THE TEMPORAL AND SPATIAL MONITORING OF WATER AND SEDIMENT PHYSICAL-CHEMICAL QUALITY FROM SAINT GEORGE BRANCH IN THE PERIOD FEBRUARY 2009 - FEBRUARY 2011

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ABSTRACT

The purpose of the study was to do a temporal and spatial monitoring of water and sediment quality in seven different locations from Saint George branch, the southern branch of the Danube Delta.

In water and sediment samples, the levels of metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and mineral oil were investigated to evaluate their potential pollution risks.

Taking into account the previous results, sampling was monthly performed in the period February 2009 - February 2011. The values obtained for the quality indicators were compared with the quality standards stipulated in the Romanian Order No.161/2006.

The monitoring activity indicated a significant organic load (BOD, COD) at all the sampling points in most parts of the investigated period. In sediments, only at the sampling point situated in Murighiol upright to the pontoon of ship supply (S6), higher concentrations of PAHs, DDTs and PCBs were detected comparing with the maximum allowed values for the second quality class.

KEYWORDS: Danube Delta, water, sediment, physical-chemical monitoring

1. INTRODUCTION

The Danube, the second largest river in Europe after Volga, flows to several countries from where it receives discharges of agricultural, industrial and urban effluents [1]. The Danube River waters flow into the Black Sea through its delta (5600 sq. km), which constitutes the largest wetland of Europe. Designated by UNESCO as a Ramsar World Heritage and a reservation of the biosphere, the Danube Delta is the third delta in ecological significance among the 300 reserves of the world. The delta wetlands have many important functions contributing to the ecological, social and economical wealth of the region. The most important threats to the Danube Delta are represented by changes in the quantity and quality of water reaching from upstream catchments.

Danube Delta Biosphere Reservation (DDBR) includes Danube Delta, the complex Lagoon Razim-Sinoe, navigable Danube up to Cotul Pisicii, the district Isaccea–Tulcea including floodable zone, the area from Lake Saraturi - Murighiol to Plopu and, finally, the Black Seaside from Chilia Branch to Midia Cape. About 14,000 inhabitants live on the reservation territory (according to 2005 statistics).

There are three categories of areas in DDBR: the first one is the core area – strictly protected area, were no human activities are allowed, except research. The second category is the buffer area, where traditional activities are allowed, and the third category is the economic area where economic activities are allowed, including commercial fishing [2].

Disturbed aquatic ecosystems, biodiversity and habitats are occurring in the Danube Delta due to a large number of activities, including navigation, intensive agriculture, fish farming and, most recently, recreation and tourist industry. In many areas of the Danube Delta, the combination of these practices had led to a decrease of the river's self-cleaning capacity but to an increase of polluted effluents resulting in a continuous deterioration of river quality [3-7]. Such activities often conduct to supplementary quanti-

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ties of nutrients and potentially hazardous substances, such as heavy metals, mineral oil, persistent organic compounds including pesticides and PCBs, into the Danube Delta ecosystems.

One of the acute problems of the inhabitants of the Danube Delta is the lack of drinking water, wastewater networks and treatment plants [8]. Using water directly from the Danube for household consumption, while the water quality has been deteriorated greatly over the reference period 1950-1960, presents a series of disadvantages, such as a high risk of disease for the population, the impossibility to promote economical activities, which requires drinking water. In addition, the local population cannot develop and practice some tourism activities, which would represent an important source of income for them.

The lack of sewerage system and wastewater treatment plants involves uncontrolled discharges of wastewaters with various loads of pollutants, which affect both human health and the quality of the environment, generating pollution and leading the degradation of the environmental factors. As recorded in a research study, water pollution in the DDBR has contributed to losses of biodiversity [9]. Therefore, a great concern is focused on water quality.

Contamination by potentially toxic metallic elements in the natural environment is one of the major problems for human health and environmental quality because these elements are indestructible, and most of them have toxic effects on living organisms when exceeding a certain concentration [10]. Trace elements may be introduced into the aquatic systems by both natural processes (eg. weathering and corrosion) and also human activities (heavy nutrient loads from agricultural fertilizers and heavy metals from industry) [11, 12]. Sediment represents one of the ultimate sinks for heavy metals discharged into the aquatic environment. Contaminants are not necessarily fixed permanently by the sediments, and under changing environmental conditions, metals may be released to the water column by various processes of remobilization. Thus, in aquatic ecosystems, sediments may be both a carrier and possible source of pollutants [13].

In 2005, the Romanian Ministry of Environment approved a Master Plan for sustainable development of DDBR. The most important issues were improvement of monitoring system for the Danube Delta ecosystems using modern surveillance; improving of infrastructure, utilities, transport and communications; support for the development of alternative economic activities in order to reduce pressure on fisheries resources.

According to Government Decision 1516/2009 [8], until 2013, the drinking water networks supply will be introduced in all communities situated in DDBR. In the same time, sewage networks and wastewater treatment plants will ensure the quality of water discharged into the Danube Delta.

Protection and conservation of this Biosphere Reserve ecosystem need a long-term assessment of the physical-chemical and biological water quality in order to provide information concerning the discharge of different pollutants, and to point out a potential trend of eutrophication.

This work is an extension of previous studies [3-5], performed between 2003-2008 as spatial and temporal monitoring of water and sediments quality in two major areas of the Danube Delta: Uzlina and Murighiol.

The results obtained in the 5 years of investigation led the idea to extend the monitoring area to other seven sampling points situated in the southeast part of the Danube Delta, on St George branch. This branch is the most southern one carrying 23% of the Danube water discharge and 21% of the Danube sediment discharge [14].

Different weather conditions, seasons, both floods and droughts, controlled or uncontrolled discharges may influence the degree of pollution of water and sediment from the investigated areas.

OCPs and PCBs are toxic organic contaminants widespread throughout the ecosystem because of their persistence and potential for bioaccumulation in the environment. These occur in water, air, soil, sediment and biota in different areas around the word [15].

In this study, different types of OCPs were analyzed: α-HCH, β-HCH, δ-HCH and γ–HCH, heptachlor, aldrine, dieldrine, endrine, 4,4-DDD, 2,4-DDE, 4,4-DDT and also individual PCB congeners (28, 52, 101, 138, 153, 180) both in water and sediment samples.

The tables and figures presented in this article try to synthesize multiple data and information obtained during two years of investigation (2009-2011). The indicators analyzed were reported to the reference values of the Romanian Order 161/2006 [16].

There were also locations (for example S1 and S2) and months (February-July), in which in the first phase of the study sampling was not performed. Samples that were not analyzed are listed in tables with NA.

In March 2009, December 2010 and January 2010, sampling was not possible to be performed because of unfavorable weather conditions, especially in winter.

The study aims at elucidating the recent contamination status as well as their usage pattern and sources. In addition, the water and sediment concentrations were compared to guideline values for sediment quality.

2. MATERIALS AND METHODS

2.1. Study area and sample collection

Water and sediment sampling was performed in seven different locations of Saint George branch: S1 -Mahmudia site before bifurcation *(45°088'N-29°095'E)*; S2 - artificial channel *(45°056'N-29°171'E);* S3 - Uzlina upstream

(45°076'N-29°222'E)); S4 - Uzlina upright to pontoon *(45°075'N-29°223'E*); S5 - Uzlina downstream *(45°070'N-29°222'E)*; S6 - Murighiol upright to the pontoon of ship supply *(45°040'N-29°185'E)*; S7 - the St. George branch at confluence with artificial channel *(45°043'N-29°192'E)* (Fig. 1).

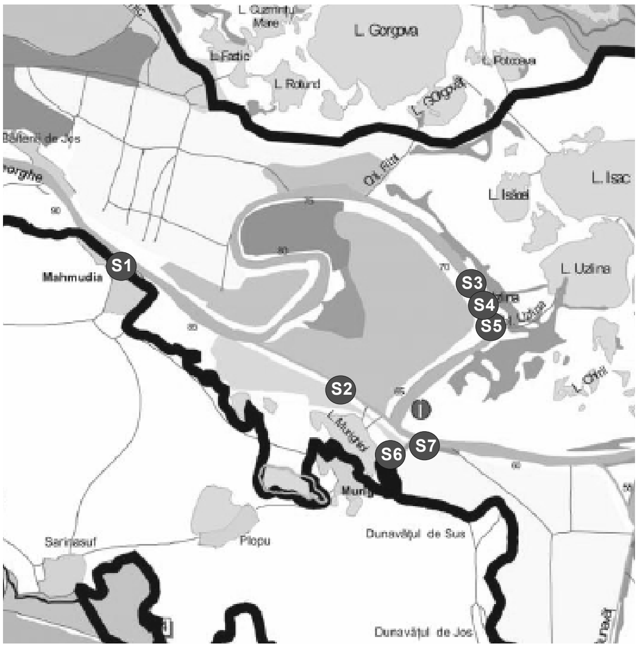

FIGURE 1 - Map of the Saint George with the sampling locations for water and sediments.

All water and sediment samples were monthly collected from February 2009 to February 2011, as momentary samples. The sampling and preservation step was done according to the recommendations of specific international guidelines (ISO 5667/ parts 1, 3, 6, 12; EN ISO 9391) [17-20].

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 within the Danube using a van Veen bottom-sampler. All samples were kept in cooling boxes at 4 °C during transportation, and analyses were performed immediately after receiving the samples in the laboratory.

2.2. Pollutants and quality indicators

In all the samples (surface water and sediments), analytical determinations of toxic metallic elements, such as arsenic, chromium, cadmium, copper, nickel, lead, mercury, iron, zinc and also organic compounds (mineral oil, PAHs, organochlorine, organophosphorus and triazine pesticides, PCBs) were performed.

2.3. Reference comparison values

The Romanian Order 161/2006, transposed from Directive 2000/60/EC, introduced a classification of the quality factors that describe the ecological conditions of surface water. This classification consists in five conditions for surface water: *very good* (I), *good* (II), *moderate* (III), *poor* (IV) and *bad* (V). The parameters evaluated for the chemical and physical-chemical characterization of water quality are temperature, oxygen, nutrients, pollution with dangerous substances, pH and the mineralization (Ca, Mg, Na). The Romanian Order 161/2006 provides two categories of chemical conditions for all aquatic, sediment and biota systems: good chemical conditions (all quality parameters for the indicators are within the limits imposed by the quality standards) and bad chemical conditions (one or more parameters exceed the limits imposed by the quality standards).

2.4. Methods and equipments

Load contents: BOD (DIN EN 1899/1, 2/03, 02); COD (SR ISO 6060: 1996).

PAHs (fluoranthene, benzo(b)fluoranthene, benzo(k) fluoranthene, benzo(a)pyrene, benz(a)anthracene, benzo (g,h,i)perylene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, anthracene, chrysene, pyrene) were determined with an Agilent 1100 HPLC equipment (fluorescence detection).

The quantitative analysis of total mineral oil was performed with an FT-IR system (Perkin Elmer, Spectrum BX II).

The quantitative determination of pesticides was performed on a GC System (Agilent Technologies 6890 N) with ECD detector for OCPs (α-HCH, β-HCH, γ-HCH, δ-HCH), with NPD detector for organophosphorus pesticides (malathion, parathion, dichlorvos) and triazine pesticides (atrazine, simazine, propazine).

Polychlorobiphenyls (PCB 28, PCB 52, PCB 101, PCB 138, PCB 153, PCB 180) were analyzed on a GC System (Agilent Technologies 6890 N) with ECD.

For the quantification of Phenol Index, a specific equipment for water sample pre-treatment and a Perkin Elmer Lambda 25 UV/VIS spectrometer were used.

Analytical techniques used for determination of metallic elements from water and sediment samples were flame atomic absorption spectrometry performed on a Thermo-Scientific M6 Dual Solaar equipment; cold-vapour technique coupled to AAS using an ATI/Unicam Solar AA 929 spectrometer; ICP-EOS technique with a Perkin Elmer Optima 5300 DV equipment.

The sediment dry weight was determined with a separate sub-sample: approximately 1 g was dried at 105 ± 2 ºC, up to constant weight. A correction to "dry matter" (quantity of metal per g dry sediment) was applied to all analytical results.

2.5. Pre-treatment of the samples

For PCB and OCP determinations, the water samples were extracted with 30 ml hexane. Polar matters were removed from the extract by adding Florisil. Non-volatile hydrocarbons from the extract were then determined by GC-ECD analysis.

For determination of organophosphorous pesticides, the water samples were extracted with 30 ml dichloromethane. Polar matters were removed from the extract by adding Florisil. Non-volatile hydrocarbons from the extract were then determined by GC-NPD analysis.

For PCB and OCP determination, the sediment samples were agitated with 30 ml acetone for 30 min, and then with 30 ml hexane for 30 min. The organic extract was cleaned with ultra-pure water in a separation funnel. The final organic extract was analyzed by gas chromatography with capillary column and ECD detection.

For determination of organophosphorous pesticides, the sediment samples were agitated with 30 ml acetone for 30 min, and then with 30 ml hexane for 30 min. The organic extract was cleaned with water in a separation funnel. The final organic extract was analyzed by gas chromatography with capillary column and detection with NPD.

For the determination of mineral oil, at first, the surface water samples were acidified (pH <5) with hydrochloric acid and then extracted with tetrachlorethylene (25 ml for each sample). The organic extracts were filtrated on sodium sulphate for retention of water traces. Polar matters were removed from the extract by adding silica gel.

The sediment samples were dried with sodium sulphate and then extracted with tetrachlorethylene (25 ml for each sample) using a mechanical shaker. The supernatant was filtrated on sodium sulphate. Polar matters were removed from the extract by adding silica gel.

For the analysis of PAHs, the surface water samples were extracted with hexane using a mechanical shaker. The extract was concentrated by evaporation and the residue taken up in acetonitrile.

The sediment samples were extracted by shaking with acetone and petroleum ether, and the supernatant was washed with ultra-pure water. The extract was concentrated by evaporation and purified by passing a SPE C18 cartridge.

The triazine pesticides were extracted from surface water samples by solid-liquid extraction on RP-C18 material and elution with methanol. The extracts were concentrated by evaporation with a rotary evaporator under reduced pressure at 30 °C to dryness. The residue was dissolved in 1ml methanol.

For determination of metallic compounds, the surface water samples were digested with supra-pure nitric acid (5 ml for each sample) and concentrated from 150 ml (sample volume) to 25 ml [21].

After drying the sediment samples at room temperature, the fractions with particle size <60 µm were used for extraction of all metallic elements. The “pseudo-total concentrations” of metallic elements dissolved in aqua regia (mixture of nitric acid and hydrochloric acid in the report 1:3) from sediment samples were compared with the reference values for the sediment quality according to the Romanian Order 161/2006.

In Tables 1 to 4, the detection limit, the quantification limit and the uncertainty of measurement (the value representing the expanded uncertainty for a coverage probability of 95%, the coverage factor is k = 2, for pollutants both in water and sediment samples) are presented.

2.6. Quality Assurance (QA) and Quality Control (QC) data

The samples were analyzed in Pollution Control Department, which is accredited by RENAR (Romanian Accreditation Association) and follows the requirements of SR EN ISO/CEI 17025:2005 standard. The Department has certification with BVQI (Bureau Veritas Quality International) in accordance with SR EN ISO 9001/2008 standard, and has periodical participation to internal and external audits.

For all the analyzed parameters, the laboratories used standard methods (ISO, SR ISO, EN, SR EN, SR, STAS, EPA), reference materials and certified reference materials. All these standard methods are validated in the laboratory according to SR EN ISO/CEI 17025:2005, and the

TABLE 1 - Performance parameters and analytical techniques applied for determination of metallic elements from surface water.

Indicator	**As**	**Ba**	**Cd**	**Co**	**Cu**	**Cr**
LOD (µg/L)	0.05	0.5	0.13	0.5	4	5
LOQ (µg/L)	0.17	1.5	0.43	1.5	11	13
U (%)	9.1	4.3	6.6	6.6	3	7.5
Analytical technique	ICP-EOS-FIAS	ICP-EOS	ICP-EOS	ICP-EOS	AAS	AAS
Indicator	**Hg**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LOD (µg/L)	0.05	5	3	1	1	1
LOQ (µg/L)	0.17	14	9.5	3.20	3	3.3
U (%)	10.4	3.1	3.2	6.6	9.9	3
Analytical technique	ICP-EOS-FIAS	AAS	AAS	ICP-EOS	ICP-EOS	AAS

FICP-EOS-FIAS: Flow injection analysis system coupled with inductively coupled plasma atomic emission spectrometry

TABLE 2 - Performance parameters and analytical techniques applied for determination of metallic elements from sediment.

Indicator	**As**	**Ba**	**Cd**	**Co**	**Cu**	**Cr**
LOD (mg/kg)	0.05	0.02	0.01	0.02	0.10	0.20
LOQ (mg/kg)	0.13	0.06	0.03	0.05	0.35	0.58
U (%)	10.3	5.1	7.1	7.2	3.5	8.2
Analytical technique	ICP-EOS	ICP-EOS	ICP-EOS	ICP-EOS	AAS	AAS
Indicator	**Hg**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
LOD (mg/kg)	0.05	0.13	0.08	0.13	0.25	0.03
LOQ (mg/kg)	0.15	0.35	0.23	0.37	0.71	0.1
U (%)	5.7	3.5	3.7	5.3	5.2	3.6
Analytical technique	CV-AAS	AAS	AAS	AAS	AAS	AAS

CV-AAS: Cold vapour atomic absorption spectrometry

TABLE 3 - Performance parameters and analytical techniques applied for determination of organic micro pollutants from surface water.

Indicator	PCBs 28, 52, 101, 138, 153, 180	Malathion, Parathion, Dichlorvos	HCH compounds, Aldrin, Dieldrin, Endrin, Alaclor, Heptaclor, 4,4-DDD; 2,4-DDE	Simazine	Triazine
LOD (µg/L)	0.001	0.003	0.001	0.1	0.1
LOQ (µg/L)	0.005	0.01	0.005	0.43	0.43
U (%)	10	8	12	9.0	7.2
Analytical technique	GC-ECD	GC-NPD	GC-ECD	HPLC	HPLC
Indicator	Propazine	PAH com-pounds*	Benz(ghi)perylene, Indeno(1,2,3cd)pyrene	Benz(a)pyrene	Mineral oil
LOD (µg/L)	0.1	0.005	0.001	0.002	0.05
LOQ (µg/L)	0.46	0.017	0.004	0.007	0.17
U (%)	7.9	5.9	6.3	5.4	4.3
Analytical technique	HPLC	HPLC	HPLC	HPLC	IR

* Fluoranthene, benzo(b)fluoranthene, benzo(k) fluoranthene, benz(a)anthracene, naphthalene, phenanthrene, anthracene, chrysene, pyrene

TABLE 4 - Performance parameters and analytical techniques applied for determination of organic micro pollutants from sediment.

Indicator	PCB 28, 52, 101, 138, 153, 180	Malation, Paration, Diclorvos	HCH isomers, Aldrin, Dieldrin, Endrin, Alaclor, Heptaclor, 4,4-DDD; 2,4-DDE	Simazine
LOD (mg/kg)	0.003	0.01	0.01	0.01
LOQ (mg/kg)	0.01	0.05	0.00	0.04
U (%)	12	10	14	9.5
Analytical technique	GC-ECD	GC-FID	GC-ECD	HPLC
Indicator	Atrazin	Propazine	PAH compounds	Mineral oil
LOD (mg/kg)	0.01	0.01	0.01	25
LOQ (mg/kg)	0.04	0.04	0.04	70
U (%)	8.4	8.6	7.5	5.5
Analytical technique	HPLC	HPLC	HPLC	IR

main performance parameters (limit of detection, limit of quantification, linearity, accuracy, precision, selectivity, the uncertainty of measurement) were established with existing equipment of the laboratories.

The department participates every year at tests for the evaluation of its capability by inter-laboratories comparisons (IMEP Belgium, IAWD Germany, CALITAX Spain, IELAB Spain, AQUACHECK LGS, Quality Infrastructure Denmark) for different groups of pollutants (organic compounds, metallic elements, inorganic compounds) from complex matrixes (surface water, wastewater, drinking water, soil, sediment, sludge). The results obtained in these inter-laboratory studies were included in the accepted range (-2 ≤ score Z ≤ 2).

3. RESULTS AND DISCUSSION

The occurrence of the selected pollutants and their temporal and spatial distribution at seven sampling points is discussed below. The values obtained for the quality elements were evaluated for their compliance with quality standards stipulated in the Romanian Order No. 161/2006 [16].

3.1. Water samples

The watercourse analyzed in studied location presented a high organic load. The BOD and COD values at S6 location exceeded the imposed limits, the highest values being 22.5 mg O_2/L for BOD and 76.8 mg O_2/L for COD (Figs. 2 and 3).

In the whole period of investigation and in all studied locations was observed a deficit of oxygen.

The level of nutrients (mineral nitrogen, total phosphorus) was almost constant and below the limit values set for a good status.

The content of heavy and toxic metals in Danube River water was in most cases below the limits according to the national legislation. The exception was iron, which was detected in water over the limits (0.5 mg /L) in S1 location (1.72 mg/L) in March 2010 (Fig. 4).

Concerning organic compounds, mineral oil, DDTs and PCBs were periodically recorded in river water being higher than the limit.

Concentrations of mineral oil in water samples from all seven location are presented in Table 1. Values below the allowed limit, and even below the method detection limit, were recorded during May-December 2010. This can be caused by the floods on the Danube in June and July 2010. The highest value, 910 µg/L (about four times more than the allowed limit) was recorded at S6 location, in June 2009.

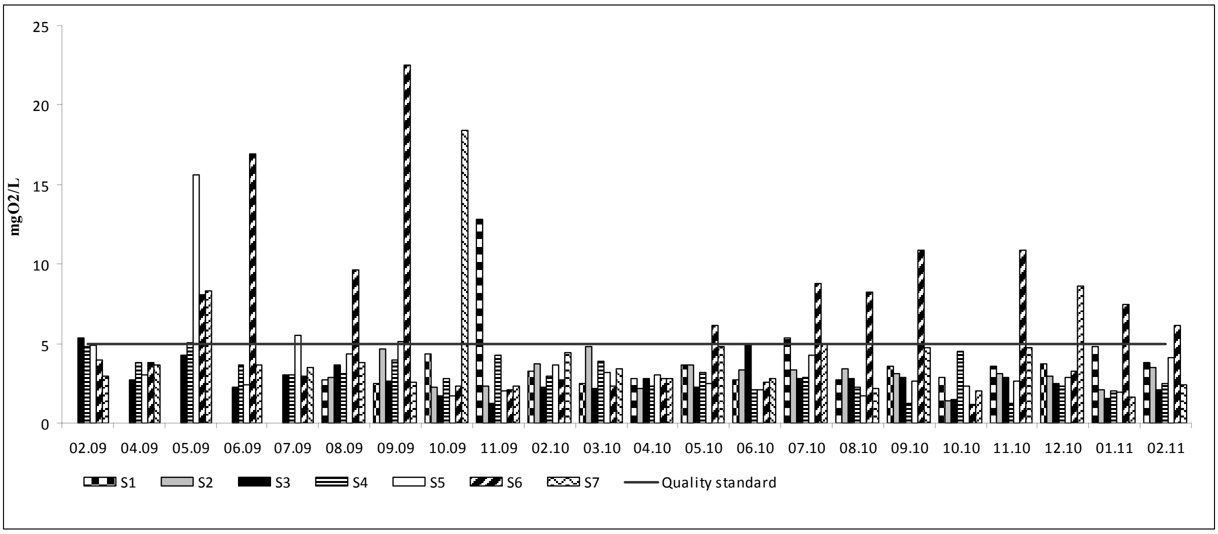

FIGURE 2 - The temporal and spatial variations of BOD in Danube River water.

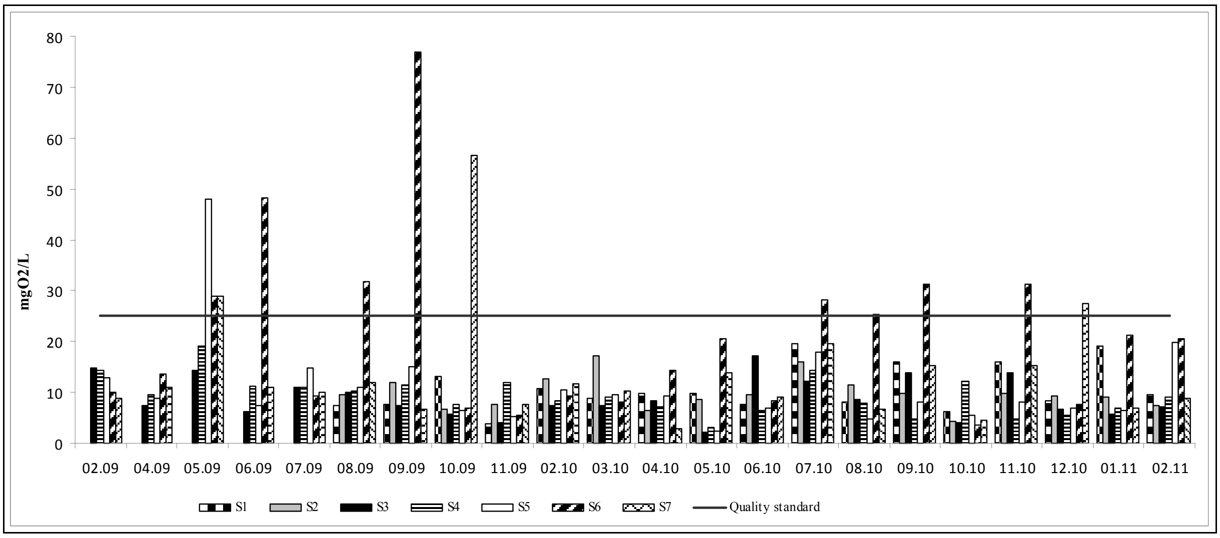

FIGURE 3 - The temporal and spatial variations of COD in Danube Rriver water.

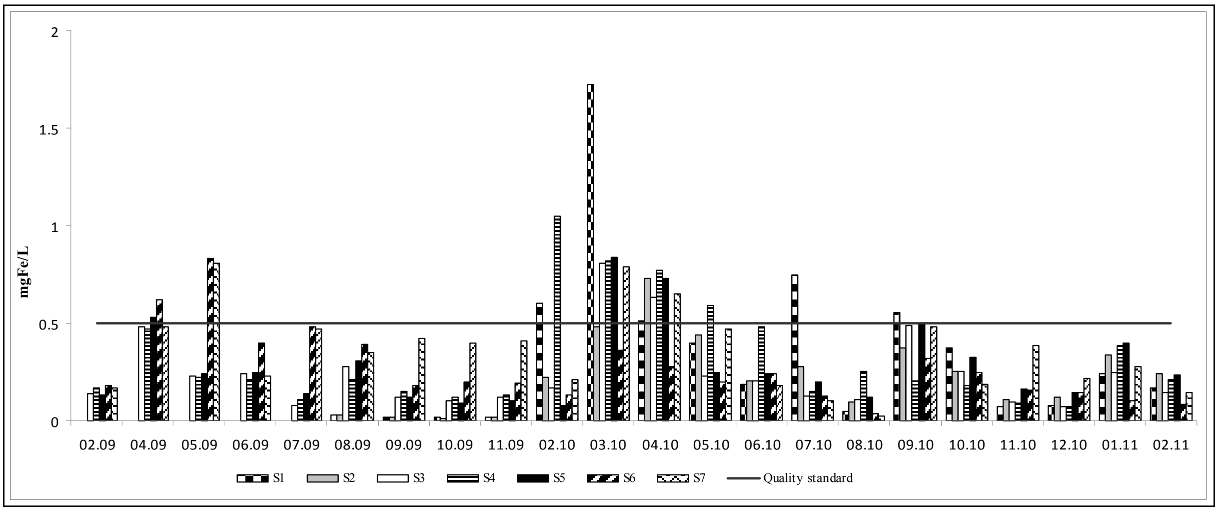

FIGURE 4 - The temporal and spatial variations of iron in Danube River water.

The variation of DDTs in Danube River water is presented in Fig. 5. The highest DDT (sum of DDT, DDE, and DDD) concentrations were detected at S7 location from April 2010 to February 2011. In January 2011, 0.649 µg/L was recorded which exceeded the limit value (0.025 µg/L). Figure 6 illustrates the composition of DDTs at S7 location in the same period. The balanced proportion of ∑(DDE + DDD)/DDT in this study indicates that degradation of DDT occurred slowly.

Other persistent organic pollutants detected in June 2009 in the surface water of the three Uzlina locations (S1, S2, S3) were PCBs, ranging from 0.003 to 0.013 µg/L.

3.2. Sediment Samples

Concentrations of heavy and toxic metals in the Danube sediments, in most samples corresponded to the norms for the aquatic organisms' protection. The exception was the presence of copper (Fig. 7), mercury (Fig. 8) and nickel (Fig. 9)

The highest value for Cu (90 mg/kg) was found in March 2010 at S7 being 2-fold higher than the admissible limit. The limit for mercury (0.3 mg/kg) was exceeded in February 2009 at S6 and S7 locations (0.48 mg/kg; 0.46 mg/kg), respectively, and in June 2009 (0.41 mg/kg; 0.38 mg/kg). Nickel recorded higher values han the admitted limit in all period and studied locations but the highest value was recorded in September 2010 at S5 (40.3 mg/kg).

In the Romanian Order 161/2006 of the Romanian Ministry of the Environment and Water Management, transposed from Water Frame Directive 2000/60/EC [16], the concentration for mineral oil in sediment is not limited. In Table 2, concentrations of mineral oil (mg/kg) in sediment samples collected from the studied locations are shown. The lowest values were recorded from July to October 2010, possibly also because of the floods from that period. The highest value was 553 mg/kg in February 2010, at S6 location.

TABLE 5 - Concentration of mineral oil (µg/L) in water samples.

Location	Month/Year															
	Mar 09	**May 09**	**June 09**	**July 09**	**Aug 09**	**Sept 09**	**Oct 09**	**Nov 09**	**Feb 10**	**Mar 10**	**Apr 10**	**May 10**	**June 10**	**Nov 10**	**Dec 10**	**Feb 10**
S1	NA^1	NA	NA	NA	320	230	170	180	576	230	230	ND^2	120	ND	ND	240
S2	NA	NA	NA	NA	330	260	160	270	589	260	170	ND	ND	ND	ND	199
S3	350	220	370	220	510	230	140	220	330	115	170	150	120	ND	ND	320
S4	370	270	390	280	470	260	160	190	575	360	400	ND	ND	ND	ND	110
S5	360	260	350	260	540	270	170	220	145	124	240	ND	ND	ND	ND	150
S6	430	340	910	390	470	250	190	580	ND	130	450	ND	110	110	110	190
S7	310	260	890	300	350	290	180	440	910	310	350	ND	ND	190	170	180

Quality Standard 200 mg/L; NA^1 = not analyzed in this period of year; ND^2 = not detected

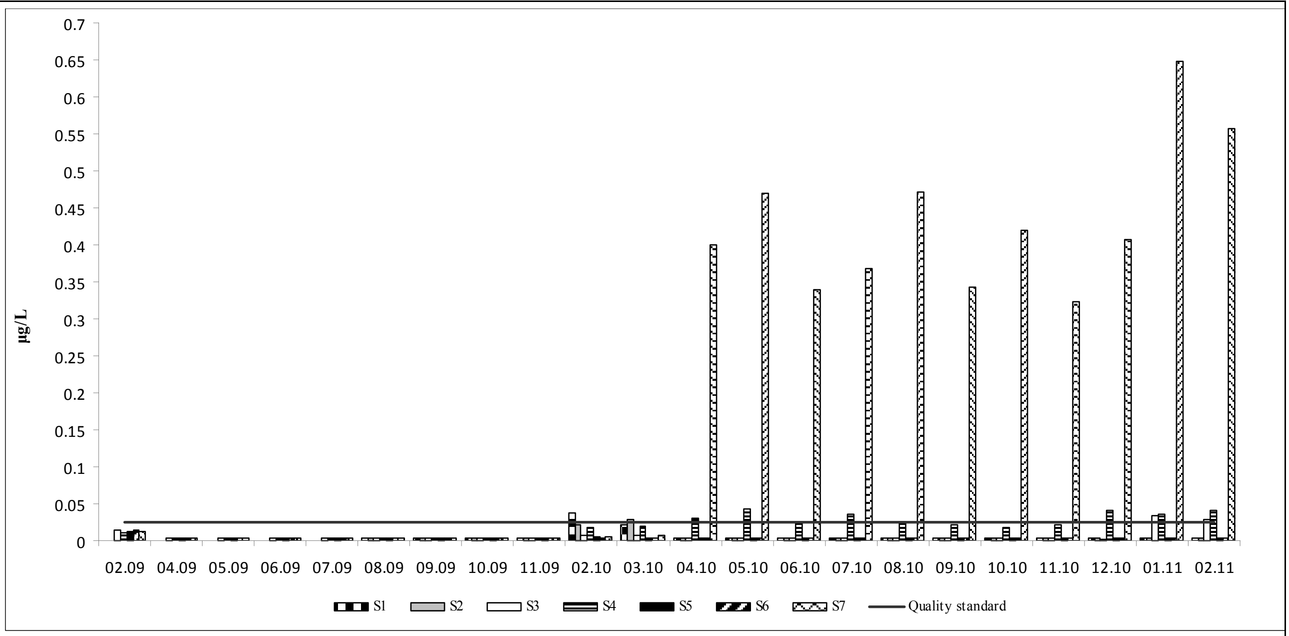

FIGURE 5 - The temporal and spatial variations of DDT/DDE/DDD in Danube River water.

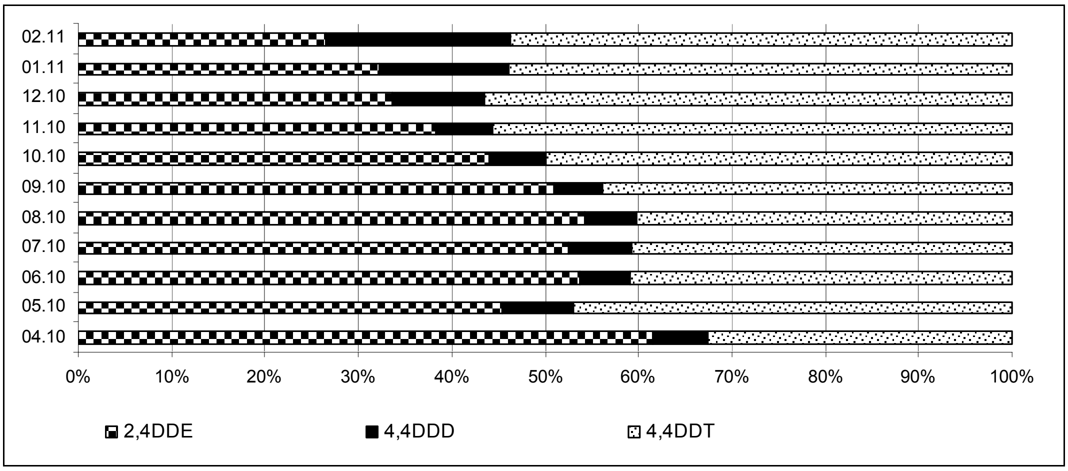

FIGURE 6 - The percentage variations of DDT/DDE/DDD in Danube River water at S7 location.

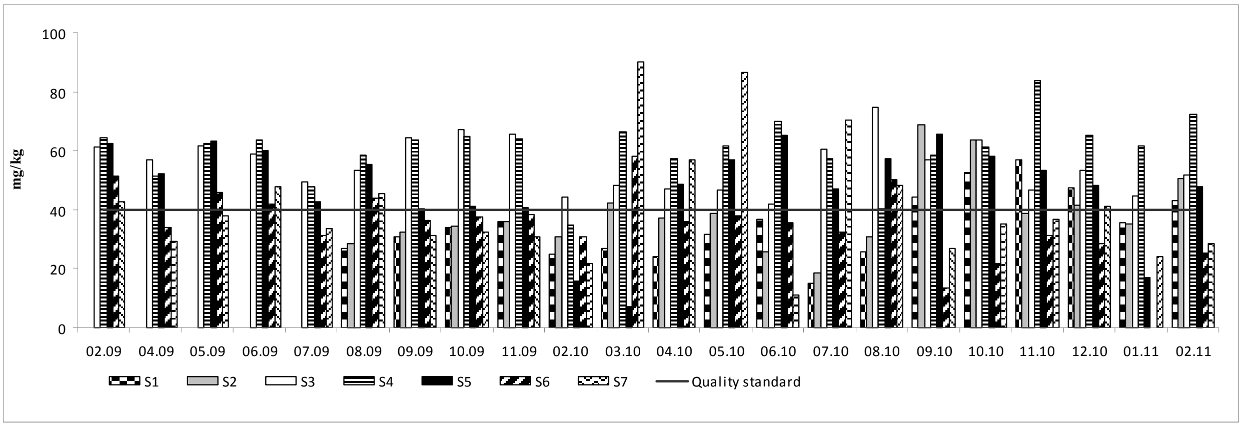

FIGURE 7 - The temporal and spatial variations of Cu in sediment.

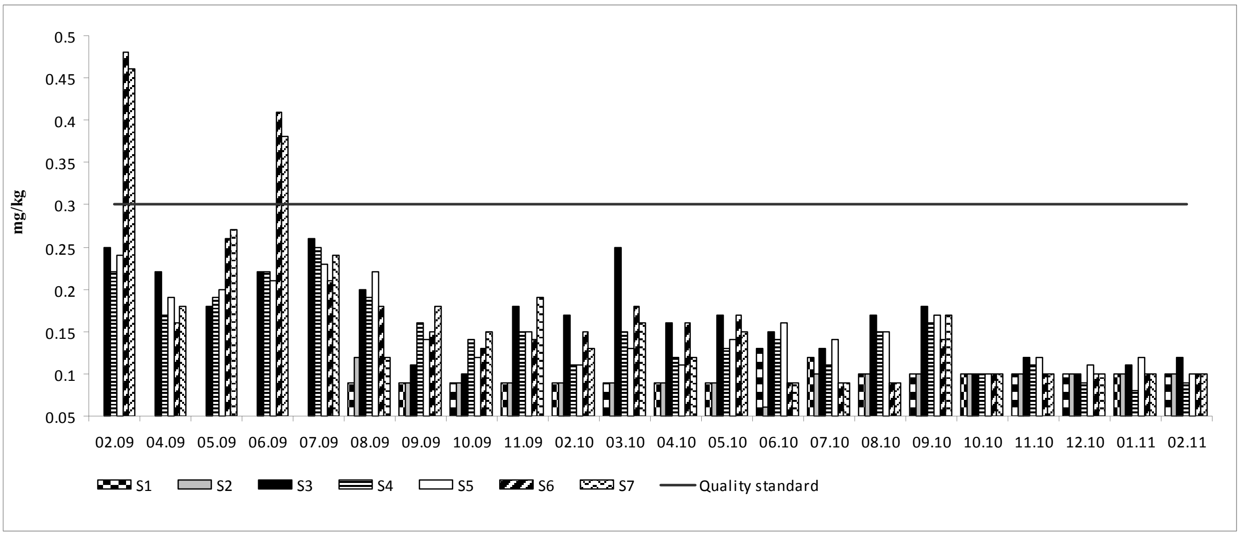

FIGURE 8 - The temporal and spatial variations of Hg in sediment.

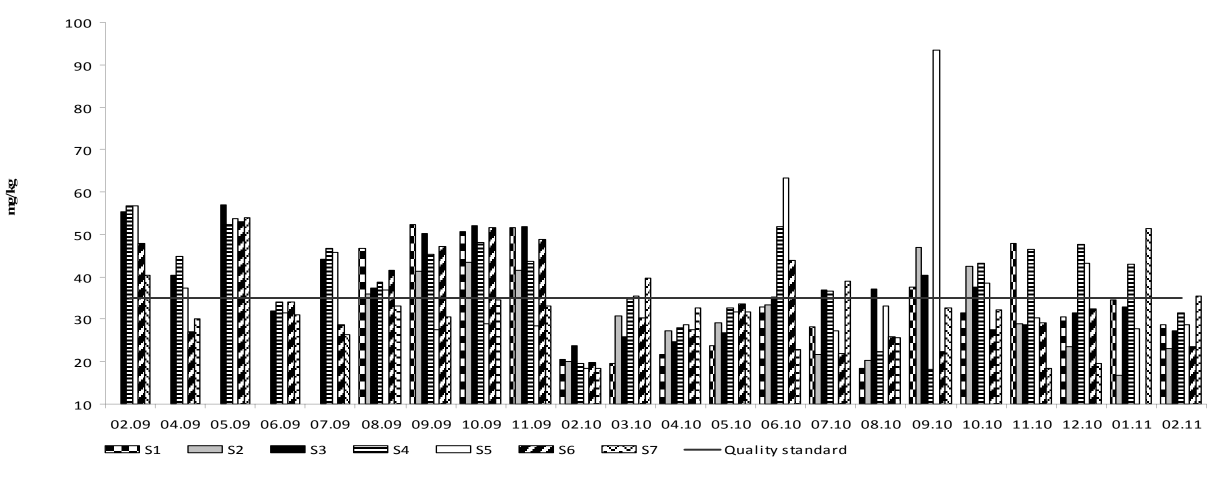

FIGURE 9 - The temporal and spatial variations of Ni in sediment.

TABLE 6 - Concentration of mineral oil (mg/kg) in sediment samples.

Loca-tion	Month / Year																	
	Apr 09	May 09	June 09	July 09	Aug 09	Sept 09	Oct 09	Nov 09	Feb 10	Mar 10	Apr 10	May 10	June 10	July 10	Nov 10	Dec 10	Ian 11	Feb 11
S1	NA[1]	NA	NA	NA	392	105	92.1	60.3	373	64.5	75.9	351	49.9	ND[2]	216	173	256	64.7
S2	NA	NA	NA	NA	93.9	70.2	61.6	37.9	452	98.2	64.5	276	54.2	ND	72.5	74.2	194	43.1
S3	ND	71.6	123	193	94.8	123	136	92	448	156	136.8	441	54.3	ND	61.7	58.3	217	41.9
S4	30.1	116	151	235	143	69.8	72.4	92	536	164	141.2	153	321	ND	113.7	98.4	195	39.6
S5	28.1	75.9	97.2	246	101.4	99.6	93.2	69.9	252	88.4	73.2	46.8	70.9	27.1	49.6	51.6	146	37.7
S6	52.9	36.4	78.7	275	309	79.7	65.3	195	553	173	90.4	56.9	84.5	26.1	55.3	48.7	NA	96.6
S7	34.6	42.1	91.4	116	125	113	86	29.9	382	134	78.8	ND	48.4	25.2	59.1	61.2	162	50.8

Loca-tion	Month / Year																	
	Apr 09	May 09	June 09	July 09	Aug 09	Sept 09	Oct 09	Nov 09	Feb 10	Mar 10	Apr 10	May 10	June 10	July 10	Nov 10	Dec 10	Ian 11	Feb 11
S1	NA[1]	NA	NA	NA	392	105	92.1	60.3	373	64.5	75.9	351	49.9	ND[2]	216	173	256	64.7
S2	NA	NA	NA	NA	93.9	70.2	61.6	37.9	452	98.2	64.5	276	54.2	ND	72.5	74.2	194	43.1
S3	ND	71.6	123	193	94.8	123	136	92	448	156	136.8	441	54.3	ND	61.7	58.3	217	41.9
S4	30.1	116	151	235	143	69.8	72.4	92	536	164	141.2	153	321	ND	113.7	98.4	195	39.6
S5	28.1	75.9	97.2	246	101.4	99.6	93.2	69.9	252	88.4	73.2	46.8	70.9	27.1	49.6	51.6	146	37.7
S6	52.9	36.4	78.7	275	309	79.7	65.3	195	553	173	90.4	56.9	84.5	26.1	55.3	48.7	NA	96.6
S7	34.6	42.1	91.4	116	125	113	86	29.9	382	134	78.8	ND	48.4	25.2	59.1	61.2	162	50.8

NA[1] = not analyzed in this period of year; ND[2] = not detected

In this study, presence of PAHs over order was detected (Fig. 10). The highest values were found at S6 location in March 2010 (24.57 mg/kg dry matter) and in February 2011 (21.3 mg/kg) while the maximum admissible values were 1 mg/kg. PAHs with highest levels detected at S6 in March 2010 were chrysene (15.15 mg/kg), pyrene (0.92 mg/kg), fluoranthene (0.83 mg/kg) and benz(b)fluoranthene (6.34 mg/kg). In February 2011, the composition of PAHs was anthracene (1.65 mg/kg), chrysene (5.28 mg/kg), fluoranthene (3.58 mg/kg), naphthalene (1.26 mg/kg), phenanthrene (5.14 mg/kg), and pyrene (1.91 mg/kg).

Chrysene recorded the highest values from the entire period of the study in April 2010 at S4 (7.29 mg/kg) and S3 (5.56 mg/kg). In April 2009, the highest values were found for anthracene (3.25 mg/kg) at S6 whereas benzo(b)fluoranthene was highest in November 2009 at S2 location(5.37 mg/kg).

DDTs (sum of DDT, DDE and DDD) and HCHs (sum of α-, β, δ- and γ-HCH) are two groups of OCPs that have been frequently detected in sediments of the previously studied locations [4, 5]. In Table 3, the concentration of DDTs is indicated as sum of DDT, DDE, and DDD in sediments, and also in Table 4, the composition of DDTs in sediments from all studied locations. S6 was a location with higher concentration of DDTs from the total concentration in which 4,4-DDD represented 61.06-92.78%, followed by 2,4-DDE (7.21–38.93% %). 4,4-DDT was not detected. These results were compared with Sudaryanto [22] regarding Mekong River Delta, where most of the samples were characterized by higher proportion of p,p'-DDE (47–96%), followed by p,p'-DDD (2.0–51%) and p,p'-DDT (0.60–27%), from total DDTs concentration. In the environment, DDT can be biodegraded to DDE under aerobic conditions, and to DDD under anaerobic conditions [23]. The higher proportions of 2,4-DDE and 4,4-DDD in this study indicate that degradation of DDT occurred significantly.

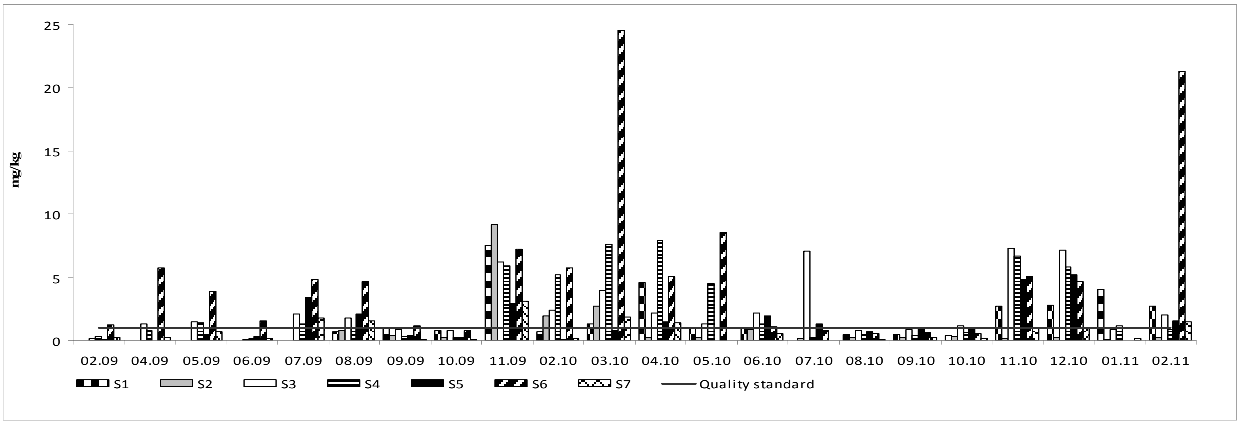

FIGURE 10 - The temporal and spatial variations of PAHs in sediment.

TABLE 7 - Concentrations of DDTs (μg/kg) in sediments.

Location	Month														
	Feb 09	Apr 09	May 09	Aug 09	Apr 10	May 10	June 10	July 10	Aug 10	Sept 10	Oct 10	Nov 10	Dec 10	Ian 11	Feb 11
S1	NA[1]	NA	NA	2.0	0.4	0.7	0.4	0.9	1.1	1.0	4.0	6.0	9.4	5.0	ND
S2	NA	NA	NA	0.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
S3	1.4	1.0	0.7	2.2	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
S4	2.0	1.0	1.0	1.8	1.7	1.2	4.0	3.5	5.0	6.0	6.1	3.9	5.7	1.8	**12.6**
S5	1.0	1.0	0.2	0.2	0.6	2.8	1.3	1.9	5.8	1.9	3.5	6.8	9.6	1.8	30.4
S6	3.0	4.0	ND	ND	8.3	**13.1**	**12.2**	**12.6**	**14.8**	**20.7**	**23.8**	**29.1**	**22.5**	**19.1**	**26.7**
S7	4.0	2.1	ND	ND	1.4	2.8	9.0	5.0	3.0	2.1	3.2	3.5	3.4	3.3	4.3
Quality standard	**∑ DDT/DDE/DDD = 10.0 μg/kg**														

NA[1] = not analyzed in this period of year; ND[2] = not detected

TABLE 8 - Compositional profiles of DDTs (μg/kg) in sediments.

	Loca-tion	Month / Year														
		Feb 09	Apr 09	May 09	Aug 09	Apr 10	May 10	June 10	July 10	Aug 10	Sept 10	Oct 10	Nov 10	Dec 10	Ian 11	Feb 11
2,4-DDE	**S1**	NA[1]	NA	NA	ND[2]	0.4	0.7	0.4	0.9	1.1	1.0	4.0	6.0	8.0	5.0	9.0
	S3	0.7	0.5	0.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	S4	2.0	1.0	0.7	ND	0.9	1.4	1.6	1.2	1.8	1.5	2.2	2.8	2.1	1.8	**2.4**
	S5	1.0	1.0	0.5	ND	0.3	0.5	0.3	0.7	0.8	1.1	2.5	1.8	1.4	1.8	**2.4**
	S6	1.5	0.2	1.5	0.4	4.3	**5.1**	**3.2**	**3.6**	**3.8**	**2.7**	**1.8**	**2.1**	**2.5**	**3.1**	**2.7**
	S7	2.0	1.1	0.8	ND	0.4	0.8	1.0	1.0	1.8	1.2	1.8	1.4	1.9	1.5	2.1
4,4-DDD	**S4**	ND	ND	ND	ND	0.3	0.8	1.3	1.1	1.7	2.4	2.1	2.9	2.2	2.0	8.0
	S5	ND	ND	ND	ND	0.3	0.7	1.0	1.0	5.0	0.8	1.0	5.0	8.0	11.0	28.0
	S6	1.5	0.2	0.2	ND	4.0	**8.0**	**9.0**	**9.0**	**11.0**	**18.0**	**22.0**	**2.7**	**24.0**	**16.0**	**24.0**
	S7	2.0	1.0	2.0	ND	1.0	2.0	8.0	4.0	1.2	0.9	1.4	1.1	1.5	18.0	2.2
4,4-DDT	**S3**	0.7	0.5	1.8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	S4	ND	ND	1.8	ND	0.5	0.6	1.1	1.2	1.5	2.1	1.8	1.1	1.4	1.6	2.2
	S6	ND	ND	12.5	1.4	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
	S7	ND	ND	1.5	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

NA[1]– not analyzed in this period of year, ND[2] – not detected

In the case of HCHs, γ-HCH (lindane) was the dominant isomer in sediments. The highest value (0,014 mg/kg) was found at S3 location in May 2009. The concentration of lindane is presented in Table 10, and of the other HCH isomers (α-HCH, β-HCH, δ-HCH) in Table 9.

The occurrence of other OCPs, like heptachlor and endrin is also presented in Table 9. At S1 location, most concentration values exceeded the quality standard.

The concentration of congener sum of PCBs detected at the studied locations is presented in Table 11, and concentration of PCBs in Table 12.

TABLE 9 - Concentrations of organochlorinated pesticides (µg/kg) in sediments.

Compound	Location	Month / Year											Quality standard
		Apr 10	May 10	June 10	July 10	Aug 10	Sept 10	Oct 10	Nov 10	Dec 10	Jan 11	Feb 11	
α-HCH	**S3**	0.3	0.8	1.0	1.0	4.0	7.0	5.0	4.0	2.0	9.0	11.0	-
	S4	0.3	0.5	0.2	0.2	0.9	1.4	2.5	1.8	2.1	2.8	2.5	
	S6	0.4	0.4	0.2	0.2	0.2	4.0	0.7	0.4	0.4	0.7	0.5	
β- HCH	**S3**	0.3	3.5	1.4	2.8	3.1	2.2	2.7	0.2	2.4	2.8	2.1	
	S4	1.9	2.5	1.5	1.6	1.7	1.2	2.4	1.6	1.9	2.3	1.8	
	S5	1.6	22.0	1.5	1.8	1.7	2.8	3.1	2.7	2.5	3.0	5.0	
	S6	2.6	3.2	2.7	3.8	3.3	4.2	3.8	2.6	2.2	2.5	3.2	
	S7	1.0	2.1	2.0	2.8	2.5	3.4	2.4	3.1	2.7	1.9	1.5	
δ- HCH	**S1**	0.3	0.8	1.1	1.3	1.5	1.2	1.6	2.0	4.0	9.0	0.2	-
	S3	0.3	0.9	0.3	0.5	0.5	1.0	4.0	7.0	8.0	6.0	8.0	
	S4	0.6	0.8	0.9	0.9	1.9	1.6	1.5	2.2	2.5	2.9	2.6	
Heptachlor	**S1**	**0.7**	**1.1**	**1.5**	**1.9**	**1.9**	**1.7**	**2.2**	**2.2**	**2.6**	**2.0**	**8.0**	0.7
Endrin	**S1**	**1.6**	**2.2**	**2.1**	**2.8**	**2.2**	**1.2**	**1.4**	**1.2**	**1.4**	**2.5**	**1.8**	0.04
	S3	**0.3**	**0.5**	**0.5**	**0.2**	**0.7**	**0.4**	**0.8**	**0.8**	**3.0**	**8.0**	**11.0**	

TABLE 10 - Concentrations of lindane (µg/kg) in sediments.

Month/ Year	Location					Quality Standard
	S3	S4	S5	S6	S7	
Feb 09	**9.0**	**45.0**	**2.0**	**6.1**	**2.8**	**0.05**
Apr 09	**5.0**	**2.0**	**2.0**	**2.5**	**2.1**	
May 09	**14.0**	**5.0**	**2.0**	**7.0**	**4.0**	
June 09	**3.0**	**3.0**	**3.0**	**7.0**	**2.0**	
July 09	**1.0**	**2.0**	**2.0**	**0.6**	**0.5**	
Aug 09	**0.2**	**0.2**	**2.0**	**8.0**	**3.0**	
Sept 09	**0.4**	**0.5**	ND[1]	**0.3**	ND	
Apr 10	**0.3**	ND	ND	**0.9**	ND	
May 10	**0.6**	ND	ND	**1.1**	ND	
June 10	**0.4**	ND	ND	**2.1**	ND	
July 10	**0.4**	ND	ND	**2.4**	ND	
Aug 10	**0.7**	ND	ND	**2.8**	ND	
Sept 10	**0.5**	ND	ND	**3.5**	ND	
Oct 10	**0.8**	ND	ND	**2.6**	ND	
Nov 10	**0.3**	ND	ND	**3.2**	ND	
Dec 10	**0.5**	ND	ND	**2.8**	ND	
Ian 11	**01.0**	ND	ND	**2.1**	ND	
Feb 11	**7.0**	ND	ND	**1.8**	ND	

ND[1]–= not detected

TABLE 11 - Concentrations of PCBs (µg/kg) in sediments.

Location	Month / Year									Quality Standard
	Feb 09	Apr 09	May 09	June 09	July 09	Aug 09	Sept 09	Oct 09	Nov 09	
S1	NA[1]	NA	NA	NA	NA	**65.0**	0.4	ND[2]	ND	**20.0**
S2	NA	NA	NA	NA	NA	**43.0**	0.4	ND	ND	
S3	0.5	4.0	1.0	0.3	ND	**74.0**	0.7	ND	ND	
S4	0.6	3.0	2.0	0.2	ND	**67.0**	0.5	ND	ND	
S5	0.8	2.0	5.0	0.5	ND	**39.0**	0.6	ND	ND	
S6	7.8	ND	8.2	7.3	4.0	**415.0**	13.6	8.7	8.7	
S7	1.1	4.4	3.2	19.8	ND	**27.03**	7.1	ND	ND	

NA[1]– not analyzed in this period of year, ND[2] – not detected

TABLE 12 - PCBs congeners in August 2009 (µg/kg) in sediments.

Congeners	Location						
	S1	S2	S3	S4	S5	S6	S7
Congener 28	61.0	41.1	64.7	63.1	37.0	348.8	25.2
Congener 52	1.7	0.2	3.4	2.8	0.3	48.7	ND[1]
Congener 101	ND	ND	0.4	0.8	0.5	4.9	0.6
Congener 153	ND	0.2	0.4	0.3	0.3	0.8	0.2
Congener 138	1.0	0.9	5.0	0.3	0.4	4.8	0.9
Congener 180	0.8	0.4	0.3	0.4	0.6	7.0	0.4
PCBs = ∑ Congeners	64.5	42.8	74.0	67.0	39.0	415.0	27.3
Quality Standard	**20.0**						

ND[1] – not detected

PCBs have been used mainly for industrial purposes, such as dielectric fluids in transformers and capacitors. They are a group of 209 related industrial compounds, which differ only in the number and pattern of chlorine atoms attached to biphenyl molecule. These compounds are termed congeners of PCBs. The patterns of chlorine substitution ultimately modify and dictate each congener's environmental fate and toxicity. Of the 209 congeners of PCBs, some have been reported to have toxicological effects.

The limit concentrations of PCBs used for regulatory purposes are based either on the "total PCB" level or, more recently, on standard individual congeners (28, 52,101, 138, 153, 180) chosen in order to cover a wide range of chlorination (from three to seven chlorine atoms), and taking into consideration their relatively high levels in samples [5]. In August 2009, exceeding values of PCBs were recorded at all sampling locations, with high values for 28 PCB congener (Table 8).

Tri- to penta-PCBs were detected for approximately 90% of total PCBs, but octa- to deca-PCBs were not detected. In addition, the relative abundances of tri-PCBs at all locations represented more than half of total PCBs. This probably was connected with congener types of technical PCBs used in August 2009 [24].

4. CONCLUSIONS

The pollution of surface water and sediments on St. Gheorghe branch from the Danube Delta with nutrients, metals and several relevant organic toxic compounds was evaluated. In this study, seven locations from the southern branch of the Danube Delta - Saint George Branch were monitored.

In water samples, concentration values of mineral oil about four times higher than the allowed limit (910 µg/L) at S6 location were recorded. The content of heavy and toxic metals in Danube River water was, in most cases, below the limits according to the national legislation; only iron values exceeded the limit. Concerning organic compounds, the mineral oil, DDTs and PCBs periodically were recorded in river water being over the limit.

At some locations, in sediment, higher concentrations of copper, nickel, mercury, lindane, PAHs, DDTs and PCBs were detected exceeding the quality standards according to Romanian legislation transposed from Frame Water Directive 2000/60/EC.

The presence of Fe, DDTs, PCBs, and mineral oil in surface water represents an acute problem for the inhabitants of the Danube Delta. The use of water directly from the river, without any treatment for household consumption, presents a series of disadvantages, such as a high risk of diseases for the population, mostly for children and old people.

Target analyses of selected pollutants showed that occasionally they were present in high concentration, and revealed the need to safeguard the quality of the river water from future deterioration, firstly by a long-term monitoring. Further studies need to be carried out also on the biota compartments (fish) from this area, in order to evaluate the occurrence of persistent organic pollutants and toxic metals in tissues, and to assess the risk of these contaminants on the ecosystem and human health.

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