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HEAVY METALS IN WATER AND SEDIMENTS OF TASAUL LAKE (2005-2006)

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ABSTRACT

The investigation of Tasaul Lake in 2005-2006 yielded the following heavy metals concentrations: in water cadmium 0.3 ±0.14 µg/l; chromium 2.6 ± 0.37 µg/l; copper 12.4 ±3.19 µg/l; lead 1.2 ± 0.47 µg/l, nickel 4.7 ± 1.66 µg/l; in sediments cadmium 0.6-3.4 µg/g dw; copper 18.6-57.4 µg/g dw; lead 26.9-125.9 µg/g dw; nickel 10.7-92.1 µg/g dw. Although higher concentrations were found in sediments, the chemical status of Tasaul Lake water was good to moderate when compared to Romanian and EU-WFD standards. The first results of the described variables for Tasaul Lake have been registered.

KEY-WORDS: heavy metals, GF-AAS, water, sediments, coastal lakes

AIMS AND BACKGROUND

Tasaul Lake with lagoon origin has had in the past marine waters impact through natural channels and freshwater input of natural tributaries. In the 1920s hydro-technical channel constructions closed the water body which was gradually transformed into a freshwater oligohaline lake (Breier, 1076). The shift from marine to freshwater conditions evolved in three stages: marine until 1925, brackish in 1925-1935 and freshwater till the present time influenced the water and sediment qualitys. After 1980, the environmental conditions were further changed by anthropogenic impact. In particular, eutrophication caused severe problems such as extensive algal blooms.

Tasaul as a shallow lake (maximum depth 4 m) is under many human pressures from its surroundings. Atmospheric pollutants emitted by the nearby petrochemical plant, industrial and municipal wastewaters, wastewaters from animal farms, surface run-off from agriculture and leaking waste landfills are just a few examples of pressures which negatively affect the Tasaul lake ecosystem.

Studies conducted during 1997-2000 on the dynamics of the main physical-chemical parameters in Black Sea coastal lakes showed the unstable character of Tasaul Lake concerning wind-induced turbulence, vaves, no stratification, big variations of temperatures (Birghila et al., 1998, Birghila & Chirila, 1997, Chirila et al., 1997, Chirila et al., 1998, Chirila et al., 2002). A property of Tasaul Lake is the alkalinity and pH values between 7.6-9.2 (Alexandrov et al., 2006), specifically for an eutrophic lake.

Heavy metals are naturally present in aquatic systems through weathering rocks. A variety of point and diffuse sources increase their concentrations beyond background level, for example industrial and municipal wastewater, atmospheric input by fossil fuels combustion from (roads and rail ways traffic, petrochemistry), mining and smelting activities in an area where also fertilizers or pesticides had a huge influence. Motorcar emissions may represent a major source of lead when alkyl-Pb additives are still in use.

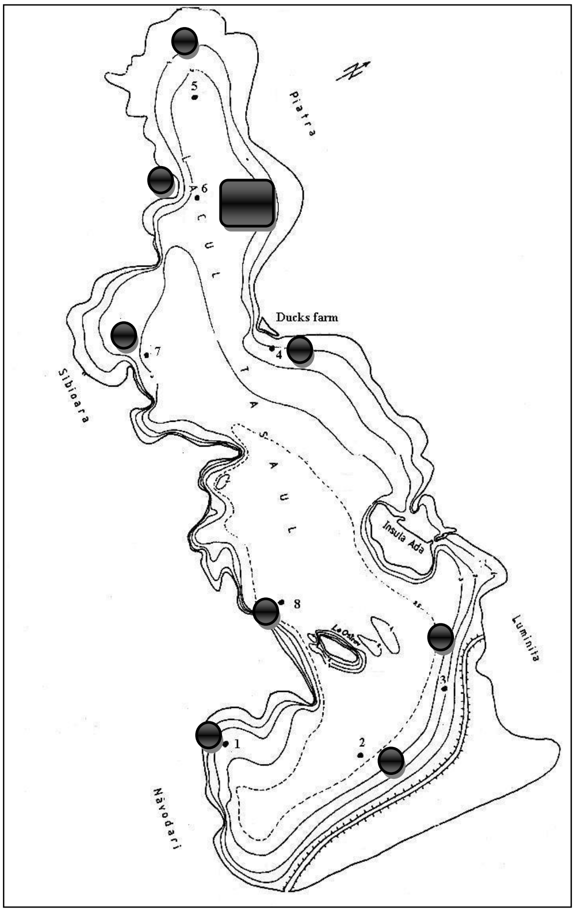
In the aquatic environment, heavy metals are present in dissolved and mostly particulate form as adsorbed to particles. Their speciation depends on the physical-chemical conditions. Metals may undergo a variety of complex reactions, ionic exchange or precipitation. Large quantities are accumulated in sediments, from which metals could be re-suspended into the water column, in certain conditions. Anoxia in sediments may also play a major role in heavy metal release. Their persistence, bioaccumulation (for Hg) and transfer along trophic food chains may cause sub-lethal and lethal effects. Therefore, monitoring of heavy metals in aquatic ecosystems is urgently needed.

The purpose of evidencing results was to document the actual (2005-2006) heavy metals investigation and possible contamination in water and sediments of Tasaul Lake, in the framework of the ESTROM project. Results are based on the other parameters investigation (hydrology, coring, water and sediment chemistry, primary production and euthrophication) which proved presence of problems, pollution, and needing hypothesis.

MATERIAL AND METHODS METHODS

Surface water and surface sediments of Tasaul Lake were sampled during 2005-2006 from eight stations horizontally distributed according to potential pollution sources: 1 - Navodari town; 2 - Petrochemical plant; 3 - Corbu mine; 4 - Birds farm; 5 - Casimcea River inflow; 6 - Pig farm; 7 - Sibioara village and 8 - Grazing field (Fig. 1).

Water samples were collected in clean HDPE (high density polyethylene) bottles and acidified up to pH 1.2-2 with Ultrapure HNO_3. Before chemical analysis, samples were preserved at 4°C. Total metal (dissolved + particulate) were directly analyzed, without any other preliminary treatment.



Sediments were dried at 105°C and well homogeneized (>2 mm fraction removed, for accuracy). Afterwards samples were weighted (around 0.05 g dry sediment) and treated with 5 ml concentrated nitric acid 65%, Suprapur Merck. Digestion procedure was carried out in a Microwave digestion system with built in, non-contact temperature and pressure measurement-type Speed wave MWS-3 (Berghof), with microwave power 1 450 W. (temperature program - step 1: 140^{0}C, ramp 5 ^{0}C/min, time 5 min; - step 2: 160^{0}C, ramp 3 ^{0}C/min, time 5 min; - step 3: 175^{0}C, ramp 3^{0}C/min, time 20 min). At the completion of this process, samples were diluted to 100 mL with de-ionized water (Water Purification System SIMPLICITY 185 MILIPORE).

Heavy metals concentrations were determined by graphite furnace atomic absorption spectrometry (GF-AAS), using an SOLAAR M6 DUAL Zeeman, Thermo Electron - UNICAM equipment.

Fig.1. Tasaul Lake - sampling stations map

Standards prepared for each element from stock solution of 1000 μg/L (Merck) were used for calibration. Three instrumental readings were averaged to one value. The accuracy of the whole analytical procedure was checked with certified reference material (BCSS 1 / marine sediment, provided by National Research Council Canada), analyzed together with sediment samples.

Sampling, pre-treatment and analytical procedures were according to the reference methods recommended for environment pollution studies (11. IAEA, 1999, IAEA-MEL, 1999).

RESULTS AND DISCUSSION

a. Heavy metals in water

The investigation of Lake Tasaul in 2005-2006 yielded the following average heavy metal concentrations in surface water samples (n = 28): cadmium 0.3 ±0.14 μg/L; chromium 2.6 ± 0.37 μg/L; copper 12.4 ±3.19 μg/L; lead 1.2 ± 0.47 μg/L; nickel 4.7 ± 1.66 μg/L.

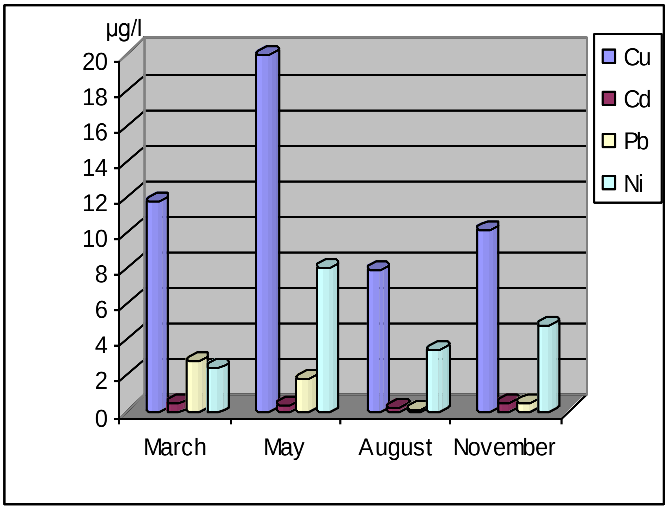


Fig. 2. Seasonal variability of heavy metals in Tasaul Lake water

The seasonal changes in heavy metal concentrations were not great and consistent (Fig. 2). Average monthly concentrations were slightly higher in spring. For example, maximum values for Cd and Pb were observed in March (0.5 and 2.8 µg/L, respectively), while Cu and Ni peaked in May (19.9 and 8.0 µg/L, respectively).

The horizontal differences in Tasaul Lake were relatively small (Fig. 3). However, some peaks occurred such as at station 5 where a Cu concentration of 22.0 µg/l (almost double than average) was measured. In contrast, the same location showed the lowest values for Cd and Pb (0.1 and 0.6 µg/l, respectively), which is half than average.

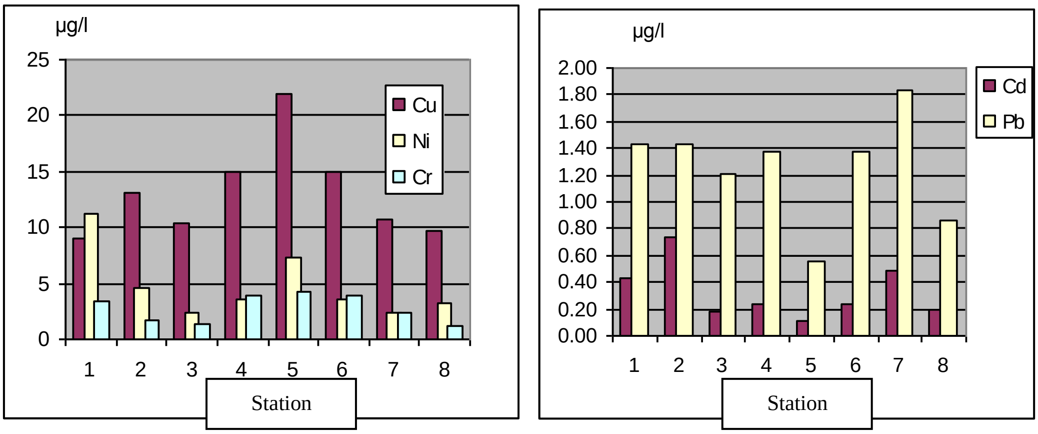
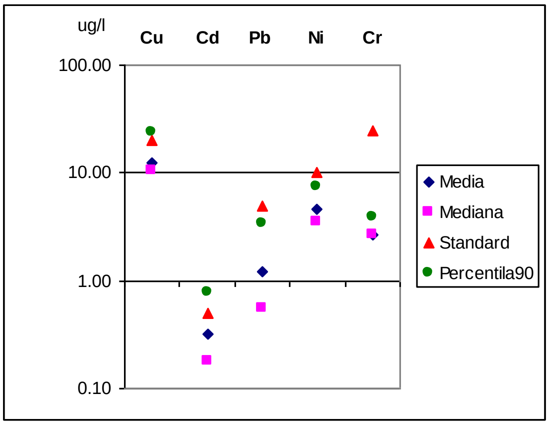


Fig. 3. Distribution of metal concentrations in Tasaul Lake

Various studies demonstrate that acidification increases the solubility and concentration of heavy metals in lake water because they are mobilized from sediments (Almer et al., 1974, Andersen & Pempkowiak, 1999).

Heavy metal contamination is rated by national and international threshold values. For example, national Romanian standards for surface waters (Ord.161/2006) are given as 0.50 µg/l for Cd, 25 µg/l for Cr, 20 µg/l for Cu, 10 µg/l for Ni, and 5 µg/l for Pb indicating good quality. In Tasaul Lake most measured concentrations were below these standards (cadmium 86%, copper 82%, nickel 93%, lead and chromium 100%).



Chromium, lead and nickel showed median values (2.7 µg/l Cr; 0. 6 µg/l Pb; 3.5 µg/l Ni) and percentiles 90th (3.9 µg/l Cr; 3.4 µg/l Pb; 7.5 µg/l Ni) which are both lower than admissible limits (Fig. 4). Cadmium and copper showed median values (0.3 µg/l Cd; 10.6 µg/l Cu) below standard, whereas percentiles 90th (0.8 µg/l Cd; 23.9 µg/l Cu) were higher than the limit (Fig. 4). In summary, the water quality of Tasaul Lake with respect to heavy metals can be rated good to medium.

Fig. 4. Classification criteria of Tasaul Lake water quality

A comparison of our results with other coastal lakes (Nuntasi, Cogealac, Sinoe, Siutghiol) investigated in the same period (2005-2006) showed that Nuntasi Lake had increased concentrations of Cu (77.9 µg/l), Cd (2.5 µg/l) and Pb (13.6 µg/l) (Fig. 5). Other differences between lakes are due to the variability in physical-chemical conditions and the different anthropogenic pressures.

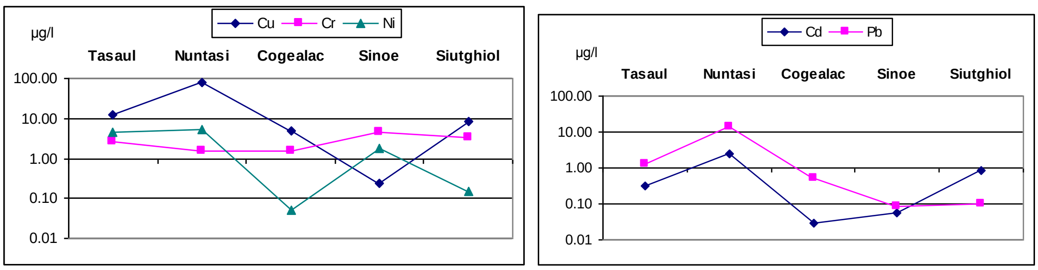


Fig. 5. Metal concentrations in Tasaul Lake compared to other Romanian coastal lakes in 2005-2006

Summarizing the results of the five lakes investigated in 2005-2006, concentrations varied between 0.03-2.5 μg/l for cadmium; 1.5-4.5 μg/l for chromium; 0.2-77.9 μg/l for copper; 0.1-13.6 μg/l for lead, and 0.05-5.4 μg/l for nickel. Investigations from 1997 in various coastal lakes (Nuntasi, Corbu, Siutghiol, Agigea, Belona, Techirghiol, Tatlageac and Neptun), using inductively coupled plasma - atomic emission spectrometry (ICP-AES), showed heavy metal concentrations of 0.1-4.3 μg/l for cadmium, 0.1-107.9 μg/l for copper, 1.2-8.9 μg/l for chromium, 6.6-198.4 μg/l for lead and 0.3-10.7 μg/l for nickel (2). We note a significant decrease of all heavy metal concentrations in the last ten years, lead in particular. This can be explained by a general decrease in heavy metal emissions due to lower release in the lake and economy-technical measures; the lower lead concentrations may be associated with the gradual reduction of alkyl-lead additives and hence smaller atmospheric pollution. It is recommended to stop all heavy metals emission.

b. ***Heavy metals in sediments***

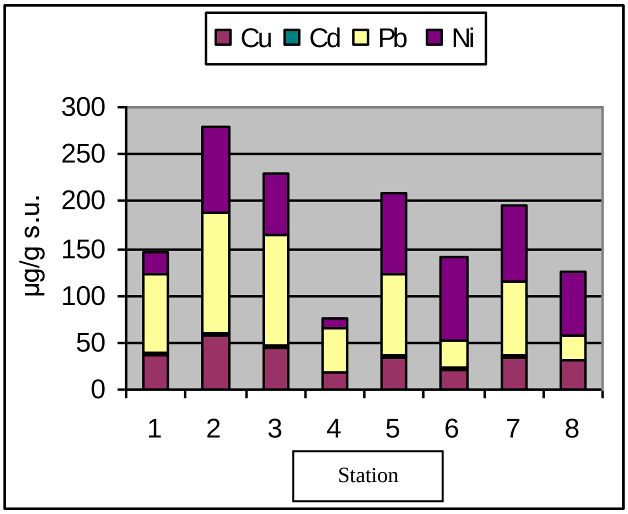


Fig. 6. Heavy metal concentrations in surface sediments

It is well known that heavy metals adsorb to particulate matter and accumulate in sediments. Mean heavy metal concentration in surface sediments of Tasaul Lake were: cadmium 0.6-3.4 μg/g dw; copper 18.6-57.4 μg/g dw; lead 26.9-125.9 μg/g dw; nickel 10.7-92.1 μg/g dw (Fig. 6). These values indicate some accumulation, congruent with the low concentrations in water, but showed quite large horizontal variation, samplied first time in the coastal zone by the coring method (Zackary & Longfellow, 2004, UNEP(DEC)/MED WG, 2006).

For instance, lead values of 117.0-125.9 µg/g dw in sediments from the southern part of the lake were observed, while in the central part values were between 26.9-45.9 µg/g dw (Fig. 6). Comparing with sediment quality criteria recommended by national legislation (Ord. 161/2006 - 0.8 µg/g Cd; 40 µg/g Cu; 85 µg/g Pb; 35 µg/g Ni), about 20-30% of copper and lead samples did not comply, whereas for cadmium and nickel the percentage is even higher. Hence, the quality of Tasaul Lake sediments can be rated as moderately polluted only compared with water samples classification and standards for it. There are first results obtained for heavy metals concentrations in Tasaul Lake sediments and could not be compared with any other previous analyses for the bottom surface.

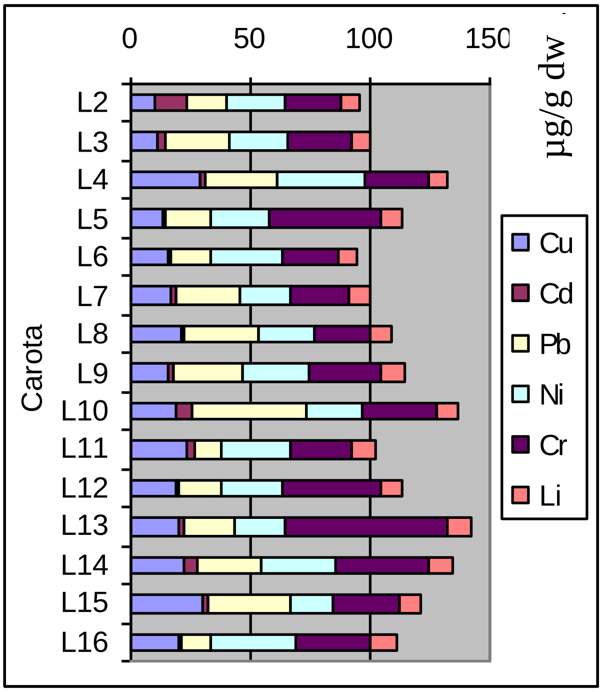


Fig. 7. The results of analysis of the sediment core (Slices in depth/Layers: L2-L16 /0-20 cm)

In opposite, the sediment core profile located between Stations 4 and 5 did not show notable trends in historical layers, except for cadmium with increased surface (0-1 cm) concentration (Fig. 7). Hence, no significant changes in heavy metals contamination occurred for the past twenty years, in coring sample. The sediment column analyse is in contrast to water concentrations that have markedly decreased in the last decade. The explanation consists in the water circulation on the bottom surface which washed the bottom surface.

Alkaline Tasaul Lake (Breier, 1976, Wallstedt & Borg, 2004) shows a tendency of decreasing heavy metal concentrations in water due to accumulation in sediments. This is in agreement with sediment studies in different Swedish lakes showing much higher heavy metal (As, Cd, Co, Zn, Fe, Mn) accumulation in sediments of alkaline lakes, while acidified lakes showed higher concentrations in the water (IAEA-MEL, 1999).

CONCLUSIONS

Tasaul Lake showed good to moderate water quality and moderate sediment quality with respect to heavy metal contamination. Their significant decrease over the last 10 years in water was not reflected in sediment depth profiles. Some increased concentrations in sediments may have a sub-lethal effect on biota in the long term. However, since threshold values given by Romanian and international standards are rarely surpassed there is not urgent need to take immediate measures with regard to Lake Tasaul contamination. Environmental protection in general and the EU WFD in particular simply request that heavy metal sources are reduced and kept at utmost minimum.

It is important to continue heavy metal monitoring in Romanian waters. More detailed investigations are needed for coastal lakes and mainly in Tasaul Lake, to better understand the mechanisms controlling the functions of this vulnerable ecosystem.

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