Comparative hydrochemistry of the five nested catchments located in the upper part of the Barcés river watershed (A Coruña, NW Spain)

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ABSTRACT

259 stream water and 21 bulk precipitation samples have been studied between April 2008 and December 2010 in order to assess baseline hydrochemical conditions in a rural area of NW Spain. Stream waters are related to five nested catchments (<10 km^2) with apparent low residence times. Their hydrochemical characteristics are closely related to bulk precipitation although clear evidences of seasonal (flushing, dilution, sediment desorption, etc.) lithological (schist vs. granite substrate) and anthropogenic (land use, contamination) effects are also described)

1. Introduction

In its eighth article, the European 2000/60/EC Water Framework Directive (WFO) states that the European Union Member States must implement programs for the monitoring of water status in order to establish a coherent and comprehensive overview within each river basin district. Apart from the hydrologic features of river basins, monitoring programs must take into account the corresponding ecological and chemical status in order to assess whether they fulfill or not given ecological objectives and, in the latter case, to design adequate management strategies aimed at achieving, when possible, a good ecological status. In the WFD, the concept of ecological status relates water quality to the assessment of certain biological, chemical and hydromorphological characteristics in the different water bodies and their comparison with given a reference conditions.

The reference condition for a water body is a description of the characteristics corresponding to pristine or nearly pristine conditions i.e. without, or with only a very minor impact from human activities. However, due to human population such circumstances have disappeared in many regions of the EU, the WFD also makes possible defining reference conditions using additional criteria like the use, when available, of time series and historical data, modeling or expert judgment.

The identification of hydrochemical reference conditions has proved to be a challenging task in many basin districts due to the fact that the majority of long term monitoring programs have focused on the large-scale river basins, where the human impact has been more pronounced. In addition, it is well known that lotic systems are typically heterogeneous due to various biotic and abiotic processes (weathering-erosion-sedimentation dynamics, biological activity, salute release/retention, flushing, land use, etc.), To this respect, the scarcity of monitoring stations or the low sampling frequency might be providing a biased picture in many EU regions.

This work presents the results of a two-and-a-half-year hydrochemical monitoring survey cantered in five nested catchments located in a rural area of the Galicia-Coast river basin district (NW Spain). The catchments are located immediately upstream of the Meirama mine reclamation site, where a big lake (area= 186 ha; mean depth 78.6 m; maximum depth= 205m; volume = 146 h m^3) is being flooded with water diverted from some of their corresponding creeks. Due to the relevance of surface

waters in the flooding as well as the implications of the future lake water quality with respect to ecological status of the Barcés river and the Cecebre reservoir (the only supply of drinking water for the city of A Coruña and the surrounding municipalities, with ~400,000 inhabitants), mine managers decided to set up their own monitoring program focused in catchments located upstream of the lake.

2. Study area and methodology

The study area covers the upper third (32.09 km^2) of the Barcés river watershed (87.9 km^2). All the catchments have an area of less than 10 km^2, which is the minimum size established by the basin district authority to implement a monitoring station (Fig. 1: SC- l = 9.4 km^2; SC-2 = 6.94 km^2; SC-3 = 3.82 km^2; SC-4= 5.17 km^2; SC-5 = 4.33 km^2). With the exception of catchment SC-4 whose bed might become dry in the summer months, the rest host perennial streams. Toe catchment with the highest altitude above the sea level is SC-2 (480 m) and is followed by SC-1, SC-4 (both 350 m), SC-3 and SC-5 (250 and 245- m, respectively). Hillsides have, in general, a moderate slope (6-25%) but steeper areas (up to 55%) might be found in SC-2 and SC-5. The local geology of the catchments is dominated by the presence of igneous and metamorphic rocks (Órdenes Schist Formation and Monte Xalo granite), whose permeability is generally low and fracture-controlled. SC- 1 and SC-4 are fully developed over schistose rocks while SC-2 is emplaced over granites. In the case of SC-3 and SC-5, the granitic substrate is partially covered by mine spoils. Soils are mainly umbrisols (humic, endoleptic), with local development of cambiso1s and anthropic regosols. On average, infiltration dominates from November to April but potential evapotranspiration is higher between May and October. Climate is typical of the Atlantic zone. Rainfall is high all year round (~1500 L/m^2; minimum values in summer and maximum in winter) and, on a yearly basis, it exceeds potential evapotranspiration (~750 L/m^2). Since 1976 the mine managers have recorded the monthly rainfall around the mine. The rainiest year recorded in the past 30 a corresponds to the year 2000, with 2069.6 L/m^2· By contrast, the driest period of the series occurred in 1988 (1037.6 L/m^2). Temperatures are mild with a markedly limited thermal range (7-17 ºC).

As was mentioned earlier the catchments are located upstream of the Meirama mine lake which is in the process of controlled flooding by the diversion of water coming from catchments SC-1,SC-3 and SC-5. Once the lake becomes fully flooded, the streams associated with the catchments SC-2 and *SC-4* will also be directed towards the lake. A preliminary hydrochemical assessment of the waters contributing to the flooding process was presented in Delgado et al. (2008) and the limnological characteristics of the lake after 2 years of flooding have been summarized by Delgado et al. (2010a, b).

In order to evaluate the hydrochemical baseline conditions in the catchments, a sampling survey (weekly from April, 2008 and biweekly since January, 2010) was progressively implemented The sampling of catchment SC-1 started in April 2008 while the systematic monitoring of catchments SC-2, SC-3, SC-4 and SC-5 started in August 2009. The measurement of temperature, specific conductance, pH, E_H and the concentration of dissolved O_2 as well as filtering of samples (0.45 µm) and preservation were performed in situ whereas alkalinity, turbidity, the concentrations of suspended solids, organic C, major constituents (Na, K. Mg, Ca, Mn, Fe, NH_4, F. CI, Br, $S0_4$, NO_3, NO_2; $HC0_3$, $P0_4$, SiO_2) and trace elements (Ag, Al, As, B, Ba, Cd, Co, Cr, Cu, Hg, Li,

Mo, Ni, Pb, Rb, Sb, Se, Sn, Sr, Ti, U, V, Zn) were measured in the laboratory. In addition to the previous parameters, the water of catchment SC-1 was analyzed for the stable isotopes of water ($\delta^{18}O_{v\text{-}smow}$ and $\delta^{2}H_{v\text{-}smow}$) and, on a monthly basis, for the concentration of 18 PCB and 16 VOC compounds. Since December 2008, the chemical quality of bulk precipitation {i.e. dry deposition + wet precipitation) has been also monitored using a funnel-and-bucket device (Friedman et al., 1992; Dämmgen et al., 2005) to which a certain volume of paraffin oil was added to minimize water evaporation. In the present work data collected up to the end of December, 2010 is used, with a total of 259 complete chemical analyses of catchment waters and 21 of bulk deposition. The quality of the water analyses was assessed computing the electroneutrality condition. In the case of the catchments, 79% of the samples had an ionic imbalance of less than 5% (mean imbalance 2.76%) while 96.5% had imbalances better than 10% (mean imbalance 3.59%). Due to the more diluted nature of bulk deposition, the ionic imbalance was poorer and only the 61% of the samples had imbalances better than 10% (mean imbalance 4.2%).

The hydrochemical data is complemented with meteorological information gathered from a weather station fixed to a floating deck anchored to the deepest point of the lake. The station records data related to the air temperature and pressure, relative humidity, rain, wind speed and direction, total and PAR radiation every 10 min.

3. Results and discussion

Fig. 2 illustrates the concentration of selected components monitored in the five nested catchments with respect to the monthly cumulative rainfall and bulk deposition. In these plots, bulk deposition has not been normalized with respect to the corresponding period rainfall in order to stress the importance of particle deposition in the dryer periods. This is notorious in the case of sulfate and alkalinity (Fig. 2C and D). Compared with the results given by Vázquez et al (2003) for **a** nearby monitoring station (Mabegondo), the averaged results show higher concentrations in nearly all the major constituents except for NO_3, SO_4 and NH_4. The difference is likely due to differences in the sampled material (true wet precipitation vs. bulk deposition). Compared with the stream water, rainwater has lower concentrations generally but typically within the same order of magnitude in catchments SC- 2 and SC-4. This suggests low mean residence time (MRT) for these catchments. SC-1 has higher concentrations than the rest of catchments what could indicate longer MRT. However, some parameters (among others, specific conductance or CI concentration; Fig. 2A and B), show a pronounced scattering and their values are too high to be derived from such a circumstance. Based on field observations, the distinct behavior of SC-1 might be attributed to contaminant flows derived from a waste processing plant located in the water divide between SC-1 and the Lengüelle River, out of the study area.

Some components of the catchment waters show a net seasonal pattern (Ca, Mg, SiO_2, Al, Co, Ni, Zn, and alkalinity) with a strong correlation with precipitation: high values are associated with the onset of rainiest periods. This can be interpreted as a result of the flushing of the substrate previously weathered in the dry season. Weathering would be more intense in the catchments partially covered by mine spoils (SC-3 and SC-5), which would explain the more pronounced flushing effect observed in them (Fig. 2E and F). Worth noting also is the seasonal behavior of As in the affected SC-1 catchment: its concentration tends to be higher in the dryer months and lower in the rainy periods. This is opposite to what has been reported before and might be related

to hydrology (i.e. dilution upon high flows), desorption from the streambed sediments or biogenic As reduction processes.

Lithology effects can also be identified in the time series. For instance, when comparing the SO_4 concentrations of the schistose SC-4 and the granitic SC-2 catchments, a nearly identical pattern is observed while the SO_4 concentration in SC-4 is always higher than in SC-2. A similar behavior but in the opposite sense is observed for As (i.e. greater concentrations in SC-2 and lower in SC-4) which shows the higher affinity of this element for granitic rocks. This is consistent with the observations performed by Calvo and Macias (1993) in a study of hydrochemical characteristics of monolithological catchments in Galicia.

4. Conclusions

The frequent monitoring at the scale of nested catchments provides important insights about the early evolution of stream water chemistry and helps in understanding significant processes that might be overlooked when working at a larger time and field scales. The present study illustrates how different effects (seasonality. lithology, hydrolo gy, contamination) introduce significant variations in the time series of the different parameters monitored. This information is very relevant when establishing the corresponding baseline conditions.

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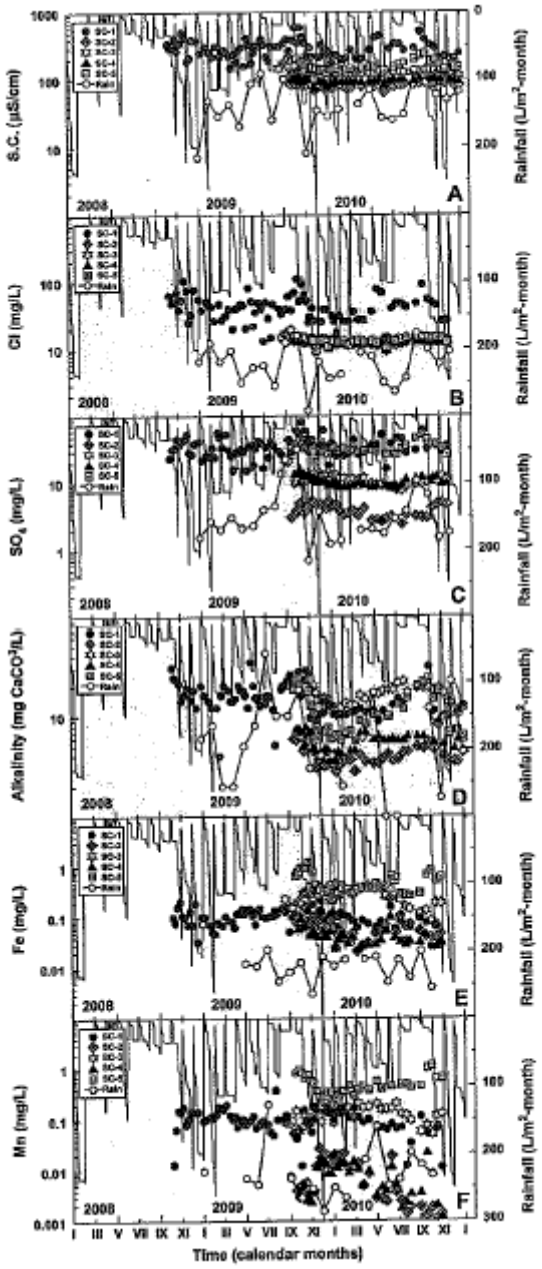
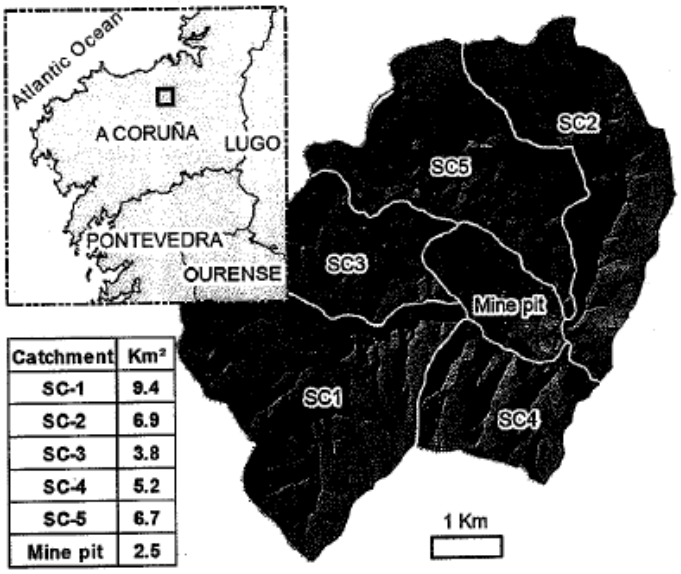


Fig. 2. Time series of precipitation bulk deposition and dissolved concentrations of a selection of constituents from the five nested catchments. SC represents the specific conductance



Catchment	Km²
SC-1	9.4
SC-2	6.9
SC-3	3.8
SC-4	5.2
SC-5	6.7
Mine pit	2.5

Fig. 1. Location map of the study area.

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