laser ablation process, the microwave plasma process, flame aerosol process, synthesis of coated particles.

The process of particle formation may be divided into four major steps: nucleation, condensation of atoms or molecules, coagulation by exchange of surface energy, agglomeration. Size limitation by charging the particle are observed at the microwave plasma process and special variants of the flame synthesis process, both of which are described later in the chapter. The most important – and certainly the oldest – process for synthesizing nanoparticles in the gas phase is that of inert gas condensation. This process applies thermal evaporation to a metal within a vacuum chamber filled with a small amount of inert gas.

The basic principle of the inert gas condensation process leads to many variants, as the systems employed differ in how the metal is introduced and subsequently evaporated. One of the most interesting possibilities is heating with an electron beam. The technical up-scaling of an inert gas condensation process may lead to the introduction of the elements that limit particle size growth. However, two possible measures exist by which particle size and particle size distribution may be controlled: (i) a reduction of the residence time of the particles in the reaction zone; and (ii) rapid cooling of the particles after they have left the reaction zone. For both measures the original diffusion-controlled process is not applicable. Rather it is necessary to replace transport via thermal diffusion with transport using a carrier gas. When used as a heat source for mass production, an electrical arc has many advantages and is utilized on a regular basis.

A system for powder production using the laser ablation process generally consists of two essential elements: the pulsed high-power laser, and

with the optical focusing system and feeding device for the precursor. In order to produce larger quantities with this process, rotating targets and automatic wire feeding systems have been developed.

The processes of chemical and physical vapor synthesis, as well as laser ablation, are purely random processes; hence, the only means by which particle size and size distribution can be influenced are the concentrations of active species in the gas, the temperature and, most importantly, the rapid cooling (quenching) of the gas after leaving the reaction zone. This situation is entirely different from that of the microwave plasma process, where the particles originating in the plasma zone carry electric charges. As a consequence, the probability for coagulation and agglomeration is significantly reduced, as the collision parameter decreases with increasing particle size.

The mechanism of nanoparticle formation in the microwave plasma differs from, that of a chemical vapor synthesis in a tubular furnace, as the reactants are ionized and dissociated. This also allows lower reaction temperatures. Among all of the processes used to produce nanoparticulate powders, the flame aerosol process is the oldest. Additionally, it is the only one to be used for mass production in the kiloton range. Although this well-established industrial process has been used for many decades, the basic principles are still not well understood, not least because the processes of powder synthesis and particle formation take place at extremely high temperatures and over very short times.

Although many applications of nanomaterials require the use of nanocomposites, the impossibility of obtaining well-distributed nanocomposites simply by blending processes led to the development of coated nanoparticles.

The processes used for particle coating must fulfill a series of requirements. The first and most important point is that the particles remain individualized and are not agglomerated. This requires either extremely low particle concentrations in the gas atmosphere, or particles that carry electrical charges of equal sign. Additionally, the temperature in the coating step must be sufficiently low so as not to destroy the matter used for coating. This condition is of particular importance when the coating consists of organic compounds.

Chapter 5, "Magnetic Properties of Nanoparticles" refers to magnetic materials, superparamagnetic materials, susceptibility and related phenomena in superparamagnets, application of superparamagnetic materials, exchange-coupled magnetic nanomaterials.

Materials are classified by their response to an external magnetic field as diamagnetic, paramagnetic, or ferromagnetic. Although, in general, all materials show inherently diamagnetic properties, only those materials not showing paramagnetic or ferromagnetic behavior in addition are known as diamagnetic.

Superparamagnetic materials excel in zero remanence and coercivity; moreover,

superparamagnetism is limited to small nanoparticle. Superparamagnetism leads, as the vector of magnetization is fluctuating thermally, to a zero coercivity. The explanation for this phenomenon is found in the magnetic crystal anisotropy. Superparamagnetism is a property of isolated noninteracting particles. In a macroscopic material consisting of many particles, dipole-dipole interaction of the particles leads to magnetically large particles that are no longer superparamagnetic. Embedding the nanoparticles in a second, nonmagnetic, phase causes the particles to be spaced further apart, such that the interaction is reduced. This led to the production of nanocomposites. In order to ensure that a technical material is superparamagnetic, the individual particles should not touch each other.

The majority of successful applications of magnetic nanomaterials use particular composites, with superparamagnetism being necessary for the application of magnetic particles, for two reasons:

- Superparamagnetic particles avoid magnetic clustering;
- Superparamagnetic particles may be either attracted or released by switching the magnetic field.

From an economic viewpoint, the most interesting applications of superparamagnetic nanoparticles are related to medicine and biology.

In general, these designs of particle may be applied to magnetic cell separation techniques. Further successful application is related to medical diagnostics. Superparamagnetic nanoparticles are used to enhance the contrast in nuclear magnetic resonance (NMR) imaging. One further potentially important application of superparamagnetic nanoparticles is that of magnetic refrigeration where, instead of using ozone-depleting refrigerants and energy-consuming compressors, nanocomposites moving in a magnetic field might be employed. The concept behind magnetic cooling dates back several decades, having been applied in low-temperature physics.

A further fascinating application of superparamagnetic particles, and one which is already widely used in technical products, is that of ferrofluids; these are stable suspensions of superparamagnetic particles in a liquid. In order to avoid the particles coagulating magnetically, they are coated with a second distance-holder phase.

In order to obtain a nanosized regular structure in the final product, with perfect distribution of the two different magnetic phases, a well-ordered regular structure is necessary within the material before the annealing stage is started. The energy product of this composite magnetic material exceeds the theoretical possible maximal value for FePt by more than 50%.

Some extremely interesting applications of this class of materials involve soft magnetic materials. The constant of anisotropy of these materials, which in most cases are metallic, is more than an order of magnitude smaller than that for soft ferrites.

Chapter 6, "Optical Properties of Nanoparticles" refers to adjustment of the index of refraction, optical properties related to quantum confinement, quantum dots and other lumophores, metallic and semiconducting nanoparticles in transparent matrices, special luminescent nanocomposites, electroluminescence, photochromic and electrochromic materials, general consideration, photochromic materials, electrochromic materials, magneto-optic applications.

In view of technical applications, the optical properties of nanoparticles and nanocomposites are of major interest. Besides their economic importance, the scientific background of these properties is of fundamental importance in order to understand the behavior of nanomaterials.

In many applications, it is necessary to adjust the index of refraction of a polymer precisely to a given value. A typical example of this is the glue used to fix or connect optical glass fibers for information transmission. One way to do this is to add nanoparticles with an index of refraction which differs from that of the polymer.

The photocatalytic activity of the nanoparticles must not lead to a self-destruction of the composite system, and it is essential to check this point before fixing a combination of polymer matrix and nanoparticles. Nanoparticles which emit at different colors may be simultaneously excited with a single light source, making multiplexed detection of different biological targets possible. Additionally, the absorption spectra of organic compounds are relatively narrow in comparison to quantum dots exhibiting a broad absorption spectrum that range deep into the UV. The only major disadvantage here is the significantly larger size as compared to organic lumophore molecules.

At present, the economically most attractive application of luminescent nanoparticles is found in biotechnology and diagnostics. For this application, it is necessary to attach antibodies, peptides, or proteins at the surface of the particles. These compounds must be selected in such a way that they attach exactly at the intended receptor.

From an economic viewpoint, electroluminescence applications have an extremely high potential for technical applications among consumer products. In electroluminescent devices, light emission is stimulated by electric fields instead of energy-rich photons.

The main advantage of devices based on electroluminescent materials lies in the fact that, in contrast to liquid crystal devices (LCDs), an external light source is no longer necessary. Although today, most electroluminescent devices function with organic materials, these compounds (which are used as the starting materials for organic light-emitting diodes). Primarily, nanoparticles made from semiconducting materials or doped insulating particles are applied as luminescent materials. Therefore, perhaps the most interesting future application will be seen in flexible display technologies.

One further interesting optical application of ceramic/polymer nanocomposites is their use as magneto-optical materials. Within this context, the phenomena under question include the Faraday effect (rotation of the plane of polarization of light in transmission), and the Kerr effect (rotation of the polarization plane after reflection at the surface of magnetic materials).

A higher concentration of ferrite particles clearly increases optical absorption. Furthermore, the strong increase in absorption for shorter wavelengths is shifted significantly to shorter wavelengths when the concentration is reduced. This blue shift may be attributed to a smaller particle size or surface phenomena on the band gap.

Chapter 7, "Electrical Properties of Nanoparticles" discuss about fundamentals of electrical conductivity in nanotubes and nanorods, carbon nanotubes, photoconductivity of nanorods, electrical conductivity of nanocomposites.

One interesting method which can be used to demonstrate the steps in conductance is the mechanical thinning of a nanowire and measurement of the electrical current at a constant applied voltage. The important point here is that, with decreasing diameter of the wire, the number of electron wave modes contributing to the electrical conductivity is becoming increasingly smaller by well-defined quantized steps.

In electrically conducting carbon nanotubes, only one electron wave mode is observed which transport the electrical current. As the lengths and orientations of the carbon nanotubes are different, they touch the surface of the mercury at different times, which provides two sets of information: (i) the influence of carbon nanotube length on the resistance; and (ii) the resistances of the different nanotubes. As the nanotubes have different lengths, then with increasing protrusion of the fiber bundle an increasing number of carbon nanotubes will touch the surface of the mercury droplet and contribute to the electrical current transport.

For technical applications outside of electronics, the electrical conductivity of nanomaterials can best be exploited as the electric-conducting phase in nanocomposites. The electrical conductivity of nanocomposites depends on percolation, the theory of which treats the properties of two-phase mixtures consisting either of conducting and insulating phases, or of a solid and pores. In the latter case, percolation leads to the formation of a network of open pores.

Assuming an electric-conducting nanocomposite - a two-phase mixture consisting of an insulating and an electrical conductive phase - the percolation threshold describes, in simple terms, the concentration of conductors required for the onset of electrical conductivity. At concentrations below the percolation threshold, there is no electrical conductivity, whereas above the threshold conductivity is observed. The percolation threshold and electrical conductivity at

saturation level are heavily dependent on the fabrication process.

Chapter 8, "Mechanical Properties of Nanoparticles" deals with bulk metallic and ceramic materials, influence of porosity, influence of grain size, superplasticity, filled polymer composites, particle-filled polymers, polymer-based nanocomposites filled with platelets, carbon nanotube-based composites.

The discussion of mechanical properties of nanomaterials is, in to some extent, only of quite basic interest, the reason being that it is problematic to produce macroscopic bodies with a high density and a grain size in the range of less than 100 nm. However, two materials, neither of which is produced by pressing and sintering, have attracted much greater interest as they will undoubtedly achieve industrial importance. These materials are polymers which contain nanoparticles or nanotubes to improve their mechanical behaviors, and severely plastic-deformed metals, which exhibit astonishing properties. However, because of their larger grain size, the latter are generally not accepted as nanomaterials. Experimental studies on the mechanical properties of bulk nanomaterials are generally impaired by major experimental problems in producing specimens with exactly defined grain sizes and porosities. Therefore, model calculations and molecular dynamic studies are of major importance for an understanding of the mechanical properties of these materials.

Filling polymers with nanoparticles or nanorods and nanotubes, respectively, leads to significant improvements in their mechanical properties. Such improvements depend heavily on the type of the filler and the way in which the filling is conducted. The latter point is of special importance, as any specific advantages of a nanoparticulate filler may be lost if the filler forms aggregates, thereby mimicking the large particles. Particulate-filled polymer-based nanocomposites exhibit a broad range of failure strengths and strains. This depends on the shape of the filler, particles or platelets, and on the degree of agglomeration. In this class of material, polymers filled with silicate platelets exhibit the best mechanical properties and are of the greatest economic relevance. The larger the particles of the filler or agglomerates, the poorer are the properties obtained. Although, potentially, the best composites are those filled with nanofibers or nanotubes, experience teaches that sometimes such composites have the least ductility. On the other hand, by using carbon nanotubes it is possible to produce composite fibers with extremely high strength and strain at rupture.

Among the most exciting nanocomposites are the polymer-ceramic nanocomposites, where the ceramic phase is platelet-shaped. This type of composite is preferred in nature, and is found in the structure of bones, where it consists of crystallized mineral platelets of a few nanometers thickness that are bound together with collagen as the matrix. Composites consisting of a polymer matrix and

defoliated phyllosilicates exhibit excellent mechanical and thermal properties.

Chapter 9, "Nanofluids" analyses aspects regarding nanofluids for improved heat transfer, ferrofluids, general considerations, properties of ferrofluids, application of ferrofluids.

Nanofluids are stable suspensions of nanoparticles in a liquid. In order to avoid coagulation of the particles, the particles must be coated with a second distance-holder phase which, in most cases, consists of surfactants that are stable in the liquid. One typical application of nanofluids containing nanoparticles is as a coolant, since the addition of only a few volume percent of nanoparticles to a liquid coolant can significantly improve its thermal conductivity, yet have no negative influence on its heat capacity. In fact, the high heat capacity of nanoparticles can actually improve the heat capacity of a coolant. When considering the technical applications of these fluids, it is not only the heat capacity and thermal conductivity but also the rheological parameters that are of vital importance. One fascinating application of superparamagnetic particles - and one which already has been widely applied in technical products - is that of ferrofluids, which are a special type of nanofluids.

A ferrofluid is a stable suspension of superparamagnetic particles in a liquid. In order to avoid magnetic coagulation of the particles they must be-coated with a: second, distance-holder phase. Ferrofluids, as magnetic materials, may be used to transfer magnetic fields or to close magnetic circuits in a simple way, without the need for any complicated and shaped parts. Besides these possibilities, the variation of viscosity as a function of an external magnetic field represents one of the most striking properties of a ferrofluid. One of the commercially most successful applications-of ferrofluids in consumer products is in loudspeakers, where the ferrofluid plays three important roles: (i) it centers the voice coil within the magnet; (ii) it acts as a coolant for the voice coil, by removing the heat caused by Ohmic losses; and (iii) it acts as damping medium.

Further broad applications of ferrofluids are in the visualization of magnetic structures and domains. This is used extensively for the quality control of all types of magnetic storage devices, such as magnetic tapes, floppy disks, or magneto-optical disks. In materials sciences, the studies of magnetic domains in alloys, garnets, and minerals and the identification of small defects in steel and weldings are typical fields of application. In such cases, small external magnetic fields are often used to enhance the contrast. Within this context, many economically extremely interesting applications may be identified. For example, in medical diagnostics ferrofluids are applied to increase the contrast of nuclear magnetic resonance (NMR) imaging.

Chapter 10, "Nanotubes, Nanorods, and Nanoplates" discusses about conditions for the formation of rods and plates, layered structures, one-dimensional crystals, nanostructures related to

compounds with layered structures, carbon nanotubes, nanotubes and nanorods from materials other than carbon, synthesis of nanotubes and nanorods.

Nanotubes, nanorods, and nanoplates are frequently observed. Whilst nanorubes and nanorods are often referred to as one-dimensional nanoparticles, nanoparticles and fullerenes, in contrast, are generally denominated as zero-dimensional structures. Although, nanorods and nanoplates are often found as more or less spherical or faceted particles, their one- or two-dimensionality is clearly visible. Notably, as very few routes of synthesis are available for the preferential delivery of aggregates that are not zero-dimensional, interest has centered on these specially shaped nanoparticles and continues to be promoted by the wide range of interesting physical properties associated with these structures. A possibility of obtaining nanorods and nanotubes is related to layered structures, where the crystal structure is built from layers held together; with van-der Waals forces rather than by electrostatic attraction. Another possibility of obtaining nanotubes is to use compounds that crystallize in only one dimension. In theory, this is the most promising way to obtain long fibers, but unfortunately the importance of this route is negligible as the numbers of compounds coming into question is small. The most important class of one-dimensional compounds is the class of silicates called allophanes.

For small particles of compounds crystallizing in layered structures, a minimum free energy can be achieved by reducing the number of dangling bonds by forming tubes; nanotubes are observed especially with this types of compound. The most prominent representative of this class of compound is graphite, although nanotubes consisting of boron nitride, the sulfides and selenides of molybdenum and tungsten, as well as many other compounds, have also been identified.

The formation of nanotubes is not limited to single graphene layers and, as for fullerenes, both "multiwall" and "single wall" nanotubes may be observed. The multiwall nanotubes consist of a series of coiled graphene layers, and can be depicted perfectly using electron microscopy. Potentially, a major application of nanotubes is as electron emitters. Electron emission in an electrical field requires a sharp tip, and the sharper the tip the lower the electrical voltage required for electron emission. This is because the electrical field at the tip controls electron field emission. Although single-wall nanotubes have the sharpest tip occurring in nature, in reality multiwall nanotubes are used as they are more readily available.

One further interesting application of carbon nanotubes exploits their electrical conductivity and large length-to-diameter ratios. Because of the huge aspect ratio, the amount of carbon nanotubes required to achieve electrical conductivity is very small, and it is possible to produce an optical transparent coating with relatively good electrical conductivity. It is also

possible to fill the interior of carbon nanotubes with metals or other compounds. As in the case of coated nanoparticles, this strategy allows two different properties to be combined within one particle. These filled carbon nanotubes may have many exciting applications.

Chapter 11, "Characterization of Nanomaterials" includes aspects on global methods for characterization, specific surface area, X-Ray and electron diffraction, electron microscopy, general considerations, interaction of the electron beam and specimen, localized chemical analysis in the electron microscope, scanning transmission electron microscopy using a high-angle annular dark-field (HAADF) detector.

When considering characterization methods, it is very important to distinguish between methods that deliver values averaged over a large ensemble of particles, and those that provide information about a limited number of particles. The most important among the latter group of methods are those that are microscopic in nature. The behavior of nanomaterials is controlled by their global properties, which provide indications of how an ensemble behaves. However, in order to understand why an ensemble behaves in a certain way, it is necessary to utilize microscopic methods. Both, X-ray and electron diffraction techniques are used to study the crystal structure of specimens, and it is also possible to obtain information on the particle size in this way. Diffraction experiments may be conducted in transmission, usually in electron diffraction, or in reflection, as it is used primarily in X-ray diffraction techniques. In order to study the shape, size, and structure of nanoparticles, electron microscopy is the best-suited technique. Today, however, as electron

microscopy is considered a broad science in its own right, within this chapter we will outline a few basic facts, aiming to avoid the impression that simply by reading these few pages it would be possible to interpret electron micrographs.

Nonetheless, the user of nanomaterials must accept that the properties of the latter materials demand a deeper insight into their physics and chemistry. Whereas, for conventional materials the interface to biotechnology and medicine is related directly to the application, the situation is different in nanotechnology, where biological molecules such as proteins or DNA are also used as building blocks for applications outside biology and medicine.

Each chapter ends with a list of References. Most of the images are colored and this fact improves significantly the understanding of various phenomena.

This valuable monograph addresses in particular the researchers who have to understand the special phenomena and potentials, with an average degree of details. It can also be use as a students course, since the nanomaterials are analyzed from an application – oriented perspective.

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Book Review

NANOTECHNOLOGY
Volume I: Principles and Fundamentals

Günter Schmid (Ed.)

WILEY-VCH Verlag GmbH&Co. KGaA, Weinheim, Germany
ISBN: 978-3-527-3173-5, X+300 pages.

The book deals with the principals and fundamentals of nanotechnology, explaining what nanoscience and nanotechnology really means and what it does not mean. Furthermore, this book contains philosophical and ethical aspects, since any new technology opens up questions concerning social consequences.

After a short introduction, where some new findings in the field of nanotechnology are briefly discussed, Chapter 2, “The Nature of Nanotechnology”, author Günter Schmid starts with various definitions of nanotechnology.

Then, the transition from nanoscience to nanotechnology is considered in a short analysis.

Nanoscience, nanoengineering and nanotechnology are represented by three steps following each other. Each step contains several of many possible examples, which will help to realize how nanoscience develops into nanotechnology. Some of the areas are still only to be found in “nanoscience”, others have already developed into the “nanoengineering” step or even into “nanotechnology”; some are present in all three fields, indicating that there is still a further need for basic research to improve or to extend existing technologies.

Also, in Chapter 2, some aspects regarding molecular motors and machines, molecular switches, single-electron memories, drug delivery, gene chips, hyperthermia, gas sensors, technologies on the nanoscale and structured surfaces are highlighted in order to demonstrate the enormous diversity of nanoscience and nanotechnology. It is shown that nano-effects can occur everywhere, both in simple materials and in complex biological structures. This makes nanoscience and nanotechnology a unique field of development. The examples discussed illustrate the universality of this future-determining technology, which in many of the most attractive

fields is still at the very beginning. Distinct fields that are still part of basic research will develop into techniques which will influence daily life dramatically. Others, usually those of easier and faster research and development, have already become routine techniques.

In Chapter 3, “Top-Down Versus Bottom-Up”, authors W.J. Parak, F.C. Simmel and A.W. Holleitner evidence, in the introductory part, that nanotechnology has evolved from different scientific fields such as physics, chemistry, molecular biology, microelectronics and material sciences. Generally, nanotechnology aims to study and to manipulate real-world structures with sizes ranging between 1 nm, which is one millionth parts of a millimeter, and up to 100 nm. The set of typical “nano”-objects includes colloidal crystals, molecules, DNA-based structures and integrated semiconductor circuits. Also, complex biological organisms, such as a human body, can be subdivided into smaller and smaller subunits.

The “top-down” strategy is introduced as to take processes known from the macroscopic world and to adopt them in such a way that they can be used for doing the same thing on a smaller scale. At present, there are several possible successor top-down nanotechnologies for industry, for example extreme ultraviolet light lithography (EUV), electron beam lithography with multicolumn processing facilities; the focused ion beam (FIB) technique and the ultraviolet nano-imprinting technique. The implementation of each of these techniques requires enormous technical challenges to be overcome.

The antipode of the top-down approach is the so-called bottom-up technique. Here a complex structure is assembled from small building blocks. These building blocks possess specific binding capabilities – often termed “molecular recognition properties” – which allow them to arrange automatically in the correct way. Self-assembly is an

essential component of bottom-up approaches. The ultimate examples of molecular recognition are biological receptor-ligand pairs: molecules that recognize and bind to each other with very high specificity. Prominent examples of such pairs are antibodies and their corresponding antigens and complementary strands of deoxyribonucleic acid (DNA).

Generally, bottom-up assembly techniques seek to fabricate composite materials comprising nanoscale objects which are spatially ordered via molecular recognition. The prime examples of the technique are self-assembled monolayers (SAMs) of molecules. A substrate is immersed in a dilute solution of a surface-active organic material that adsorbs on the surface and organizes via a self-assembly process. The result is a highly ordered and well packed molecular monolayer. The method can be extended towards layer-by-layer (LBL) assembly, by which polymer light-emitting devices (LEDs) have already been fabricated. The self-assembly technique also allows positioning of single molecules between two metal electrodes and subsequently into an experimental circuit. By this set-up, quantum mechanical transport characteristics of single molecules, such as photochromic switching behavior, can be studied in order to build electronic devices with new functionalities.

A typical application of this technique is the formation of networks of metallic nanowires, that is, metals are vapor deposited on to a preformed template matrix made out of copolymers. The polymer networks can be used as two- or even three-dimensional templates. Generally, there is a wide range of materials which can be engineered by bottom-up techniques, such as: nanotweezers, nanomorphors, patterning, quantum dots.

Chapter 4, "Fundamental principles of Quantum Dots", authors W.J. Parak, L. Manna, T. Nann, analyses some considerations on these new trends which involve the ability to fabricate, characterize, and manipulate artificial structures, whose features are controlled at the lower nanometer scale, in areas of research as diverse as engineering, physics, chemistry, materials science and molecular biology. Research in this direction has been triggered by the recent availability of revolutionary instruments and approaches that allow the investigation of material properties with a resolution close to the atomic level. Strongly connected to such technological advances are pioneering studies that have revealed new physical properties of matter at a level which is intermediate between the atomic and molecular level and bulk.

Nanoscale materials are presented as intermediates between atomic and bulk matter.

A few examples are given to explain why the behavior of nanoscale materials can be very different from that of their bulk and from their atomic counterparts and how quantum mechanics can help us in rationalizing this. A bottom-up approach and a simplified picture of a solid are given as being a very

large molecule, where the energy levels of each individual atomic component have merged to form bands. The electronic structure of a quantum dot being intermediate between the two extreme cases of single atoms and the bulk, will then be an easier concept to grasp. The mole of a free electron gas and the concept of quantum confinement are used to explain what happens to a solid when its dimensions shrink one by one. This leads to a more accurate definition of quantum wells, quantum wires and quantum dots. The electronic structure of quantum dots is examined in more detail.

In Chapter 5, "Fundamentals and Functionality of Inorganic Wires, Rods and Tubes", authors J.J. Schneider, A. Popp and J. Engstler, the physical properties of 1D inorganic structures are discussed first, followed by a section devoted to general techniques for the synthesis of inorganic wires, rods and tubes. The chapter then highlights some of the material developments made over the last few years in the very active area of nanostructured inorganic rods, wires and tubes with respect to their scientific materials functionality. The field carbon nanotubes (CNTs) is touched upon in this chapter as far as sensing and nano-micro integration in functional devices are concerned.

The interest in nanostructured materials often arises from the fact that the small size connected with nanoscaled matter creates new chemistry. For example, the extremely high number of interfaces connected with small-scale matter, be it in 0D (particles), 1D (wires, rods, tubes), 2D (films), dimensions create high chemical reactivity. Interfaces control important material properties such as catalytic activity or analytical sensing behavior in addition to electronic properties of nanomaterials, which are highly dependent on such interfacial contacts of individual nano-building blocks and also on the individual QSE of the nano-building blocks. Besides such effects connected with the nanoscale regime, morphological properties of assembled nanomaterials such as habit (size, shape) and surface structure are also important for new and desired materials properties arising from the sequential build-up of larger structures from nano-building blocks.

Chapter 6, "Biomolecule-Nanoparticle Hybrid Systems", authors M. Zayats, I. Willner, is aimed at summarizing the different venues where the unique optical and electronic properties of biomolecule-NP hybrid systems have been applied and to discuss future opportunities in the area. The discussions include issues such as metal nanoparticles for electrical contacting of redox proteins, metal nanoparticles as electrochemical and catalytic labels, metal nanoparticles as microgravimetric labels, semiconductor nanoparticles as electrochemical labels for biorecognition events, metal nanoparticles as optical labels for biorecognition events, semiconductor nanoparticles as optical labels, semiconductor nanoparticles for photoelectrochemical applications, biomolecules as

catalysts for the synthesis of nanoparticles, biomolecule growth of metal nanowires.

The analytical applications of biomolecule-NP hybrid systems have seen tremendous advances in the last decade. The electronic properties of metallic NPs were used to electrically communicate redox proteins with electrodes and to develop amperometric biosensors. The catalytic functions of metallic NPs were broadly applied to develop amplification methods for biosensing events, and the localized plasmonic features of NPs were extensively used to develop new optical methods that probe biorecognition events and design novel biosensor configurations. Optical phenomena such as the surface-enhanced fluorescence are Raman signals by dye-modified metallic NPs, the coupling of the localized plasmon of metallic NPs with surface plasmonic waves, the interparticle plasmon coupling in metallic NP aggregates and the reflectance of NPs were creatively used to image biorecognition events and to develop optical biosensors. Similarly, the coupling of biomolecules to semiconductor NPs (quantum dots) demonstrated the utility of these systems to assemble new optical and photoelectrochemical biosensor systems. The size-controlled emission properties of semiconductor QDs, as a result of the quantum confinement of the electronic levels in the nanoparticles, allow the multiplexed analysis of different targets and the design of high throughput analyses in array formats. The development of photoelectrochemically based biosensors by the use of biomolecule-semiconductor hybrid systems highlights the bridge between the optical and electronic applications of biomolecule-NP hybrids for biosensing.

The development of biomolecule-NP-based sensors reached the level of practical applicability, and various analytical systems for clinical diagnostics, the analysis of food products, environmental pollutants and homeland security biosensors are expected to emerge from these hybrid nanocomposites.

Chapter 7, “Philosophy of Nanosciences”, author A. Nordmann, addresses some aspects of philosophy of technoscience, which asks for nanotechnological, biomedical or semiconductor research the four questions that were identified above: what is the role of theory and theory-development in nanoscale research and what kinds of theories are needed for nanotechnological development?; what are the preferred methods and tools and the associated modes of reasoning in nanoscientific research?; what is nanoscience and how are its objects constituted?; and what kind of knowledge do technoscientific researchers typically produce and communicate? The four main sections of this chapter will address these questions – and in all four cases, strictly philosophical considerations will shade into societal dimensions and questions of value. Other problems, such as applying

theory to the nanoscale: fitting versus stretching, mute complexity, from successful methods to the power of images, technoscientific methodology: quantitative versus qualitative, “ontological indifference”: representation versus substitution, images as the beginning and end of nanotechnologies represent an important part of this chapter. This chapter did not survey a revolutionary development, but pragmatic and problematic integrations of pre-existing scientific knowledge with the novel discoveries at the nanoscale.

Chapter 8, “Ethics of nanotechnology. State of the Art and Challenges Ahead”, author A. Brunwald, is a study on current and foreseeable developments in nanotechnology from the viewpoint of philosophical ethics. This overview is complemented by two in-depth case-studies of ethical aspects in nanotechnology: the challenge of dealing with possible risks of nanoparticles and the role of the precautionary principle and the human enhancement case, which is directly related to nanotechnology via the debate on “converging technologies”. Dealing constructively and in a rational way with these ethical challenges requires specific conceptual and methodical developments. In particular, some effort has to be invested into handling the dimension of the future in normative as well as epistemological regard in a non-partisan way.

The last Chapter, 9, “Outlook and Consequences”, author Günter Schmid, summarizes the main findings and ideas from the whole book, in order to demonstrate the innovative power of nanoscience and technology. The conclusion at the end is that there is no doubt that nanotechnology will change our lives, but it depends on us what this change will look like.

This is considered to be one of the first books which deals with the various fields on nanotechnology. In addition to the principles and fundamentals, treated in this volume, information technology, medicine, energy, tools and analytics as well as toxicity could be the subjects of subsequent other books. Developed fields of nanotechnology and future areas of nanotechnological applications are described and discussed.

The book addresses scientists, teachers/professors and students involved in this important and advanced field of fundamental and applicative science.

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Mauch K., Vaseghi S., Reuss M., (2000), *Quantitative Analysis of Metabolic and Signaling Pathways in Saccharomyces cerevisiae*. In: *Bioreaction Engineering*, Schügerl K., Bellgardt K.H. (Eds.), Springer, Berlin Heidelberg New York, 435-477.

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Handbook of Chemical Engineer, (1951), (in Romanian), vol. II, Technical Press, Bucharest.

Symposium volumes: Names and initials of authors; year; article title; full title; symposium abbreviated; volume number; place; date; page number:

Clark T. A., Steward D., (1991), *Wood and Environment*. Proc. 6th Int. Symp. on Wood and Pulping Chemistry, Melbourne, vol. 1, 493.

Journal papers: Names and initials of authors; year (between brackets); full title of the paper; journal abbreviated in accordance with international practice (italic); volume number (bold); first and last page numbers;

Tanabe S., Iwata H., Tatsukawa R., (1994), Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals, *Sci. Total Environ.*, **154**, 163-177.

Patents: Names and initials of authors; year; patent title; country; patent number:

Grant P., (1989), Device for Elementary Analyses. USA Patent, No. 123456.

Dissertations: Names and initials of authors; year; title; specification (Ph. D. Diss.); institution; place: Aelenei N., (1982), *Thermodynamic study of polymer solutions*. Ph. D. Diss., Macromol. Chem. Inst. Petru Poni, Iasi.

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