THE EVOLUTION OF THE PHYSICAL-CHEMICAL QUALITY STATE OF THE DANUBE DELTA AQUATIC ECOSYSTEM IN THE PERIOD MAY-OCTOBER 2005/2006

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ABSTRACT

The objective of this paper is to provide useful data concerning the quality of the Danube Delta aquatic ecosystem (surface water and sediment). Samples were collected from May to October in two consecutive years (2005 and 2006) from two different locations situated on Sfantul Gheorghe (Saint George) branch (Murighiol and Uzlina). A particular observation is that a high concentration of polyaromatic hydrocarbons (PAHs) was recorded in the sediments collected from Murighiol confirming the pollution of the environment from that area.

The comparative analysis of the quality characteristics of the Danube Delta aquatic ecosystem in 2005 and 2006 (by physico-chemical determinations) emphasized a dynamic character of water quality that can lead to unfavorable stages and, thus, to worse life conditions for aquatic organisms.

KEYWORDS: Danube Delta, water, sediment, physical-chemical characterization, pollution, PAH.

INTRODUCTION

The Danube Delta Biosphere Reservation has a total surface of almost 580,000 ha and includes the Danube Delta, the Razim–Sinoe Complex, the Danube seaboard till Cotul Pisicii, and the lake Saraturi–Murighiol. More than 50% from this surface (312,440 ha) are represented by aquatic and terrestrial natural ecosystems included in the universal patrimony.

Surface water and sediment samples were taken from two locations on Sfantu Gheorghe branch – *Murighiol* and *Uzlina*. In *Murighiol*, samples were collected from a canal near Murighiol Lake. Usually, a large number of vessels pass through this place, and this explains the presence of oil spots on the surface of the Danube. Another problem in this location is the direct release of wastewater from the nearby houses into the Danube. In *Uzlina*, samples were collected from the Cormoran Complex, a place with intensive naval activity (speed boats, motor boats, fishing boats). Cormoran Complex has its own domestic wastewater treatment station, and the treated water is dumped into the Danube. The place from where the samples have been collected is situated on a jetty.

The major sources of pollution in the Danube Delta Biosphere Reservation with different organic and inorganic pollutants are the economic agents and the naval transportation. The presence of heavy metals in this area has negative effects on the environment. Most part of heavy metals associate with the particles in water and accumulate in the sediments. The binding mechanism is a very important parameter for the risk assessment of the pollution level in this ecosystem while mobility and availability are highly dependent on the strength of binding.

In a previous study, the extraction and determination techniques for heavy metals from sediments were tested [1]. The results of this study led to the conclusion that the optimum method for extraction of Cu, Mn, Zn, Fe, Pb, Cd, Cr, Ni and Hg is that presented in the French standard NF X31 – 120/1992 [2].

The results of the study concerning the physico-chemical quality state of the deltaic ecosystems from Uzlina and Murighiol, carried out in the period April-October 2003 and 2004 [3] showed an oxygen deficit and the presence of some chemical parameters (heavy metals, phenolic compounds, mineral oil, o-phosphates, lindane) in concentrations which exceed the reference values [4].

The Norm 161/2006 [5] (transposed from Directive 2000/60/EC) introduced a classification of the quality factors that describe the ecological conditions of surface water. This classification consists of 5 conditions for surface water: *very good* (I), *good* (II), *moderate* (III), *poor* (IV) and *bad* (V). The parameters evaluated for the chemical and physico-chemical characterization of water quality are temperature, oxygen, nutrients, pollution with dangerous substances, mineralization, and pH. The Norm provides two categories of chemical conditions for all aquatic, sediment and biota systems:

- good chemical conditions: all quality parameters (indicators) are within the limits imposed by quality standards;

- bad chemical conditions: parameters exceed the limits imposed by quality standards.

Due to the dynamic character of water quality, after a first study carried out in the years 2003 and 2004, the investigations were continued in the next years (2005 and 2006), and the obtained results were compared. The results of the analyses provide relevant information on the ecosystem quality, focusing on the physico-chemical characteristics, and also an overview of the evolution of the pollution level in time.

MATERIALS AND METHODS

Sampling

Water and sediment samples were taken monthly from May to October 2005 and 2006 from 2 locations: Murighiol and Uzlina (see map of the Danube Delta in Fig. 1). The sampling and preservation step was done according to the recommendations of specific international guides [6-10].

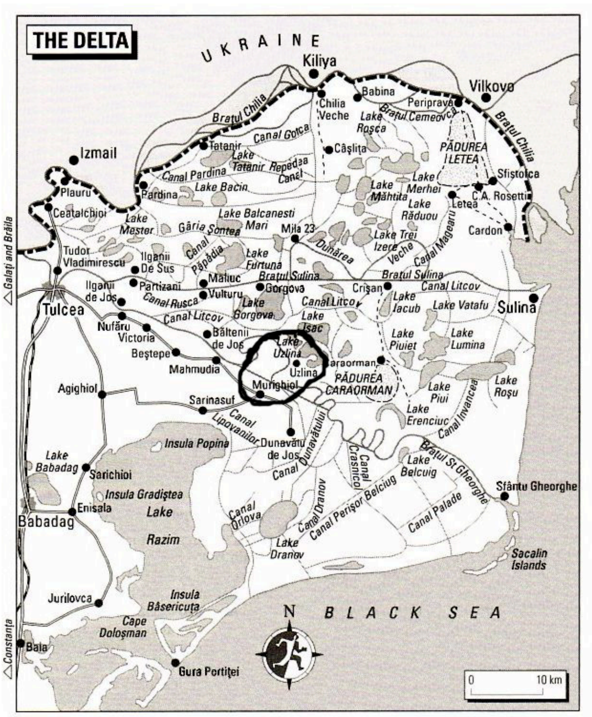

FIGURE 1 - The map of Danube Delta:
Uzlina and Murighiol locations on Saint George branch.

Water samples were collected and stored in glass bottles. From each sampling location, 10 L of water were collected. The sediment samples were taken from 2-3 m depth within the Danube using a van Veen bottom water sampler. All samples were kept in cooling boxes at 4 ^{0}C during transportation, and the analyses were performed immediately after receiving the samples in the laboratory.

Analysis

The analyses performed on water and sediment samples are presented in Table 1.

Analytical methodology applied for the determination of organic pollutants

a. Water samples

- **Polyaromatic hydrocarbons (PAHs):** Fluoranthene, benzo(b)- and benzo(k)fluoranthene, benzo(a)pyrene, benz(a)anthracene, benzo(g,h,i)perylene, indeno (1,2,3-cd) pyrene, naphthalene, phenanthrene, anthracene, chrysene, and pyrene were determined from surface water with Agilent 1100, HPLC equipment, fluorescence detection and column LiChrospher® PAH (L=250 mm, i_d= 4.6 mm, θ=5 μm) in accordance with SR EN ISO 17993/2004 standard (clean-up on silica gel column);
- The quantitative analysis of total **mineral oil** content was performed with an FT-IR system (Perkin Elmer Spectrum BX II), clean-up step on silica gel column;
- **Pesticides:**
  - For **organochlorine pesticides** (α-, β-, γ-, δ-HCH), clean-up step was performed using a silica gel column; the quantitative determination was performed on a GC system (Agilent Technologies 6890 N*)*, with ECD and a TR-1 column (Thermo; L=30 m, i_d =0.32 mm, θ=0.25 μm)
  - For **organophosphorus** (malathion, parathion, dichlorvos) and **triazine pesticides** (atrazine, simazine, propazine), a GC system Agilent Technologies type 6890 N was also used, but with NPD and a CP-Sil-5CB column (L= 30 m, i_d= 0.33 mm, θ =0.25 μm)
- **Polychlorobiphenyls** (PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180) were analyzed on a GC System as described above for organochlorines, after a clean-up on a silica gel column

b. Sediment samples

For sediment samples, determinations were carried out in accordance with the European Standards (Table 1) using the same equipment and clean-up procedure as for water samples.

Analytical methodology applied for the determination of heavy metals

a. Water samples

In order to analyze the content of heavy metals from water samples, the pretreatment step was done according to the standard SR EN ISO 15587-1/2003 [11].

TABLE 1 - Parameters analyzed in water and sediment, and the methods of analysis.

No	Parameters	Methods of analysis	No	Parameters	Methods of analysis
	WATER				
1	pH	SR ISO 10523:1997	19	Sodium	STAS 3223-2 / 80
2	Conductivity	SR EN 27888:1997	20	Chromium total	SR ISO 9174:1998
3	Residue filterable	STAS 9187:1984	21	Copper	SR ISO 8288:2001
4	Dissolved oxygen	STAS 6536:1967	22	Cadmium	SR ISO 8288:2001
5	BOD_5	SR EN 1899/2:02	23	Iron (Fe^{2+} + Fe^{3+})	SR ISO 13315:1996
6	COD-Cr	SR ISO 6060:1996	24	Zinc	SR ISO 8288:2001
7	Ammonium $N\text{-}NH_4^+$	SR ISO 7150/1-00	25	Manganese	SR 8662/2:1996
8	Nitrate $N\text{-}NO_3^-$	STAS 8900/1:1971	26	Nickel	SR ISO 8288-2001
9	Nitrite, $N\text{-}NO_2^-$	SR 6777-96	27	Lead	SR ISO 8288-2001
10	Total Nitrogen	SR ISO 10048-2001	28	Anionic surfactants	SR ISO 7875/1:1996
11	Ortho-phosphate ($P\text{-}PO_4^{3-}$)	SR EN 1189:2000	29	Phenol index	SR ISO 6439:2001
12	Total phosphorus	SR EN 1189:2000	30	Mineral oil	SR 7877/2:1995
13	Chloride	SR ISO 9297-01	31	PAH compounds	SR EN ISO 17993 / 2004
14	Sulfate	EPA427C	32	Organochlorine Pesticides	SR EN ISO 6468:2000
15	Arsenic	SR EN 26595-02	33	Organophosphorus Pesticides	SR EN ISO 6468:2000
16	Mercury	SR EN 1483-2003	34	Triazine Pesticides	SR EN ISO 6468:2000
17	Calcium	SR ISO 7980/97	35	PCB	SR EN ISO 6468-2000
18	Magnesium	SR ISO 7980/97			
	SEDIMENT				
1	Copper	SR ISO 11047:1999	9	Arsenic	SR EN 26595/1-97 SR ISO 11466-99
2	Zinc	SR ISO 11047:1999	10	Lead	SR ISO 11047:1999
3	Cadmium	SR ISO 11047:1999	11	PCB	SR ISO 14507: 2000 SR EN ISO 6488-00
4	Mercury	SR EN 1483-2003 SR ISO 11466-1999	12	Lindane (γ-HCH)	SR EN ISO 6468: 00 SR ISO 14507: 2000
5	Chromium	SR ISO 11047:1999	13	Total PAHs	SR ISO 13877-1999
6	Nickel	SR ISO 11047-1999	14	Mineral oil	SR ISO/TR 11046-98 Method B
7	Iron	SR ISO 13315:1996 SR ISO 11466-1999	15	Mobile species of heavy metals	NF X 31 – 120/1:1992
8	Manganese	SR 8662/2:1996 SR ISO 11466-1999			

The quantitative determination of some metals (**cadmium, copper, iron, lead, manganese, nickel, zinc**) was performed with an UNICAM SOLAR type 929 atomic absorption spectrophotometer, using a mixture of air-acetylene, but for **chromium**, of acetylene-nitrogen protoxide for flame combustion. **Mercury** determination was performed by cold vapor technique after 24-h oxidation of the organic matter with potassium permanganate. For **arsenic,** a hydride generator coupled with an AAS system was used. **Calcium, magnesium** and **sodium** were directly analysed from water samples by F-AAS (air–acetylene for Mg and acetylene–nitrogen protoxide for Ca) and AES (atomic emission spectrometry) with air-acetylene flame for Na.

b. Sediment samples

Dry sediment (at room temperature) with particle dimension lower than 60 µm was digested with a mixture of aqua regia (21 ml HCl 37% + 7 ml nitric acid 65%) [12]. The total concentration of metals (**Cd, Cu, Cr, Fe, Pb, Mn, Ni, Zn**) was determined in liquid solution.

For **mercury**, the digestion procedure was performed in a microwave laboratory system (Ethos Millestone) on dry sediment mixed with 10 ml nitric acid, using the following program: power -700 W, time -10 min, maximum temperature 130 ºC)

For **arsenic,** it was necessary to treat the dry sediment with 10 ml of nitric acid and 15 ml of sulfuric acid.

Analytical methodology applied for the analysis of inorganic parameters

For the quantification of inorganic parameters (a**mmonium, nitrate, nitrite, total nitrogen, o-ophosphate, total phosphorus**), specific equipment for pretreatment of water samples and a Perkin Elmer Lambda *25* UV/VIS spectrometer were used.

The same equipment was used for the determination of a**nionic surfactants** [13] and **Phenol Index**.

Mobile form of metallic elements

The working procedure was as follows: 4 g of dry sediment (particle size <60 µm) were mixed with 40 ml of buffer solution of 1 M ammonium acetate and 0.01 M EDTA (pH = 7.2 ± 0.2). The obtained suspension was shaken at 20 ºC for 2 h with 40 rpm. The solution was centrifuged and then analyzed using AAS methods.

Chemical reagents

- Reference materials, standard solution traceable to SRM from NIST (1000 mg/L, CertiPUR, Merck quality) for all metallic elements;
- Reference material for PAH compounds Kit 610-N, Supelco quality;
- Reference materials for organochlorine, organophosphorus and triazine pesticides, Pestanal, Riedel-de-Haën quality;

- Reference material for PCB–mix, Oekanal, Riedel-de-Haën quality and PCBs (28, 52, 101, 138, 153, 180), Promochem quality;
- Reference materials for mineral oil: n-hexadecane (Oekanal, Riedel-de-Haën quality), benzene (Sigma-Aldrich quality), isooctane (for spectroscopy, Uvasol, Merck quality);
- Reference materials, standard solution traceable to SRM of NIST for ammonium, nitrate, nitrite, chloride, sulfate, phosphate (1000 mg/L, CertiPUR, Merck quality);
- Buffer solution for pH (4.01; 7.00; 9.21) from Mettler Toledo;
- Potassium chloride solutions (nominal 0.015 mS/cm, 0.147 mS/cm, 1.41 mS/cm), certified reference material for the measurement of electrolytic conductivity, traceable to SRM from NIST and PTB;
- Organic solvents: methyl chloride (GR for analysis, Chimopar), carbon tetrachloride (pro analysi, Merck), n-hexane (SupraSolv, Merck), chloroform (SupraSolv, Merck), acetone (Suprasolv, Merck), petroleum ether (Reag. Ph. Eur, Merck);
- Silica gel 40 (0.063–0.200 mm) for column chromatography, Merck;
- Hydrochloric acid (37%, GR for analysis, Merck), nitric acid (65%, GR for analysis, Merck), sulfuric acid (98%, GR for analysis, Merck);
- Chemical substances for determination of inorganic compounds, GR for analysis, Merck quality

Quality Assessment

The laboratory is accredited by RENAR (Association for Accreditation from Romania), and follows the requirements of ISO 17025/2005 standard. The laboratory has certification with BVQI (Bureau Veritas Quality International) in accordance with ISO 9001 standard, and has periodical participation to internal and external audits.

For all the analyzed parameters, the laboratory uses standard methods (ISO, SR ISO, EN, SR EN, SR, STAS, EPA), reference materials and certified reference materials. All these standard methods were verified and the main performance parameters (limit of detection, limit of quantification, linearity, accuracy, precision, selectivity, the uncertainty of measurement) were established with the existing equipment from the laboratory.

The laboratory participates every year at tests for the evaluation of its capability by inter-laboratory comparisons (IMEP Belgium, IAWD Germany, CALITAX Spain, Quality Infrastructure Denmark) for different groups of pollutants (organic compounds, metallic elements, inorganic com-pounds) from complex matrixes (surface water, wastewater, drinking water, soil, sediment, sludge).

RESULTS AND DISCUSSION

A large database was obtained after two years of physico-chemical evaluation of surface water and sediments from the Danube Delta. The evolution of the concentrations found in the water samples during the last two years, and the comparison of these results with the reference values imposed by the Norm 161/2006 [5] are presented in Figs. 2-8 for Murighiol and Figs. 9–13 for Uzlina.

The values were compared with the second-class quality factor for surface water. The following physico-chemical changes took place in the water samples investigated in 2006, in comparison with those of 2005:

In Murighiol (water samples)

- The water bodies presented a high organic load (based on COD and BOD levels) from July till October 2006; the values were higher than the acceptance limits (class II quality), thus in September were registered the highest BOD (27 mg O_2/L, class V) and COD (67 mg O_2/L, class III) values;
- Nitrogen compounds (represented by total nitrogen and nitrate ions) were also higher in 2006 than in 2005, but only in July and August the total nitrogen values exceed the admissible value; nitrate concentration was higher than the admissible value for class II quality of surface water (3 mg N/L) in almost all the investigated months;
- The total concentration of phosphorus was higher than the reference value only in May 2006; all the other values, including those for ortho-phosphorous and phosphoric compounds were situated under the admissible values in both years;
- The heavy metal concentrations were below the reference values, excepting iron and manganese; for iron, high values were recorded in 2006 from July to October, being higher than the admissible and also the values detected in 2005; the situation was similar concerning manganese concentration, and its values from July to October were higher than the limit value (0.1 mg/L);
- An unexpected increase of chloride ions concentration was observed in July 2006, and persisted at this high level also in the next months (140–200 mg/L); this increase is also reflected in the higher values of conductivity and the filterable residue in the same period;
- The dissolved oxygen is lower than the admissible value throughout all the investigated periods; this fact causes detrimental effects on aquatic organisms because content of dissolved oxygen is an essential factor for living organisms;
- Other pollutants detected 2006 in surface water were PAHs (benz(a)anthracene and fenanthrene); their concentrations were higher than the admissible values in 3 different months;

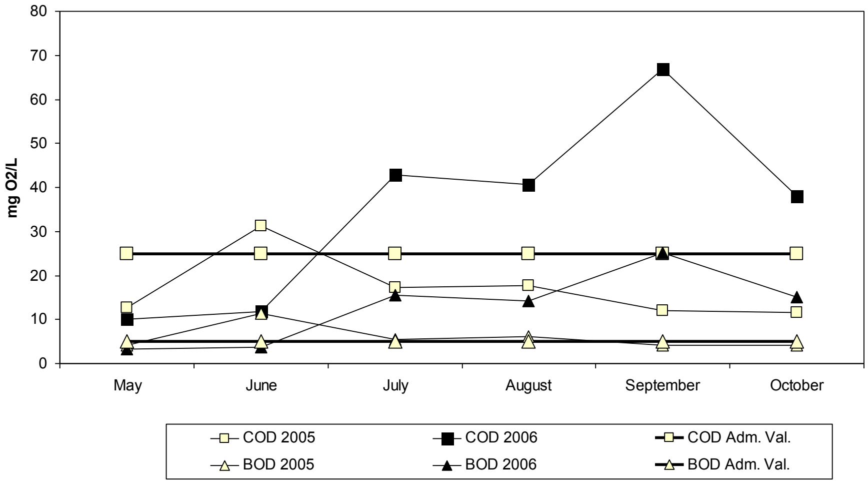

FIGURE 2 - MURIGHIOL- ORGANIC LOAD.

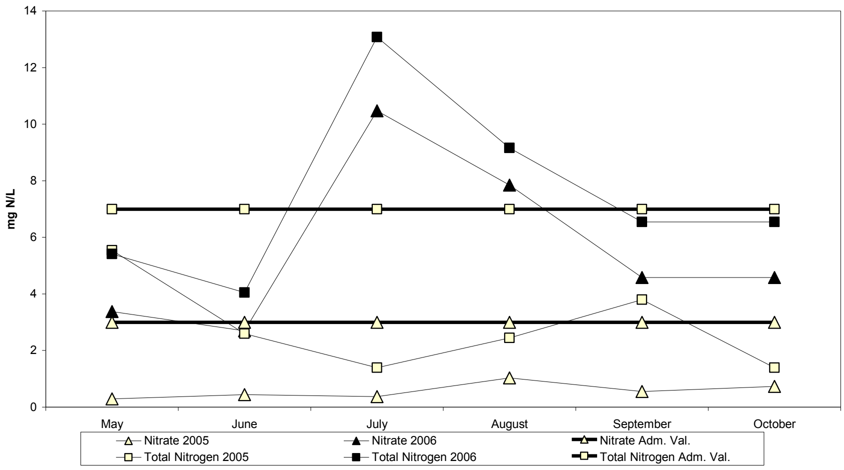

FIGURE 3 - MURIGHIOL - NITROGEN COMPOUNDS.

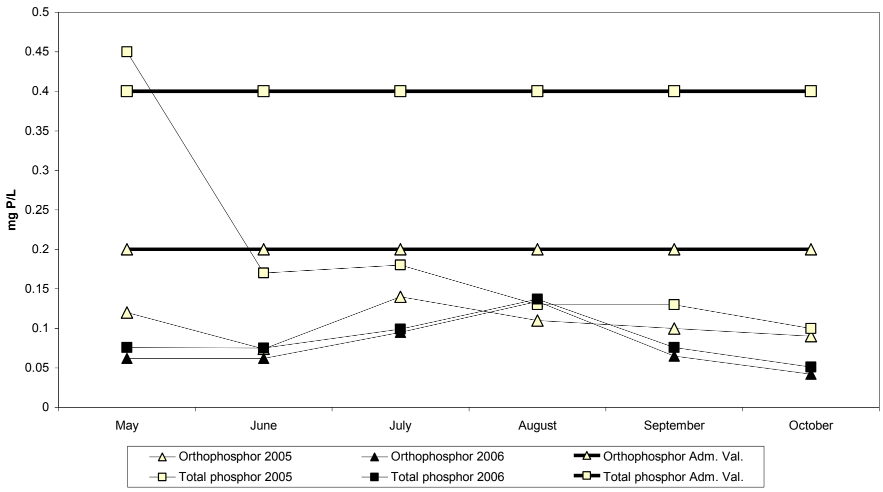

FIGURE 4 - MURIGHIOL - PHOSPHOR COMPOUNDS.

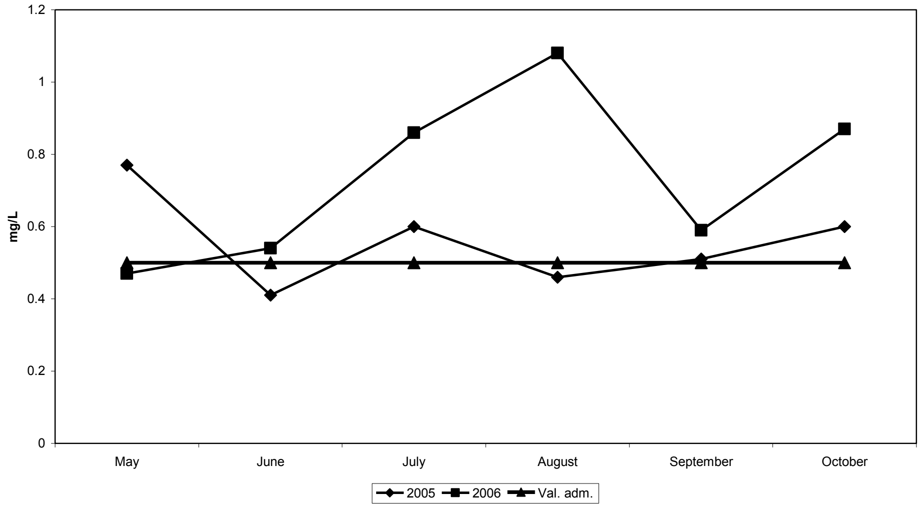

FIGURE 5 - MURIGHIOL – IRON.

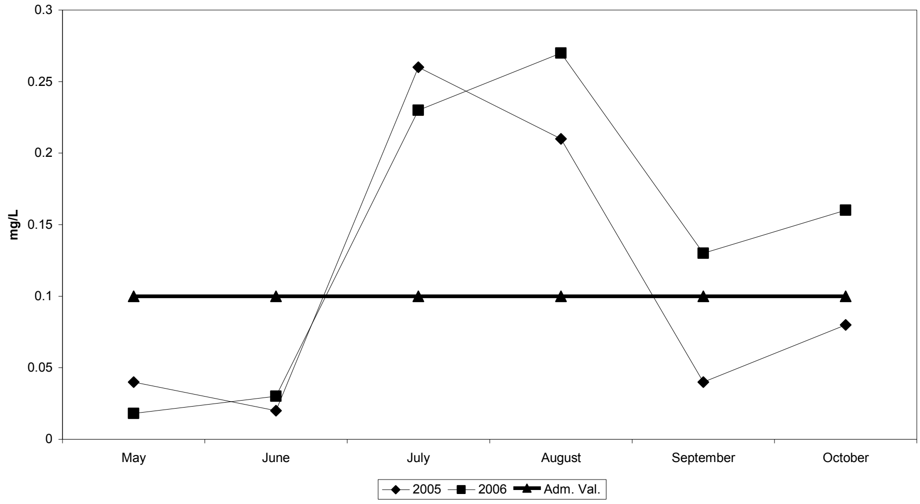

FIGURE 6 - MURIGHIOL- MANGANESE.

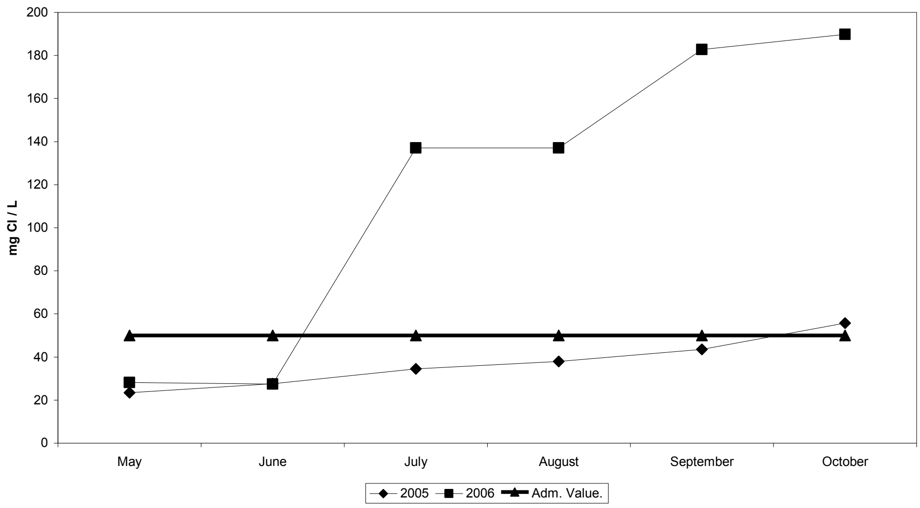

FIGURE 7 - MURIGHIOL – CHLORIDE.

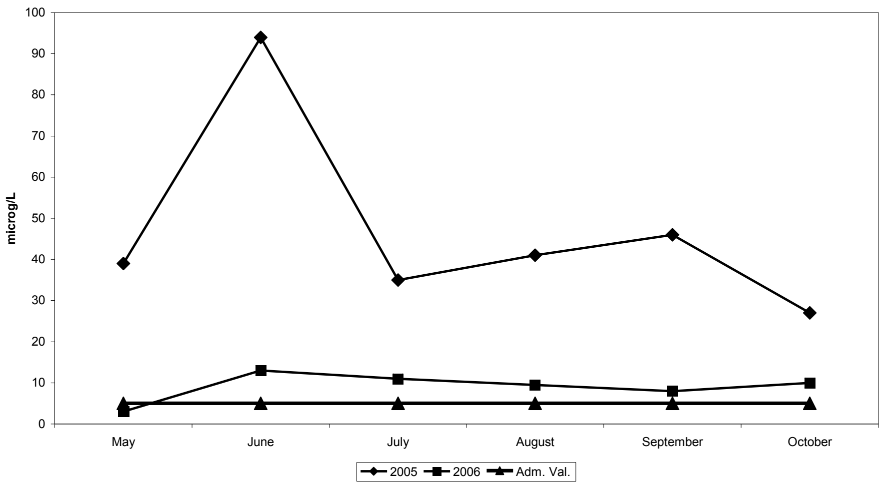

FIGURE 8 - MURIGHIOL - PHENOL INDEX.

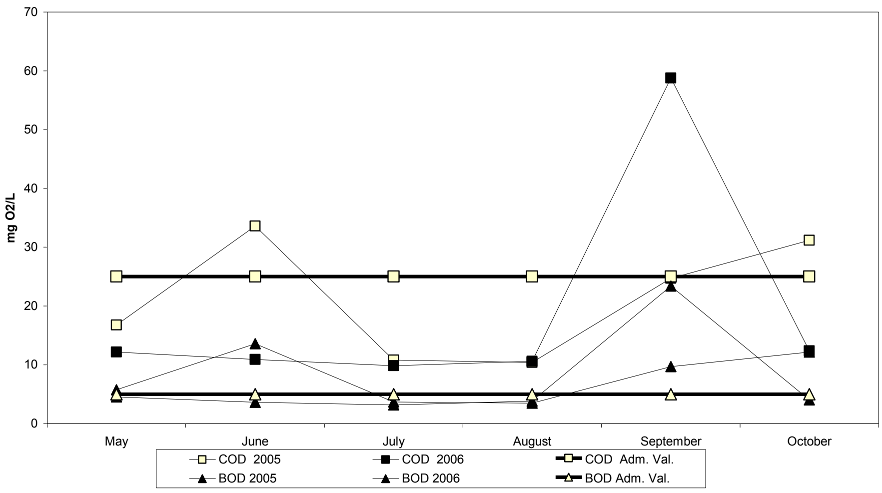

FIGURE 9 - UZLINA - ORGANIC LOAD.

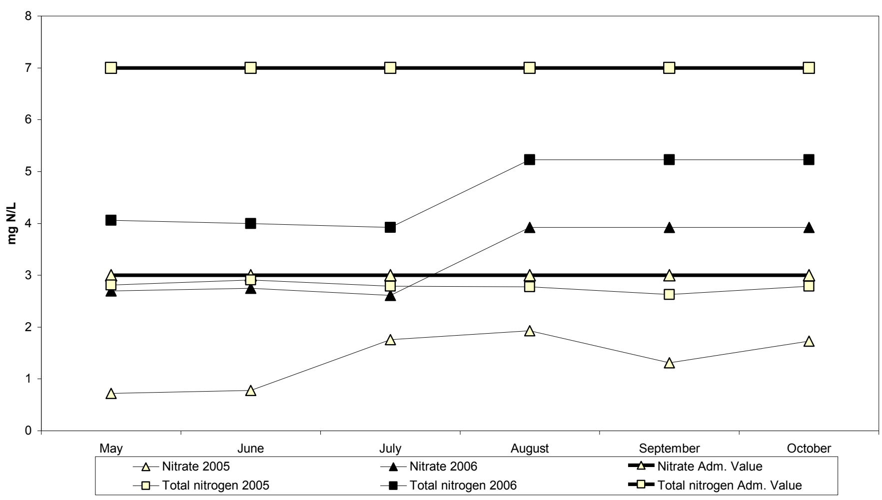

FIGURE 10 - UZLINA - NITROGEN COMPOUNDS.

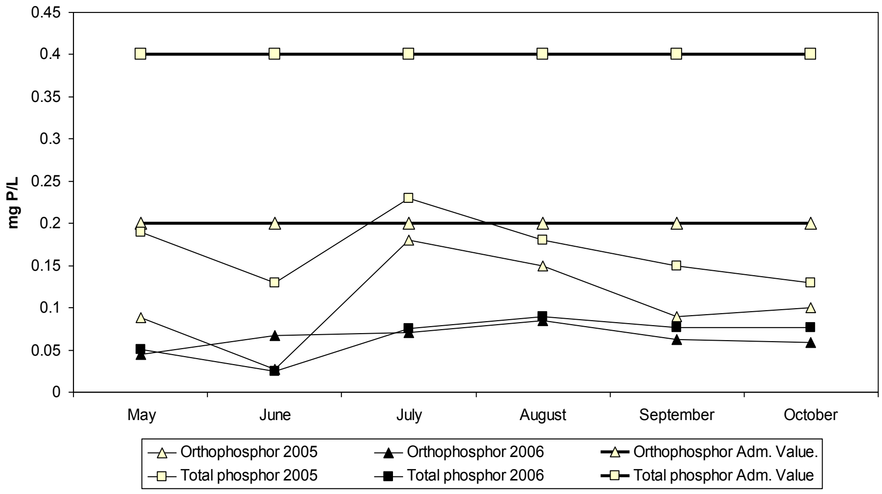

FIGURE 11 - UZLINA - PHOSPHOR COMPOUNDS.

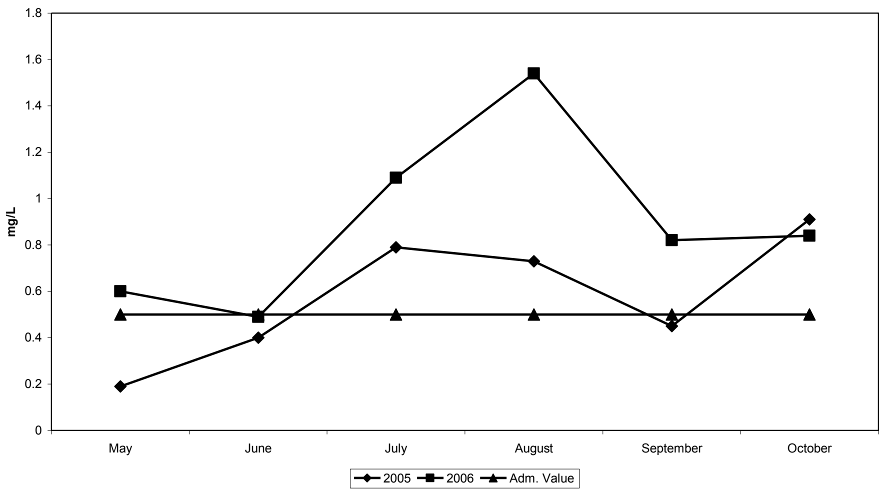

FIGURE 12 - UZLINA – IRON.

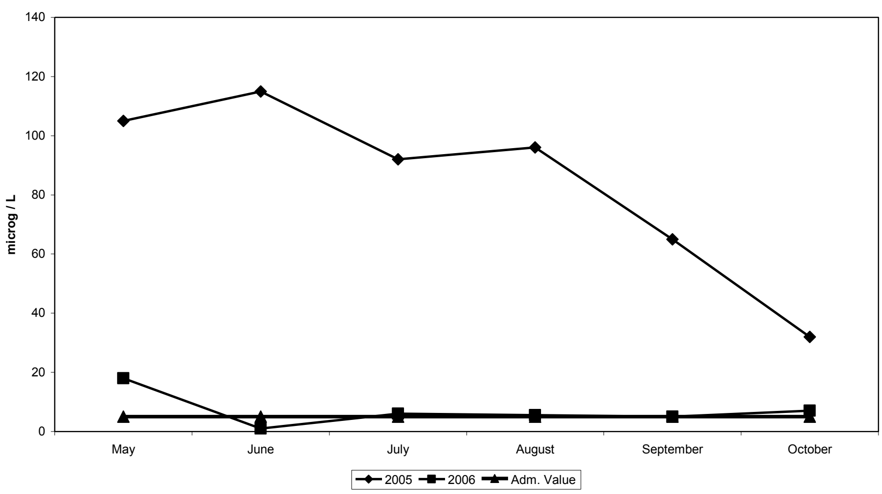

FIGURE 13 - UZLINA - PHENOL INDEX.

- Phenol index exceeded the reference value during the whole measurement periods n 2005 and 2006; this fact influences ecological state of water-bodies

In Uzlina (water samples)

- The surface water from Uzlina has a better quality than that collected from Murighiol, due to the fact that Uzlina is situated on an open field and water flow is much higher, having a good traffic and an uninterrupted flowing;
- Concerning the organic load (BOD and COD), the highest concentration recorded for both years was in September 2006 (23.4 mg O_2/L for BOD, class V and 58.8 mg O_2/L for COD, class III), whereas the other values from 2006 are below the limits;
- Nitrate concentrations presented an increase from August to October, and the values did not correspond to class II according to the national norm; all total nitrogen values are under normal limit (7 mg N/L);
- The concentration of phosphoric compounds are lower in 2006 than in 2005, and under the limits;
- Iron concentrations are higher than the admissible value in 2006 in all investigation periods, and reflect the influence of pollution;
- A decrease of phenol index level was observed in 2006, but not within the tolerable limit for aquatic life ecological protection (101 µg/L - the highest value in 2005; 13 µg/L - the highest value in 2006).

The analyses of sediment samples (Tables 2 and 3) show a relatively uniform distribution of the results during the investigated periods at both locations. Table 4 contains the uncertainty of measurement for the analyzed pollutants from the sediment sample.

TABLE 2 - Comparison of analyses from Murighiol sediments (total concentration).

No	Parameter	MU	MAY		JUNE		JULY		AUGUST		SEPTEMBER		OCTOBER		Order 161/06
			2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	
1	Copper	mg/kg dm*	**42.7**	**55.4**	**67**	**45.3**	**43.1**	**52.3**	**41.6**	34.4	40	28.6	**46.7**	**41.6**	**40**
2	Zink	mg/kg dm	123	105	143	109	113	**157**	116	120	108	60.8	111	83.7	**150**
3	Cadmium	mg/kg dm	< 0.5	<0.5	0.69	<0.5	1.3	<0.5	1.1	<0.5	1.5	<0.5	<0.5	<0.5	**0.8**
4	Chromium	mg/kg dm	32.3	21.7	38.9	22.2	25.7	36.2	28.1	24.2	35.9	17.6	54.6	24.1	**100**
5	Lead	mg/kg dm	30.3	25.7	26.2	30	30.6	27.9	36.2	16.7	29.4	19.4	35.3	21.2	**85**
6	Mercury	mg/kg dm	0.13	<0.1	0.16	<0.1	<0.1	<0.1	<0.1	<0.1	0.17	<0.1	<0.1	<0.1	**0.3**
7	Arsenic	mg/kg dm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**29**
8	Nickel	mg/kg dm	-	33.4	-	31.5	-	**41.4**	-	27.6	-	19.0	-	29.1	**35**
9	Lindane	mg/kg dm	-	**0.009**	-	**0.013**	-	**0.012**	**-**	**0.017**	-	**0.014**	**-**	**0.015**	**0.00005**
10	Mineral oil	mg/kg dm	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	**< 100**
11	PAH total	mg/kg dm	-	**6.36**	-	**7.84**	-	**10.89**	**-**	**13.53**	-	**7.44**	**-**	**4.54**	**1**
12	Benz(a) anthracene	mg/kg dm	0.05	0.38	0.03	0.44	< 0.02	0.16	< 0.02	0.43	0.056	0.41	< 0.02	0.2	-

TABLE 3 - Comparison of analyses from Uzlina sediments (total concentration).

No	Parameter	MU	MAY		JUNE		JULY		AUG.		SEPT.		OCT.		Order 161/2006
			2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	2005	2006	
1	Copper	mg/kg dm*	**81.2**	**58,8**	**69**	**55,9**	**80.5**	**53,8**	**76.8**	**55,6**	**63.2**	**55,4**	**46.7**	**56,5**	**40**
2	Zink	mg/kg dm	**191**	**175**	**162**	**158**	**184**	**173**	**172**	**169**	137	130	**155**	134	**150**
3	Cadmium	mg/kg dm	**1.05**	<0.5	0.58	<0.5	**1.5**	<0.5	**1.4**	<0.5	0.67	<0.5	<0.5	<0.5	**0.8**
4	Chromium	mg/kg dm	52.3	48.9	43.1	42.4	46.7	38.2	47.2	39	43.8	37.1	53.4	40.7	**100**
5	Lead	mg/kg dm	35.1	46	28.9	28.9	36.7	18.8	33.3	21	34.8	30.7	27.7	29.2	**85**
6	Mercury	mg/kg dm	0.15	<0.1	0.18	<0.1	<0.1	<0.1	<0.1	<0.1	0.18	<0.1	<0.1	<0.1	**0.3**
7	Arsenic	mg/kg dm	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	**29**
8	Nickel	mg/kg dm	**-**	**56.9**	**-**	**56.3**	**-**	**46.1**	**-**	**50.4**	-	**49.3**	-	**51.1**	**35**
9	Lindane	mg/kg dm	-	**0.01**	-	**0.011**	-	**0.011**	**-**	**0.014**	-	**0.013**	**-**	**0.01**	**0.00005**
10	Mineral oil	mg/kg dm	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	< 25	**< 100**
11	PAH total	mg/kg dm	-	**1.26**	-	0.56	-	**7.66**	**-**	**4.27**	-	0.35	**-**	1.00	**1**
12	Benz(a) anthracene	mg/kg dm	0.039	<0.01	0.04	<0.01	< 0.02	0.05	< 0.02	0.03	<0.02	0.01	< 0.02	0.02	-

* dry matter

TABLE 4 - Uncertainty of measurement for the analyzed parameters from sediment samples (mg/kg).

No	Parameters	Value	No	Parameters	Value	No	Parameters	Value
1	Copper	± 2	9	PCB	± 0.01	17	Benzo(a)pyrene	± 0.01
2	Zinc	± 3	10	γ-HCH	± 0.0001	18	Benz(a)anthracene	± 0.01
3	Cadmium	± 0.5	11	Mineral oil	± 0.01	19	Benzo(g,h,i)perylene	± 0.01
4	Mercury	± 0.1	12	Fluoranthene	± 0.01	20	Indeno(1,2,3-cd)pyrene	± 0.01
5	Chromium	± 2	13	Phenanthrene	± 0.01	21	Naphthalene	± 0.01
6	Nickel	± 1.5	14	Anthracene	± 0.01	22	Benzo(b)fluoranthene	± 0.01
7	Arsenic	± 1	15	Chrysene	± 0.01	23	Benzo(k)fluoranthene	± 0.01
8	Lead	± 4	16	Pyrene	± 0.01			

In **Murighiol**, the sediment samples contained:

- Total heavy metals (Zn, Cd, Cr, Ni, Pb, Hg, As) under the reference values for the sediment quality according to the Romanian Norm 161/2006;
- A major problem in Murighiol was the high concentration of total PAHs (between 4.5-13.5 mg/kg d.m., much more than 1 mg/kg d.m., the limit value); this problem may be older, because the previous legislation concerning sediment quality proposed for measurement only benz(a)anthracene, not all the 12 compounds presented in the new Norm 161/2006. For this reason, in 2005 only benz(a)anthracene was analyzed in sediment;
- For copper, values higher than the limit were recorded (40 mg/kg d.m.); in the Norm 161/2006, the limit value for Cu is 5 times lower than in the previous legislation; in all investigated months, copper level was in the range 29–67 mg/kg d.m;
- Lindane concentrations exceeded the limits (a very low concentration imposed by the Norm 161/2006, 0.00005 mg/kg d.m.) in 2006 and show a specific organic pollution.

In **Uzlina**, the sediment samples contained:

- Copper between 45-80 mg/kg d.m., values higher than the admissible limit;
- Composition of the sediment with high concentration of zinc (more than 150 mg/kg d.m.) generating the risk of pollution with mobile forms of Zn;
- Total concentration of other metallic elements, such as Cr, Pb, Hg, and As were under the limit values for the quality of sediment;
- The concentrations of cadmium in 2006 were lower and at the normal level; but in 2005, in 3 different months, higher concentrations of Cd compounds than the limit value (0.8 mg/kg d.m.) were recorded;
- Geo-morphological structure of the sediment presented nickel compounds in concentrations between 46-67 mg/kg d.m., which were higher than the limit (35 mg/kg d.m.);
- For PAHs, values over the prescribed limit were recorded in May, July and August, but the concentrations were not as high as in Murighiol location;
- Lindane was present in all the investigated months in concentrations between 0.01-0.014 mg/kg d.m, values higher than the limit (0.00005 mg/kg d.m.).

The study of the **availability of heavy metals** (Cd, Cu, Cr, Zn, Ni, Pb, Mn, Fe and Hg) to migrate from sediments into aquatic bodies (Figs. 14 and 15) emphasized the following aspects:

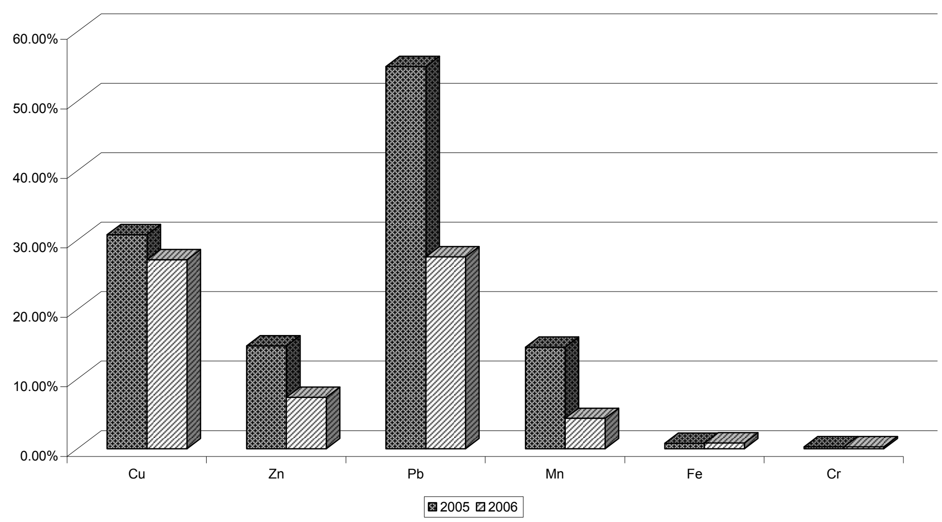

FIGURE 14 - Average of mobility percentage of heavy metals from Murighiol location in the periods May-October 2005/2006.

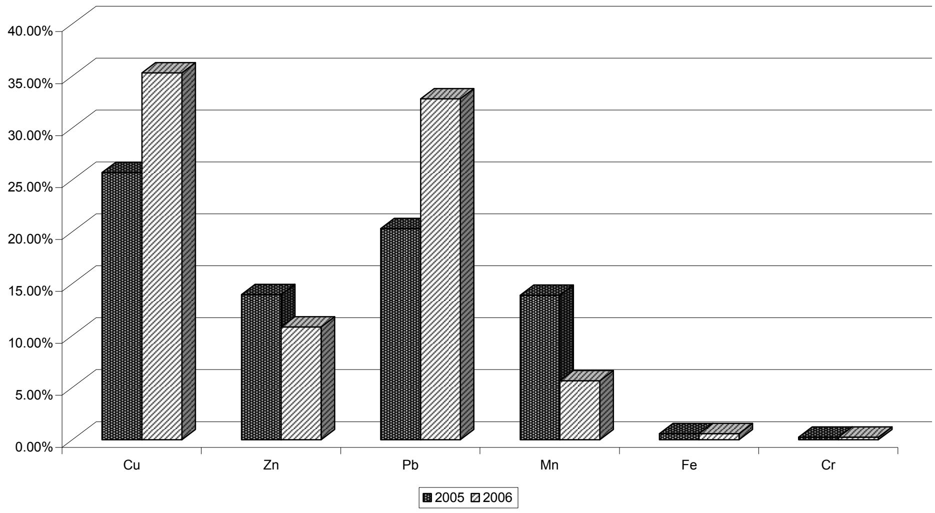

FIGURE 15 - Average of mobility percentage of heavy metals from Uzlina location in the periods May - October 2005/2006.

- Total concentration of chromium (Cr^{2+} + Cr^{3+}) in sediment (Uzlina and Murighiol) during the investigation was between 18-49 mg/kg; the results show that this element is not in exchangeable forms, being bound by crystalline iron oxides (poorly and strongly), organic matter, and in residual forms;
- Generally, the percentages of mobility for all elements wereas lower in 2006, except the values for Cu and Pb in Uzlina, and the concentration of mobile forms of Zn and Mn in both locations;
- Concentration of mobile copper was higher in 2006 than in 2005 at both locations. The same was detected for lead in Uzlina location; this fact is due to an increase of mobility percentage; the total concentrations of Cu were lower in 2006 than in 2005, but the mobility percentage was higher; for Pb, the total concentration was in the same range or lower, but higher amounts of mobile Pb were detected because it was easier available than in 2006;
- Cadmium and mercury metallic species were not in mobile status inside the sediment bodies;
- Even when nickel was over the limit in the sediments from Uzlina, this element presented low levels of mobile form (1-3 mg/kg d.m.), thus not being a pollution factor in water-bodies;
- 2006, mobile forms of iron were in the same range than in 2005, at both locations.

CONCLUSIONS

The measured values were momentary and showed the character of contamination levels, relevant for the location and investigation period.

The compounds found in concentrations higher than reference limits show a potential pollution of water, an alteration of water quality, and a decrease of biological activity.

The watercourses presented a deficit in dissolved oxygen, and under saturation, not satisfying the regulations (7 mg/L O_2) concerning the conditions for protection of aquatic organisms.

High concentration of organic load (on the basis of COD and BOD), phenol index, some PAHs and metallic elements (iron and manganese) were detected at both locations, affecting the favorable living conditions for the aquatic organisms.

A major ecological problem was the detection of high PAH levels (4.5-13.5 mg/kg d.m. in Murighiol, and 0.35–7.7 mg/kg d.m. in Uzlina) in sediments. PAHs are persistent substances and, therefore, pollution may be older than from investigation period 2006.

The quality of Murighiol water and sediment was strongly affected by organic pollutants, thus corresponding to **bad chemical conditions**, because some important parameters (PAHs, dissolved oxygen, organic load) overtopped the limits.

In Uzlina, quality of water and sediment was better than in Murighiol, and closer to **good chemical conditions** than to bad ones. Concentrations over the limits were momentary, not reflecting the whole period of investigation. Even if the total levels of heavy metals exceeded limit values (Cu, Zn and Ni), the study of mobility showed that the mobile elements cannot affect living organisms from water-bodies. In this location, the auto-purification and biological activities of the river took place in good condition.

Earlier, water and sediment samples collected from Uzlina and Murighiol were investigated in the intervals April–October 2003 and 2004.

In April 2005 and 2006, sampling from these two locations was not possible because of floods with a very high level of water-flow.

The variation of parameters during all investigated periods in Uzlina and Murighiol were strongly influenced by the climatic conditions (drought, flood).

In springs of 2003 and 2004, when it was a very dry weather without rains, highest values were recorded for:

- organic load (BOD, 118 mg O_2/L; COD, 295 mg O_2/L) in Murighiol, June 2004;
- Iron (8 mg/L) in Murighiol, June 2003;
- Manganese (0.64 mg/L) in Murighiol, June 2003.

In spring–summer periods of 2005 and 2006, a better quality of the surface water was recorded, especially as a result of strong dilution of water. But in autumn, it was noticed a return to the normal flow of water, which modified the quality of surface water in a negative way.

During all the periods 2003–2006, the quality of sediment slowly changed. The temporary high volume of water carried big quantities of alluvium and ensured the mixture of sediments, explaining the presence of Cd and Hg in sediments structure in 2005 (low values, without problem for the environment).

These conclusions show dynamic variations of physico–chemical characteristics of water courses in the investigated locations, and explain the necessity to continue the studies in the next years.

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REFERENCES

[1] Vasile, G.G., Cruceru, L., Petre, J. and Nicolau, M. (2005) Analytical investigation concerning biodisponibility of heavy metals from Danube Delta sediments, Revista de Chimie, vol 56, No 8, 790-794

[2] *** NF X 31 – 120/1992: Soil quality - Measurement of heavy metals from soil after extraction with a mixture of ammonium acetate and EDTA

[3] Vosniakos, F., Petre, J., Vasile G.G., Cruceru, L., Nicolau, M., Mitrita, M., Iancu, V. and Cruceru, I. (2006) Evaluation of the physical-chemical quality state of the Danube Delta Aquatic Ecosystem during the period 2003-2004, Fresenius Environmental Bulletin 15 (5), 401 – 408.

[4] The Ministry of Water and Environmental Protection of Romania, Order no 1.146/2003 for the approval of the Norm concerning the reference objectives for the surface water quality classification, Official Monitor of Romania, Part 1, No 197;

[5] The Ministry of Environmental and Water, Order no. 161/2006 for the approval of the Norm concerning the reference objectives for the surface water quality classification (including quality standards for sediments), Official Monitor of Romania, Part 1, No 511 bis, in force in Romania since 13.06.2006;

[6] *** SR ISO 5667/1:1998, Water quality. Sampling. Part 1: Guidance on the during of sampling programmers;

[7] *** SR ISO 5667/2:1998, Water quality. Sampling. Part 2: Guidance for the sampling techniques;

[8] *** SR ISO 5667/3:2002, Water quality. Sampling. Part 3: Guidance on the preservation and handling of samples;

[9] *** SR ISO 5667/6:1997, Water quality. Guidance for the sampling of rivers and streams water;

[10] *** SR ISO 5667-12/2001, Water quality: Guidance on sampling of bottom sediments;

[11] *** SR EN ISO 15587-1/2003, Water quality: Digestion for determination metallic elements from water. Part 1: Digestion with aqua regia;

[12] *** SR ISO 11466-99, Soil quality: Extraction of micro elements with aqua regia;

[13] *** SR EN 903 / 2003, Water quality: Determination of anionic surfactants by measurement of the methylene blue index MBAS.

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