Selected metals in the sediments of River Sava, Slovenia

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Abstract: In order to determine the anthropogenic contribution of selected metals (Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn) to background levels, concentrations of these metals were measured in sediments at several downstream locations. An extracting procedure using 25 % (v/v) acetic acid was applied for estimation of the extent of contamination with heavy metals originating from anthropogenic activities. In addition, a normalization technique was used to determine background, naturally enriched and contamination levels. Aluminum was found to be good normalizer for most of the measured elements. The results suggest that an anthropogenic contamination of certain metal is not necessarily connected to easily extractable fraction in 25 % acetic acid. As a consequence of anthropogenic activities the elevated levels of all measured elements were found near Acroni Jesenice steelworks and at some locations downflow from biggest cities.

Key words: heavy metals, acetic acid extraction, normalization, river sediments, Slovenia

Introduction

Several studies used the normalization approach to quantify the degree of anthropogenic pollution in different water environments. Usually the Al as a major constituent of alumosilicates (Din, 1992; Tam & Yao, 1998) and Fe as a clay mineral indicator element (Morse et al., 1993; Kennicutt et al., 1994; Tam & Yao, 1998) have been used. As total metal concentration in sediment does not give adequate data about metal origin it also does not provide any data about metal solubility, mobility and potential bioaviability in sediment. To study the bioaviability of the metals in sediment several extraction techniques with different chemical extractants in single step and/or in sequence have been developed (Houba et al., 1996; Tack & Verloo, 1996; McGrath, 1996; Quevauviller, 1997; Mainz et al., 1997; Ščančar et al., 2000). Chemical partition of sediments is used also to deduce the source and pathways by which natural and anthropogenic heavy metals have entered the environment. For marine sediments a method based on the comparison of data for total metal concentration and the portion extractable in acetic acid was suggested to asses the extent of heavy metal contamination originating from anthropogenic activities (Loring & Rantala, 1992; UNEP/IOC/IAEA, 1995).

Results and discusion

In general, the highest total metal concentrations in sediments were found at Moste hydro power plant reservoir, which is influenced

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by effluents from Acroni Jesenice steelworks. Concentrations of metals from the Sava River upstream (sampling sites S1 to S6) are low and represent their geochemical background with exception of Cd. Cd is higher in upper flow and at HPP Moste and it is probably a consequence of uncontrolled anthropogenic source in upstream region. The highest Hg concentrations (0.7 – 1.5 mg/kg) were found downstream at sampling locations V5, V6 and V7, due to effluents from Hrastnik chlor-alkali plant (TKI Hrastnik), which used "mercury cell" until year 1997 and has since changed to membrane technology.

Basically two patterns were distinguished on normalization scatter plots. Among metals where the concentration represents their natural background (Co) almost all data points are located within the limits of the 95 % confidence band of the regression line, except LJ11 and LJ2, which represent sampling locations on the Ljubljanica upstream and downstream Ljubljana waste water treatment plant. The metals that show the anthropogenic contribution (Cd, Cr, Cu, Fe, Ni, Pb, Zn) have elevated Me/Al ratio at same locations. Concentration of Cd shows natural background at locations downstream from HPP Moste while the levels in sediments at upper flow and in HPP Moste reservoir show anthropogenic contribution most probably due to local input from Acroni Jesenice steelworks. The normalization of the data showed higher Me/Al ratios for Cu and Fe only in sediments collected in HPP Moste reservoir while the Me/Al ratios for Cr, Ni, Pb and Zn show anthropogenic contribution in sediments from HPP Moste reservoir and at certain locations around Ljubljana, especially at sampling locations LJ2 and LJ10.

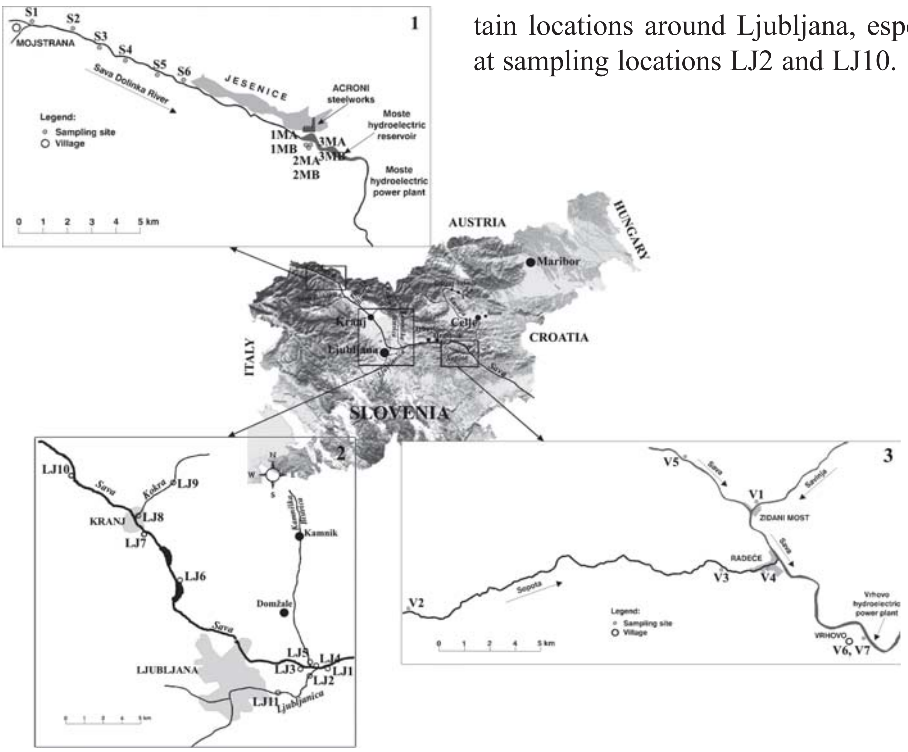

Figure 1. Sampling locations in Sava River and its inflows.

Cd was most soluble in sediment at downstream locations (LJ and V stations). The percentage of extractable Cd was 26 to 76 %, while at upstream locations Cd was strongly bound, with extractable fraction only between 2 and 8 %. The geochemical normalization of Cd to Al indicates the anthropogenic source (industrial or municipal) at upstream locations (S and M), while acetic-acid extraction shows that Cd is strongly bound at those locations. At downstream locations lower Cd concentrations were found, indicating weaker bound.

Co, Cr, Cu and Zn showed very uniform distribution of extractable fraction along Sava River. For Ni and Pb the soluble fraction were the highest in sediments collected at HPP Moste (Ni: 40 – 47 %; Pb: 79 – 100 %) and significantly lower at up- and downstream locations (Ni: 5 – 19 %; Pb: 9- 22 %) and show the same distribution pattern as normalization to Al. The lower percentage of extractable metal was found for Cr (2 – 21 %) followed by Cu (3 – 28 %), Co (6 – 34 %) and Zn (17 – 48 %). Extractable fraction of Cr, Cu, Co and Zn do not show the same distribution pattern as geochemical normalization. It can therefore be concluded that Ni and Pb in sediments from HPP Moste reservoir originate from anthropogenic activities, while solubility of other metals is not necessary

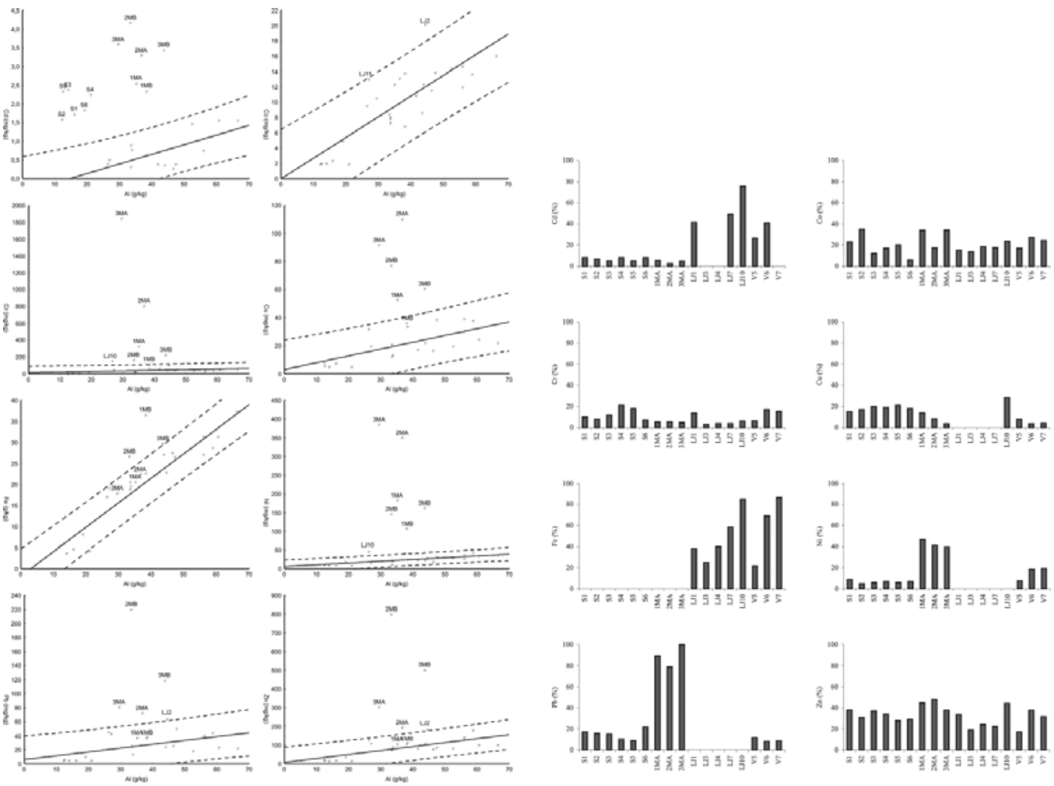

Figure 2. a) scatter plots Me/Al for surface sediments in Sava River. Solid lines represents regression line and dashed lines represent the 95 % confidence band and b) percentage of metals in the fraction soluble in 25 % ($^{v}/_{v}$) acetic acid.

connected to anthropogenic contribution of those metals to their natural background concentrations.

CONCLUSIONS

To obtain as much as possible information about elements behavior and origin in sediments the measuring of total element concentration is not enough. The geochemical normalization to element, which is abundant in certain sediment give adequate information on origin of element (i.e. natural or anthropogenic), while acetic acid extraction does not give any information on origin, but it gives some information on mobility and bioavailability of the certain element.

The results obtained from total metal (Al, Cd, Co, Cr, Cu, Fe, Hg, Ni, Pb and Zn) concentration, acetic acid extraction (25 %, v/v) and normalization to Al indicate that sediment in HPP Moste is the most polluted area in the Sava River flow by Cd, Cr, Cu, Ni, Pb and Zn. Elevated concentrations of Co, Cr, Pb and Zn were also observed at location on the Ljubljanica River just downstream Ljubljana waste water treatement plant (LJ2). At other locations the concentrations of those metals represent their natural background. The results obtained by acetic acid extraction agreed well with normalization to Al for Pb and Ni. For other analyzed metals the acetic acid soluble fractions not connected to anthropogenic activities.

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