AQUATIC ECOSYSTEM QUALITY ASSESSMENT OF THE DANUBE DELTA IN THE PERIODS APRIL-OCTOBER 2007 AND 2008

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ABSTRACT

The present paper is focused on the quality assessment of surface water and sediment of the Danube Delta biosphere. Information is presented on water and sediment quality variations in organic/inorganic pollutants and heavy metals over a 2-years period (2007 and 2008) from April to October. Samples have been collected monthly from two different locations situated on St. George branch Murghiol and Uzlina, respectively.

The analyses were performed by GC-ECD for orga-nochlorine insecticides and polychlorinated biphenyls (PCBs), GC-NPD for organophosphorus and triazine pesticides, HPLC-Fluorescence/UV for PAHs and phenylurea herbicides, IR for mineral oil, and AAS for metals.

The monitoring results have shown, at both sampling points, a significant high organic load (BOD_5, COD-Cr) of the water-bodies during all investigated periods, potentially threatening the river's self-cleaning capacity. In sediment, an essential and dynamic part of the river basin, Cu was the predominant pollutant in all samples at levels (41-194 mg/kg dry weight) higher than the quality standard (40 mg/kg d.w.) according to the Romanian legislation (transposed from Directive 2000/60/EC).

KEYWORDS: Danube Delta, water, sediment, organic pollutants, inorganic pollutants, monitoring.

INTRODUCTION

The Danube River, the second largest in Europe with a length of 2780 km and a catchments area of 817,000 sq. km, provides essential water resources for a population of over 70 million people living in the 8 countries along its course, and 6 additional countries in its extended catchment area [1]. At the same time, the river receives discharges of agricultural, industrial and urban effluents.

The Danube River waters discharge into the Black Sea through its delta (5600 sq. km), the second largest natural wetland in Europe, that has the richest ornithological fauna including rare species of birds, such as Dalmatian pelicans (*Pelecanus crispus*), pygmy cormorants (*Phalacrocorax pygmeus*) and the great white egrets (*Egretta alba*) [2]. This area is of high environmental, economic and social value. It supports drinking water supply, agriculture, industry, navigation, fishing, tourism and recreation. All these activities are potential sources of pollution with metals, mineral oil, persistent organic compounds including pesticides and PCBs, resulting in deterioration of river quality and, consequently, the disturbance of the aquatic ecosystems as well as their biodiversity and habitats. Some of the organic pollutants are hydrophobic and, therefore, readily bind to particle fraction in surface waters. Via sedimentation processes, these chemicals are deposited to the bottom remaining for a long time in sediment due to their long half-life times [3]. These organic pollutants as well as the toxic metals retained in sediment can be taken up and retained in benthic chains to higher trophic levels [4]. Examination of metals and persistent organic pollutant levels in sediment may give basic information on the contamination status, sources and ecological risks of these chemicals in the aquatic environment [5]. Some recent data about contamination with organochlorine pesticides, PCBs and polybrominated diphenyl ethers of sediment and biota (intervertebrates, 11 fish species and cormorant tissues) reported on the presence of DDTs in all samples collected in 2001 [2]. Protection and conservation of this Biosphere Reserve ecosystem need a long-term assessment of the physico-chemical water quality in order to provide information concerning the discharge of different pollutants, and also to point out a potential trend of eutrophication. The data obtained [6, 7] in previous studies carried out during a 4-years period (2003-2006) concerning long-term trends of the Danube Delta aquatic ecosystem status from Uzlina and Murighiol locations put in evidence an oxygen deficit, a high concentration of organic load and the presence of some chemical parameters (phenols, PAHs, mineral oil, orthophosphates, lindane and some metallic elements, such as iron, manganese and copper) in concentrations which exceed the quality standards for water-bodies. Even if the total concentration levels of metals (Cu, Zn, Ni) in sediments exceeded the quality standards, the study of their availability to migrate into the overlying water showed that the mobile elements cannot affect living organisms from water-bodies, al-though a continuous in-going of these pollutants in the abiotic compartment (water and sediment) can affect the water as a complex life support system. As a consequence, the occurrence of these pollutants should be periodically controlled.

The aim of this study was to continue the water and sediment quality monitoring in Danube Delta at Uzlina and Murighiol locations. The main objectives were the identification and quantification of the most important inorganic and organic pollutants in water and sediment at both locations, the evaluation of their compliance with standards, and the long-term trends of the ecosystem`s chemical status.

MATERIALS AND METHODS

Study area and sample collection

Water and sediment sampling was performed in two locations on St. George branch, *Uzlina* and *Murghiol.* This branch is the most southern branch carrying 23% of the Danube water discharge and 21% of the Danube sediment discharge [8]. This highly sinuous branch was cut off in 1984-1988 by an artificial canal opened to shipping which caused significant changes of the river flow velocity in the natural channel. The main flow (82%) was captured by the artificial canal which has also an increased velocity. In *Uzlina (45°4'N-29°14'E)* situated on the natural channel, samples were collected from the Cormoran Complex, a place with intensive naval activity. Cormoran Complex has its own domestic wastewater treatment station, and the treated water is dumped into the river. However, many houses in this area are discharging water directly into the river. In *Murghiol (45°2'N-29°10'E)*, samples were collected from the artificial canal near Murghiol Lake. These two locations situated on two different channels, in an area of natural fish reproduction and a pelican colony, are tourist villages in continuous expansion with ports and fuel stations for boats.

A total of 28 samples, including 14 water and sediment samples (momentary samples), were collected from April to October in 2007 and 2008 from each location. The sampling and preservation step was done according to the recommendations of specific international guidelines [9-14]. All water samples were collected and stored in 1-L pre-cleaned amber glass bottles that had been rinsed thoroughly with nitric acid and analytical-grade pentane in order to remove all heavy metals and organic residues. From each sampling location, 10 L of water were collected. The sediment samples were taken from 2-3 m depth within the river using a *Van Veen Bottom Sampler*. The sediment samples were put into glass jars and thoroughly homogenized. The 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.

Chemicals and Analytical Methodology

The chemicals, analytical methodologies and quality controls used by the laboratory for the determination of selected physical and chemical parameters have been presented in a previous paper [7]. The analytical procedures used in this study are briefly presented here. Prior to analysis, water samples were filtered through 0.45-µm glass fiber filters in order to remove suspended particles. For the quantitative analysis of the adsorbed organic pollutants, the sediment samples were frozen at -20 °C and then lyophilized. The lyophilized samples were ground and homogenized with mortar and pestle, and finally sieved through a 63-µm sieve.

Insecticides

Sample treatment was based on liquid-liquid extraction with enrichment factors of 1000. The organophosphorus insecticides were extracted from acidified (pH 3.5-4.5) water samples with dichloromethane. The treatment conditions for triazine pesticides were the same but at pHs between 6-9. The organochlorine insecticides and PCBs were extracted with hexane from water samples at pHs 5-7.5. The freeze-dried river sediment sub-sample was extracted with acetone and then petroleum ether. After clean-up on a silica gel column and concentration by evaporation of the solvent layer, the analytes were reconstituted with 1 ml acetone. Insecticides were determined by GC analysis (Agilent GC *6890* N, equipped with NPD for organophosphorus and triazine insecticides as well as ECD for organochlorine insecticides and PCBs - PCB 28, PCB 52, PCB 101, PCB 118, PCB 138, PCB 153, PCB 180). The fused silica capillary columns used were a CP-SIL-5CB (30 m x 0.32 mm i.d. x 0.25 µm film thickness) for organophosphorus (malathion, parathion, clorpyrifos, mevinphos, dichlorvos, triclorfon) and triazine (atrazine, simazine, propazine) insecticides, and a TR1 Thermo column (30 m x 0.32 mm i.d. x 0.25 µm film thickness) for organochlorines (α-, β-, γ-, δ-HCH, heptachlor, aldrin, dieldrin, endrin, DDTs).

Phenylurea herbicides

Determination of phenylurea herbicides (diuron, linuron, monolinuron, isoproturon) from water samples was carried out according to EN ISO 11369:1997. Solid-phase extraction procedure (SPE) was applied prior to analysis using a disposable Vacuum Manifold System (Vacuubrand GmbH, Wertheim, Germany) and solid-phase extraction cartridges (Macherey-Nagel, Dueren, Germany). The SPE cartridges (Chromabond C18 Hydra, 6 ml, 2000 mg) were conditioned with 3 x 3 ml methanol, and then with 3 x 3 ml

HPLC-grade water, taking care not to let the cartridges dry out. The passage of the samples (volume 1 L) through the cartridges was carried out at a flow-rate of 10 ml/min by means of a vacuum pump. After the retention step, the cartridges were cleaned with 10 ml of HPLC-grade water and dried under a gentle stream of air (45 min, room temperature). The retained compounds were eluted with 10 ml of methanol. The obtained solutions were evaporated to dryness by means of a rotary evaporator, at 35 °C. The dry residue was dissolved in 1 ml acetonitrile. Liquid-chromatographic separation of the herbicides was performed using an Agilent 1100 system (Agilent Technologies, USA), equipped with a degasser, quaternary pump, autosampler, column thermostat and multiple wavelength detector (MWD), on a Zorbax Eclipse XDB-C18 analytical column (150 x 4.6 mm, 5 µm particle size, Agilent Technologies). The HPLC separations were carried out at 25 °C with a flow-rate of 1 ml/min under isocratic conditions. The injection volume was 10 µl, and the elution of the compounds into the chromatographic column was performed with acetonitrile/water (65/35, v/v).

Mineral oil

The water samples were acidified with hydrochloric acid to pH <5, and then the samples were extracted with carbon tetrachloride. The solvent layer was purrified on a silica gel column and dried with anhydrous sodium sulfate. The sediment samples were firstly dried with Na_2SO_4 and then ground as well as homogenized using a mortar and pestle before extraction with carbon tetrachloride. Concentrations of total mineral oil were determined by screening infrared spectra on a FT-IR Spectrum BX II (Perkin Elmer, USA) in the wavelength range between 2800-3100 cm^{-1} and comparing peak maxima (CH_3 groups at 2958 cm^{-1}, CH_2 groups at 2925 cm^{-1}, and CH groups at 3030 cm^{-1}) with a calibration curve made using a standard mix of 37.5% isooctane, 37.5% *n*-hexadecane and 25% benzene.

RESULTS AND DISCUSSION

A large database was obtained after two consecutive years of physico-chemical evaluation of surface water and sediments from the Danube Delta. The values obtained for the quality elements were evaluated for their compliance with quality standards stipulated in Statutory Order No. 161/2006 of the Romanian Ministry of the Environment and Water Management transposed from Water Frame Directive (WFD) [14, 15].

The WFD classification scheme for water quality includes 5 status categories: high, good, moderate, poor and bad. The objective regulation is to achieve “good status” for all surface waters, and, for that reason, it sets concentration limits of this on a large number of dangerous substances that pose a particular risk to animal and plant life in the aquatic environment, and also to human health.

The occurrence of the selected pollutants and their temporal distribution at both sampling points, as well as their compliance with the quality standards are discussed below. The mass concentrations of the individual chemical parameters determined in the sediment samples are reported in terms of dry weight.

Water samples

A high organic load was observed during the whole period of investigation. The COD-Cr and BOD_5 values at Murighiol were characteristic for poor chemical status category. The COD-Cr values ranged in the last two monitoring years from 19.2 to 76.8 mg O_2/L with a mean value of 47.0 mg O_2/L. BOD_5 values varied similarly, ranging between 7.3 and 30.9 mg O_2/L with a mean value of 17.2 mg O_2/L. This almost constant organic overloading explains the deficit of water courses in DO suggesting a high biological action. Comparatively to Murighiol river water, the level of organic load at Uzlina is lower, with mean values of 31.7 mg O_2/L for COD-Cr and 10.5 mg O_2/L for BOD_5 (Figs. 1 and 2).

No significant changes were observed in nutrient (mineral nitrogen, total phosphorus) concentrations during the whole period of investigation, their level being almost constant and below the limit values set for a good status.

Excess of chloride and sodium ions was detected in 2007 from April till September in Murighiol, with values ranging from 104 to 198.4 mg/L and 53.9 to 189 mg/L, respectively, compared to 50 mg/L admitted by the regulation for a good status in both cases (Fig. 3). This high salinity was recorded only in the artificial canal and we can conclude that this is a local contamination, probably due to the influence of the neighboring salt lakes. Since high concentrations of chloride ions were recorded also in other previous years (2004 and 2006), further investigations on the determination of their input origin are needed.

The metal load grade of the water-body has been generally low. Higher levels of iron, chromium, manganese and nickel were measured occasionally in 2007. The highest concentrations of these metals were recorded in June, for Murighiol location: 70 µg/L for Cr, 160 µg/L for Mn, 3.72 mg/L for Fe and 460 µg/L for Ni. High values for Ni, specific for a bad chemical status of the water stream, occurred also in the autumn months (180 µg/L in September and 140 µg/L in October). In Uzlina, there have been recorded relatively high values only for iron in 2007 (1.72-2.05 mg/L), exceeding the stipulated value (1.0 mg/L) for a moderate chemical surface water category. As shown in Fig. 4, high iron concentrations occur in the same months in both channels indicating anthropogenic contamination of the river before the cutoff of the St. George branch. The observed variation of heavy metals in the river water can be expected to be caused by influx of contaminants into the Danube through the tributaries polluted by mining and ore treatment activities. In the next year, there has been a general decrease in metal concentrations, with values below the limits set for a good water quality status. Similar low concentrations of trace metals have been measured in two

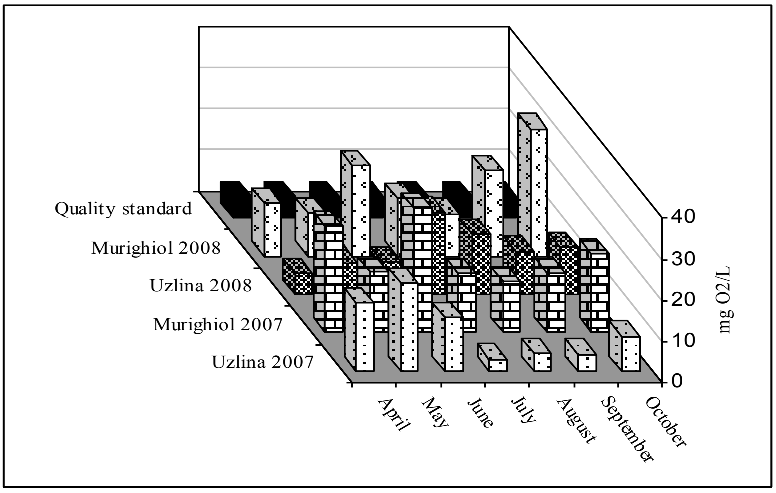

FIGURE 1 – The temporal and spatial variation of BOD_5 in the River Danube water samples.

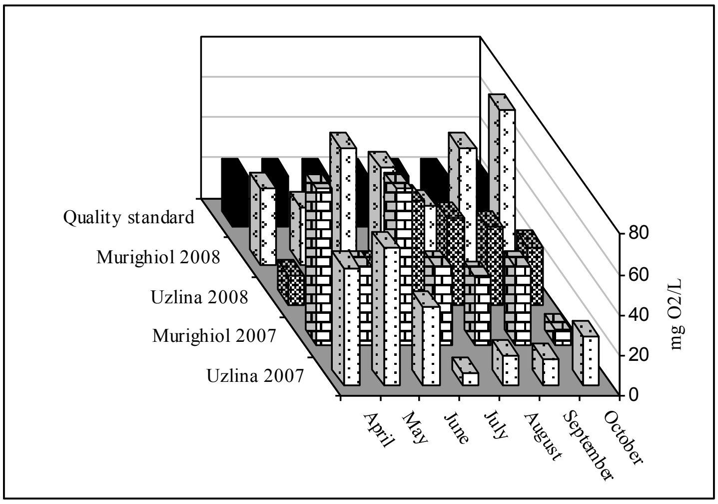

FIGURE 2– The temporal and spatial variation of COD-Cr in the River Danube water samples.

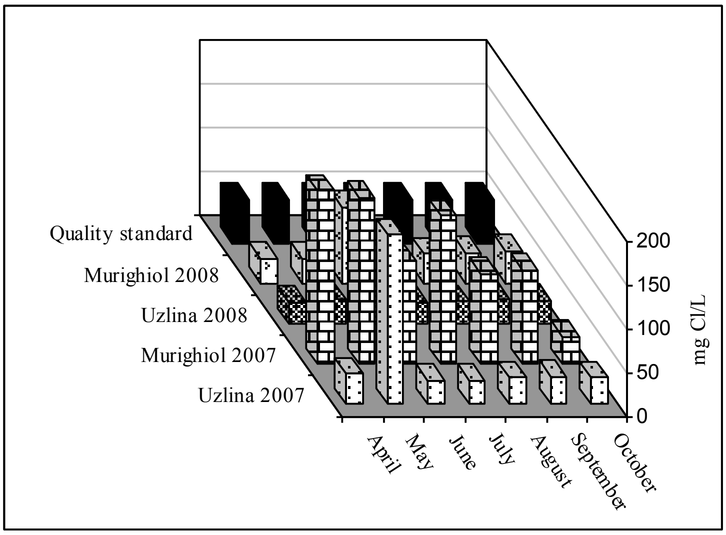

FIGURE 3 – Temporal variation of chloride ions in the River Danube water samples.

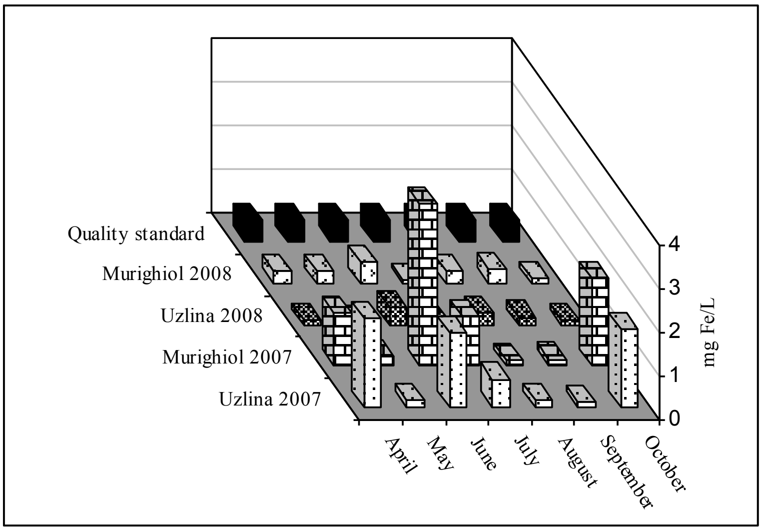

FIGURE 4 – The temporal and spatial variation of Iron concentration in the River Danube water samples.

investigation campaigns carried out in 1995 and 1997 in the three branches of the Danube River, except for copper [16]. The results of our very wide studies of the two locations during 6 years suggest that copper pollution decreased drastically in the last three years in river water.

Generally, the concentrations of organic pollutants found in the tested surface water were not high. Relatively higher levels of mineral oil occurred in the spring of 2007 in Murighiol (0.23-0.27 mg/L) as well as in Uzlina (0.26-0.32 mg/L), decreasing drastically in the next period to below the limit of detection (LOD) of the analysis method. Considering the fact that the mineral oil occurred in both locations at the same time and in similar concentrations, it can be concluded that the contamination took place through accidental discharges elsewhere before river bifurcation. Organochlorine pesticides, such as heptachlor and lindane (γ-HCH) were found in water only in spring months. Thus, heptachlor was detected in spring 2007 at both location in concentration of 0.01 μg/L (50 times higher than the limit), and lindane occurred in spring 2008 in a mean concentrations of 0.034 μg/L. The occurrence of organochlorines in surface water only during spring could be caused by their illegal use as pesticides in agriculture and vector control. Other persistent organic pollutants detected during spring 2008 in the surface water of the two channels were PCBs (concentrations 0.025-0.48 μg/L). Of the 12 PAHs investigated, only benzo[b]fluoranthene occurred in the artificial canal during April and May 2008 in high concentrations (0.028-0.031 μg/L) exceeding the limit sets for a good water quality status. With regard to the artificial canal, the water quality status in the natural channel is better indicating a self-purification activity probably due to its present weak flow.

Sediment samples

Zn, Cd, Cr, Pb and As amounts in sediment were generally low in both locations, but the concentrations of Cu and Ni exceeded in both years the quality standards: 40 mg/kg for Cu and 35 mg/kg for Ni. In Murighiol location, the concentrations of copper ranged from 41.0 to 49.2 mg/kg and that of nickel from 41.5 to 71.9 mg/kg with a higher value recorded in June 2008 (110.5 mg/kg). Similar Cu and Ni concentration levels were found in the sediments collected from Uzlina. At this sampling point, the highest value of Cu (194 mg/kg) was recorded in July 2007 (Figs. 5 and 6). On the basis of the element data obtained in the period 2003-2008, it has been observed that the concentration of Cu in sediment samples collected from both locations remained relatively stable, suggesting an historical anthropogenic contamination. Although nickel has been investigated only in the past 3 years, the same anthropogenic origin could explain its presence in high concentrations. In 2006, intra-annual variation of this element ranged in Uzlina between 46.2-56.9 mg/kg and Murighiol from 16.0 to 41.4 mg/kg [7]. High levels of Cu and Ni concentrations have been also reported in an assessment of element concentrations in Danube river sediments carried out in 2001. Cu and Ni concentrations found along the river ranged from 31.3-662.9 mg/kg and from 24.6-142.8 mg/kg, respectively [17].

High concentrations of mercury were found in 2007 at both sampling points from July till October ranging from 0.35 to 0.99 99 mg/kg (Fig. 7). In Uzlina, this toxic element was detected also in the following spring in concentrations exceeding the qualitative standard (0.3 mg/kg). From the beginning of the monitoring study (2003), Hg occurred for first time in high concentrations. Fortunately, this element was not detected in the water and studies undertaken in this work on the mobility of Hg showed that this toxic metal is not present in sediment in a mobile form. Special attention should be paid to this element in future investigations to determine the origin of its occurrence. A strong Hg pollution was reported in the past from the catchment of the Vah River (Slovakia), a Danube tributary [18].

TABLE 1 – Concentration of mineral oil (mg/kg) in Danube sediment samples.

Year	Location	Month						
		April	May	June	July	August	September	October
2007	Uzlina	113.3	108.5	101.3	47.0	45.5	45.0	56.3
	Murighiol	111.2	109.5	136.1	132.7	126.2	92.1	84.3
2008	Uzlina	375.4	287.9	71.1	<25	<25	<25	<25
	Murighiol	250.5	188.2	28.0	<25	<25	<25	<25

Mineral oil was found in sediment samples in concentration levels ranging between 28.0 and 375.4 mg/kg, higher peaks being observed mainly in spring months (Table 1). Concentrations of mineral oil adsorbed in sediments were gradually reduced to below the LOD of the method of analysis, probably as a result of microbial degradation and/or being transported by the water streams into the Black Sea. One of the most contaminated sediment sites with petroleum hydrocarbons in the Black Sea is considered to be situated near the Danube Delta (220 mg/kg) and is associated with river inputs [19]. Our earlier studies [6, 7] have shown that mineral oil occurrence in all the river compartments has an anthropogenic origin, probably by an accidental spillage of this pollutant into the river.

The presence of high PAH levels at both sampling points is not surprising because they were detected almost constantly in the previous years of investigations in concentrations ranging from 0.35 to 13.5 mg/kg, with higher values in Murighiol. In this study, the PAH concentrations in Murighiol (1.24-10.26 mg/kg) exceeded the value of qualitative standard set as 1 mg/kg in both years (Fig. 8). Their concentrations in Uzlina location are generally increasing in 2008 (1.12-2.78 mg/kg) compared to the previous year values (1.01-1.27 mg/kg), but their concentrations were not so high than in Murighiol location. Anthropogenic PAHs enter the riverine environment through a variety of routes including domestic and industrial outfalls, atmospheric deposition or direct spillage of petroleum products. An approach commonly used in the literature to distinguish between petrogenic and pyrolytic PAH origin is based on PAHs isomeric ratios, such as anthracene/ anthracene+fenanthrene (Ant/178), fluoranthene/ fluoranthene+pyrene (Flu/202) [20-23]. PAHs in sediment with Ant/178 <0.1 are from petroleum contamination while Ant/178 >0.1 are of combustion source. Similar logic will be applied to the Flu/202 ratio, where values >0.5 are mainly from combustion of grass, wood and coal; PAHs with 0.5 > (Flu/202) > 0.4 are mainly from combustion of petroleum, and Flu/202 <0.4 are of petroleum contamination [24]. Since many possible contamination sources may be coexisting in sediment samples, both ratios mentioned above were used in the present study to assess the input sources of PAHs. Anthracene and fenanthrene were detected at both locations only from April till May in each year, and the ratios Ant/178 were in the range of 0.23-0.90 indicating a combustion source in sediments. In 2008, when PAH contamination was observed, the ratios Flu/202 were less than 0.4 from April till October with a mean of 0.27 in Uzlina and 0.34 in Murighiol, indicating a petroleum contamination source. These characteristics indicate that the associated PAHs could be a mixture of pyrolytic and petrogenic origin. The total PAH concentrations in sediments from the studied area are similar to the levels found in Inner Clyde Estuary (0.63-23.711 mg/kg) [23] and Pearl River Delta (1.291-9.871 mg/kg) [25]. In the Black Sea, highest PAH concentrations were observed at the sediment sites influenced by the Danube (0.638 mg/kg) [16].

The results for organochlorine pesticide levels (OCPs), found occasionally in sediment samples collected from Uzlina and Murighiol sampling points, are shown in Table 2. Heptachlor identified in water-body in June 2007 was also detected in sediment from Uzlina in April (2.30 µg/kg) and Murighiol in May (4.68 µg/kg). Lindane was found in sediments in concentrations ranging from 1.30 to 8.00 µg/kg in Murighiol and from 2.29 to 6.00 µg/kg in Uzlina. β-HCH isomer has also been detected during spring in concentrations ranging between 1.60-7.50 µg/kg in Uzlina, but only in April in Murighiol (2.61 µg/kg). DDT compounds occurred in sediments only in 2008 from April till June in concentrations ranging from 2.70 to 70 µg/kg, the highest value being recorded in Murighiol. Other OCPs detected in 2008 were α-HCH (1.30-1.75 µg/kg) in Murighiol, aldrin (0.018-0.27 µg/kg) and endrin (12-24 µg/kg) at both sampling points, whereas δ-HCH, dieldrin, triazine pesticides and phenylurea herbicides were not detected. Only limited amount data on the organochlorine residues in sediments from Danube Delta exist. Sediment samples collected in 2001 from 3 lakes of the Danube Delta have shown high organochlorine values. HCHs ranged from 0.9 to 9.0 µg/kg with a higher contribution of lindane (range 31-76%). DDTs were found in higher concentrations than HCHs, and ranged from 0.7 to 33 µg/kg [2]. Elevated concentrations of lindane (up to 40 µg/kg) and DDTs (up to 72 µg/kg) have been reported in the Black Sea sites influenced by the Danube Delta [26]. Comparable concentration levels of lindane (5.00 µg/kg wet wt.) were also recorded in the samples collected from Kizilirmak river, as well as DDTs in the Mert stream sediments (71 µg/kg wet wt), both discharging into Black Sea coast of Turkey [27].

This study has shown that some organochlorine compounds (lindane, heptachlor, endrin, DDTs) were present mainly during spring in sediments samples collected from

TABLE 2 - Concentrations of organochlorine pesticides (μg/kg) in Danube sediment samples.

Compound	Location	April		May		June		October
		2007	2008	2007	2008	2007	2008	2008
α-HCH	Murighiol	ND*	1.40	ND	1.30	1.75	ND	ND
	Uzlina	ND	ND	ND	ND	ND	ND	ND
β- HCH	Murighiol	2.61	ND	ND	ND	ND	ND	ND
	Uzlina	7.5	ND	1.9	ND	1.6	ND	ND
γ- HCH	Murighiol	1.30	6.00	4.21	4.40	ND	ND	8.00
	Uzlina	2.62	4.50	2.29	ND	ND	ND	6.00
Heptachlor	Murighiol	ND	ND	4.68	ND	ND	ND	ND
	Uzlina	2.3	ND	ND	ND	ND	ND	ND
DDTs	Murighiol	ND	70	ND	27	ND	2.90	ND
	Uzlina	ND	2.7	ND	12.00	ND	ND	ND
Aldrin	Murighiol	ND	ND	ND	ND	ND	0.27	ND
	Uzlina	ND	ND	ND	0.018	ND	ND	ND
Endrin	Murighiol	ND	ND	ND	ND	ND	ND	12
	Uzlina	ND	ND	ND	ND	ND	ND	24

*ND – not detected

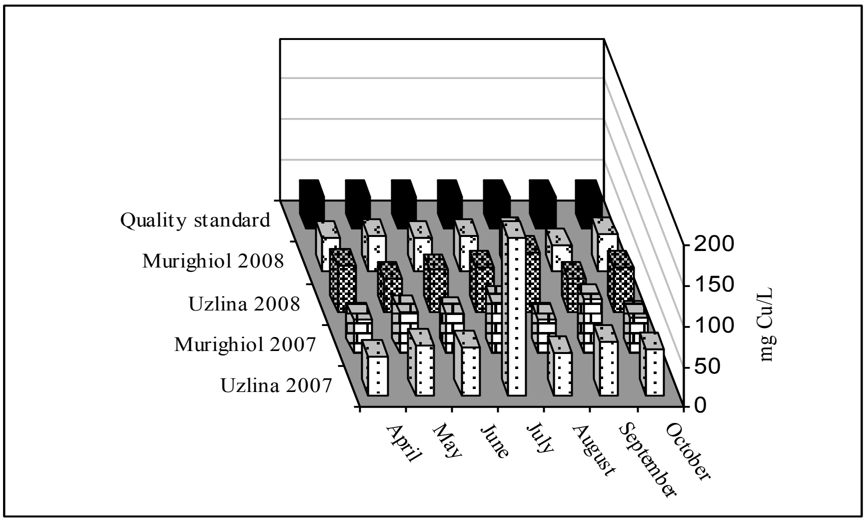

FIGURE 5 – The temporal and spatial variation of total Cu concentration in sediment samples.

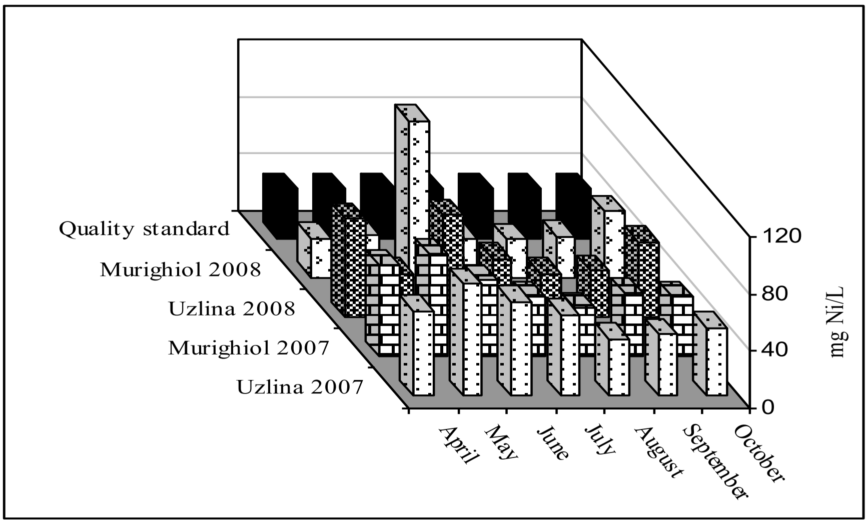

FIGURE 6 – The temporal variation of total Ni concentration in sediment samples.

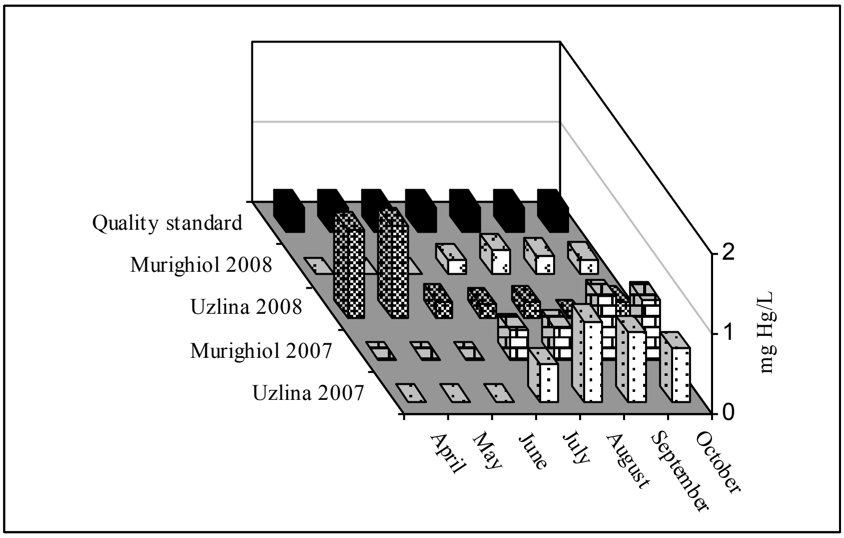

FIGURE 7 – The temporal and spatial variation of total Hg concentration in sediment samples.

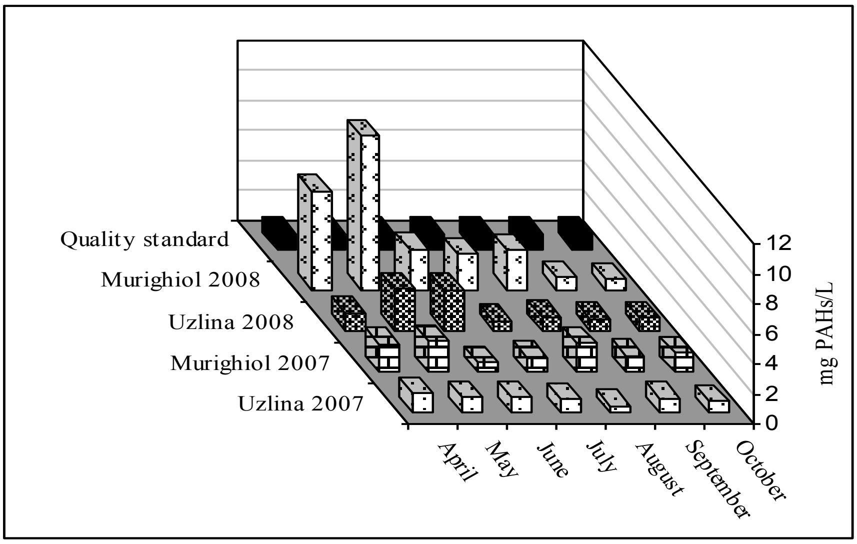

FIGURE 8 – The temporal variation of PAHs concentration in sediment samples.

both sampling points indicating substantial usage of these compounds as pesticides in the river area.

Mobility of heavy metals

It was recognized that only the determination of the total content of heavy metals was not sufficient to assess potential impact on the environment exerted by contaminated sediments. This evidence is due to the fact that only a small part of the metal present in sediment may take part in short geochemistry processes and (or) to become biologically available [28].

The study concerning the availability of metals analyzed in sediments (Cd, Cu, Cr, Zn, Ni, Pb, Mn, Fe and Hg) to migrate into the overlying water showed that Cd, Hg and Cr were not present in a mobile form in sediment samples collected from both locations. The annual average percentages of the mobility of the heavy metals obtained by single extraction procedure described elsewhere [7] are reported in Fig. 9. The results show that the behavior of the studied metals differs considerably, but the mobile form concentrations of each element from Uzlina and Murighiol sediment samples had intra-annual comparable values. The study highlights that at both sampling points Cu, Pb, Zn and Mn amounts present in a mobile form were substantial higher in 2008 than in the previous year. Thus, Pb was the most mobile metal with an average of 29 % in 2007 and increasing to 67 % in the following year. Cu average mobility percentage was 19 % in 2007 and 41 % in 2008. Although the mobility percentage of lead was higher than that of copper, the least was constantly detected in exceeding concentrations and its potential to contaminate the wa-

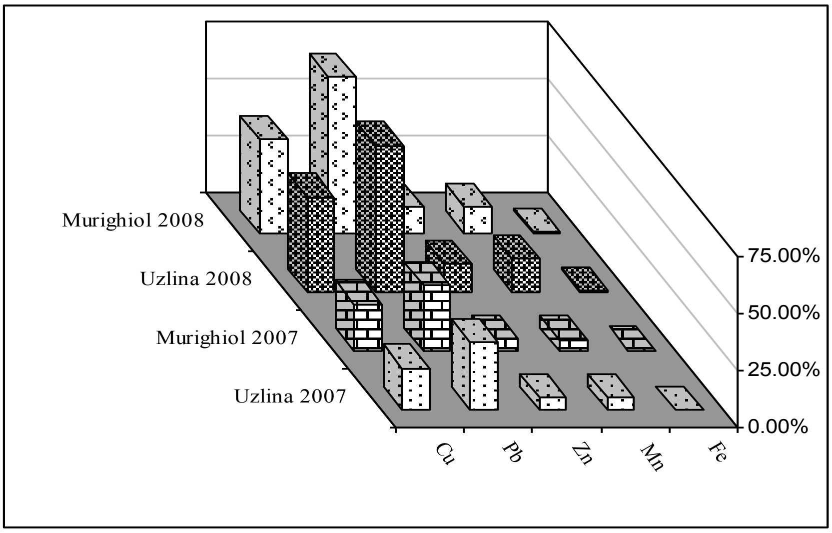

FIGURE 9 – The average of mobility percentage of metals from Uzlina and Murighiol sediment samples.

ter-body was higher. Our earlier studies [6, 7] have shown that Cu and Pb are of particular concern because of their high mobility percentages. Even though nickel was found in high concentrations in sediments, its availability to migrate from this matrix is quite low (1.2-3.1 mg/kg), consequently with a reduced potential to contaminate the overlying water. Generally, heavy metals of anthropogenic origin reach the aquatic environment as inorganic complexes or hydrate ions which are easily adsorbed on sediments through relatively weak physical and chemical bonds [29]. The con-siderable mobile fractions of Cu and Pb found in the collected sediments can be attributed to the input of these metals from anthropogenic sources. A variety of sources might be responsible for the contamination of the Danube River environment with heavy metals, the most important being mining and smelting activities.

CONCLUSIONS

The pollution of the Danube Delta branch (St. George) surface water and sediment with nutrients, metals and several relevant organic toxic compounds was evaluated. The measured values were momentary ones showing the character of contamination levels, relevant for the location and the investigation period.

Several organic toxic compounds were detected in the water and sediment samples during the monitoring period. Although their concentration levels were generally low, a seasonal influence was observed in the concentrations of some organochlorine insecticides (lindane, heptachlor, endrin, DDTs), mineral oil, PAHs and PCBs that were higher from April to June.

From all metals studied, Cu, Pb and Ni appear to be of particular concern because of their high total concentration levels found in the sediments of both channels. The large amounts of Cu and Pb found in mobile fractions of the sediment samples may have significant adverse impact on chemical and ecological status of the river water, especially during the low-flow seasons.

Target analysis of selected pollutants showed that they were present, occasionally in high concentration, in the investigated samples, 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, birds) 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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