Spatio-Temporal Variability of Dissolved Metals in the Surface Waters of an Agroforestry Catchment with Low Levels of Anthropogenic Activity

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Abstract. Evaluation of levels and spatial variations of metals in surface waters within a catchment are critical to understanding the extent of land-use impact on the river system. The aims of this study were to investigate the spatial and temporal variations of five dissolved metals (Al, Fe, Mn, Cu and Zn) in surface waters of a small agroforestry catchment (16 km²) in NW Spain. The land uses include mainly forests (65%) and agriculture (pastures: 26%, cultivation: 4%). Stream water samples were collected at four sampling sites distributed along the main course of the Corbeira stream (Galicia, NW Spain) between the headwaters and the catchment outlet. The headwater point can be considered as pristine environment with natural metal concentrations in waters because of the absence of any agricultural activity and limited accessibility. Metal concentrations were determined by ICP-MS. The results showed that metal concentrations were relatively low (Fe > Al > Mn > Zn > Cu), suggesting little influence from agricultural activities in the area. Mn and Zn did not show significant differences between sampling points along main stream, while for Fe and Cu significant differences were found between the headwaters and all other points. Al tended to decrease from the headwaters to the catchment outlet.

1. Introduction

Local conditions such as topography, hydrology, geology and soil uses in catchment areas, as well as local precipitation rate and climate determine the wide range of water chemistry conditions observed in streams. Generally, the solutes of surface water are mainly derived from the weathering of rocks and erosion of soils in the drainage basin [1]. Heavy metals are not only regarded as natural trace components of the aquatic environment but are also commonly known as environmental pollutants particularly receiving input from anthropogenic activities through the discharge of industrial and domestic wastewater as well as agricultural drainage to the rivers [2]. Metals are important parameters in water-quality assessment. They occur in the environment in a variety of forms, and their bioavailability is controlled by conditions such as pH and ligands, which can be highly impaired by human activities.

Groundwater, because of the long-term contact with rocks and mineralized soils, usually contain greater concentrations of heavy metals than surface waters. There is a considerable temporal and
spatial variation in concentrations of heavy metals in surface waters. Generally, the heavy metal concentrations of rivers tend to increase from source to mouth and to vary inversely with discharge, which dilutes the natural and industrial contaminations. Understanding of the spatio-temporal distribution of heavy metals and identification of the sources in the river systems is a prerequisite for the protection and sustainable utilization of the water resources. Regularly monitoring and evaluating the quality of river water are required for integrated management of water resources [3].

In the present study, we analysed the spatial and temporal variability of surface water quality concerning to the dissolved metal concentrations (Al, Fe, Mn, Cu and Zn) in water of Corbeira stream, a tributary of Mero River, located in a rural area of Galicia (NW Spain).

2. Material and Methods

2.1. Study Area

This study was carried out in the Corbeira catchment, a small agro-forestry catchment (16 km²) located in the headwaters of the Mero River basin (A Coruña, NW Spain), draining terrains developed on basic schist of the Órdenes Complex, whose main constituents are biotite (sometimes chlorite), calcium plagioclase and amphiboles. The catchment elevation ranges from 60 m to 470 m above sea level. Hillslope steepness reaches an average of 19%. The stream length is 10 km and the mean stream slope gradient is 2.9%. The most common soil types in the catchment are Umbri-sols, which predominantly occupy the forest areas, and Cambisols (25% of the total area) that are found mainly in the agricultural areas of the catchment [4]. The topsoil is characterized by silt and silt-loam textures, acid pH (4.5 - 5.6), high organic matter contents (4.4 - 10.5%), with the highest values in the forest soils (mean 8.5%) and the lowest in the cultivated soils (mean 5.3%). The main land uses are forestry (65%, mostly Eucalyptus sp and Pinus sp) and agriculture (30%) including grasslands and croplands. Impervious areas (roads and built-up areas) cover about 5% of the catchment and are mainly distributed in the agriculture zone. The population density of the catchment is low (35 inhabitants per km²). Organic (mainly manures and cattle and pig slurry) and inorganic fertilizers are commonly applied to the agricultural area throughout the year, including the wet period (October to March). The mean annual temperature is 13 °C and the rainfall is approximately 1040 mm. The hydrological regime is pluvial, with maximum discharge in December (winter) and low flows from June to September (summer). Detailed information about location, climate and hydrological regimes, and transport of metals in this area was provided in [5-8], and details of soils in [7, 8].

In the Corbeira stream four points were sampled along the main channel (P1, P2, P3 and P4), each of them being located at the outlet of a sub-catchment. P1 (headwater point) receives water from a forest area, and it can be taken as an approach to the catchment metal background due to the absence of anthropogenic activity in this area. P2 and P3 are located 2.99, and 4.12 km from the headwater point, respectively. In the sub-catchments represented by P2 and P3 the forest cover is about 67.5% of the total area of each sub-catchment; at the same time, the agricultural use of the soil (mainly grasslands) is increasing from headwaters to the catchment outlet. A greater agricultural activity of the Corbeira catchment is located between P2 and P3. In the sub-catchment represented by P4 (catchment outlet) the forest cover falls to 65.4% of its total area and the percentage of agricultural land increases.

2.2. Sampling procedure and analysis

A total of 100 water samples were collected bimonthly in Corbeira stream (low and high flows) between 28 December 2004 and 30 September 2008. Water samples were collected in polyethylene bottles, which were pre-washed in a 10% solution of HNO₃ and then rinsed with Milli-Q water. Water samples were analysed for dissolved Al, Fe, Mn, Cu and Zn concentrations (measured with ICP-MS). For determination of dissolved fractions, samples were filtered using 0.45 µm pore diameter membrane filter and then acidified with (1:1) nitric acid to pH < 2. Further details of the water sampling and analysis can be found in [5].
2.3. Statistical analysis
All statistical analyses were performed with the package IBM SPSS Statistics 19. Due to the presence of outliers and the absence of normality, nonparametric tests for spatial analysis were applied, both to identify differences among points, and between which points there are significant differences in the pairwise comparisons.

3. Results and discussion
3.1. Spatial variation
Table 1 shows the statistical summary of the concentrations of Al, Fe, Mn, Cu and Zn in the samples collected at the four points of the main channel of the Corbeira stream. The results showed that dissolved metal concentrations were relatively low (Fe > Al > Mn > Zn > Cu), in agreement with the water pH values close to neutrality [5], suggesting little influence from agricultural activities in the area. In spite of this, a wide range of concentrations was detected for all metals in each sampling point (table 1).

|       | Al   | Fe   | Mn   | Cu   | Zn   |
|-------|------|------|------|------|------|
| P1    |      |      |      |      |      |
| Median| 16.4 (a) | 26.5 (a) | 0.29 | 0.15 (a) | 0.15 |
| Minimum| 6.1  | 7.6  | 0.09 | 0.05  | 0.01 |
| Maximum| 197.5 | 166.8 | 3.14 | 3.14  | 2.60 |
| P2    |      |      |      |      |      |
| Median| 12.6 (a, b) | 42.6 (b) | 0.51 | 0.32 (b) | 0.26 |
| Minimum| 6.0  | 4.3  | 0.08 | 0.14  | 0.05 |
| Maximum| 85.3 | 130.8 | 10.82 | 1.08  | 13.04 |
| P3    |      |      |      |      |      |
| Median| 11.0 (b) | 39.3 (b) | 0.91 | 0.32 (b) | 0.47 |
| Minimum| 5.0  | 3.4  | 0.07 | 0.17  | 0.05 |
| Maximum| 76.1 | 120.1 | 8.51 | 1.09  | 13.63 |
| P4    |      |      |      |      |      |
| Median| 10.2(b) | 56.0 (b) | 0.57 | 0.31 (b) | 0.20 |
| Minimum| 4.1  | 4.8  | 0.09 | 0.14  | 0.05 |
| Maximum| 75.4 | 105.3 | 7.81 | 1.07  | 14.50 |

(a) and (b) indicate the existence of significant differences in concentration between sampling points.

There were significant differences (p < 0.05) for Fe and Cu concentrations between P1 (headwaters) and all other points, and for Al contents between P1-P3, and P1-P4, while for Mn and Zn concentrations, no significant differences were observed between sampling points. When the median values of the study metal concentrations were examined, different spatial trends were observed. Thus, there was an increasing trend of Fe concentration from upstream (P1: headwaters) to the downstream (P4: catchment outlet), probably due to the higher volume of groundwater prevailing at the catchment outlet. However, the median values of Mn and Zn increased from P1 to P3 decreasing in the catchment outlet. Cu increased significantly from P1 to P2 remaining constant until P4. Unlike the other metals, median Al concentrations exhibited a progressive decrease from headwaters to the catchment outlet. Median Al concentrations in P1 were 1.6 times greater than in the catchment outlet. This fact can be explained by the smaller particle size of the suspended solids (SS) recorded in the headwater stream compared to those of the other points. Significant and positive relationships between dissolved Al concentrations and SS contents were observed at all sampling points (data not shown). However, the slope of the regression line was higher in P1, which suggests that, for the same concentration of SS in the water, dissolved Al concentrations are usually higher in the headwaters. Al-rich colloidal particles may have passed through the 0.45 µm filter and counted as dissolved Al [5].
3.2. Temporal variation

Previous studies on the metal loads of Corbeira stream have highlighted the role of high flows on metal export [9, 10]. For this reason, the temporal evolution of metal concentrations in the Corbeira stream is analysed essentially on the basis of the discharge. High-flow periods were frequent between the years 2004 and 2006, except for their respective summer months. By contrast, 2007 was the driest year of the study period and as consequence the annual streamflow was the lowest of the study period, the Corbeira stream being maintained mainly under base-flow conditions [11].

Figure 1. Temporal variability in metal concentrations in each sampling point

Figure 1 shows an example of the temporal distribution of the concentrations of some metals here studied. The observation of this figure allows verifying the existence of several similarities in the concentrations distribution of all the metals throughout the study period, except for concentrations measured during the year 2007. Al and Cu reveal higher concentration values, as well as greater variability from the beginning of the study period until the end of 2006, whereas during the remaining study period (years 2007-2008) these metals exhibit a much more stable behaviour and similar concentrations at all the points. Fe is the metal that most fluctuates and concentrations distribution, especially during 2007, differs from that of Al and Cu.

The concentration peaks of all metals are linked to rainfall-runoff episodes that occurred during waters sampling, with the exception of those peaks of Fe and Mn recorded during the year 2007, which are probably linked to higher concentrations of Fe and Mn (dissolved) on groundwater compared with near-surface water [12].
Thus, the peaks of Al, Fe, Mn, Cu and Zn recorded on 28 December 2004 were generated with a rainfall-runoff event that caused high SS concentrations due to the rills developed in some agricultural fields nearby to the points P2 and P3. These metal concentration peaks can reflect the presence of these metals in colloidal forms, which could induce an increase in the concentration of dissolved metals at points receiving runoff waters, mainly in those involved in the processes of more or less intense erosion, as is the case of the waters collected at point P2 and P3. On the other hand, the unanimous increase of Al, Fe and Cu concentrations and to a lesser extent Zn, registered on 6 October 2006 (figure 1), coincided with a rainfall-runoff event that recorded the highest rainfall volume of the study period, as well as high SS concentrations. As a consequence, a higher washing of these metals from the soils to stream can be occur, as well as an increase of their microparticulate fraction.

Finally, it should be pointed out that the increase in metal concentrations occurred in 2008, especially notable for Fe and Mn (figure 1), is again related to runoff events and with the increase of colloidal particles carrying these metals.

4. Conclusions
The results from the analysis of stream water collected from four points along main stream showed that dissolved metal concentrations were relatively low (Fe > Al > Mn > Zn > Cu), suggesting little influence from agricultural activities in the area. The statistical results revealed no common trend in the spatial variability of the metal concentrations measured at the four sampling points. For Mn and Zn concentrations no significant differences were observed between sampling points, while for Fe and Cu significant differences were found between the headwaters and all other points. Al tended to decrease from the headwaters to the catchment outlet probably due to the smaller particle size of the suspended solids recorded in the headwater stream compared to those of the other points.

Temporal variations in dissolved metals suggest that metal concentrations are controlled by rainfall-runoff episodes that occurred during waters sampling, with the exception of those peaks of Fe and Mn recorded during the year 2007, which were probably more linked to groundwater.

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