

Assessment of toxic metals mobility in water-sediment environment of the Lambro Creek, Italy.

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Abstract

Metals enter streams through a variety of natural and anthropogenic sources. Source of pollution, localized or diffused, may alter the values of physicochemical parameters, which effect the mobility of metals in an aquatic environment. This paper evaluates the impact of local wastewater treatment plant (WWTP) discharge, as well as diffuse sources of pollution on metals behavior in water, sediment and biota of the Lambro creek, Salerno Province, Southern Italy. Water, sediment and biotic samples were collected in different sites of the creek, during two different periods of the year. Together with the most common physicochemical parameters (pH, conductivity, dissolved oxygen, COD, NO₃-N, etc.), the concentration of potentially toxic metals (Cu, Zn, Pb, Cr and Ni) in different geochemical fractions of sediment and accumulation in biotic tissues were measured. The results showed that the creek was not polluted by metals dominant in urban streams (Cu, Zn and Pb) compared to sediment quality guidelines (SQG) values. The availability of metals in most readily available fraction was found in order of Zn>Cr>Ni>Pb>Cu. Likewise, the distribution coefficient (K_d) values showed the preference of Cu and Cr to bind with sediments while, for Pb and Zn, it indicated the preference to occur in dissolved form.

Keywords: sediment, pollution, metals, mobility, biota

1. Introduction

Toxic metals are among the most common environmental pollutants and their occurrence in aquatic ecosystem indicates the presence of natural and anthropogenic sources of pollution. Once discharged through stormwater drains, combined sewer overflows, waste water treatment plants, illegal discharges, etc. (Komínková *et al.*, 2016), they are either accumulated in sediment particles or remain insoluble in overlying water of water receiving bodies. Sediments act as a sink as well as source of metals in aquatic environment because metals are not constantly bound to sediments and can be released into water column due to changes in physicochemical variables such as pH, redox potential, salinity, hardness, etc. induced by environmental changes. Measurement of total

concentration of metals provides inadequate information to assess bioavailability or toxicity of metals, owing to their mobility, potential toxicity and bioavailability depends on different chemical forms in which they are present in sediments (Baran and Tarnawski, 2015). Metals bound to exchangeable, reducible and oxidisable fraction of sediment are susceptible to released into water column that becomes bioavailable and poses threat to aquatic biota. Small urban streams are more vulnerable to discharges compared to big rivers because of their limited flow. Even a small amount of pollutant discharge can alter the existing balance of the creeks (Race *et al.*, 2015). Several studies assessing the toxic metal pollution have been dedicated to world great rivers such as the Yangtze, China (Song *et al.*, 2011), the Hindon River, India (Chabukdhara and Nema, 2012) etc. However, studies related to the fate of toxic metal in small urban creeks are rare. Hence, it is necessary to understand precisely the potential and actual impacts of elevated level of toxic metals in biota, sediment and water of small creeks that proves to be beneficial for pollution control strategies and approaches to water quality management. The objectives of this study were: 1) to assess toxic metal concentration in water, sediment and biota of the Lambro Creek, Italy affected by municipal wastewater treatment plant, 2) to investigate the distribution of toxic metals in different geochemical fractions of sediment using sequential extraction and 3) to investigate the influence of pH and leaching time in remobilization of metals.

2. Methodology

2.1 Sampling

Sediment, water and biota samples were collected along the Lambro Creek, Salerno, Southern Italy at four and six different sites during the month of May and June 2016, respectively. Sampling points are hereby termed L1, L2, L3, L4, L5 and L6. Sampling sites L1 and L2 are situated at coast of the Tyrennian sea and mouth of the creek, respectively, whereas, L3, L4 and L5 are situated at a suitable distance downstream from local wastewater treatment plant. L6 is close to the source of the creek (Figure 1)

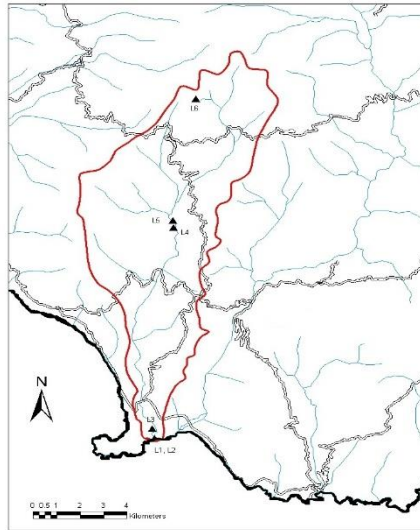


Figure 1. Sampling sites along the Lambro Creek (Southern Italy).

Water samples collected approximately from the midpoint of the stream below the water surface at the depth from 5–20 cm, were transported to the laboratory, acidified by HNO₃ (super grade) and stored at 4 °C in acid prewashed PE bottles for later analysis of metal contents. Approximately 2 kg of bottom sediment down to 5 cm depth were collected using a plastic scoop. In order to obtain homogeneous composition of sediment, subsamples from five to eight different points in each site was composited. Samples after transport to the laboratory was kept for drying in a room condition. The dried samples were homogenized and sieved into different fractions (1–2 mm, 0.5–1 mm, 0.3–0.5 mm, 0.15–0.3 mm, 0.015–0.15 mm and <0.015 mm) through successive sieving sessions. Considering the grain size distribution of sediments in urban creeks, the sediment fraction having <0.5 mm size was chosen for chemical analysis (Pollert *et al.*, 2000). Biotic samples were collected using the standard method Three Minutes Semiquantitative Kick Sampling (Storey *et al.*, 1991). Three different families of benthic organisms were selected according to their abundance in the creek from different sampling points. After transport to the laboratory, organisms were separated according to their family and species level. The samples were frozen and freeze-dried using a lyophilizer (Christ Alpha 2–4 LSC plus).

2.2 Chemical analysis

Concentration of metals (Cr, Cu, Ni, Pb and Zn) in filtered water sample through 0.45 µm pore size cellulose nitrate membrane filters analysis was analyzed using NexION 350X ICP-MS Spectrometer (by PerkinElmer, Inc., MA, USA). The pH, conductivity and DO were measured in the field on the day of sampling using multiparameter probes (Hach, Loveland, CO, USA). COD and nitrate was determined using acidic dichromate solution followed by spectrophotometry according to standard methods (APHA, 1998) and ion chromatography (IC 761 compact by Metrohm Ltd., Switzerland), respectively. Sediment samples were digested according to the US EPA 3051 microwave (MW) digestion method (slightly modified by Nábělková, 2005). The partitioning of metals in specific

geochemical fractions of sediment was accomplished through sequential extraction according to the BCR procedure described by Pueyo *et al.* (2008) (the last step adapted from US EPA 3051 microwave (MW) digestion method slightly modified by Nábělková, 2005). The organic matter content of sediment samples was determined gravimetrically by loss on ignition (LOI). In order to reduce experimental errors, all experiments were performed at least in duplicates. The biotic samples were digested according to the method described by Komínková, (2006). Organisms having a mass of 1 g approx. after lyophilization were treated with HNO₃ and H₂O₂ (9:1 ml) and digested in a microwave oven. The concentration of metals in all extracts was determined using ICP-MS (NexION 350X).

2.3 Remobilization test

Remobilization test was carried out by a batch adsorption test method based on EPA methodology. Sediment sample of known mass (3 g approx.) was mixed with 30 ml (liquid/solid ratio = 10) of distilled water adjusted initially to two different pH values (2 and 6). The mixture was placed in a horizontal shaking device and shaken at 220 rpm. At predefined time-intervals (15 min and 3 hrs.), suspension was taken over to determine the changes of metal concentrations in water. The solution was then centrifuged and filtered. Subsequently, the sample was acidified with a drop of HNO₃ (super grade) and stored at 4 °C for later analysis of metal contents in the supernatant. The concentration of metals was determined using ICP-MS (NexION 350X).

2.4 Data Interpretation

The partitioning behavior of metals between a solid matrix and water was expressed by the distribution coefficient (K_d) defined as a logarithmic ratio between pollutant concentration in sediment and its concentration in water indicating the medium crucial for the risk assessment (EPA, 1999). K_d values of 3 and less identify metals occurring mostly in dissolved form while, above 4, it refers metals preference to bound to sediment (Borovec *et al.*, 1993). It is calculated as,

$$K_d = \log \frac{C_s}{C_w}$$

where, C_s is the metal concentration in sediment (mg/kg) and C_w is the metal concentration in water (mg/l) at equilibrium. Metal concentrations in the tissue of macroinvertebrates was assessed by the biota sediment accumulation factor (BSAF) according to Rand, (1995):

$$BSAF = \frac{C_o}{C_s}$$

where, C_o is the metal concentration in tissue (mg/kg).

3. Results and discussion

3.1 Water

Water quality parameters were observed as supplementary data to gain information about dominant hydrochemical conditions of study sites. Spatial variations of pH values were identical among the sites and varied from 8.1 to 8.3 during 1st sampling, while it varied from 7.9 to 8.9 during 2nd sampling. Dissolved oxygen ranged from 8.67 to 9.94 mg/l (saturated DO range 9.06–10.5 mg/l) and 8.8 to 13.1 mg/l (saturated DO range 8.85–10.17 mg/l) during 1st and 2nd sampling, respectively. The level of pollution attributed to COD and NO₃-N were identified with different values according to Italian norms (D. Lgs. 152/2006). COD was high at site L5 downstream of WWTP during both samplings (54.5 and 50.5 mg/l, respectively) and categorized in level 5 according to Italian norms. The level of COD decreased downstream flow along the creek. The spatial variations in NO₃-N ranged from 0.7 mg/l to 2.1 mg/l, the highest value was obtained in mouth of the creek (L2) and presents the risk of eutrophication. The metal concentration in water ranged from 0.9–6.3 and 1.5–4.8 for Cr, 0.05–0.1 and 0.06–0.54 for Cu, 6.32–7.1 and 0.03–4.5 for Ni, 0.02–0.38 and 0.03–2.4 for Pb and 0–2.8 and 0–79.3 µg/l for Zn during 1st and 2nd sampling, respectively. The lowest concentration of studied metals was measured at L6 except Zn where it was measured under detection limit. The values were evaluated in view of background median concentration of Italian stream water for Cr (0.285 µg/l), Cu (1.12 µg/l), Ni (1.35 µg/l), Pb (0.099 µg/l) and Zn (3.17 µg/l) (De Vivo *et al.*, 2008). The results revealed that Cr and Ni at all sites (except Ni at L4 and L6 during 2nd

sampling) Pb at L5 (2nd sampling), and Zn at L3 and L5 (during 2nd sampling) possess acute risk to aquatic biota showing the concentration above the background values. Higher concentration of Pb and Zn in L5 and L3 can be related, respectively, to the discharge from local WWTP and storm water runoff from a busy road and parking lot near recreational park.

3.2 Sediment

Sediment of the Lambro Creek was characterized as coarser fractions (1–2 mm and 0.5–1 mm) dominant in both samplings with 12–47 % and 34–62 % of the total, respectively. Fine sand fraction (0.15–0.3 mm) was higher at sampling points L4 and L5 during 1st sampling while, L6 had the highest fine sand fraction during 2nd sampling. The organic matter content was found within a range of 1–5 % during both sampling periods showing high correlation with clay and silt fraction ($r = 0.7$). Total metal concentrations were compared with the consensus based sediment quality guidelines (SQGs) for fresh ecosystems (MacDonald *et al.*, 2000) to estimate the degree of contamination. Threshold effect concentration (TEC) and probable effect concentration (PEC), respectively, are the indices of SQGs that describes the contaminant concentration below which no adverse effects are expected to occur and above which adverse effects are expected to occur more often. The creek was found with low concentration of metals dominant in urban streams such as Cu (5–16 mg/kg), Zn (40–87 mg/kg) and Pb (3–5 mg/kg) compared to TEC (31.6, 121 and 35.8 mg/kg) and PEC (149, 459 and 128 mg/kg) values. Likewise, Cr and Ni exceeded PEC level (Cr 111 mg/kg and Ni 48.6 mg/kg) at L3 (125 mg/kg) and L3 (74 mg/kg) and L4 (53 mg/kg), respectively, during 1st sampling while, during 2nd sampling, Cr and Ni exceeded TEC levels (Cr 43.4 and Ni 22.7 mg/kg) indicating a possible negative effect on biota at all sampling points except Cr (33 mg/kg) at L6. The chemical partitioning of metals in different phases analyzed namely, exchangeable or acid soluble, reducible, oxidisable and residual is shown in Figure 2. The highest availability of Zn in readily available exchangeable fraction was evident during 1st sampling. With respect to the results, the availability of metals in most readily available fraction can be generalised as Zn>Cr>Ni>Pb>Cu.

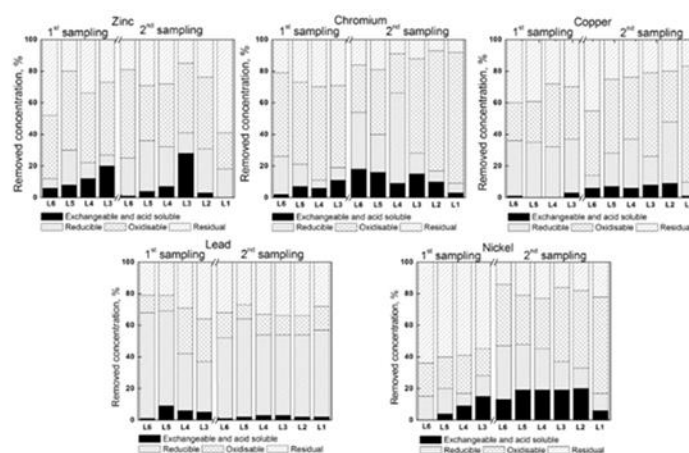


Figure 2. Proportion of metals bound to geochemical fractions of sediment.

Table 1. BSAF of toxic metals in biota (H.- *Hydropsychidae* and B.- *Baetidae*)

Sites	Sampling	Cr		Cu		Ni		Pb		Zn	
		H.	B.	H.	B.	H.	B.	H.	B.	H.	B.
L5	1 st	0.9	2.6	1.9	0.1	0.5	0.3	0.3	0.6	2	1.3
	2 nd	0.9	22.4	0.9	2.4	0.6	0.7	0.3	0.4	1.8	4.4
L4	1 st	1.1	–	2.2	–	0.8	–	0.4	–	1.3	–
	2 nd	1.4	0.8	1.6	0.9	1.5	0.9	1.3	0.2	1.2	2.8
L2	1 st	0.1	–	0.4	–	–	–	0.2	–	0.8	–
	2 nd	0.5	–	0.3	–	0.9	–	0.2	–	1.6	–

The percentage of Zn associated with oxidisable and residual fractions constituted, respectively, 40–50 % and 20–48 % during 1st sampling and 23–56 % and 15–60 % during 2nd sampling. Cr bound to exchangeable and acid soluble fraction showed a drastic increase at sampling sites L5 and L6 during 2nd sampling. Cu almost did not occur in exchangeable fraction during 1st sampling while, during 2nd sampling, it was observed up to 9 % of the total concentration. Cu is predominantly found retained in sediment fraction with a high amount of organic matter because of the high stability constant of organic Cu compounds (Morillo *et al.*, 2004). Similarly, Pb has high tendency to form complex compounds with Fe/Mn oxides and hence, predominate in reducible fraction of sediment (Xiangdong *et al.*, 2001). The results of distribution coefficient (K_d) revealed that Zn at L3 and L5 during 2nd sampling was most available metal in dissolved form. However, during 1st sampling at L3, Zn showed a tendency to bind with sediments. K_d values of Cu and Cr indicated that these metals preferentially bound to sediments. In contrast, the values of K_d obtained for Ni showed an ambiguous result between two samplings. Similarly, Pb was easily released into water at L5 during both samplings.

3.3 Remobilization of metals

The remobilization results showed the highest mobility of Cr at L3 within a range of 6.0–8.4 mg/kg followed by L5, L4 and L6, respectively, at pH 2 and leaching time of 3 hrs. In contrast, the influence of pH and leaching period was not significant in release of Cr at creek's mouth (L2) and marine coast (L1). Lower concentration of Cr release was evident at pH 6 compared to pH 2 at L7, L2 and L1. Cu release was higher at L3 during 3 hrs. of leaching at pH 2. Similarly, for both pH values, Cu release from marine sediment was higher than sediment from creek's source. There was a clear increasing trend of Zn release as creek flows from source to mouth, however, negligible remobilization was observed at mouth of the creek and marine coast. Lower release is supported by negligible amount of Zn bound to exchangeable fraction in marine sediment. The highest Ni release was observed at L3 when leached at pH 2 for 3 hrs. Likewise, the highest concentration of Pb released was observed at L4, whereas, the lowest release was observed at L5 followed by L7.

3.4 Biota

The toxic metals accumulation in tissues of macroinvertebrates are presented in terms of BSAF in Table 1. BSAF greater than 1 indicates accumulation of metals in biota to concentration higher than sediment concentration. The results showed that *Hydropsychidae* accumulated higher level of Zn at L5. During 2nd sampling, significant decrease in BSAF of Cu at L5 and increase in BSAF of Zn at L2 was observed. It is worth mentioning that the monitored sites are impacted by human activities in different scale and may alter bioavailability of metals in keeping with the sequential extraction analysis (Figure 2). Similarly, for *Baetidae*, Cr and Zn exceeded BSAF of 1 during both samplings, while, Cu showed BSAF>1 during 2nd sampling at L5. For Zn, BSAF>1 was observed at L4 during 2nd sampling.

4. Conclusion

This study shows the impact of municipal wastewater treatment plant discharge on mobility and bioavailability of toxic metals in sediment water environment of the Lambro Creek. Water contamination results showed threat of Pb and Zn to aquatic biota at site below the WWTP discharge and site in the proximity of recreational park compared to Italian background values. It can be said that traditional WWTPs could be not enough to treat the pollutants in efficient way. Regardless of the expectation, the contamination level at sites close to the source of creek reveals that even in environment with low anthropic impact there can be possibility of contamination. For better understanding the fate of toxic metals in water-sediment environment, a thorough study of various small creeks not only in proximity of the city but also outside the city area impacted by different drainages seems necessary.

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