Geophysical Research Abstracts
Vol. 21, EGU2019-17252, 2019
EGU General Assembly 2019

Evaluation of As and metal availability in sediments from river catchments with different land use in northern Portugal

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The Northern region of Portugal shows contrasting land uses which are attributed mainly to the geomorphology and climate. Given this heterogeneity, land management practices infer differences in the factors that contribute to non-point source pollution. Recent studies support concerns related to soil losses and land use conflict, high levels of P, metals and organic contaminants in the regional fluvial systems. This study aims to recognize the pattern of spatial and temporal distribution of metal contents in streambed sediments, and its potential availability, in two catchments with distinct geomorphology and connectivity, land use and under environmental pressures: (i) textile industry and livestock production in River Vizela; (ii) intensive agriculture in Vilariça Riverine.
Sediment samples were collected at the end of the dry season (September) and the end of the rainy season (May); the 63μm fraction was studied for As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn and V. To assess the contents, potential mobility and possible origins (natural/anthropogenic) of these elements, a sequential chemical extraction approach was used, considering five fractions: metals bound to carbonates as exchange cations in the soluble phase (F1); Mn oxides (F2); Fe amorphous compounds (F3); organic matter (F4); crystalline Al and Fe oxides (F5). The element concentrations were obtained by ICP-OES.
The results showed that: (i) As and metal contents distributed among the most mobile geochemical phases decreased in the following order: F1>F3>F2; (ii) the affinity to the organic phase, F4, was low; (iii) the F5 fraction revealed high amounts of Cr, Fe, Ni and V, whereas Mn and Cd were not detected. When comparing both catchments, differences were observed. Manganese, Cd and Pb dominated in fraction F1 in both catchments, but in Vizela catchment Zn and Co were also high. In F2, the Vilariça catchment presents several elements, whereas in the Vizela catchment these are not detected, except for Cd in one sample from the rainy season.
Manganese, Cd, Pb, and Cu, present in higher proportions in the most labile fractions suggesting the contribution of anthropogenic activities, assigned to distinct sources, were the metals with a higher potential risk of mobility to the water column. Chromium, Fe, V and Ni presented relatively higher contents in the residual fraction, expressing a significant contribution from a lithological source.
Some samples show total contents of metals that can be indicative of localized threat to fluvial ecosystems, in particular Cd, Cu, Pb and Zn. In both catchments, Cd contents were above the PEL values for the dry season. In the wet season, in the Vilariça catchment, these values decreased significantly and were below the PEL values, but in Vizela catchment only two samples were under PEL. This distribution could be explained by the occurrence of Cd mostly in the soluble phase as an exchange cation.