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18. Long-term nutrients and heavy metals concentration dynamics in aquatic ecosystems of Danube Delta

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Abstract: This study aims to make an overview of the last fifteen years of contamination freshwater, in the Danube river, branches and delta lakes. The water quality of the river and Delta lakes was described by analysing the data for nutrients and some heavy metals. The concentrations elements (Zn, Cd, Cu, Pb) in the water are compared with heavy metals in fish, captured in natural delta lakes. Bioconcentration factor (BCF) is described in some commercial fish species.

Keywords: Water Framework Directive; ecological status; eutrophication, heavy metals, nutrients, fish, bioconcentration factor

INTRODUCTION

The Danube is the EU's largest international river basin district, stretching across ten Member States and nine neighboring countries. The Danube illustrates the great variety in Europe's waters: includes mountain streams in the Carpathians and the Alps as well as major rivers, groundwater bodies across many different geological formations, and the Danube Delta and Black Sea coastal waters (Figure 1).
The Romanian geographic literature referring to the Danube Delta (Gastescu and Driga 1989), describe the area downstream the first bifurcation of the Danube river, bordered by the Black Sea to the east, the Chilia branch to the north and Razim-Sinoe lagoon complex to the south. Compared to the Black Sea level, only 20.5% of delta areas is below 0 m, the major proportion being above 0 m (79.5%).

The Danube is transporting higher amounts of water during spring and at the very beginning of winter. The discharge is smaller in the summer-autumn period. This water flow pattern determines some of the specific features of the ecosystems abiotic compartment: flooding plays the most important role in water renewal and the removal of some important quantities of N, P, H_2S (that contribute to water eutrophication) and the deposition of suspended sediment load; depending on the duration of the flooding period, there are temporary changes in the terrestrial, semi-aquatic and aquatic environments, these changes have a major influence on the structure of the living communities.

As a result of these changes, the flooded terrestrial and aquatic ecosystems play an important role in the increase of the primary production of the aquatic ecosystems. After the flood period has ended, the secondary production of the Danube Delta terrestrial and aquatic ecosystems depends on their primary and secondary production during flooding. This regular take-over of functions by the different types of ecosystems, during flooding stages, is an important characteristic of the delta system reflecting its completeness (Gastescu *et al*. 1998).

Danube river splits in three main branches, Chilia, Sulina and Sf. Gheorghe. The first bifurcation of the Danube, Chilia branch at the beginning split off in Tulcea branch (city Tulcea) and downstream the city the southern branch Sf. Gheorghe (Saint George). The middle branch is Sulina, used for navigation to the Black Sea (Fig. 1).

Some important hydrological parameters of the Danube and the main branches are:

- a flow speed of 0.3-0.5 m/s at low water levels and 0.6-1.2m/s at high water levels,
- the turbidity due to the alluvia in suspension of 290 gr/m^3,
- the uniformity of the distributed dissolved oxygen of 10-11 mg/L,
- the mineralisation of about 340 mg/L, and the hydro-chemical type of the water is calcium

These parameters provide good conditions for life, for the development of biocenoses and of characteristic populations (phytoplankton, zooplankton, macroinvertebrates). These compartments build up the trophic chains which make possible the existence of the diverse fish species.

The total area of Danube Delta is about 5600 km^2 for this only 3300 km^2 is located in Romania the other part is situated in Ukraine (Oosterberg *et al.* 2000).

From the point of hydrographic characteristics, Danube Delta is divided in two main subunits: the fluvial delta, situated to the west and the fluvio-marine delta in east part, up to the Black Sea (Figure 1).
The recent inventory of the Danube Delta lakes acording to the literature (Gastescu *et al*, 2008), show more than 300 lakes with a total area of 25,666 ha (7.82% of total Delta area).

The lakes chosen for these paper are from two aquatic complexes: one from fluvial delta area (Gorgova-Isac complex with lakes Cuibul cu Lebede 196 ha, Isac 1020 ha, Uzlina 483 ha), and another from the fluvio marine delta part (Matita-Merhei complex with lakes Merhei 1057 ha, and Miazazi 130 ha) (Fig. 1).

Lakes in the Danube Delta are not isolated, being part of a large riverine system. From the hydrological point of view the river and floodplains must be considered as an indivisible unit because of their common water, e.g.: all the lakes for each aquatic complex are interconnected by channels.

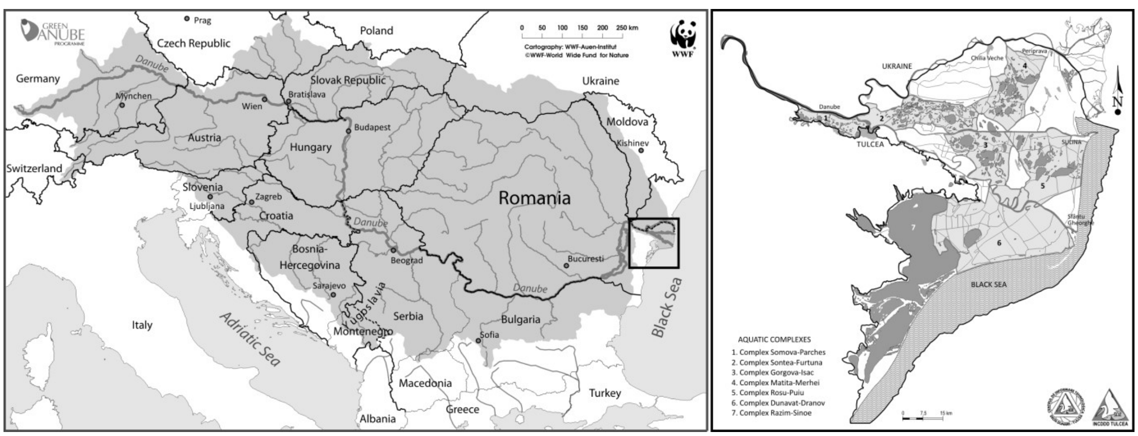

Figure 1 The location of the Danube river, branches and delta lakes complexes described in the term paper (Danube Delta National Institute - map for aquatic complex).

A major role in terms of danger to the Danube Delta aquatic ecosystem is played by heavy metals, which stand out by their persistence and accumulability. Monitoring programs for nutrients and heavy metals on freshwater ecosystems and research effects on fish species have been widely studied because of their economic and regression value. (Tudor *et al.* 2006).

MATERIAL AND METHODS

In the monitoring program of Danube Delta National Institute for Research and Development, water samples were collected in accordance with SR ISO 5667/1998. For heavy metals, it was taken 500 mL of water and fixed with 2.5mL concentrated nitric acid. Determination of the total heavy metal concentration is on an unfiltered water sample (Teodorof *et al*. 2015).

For the analysis of heavy metals in the fish muscles tissue, was collected about 10g of samples of each individual adult species. The adult fish (ten individual for each species) was colected once a year in summer. All reagents used have high chemical purity and are Merck. For the heavy metals extraction was uses concentrated nitric acid and residues.

Calibration solutions for all the heavy metals the flow charts and the calibration curves were made. The calibration curves were made using the Perkin Elmer Pure Plus Atomic Spectroscopy Standard, certified reference material 10 µg/mL, Multi-element ICP-MS calibration STD.3, matrix 5% HNO3. The calibration curves are linear and they are made in five points. Using the Excel interface for each calibration curves were calculated the equations and the R^2 coefficients. The values of 0.9994 – 0.9997, represents a very good correlation between the intensity and the standard concentrations (Teodorof *et al*., 2009; Burada *et al*. 2014).

The Water Framework Directive (WFD; 2000/60/EC; European Parliament and Council 2000) and its transposing legislation (Normativ din 16/02/2006) require an evaluation of ecosystem quality in rivers, lakes and transitional waters, based on a variety of 'quality elements', including fish.
The classification must be based on an evaluation of current status of the fish community relative to the value at reference conditions—the ecological quality ratio (EQR)—for the various rivers, lakes and transitional waters.

RESULTS AND DISCUSSIONS

One of the main environmental problems related to the water bodies in the Danube - Black Sea region is due to the high content of nutrients that flows into the Black Sea, both via the rivers and directly from land'based sources. Eutrophication is the main problem threatening the biodiversity and the economic potential of the riverine ecosystems of Danube delta (Galatchi and Tudor, 2006).

In the Danube river the median phosphorus concentration between 1997-1998 was 0.12-0.17 mg P/L, (Oosterberg *et al*. 2000), up-to-date 0.12 mg P/L in 2015 (DDNI laboratory, unpublished data). In the lakes the variation of total phosphorus is more evident than in the river in 2003 when the water level was very low because of the lack of precipitation. The concentration of total phosphorus is lower in Delta lakes than in river in 2012-2015, period (Fig. 2).

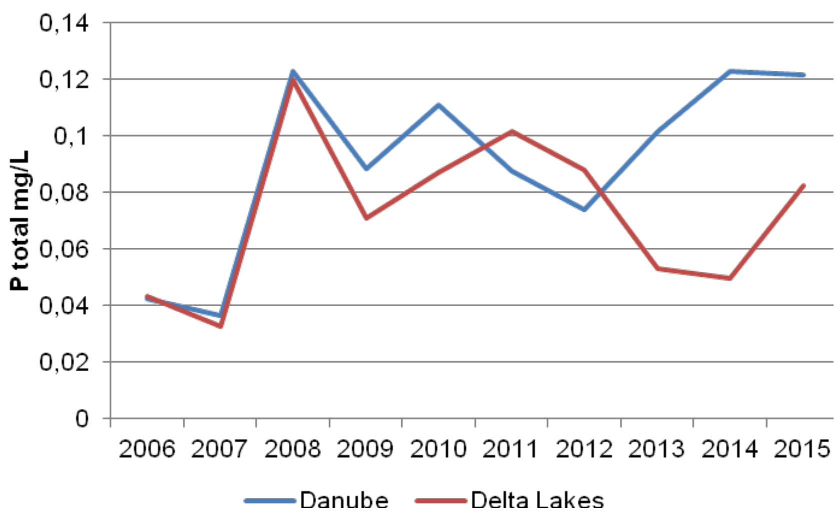

Figure 2 The variation of P-total 2000 to 2015 (median) in Danube river and Delta lakes

The limits of total phosphorus for a good ecological status in accordance with Directive and Romanian legislation are situated 0.15 mg P/L "high ecological status" and >1.2 "bad ecological status".

The median total nitrogen concentration in the Danube river is 8.5 mg N/L. High values in 2008 (19.09 mg N/L in river and 13.62 mg N/L in lakes), coincide with the flood pulse (figure 3).

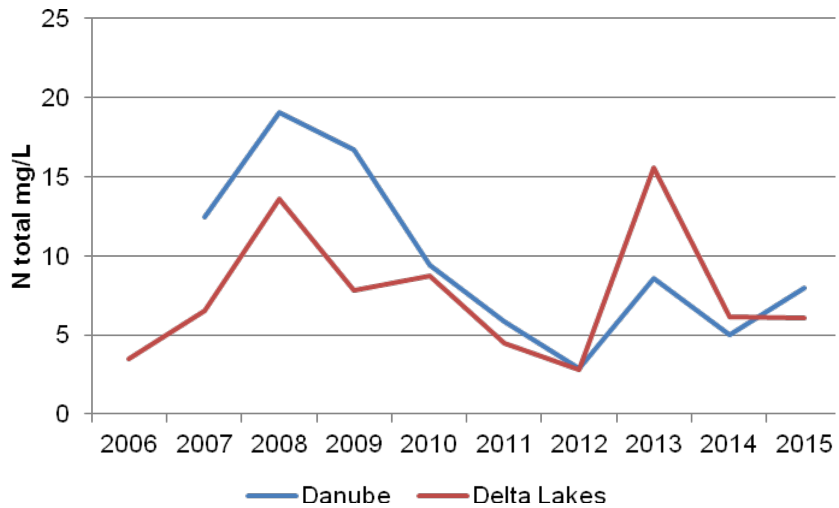

Figure 3 The variation of N-total 2006 to 2015 (median) in Danube river and Delta lakes

In the Delta lakes the total nitrogen concentration is generally lower than in the river-branches (Danube). The total nitrogen concentration in accordance with Directive and RO 161/2006 is situated below 1.5 mg/L- I quality class "for a high ecological status" and >16 mg/L – V quality class "bad ecological status".

The concentration of nutrients in shallow lakes is the resultant of many processes, the most important of which are the external nutrient loading, sedimentation and adsorption, resuspension and desorption, bacterial transformations, uptake by aquatic vegetation and phytoplankton. These processes have not been yet quantified in Danube delta lakes.

Danube river-branches water contains approximately 10 mg/L total Nitrogen concentrations that means II-III quality class "Moderate ecological status" in accordance with Water Framework Directive (WFD).

All the **heavy metals** concentrations values from water are reported to the Romanian Order 161/ 2006 which is the transposed of Water Framework Directive (WFD) into Romanian Legislation.
The classification into the quality classes was made in accordance with Romanian Order 161/2006, regarding the classification of surface water quality to determine the ecological status of water bodies. Elements and biological quality standards, chemical and physico-chemical for setting ecological status of surface waters, Annex C, Elements and chemical, physico-chemical quality standards in water .
The maximal limits recommended by EU 2008 for metals in water are in Table 1.

Table 1. Standard limits in water for Cadmium (Cd), Zinc (Zn), Copper (Cu), Lead (Pb) according by WFD.

Water quality indicators for heavy metals	U/M	Quality class				
		High	Good	Moderate	Poor	Bad
Cadmium (Cd) mg/L	mg/L	0.0005	0.001	0.002	0.005	>0.005
Zinc (Zn) mg/L	mg/L	0.1	0.2	0.5	1	>1
Copper Cu mg/L	mg/L	0.02	0.03	0.05	0.1	>0.1
Lead Pb mg/L	mg/L	0.005	0.01	0.025	0.05	>0.05

In delta lakes waters, reported average Cd concentrations range from 0.001-0.024 mg Cd/L, and have generally decreased since the end of the 2011s.

For their environmental risk assessment, Cadmium concentration in water in the last four years 2012-2015 is moderate, according classification of ecological status (Table 1, Fig. 4)

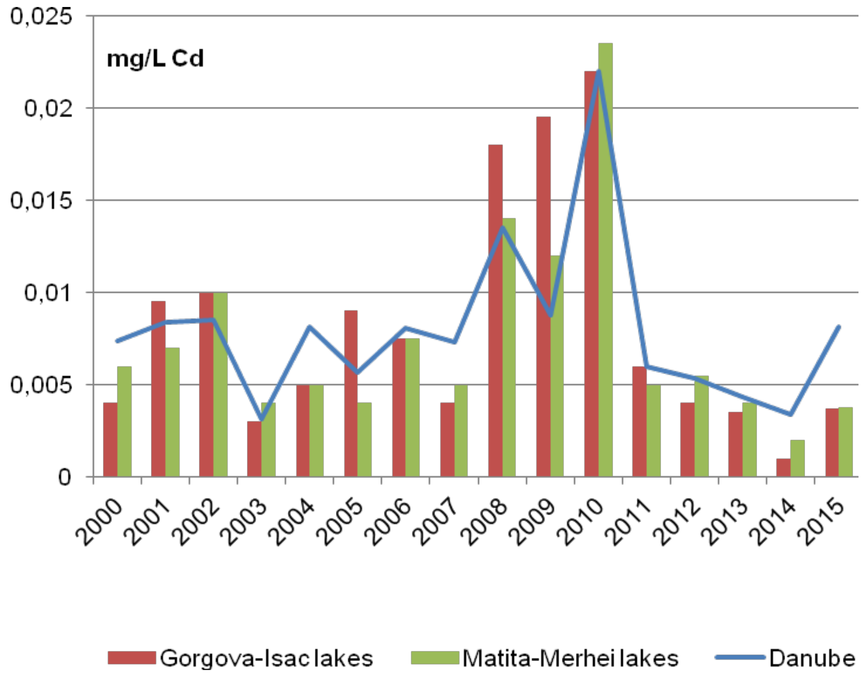

Figure 4 Cadmium concentration (mg/L) in water of the Danube river and delta lakes (median per year).

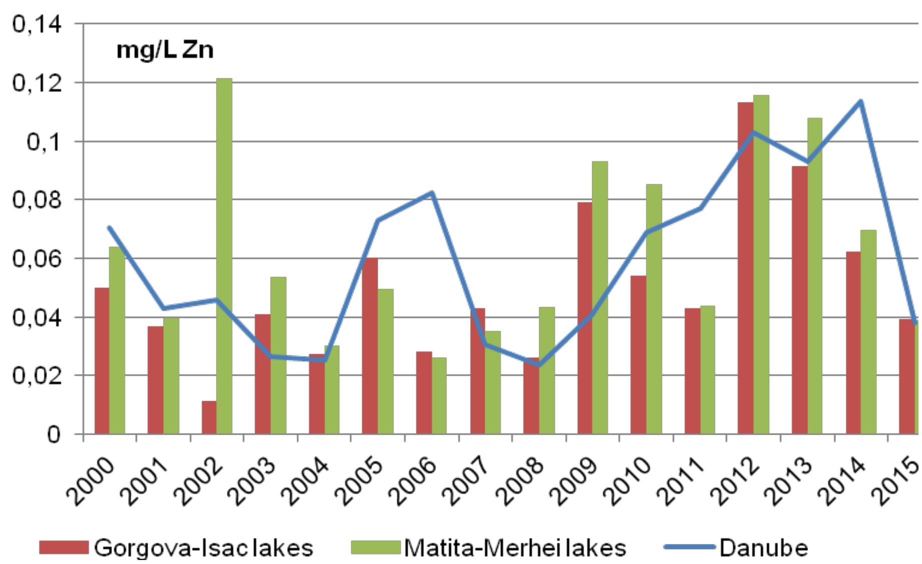

Figure 5 Zinc concentration (mg/L) in water of the Danube river and delta lakes (average per year).
Zinc (Zn) in Danube and delta lakes are in a “good ecological status” (Fig. 5).
The Copper concentrations was high in 2006 in Danube river 0.2385 mg Cu/L after that the limits was under 0.05 mg Cu/L which represents “good ecological status” (Fig. 6).

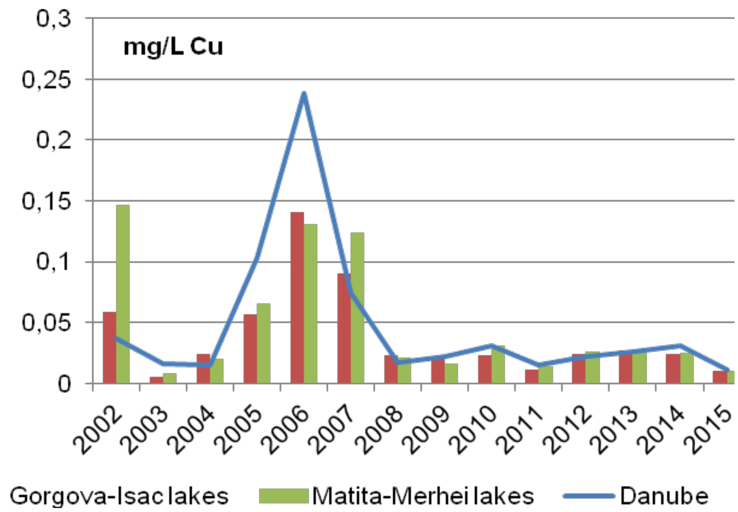

Figure 6 Copper (Cu) concentration (mg/L) in water of the Danube river and delta lakes (median per year).

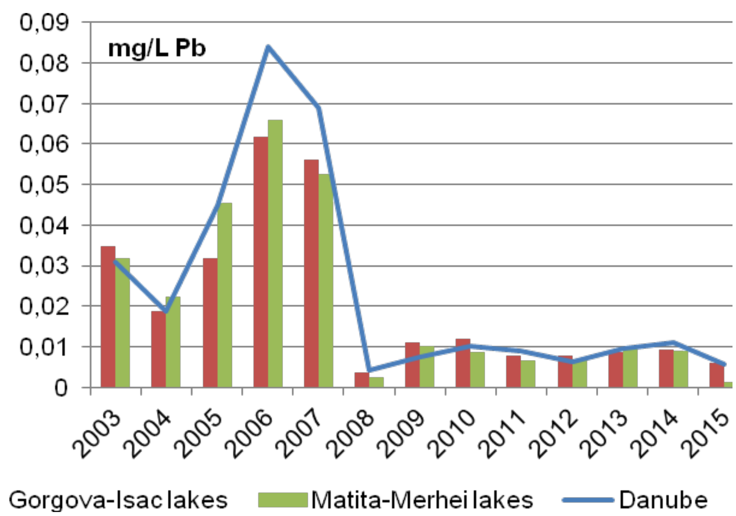

Figure 7 Lead (Pb) concentration (mg/L) in water of the Danube-river and delta lakes (average per year).

The Lead (Pb) concentrations started in 2003 with a high concentration in Danube river 0.030 mg/L and in delta lakes was much more 0.035mg/L which means "poor ecological status", The highest concentration value in water was in 2006 0.084 mg Pb/L in Danube river and 0.065 mg Pb/L in Matita-Merhei complex lakes (Fig. 7), according with WFD representing "bad ecological status" (Table 1).

The heavy metal concentrations for each fish species samples in this study are in a total forms. Metal contents were ranging in the following intervals: **Zn**: 0.437 (carp) – 84.652 (rudd) mg/kg, **Pb**: 0.091(rudd) – 3.866 (perch) mg/kg; **Cd**: 0.030 (rudd) – 3.329 (rudd) mg/kg; **Cu**: 0.253 (tench) – 4.443(zander) mg/kg. Analysis of heavy metals in fish shows maximum values in predatory fish species: rudd, zander and perch.

Bioconcentration factors (BCFs) are used to relate pollutant residues in aquatic organisms e.g. fish species, to the pollutant concentration in ambient waters.

Table 2 Bio-concentration Factors BCF of fish species in Danube delta lakes

Fish species		Zn BCF value	Cd BCF value	Cu BCF value	Pb BCF value
perch	*Perca fluviatilis*	317.67	38.22	62.32	21.25
gibel carp	*Carassius auratus gibelio*	318.69	31.42	59.31	50.58
carp	*Cyprinus carpio*	381.14	10.22	34.20	22.51
tench	*Tinca tinca*	154.56	31.94	37.93	40.74
bream	*Abramis brama*	34.16	29.12	67.57	18.07
rudd	*Scardinus erythrophthalmus*	378.52	25.98	48.59	25.17
zander	*Lucioperca lucioperca*	260.71	61.05	47.36	20.84
catfish	*Silurus glanis*	213.73	14.76	67.13	18.16
pike	*Esox lucius*	558.17	31.03	57.88	17.69

The guidelines of the European Chemicals Agency (ECHA) for REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) suggest using logP for screening (if logP < 4.5, then the substance is non-bioaccumulative). LogP is the logarithm of the partition coefficient between octanol and water. It is considered very important to assess the bioaccumulation potential of a substance (Lombardo et al., 2010).

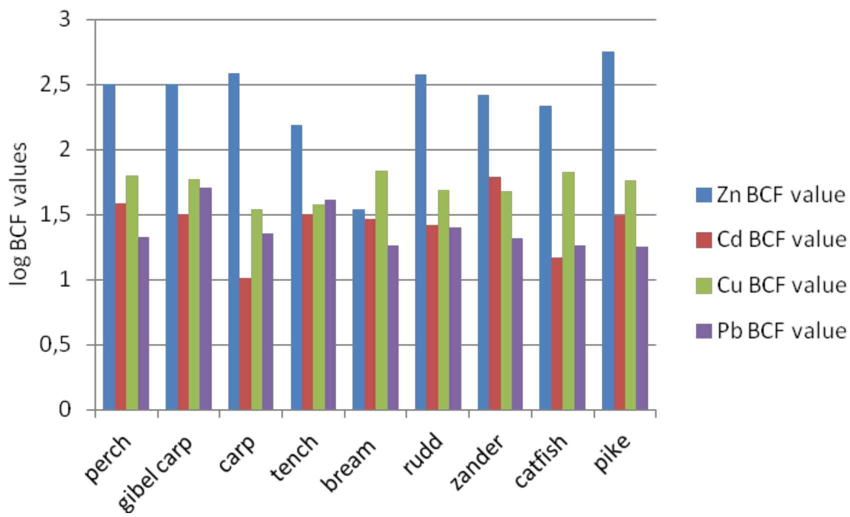

Figure 8 The result of log BCF values in some fish species from Danube Delta lakes

The result of the Bioconcentration factors BCF value are non-bioaccumulative from investigated fish species.

CONCLUSIONS

The values of heavy metals concentrations in the Danube river are higher than concentration in lake ecosystems. Our possible explanation could be the more intense sedimentation processes occurring in Danube compared to lakes coupled with the fact that heavy metals are combined with suspended matter.

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