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EVOLUTION OF PHYSICOCHEMICAL QUALITY OF THE DANUBE DELTA AQUATIC ECOSYSTEM STATE IN THE PERIOD MAY-OCTOBER IN 2003-2005

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Abstract. The main objective of this paper is to provide data on the Danube delta quality based on the long-term specific indicators of laboratory analysis results. There were investigated the physicochemical properties of water and sediment samples collected from the Uzlina and Murighiol locations during the period May-October of the consecutive years 2003, 2004 and 2005. The comparative analysis of the quality characteristics of the Danube delta aquatic ecosystem in these three years emphasised a dynamic character of the water quality that can determine an evolution into the unfavourable stages which lead to worsen life conditions for aquatic organisms.

Keywords: water, sediment, the Danube delta, evolution, physicochemical parameters.

AIMS AND BACKGROUND

Monitoring is a 'continuous standard measurement and observation'[1]. The primary objective is to measure the impact of environment (because of human intervention through industrial activities, agricultural and transport) on water quality and the suitability of water quality for future use. Chemical analysis of sediments provides an efficient tool for water quality management. Sediment is an integral and dynamic part of river basins. Sediment originates from the weathering of minerals and soils upstream and is susceptible to transport downstream by the river water[2]. Monitoring of sediment contaminants and assessment of sediment quality are usually carried out with the objectives of determining the extent to which the sediments are a source for contaminants and evaluating the effects of these contaminants on the environment of the investigated water body.

The knowledge of the fixation mechanisms of heavy metals is an important parameter for the risk assessment concerning the pollution of the ecosystems.

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Mobility and availability are highly dependent on the way and the strength of the fixation of the heavy metals by the sediments components.

The release of heavy metals into the aquatic environment is known to cause detrimental effects to the environment. Most heavy metals entering water bodies become associated with particulates and as a result of setting time, accumulate in bottom sediments of the receiving water.

For these reasons is very important to monitor the quality of the river water and also the quality of sediments from the water body.

The main objective of this paper is the monitoring of the Danube delta aquatic ecosystem in two location, Uzlina and Murighiol, sites from Sfantu Gheorghe branch. The results of the analyses provided relevant information on the ecosystem quality, with the focus on the physicochemical determination

The tasks performed in order to obtain a correct average evaluation of the quality state of the monitoried aquatic ecosystems were:

- Physicochemical characterisation of the momentary water samples monthly collected from the Uzlina and Murighiol location;
- Determination of the chemical quality parameters of sediment specified in the Norm concerning the reference objective for the surface water quality classification[3];
- Evaluation of the harmonisation with the quality class with the aim to establish physicochemical water quality in accordance with the limiting values specified in the Norm[6];
- Study of the mobility of heavy metals from sediment into water body.

Corroboration of the results on the physicochemical parameters determination with the biological, bacteriological, radioactivity parameters makes possible the appreciation of the pollution risk in the surveyed aquatic basin and the intervention of the Danube Delta Biosphere Reserve Association (DDBRA), in damage case.

EXPERIMENTAL

Samples were taken from water and sediment stock compartments from the Uzlina and Murighiol locations during sampling campaign period May-October 2003, 2004 and 2005. The collected samples represent momentary water and sediment samples. The samples were taken in accordance with the recommendations of the specific guides of sampling[4-6]. The water samples were preserved when collected in accordance with the prescriptions of the used specific methods of analysis. The sediment samples collected for investigation of inorganic and organic constituents were stored in glass jars, air-tight containers, at 4°C to avoid the process of oxidation. The samples were analysed as soon as possible after collection.

The water quality parameters which were monthly analysed were: pH, conductivity, dissolved oxygen, residue filterable, COD-Cr, BOD_5, heavy metals

(Fe, Mn, Zn, Cd, Cr, Cu, Ni, Pb, As and Hg), ammonium, nitrate, total nitrogen, *o*-phosphate, total phosphorus, chlorides, sulphates, anionic surfactants, mineral oil, PAHs, phenol index, Lindane, Atrazine and PCB.

The sediment samples were subjected to the following analyses: the mobile and total content of metals (copper, zinc, cadmium, chromium, lead, mercury and arsenic), γ-Lindane and benzo(a)pyren.

The analyses were done from homogeneous water and sediment samples[7]. Separation of the taken sediment was carried out in the laboratory and fraction <63 μm was prepared for further laboratory analysis. An aliquot of the prepared sample was digested in a microwaves digestion apparatus in accordance with the AAS standard method for the determination of total heavy metals. Another part was lyophilised, extracted and quantitatively analysed for the adsorbed organic pollutant presence.

For mobile forms of heavy metals from sediments the analyses were performed in accordance with the French standard NF X31-120/1992 (Ref. 8).

The working conditions consisted in: 40 g of pre-treated sediment were mixed with 40 ml of buffer solution of 1M ammonium acetate and 0.01 M EDTA. The obtained suspension was shaken 2 h with 40 rot./min. The solution obtained were filtered and than analysed by flame AAS method.

RESULTS AND DISCUSSION

The results of the study concerning the physicochemical quality state of the deltaic ecosystems from the Uzlina and Murighiol locations, carried out in the period May-October of years 2003-2005, showed an oxygen deficit and the presence of some chemical parameters (heavy metals, phenol compounds, mineral oil, *o*-phosphates, Lindane) in concentrations which exceed the reference values in principal in 2003 and 2004. In the same period of 2005, the results of physicochemical parameters showed that majority of pollutants are in normal limits for class II of water quality[3].

The temporal evolution of the parameters which presented higher concentrations compared with the references values[3] is presented in Figs 1-10.

The changes in the physochemical quality of the investigated water body from the Danube delta in the Uzlina and Murighiol locations in 2005 in comparison with the proceeding years are as follows:

– Uzlina location:

- higher organic load (BOD) in September and October, lower organic load during the other months;
- high concentration of iron, but lower than in proceeding years;
- concentration of phenol compounds in July and August higher than that for class IV and similar with the concentration recorded during last years;

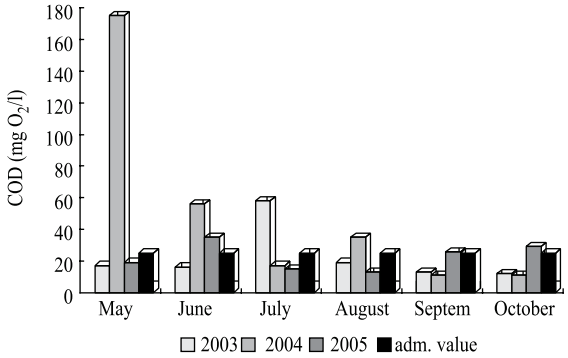

Fig. 1. Variation of COD concentration in the Uzlina location

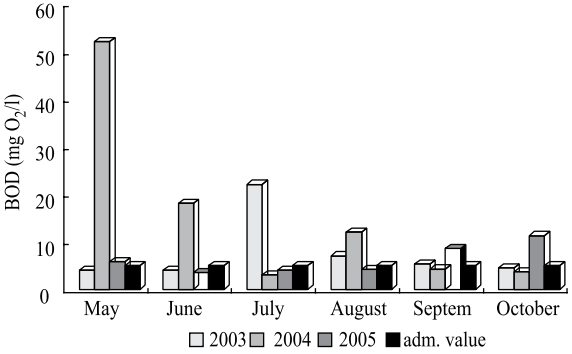

Fig. 2. Variation of BOD concentration in the Uzlina location

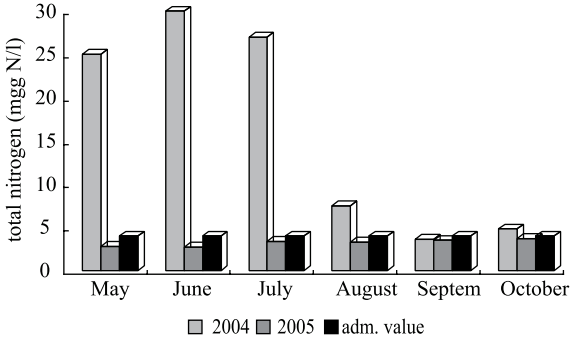

Fig. 3. Variation of nitrogen concentration in the Uzlina location

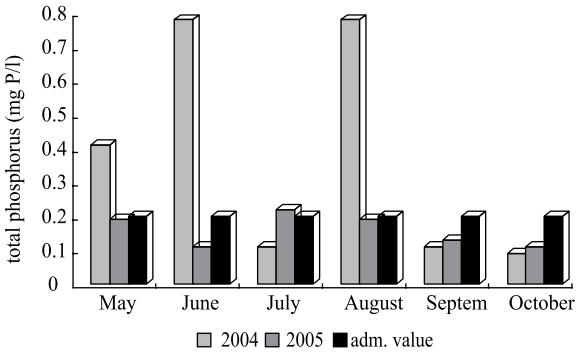

Fig. 4. Variation of total phosphorus in the Uzlina location

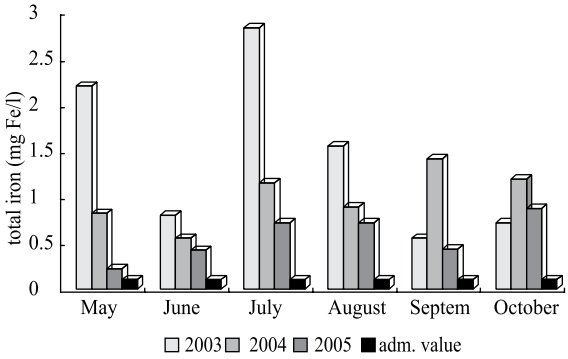

Fig. 5. Variation of total iron in the Uzlina location

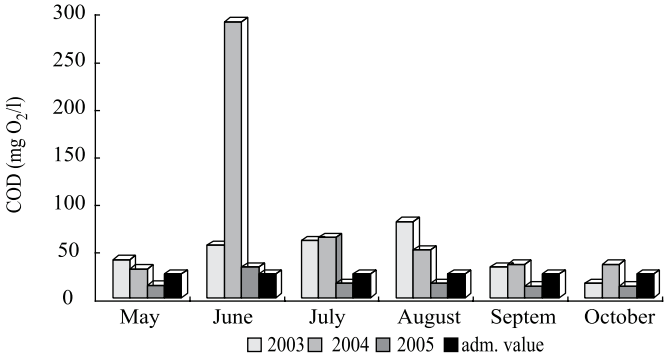

Fig. 6. Variation of COD concentration in the Murighiol location

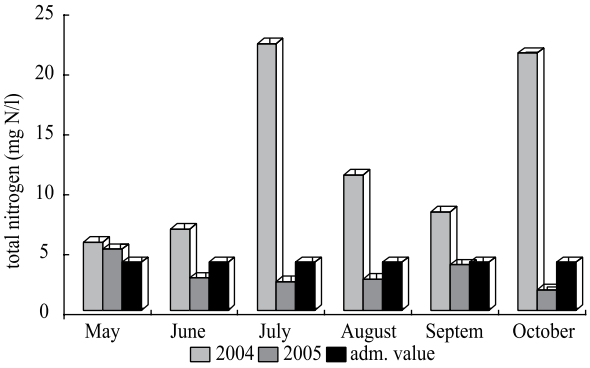

Fig. 7. Variation of total nitrogen in the Murighiol location

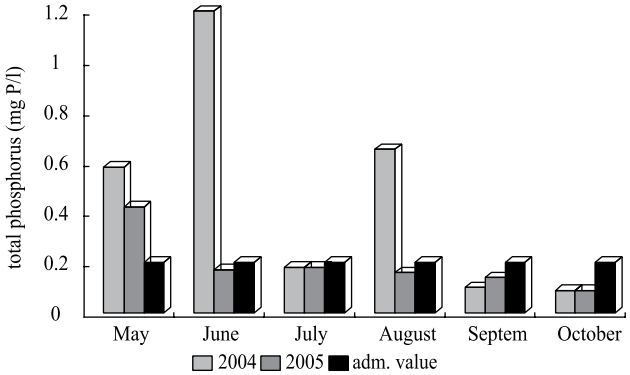

Fig. 8. Variation of total phosphorus in the Murighiol location

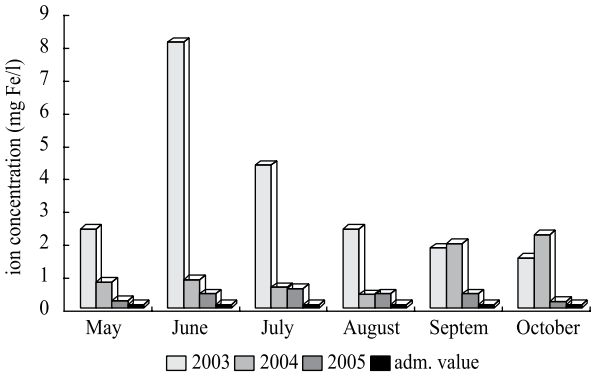

Fig. 9. Variation of total iron concentration in the Murighiol location

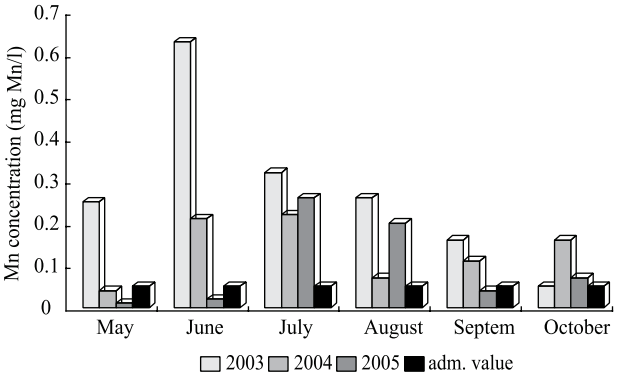

Fig. 10. Variation of manganese concentration in the Murighiol location

● lower lever of nitrogen, phosphorus compounds, copper and manganese.

– Murighiol location:

● lower organic load (both COD and BOD);

● lower concentration levels for orthophosphates, nitrogen compounds;

● high concentration of iron, but lower than in proceeding years;

● lower concentration of manganese with two exceptions in July and August 2005 when were recorded higher values than in 2004.

The concentrations of total heavy metals extracted with 'aqua regia' from sediment samples had a uniform distribution along the entire period of time in both locations and are situated under the reference value for river sediment. Comparing with proceeding years, mercury and cadmium were founded in the body of sediment, but the values are situated in normal levels of concentration. These changes may be a cause of strong floods, who affected the whole territory of Romania in 2005 and the hydrodynamic conditions of many rivers were altered.

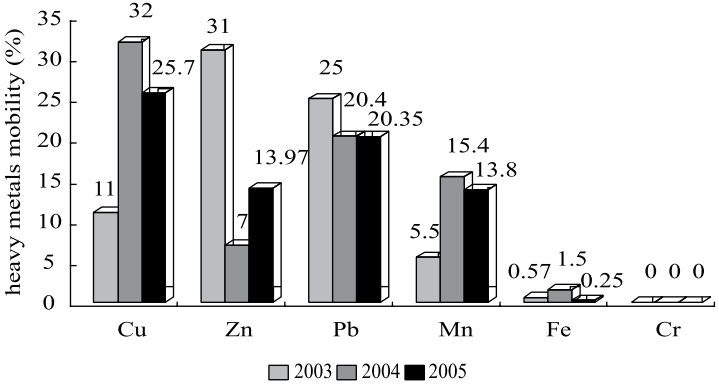

Fig. 11. Percentage of mobility of heavy metals from sediments sampled from the Uzlina location

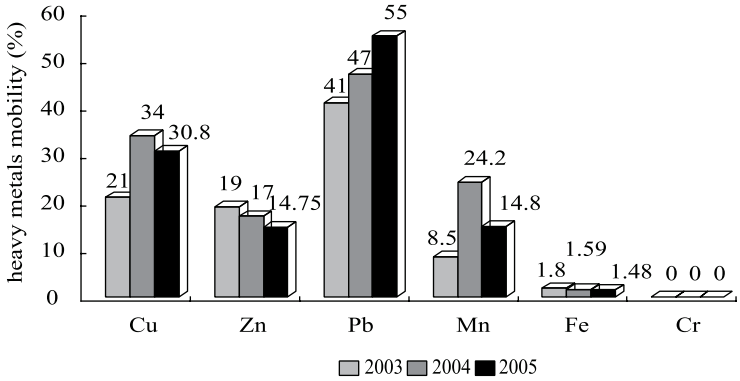

Fig. 12. Percentage of mobility of heavy metals from sediments sampled from the Murighiol location

The study of the availability of the following heavy metals: Cu, Zn, Pb, Mn, Fe and Cr to migrate from sediment into aquatic body (Figs 11 and 12) emphasises the following aspects:

– Uzlina:

● the concentrations of Zn, Cu, Mn and Fe in mobile form were higher during this year, because of the increase of the total concentrations (Cu, Mn and Fe) and the mobility (Zn);

● the concentration of mobile Pb was situated in the same range.

– Murighiol:

● the sediments presented lower percentages of mobility than in 2004;

● the concentration of Pb in mobile phase decreased in 2005 and that can be due to the lower total concentration of this metal in sediments;

● the increase of about 2.5 times of the manganese concentration in mobile form (similar during 2004);

● there have not been recorded significant changes of Zn, Fe, Cu mobile form concentration.

In both locations, total Cr, Cd and Hg in mobile phases were not found.

CONCLUSIONS

The pollutants found out in concentrations that exceeded the limits represent a potential for water quality alteration by negative influences on autopurification of the river by the diminution of the biological activity.

The measured values were momentary values and showed only the character of the contamination level relating to the period and locations of the investigation campaign development.

In general, in 2005, all the investigated parameters from watercourse were situated in the limits for the references value for II class quality, in principal thanks to dilution of water (strong floods in different counties of Romania, with the major impact to the rivers).

The adsorbed heavy metals concentrations in the sediment particles smaller than 63 μm (Cu, Zn, Cr and Pb) were in a relative uniform distribution within the scheduled investigation, in the both locations and below the established criteria for the pollution. Arsenic was below the determination limits of the analytical method used. Regarding heavy and toxic metals, it can be generally concluded that the sediments were favourable for the aquatic organisms' development in the watercourses.

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