

# WHICH IS THE INFLUENCE OF ANTHROPOGENIC INPUTS ON METAL CONTAMINATION PATTERN IN SURFACE BOTTOM SEDIMENTS FROM A URBAN RIVER CATCHMENT?

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## Introduction

During the 19th and 20th centuries the main sources of metals in aquatic environments were anthropogenic inputs, especially in urban catchments, mainly from industrial or urban effluents. Additionally, it has been reported that most of the metals in aquatic systems are associated with the particulate phase, which acts as a vector and reservoir of contaminants (Owens and Xu, 2011). Suspended particulate matter found in rivers may have a natural origin (geological weathering) or anthropogenic origin. Moreover, although sediment-associated metals accumulate in the river during periods of low discharge, they are resuspended and transported downstream during flood events, especially during higher-magnitude floods, where the risk of metal mobilization increases.

In this context, this work aims to: i) determine the sites with the highest potential of risk from sedimentassociated metals and identify their source of contamination; ii) assess the impact of natural or anthropogenic disturbances such as the occurrence of a high-intensity flood and construction of a high-speed rail on source variability and change in metal composition in river-bottom sediments.

## Materials and methods

Nine surface bottom sediment (SBS) samples were collected from the main river bank and from tributaries, during the sampling campaigns of October 2011 and October 2012. SBS were collected using a plastic spoon and sealed in clean polyethylene bags.

In the laboratory, SBS were air-dried and ground with a pestle and mortar for homogenization. Pseudototal metal content was measured in three replicates of the fine fraction (<63  $\Box$  m) at each sampling point. A sequential extraction method (BCR 701) was performed in three replicates of sediments. This extraction was divided into four operationally defined fractions: F<sub>1</sub> (soluble species, carbonates and exchangeable metals); F<sub>2</sub> (Fe/Mn oxi-hydroxides); F<sub>3</sub> (organic matter and sulphides); and F<sub>4</sub> (residual fraction). Finally, the metals under consideration (Fe, Mn, Cu, Cr, Ni, Pb and Zn) in the extracts and pseudo-total digestion were determined by ICP-OES. Total sulphur, nitrogen and carbon were also measured.

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#### **Results and discussion**

Untreated industrial effluents (about 6,773 m<sup>3</sup> y<sup>-1</sup>) contribute significantly to the pseudo-total metal content, the organic matter load (16,035 kg  $O_2$  y<sup>-1</sup>) and the suspended sediment load (19,017 kg y<sup>-1</sup>) in rivers. This fact is reflected in those streams which still receive or have received untreated or partially treated wastewater effluents for a long time, which explains their higher organic matter, nitrogen and sulphur concentrations in fine sediments. Organic-rich material also determines the metal distribution in fine sediments. Therefore, a substantial amount of Cu, Cr and Pb was bound to the oxidisable fraction (F<sub>3</sub>), which means that these metals are favoured to form complexes with humic substances when there is an important organic input.

Apart from that, uncontrolled industrial inputs could be partially responsible of the higher metal concentrations in the fine sediments and of the Zn, Mn and Ni distribution in the exchangeable/carbonates and reducible fractions ( $F_{1,2}$ ), which might be susceptible to remobilization if the physicochemical conditions of the river change and, consequently, they could be more available to aquatic biota.

Determination of the global contamination factor (GCF, Naji et al., 2010) in fine sediments has made it possible to identify the extremely high potential risk for the aquatic environment due to metal pollution in those sites strongly affected by anthropogenic inputs, Zn being the most potentially toxic element for organisms in the Deba River catchment, followed by Cu and Cr.

The recent construction of the Albertia rail tunnel has provided direct evidence of the presence of these sulphated facies in the southwest of this catchment where large quantities of sediments were extracted and deposited around the tunnel. As a consequence of CaSO<sub>4</sub> accumulation in river sediments, where anoxia conditions were detected, the precipitation of Fe-, Zn-, Ni- and Cu-sulphides were favoured (F<sub>3</sub>).

It can be concluded that intense rainfalls play two different roles. On the one hand, they drag and deposit sediments from soils to the river channel, particularly when runoff is important and, on the other hand, rainfalls generate flood events which result in a decrease in metal concentrations in channel bottom sediments, as observed in the 2012 campaign in some sampling sites.

#### Conclusions

This study gives a better insight into the influence of anthropogenic factors (infrastructure construction and industrial and wastewater inputs) and hydrological factors (high-magnitude flood events) on metal and organic contamination and on the source variability of sediments taken from the Deba River urban catchment.

#### References

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