



“Gheorghe Asachi” Technical University of Iasi, Romania



CHANGE OF THE GROUNDWATER QUALITY FROM INDUSTRIAL AREA ORADEA, ROMANIA, USING GEOGRAPHIC INFORMATION SYSTEMS (GIS)

Tamara Romocea^{1*}, Aurelia Oneț^{1*}, Nicu-Cornel Sabău¹, Cristian Oneț¹, Grigore Vasile Herman², Emilia Pantea¹

¹*Faculty of Environmental Protection, University of Oradea, Magheru 26 Street, Oradea, 410048, Romania*

²*Faculty of Geography, Tourism and Sport, University of Oradea, University 1 Street, Oradea, 410087, Romania*

Abstract

During the years 1965-1985, a veritable industrial platform was developed in the west part of Oradea, Bihor County, Romania. It stretches on an area of 9 sq. km. and is placed in the meadow of Crisul Repede River. Throughout that period, several industrial facilities were built that lately became sources of pollution for the environment. The purpose of the present paper is to study the influence of historical stages of industrialization and restructuring of enterprises in Western Oradea, addressing the evolution of groundwater quality, by mainly using geospatial analysis means. The evolution of some parameters in the water samples taken from drilling wells which characterize the groundwater quality were analyzed over a period of 30 years by using a pre-existing database, provided by the Romanian Waters National Administration – Crisuri branch. The ArcGIS system was used to highlight the spatial trends of the analyzed indicators on 16 maps. The available values have been incorporated into a pre-existing database, developed in ESRI ArcGIS 9.3. The results regarding the industrial sources indicated an extensive pollution process of the groundwater in the years 1977, 1990, and a reduction of the pollutants' concentrations in the recent monitoring years. Contrary to this evolution, the nitrate concentration increased toward 2008, exceeding the admitted limits. It is also noted, that until 1990 the pollution of the groundwater is rather of industrial nature and after 1990 the level of industrial pollution decreases, as in the restricted areas the agricultural pollution is amplified.

Key words: groundwater, geographical information system, industrial facilities, quality evolution, spatial and temporal distribution of indicators

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1. Introduction

Groundwater constitutes the largest reservoir of freshwater on Earth. Directive 2006/118/EC that is part of Framework Directive 2000/60/EC on water refers to the protection of groundwater against pollution and quality deterioration. The measures specified for this purpose include the establishment of criteria for assessing the good chemical condition of the groundwater and criteria for identifying and reversing significant upward trends. According to

these provisions the significance of water quality trend can be treated either statistically or environmentally (Blum et al., 2010; Enea et al., 2017).

The first legal provisions on environmental protection have been adopted in our country in 1973 (Environmental Law No.9/1973). Environmental policy has continuously developed in Romania after 1990. Since 1996 it has been noticed that environmental principles, priorities and objectives have tried to align to the European Community strategy. The National Program for EU membership has forced

* Author to whom all correspondence should be addressed: e-mail: tamararomocea@yahoo.com; aurelia_onet@yahoo.com

the Romanian government to develop an environmental policy in accordance with the strategy set by the European Community. After 2007 (Romania's admission year) the Romanian environmental legislation has been harmonized with the European legislation and the institutional reform has made remarkable progress. This is why, the company-related environmental policies have become more responsible.

Groundwater content is determined by several natural factors, such as chemical reactions between water and solid fraction (soil or sediment), biochemical reactions, interactions with the surface waters, especially human activities (Onet et al., 2018). The municipal and industrial wastewater, whether treated or not, is a constant source of pollution which affect the groundwater hydrochemistry. In addition, groundwater may be affected by non-point sources of pollution caused by the runoff from irrigation facilities and waste treatment in urban areas (O'Connor, 2010). Anthropogenic phenomena such as the industrial development, urbanization, agricultural irrigation, water pollution as well as changes in irrigation practices, greatly influence the groundwater resources. These human impacts on groundwater chemistry have been studied intensively (Cîrfină and Traistă, 2014; Wenke et al., 2014). Kasperczyk et al. (2016), studied the pollution indicators in groundwater of two agricultural catchments in Lower Silesia (Poland) and they concluded that chemical composition of groundwater is influenced by a variety of factors related to both natural causes and anthropogenic activities. Groundwater resources can be influenced both by climate change and human activities. The combination of climate change and irrational use of the groundwater have caused a general decline in the groundwater levels, resulting in their depletion, landslides and intrusions of saltwater in deltaic areas and in alluvial plains (Romoccea and Josan, 2004).

Studies regarding the spatial changes of the groundwater quality were conducted also, by Farsang et al. (2017). They studied the concentrations of 12 inorganic contaminants from 28 wells in Szeged, Hungary. The concentrations values have shown a remarkable contamination throughout the city. The chemical composition of the groundwater may be constantly affected by ancient human activities (Kasprzak et al., 2013). Other researcher found no evidence that groundwater chemistry is determined by the depth of captured aquifer interval. The main processes that control the chemistry of all analyzed water are cation exchange and feldspar weathering (Marić et al., 2014). The aim of this study is to observe the evolution of certain chemical parameters which characterize the groundwater in the western area of Oradea (Romania), over a period of 30 years, out of which 12 years covering the period of communist development and the remaining years covering the period after 1989. This study has in view the opportunity to emphasize the degree of water

degradation, human pressure and their potential impact on the possibilities of use.

The present study focused on the relationship between the quality of the groundwater from an industrialized urban area and the history of the property forms, political views and development of environmental legislation in Romania.

2. General presentation of the study area and the history of its industrial development

Oradea is the capital of Bihor County. The county is located in the NW of Romania between the parallels of 46.23 and 47.35 north latitude and meridians of 22.48 and 21.26 east longitude and covers an area of 7544 sq. km. It is situated on the north-western border of Romania with the Hungarian neighboring counties of Hajdu-Bihar and Bekes. The municipality has a population of approximately 180,000 inhabitants. The town lies at the transition from a hilly landscape, represented by Oradea Hills, to a plain area represented by Banato-Crisana Plain. Crisul Repede River crosses the town from south to north-west (Fig. 1). The groundwater in the area is stored in Crisul Repede alluvial cone which is developed on both banks.

During 1965-1985, a veritable industrial platform was developed in the western part of Oradea. It covers an area of 9 sq. km. and is placed within a short distance from the city's most populated district, in the meadow of Crisul Repede River (Fig. 2).

The relief, the platform was built on, is flat and the soil has an alluvial structure, composed of gravels and sands with a considerable thickness. The region's groundwater is plentiful and close to the topographic surface (Romoccea and Josan, 2002). Throughout that period, several industrial facilities were built that have become sources of pollution for the environment affecting especially the air, soil and groundwater (see environmental reports from the environment agency). The most important of them are listed below.

In 1965, Alumina Factory was set up. It processed the bauxite extracted from the region and transformed it in calcined bauxite through the Bayer process. In 1999 the factory was closed. In 1966 the thermal power station, CET I, was put into operation. It worked on lower coal extracted from the mining areas nearby. The dump of ash and slag, in which the slurry resulting from the wastewater treatment station is stored and transported in hydro-mix and is located nearby. Since 2016 the station has been operating on natural gas.

The manufacture of chemical products in Oradea has a rather old history. Sinteza Chemical Plant was set up in 1959. In 1967-1970, facility for manufacturing organo-phosphorous (pesticides for agriculture) was built. Also, a large investment was put into operation - the Department of Inorganic Pigments (chromium green, iron red, lead yellow).

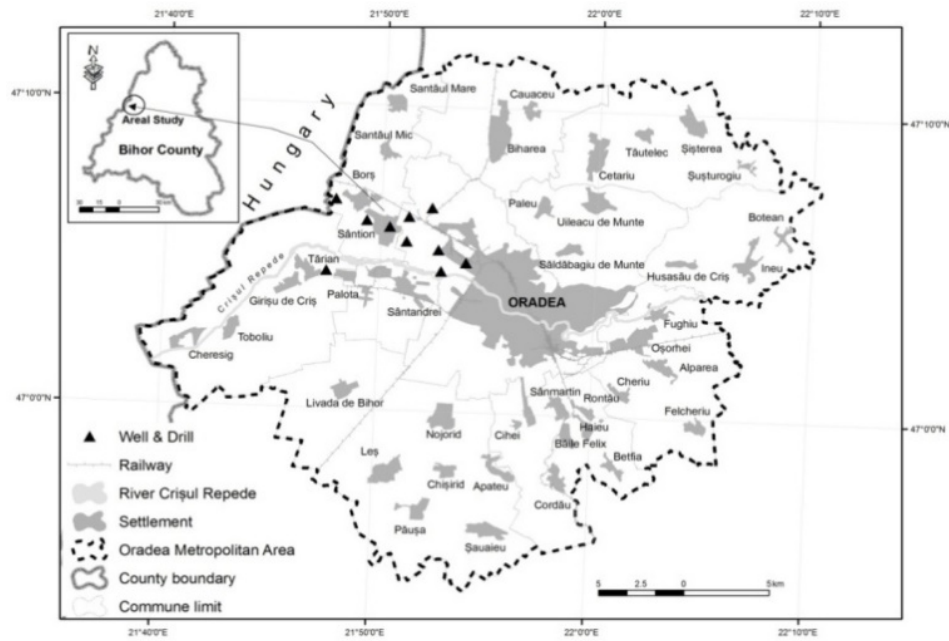


Fig. 1. Oradea and Metropolitan Area

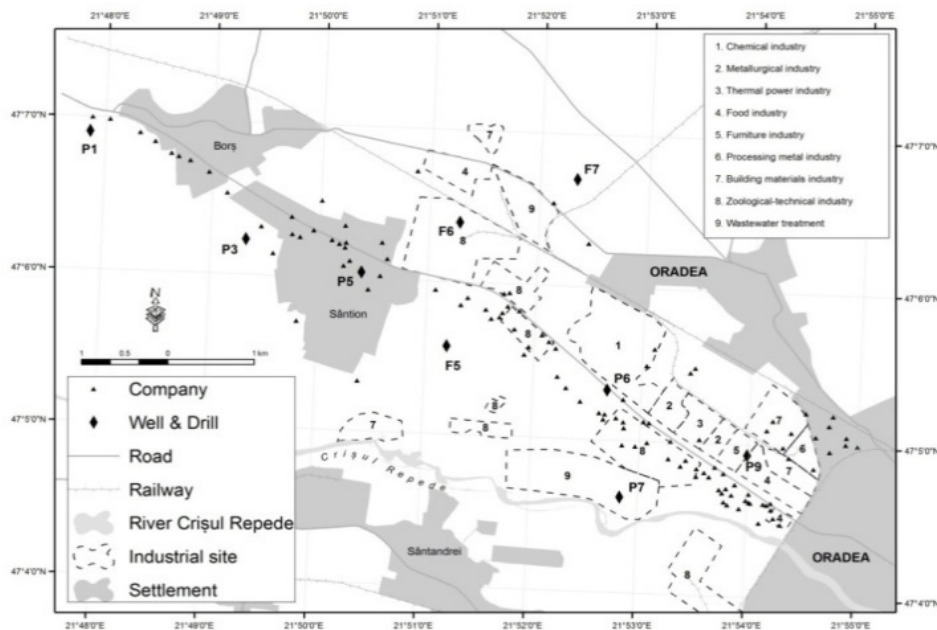


Fig. 2. Industrial area in Oradea

This was followed by other facilities for the production of many other chemicals. Since 2000, the departments of the enterprise have closed one by one. In 1968, a sugar factory was established. It's still working today, as part of the large DIAMANT Company, having as shareholders the German company Pfeifer & Lange and the French Cristal Union group. In the same period, the company begins the construction of some greenhouses in the vicinity of the road to Borș Customs. The plant stretched on almost 100 ha and was the second largest exporter of vegetables in the country. Around 2007, the greenhouses went into liquidation. S.C. ECO Bihor

SRL was founded in early 2004 by the company Keviép Kft., near the former lakes in which, over time, the slurry coming from Alumina plant and the thermal power plant Oradea and the domestic waste have been stored, and being clogged up at present.

S.C. ECO Bihor SRL Oradea is operating and managing the county ecological landfill, for a period of 20 years through a public-private partnership with the Local Council of Oradea. The municipal water treatment plant placed on the right bank of Crișul Repede River, south of the European Road E60, collects the domestic and industrial wastewater from Oradea and the neighboring villages.

Downstream to the water treatment plant there are biological ponds of about 50 ha, from which water is discharged into Crisul Repede River, in a controlled way and with the approval of the Inspectorate of Environment and Directorate of Crisuri Waters.

Industrial companies currently operating in the study area have a limited activity which is much different in comparison to the situation during the period 1965-1985. Most of them have been forced to restructure their production so that, in the context of the EU environmental legislation already implemented in Romania, their impact on the environment is normal.

2. Material and methods

In pursuit of this research, in order to examine the variation of the parameters chosen to characterize groundwater condition, a pre-existing database was used, provided by the Romanian Waters National Administration – Crisuri branch. This database contains the results of the analyses carried out over many years, for several drillings and a large number of water quality indicators. Out of the multitude of available data, the most significant ones were chosen for achieving the purpose of the study, that is a few relevant indicators and several years of reference for the industrial development area had to be chosen.

The determination of the groundwater quality in the first phreatic layer is made on the morphological units of the catchment basins through hydrogeological stations. This includes one or more observation wells, which allows the multiplication of the number of observation points within a hydrogeological system. This fact allows the highlighting of either the local specificities, or, on the contrary, the homogeneity of water composition. To highlight the potential sources of pollution and their impact on water quality, there is pollution tracking wells around the important pollution sources.

Starting with 1977, in the western part of Oradea, a well hydrogeological system was set upon two perpendicular alignments. One of the alignments is located on the east-west direction (includes wells P1, P3, P5, F5, P6 P9.) and the other one on the north-south direction (consisting of wells P7, F6, P5, P2). Over time, the concepts of management and purposefulness were better crystallized, with regard to the wells networks used for the study of groundwater (Romocea and Josan, 2002).

The wells which are the subject of this study are divided into pollution tracking wells (P1, P2, P3, P5, P6, P7, P9) and drillings which are part of the National hydrogeological network (F5, F6, F7). The former is included in the operational national monitoring program. Since the beginning of the system construction, there were collected and analyzed four samples of water per year, one for each season. The manner of sampling and analysis were established by the Water Basin Administration (ABA) Crisuri, Bihor. For this study, a large number of parameters, determined over a period of 30 years have

been analyzed. Over the years there have been changes in the number of parameters analyzed or situations where, for reasons unknown today, certain parameter values were not reported. These facts somehow limited the possibilities of selecting the types of the parameters and the years under consideration. For this reasons, have been studied 24 annual average values.

The analyzed wells were chosen so as to provide adequate spatial coverage of the area under study. When making the choice, we have taken into account the possibility of obtaining information on neighborhoods (Chartier, 2005). The wells are located mostly in the industrial area in the western part of Oradea, but also in predominantly agricultural areas. The regime of these areas has changed over the studied period. Except for the well P2 which is located on the left bank of Crisul Repede, wells P1, P3, P5, P6, P7, P9, F6 and F7 are located on the right bank, all downstream of Oradea. The location of the analyzed hydrogeological wells is established so as to monitor the industrial enterprises' influence on the groundwater quality in the area and the temporal evolution of their pollution (Fig. 3).

The groundwater in the studied area is part of the groundwater body ROCR01, a cross-border body of water, developed in the alluvial cone of Crisul Repede. It is located at depths between 2.00 m and 8.00 m, the thickness of the water-bearing horizon having around 15- 17 m, in the area Western Oradea - Bors. The aquifer layer has a maximum development in Bors, where it has been captured on a thickness of 19 m. This cone, well-developed downstream of Oradea, also has a large extension beyond the Hungarian border. It has developed on both sides of Crisul Repede River.

The typical structure is that of a cone, made up of sands, gravels and boulders, of a great variety of grain-size; the lithological structure is generally crossed, sometimes with inter-layers of clay. The flow direction is regionally from the east to the west. The groundwater of this body is fed by precipitation and subordinate in the cone zone on Crisul Repede in Oradea, and by surface waters during high water periods. The effective infiltration is generally low and falls into the range of 15-60 mm water column per year which gives the body of water a mid-range and good degree of surface protection.

In the industrial area of Oradea, the groundwater is drained, south of the natural course of Crisul Repede and north of its tributary Crisul Mort river which flows on the direction east – north-west and flows on the territory of Hungary. The main hydrogeological parameters of discharge are flow $q = 1$ to $20 \text{ dm}^3 \cdot \text{s}^{-1} \cdot \text{m}^{-1}$ and transmissivity $T = 100\text{-}2000 \text{ m}^2 \cdot \text{day}^{-1}$. In terms of hydro chemical profile, waters in the study area are very different. Thus, there are bicarbonate - calcium - magnesium water types, chloric - sulfate, calcium - magnesium waters etc.

From this body of water, over 66 million m^3 of groundwater is extracted annually from the municipal capture, through four drains, especially built for this purpose.

The notion of water quality is necessarily associated to a domain of use, to a particular purpose, or a reference. In this study, the values of the selected parameters have been compared to the maximum admissible concentrations in drinking water quality standard (Law no. 458/2002, as amended and supplemented).

The ArcGIS system was used to highlight the spatial and temporal trends. A geographical information system (GIS) allows visualization, analysis and interpretation of the available data, in order to understand the evolution trends. M. O'Connor (2010) studied the influence of bedrock on the groundwater geochemistry using geospatial analysis tools to estimate the spatial trend of the groundwater chemistry in the north of the New York City. He used an ArcGIS database to generate contour plots for the studied chemical elements. This technique has also been used by other researchers (Biali and Statescu, 2013; Johnston et al., 2001; Longley et al., 2005; Moody and Jacko, 2012).

The available values have been incorporated into a pre-existing database, developed in ESRI ArcGIS 9.3. ArcGIS Spatial interpolation techniques were designed to estimate and analyze trends indicators of concentration in the study area. The spatial interpolation method utilized in this study was kriging interpolation. Using this method, which is based on the theoretical principals that compares data located in close proximity to a reference point being examined, were analyzed and extrapolated the data collected in the 11 drillings in the areal studied (Oliver, 1990). The semivariogram chosen for the study was the spherical model. The spherical model shows a progressive decrease of spatial autocorrelation and an equivalently increase in semivariance until some distance, beyond which autocorrelation is zero (O'Connor et al., 2010; Johnston et al., 2001). This way, simulations of the spatial and temporal distribution of the analyzed indicators were performed (Figs. 4-7).

The results were analysed using variance analysis (ANOVA) in order to determine the statistical significance of differences between the means of each studied parameter. The statistical methods used to determine the significance of differences between the average values of the quality parameters monitored in the studied wells, during the years 1977-2008, was the one-way analysis of variance (ANOVA). The ANOVA results were generated using the GNU PSPP Statistical Analysis Software (PSPP Users' Guide, 2016).

3. Results

The results have been materialized in 16 maps which simulate the spatial and temporal distribution of the analyzed indicators values (Figs. 4-7) and in 4 tables (Tables 1-4) which present the statistical analysis of the mean values of the concentrations of groundwater quality parameters.

3.1. Study of the evolution trend of the permanent residue parameter

In terms of the permanent residue values, in 1977, values were recorded above the maximum admitted limit of 800 mg/l for the wells P6, P7, P9, F5, F6, F7 and in 1990 for the wells P1, P3, P5, P6, P7, P9, F5, F6, F7. In 1997 the wells P1, P3, P5, P6, P7, P9, F6 recorded values above the maximum admitted and in 2008 the underground water coming from wells P1, P3, P6, P7, F6 recorded high levels of permanent residue. The highest value of permanent residue ($1754.75 \text{ mg} \cdot \text{dm}^{-3}$) was recorded in 1977 in the well P7 located near the Wastewater Treatment Plant of the city. In conclusion, between the years 1977 and 1990 there is a noticeable shift of the frontline ionic pollution on the groundwater flow direction. In the following periods, there is a stabilization of this parameter (Fig. 4).

3.2. Study of the evolution trend of the sulfate parameter

In 1977, the concentrations of sulfates in the groundwater were above the maximum permissible for wells P6, F6, F7, the highest concentration ($637, 909 \text{ mg} \cdot \text{dm}^{-3}$) occurring in the groundwater coming from the well F7, located near Oradea ecological landfill. In 1990, the groundwater samples coming from wells P1, P3, F6, F7 recorded higher values compared to the maximum permissible value. The minimum values are recorded in 1997 followed by a slight increase in 2008 (Fig. 5).

3.3. Study of the evolution trend of the nitrate parameter

In 1977 and 1990 there were recorded no values of nitrate concentration in the groundwater above the maximum permissible limit of $50 \text{ mg} \cdot \text{dm}^{-3}$ as opposed to 1997 and 2008 when there were exceeding of the maximum admitted values for wells P1, P3, P5, P7, F6 and F7. The highest concentration of nitrates was recorded in 2008 for well P3 (agricultural area) having a value of $144.2 \text{ mg} \cdot \text{dm}^{-3}$.

3.4. Study of the evolution trend of the lead parameter

In 1977, concentrations of lead in the monitored groundwater showed values above the maximum permissible for the wells P1, P2, P3, P5, P7, F5, F6 and in 1990 for the wells P1, P3, P5, P6, F5, F6.

The same situation was recorded in 1997 when the groundwater coming from the wells P5, P6, P7, F6 and F7 showed high concentrations of lead, above the maximum allowed limit. In 2008, there were recorded no exceeding beyond the maximum allowed. The highest concentration of lead ($0.294 \text{ mg} \cdot \text{dm}^{-3}$) was recorded in the groundwater from the well P3 located in the agricultural area Sântion, Bihor County in 1977.

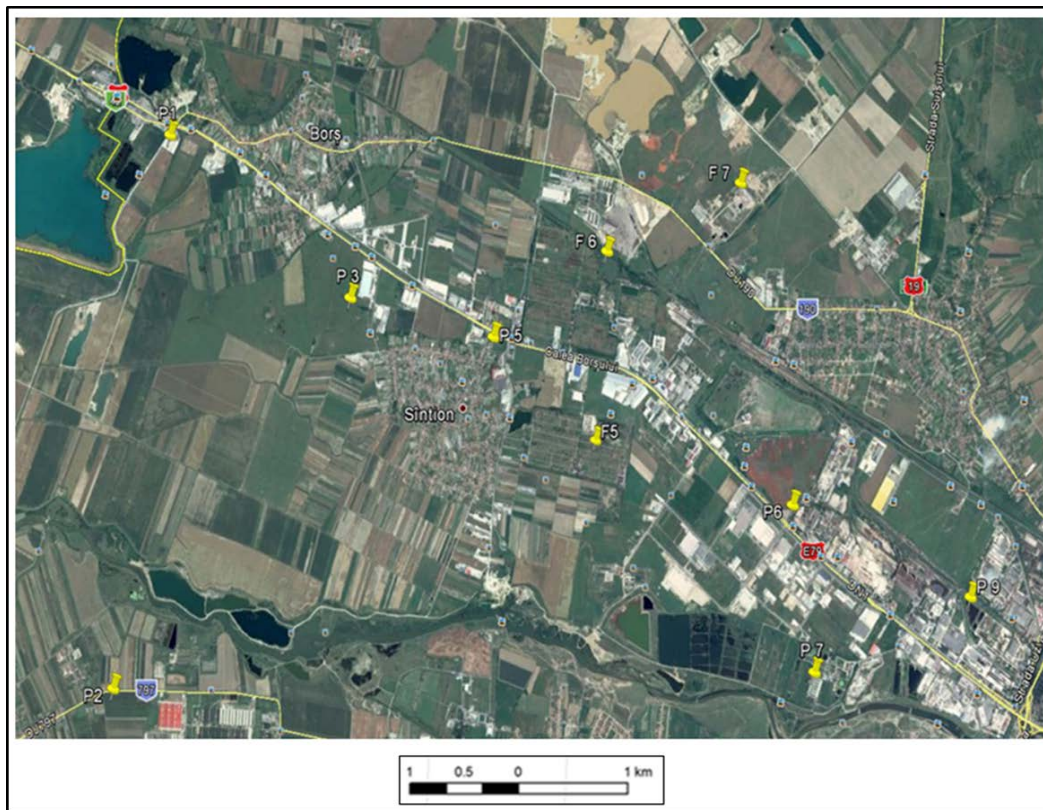


Fig. 3. The site of hydrogeological wells and boreholes

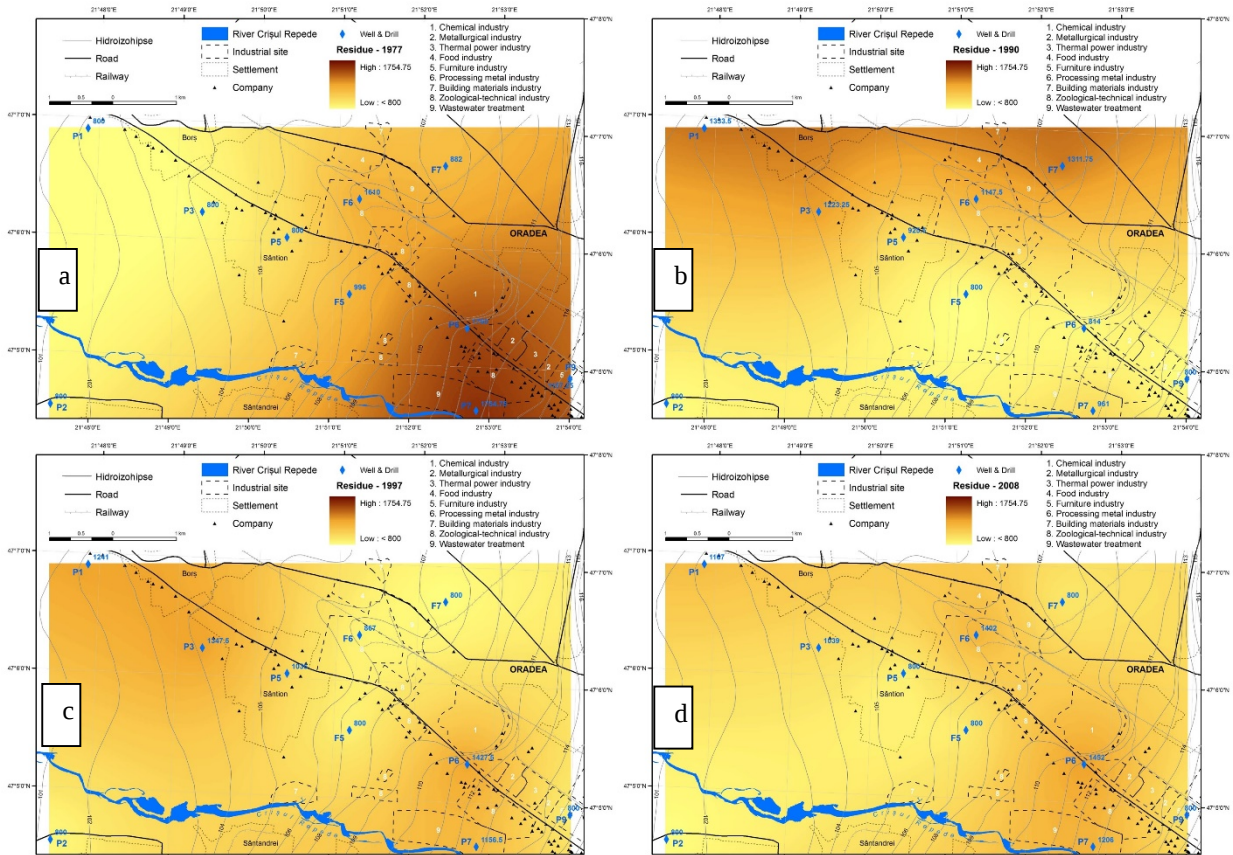


Fig. 4. Evolution of the permanent residue concentrations in the groundwater of Oradea industrial area: (a) year 1977; (b) year 1990; (c) year 1997; (d) year 2008

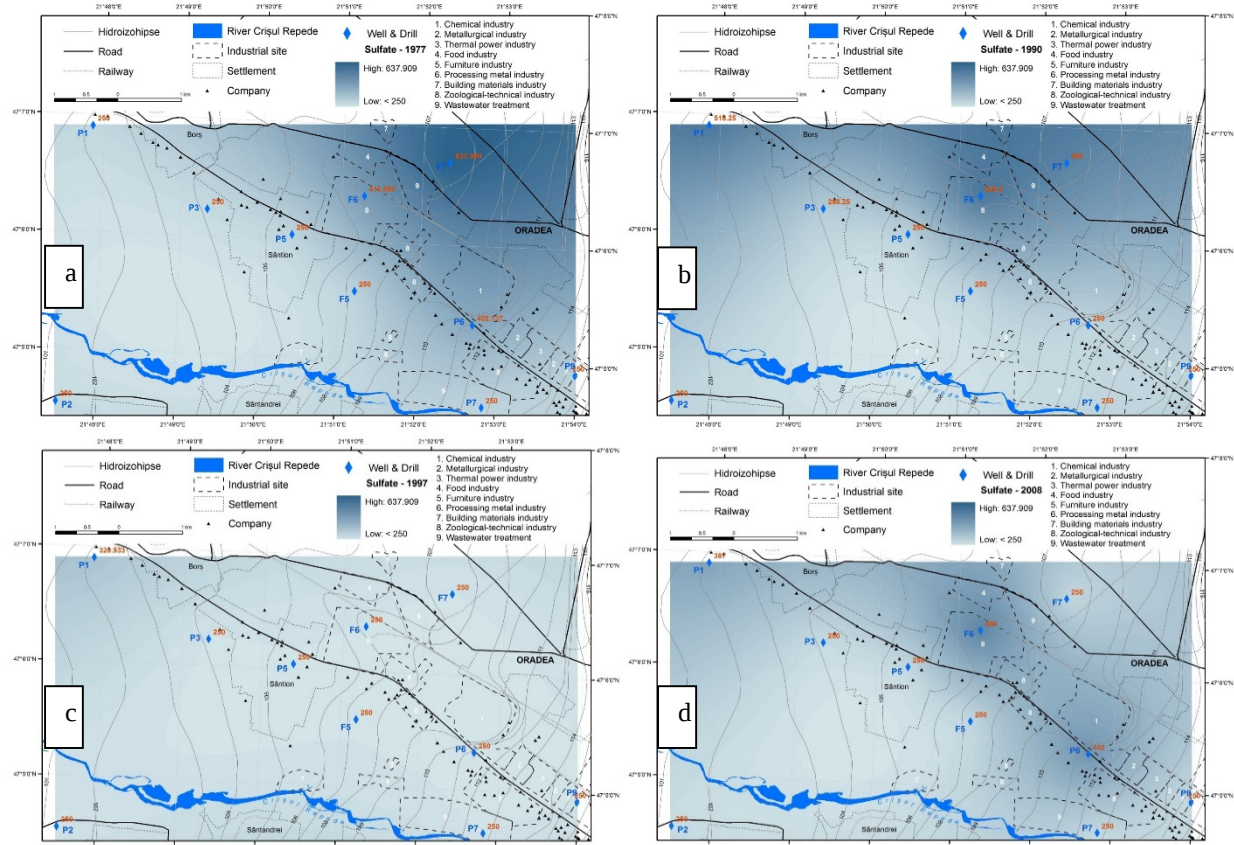


Fig.5. Evolution of the sulfate ion in the groundwater of Oradea industrial area:
(a) year 1977; (b) year 1990; (c) year 1997; (d) year 2008

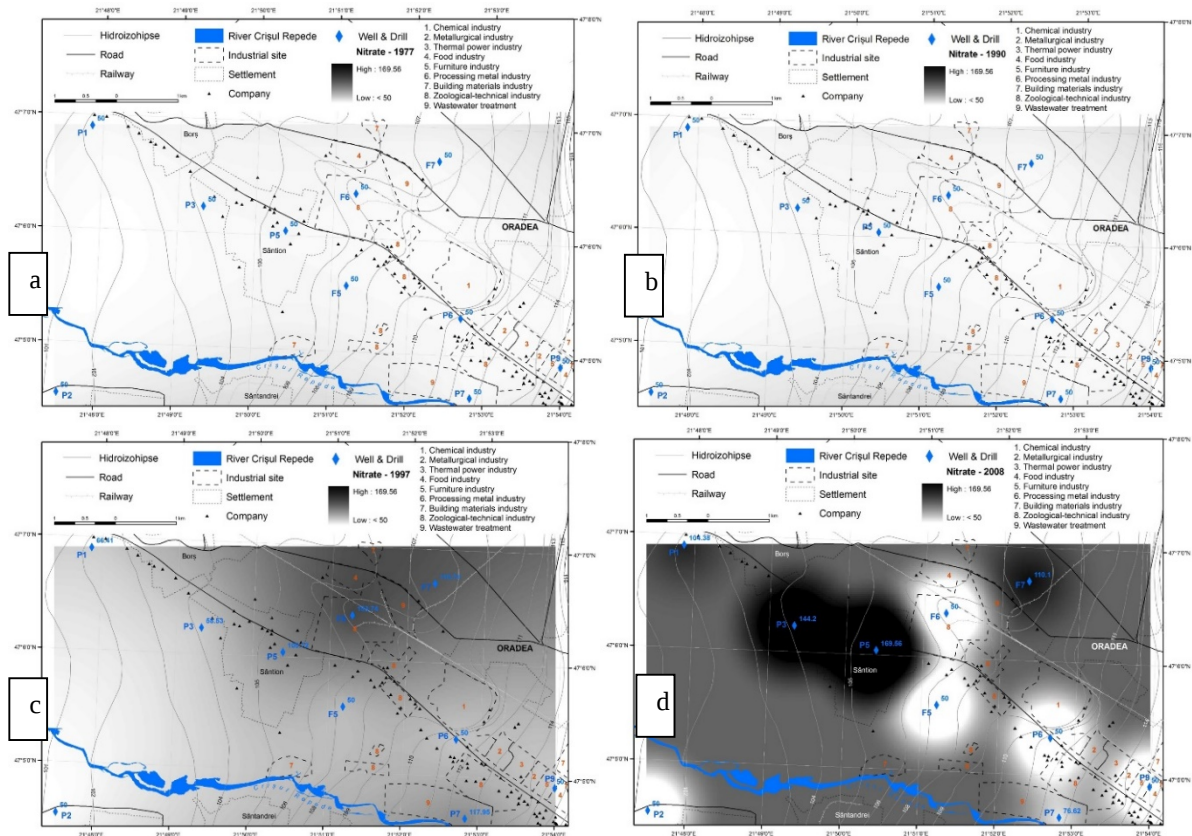


Fig. 6. Evolution of nitrates in the groundwater of Oradea industrial area:
(a) year 1977; (b) year 1990; (c) year 1997; (d) year 2008

Table 1. ANOVA analysis of the mean values of permanent residue concentrations (mg·dm⁻³)

<i>Wells</i>	<i>N</i>	<i>Min.</i>	<i>Max.</i>	<i>Mean</i>	<i>Std.Deviation</i>	<i>Std.Error</i>	<i>F</i>	<i>Significance</i>
P1	24	381	1430	995,5	384,56	62,63	38,13	0,000
P3	24	460	1710	1051,42	357,43	72,96	13,26	0,000
P5	24	356	2461	955,96	536,05	109,42	14,03	0,000
P6	24	404	2270	1273,00	451,31	92,12	18,07	0,000
P7	24	821	2247	1235,96	334,73	68,33	4,66	0,007
P9	24	180	1565	442,08	365,11	74,53	20,13	0,000
F5	24	235	1296	605,75	253,76	51,80	3,59	0,020
F6	24	570	1920	1216,46	321,94	110,73	9,83	0,000
F7	24	523	1390	862,38	270,57	55,23	10,74	0,000

Table 2. ANOVA analysis of the mean values of sulfates concentrations (mg·dm⁻³)

<i>Wells</i>	<i>N</i>	<i>Min.</i>	<i>Max.</i>	<i>Mean</i>	<i>Std.Deviation</i>	<i>Std.Error</i>	<i>F</i>	<i>Significance</i>
P1	24	75,05	374,65	318,16	189,93	38,77	5,43	0,003
P3	24	54,48	380,00	181,36	76,04	15,52	7,51	0,001
P5	24	49,45	264,60	156,57	57,69	11,78	12,54	0,000
P6	24	74,00	716,43	257,14	166,68	34,02	6,52	0,001
P7	24	9,05	232,27	116,55	69,52	14,19	7,75	0,000
P9	24	7,75	126,63	48,34	33,96	6,93	7,70	0,001
F5	24	34,00	128,88	64,57	27,42	5,60	7,47	0,001
F6	24	26,72	640,00	311,55	202,75	41,39	21,09	0,000
F7	24	80,00	649,59	380,57	199,24	40,67	32,37	0,000

Table 3. ANOVA analysis of the mean values of nitrates concentrations (mg·dm⁻³)

<i>Wells</i>	<i>N</i>	<i>Min.</i>	<i>Max.</i>	<i>Mean</i>	<i>Std.Deviation</i>	<i>Std.Error</i>	<i>F</i>	<i>Significance</i>
P1	24	6.92	118.12	56.66	33.76	6.89	19.25	0.000
P3	24	3.70	158.73	56.05	46.90	9.57	26.07	0.000
P5	24	4.45	179.77	76.51	54.91	11.21	18.40	0.000
P6	24	0.47	17.36	4.57	4.52	0.92	13.60	0.000
P7	24	0.45	126.24	41.77	46.14	9.42	66.91	0.000
P9	24	0.03	39.44	8.49	10.48	2.14	2.92	0.042
F5	24	1.16	72.42	25.97	23.69	4.84	11.80	0.000
F6	24	2.94	237.53	44.32	57.58	11.75	15.43	0.000
F7	24	3.13	148.75	53.80	48.01	9.80	28.48	0.000

Table 4. ANOVA analysis of the mean values of lead concentrations (mg·dm⁻³)

<i>Wells</i>	<i>N</i>	<i>Min.</i>	<i>Max.</i>	<i>Mean</i>	<i>Std. Deviation</i>	<i>Std. Error</i>	<i>F</i>	<i>Significance</i>
P1	24	0	0.191	0.02	0.04	0.01	1.07	0.411
P3	24	0	1.137	0.10	0.31	0.06	2.89	0.044
P5	24	0	0.160	0.02	0.03	0.01	0.98	0.458
P6	24	0	0.098	0.02	0.03	0.01	1.73	0.178
P7	24	0	0.086	0.01	0.02	0.00	2.35	0.083
P9	24	0	0.123	0.01	0.02	0.01	1.77	0.171
F5	24	0	0.058	0.01	0.01	0.00	1.87	0.149
F6	24	0	0.101	0.01	0.02	0.00	1.39	0.275
F7	24	0	0.057	0.01	0.01	0.00	3.98	0.013

The elevated concentration of lead exceeding by almost 30 times the maximum admissible concentration in 1977, suggests the possibility of a serious accidental pollution (fig. 7). Since the location of the P3 drilling is near the European route E79 (Borşului Road) it is supposed that the source of lead pollution is the road transport. In other wells located near this road as P5 and P6, no exceptional concentrations of lead were registered in 1977.

The concentrations of the groundwater quality parameters (permanent residue, sulphate and nitrate) varied significantly in the studied period (years 1977-

2008) (tables 1, 2, 3). The lead levels did not vary significantly in the years studied except for the concentrations recorded at the well P3 (Table 4).

4. Discussions

The main purpose for monitoring the water drillings is to assess the conditions of the groundwater quality in the aquifer system. An inadequate distribution of sampling wells could produce insufficient or redundant data regarding the groundwater quality.

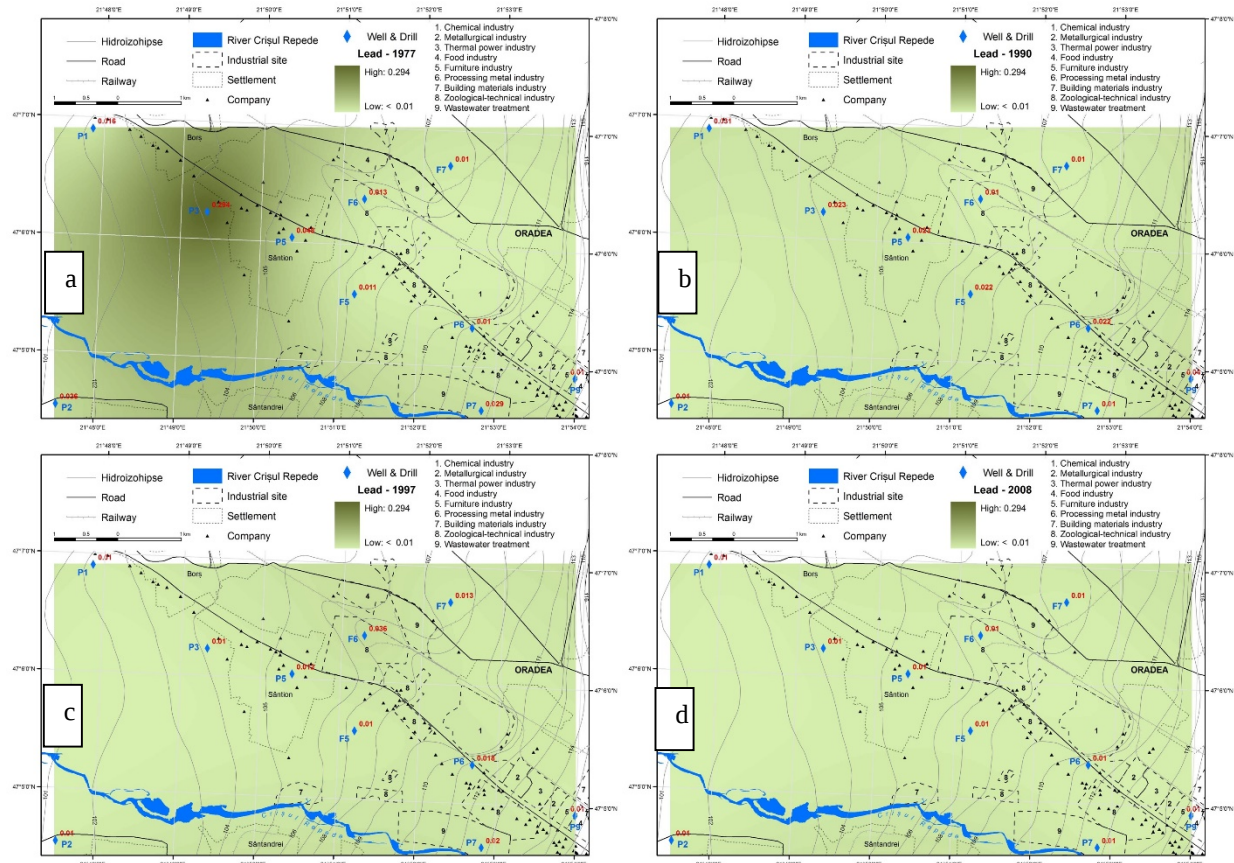


Fig. 7. Evolution of lead in the groundwater of Oradea industrial area:
(a) year 1977; (b) year 1990; (c) year 1997; (d) year 2008

An optimal selection of the representative monitoring locations can be obtained by considering the natural and anthropogenic potential of the sources of pollution, the hydrological adjustment and the assessment of all existing data regarding the monitoring networks. More researches are currently focused on assessing areas that require the monitoring of the groundwater quality (Zhang et al., 2014). The proposed approaches highlighted the efficiency of the existing network of monitoring wells, taking into account not only the samples collected from wells but also the hydrogeological characteristics of the aquifer and the anthropogenic pollution potential in the study area (Narany, 2014; Rusinga and Taigbenu, 2005). Analyses on groundwater quality by monitoring the concentrations of inorganic chemicals in water samples taken from drilling wells were also made by many researchers who obtained preliminary data for these areas, regarding groundwater quality and their geochemical trend, noting the presence of high concentrations of aluminum, iron, mercury, manganese, arsenic and lead (Chiarenzelli et al., 2007; Nystrom, 2007).

The permanent residue and sulfates are part of water salinity indicators. The value of the permanent residues is a direct way of expressing its degree of mineralization. The high levels of these parameters (besides the natural level of water mineralization) most often indicate groundwater pollution of an

industrial nature. The parameter is suggestive, taking into account the specificity of the industrial objectives which might be polluting sources in the industrial area under study: coal thermal plant, chemical and alumina processing plants (Preda et al., 2018). Sulfates are found in almost all natural waters, due to their solubility (Huber et al., 2012). They are a major component of rainwater.

They may occur in polluted waters due to the oxidation of pyrite or hydrogen sulfide. Burning fossil fuels is also a major source of pollution. Evolution of the sulfate ion concentration is similar to the evolution of the fixed residue. The process of pollution with sulfate follows the course of the groundwater flow starting with 1977 until 1990. Nitrates are found naturally in the groundwater in relatively low concentrations. Concentrations above $10 \text{ mg} \cdot \text{dm}^{-3}$, usually prove an anthropic intrusion.

The nitrate ion can get into the groundwater as a result of washing the soil on which chemical fertilizers containing nitrogen or manure are used, and which are not fully used by plants, or as a result of soil pollution with substances coming from the uncontrolled fermentation of the sewage and waste from livestock farms. Wastewater treatment plants from urban agglomerations and waste water from the food industry are also important sources of nitrate pollution (Fig. 6.)

In Romania, a number of researches have been focused on the study of the nitrate pollution of the groundwater by emphasizing that the impact of human activities has long-term effects on the groundwater quality. Pollution that occurred decades ago, due to agriculture, industry and other human activities can threaten today the water quality and in some cases there is a risk that future generations could be exposed to the effects induced by this phenomenon of pollution (Dumitru and Botau, 2011). Nitrogen fertilizers used in agriculture are highly soluble and they are levigated by rainfall. The presence of higher concentrations of nitrate in the monitored groundwater coming from wells P1, P3, P5, P7, F6 and F7 is due to the agricultural use of nitrogen fertilizers in the former greenhouses of Oradea and also to the active sludge from the waste water treatment plant of S.C. Zaharul factory (Fig. 6). Based on this data, the nitrate pollution of the zones located outside the industrial area becomes obvious. The return (retrocession) of the agricultural land to its private owners represented by the residents of the rural areas attracted the intensive and unreasonable use of chemical and organic fertilizers. The transfer of nitrates in the unsaturated zone is a complex phenomenon. Penetration of nitrates from soil into the groundwater is relatively slow, the descent speed being of 1-2 m/year. The penetration usually occurs in winter, because during the spring and summer, rain is quickly taken over by vegetation. Although slow, the penetration of nitrates is continuous. There are no retention phenomena (sorption is negligible), or oxidation-reductive transformations (Kubare et al., 2010). The movement of nitrates in the saturated zone has the velocity of the water which generally is rather low. The possibility of converting nitrates in the groundwater is very low. The accidental lack of air or the presence of pyrite and denitrifying bacteria can cause denitrification. Another situation in which denitrification is possible is when the groundwater is connected to the bedrock of a watercourse. At the top of the alluvia formed in the riverbed, often a thin layer of silt arises and blocks communication between the groundwater and the atmosphere.

In the absence of atmospheric oxygen, the water bacteria may consume the oxygen from the nitrate ion, converting nitrogen into molecular nitrogen. Unfortunately, this phenomenon is not intense enough to have a role in water remediation (Biali and Statescu, 2013). Normally, the quantity of lead in the groundwater is low, due to the low solubility of the lead compounds (Sadeghi et al., 2017). A consequence of this fact is the accumulation of lead in the superficial soil layers until shallow depths, in the range of units or tens of cm. However, there are several factors that can increase the risk of mobilizing lead towards groundwater: clay soils for lead in suspension, soils composed of coarse sand, acidic soils, ground water with a pH below 6, the prolonged contact of lead with the ground (Mikołajków, 2003).

After analyzing the spatial and time distribution of the possible industrial polluters and the direction of leakage of the groundwater, upstream of the P3 drilling, Sinteza chemical factory (which produces pigments and stabilizers based on lead) can be identified as other polluter all together with Oradea Power Plant and Cemtrade Factory which produces alumina.

5. Conclusions

Environmental issues have strong political, social, economic, scientific and industrial connotations. They can not be included in a specific framework because they are connected to various aspects of the society.

In order to examine the variation of four parameters (permanent residue, nitrate, sulfate and lead) chosen to characterize the groundwater condition, a pre-existing database provided by the Romanian Waters National Administration – Crisuri branch, was used. This database contains the results of the analyses carried out over many years for several pollution tracking wells and drillings. Since the beginning of the system construction, there were collected and analyzed four samples of water per year, one for each season. For this study have been studied and interpreted 24 annual average values.

The geographic information systems are able to put together geographical, social and physico-chemical data in an overall picture of the studied companies. By using the ArcGIS system in this study for four years, the spatial and temporal trends of the water analytical parameters were highlighted, which are integrated in the context of historical stages of industrialization and restructuring of companies in the study area. There was also made a link between the chemistry and quality of the groundwater and the potential impact of anthropogenic pressures.

Changes in the concentrations of the four studied parameters: permanent residue, sulfate ion, nitrate ion and lead ion are well highlighted on all the sixteen maps. The statistically interpretation of the results made with one-way ANOVA method, reveal that with the exception for the lead parameter, the mean values of the other groundwater quality parameters (permanent residue, sulphate and nitrate) varied significantly in the studied period.

The temporal evolution of the analyzed parameters indicates that the biggest problems related to the groundwater quality in the industrial area of Oradea were recorded in 1977 and 1990, years that characterize a boom in the industrial production in Romania.

Reduction of the pollutant concentrations in the recent years of the monitoring (2008) is related to the regenerative power of the aquatic environment, aided by the restructuring of the companies recognized as highly polluting and especially to the implementation of the environmental legislation asked by the European Community.

References

- Biali G., Statescu, F., (2013), Mapping nitrate levels in groundwater using GIS, *Environmental Engineering and Management Journal*, **12**, 807-814.
- Blum A., Lopez B., Guilbert M., Noel Y., Chery L., (2010), National assessment of groundwater monitoring efforts from ADES. Indicators for assessing the qualitative and quantitative status of groundwater: examples of achievements and recommendations, Final Report, On line at: <https://ec.europa.eu/research>.
- Cîrîină D., Traistă E., (2014), Research on the influence of metallurgical industry waste on soil and groundwater quality, *Journal of Chemical Technology and Metallurgy*, **49**, 311-315.
- Chartier R., Meilhac A., Souadi T., Rouxel E., Giraud F., Nguyen D., Bouroullec I., Pinson S., Le Guern C., Lamotte C., Nguyen-The D., (2005), Monitoring of groundwater quality for classified installations and polluted sites. State of play and methodology of data banking, Final Report, BRGM/RP-53784-FR, On line at: <http://infoterre.brgm.fr/rapports/RP-53784-FR.pdf>.
- Chiarenzelli J., Shrady C., Cady C., General K.E., Snyder J., Benedicto-Debo A., David T., (2007), Multi-Element analyses of private wells on the St. Regis Mohawk Nation (Akwasasne), *Northeastern Geology and Environmental Science*, **29**, 167-175.
- Dumitru M., Botău O., (2011), Nitrate pollution in phreatic groundwater basin Crișul Repede, *University of Oradea Annals, Geography Series*, **21**, 30-38.
- Enea A., Hapciuc O.E., Iosub M., Minea I., Romanescu G., (2017), Water quality assessment in three mountainous watersheds from eastern Romania (Suceava, Ozana and Tazlău rivers), *Environmental Engineering and Management Journal*, **16**, 605-614.
- Environmental Law No. 9, (1973), Romanian Government, On line at: http://www.parlament.ro/pls/legis/legis_pck.htm.
- Farsang A., Fejes I., Tóth M.T., (2017), Integrated evaluation of urban groundwater hydrogeochemistry in context of fractal behaviour of groundwater level fluctuations, *Hydrological Sciences Journal*, **62**, 1216-1229.
- GNU PSPP Statistical Analysis Software, (2016), PSPP Users' Guide, Free Software Foundation, On line at: <http://www.gnu.org/software/pspp/manual/pspp.pdf>.
- Johnston K., VerHoef J.M., Krivoruchko K., Lucas N., (2001), *Creating a Surface with Geostatistical Techniques, Using Analytical Tools when Generating Surfaces*, In: *Using ArcGIS Geostatistical Analysis*, ESRI, United States of America, 131-219.
- Huber G., Knafla A., Vickerman L., Bell G., (2012), Summary of Research on Sulfate Behavior in Soil and Groundwater: Implications for Subsoil Sulfate Guideline Development, *PTAC Soil and Groundwater Forum Calgary*, 52.
- Kasperczyk L., Modelska M., Stasko S., (2016), Pollution indicators in groundwater of two agricultural catchments in Lower Silesia (Poland), *Geoscience Records*, **3-1**, 18-29.
- Kasprzak A., Motika J., Wardas-Lasoń M., (2013), Changes in the chemical composition of groundwater in Quaternary Aquifer in Old Krakow, Poland (Years 2002-2012), *Geology, Geophysics & Environment*, **39**, 143-152.
- Kubare M., Mutsvangwa C., Masuku C., (2010), Groundwater contamination due to lead (Pb) migrating from Richmond municipal landfill into Matsheumhlope aquifer: evaluation of a model using field observations, *Drinking Water Engineering and Science*, **3**, 251-269.
- Longley P.A., Goodchild M.F., Maguire D.J., Rhind Query D.W., (2005), *Measurement and Transformation*, In: *Geographic Information Systems and Science*, John Wiley & Sons, Ltd., 2nd Edition, Wiley Publishing House, England, 315-340.
- Law no. 458, (2002), Quality of drinking water, Commission Regulation (EC), On line at: <http://publications.europa.eu/en>.
- Marić N., Kurilić M.S., Matić I., Sorajić S., Zarić J., (2014), Groundwater quality on the territory of Kikinda municipality (Vojvodina, Serbia), *Environmental Earth Sciences*, **2**, 525-534.
- Mikołajków J., (2003), Laboratory methods of estimating the retardation factor of migrating mineral nitrogen compounds in shallow groundwater, *Geological Quarterly*, **47**, 91-96.
- Moody R., Jacko A., (2012), Implementation of GIS-Based Applications in Water Governance, *Water Resources Management*, **26**, 517-529.
- Narany T.S., Ramly F.M., Aris A., Sulaiman W., Fakharian K., (2014), Spatial assessment of groundwater quality monitoring wells using indicator kriging and risk mapping, Amol-Babol Plain, Iran, *Water*, **6**, 68-85.
- Nystrom E.A., (2007), Groundwater quality in the St. Lawrence River Basin, New York, U.S. *Geological Survey Open-File Report 2007-10066; US Geological Survey: Washington, DC, USA*.
- O'Connor M., Zabik M., Carol C., Cousens B., Charenzelli J., (2010), Multi-element analysis and geochemical spatial trends of groundwater in rural northern New York, *Water*, **2**, 217-238.
- Oliver M.A., (1990), Kriging: A Method of Interpolation for Geographical Information Systems, *International Journal of Geographic Information Systems*, **4**, 313-332.
- Onet C., Teusdea A., Onet A., Pantea E., Sabau N.C., Laslo V., Romocea T., Agud E., (2018), Comparative Study Of Dairy And Meat Processing Wastewater Characteristics, *Environmental Protection and Ecology*, **19**, 508-514.
- Preda E., Mincea M.M., Ionașcu C., Botez A.V., Ostafe V., (2018), Contamination of groundwater with phenol derivatives around a decommissioned chemical factory, *Environmental Engineering and Management Journal*, **17**, 569-578.
- Romocea T., Josan N., (2002), *The Anthropogenic Influences upon the Phreatic Water Quality in the West Side of Oradea*. Proc. of the International Conference Preventing and Fighting Hydrological Disaster, Timisoara.
- Rusinga F., Taigbenu A. E., (2005), Groundwater resource evaluation of urban Bulawayo aquifer, *Water*, **31**, 23-34.
- Sadeghi M., Karimi H., Alijanvand H.M., (2017), Removal of lead ions from industrial wastewater using precipitation process, *Environmental Engineering and Management Journal*, **16**, 1563-1568.
- Wenke W., Yang Z., Kong J., Cheng D., Duan L., Wang Z., (2013), Ecological impacts induced by groundwater and their thresholds in the arid areas in northwest China, *Environmental Engineering and Management Journal*, **12**, 1497-1508.
- Zhang X., Qian H., Chen J., Qiao L., (2014), Assessment of groundwater chemistry and status in a heavily used semi-arid region with multivariate statistical analysis, *Water*, **6**, 2212-2232.