METAL POLLUTION STATUS OF SUSPENDED PARTICULATE MATTER AND THE INFLUENCE OF ANTROPOGENIC ACTIVITIES OF THE DEBA RIVER URBAN CATCHMENT

Jon García-García[a], M. Martínez-Santos[a], E. Ruiz-Romera[a] , J. Unda-Calvo[a]

[a] University of the Basque Country, Department of Chemical and Environmental Engineering, Bilbao, Basque Country, Spain
jon.garciag@ehu.eus

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Introduction

Inflows of metals in river basins due to urban development is a constant concern (Li et al, 2008) because of the importance of metals toxic impact on aquatic organisms due to their persistence, toxicity and bioaccumulative nature (Davutluoglu et al, 2011). Sediments act as vector and reservoir of anthropogenic pollutants that accumulate over time (Owens and Xu, 2011). However, they can become a source due to changes in environmental conditions (Violintzis et al., 2009). Natural and anthropogenic disturbances can lead these changes (Martinez-Santos et al., 2015).

This study was conducted at the Deba River urban catchment (Basque Country, Northern Spain) and aims to: i) determine the metal contamination status of the Suspended Particulate Matter (SPM) along Deba River catchment and ii) assess the impact of anthropogenic disturbances such as wastewater treatment plant and non-depurated wastewaters on SPM-associated metal toxicity.

Materials and methods

Water samples were collected from 8 sampling points along the catchment during 9 sampling campaigns between January 2015 and January 2016.In the laboratory, samples were filtered through 0.45µm filters. The content of pseudo-total particulate metal (Fe, Mn, Zn, Ni, Cu, Cr and Pb) in the filter was measured by ICP-OES after microwave acid digestion. Geo-accumulation index (Igeo), and Pollution Load Index (PLI) were used to determine the polluted zones (Davutluoglu et al., 2011). The toxicity of SPM was approximately determined by PELQ (Violintzis et al., 2009), and Accumulation Factor (AF) was used to estimate the effect of different anthropogenic disturbances (Oke et al., 2013).

Results and discussion

Metal (Mn, Zn, Ni, Cr, Cu and Pb) contents in SPM show high variability between sample sites and sample campaigns, whereas Fe content remains more constant. Spearman's correlation matrix shows strong positive correlation ($r = 0.70 – 0.90$) between Mn, Zn, Ni, Cu, Cr and Pb. The correlation is weaker ($r = 0.30 – 0.60$) with Fe content. It could be due to two Fe sources: lithogenic and anthropogenic, whereas the other metals have mainly an anthropogenic source. The discharge and suspended solid concentration (SSC) show a significant negative correlation with the particulate metal content, which could be due to a dilution effect by metal-poor soil-born particles (Nicolau et al., 2012). Principal Component Analysis (PCA) distributes samples in two groups: i) samples with high SSC (20 – 400 $mg \cdot l^{-1}$) that were taken under high flow conditions (52 – 88 $m^3 \cdot s^{-1}$), and ii) samples with low SSC (1.5 – 12 $m^3 \cdot s^{-1}$) that were taken under low flow conditions (1.5 – 12 $m^3 \cdot s^{-1}$).

Igeo indicates no pollution for Fe, Mn, Ni, Cr and Cu under high flow conditions. Pb pollution is minimal except at O1, where it is moderate, and Zn presents moderate to strongly contamination except upstream (M1 and E1) were is low. When the discharge decreases, Igeo values increase (iron maintains unpolluted or with minimal pollution). O1 presents the maximum Mn and Pb pollution degree (twice of the rest of sampling sites). The same occurs at E2 sites with Zn, Cu and Cr. PLI shows the same behaviour as Igeo in relation with flow condition and it increases from upstream (M1 and E1) to downstream. With low discharge conditions PLI is high (1.8 – 3.3) in all sampling points, and very high at O1 (4.0) and E2 (3.9), which suggest higher potential to cause secondary pollution.

Under high flow conditions the toxicity is medium-low (PELQ between 0.6 – 1.4), and it increases to high (2.4-3.1) at O1 and D4 and specially (8.0) at E2 with low discharge. All metals (except Fe) show an AF higher than 1 which increases from upstream to downstream. The AF between D1 and D2 is 1.6 supposing a PELQ increase of a 16.5% which could be related with the wastewater treatment plant located between them. The Mn AF (1.7) between D2 and D3 could be due to batteries factory located upstream next to Oñati tributary. In Ego tributary PELQ increases a 365% from upstream to downstream, mainly associated with Zn (AF = 40.5) and to a lesser extent with Cu (AF = 5.7), Cr (AF = 2.9) and Ni (AF = 1.6). The increase of toxicity in the catchment from M1 to D4 is 200%, mainly due to Zn (AF = 7.0) probably from Ego tributary and to Mn (AF = 4.5) from Oñati tributary which reflect that those streams have received untreated wastewater effluents for a long time.

Conclusions

Metal content in SPM is strongly affected by discharge and SSC, so the hydrologic is a very important factor to be taken in mind in order to do a correct pollution evaluation. Metal pollution, and the associated risk, increases from upstream to downstream, mainly after untreated municipal and industrial wastewaters inputs.

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