Fluvial transport patterns of dissolved trace metals to the Ria of Cedeira

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Abstract

Samples of water were withdrawn monthly close to the Das Mestas River mouth, out of the tidal influence, from October 2011 to September 2012 (covering a hydrological year). After filtration through 0.45 policarbonate membrane, nine trace metals were analyzed (Al, Co, Cu, Cr, Fe, Mo, Ni, Pb and V) in the dissolved phase. All procedures were made following trace-metal-clean techniques. Three groups of metals were distinguished: Al, Co, Ni, Cu and Pb correlated with the SPM and the DOC indicating they are related with soil leaching; Iron is related with Chl-a so its behavior depends on the biologic activity; lithological influence on Cr, Mo and V patterns was observed.

Keywords:

River load, trace element, Das Mestas River, NW Iberian Peninsula.

1. Introduction

Several authors [*e.g.* Bernardez *et al.*, 2013; Nicolau *et al.*, 2006; Meybeck and Helmer, 1989] point that large rivers, especially those affected by human activities, are widely studied, but exists a lack of knowledge on small rivers. Since continental surface waters cover a wide range of concentrations (especially in small drainage basins) related to different environmental factors, Meybeck and Helmer [1989] state that a global reference level for rivers cannot be set. These authors, recommend that regional baseline values should be established, taking into account the local lithology, climate, vegetation and drainage patterns of nutrients and organic matter. This paper intent to identify variation patterns of nine dissolved trace metals (*i.e.* Al, Co, Cr, Cu, Fe, Mo, Ni, Pb and V) in a temperate watercourse, the Das Mestas River (NW Iberian Peninsula).

2. Material and Method

2.1. *Study area.*

The Das Mestas River is the main flow of continental water discharging into the Ria of Cedeira. The river course has 18 km long and an average flow of 2.09 $m^3 \cdot s^{-1}$, ranging from 0.48 to 34.37 $m^3 \cdot s^{-1}$ (daily data from January 2011 to January 2013). Its watershed has a total area of 81.84 km^2 supporting an average population density of 62 inhab·km^{-2}, spread in small towns. The land use in this area is composed basically agriculture, eucalyptus plantations (57%), crops (24%), pastures and meadows (10%). The river crosses a variety of lithology including serpentinites, acid metabasites and metavulcanites, felsic-gneiss schists and metabasites.

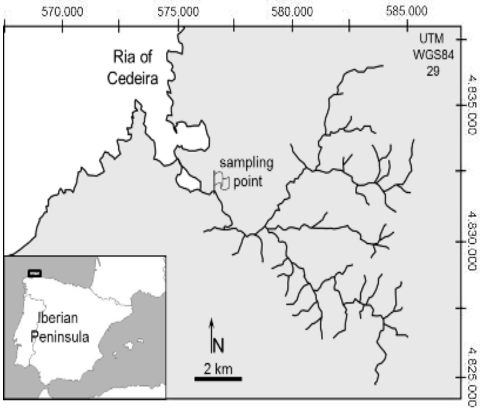

Figure 1. The Das Mestas River drainage net.

2.2. *Sampling, sample treatment and analysis.*

Samples of water were taken monthly from October 2011 to September 2012 at Porto do Cabo (43º 37.543'N; 8º 02.405'W). Temperature, pH and conductivity were recorded. Afterwards, samples were filtered inside a class-100 laminar flow bench (Cruma 670FL) placed inside the clean laboratory (class-10000). The filtration was undertaken using 0.45 µm acid-clean polycarbonate membranes (Gelman). Samples were acidified to pH<2 with suprapur 30% HCl (Merck). All procedures during sampling, handling and analysis were made following trace-metal-clean techniques [EPA, 1996].

Trace metals in the dissolved phase (Al, Co, Cu, Cr, Mo, Ni, Pb and V) were determined by Inductively Coupled Plasma–Mass Spectrometry (ICP-MS, Thermo-Elemental X-Series) [American Public Health Association, 1995]. Iron was analyzed by Electrothermal Atomic Absorption Spectrometry (ETAAS, Varian SpectrAA 220 with Zeeman background correction). Samples to determine chlorophyll-a (Chl-a) were immediately filtered (Whatman GF/F 25 mm diameter filter) and Chl-a determined by spectrofluorimetry. Dissolved oxygen was quantified by the Winkler method. Dissolved organic carbon (DOC) was determined using a Shimadzu TOC-VCSH analyzer.

3. Results.

Range distributions as box and whisker graphs are presented in figure 2, where the length of the box represents the interquartile range containing 50% of the values. Mean trace element concentrations (horizontal dotted line) were as follows: 17.5 µgAl·L^{-1}; 0.034 µgCo·L^{-1}; 0.37 µgCr·L^{-1}; 0.40 µgCu·L^{-1}; 60 µgFe·L^{-1}; 0.06 µgMo·L^{-1}; 0.39 µgNi·L^{-1}; 0.020 µgPb·L^{-1}; 25 µgV·L^{-1}. The straight horizontal line inside the box indicates the median. The whiskers are lines that extent from the box to the highest and lowest values excluding outliers and extremes. Outliers handling represent the 5 and 95 percentile.

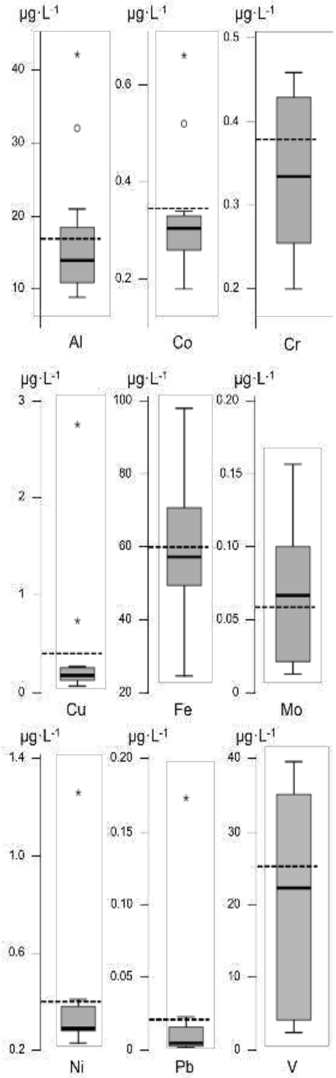

Figure 2. Trace metal concentrations.

To study metal groupment, two statistical procedures were employed; (i) a cluster analysis (left figure 3) where variables were typified to avoid aggregation by concentration similarity; (ii) correlation between all the measured variables was checked and as result a correlation matrix was obtained. It was considerate as relevant those correlation coefficients over 0.612 (critical value of r, n=14, 1-tailed testing, α=.01), two extra samples (October 2012 and January 2013) were also included. Parameters with coefficients under the critical value of r have not been considered (discharge, temperature, conductivity, pH and dissolved O_2 saturation).

Based on the cluster dendrogram, metals can be grouped as follows: a group consisting of Al, Co, Ni, Cu and Pb, all with a significant direct correlation with suspended solids (SPM) and dissolved organic carbon (DOC). Correlations of SPM with those metals varied between 0.63 and 0.92; correlations with DOC ranged resulted 0.62 and 0.89. These results suggest that metals distribution in the dissolved fraction is ruled by the amount of suspended matter and nature of sediment particles. This was particularly clear during the flooding events induced by the first rains after the fall. A second group was found with Cr and V (Cr-V

0.92) both indirectly correlated with Mo (-0.93 and -0.85 respectively). An indirect correlation was also found between Fe concentrations and Chl-a (-0.70).

Figure 3 (right) shows the temporal variation of the three metal groups. In order to present all the data in the same scale concentrations were typified by dividing by the mean value calculated for all the period. The straight gray line represents the value 1 (mean) while curves show the variations in concentration respect to the mean. Discharge data is also present as a black shadow.

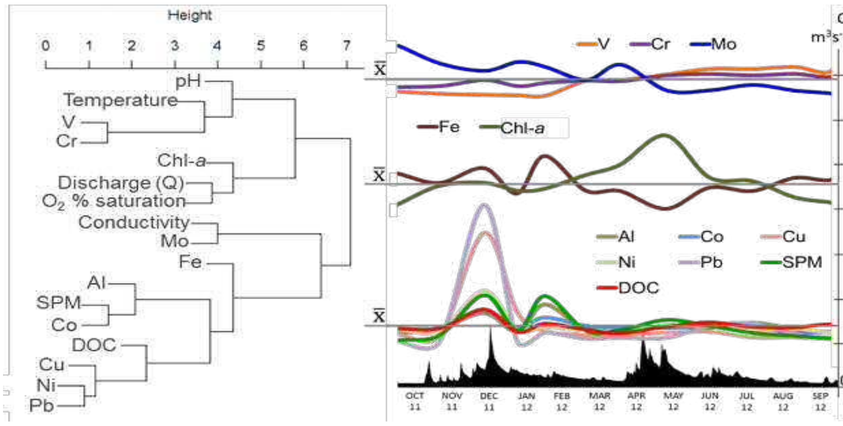

Figure 3. Grouping. Cluster dendrogram in the left side (R statistics software). In the right the daily discharge (Q) and the studied variables as curves in the three identified groups.

4. Discussion.

The increase of dissolved Al, Co, Ni, Cu and Pb with the SPM suggest that as suspended matter increased metals desorb from the solids. Higher metal concentrations were reported by Nicolau et al. [2006] after flooding events in small Mediterranean rivers, especially when rain occurred after long dry periods. These authors attribute this phenomenon to the transport by runoff of particles washed from the upper soil horizon. On the other hand, Mokhtar *et al.* [2009] related an increase in dissolved ions with the decay of organic matter in forest floors. The increase in metal concentration of Al, Co, Ni, Cu and Pb after first rains of November and December could be linked to the decomposition of organic matter deposited combined with soil leaching by the rain after summer.

Time course variation of Cr, Mo and V levels showed no seasonal pattern. Concentrations of V (mean value 20±15 $\mu g \cdot L^{-1}$) were higher than those found for in similar freshwater systems, rivers Sor, Mera and Landro [Bernárdez *et al.*, 2013]. Shiller and Mao [2000] hold that dissolved V in surface waters might be indicative of the local lithology, among others. Therefore V concentrations should be related with the higher contents of V in the regional soils reported by

Macías-Vázquez and Calvo-Anta [2009] in those over basic and ultrabasic rocks (180 and 111 mg·kg^{-1}, respectively) present within the Das Mestas basin.

The variability of Fe concentrations with Chl-a in a seasonal basis is related with the primary production.

5. Conclusion remarks.

Metal concentrations in the dissolved phase of the aquatic system of the Das Mestas River can be mainly related with seasonal parameters. Concentrations of Al, Co, Ni, Cu and Pb increases by soil drainage after the fall while the rest of the period trend to remain almost constant. Iron concentration decreases when phytoplankton grows. Cr, Mo and V do not show any seasonal pattern and may be related to the local mineralogy.

Acknowledgments

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