Science of the Total Environment 646 (2019) 121–133

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Evaluating the role of particle size on urban environmental geochemistry of metals in surface sediments

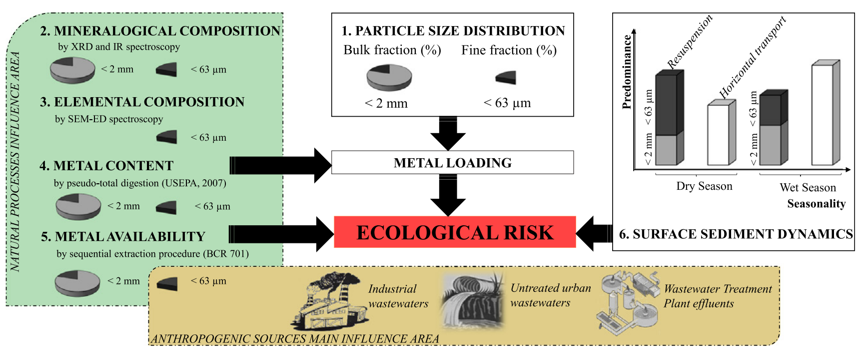
Jessica Unda-Calvo [a,*], Estilita Ruiz-Romera [a], Silvia Fdez-Ortiz de Vallejuelo [b], Miren Martínez-Santos [a], Ainara Gredilla [c]

[a] Department of Chemical and Environmental Engineering, University of the Basque Country (UPV/EHU), Plaza Ingeniero Torres Quevedo 1, Bilbao 48013, Basque Country, Spain
[b] Department of Analytical Chemistry, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), E-8940 Leioa, Basque Country, Spain
[c] Department of Applied Chemistry, Faculty of Chemistry, University of the Basque Country (UPV/EHU), E-2018 San Sebastián, Basque Country, Spain

HIGHLIGHTS

- Non-destructive and invasive methodologies for surface sediment characterization
- Metal geochemistry variation in particle size distribution controls availability.
- Natural processes and human activities are sources of available metals.
- Higher ecological risk was identified in the dry compared to the wet season.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 March 2018
Received in revised form 13 July 2018
Accepted 13 July 2018
Available online xxxx

Editor: Xinbin Feng

Keywords:
Surface sediment
Particle size, geochemistry
Ecological and health risk
Urban environment

ABSTRACT

In this study, non-destructive techniques (X-ray Diffraction, Infrared and Scanning Electron Microscopy with Energy Dispersive spectroscopies) and invasive procedures (pseudo-total and sequential metal extraction methodologies) were used to highlight the significance of evaluating different particle sizes of sediments for assessing the potential environmental and health implications of metal geochemistry in an urban ecosystem.
The variability in composition and properties between bulk (<2 mm) and fine (<63 μm) fractions influenced the availability, and by extension, the toxicity of metals. Indeed, the fine fraction presented not only higher metal pseudo-contents, but also greater available metal percentages. Besides the larger surface area per unit of mass and the high content of clay minerals, it was observed that it was principally Fe/Mn oxyhydroxides that favour adsorption of metals on the fine surface sediments. However, although we demonstrated that the origin of metals in the bulk surface sediments was predominantly lithogenic, use of the <2 mm fraction proved to be a useful tool for identifying different sources of available metals throughout the Deba River catchment. Specifically, discharges of untreated industrial and urban wastewaters, and even effluents from wastewater treatment plants were considered to greatly increase the health risk associated with metal availability. Finally, an evaluation of sediment dynamics in different hydrological conditions has highlighted the role played by each particle size as a vector of metal transport towards the coastal area. While resuspension of fine surface sediments notably induced significantly higher particulate metal concentrations in water during the dry season, resuspension of bulk surface sediments and, fundamentally, downstream transport of suspended particulate matter became more relevant and lowered the ecological risk during the wet season. Greater attention therefore needs to be paid to the new

* Corresponding author.
E-mail address: jessica.unda@ehu.eus (J. Unda-Calvo).

https://doi.org/10.1016/j.scitotenv.2018.07.172

hydrological scenarios forecast to result from climate change, in which longer seasons with low river discharges are forecast.

1. Introduction

According to World Population Prospects (United Nations, 2017 Revision), the world's population is projected to grow from nearly 7.6 billion in 2017 to 8.6 billion in 2030. Intense development of human activity, driven by demographic growth, will greatly impact environmental quality and by extension, human health (Ghanem, 2018). Several studies have addressed the impact of urbanization on the quality of aquatic environments, including high loadings of nutrient and microbial contaminants from both septic systems and wastewater treatment plants (WWTPs) (Carey et al., 2013; McGrane et al., 2014), volatile organic compounds from vehicular emissions (Mahbub et al., 2011) and metals, mainly from industrial or urban effluents (Gupta et al., 2010; Buzier et al., 2011), among others.

Sediment is a good indicator of pollution loads in rivers since it is subject to a continuous accumulation of pollutants, especially metals (Devesa-Rey et al., 2010; Bartoli et al., 2012). These contaminants are considered to pose a serious threat to ecological and human health because of their non-biodegradable, toxic and persistent nature, as well as their capacity to enter the food chain (Burghardt, 1994; van Kamp et al., 2003; Armitage et al., 2007). The percentage of total metal content in the sediment that is available for absorption into the systemic circulation system and that has a toxic impact on human health, will depend firstly on environmental availability (Lanno et al., 2004; Harmsen, 2007), which is in turn related to its chemical forms or types of binding (Saracoglu et al., 2009; Sungur et al., 2014). The physical and geochemical properties of sediments such as surface to volume ratio, mineralogical composition and organic matter are considered to influence chemical distribution of metals (Simpson and Batley, 2009; Campana et al., 2012; Saeedi et al., 2013; Zhang et al., 2014). However, particle size determines all these properties and, therefore, it is the cornerstone parameter (Maslennikova et al., 2012).

To date, numerous researchers have used different analytical techniques (X-ray Diffraction, Infrared and Scanning Electron Microscopy or Inductively Coupled Plasma) to individually investigate the grain size effect over: the mineralogical and elemental composition (Zhou et al., 2015) or the metal chemical speciation (Liang et al., 2018); as well as the mineralogical effect over the metal content (Xie et al., 2018). However, considering all these techniques as a whole may be more suitable to bind the particle size effect on the geochemistry of sediments with the metal accumulation, distribution and environmental impact.

In urban environments, geochemical patterns observed in different particle sizes of sediments help to differentiate the contribution to metal availability of non-anthropogenic sources from human activities (Chiprés et al., 2009). Indeed, sediment records the geochemical composition of the provenance bedrock and the intensity of chemical weathering and hydraulic sorting (Lapworth et al., 2012; Zhao and Zheng, 2015; Kirkwood et al., 2016; Darwish, 2017). During chemical weathering of the bedrock, water-soluble elements are chemically dissolved in water, whereas water-insoluble elements are physically transported by the water current (Zhao and Zheng, 2014). Consequently, despite the high adsorption capacity of minerals, the chemical dissolution of soluble ones might promote the availability of metals previously retained in their lattice.

Additionally, after elucidate the source and magnitude of available metals in each particle size, sediment dynamics become decisively important in addressing the ecological consequences of seasonal variations in river discharge. Indeed, the physical processes involved in sediment dynamics include erosion, transport, deposition, and resuspension (ICES, 2011), which are the result of interactions between several variables such as water discharge or grain size distribution (USEPA, 1999; Apitz, 2012). According to future climate change predictions, alterations in the seasonal precipitation (magnitude and duration) and, consequently, river flow variations are expected. Therefore, deeper knowledge into sediment dynamics will be crucial for a better estimation of metal environmental risk, based on the new hydrological scenarios.

The overall aim of this study is therefore to identify the relevance of analysing different particle sizes, as a more reliable reflection of the environmental geochemistry of metals in surface sediments from an urban catchment and the associated ecological and human health risk. The specific objectives were (i) to use different methodologies for mineralogical, elemental and metal characterization of surface sediments, (ii) to identify natural processes and/or sources of anthropogenic contamination influencing the environmental and health risk associated with the availability of metals in surface sediments, and (iii) to evaluate the influence of seasonality on physical mechanisms governing metal migration towards the coastal area. We hypothesized that combined analysis of different particle sizes of surface sediment will provide us more comprehensive and detailed information about the environmental geochemistry of metals in a catchment subjected to multiple pressures.

2. Materials and methods

2.1. Study area and sampling

The Deba River runs through the catchment (538 km^2) to the Bay of Biscay, receiving inflows from several tributaries, including the Ego and Oñati streams (Fig. 1). The geology of the catchment mainly consists of a succession of sedimentary rocks, predominantly an alternation of sandstones and mudstones in the northern and western part, marls in the central area, and limestones in the southern region. In contrast, igneous rocks dominate the area of confluence of the Ego tributary and the main river (Fig. 1A).

The Deba River catchment possesses certain characteristics which are distinctive of a typical urban environment. These include dense population, a relatively high level of productivity, primarily driven by non-agricultural activities, infrastructures, buildings, and an extensive motor transportation network (Wong et al., 2006; Fig. 1B).

Surface waters receive treated effluents from three wastewater treatment plants (Fig. 1B). The Apraitz (95,000 population equivalent (pe)) and Mekolalde (35,000 pe) WWTPs have been operating since 2007 and 2008, respectively. The Epele WWTP (90,000 pe) only came into continuous operation in May 2012; previously, organic-rich wastewaters from the towns of Arrasate and Oñati were discharged into the Deba River and Oñati stream. In June 2014, the sewer from Ermua-Eibar was also connected to the Apraitz WWTP and untreated urban wastewater (UWW) from these municipalities is no longer discharged into the Ego stream. However, according to data from Gipuzkoa Provincial Council, about 6773 $m^3\ y^{-1}$ of untreated industrial wastewater (IWW) from metal-working, the automotive industry, galvanising, smelting factories and electrical appliance manufacturers are also discharged into the Deba River and its tributaries (Martínez-Santos et al., 2015). In this context, surface sediments are characterized by having a high content of metals, nutrients and organic compounds, principally in areas of greatest urbanization and industrialization. Previous studies have shown that discharges of effluents from WWTPs and even IWW and UWW throughout the catchment are responsible for the declining quality of surface sediments, posing a potential risk for the ecosystem (Unda-Calvo et al., 2018) and for human health (Unda-