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Assessment of metal pollution in the Lambro Creek (Italy)

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ABSTRACT

This study assessed the effect of metal pollution in the Lambro Creek (Southern Italy). Water, sediment and biota were collected at six sampling sites (June) for metal concentration assessment (Cr, Cu, Ni, Pb and Zn). Sequential extraction was performed to determine the distribution of metals in different geochemical sediment fractions. The influence of pH and leaching time on the release of metals from sediment to the water column was investigated via remobilization tests. A battery of toxicity tests (*Vibrio fischeri*, *Raphidocelis subcapitata*, *Phaeodactylum tricornutum*, and *Daphnia magna*) with multi-endpoints (bioluminescence, growth inhibition, and immobilization) was used to determine the overall toxicity in sediment water extracts. The results showed that metals did not exceed the probable effect concentration levels, with Cr concentration exceeding the threshold effect concentration level at all sampling points except for the one closer to the source of the creek, suggesting potential negative effect on the biota. Considering the cumulative criterion unit, sediment contamination was moderate at all sampling sites, except for L3 and L5 where biota was exposed to a very high risk. With respect to sequential analysis, the most readily available fraction of metal can be generalised as Ni > Cr > Cu > Zn > Pb. For better understanding the fate of metals in the water-sediment environment, their biogeochemical cycles should also be investigated in small creeks including both fresh (watercourse) and saltwater (river mouth) sediments.

1. Introduction

Metals enter streams through a variety of natural and anthropogenic sources (Balintova et al., 2016; Galdiero et al., 2015, 2016; Libralato et al., 2016a, 2016b; Satyro et al., 2017). Stream water quality is affected by materials from dry and wet atmospheric depositions, traffic and industry related activities, or released from roofs and building sidings, commercial and industrial discharges (Ball, 2002; Gasperi et al., 2010; Libralato et al., 2011; Race et al., 2016), including new emerging contaminants as well (Lofrano et al., 2016). Rainwater runoff discharged through the storm water drainage or combined sewer overflow systems not only influence the physico-chemical variables of the receiving water bodies, but could also adversely impact organisms living in the water column and bottom sediment (Barałkiewicz et al., 2014). Streams are also affected by metals and other pollutants from illegal discharges, such as domestic wastewater connected directly to a sewer without any legal permission (Komínková et al., 2016). Metal concentrations might serve as indicators for assessing sediment contamination; however, it is not sufficient to assess their potential environmental impact because mobility, potential toxicity and bioavailability depend on the chemical forms in which they are present (Baran and Tarnawski, 2015). The behavior of heavy metals in urban streams is often influenced by various water and sediment characteristics such as pH, redox potential, salinity, temperature, content of organic matter, and particle size distribution (Caetano et al., 2003; Cantwell et al., 2002). A decrease in dissolved oxygen (DO) concentration and redox potential (Eh) caused by biodegradable organic substances in receiving waters may affect the release of metals from sediment to water. Changes in pH can strongly affect the remobilization of metals in water through precipitation/dissolution and adsorption/desorption processes (Ho et al., 2013; Race, 2017). Other quality indicators of freshwater ecosystem are macroinvertebrates, ensuring a wide range of sensitivities to changes in both water quality and habitats (Hussain and Pandit, 2012). Biota metal content is governed by bioconcentration dynamics (species-by-species specific) depending on seasonality, developmental stage, behavior, sex, and exposure

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conditions (Eggleton and Thomas, 2004). Accumulation of a tangible quantity of metals in aquatic biota may have dramatic consequences on the biodiversity and potential toxicological risk to human populations consuming contaminated food (Komínková et al., 2016).

Previous studies (Varol and Sen, 2012; Tang et al., 2013; Harguinteguy et al., 2013; Shafie et al., 2014) investigated the fate of toxic metals in large urban riverine systems, but their impact in small urban creeks is understudied (Hnatuková et al., 2009; Barałkiewicz et al., 2014; Komínková et al., 2016; Nábělková and Komínková, 2006).

The aim of this research was to assess Cr, Cu, Ni, Pb and Zn in water, sediment (i.e. considering various geochemical fractions), and biota (i.e. body tissues of macroinvertebrates) collected from the Lambro Creek (Italy) in order to try to fill the gaps to the knowledge about downstream transport, deposition and release under changing environmental conditions, and to look for optimal strategies for pollution control and water quality management. Remobilization tests were carried out to understand the influence of pH and leaching time variation on the release of metals from sediment to water. Toxicity tests integrated the final assessment of sediment water extracts (*Vibrio fischeri*, microalgae *Raphidocelis subcapitata* and *Phaeodactylum tricornutum,* and crustacean *Daphnia magna*).

2. Methodology

2.1. Study area

The Lambro Creek (Salerno province) flows into the Eastern Tyrrhenian Sea near Palinuro (Italy). Its catchment basin falls within Cilento e Vallo di Diano National Park. The creek is about 24 km long with a catchment area of approximately 300 km^2 and an average flow of 3.4 m^3/s. The area could be suffering due to tourism pressure (especially during summertime), illegal dumping and residential areas, agricultural activity, and discharges from wastewater treatment plant (WWTP). Six sampling points (L1, L2, L3, L4, L5 and L6) were identified along the creek (Fig. 1) for the collection of water, sediment and macroinvertebrate specimens in June 2016.

Sampling points L1 (40°01'47.4"N 15°17'55.1"E) and L2 (40°01'46.8"N 15°17'55.3"E) are located along the coast in front of the creek mouth and in the mouth itself. L3 (40°01'59.2"N 15°17'51.9"E), L4 (40°07'36.2"N 15°19'00.0"E) and L5 (40°07'51.91"N 15°18'56.36"E) are located downstream from the local WWTP discharge. L6 (40°9′31.00"N 15°20'56.00"E) is close to the source of the creek.

Water samples were collected approximately from the midpoint of the creek, immediately below the water surface at a depth from 5 to 20 cm, according to Komínková et al. (2016), in acid pre-washed polyethylene (PE) bottles. Refrigerated samples were transported to the laboratory, filtered, acidified with HNO_3 (super grade), and stored at 4 °C for later analysis of metal content. Basic physico-chemical parameters such as pH, conductivity, DO, nitrate (N-NO_3^-) and chemical oxygen demand (COD) were determined on the day of sampling.

Sediment sampling was carried out by collecting approximately 2 kg of bottom sediment, down to 5 cm depth, using a plastic scoop; from five to eight sub-samples were integrated in order to minimize the differences in sediment composition. Sediment samples were transported to the laboratory and air dried. Each dried specimen was 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 sequential sieving sessions. Considering the grain size distribution of sediment in urban creeks, the sediment fraction having < 0.5 mm size was chosen for chemical analysis, according to Race et al. (2015) and Komínková et al. (2016).

Macroinvertebrates were collected using the standard method of Three Minutes Semi-quantitative Kick Sampling (Storey et al., 1991). A hand net of 0.5 mm mesh size was placed near the bottom substrate, disturbed by the foot, and then removed from the bottom. Two different families of benthic organisms were selected from different sampling points according to their abundance in the creek. They were *Hydropsychidae* (Caddisfly) and *Baetidae* (Mayfly), which are filter feeders and scraper feeders (Ramirez and Gutierrez, 2014) respectively. L6 was considered as the reference site. Samples were preserved in ethanol in PE bottles sorted and freeze-dried (Christ Alpha 2–4 LSC plus).

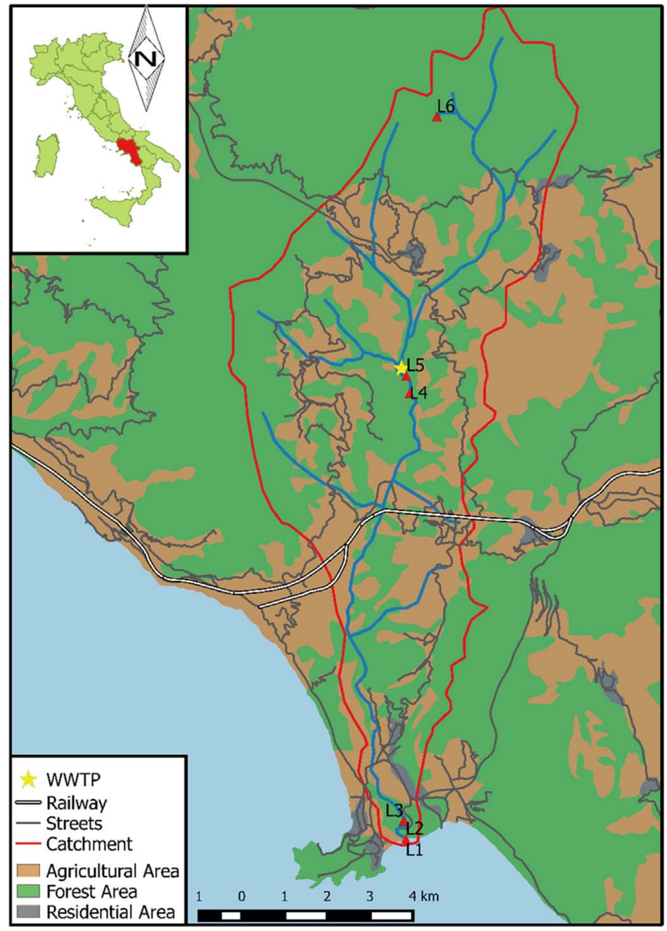

Fig. 1. Sampling points along the Lambro Creek L1-L6 and WWTP.

2.2. Chemical analysis

2.2.1. Water

Water samples were filtered (0.45 µm pore size – cellulose nitrate membranes), acidified (super grade HNO_3), and stored at 4 ± 1 °C for later analysis. Samples were analyzed for Cr, Cu, Ni, Pb and Zn using an inductively coupled plasma mass spectrometer (ICP-MS) (NexION 350X, PerkinElmer, Inc.). A multi-parametric probe (Hach, Loveland, CO, USA) was used for pH, conductivity and DO field measurement. COD was determined using acidic dichromate solution followed by spectrophotometry, according to standard methods (APHA, 1998). N-NO_3^- was determined using ion chromatography (IC 761 compact by Metrohm Ltd., Switzerland).

2.2.2. Sediment and biota

Sediment samples were digested according to the US EPA 3051 microwave (MW) digestion method (Nábělková, 2005 mod.). A sediment mass of approximately 1 g was extracted with HNO_3 (67% v/v) and (30% v/v) in a volumetric ratio of 9:1. The mixture was digested in a microwave oven (Milestone START D) at 108 °C for 20 min. The digests were filtered after adequate cooling and diluted to 50 mL volume with deionized Milli-Q water. Filtrates were stored in PE falcons at 4 °C for later analysis. The partitioning of metals in specific geochemical fractions of sediment, which can be extracted selectively by using