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HYDROLOGICAL MODELING OF ARSENIC IN THE DANUBE DELTA

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Abstract

The Danube River forms one of the largest and most complex deltas at the Black Sea, being a Biosphere Reserve, UNESCO World Heritage and Ramsar site. This study assesses the spatial variability of arsenic contamination of the water in the Danube Delta. Water samples were collected during all seasons in 2013 from the south-east of the Danube Delta and analyzed through HG-AAS method for arsenic. Data were handled using two different approaches. First, a complex hydrological model was compiled, using the USEPA WASP modeling software. Secondly, the field measurements were interpolated using GIS software's kriging method to generate prediction maps for the arsenic concentrations. The prediction maps validated the results of the hydrological model, showing that the spatial and seasonal variability of the arsenic concentrations differs depending on the source of the pollution wave, originating upstream in some cases, or being influenced by the marine system. Arsenic constantly recorded noticeable variations but at lower concentrations, within the range [0.5-5.88] μg/L.

Since arsenic is not destroyed in the environment, WASP model can be extended to the entire Delta and beyond, to study the fate and transport of pollutants on a larger scale. In other case, field observations and sampling would need much more human and financial efforts.

According to our knowledge this is the first study which assesses the spatial distribution (hydrological modeling/GIS) of arsenic concentrations in the Danube Delta.

Keywords: arsenic, Danube Delta, GIS, WASP modeling

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1. Introduction

1.1. Background of actor-network theory (ANT)

The Danube River is the second largest river in Europe. The basin has over 300 tributaries from 19 countries with a total population of 83 million inhabitants (2002 census). Over the last 50 years, the water quality has become an important issue for the Danube River. The first attempt to map the water quality in the Danube River was made by Liepolt (1967). Between the '50s and '80s, the major issues were located in the Upper Danube region, but the construction of waste water plants improved the water quality. After the '70s, the Middle and Lower Danube River water quality deteriorated rapidly due to intense industrialization, low pollution control and inputs from highly contaminated tributaries (Popa et al., 2018; Sommerwerk et al., 2009).

The Danube Delta is located on the NW coast of the Black Sea and includes the region between the three main branches formed from the Danube River – Chilia, Sulina and Sfântu Gheorghe (Sommerwerk et al., 2009). It is one of the largest European deltas and one of the best conserved deltas from the world (Biosphere Reserve, UNESCO World Heritage and Ramsar site) (Szilassi, 2004), being an important area which supports a high diversity of life – over 1,600 plant species and over 3,800 animal species (Florescu and Moldoveanu, 2017; Wohl, 2012).

Mathematical modeling became an important branch of the environmental quality assessment.

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Models are often used in addition to monitoring data to estimate environmental concentrations and to study the fate/transport of pollutants (Williams et al., 2010). The Water Quality Analysis Simulation Program – WASP (Ambrose et al., 2009; Wool et al., 2001, 2006) is a dynamic compartment-modeling program linked with a hydrodynamic model, developed by the USEPA for analyzing aquatic systems. It interprets and predicts the reaction of the water quality to the natural phenomena and anthropogenic impact. WASP includes different models for a specific analysis of several contaminants. WASP hydrological model was used to examine major issues, like the eutrophication of the Tampa Bay, Neuse River and Estuary, Potomac Estuary, PCB contamination of the Great Lakes, insecticide contamination of the James River, VOC contamination of the Delaware Estuary or heavy metal contamination of the Deep River (North Carolina) (Wool et al., 2006). WASP model has been successfully applied before in the Danube River, for analyzing a decoupled floodplain along its course in Austria (Preiner and Hein, 2013).

Spatial data are studied through spatial statistics. Geostatistics is a branch of spatial statistics. Its main objective is to interpolate values to a continuous field using sparsely observed data. It was developed initially in the mining field by D.G. Krige, for predicting gold grades in unexploited ores. In the 60`s, Matheron contributed to extend this method for random field data, calling it “kriging”. Kriging is a central tool of geostatistics and had been used almost synonymously. It has become an indispensable tool for fields like environmental sciences, epidemiology, forestry, hydrology, geology etc. (Meuli, 1997; Mase, 2014; Rogozan et al., 2016). Arsenic is an ubiquitous element, thus it can occur in water both from natural sources (geological background), being a natural element of the earth’s crust, and anthropogenic activities, especially industrial waste water generated by mining, nonferrous metallurgy or other activities. The long-term presence of As as a pollutant in the Danube Delta is demonstrated by the enrichment in the 5-30 cm range of lacustrine sediments, where water conditions allow pollutants to be deposited (Dinescu et al., 2004). Naturally occurring concentrations in surface waters range between 1-2 μg/L (WHO, 2011). Previously in our study (Gati et al., 2013), Lead, Cadmium and Mercury have been found in water, but only arsenic was constantly present and had the required spatial variability to be modeled, showing a significant correlation between the aquatic-sedimentary environments, suggesting a balance in mobilization processes.

In this regard, the main objectives of this study were to assess the arsenic contamination of the water and to investigate the spatial variability of arsenic concentrations in the SE of the Danube Delta in each season, by creating prediction maps through the WASP model and Geographical Information System, and therefore comparing the results of the two different approaches.

2. Material and methods

2.1. Study area and sampling

The study area is characterized by the fewest point sources of anthropogenic contamination in the Danube Delta, so it would describe the pollution generated upstream the Delta and support the theory of transportation of metals. The sampling was performed seasonally during 2013 in the S-E of the Danube Delta (Fig. 1), at the end sector of Sf. Gheorghe Branch of the Danube River, near the locality with the same name (44º53’N and 29º36’E). There were 13 sampling sites whence the sampling covered all four seasons of 2013 (March 1-5, May 1-5, July 5-10 and September19-22), summing up to a number of 45 samples. Due to the freezing conditions on the Danube and channels, winter sampling session was conducted at the beginning of March, although it can be considered as winter session, considering the water temperature, specific for January.

Water samples were collected at 20-30 cm under the water surface in 50 mL polyethylene demineralized containers, conserved through acidification at pH<2 with 0.25 mL of concentrated HNO_3 solution, and kept at 4ºC during transportation.

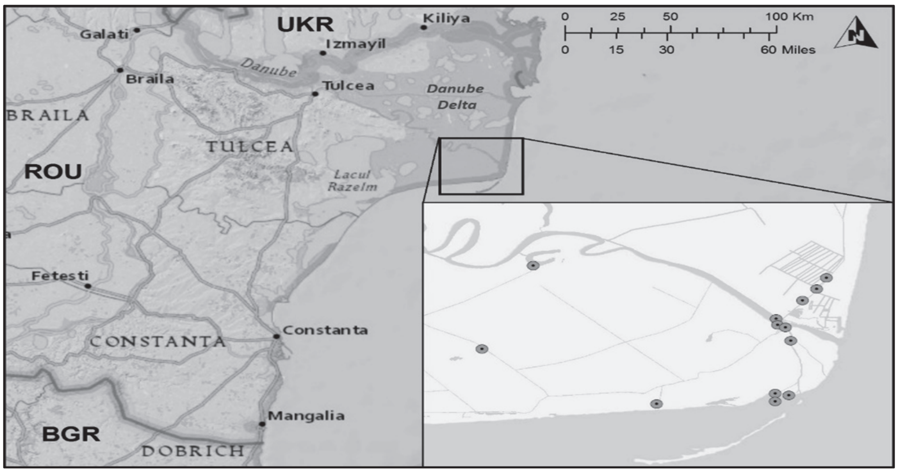


Fig. 1. Location of the study area in Romania and in the Danube Delta (Gati, GIS map)

2.2. Analysis

The water samples were analyzed for arsenic (As) using a Zeenit 700P Spectrophotometer (AAS) using the HG-AAS (Hydride Generation) method. Quality control was performed through specific methods, to evaluate the accuracy of our analyses, according to the Romanian Accrediting Association (RENAR) standards and certifications. RENAR is a member of EA-MLA, ILAC-MLA and IAF-MLA, certificated under SR EN ISO/CEI 17011.

An external standard curve method was used for the calculation of the concentrations. The calibration curve was plotted between 0-10 µg/L. A control sample was prepared using NIST SRM 3103a. The calibration curve was plotted every day (with batch analyses up to 10 samples per day) using MRC ChemLab. The control sample was prepared with other standard solution than the one used for the calibration curve. The control and blank samples were analyzed before, after every 10th, and after the last sample. The method detection limit (MDL) (RL, 2011) was 0.5 µg/l, and the uncertainty of the method (Ellison et al., 2000; ISO/CEI, 2010) was 12.62 %. Proficiency Test samples indicated z scores of 0.01/0.04. A Shewhard control diagram was computed using the results of the control samples, with daily and long-term interpretations. The laboratory participated in inter-comparison analyses organized by ROLAB (accredited by RENAR).

2.3. Hydrological modeling

Water quality modeling plays an increasingly important role in water environment protection, management and decision-making support. It helps to predict and assess water quality responses to natural phenomena and anthropogenic pollution (Peng et al., 2010).

WASP is a dynamic compartment-modelling framework for aquatic systems that divides the water column and underlying benthic system in segments. They can be arranged in a zero-, one-, two-, or three-dimensional configuration to achieve any required spatial resolution. The WASP modelling framework consists of a simple flow module (including net flows, gross flows, and kinematic wave propagation), several different kinetic modules, including heat (HEAT), toxicants (TOXI), nutrients (EUTRO), and mercury (MERCURY), and the time-varying processes of advection, dispersion, point and diffuse mass loading, and boundary exchange (Bird and Dortch, 1988; Sunderland et al., 2010).

The basic principle of WASP is the conservation of mass. The masses of the water volume and water quality constituents are tracked and accounted in time and space using a series of mass balancing equations. The mass balance equation for dissolved elements must account for all the material entering and leaving through direct and diffuse loading, advective and dispersive transport and transformation of physical, chemical and biological order. The mass balance equation that describes the infinitesimally small fluid volume is (Wool et al., 2001) (Eq. 1):

$$\frac{\partial C}{\partial t} = -\frac{\partial}{\partial x}(U_x C) - \frac{\partial}{\partial z}(U_z C) + \frac{\partial}{\partial x}(E_x \frac{\partial C}{dx}) + \frac{\partial}{\partial y}(E_y \frac{\partial C}{dy}) + \\ + \frac{\partial}{\partial z}(E_z \frac{\partial C}{dz}) + S_L + S_B + S_K \tag{1}$$

where, C - concentration of the water quality constituent, mg/L or g/m^3 ; t - time, in days; U_x, U_y, U_z - longitudinal, lateral, and vertical advective velocity, m/d, E_x, E_y, E_z - longitudinal, lateral, and vertical diffusion coefficient, m^2/d; S_L - direct and diffuse loading rate, g/(m^3·d); S_B - boundary loading rate (including upstream, downstream, benthic, and atmospheric), g/(m^3·d); S_K - total kinetic transformation rate (positive is source, negative is sink), g/(m^3·d).

By expanding this infinitesimally small fluid volume to the model's computational segments, and by assuming vertical and lateral homogeneities, the previous equation can be simplified to Eq. (2) (Wool et al., 2001):

$$\frac{\partial}{\partial t}(AC) = \frac{\partial}{\partial x}(-U_x AC + E_x A \frac{\partial C}{dx}) + A(S_L + S_B) + AS_K \tag{2}$$

where, A - cross-sectional area, m^2.

The analysis of model input and output data is critical for the quality of modeling because these allow the modeler to interpret certain aspects of the water body (Peng et al., 2010). Model input consists of chemical loadings and properties, flows, transport and transformation processes. The output represents the average concentration per water segment [µg/L]. (Williams et al., 2010).

Table 1. WASP model input

Model	***Input***	***Observations***
Time range	10/2012- 10/2013	
Model Type	Simple Toxicant (TOXIWASP)	
Hydrodynamics	1-D Kinematic wave	
Bed Volumes	Static	
Print interval	once a day	
Segments	9	Length, width, min. depth (m), slope (%), bottom roughness (m)
Toxicant	Arsenic (µg/L)	Density (g/cm^3), max. concentration (µg/L)
Loads	Segment 1, 4	Observed concentrations (µg/L) → system inflow boundaries

Table 2. Segmentation of the studied water system for setting up the hydrological model

WASP Segment	***Location***
1. Sfântu Gheorghe Branch (1)	Upstream Central Channel discharge
2. Sfântu Gheorghe Branch (2)	Connection with Central and Turcesc Channels
3. Sfântu Gheorghe Branch (3)	Downstream Sfântu Gheorghe locality, discharge to the Black Sea
4. Central Channel (1)	Upstream the cormorant settlement
5. Central Channel (2)	Downstream the cormorant settlement
6. Turcesc Channel (1)	Upstream the bifurcation with Serednie Ch.
7. Turcesc Channel (2)	Downstream the bifurcation with Serednie Ch.
8. Serednie Channel	The full length of Serednie backwater
9. Melea Lagoon	Connecting Turcesc Ch. with the Black Sea

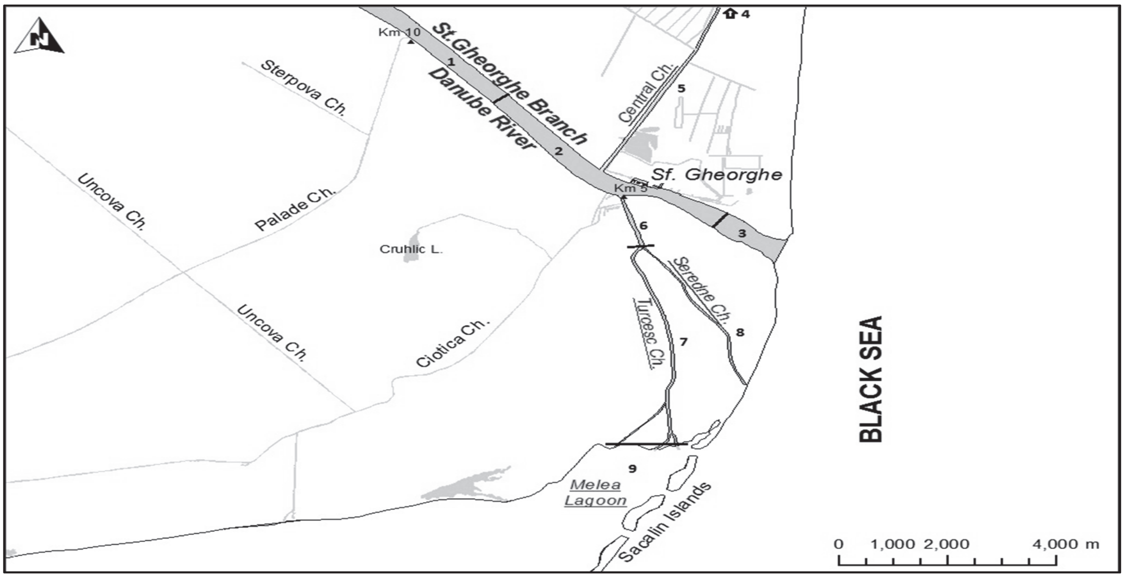


Fig. 2. The studied area, modeled water system and the applied segmentation

The flow distribution of the studied system was divided in a schematic network, a scaled-down version of the work of Mikhailov (2004). The segments were created to divide the water system into sections where changes of the arsenic concentration are most likely to be observed. Each segment was delimited within the model with its specific length, width, depth, slope and bottom roughness, and a hydrological network was created by assuming the flow and exchange functions. The segments are presented in Table 2.

The model was run using the TOXI simulation (Simple Toxicant), based on the concentration of arsenic in the points of advection into the aquatic network – at segments 1 and 4. The path of the contaminant was then modeled with a time step of one day. The variable hydrological parameters were adjusted according to the seasonal variations.

The model network was created and divided respecting the segments, as a vector-based polygon digital map, and was then loaded into the Graphic Post-Processor unit of the WASP program. The average arsenic concentration of each segment was exported for each period coinciding with the field observations.

2.4. Geostatistical analysis

Geostatistical methods are based on statistical models that use autocorrelation and statistical relations between the measured points. The statistical dependences are estimated using semivariogram and covariance functions and they depict the spatial autocorrelation of the measured samples. These functions can be written as (Oliver, 1990) (Eqs. 3-4):

$$\gamma(S_i,S_j)=\frac{1}{2}\mathrm{var}\left[Z(S_i)-Z(S_j)\right] \tag{3}$$

Semivariogram

$$C(S_i,S_j)=\mathrm{cov}\left[Z(S_i),Z(S_j)\right] \tag{4}$$

Covariance

where: *var* – variance, *cov* – covariance, S_i, S_j – locations.

The kriging method is similar to the spline and IDW (Inverse Distance Weighted) methods, attributing weights to nearby measured values to derive a prediction for an unsampled location. The general formula for this type of interpolation can be written as follows (Oliver, 1990) (Eq. 5):

$$\hat{z}(S_0)=\sum_{i=1}^{N}\lambda_i Z(S_i) \tag{5}$$

where, $Z(S_i)$= the measured value at the location *i*; λ_i= an unknown weight for the measured value from the location *i*; S_0= the prediction location; *N*= the number of measured points.

In the kriging method, the weight (λ_i) depends on both the distance between the measured points and the prediction location, and the spatial arrangement of the measured points. Therefore, in this method, the weight depends on the fitted model of the measured points, of the distance to the prediction location and the spatial relation between the surrounding measured points (Oliver, 1990).

Statistical dependence among the spatial variables is related to the distance between the sampling points and the direction of movement from one to another. Geostatistical methods usually imply the Euclidian distances between locations (Krivoruchko and Gribov, 2004). The water system creates linear discontinuity in a normal prediction surface. Therefore, to predict the path of the contaminants in the aquatic system, the method implies the use of barriers, to separate the water from the land. IDW and kriging support the use of barriers. The vector-based polygon digital map created for WASP Graphic Post-Processor, with no segmentation, was applied as barrier, using kriging interpolation instead of IDW, which is a deterministic method that uses non-Euclidean distances. The structural analysis of the model was made using the semivariogram function. The empirical semivariogram provides information about the spatial autocorrelation of the points, however, in order to make spatial predictions, a continuous function needs to be fitted. There are several types of models for the semivariogram function, like linear, circular, spherical, exponential and others. For this model, a circular function was used. In order to limit the influence of more distant samples on the prediction of an unsampled location, the search radius was limited to only two neighbors (upstream and downstream).

Table 3. Kriging interpolation input

Kriging type	***Ordinary***
Output type	Prediction
Function	Semivariogram
Model	Circular
Neighborhood type	Standard
No. of neighbors	2
Mean prediction error	[0.004-0.08]

Therefore, the results of the spatial analysis are prediction maps that reveal the arsenic concentration throughout the study area for each set of observations. The maps were created using ESRI ArcGIS software.

3. Results and discussion

The results for the arsenic measurements (Table 4) showed the highest values in March > July > September > May. The highest variation was also observed in March and the lowest in September. The paper continues with the presentation of the prediction maps generated by the WASP model (Fig. 3) and the field measurement based spatial analyses generated by the GIS software (Fig. 4).

The arsenic concentration in the water was observed to vary from one season to another. This is expected, as the Danube River has a very large catchment, with an area of 817.000 km^2 (Panin, 2003), and there are many pollution sources.

Table 4. Arsenic measurements results

As (µg/L)	***Average***	***Median***	***S.D.***	***Min***	***Max***
March	2.02	1.94	1.4	0.5	5.88
May	0.59	0.624	0.21	0.5	0.94
July	1.2	0.8812	0.78	0.5	3.15
September	1.28	1.295	0.18	0.81	1.57

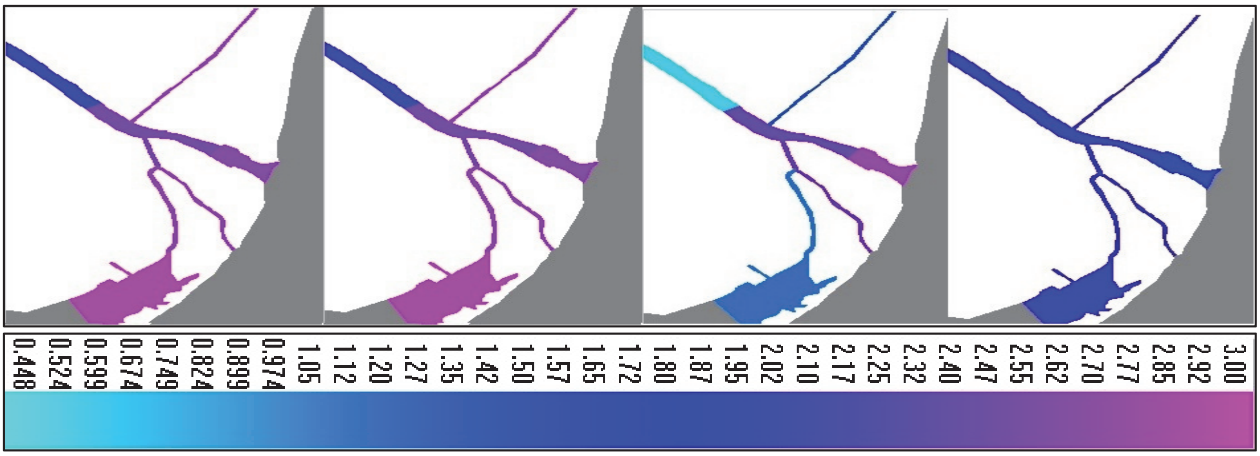


Fig. 3. Prediction maps of the arsenic concentration (µg/l) generated by the WASP hydrological model. From left to right are the months of March(4a), May(4b), July(4c) and September(4d) 2013

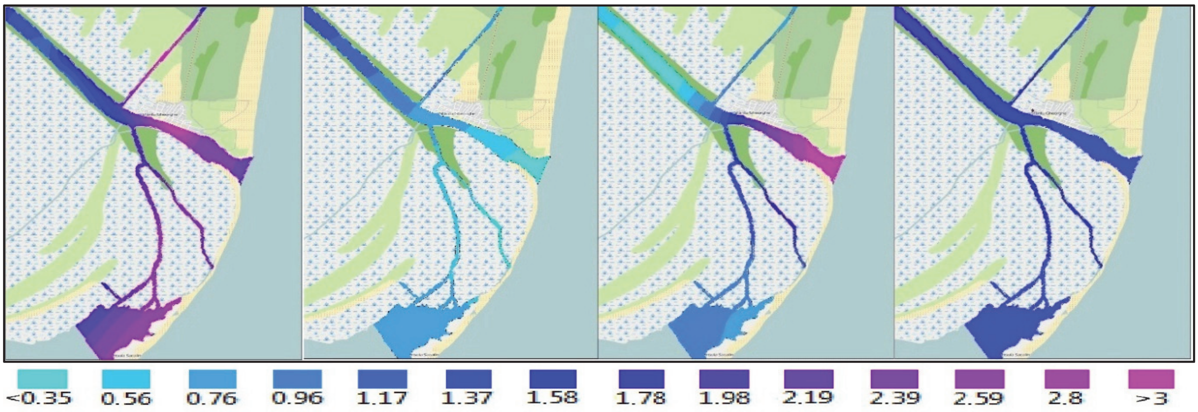


Fig. 4. Prediction maps of the arsenic concentration (μg/l) from field measurement based spatial analyses. From left to right are the months of March(5a), May(5b), July(5c) and September(5d) 2013

According to the International Commission for the Protection of the Danube River (ICPDR), the most important heavy metal pollution sources are - waste and wastewaters from the cities throughout the Danube`s catchment; industry (mining, metallurgy, power plants); fluvial transport; natural causes. For the reference year 2002, the ICPDR inventory included 987 municipal, 306 industrial and point sources (ICPDR, 2004). From the European Environment Agency's (EEA, 2014) waterbase – emissions to water, we can conclude that for the years 2010-2012, the mean arsenic emissions to water from industrial and urban sources amounted to over 2200 kg per year. Assuming a constant emission rate, a basic calculation states that this value can lead to an increase of As concentration in the Delta's apex with 0.011 μg/l. However, we need to take into account that there are several non-EU countries in the Danube River Basin that are not reporting to EEA. From various measurements (2006-2012) from the TransNational Monitoring Network (TNMN, 2012) program, part of the ICPDR, on the main tributaries of the Danube River's Lower Section (Morava, Drava, Tisa, Sava, Iskar, Yantra, Siret, Olt, Prut, Arges and Jiu) As concentrations before their confluence with the Danube varies between 1.13 – 4.33 μg/L with an average of 2.26 μg/L. The highest concentration was measured in the Iskar River, known to be contaminated with metals due to mining activities (Bird et al., 2009). The flow weighted average As concentration is 1.92 μg/L. The flow rate of these tributaries accounts for over 50% of the Danube River's flow rate before the Delta's apex. The closest point source is located 120 km upstream, in Tulcea city (~75.000), which did not have a Wastewater Treatment Plant until 2014.

The measured arsenic concentrations in the study area are within the normal range (0.5 – 5.88 μg/l) according to the Romanian Standard 161/2006 (transposition of the 2000/60/CE Directive), the allowable concentration for arsenic in surface waters being 10 μg/L. This is the same as the US EPA's (http://water.epa.gov) MCL (maximum contaminant level) and WHO guidelines (WHO, 2011), for drinking water. This value is set as close as possible to the health goals, considering the cost-benefit criteria (http://water.epa.gov). The health-protective value for As-induced noncancer chronic toxicity is under 2 μg/L, but it isn't economically feasible to treat the drinking water to this level (OEHHA, 2004). Also, the value of 10 μg/L is equivalent to the ATSDR's Minimum Risk Level (MRL) for chronic oral exposure to inorganic As, assuming an adult of average weight, drinking 2L of water per day (0.3 μg As/kg/day).

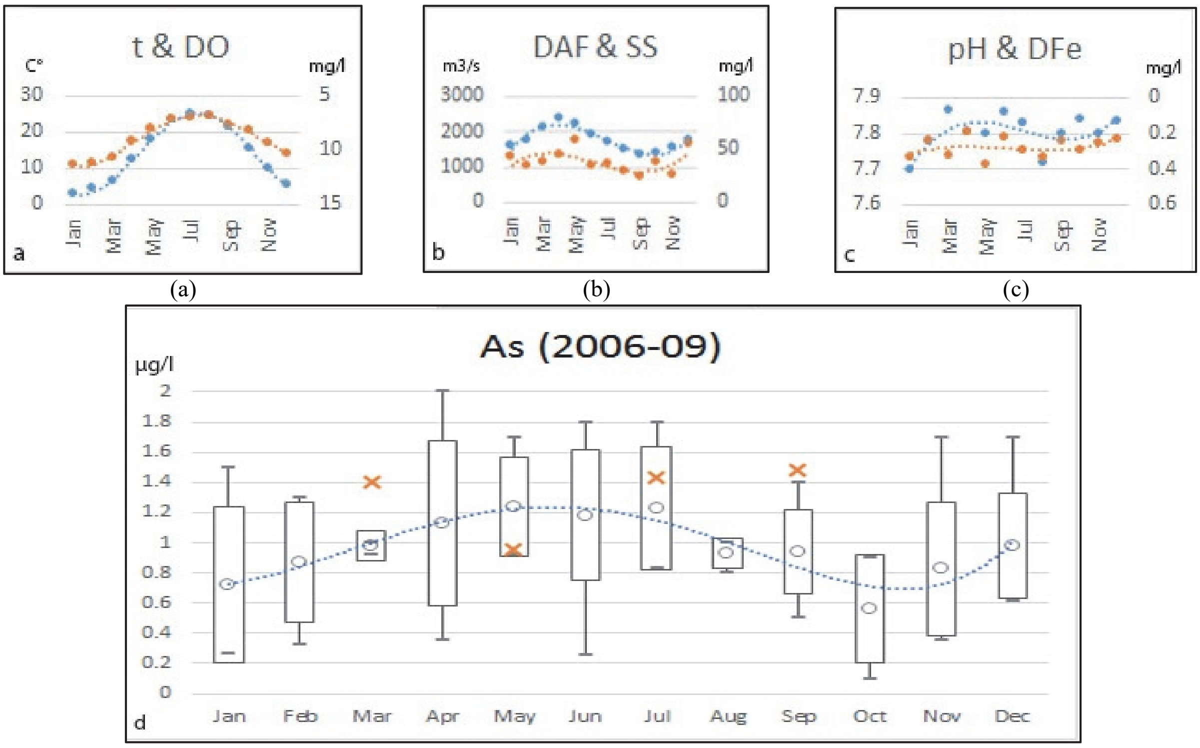
Data were gathered from the monitoring point of the TNMN program located on Sf. Gheorghe Branch (N44.88462; E29.60945), for the period 2006 – 2009. These were analyzed to create a monthly multiannual pattern (Fig. 5) and a trend line was added using a polynomial order 3 function. We considered these as normal values for the recent period and we relied on them for referencing our results.

According to the WASP model, we can say that the arsenic contamination comes in plumes, as it can be seen in the generated prediction maps (Fig. 3). This pattern is validated by the observed values, modeled by the field measurement based spatial analyses (Fig. 4). The highest arsenic contamination was modeled and observed in March, when a contamination plume can be seen passing along the water system. In May, lower concentrations were measured, and the plume can be seen appearing in the water system. Another shorter plume was observed in July, as for September, the arsenic concentration had a low spatial variability. Our measured values of arsenic are not fitting in the multi-annual monthly values and trend of TNMN measurements (Fig. 5d). These can be linked with the conditions created by the hydrological status of the Danube River, as the lowest flow rate was recorded in September, measuring 37% lower than the multi-annual average value, while in March, May and July, the flow rate measured 8%, 50%, respectively 33% higher, according to the Romanian National Institute of Hydrology and Water Management "INHGA" (2013). Our measured pH values were out of the normal range (Fig. 5c), with lower values in March (6.4) and higher in the rest of the sampling months (8.6, 8 and 8.5). The temperature was also lower than the normal values (Fig. 5a) in March (3.1°C), and

September (18.7°C), normal in July (24.5°C) and higher in May (20.1°C). Ungureanu et al. (2004) observed an association between the values of water temperature and pH in the Sf. Gheorghe Branch. At temperatures under 15°C the pH varies inversely, while over 25°C, it varies directly.

In order to study the relations and influences between the physico-chemical variables and the As concentration, the TNMN (2012) data from the Sf. Gheorghe Baranch were subjected to statistical tests. The Pearson correlation revealed that the As concentration is influenced by suspended sediment (-.376, p<.001), pH (.348, p<.001), temperature (.217, p=.018), dissolved Fe (-.2, p=.09), daily average flow (-.169, p=.401) and dissolved O_2 (-.08, p=.384). According to Ungureanu et al. (2004), the concentrations of the metals associated to suspended sediments are influenced by the content in clay minerals. A linear regression model with stepwise method (F probability) was computed. This test selected three predictors as significant – suspended sediments, pH and dissolved Fe. The regression's ANOVA test revealed the value of p<.001. The B coefficient for the constant (intercept) is -1.77 (s.e.=1.045, 95% C.I. [-3.85 – .318], t=-1.69, p=.095), for suspended sediments B=-.006 (s.e.=.002, 95% C.I. [-.009 – -.002], t=-3.38, p=.001), for pH B=.422 (s.e.=.132, 95% C.I. [.16 – .69], t=3.19, p=.002), and for dissolved Fe B=-1.08 (s.e.=.457, 95% C.I. [-1.99 – -.166], t=-2.36, p=.021). The variation of the sediment discharge is influencing many metals (Al, Cu, Zn, As, Be, V). In the study of Ungureanu et al. (2004), they all presented the same seasonal variability. Moreover, due to its high correlation with the flow rate, a higher proportion of the effect magnitude can be assigned to this, while it is more of an indirect order. Arsenic is highly related to Fe, as large quantities of it co-precipitates with iron (Nikilaidis et al., 2004), and is remobilized from sediments via the redox-controlled dissolution of Fe oxide phases (Martin and Pedersen, 2002), especially in fall and winter (La Force et al., 2000). Also, water temperature above ~15°C (Masson et al., 2007) and high pH conditions, over 8.5 can lead to large scale release of As from sediments (Smedley and Kinniburgh, 2002).

Because the channels where we have sampled are much narrower than Sfântu Gheorghe Branch, they can take a much lower flow rate and the water velocity is usually low, especially in the area of Turcesc Channel (Segments 6,7 and 8), where conditions are close to a backwater, near the discharge to Melea Lagoon (S.9). WASP model results show that Serednie Channel (S.8) can hold the contamination plume for the longest time (up to 20 days), having the outflow blocked by a sand belt. The Turcesc Channel (S.6,7) can hold the plume for 4-6 days. The Melea Lagoon (S.9) is subjected to very few coastal currents, as it is sheltered by the Sacalin Islands.



(a) (b) (c)

(d)

Fig. 5. Arsenic measurements in Sf. Gheorghe Branch from the TNMN (2012) program between 2006-2009, a – temperature(blue) and dissolved oxygen(red), b – daily average flow(blue) and suspended sediments(red), c – pH(blue) and dissolved Fe(red), d – total arsenic, with mean(circle), +/- S.D.(box) and minimum/maximum(line), our measured values on the same sector(**X** mark). Dotted lines represent trends – polynomial order 3 functions

The Central Channel (S.4,5) is also a more delayed water system (8-10 days), as it is connected to a large lake complex – Puiu-Rosu – subjected to increasing eutrophication and sedimentation (Pinay, 1992). It is known that lakes within a delta act like a filter for water contaminants. The deltaic lakes and swamps play an important role of buffer-reservoirs and filters, since the residence period for the water in these depressions can reach 3-4 months (Panin, 2003). Due to these phenomena, higher levels of arsenic can occur in the channels and lagoons, while the main plume could have passed. The water level of the Danube and the lakes rises between April and June and then decreases in September and October (Durisch-Kaiser et al., 2008). According to Hasegawa et al. (2010) inorganic As is frequently converted to more complicated organoarsenical compounds in eutrophic lakes. So, even though the lakes and swamps can recontaminate the water system, the resulted organic As can be less harmful (WHO, 2011).

Our observed data suggest that higher than normal As concentrations can occur in conditions created by low-flow, like those observed in September 2013. According to Mauser et al. (2008), more frequent and severe low-flow conditions are expected due to a predicted decrease in rainfall in the Danube River Basin. In addition, by 2030, the contribution to the Danube coming from ice-melt, considered a clean water source, will be as low as 20% (Weber et al., 2010). In this case, without a strict management of toxic pollutants, sensitive areas will be severely affected by toxic plumes.

Water quality doesn’t affect directly the population living in the Danube Delta, as it is not considered a drinking water source. But people in the Danube Delta depend on natural resources and wildlife, with more than 40% of them being officially registered fishermen (Boja and Popescu, 2000). Fish tend to bioaccumulate heavy metals from water (Mendil et al., 2010), and this can increase the exposure risk of the local population, especially that 90% of the dietary As exposure comes from fish and seafood (Borak and Hosgood, 2007). In our previous studies (Gati et al., 2013) we found As in fish ranging between 0.13-0.38 mg/kg WW. Also, birds are an important link in the Danube Delta’s ecology, more than 300 species passing, breeding or some of them spending the winter. They are also at risk due to the environmental pollution, heavy metals having adverse effects on the reproduction and development of birds (Lucia et al., 2010).

The resulting prediction maps generated by the WASP Graphic Post-Processor (Fig. 3) are less smooth than the ones generated by the GIS spatial analysis (Fig. 4), but they present the same trends in changes of the As concentrations. WASP model results are validated by the field measurement based spatial analyses, meaning that it can be successfully applied in complex water systems like river deltas. Smoother prediction maps could be achieved by multiplying the number of segments, resulting in a better resolution, although computational time will increase significantly. As in this case study, a compromise has to be made, depending on the desired outcome. There are cases where time is more important than resolution, like studying an accidental spill and making decisions before the plume reaches sensitive areas. There are also cases where the outcome needs good resolution, like developing Total Maximum Daily Loads (TMDL) from industrial point sources in order to protect these sensitive areas. Pollutants like arsenic are not destroyed in the environment, they only change their chemical state or form. In this order, a WASP water quality model can be extended to the entire Delta and beyond, by separate models, to enhance computation capabilities and to study the fate and transport of pollutants on a larger scale. For this kind of studies, field observations and sampling would need much more human power, time and financial efforts. WASP model has not had an external peer-review, though it was cited in the peer-reviewed literature for its application in water quality (Williams et al., 2010).

The time and computational costs for setting up and running the WASP model are much higher than those implied by using the geostatistical method, and the data needed is also much more complex. Even so, the flexibility and ability of WASP model to perform complex calculations makes it useful in understanding environmental trends and patterns without needing complex field observations.

4. Conclusions

Arsenic showed spatial and temporal variability, but within normal values, according to Romanian laws.

Comparing the simulation results of WASP model with the spatial analyses of the observed arsenic concentrations, we conclude that it was applied effectively to this water system, consistently predicting the trend change of the studied indicator and its path through the modeled system.

Because arsenic persists in the environment, WASP model can be extended to the entire Delta and beyond, to study its fate and transport on a larger scale. Otherwise, field observations and sampling would need much more human and financial efforts.

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