Factors Controlling the Metal Levels in Headwater Stream Draining an Agroforestry Catchment (Galicia, NW Spain)

Laura Palleiro 1, M. Luz Rodriguez-Blanco 1, M. Mercedes Taboada-Castro 1, M. Teresa Taboada-Castro 1

1 Faculty of Sciences, Centre for Advanced Scientific Research (CICA), University of A Coruña, 15071 A Coruña, Spain

E-mail address: teresa.taboada@udc.es

Abstract. Concentrations of Al, Fe, Mn, Cu and Zn (dissolved and particulate), suspended sediment, dissolved organic carbon, and pH and discharge were determined during a 3-year period in a stream water of an agroforestry catchment in Galicia (NW Spain). The objective of this study is to investigate the role of these variables in the control of dissolved and particulate concentrations of each metal in the stream water. The soils in the catchment are developed on metamorphic schist. Stream water samples were collected at the catchment outlet every 15 days and more frequently with increased stream flows. Metal concentrations were measured by ICP-MS. Pearson correlation coefficients were calculated to examine the possible associations between metals and the four variables under consideration. Stepwise multiple regressions were applied to determine which predictor variables have the strongest influences on controlling concentrations of each metal in the stream. The results showed that metal concentrations were relatively low (Fe > Al > Mn > Zn > Cu), but particulate metals were predominant over those dissolved. Stepwise multiple regression analysis revealed that the most important variable to explain dissolved concentrations for Al, Fe and Cu was the dissolved organic carbon, whereas the suspended sediment was a good predictor of particulate metal levels.

1. Introduction
Metal concentrations of river water and sediment are usually controlled by the abundance of metals in the rocks and soils of the catchment, and their geochemical mobility; however, anthropogenic impacts have greatly affected availability and cycling. Understanding factors controlling mobility of trace metals in surface waters is critical to assessing potential impacts from metals on the hydrosphere. Cycling of metals is complex because many factors influence the mobility and transport of metals to and within surface water systems, such as properties of the metals themselves, pH, ionic strength, dissolved organic matter (DOC), suspended sediment (SS), etc. Each metal has unique chemical properties, including solubility and binding affinities, which affect its speciation and mobility [1]. Acidity is a “master variable” because of its control over metal solubility and speciation. Low pH increases the solubility of many metal cations and reduces the capacity of metals to remain adsorbed to solids due to protons competition for negatively charged binding sites [2]. DOC can bond metals and thus increase metal solubility reducing their toxicity and bioavailability, while DOC degradation releases organically bound metals, thereby increasing their bioavailability [3]. SS in natural waters are...
characterized by a great diversity, and they generally include minerals, clays, organic particles, biological debris, and inorganic particles coated with organic matter that provide abundant binding sites for metals removing them from solution [1]. Few studies have investigated factors controlling metal concentrations in uplands and streams of forested catchments. The aim of this study is to determine factors which control dissolved and particulate Al, Fe, Mn, Cu and Zn concentrations in a headwater stream draining an agroforestry catchment in NW Spain. Although metal concentrations may be related to numerous factors, we attempt to explain variability using four variables: pH, DOC, SS and discharge (Q).

2. Material and Methods

2.1. Study area
The study was conducted in the headwater of the Mero River Basin (A Coruña, Galicia, NW Spain) which drains an area of 65 km² with three different land uses: forest (53%) with mainly pine and eucalyptus, pasture (38%), cultivation (4%), and impervious areas (5%). The soils are developed on basic metamorphic schist of the Órdenes Complex (IGME, [4]) and main soil types are Umbrisols and Cambisols (IUSS Working Group WRB, [5]), which are usually deep because of intense weathering. The surface soil layer has silt and silt-loam texture and acidic pH (mean 5.6). The mean organic matter content in the upper horizon ranges from 4.1 to 14.3%, with the highest values in the forest soils and the lowest in the cultivated soils. The area’s climate is humid temperate and rainfall (mean annual of about 1194 mm) is usually concentrated in autumn and winter. The hydrological regime is pluvial. Additional information of this basin can be obtained from [6, 7 and 8].

2.2. Monitoring, sample collection and analysis
The monitoring period comprised three hydrological years, from October 2005 to September 2008. Stream water samples were collected at the basin outlet every 15 days and more frequently at 2-8 h intervals during storm events. A total of 1100 water samples were analyzed that provided a detailed temporal record of metal concentrations in stream water under a range of flow conditions. The stream water level was monitored continuously at the basin outlet (logged at 10-min intervals) and then converted into discharge values (m³·s⁻¹) using the rating curve technique, based on field discharge measurements.

Water samples were collected in polyethylene bottles, which were prewashed in a 10% solution of HNO₃ and then rinsed four times with Milli-Q water. Water samples were analyzed in the laboratory for metals (Al, Fe, Mn, Cu, Zn), pH (determined with a pH meter Crison micro pH 2000), DOC and SS. The total metal concentrations were determined after digesting 50 mL of unfiltered subsamples with ultra-high purity acids (1 mL HNO₃ + 3 mL HCl) in a block of graphite. Subsamples for dissolved metals were filtered through 0.45 μm pore diameter membrane filter and then acidified with nitric acid to pH < 2. Metal particulate concentrations were calculated from the difference between total and dissolved concentrations. Al, Fe, Mn, Cu and Zn concentrations (total and dissolved) were measured by ICP-MS. Three replicates were made on each sample. Replicate samples for all the measured variables generally agree. SS concentrations were determined gravimetrically after passing the water samples through filters (0.45 μm). DOC after sample filtration (0.45 μm) was determined using a Total Carbon Analyzer Shimadzu 5000A. Further details of the water sampling, discharge monitoring and analysis can be found in [6, 7].

Pearson correlation coefficients were calculated to assess the relationships between the metal concentrations and the study variables. Stepwise multiple regressions were applied to determine which predictor variables have the strongest influences on controlling concentrations of each metal in the stream. All statistical analyses were performed with the “R” program.

3. Results and Discussions
A marked variability in metal concentrations as well as in Q, pH, DOC, and SS values was observed (Table 1). Q oscillated between 0.2 and 22.1 m³·s⁻¹; pH values ranged from 5.9 to 7.5; DOC values
fluctuated between 0.6 and 7.1 mg L\(^{-1}\), and SS varied from 0.5 to 646 mg L\(^{-1}\). The SS variability was probably associated with hydrological changes and the existence of sediment source areas near or well connected to the stream, as it has already been reported for this basin [9]. The total metal concentrations also varied significantly, especially the particulate fractions, in part reflecting the relatively high variability in SS levels. The mean abundance order of the metal contents in the particulate phase was Fe>Al>Mn>Zn>Cu, while it was reversed for Mn and Zn in the dissolved phase. The particulate metals showed a similar pattern to the total metals in the topsoil of the Mero Basin, where they appear predominately linked to residual phases, i.e., embedded in the crystal lattice of minerals [8]. For all metals, the particulate concentrations were significantly higher than the dissolved ones (Table 1), suggesting that the transport of these metals is linked to particles’ transport. When the mean dissolved metals in the catchment were compared to the world mean concentrations of unpolluted rivers [10], only Znd showed higher concentrations in the Mero River because of the high Zn content in the schists of the study area. However, both the dissolved and particulate metals were slightly lower than those determined by Soto-Varela et al. (2014) in a stream adjacent to the study area, with similar characteristics to those of the Mero Basin.

Table 1. Dissolved (d) and particulate (p) metal concentrations (μg L\(^{-1}\)) and other variables

| Type | Min. | Max. | Mean |
|------|------|------|------|
| Ald  | 1.8  | 211.0| 23.0 |
| Alp  | 4.3  | 21144.5| 1287.3|
| Fed  | 1.4  | 231.5| 42.8 |
| Fep  | 4.8  | 19871.0| 1466.9|
| Mnd  | 0.1  | 9.5  | 1.0  |
| Mnp  | 0.2  | 807.8| 60.1 |
| Cud  | 0.1  | 1.3  | 0.4  |
| Cup  | 0.1  | 19.1 | 1.2  |
| Znd  | 0.1  | 24.1 | 1.8  |
| Znp  | 0.1  | 49.1 | 4.2  |
| Q (m\(^3\) s\(^{-1}\)) | 0.2 | 22.1 | 2.0  |
| pH   | 5.9  | 7.5  | 6.8  |
| SS (mg L\(^{-1}\)) | 0.5 | 646.0| 44.0 |
| DOC (mg L\(^{-1}\)) | 0.6 | 7.1  | 2.7  |

The correlation analysis (Table 2) showed that there were positive and significant relationships between Q and particulate metals, indicating that increases in Q were associated with increments of particulate metals. However, in the dissolved phase only Fed and Mnd had inverse relationships with Q, which is frequently linked to either dilution processes or higher Fed and Mnd concentrations on groundwater compared to near-surface water [11]. The water pH presented negative correlations with all particulate metals. If stream geochemistry was dominated by pH, one would expect an increase in particulate metals with increasing pH. However, this did not happen, but the pH was negatively related to the SS and Q. Therefore, particulate metal concentrations were largely controlled by the SS concentrations.

As regards dissolved metals, only the Ald, Znd and Cud showed inverse relationships with pH. All dissolved metals, except Znd, were correlated with DOC. All particulate metals as well as dissolved metals, except for Mnd, showed positive and significant relationships with SS. These observations showed a relevant influence of the solid particles on the metal concentrations, as was reported by [12] in a catchment next to the study area. The dominant control of particulate metal concentrations is the supply of SS. Suspended sediment availability can vary considerably through time, as was found by [9] in the Corbeira catchment.
Table 2. Pearson correlation matrix. Correlations significant at $p < 0.01$ in bold

|     | Q     | pH    | SS    | DOC   |
|-----|-------|-------|-------|-------|
| Q   | 1     |       |       |       |
| pH  | -0.22 | 1     |       |       |
| SS  | 0.17  | -0.42 | 1     |       |
| DOC | -0.15 | -0.38 | 0.36  | 1     |
| Ald | 0.06  | -0.40 | 0.67  | 0.69  |
| Fed | -0.31 | 0.05  | 0.33  | 0.53  |
| Mnd | -0.21 | 0.01  | 0.09  | 0.17  |
| Cud | 0.05  | -0.44 | 0.53  | 0.39  |
| Znd | 0.02  | -0.32 | 0.66  | 0.07  |
| Alp | 0.15  | -0.42 | 0.94  | -     |
| Fep | 0.15  | -0.41 | 0.96  | -     |
| Mnp | 0.13  | -0.42 | 0.95  | -     |
| Cup | 0.13  | -0.43 | 0.95  | -     |
| Znp | 0.20  | -0.32 | 0.87  | -     |

Table 3. Results from stepwise regressions for dissolved and particulate metal concentrations

| Equation                      | Adjusted $R^2$ | p-value | Independent variable | t values |
|-------------------------------|----------------|---------|----------------------|----------|
| Ald = 31.1 + 8.8 DOC + 0.1 SS - 5.4 pH | 0.61           | < 0.01  | DOC, SS, pH          | 26.1, 16.5, -3.1 |
| Fed = 3.2 + 16.3 DOC - 2.6 Q | 0.57           | < 0.01  | DOC, Q               | 33.6, -11.6 |
| Mnd = 0.53 * Q^{2.59}       | 0.20           | < 0.01  | Q                    | -        |
| Cud = 0.6 + 0.1 DOC + 7.7 E-3 SS - 7.5 E-2 pH | 0.63           | < 0.01  | DOC, SS, pH          | 30.7, 13.0, -4.2 |
| Znd = -1.1 + 2.4 E-2 SS + 0.6 DOC | 0.42           | < 0.01  | SS, DOC              | 21.6, 9.6 |
| Alp = 25.5 SS + 155.5        | 0.85           | < 0.01  |                      |          |
| Fep = 29.2 SS + 169.7        | 0.88           | < 0.01  |                      |          |
| Mnp = 1.1 SS + 11.3          | 0.88           | < 0.01  |                      |          |
| Cup = 0.02 SS + 0.24         | 0.86           | < 0.01  |                      |          |
| Znp = 0.05 SS + 2.10         | 0.61           | < 0.01  |                      |          |

The above results suggest that metal concentrations cannot be explained adequately by a single predictor variable. The results of the multiple regressions (Table 3) showed that the combination DOC–SS–pH increased the explained variance for Ald and Cud (in both cases it was higher than 60%), whereas the pair DOC–Q improved the variability explained for Fed (57%). The SS was the most important vector for Znd, whereas the DOC was a second driving force. The regression was only significant with Q for Mnd, but this variable explained only 20% of its variance. The SS explained a high variability of particulate metal concentrations, more than 85% for each of them, except for Zn (61%).
4. Conclusions
The metal concentrations in stream water were relatively low and followed this sequence: Fe > Al > Mn > Zn > Cu. Particulate metal concentrations were significantly higher than dissolved ones for all metals. The DOC concentration was the best geochemical variable that explains the variance for Ald, Fed, Cud, whereas SS was the main parameter controlling the concentration for Znd and largely for particulate metals, and Q is the only factor explaining a small proportion of the variance (20%) for Mnd.

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