

**INVESTIGATION OF PHYSICAL AND CHEMICAL QUALITY
OF SURFACE WATER AND SEDIMENT IN SEVEN LOCATIONS
FROM DANUBE DELTA, IN THE PERIOD 2009-2011**

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The purpose of this paper was to investigate distribution of organic and inorganic contamination in water and sediment in different locations of Saint George Branch -the southern branch of the Danube Delta. Concentrations of dissolved oxygen, nutrients, metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), mineral oil were analyzed in water and sediment samples and the results were compared to those obtained in the previous works [1,2,3,4].

Sampling was monthly performed in the period 2009-2011 from seven locations of Saint George Branch from the Danube Delta.

The obtained values 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 [5].

In Danube river water, the content of heavy and toxic metals was in most cases below the limits according to the national legislation, only iron values

exceed the limit. Concerning organic compounds, mineral oil, DDTs and PCBs periodically were recorded in river water over the limit.

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

Keywords: Saint George Branch, water, sediment, physical-chemical investigation, seven locations

The Danube River with a length of 2780 km is the second largest river in Europe and drains an area of 817,000 sq. km. The Danube River discharges into Black Sea through a delta, which is the second largest natural wetland in Europe. The Basin is characterized by an aquatic ecosystem with numerous important wetlands and floodplains. It is of high environmental as well as economic and social value. It supports drinking water supply, agriculture, industry, fishing, tourism and recreation, power generation, navigation, etc. [1]. The use of water resources for economic activities and the release of wastewater without adequate treatment produced changes in the hydrological system. Problems of water quality and quantity have been created, including significant environmental damages, with resulting impairment of public health and quality of life [1].

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.

The results obtained in 5 years of investigation between 2003-2008 [2,3,4,5] 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 branch and carries 23% of the Danube water discharge and 21% of the Danube sediment discharge [6].

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.

The tables and figures presented in this article tried to synthesize multiple data and information obtained during 3 years of investigation 2009-2011. Average values were calculated for each indicator in different seasons (winter, spring, summer, autumn). These averages were compared with other and the results are presented in Figures 2-13.

The indicators analyzed were reported to the reference values of the Romanian Order 161/2006 [7].

There were also locations (for example S1 and S2) and month (February-July) in which in the first phase of the study sampling was not performed. In March 2009, December 2010 and January 2010 sampling was not possible to be performed because of unfavorable weather condition, especially in winter time.

The study aims at elucidating the recent contamination status, connection between the four seasons, weather conditions of each year and values above the limit of some compounds analyzed. In addition, the water and sediment concentrations were compared to guideline values for sediment quality.

MATERIALS AND METHODS

Study area and sample collection

Water and sediment sampling was performed in seven different locations from Saint George branch : S1-Mahmudia site before bifurcation ($45^{\circ}088'N-29^{\circ}095'E$); S2- artificial channel ($45^{\circ}056'N-29^{\circ}171'E$); S3-Uzlina upstream($45^{\circ}076'N-29^{\circ}222'E$); S4-Uzlina upright to the pontoon ($45^{\circ}075'N-29^{\circ}223'E$); S5- Uzlina downstream ($45^{\circ}070'N-29^{\circ}222'E$); S6-Murighiol upright to the pontoon of ship supply($45^{\circ}040'N-29^{\circ}185'E$); S7-the St. George branch at confluence with artificial channel ($45^{\circ}043'N-29^{\circ}192'E$). (Fig1)

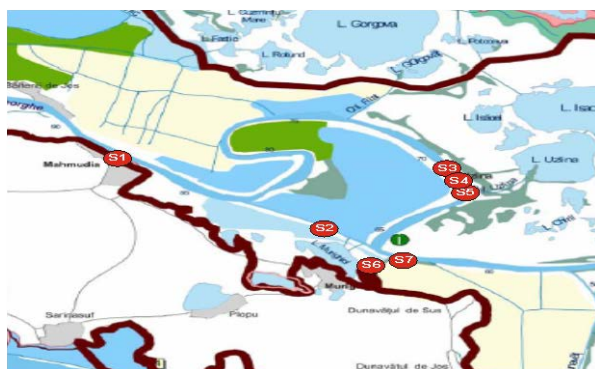


Figure. 1. Map of the Saint George branch with the sampling locations for water and sediments

All water and sediment samples were monthly collected from February 2009 to August 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) [8-11].

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 $4^{\circ}C$ during transportation and the analyses were performed immediately after receiving the samples in the laboratory.

Pollutants and quality indicators

In all the samples (surface water and sediments) were performed analytical determinations of toxic metallic elements such as arsenic, chromium, cadmium, copper, nickel, lead, mercury, iron, zinc and also organic compounds (mineral oil, polyaromatic hydrocarbons - PAH, organochlorine, organophosphorus and triazines pesticides, polychlorobiphenyls - PCB).

Reference comparison values

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 situated in the limits imposed by the quality standards) and bad chemical conditions (one or more parameters exceed the limits imposed by the quality standards).

Methods and equipments

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

Polyaromatic hydrocarbons, PAH's (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 Agilent 1100, HPLC equipment with fluorescence detection.

The quantitative analysis of *total Mineral oil* content was performed with an FT-IR System type Perkin Elmer Spectrum BX II.

The quantitative determination of *pesticides* was performed on a GC System (Agilent Technologies 6890 N) with ECD detector for organochlorine pesticides (α -HCH, β -HCH, γ -HCH, δ -HCH), with NPD detector for organophosphorus pesticides (Malathion, Parathion, Dichlorvos) and triazines 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 type 6890 N, with ECD detector.

Analytical techniques used for determination of metallic elements from water and sediment samples were flame atomic absorption spectrometry performed on THERMO SCIENTIFIC M6 DUAL SOLAAR equipment; cold-vapor technique coupled to AAS using an ATI UNICAM SOLAAR 929 Spectrometer; ICP-EOS technique with PERKIN ELMER OPTIMA 5300 DV equipment.

RESULTS AND DISCUSSION

The occurrence of the selected pollutants and their temporal and spatial distribution in 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 [7].

Water samples

In all period the water course analyzed in the studied locations presented a high organic load. The BOD and COD values at S6-Murighiol upright to the pontoon of ship supply location, exceeded the imposed limits in summer of 2011, the highest values being of 14.2 mg O₂/ L for BOD and 34.69 mg O₂/ L for COD (Figures 2 and 3).

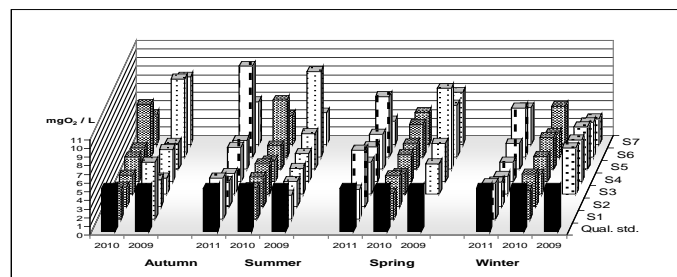


Figure 2: The temporal and spatial variation of BOD in Danube river water

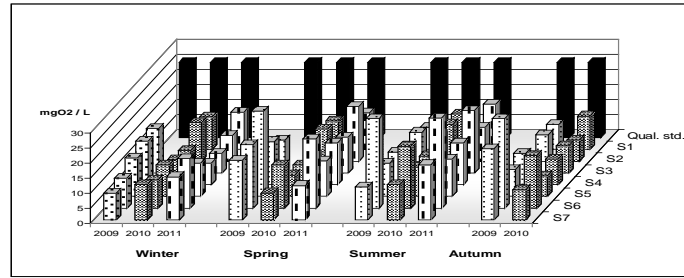


Figure 3: The temporal and spatial variation of COD in Danube river water

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

The level of nutrients (mineral nitrogen, total phosphorous) 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 S4-Uzlina upright to the pontoon location (1.05 mg / L) in February 2010 (Figures 4).

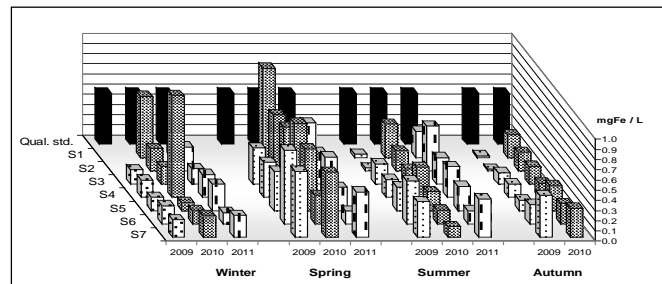


Figure 4: The temporal and spatial variation of Iron in Danube river water

Concerning organic compounds: mineral oil, DDTs and PCBs periodically were recorded concentration over the limit.

Concentrations of mineral oil in water samples from all seven locations are presented in Figures 5. 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 in S6-Murighiol upright to the pontoon of ship supply location, in June 2009 and in S7-the St. George branch at confluence with artificial channel, in February 2010.

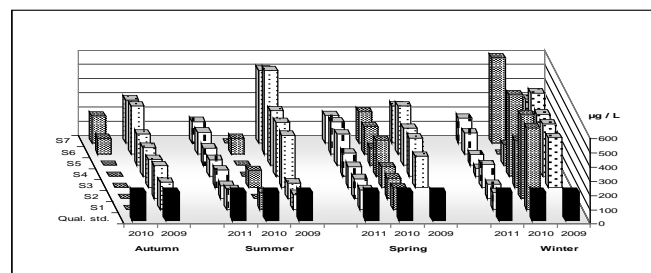


Figure 5: The temporal and spatial variation of Mineral Oil (µg/L) in Danube river water

The variation of DDTs in Danube river water is presented in Figure 6. The highest DDTs (sum of DDT, DDE, and DDD) concentrations are detected in S7-the St. George branch at confluence with artificial channel location, from April 2010 to August 2011. In March 2011 was recorded the value of 0.625µg/L which exceeded the limit value (0.025 µg/L). Figure 7 illustrates the composition of DDTs in S7-the St. George branch at confluence with artificial channel location in the same period. The balanced proportion of $\Sigma(\text{DDE} + \text{DDD}) / \text{DDT}$ in this study indicates that degradation of DDT occurred slowly.

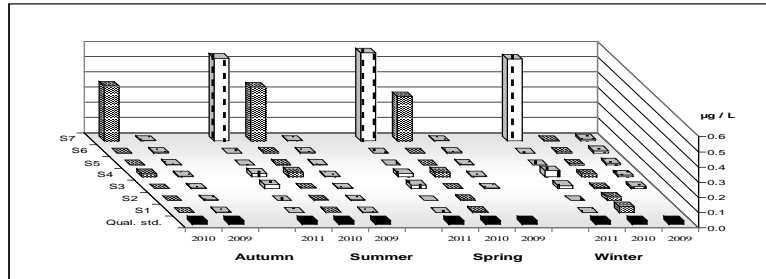


Figure 6: The temporal and spatial variation of DDT/DDE/DDD in Danube river water

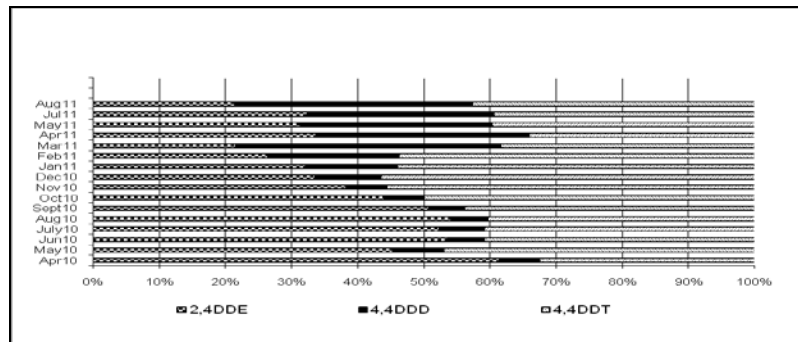


Figure 7: The percentage variation of DDT/DDE/DDD in Danube river water in S7-the St. George branch at confluence with artificial channel location

Other persistent organic pollutants detected in June 2009 in the surface water of the three locations from Uzlina (S1 Mahmudia site before bifurcation, S2-artificial channel, S3- Uzlina upstream) were polychlorinated biphenyls (PCBs), which concentrations ranged from 0.003 to 0.013 µg/L.

Sediment Samples

In most samples the concentrations of heavy and toxic metals in the Danube sediments, correspond to the norms for the aquatic organisms' protection. The exception was the presence of copper (Figure 8), mercury (Figure 9) and nickel (Figure 10).

The highest average value for copper two times higher than the admissible limit was found in autumn 2010 in November (with nominal value of 83.80 mg/kg) in S4-Uzlina upright to the pontoon location. The limit for mercury (0.3 mg/kg) was exceeded in winter 2009 in S6-Murighiol upright to the pontoon of ship supply and S7-the St. George branch at confluence with artificial channel locations (0.48 mg/kg respectively 0.46 mg/kg), in February. Nickel recorded higher

values than the admitted limit in all period and studied locations but the highest value was recorded in September 2010, in S5- Uzlina downstream (93.5 mg/kg).

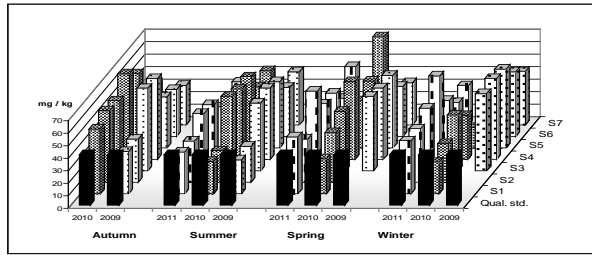


Figure 8: The temporal and spatial variation of Cu in sediment

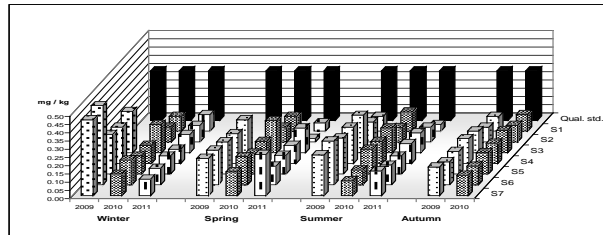


Figure 9: The temporal and spatial variation of Hg in sediment

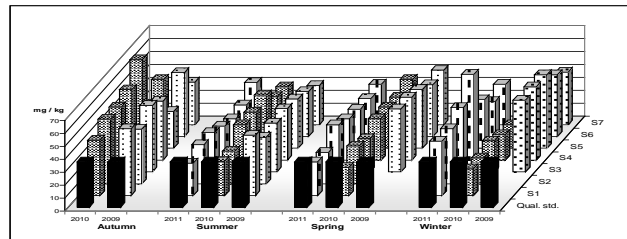


Figure 10: The temporal and spatial variation of Ni in sediment

In the Romanian Order 161/2006 of the Romanian Ministry of the Environment and Water Management, transposed from Water Frame Directive 2000/60/EC [7], the concentration for mineral oil in sediment is not imposed. In Figure 11 are presented concentrations of mineral oil (mg/kg) in sediment samples collected from all the locations. The lowest values were recorded from July to October 2010, possibly because of the floods from that period. The highest value was 553 mg/kg in February 2010, in S6-Murighiol upright to the pontoon of ship supply location.

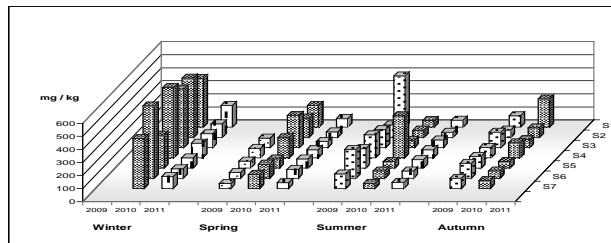


Figure 11: The temporal and spatial variation of Mineral Oil (mg/kg) in sediment

In this study, the presence of polycyclic aromatic hydrocarbons (PAHs) over order limits was detected (Figure 12). The highest values were found in S6-

Murighiol upright to the pontoon of ship supply location in February 2011 (21.3 mg/kg) while the maximum admissible value was 1 mg/kg .

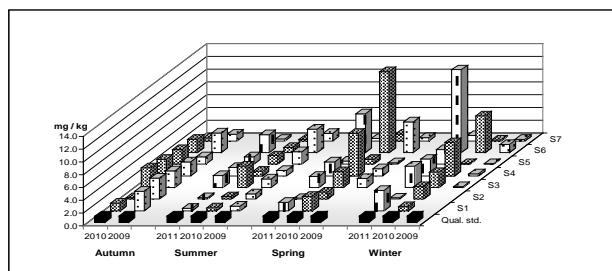


Figure 12: The temporal and spatial variation of PAH in sediment

DDTs (sum of DDT, DDE, and DDD) and HCHs (sum of α -HCH, β - HCH, δ -HCH, and γ -HCH) are two groups of OCPs that have been frequently detected in sediments of the previous studied locations [4,12]. S6-Murighiol upright to the pontoon of ship supply was a location with higher concentration of DDTs in autumn of 2010, with nominal value of 29.10 μ g/kg in November (Figure 13).

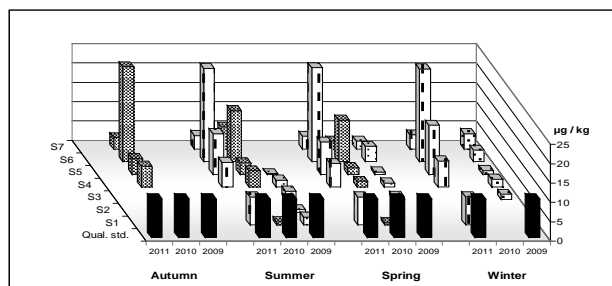


Figure 13: The temporal and spatial variation of DDTs (μ g/kg) in sediment

In the case of HCHs, γ -HCH (Lindane) was the dominant isomer in sediments. The highest value (0,05 mg/kg) was found in S3- Uzlina upstream location in August 2011.

In all studied period in S1- Mahmudia site before bifurcation and S3- Uzlina upstream locations concentration values of endrine exceeded the quality standard and in S1- Mahmudia site before bifurcation location, heptachlor concentration.

The highest concentration of PCB's, were detected in August 2009, in all studied locations.

CONCLUSIONS

In this study were monitored seven locations from the southern branch of the Danube Delta- Saint George Branch in different weather conditions (floods and droughts), seasons, who may influence the degree of pollution of water and sediment from the investigated areas.

The pollution of surface water and sediments on St. George branch from the Danube Delta with nutrients, metals organic load and several relevant organic toxic compounds was evaluated.

The analyzed period included a dry year (2011), a rainy year with floods in June (2010) and a normal year (2009).Organic loading as BOD and COD was higher

in 2011 than 2009 and than 2010:2011>2009>2010. Also the mineral oil concentrations were lower in 2010, during floods.

In water samples were recorded high concentration values of mineral oil and organic load in summer, in S6-Murighiol upright to the pontoon of ship supply location.

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 exceeds the limit. Concerning organic compounds, mineral oil, DDTs and PCBs periodically were recorded in river water over the limit.

In some locations, in sediment were detected higher concentrations of copper, nickel, mercury, Lindane, PAHs, DDTs and PCBs who exceeded the quality standards according to Romanian legislation transposed from Frame Water Directive 2000/60/EC. Results show that in S6 location mineral oil and PAH's concentrations are higher in winter and concentrations of copper, nickel and DDT s are higher in autum.

The presence of iron, DDTs, PCBs, mineral oil in surface water may create adverse effects on human health and ecosystems.

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

Bibliography

- [1] MALJEVII, E., BALAI, M., Desalination, 213 (2007), p.135–140.
- [2] VASILE, G., PETRE, J., MITRITA, M., IANCU, V., PASCU, L., NICOLAU, M., CRUCERU L., VOSNIAKOS, F. International symposium the environment and industry, 25-27 october 2007, Bucharest, Romania.
- [3] PASCU, L., PETRE, J., VASILE, G., IANCU, V., STANILOAE, D., DINU, C., NASTAC, E., CRUCERU, L., NICOLAU, M., International symposium the environment and industry, 28-30 october 2009, Bucharest, Romania.
- [4] VOSNIAKOS, F., PETRE, J., PASCU, L., VASILE, G., IANCU, V., STANILOAE, D., NICOLAU, M., CRUCERU, L., GOLUMBEANU, M., Fresenius Enviromental Bulletin, **19**, nr.1, 2010, p. 20-29.
- [5] PASCU, L., PETRE, J., VASILE, G., IANCU, V., STANILOAE, D., DINU, C., NICULESCU, M., NASTAC, E., CRUCERU L., NICOLAU, M., A-31-a Conferinta Nationala de Chimie, 6-8 octombrie 2010, Ramnicu-Valcea, Romania.
- [6] Jugaru Tiron, L., Le Coz, J., Provansal, M., (2009), , Geomorphology (106), 186-197.
- [7] 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.
- [8] SR ISO 5667/1:2007, Water quality. Sampling. Part 1: Guidance on the design of sampling programmers and sampling techniques
- [9] SR ISO 5667/3:2002, Water quality. Sampling. Part 3: Guidance on the preservation and handling of samples
- [10] SR ISO 5667/6:1997, Water quality. Guidance for the sampling of rivers and streams water
- [11] SR ISO 5667-12/2001, Water quality: Guidance on sampling of bottom sediments
- [12] Vosniakos, F., Vasile, G., Petre, J. (2008) The evolution of physical-chemical quality state of the Danube Delta Aquatic Ecosystem in the period May-October of years 2005 and 2006. Fresenius Environmental Bulletin 17(1), 372 – 389.