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Abstract

The presence of contaminants in montane environments has been a topic of increasing interest lately, due both to the ease with which they can accumulate in great quantities after being transported long distances and the various nocive effects on the nearby populations. This study aimed to determine the presence of airborne arsenic pollution in Valle de Respomuso, a glacial valley situated in the Spanish part of the Central Pyrenees which springs provide drinking water to the nearby populations and which holds a reservoir where large As quantities have already been found. In order to test the importance of atmospheric deposition, montane snowpacks were analyzed looking for As, as well as other pollutants, in order to get some information about the possible consequences of this contamination for the surrounding ecosystems and human populations. High levels of deposited arsenic (up to 13 and 15.70 µg As L-1) were found in the snow, following a pattern of deposition highly related to the dominant surface winds coming from the North West and West. This source of contaminants might be the source of severe health problems on the inhabitants of the local populations. Our data suggest that part of this arsenic originates from long-range transport by the wind, with 2 of our study sites showing significantly higher dissolved

arsenic concentrations in snowpacks, with levels above the guidelines given by the World Health Organization. However, the origin of this contaminant remains unclear. The summer snowpack melting addressed is as a secondary effect of the global change in our montane environments and support the mobilization of the trace metals accumulated in these reservoirs into the water and sediments.

Keywords: Arsenic, snowpack, atmospheric deposition, Pyrenees, high altitude.

1. Introduction

Proper assessment of pollution levels present in a given ecosystem is a prioritary ecological issue, since the prediction of its impact on both the ecosystem and the population health is essential to find a solution. Also, atmospheric deposition of heavy metals on natural environments has been a pollution pathway of growing importance, due to the great urban and industrial growth of the developing countries. (Chukanov *et al.* 2006; Klavins *et al*. 2000; Yuan *et al*, 2004; Lavilla *et al*. 2006; Zaharescu *et al*. 2009a).

Atmospheric deposition of air pollutants is a very important factor influencing the quality of montane waters (McBean & Nikleva 1986; Schnoor & Stumm1986; Halstead *et al*. 2000) Consequently, the atmospheric composition of the areas where these pollutant-transporting air masses originate is much related to the suitability of said water resources for human use (Mosello *et al*. 2001). Precipitations, as well as surface winds, are important mechanisms for deposition of pollutants that have undergone long-range atmospheric transport. Hence, the capability of atmospheric water to work as a vehicle for transport of pollutants hundreds of kilometres away from the source is a cause of impact on both ecosystems and human health. Since precipitation is a source of

water used for an important number of uses by the human population (Reuss & Johnson 1985; Schindler 1988)

Nowadays snow is stated as an indicator of environment contamination, due to the fact that in high-altitude montane environments the main sources of water come from snowmelt and precipitations, which gives the atmospheric inputs a great impact on the water chemistry, especially in areas with slow-weathering rocks.

The transport of pollutants across long distances by wind and precipitations is consequently an important ecological issue affecting these environments, because all this pollutants will accumulate in the seasonal snowpacks and be released directly to the water system, seriously affecting both terrestrial and aquatic wildlife. Thus, the monitoring of snow composition is vital to trace and quantify the levels of atmospheric deposition in alpine and subalpine environments (Grimalt *et al.* 2001; Carrera *et al.* 2002; Campbell *et al.* 1995; George *et al.* 2008; Araratyan *et al.* 1998; McBean & Nikleva 1986; Schnoor & Stumm 1986; Halstead *et al.* 2000).

Arsenic (As) is present in the atmosphere in both soluble and insoluble forms that, once the air masses reach high altitudes or latitudes, deposite on land and water surfaces, including snowpacks.

This study focuses itself in summer snowpacks, historical remains of recent extintic glaciars, which are extensions of snow (that in our study area usually have sizes up to 10 square Km) enduring from the winter and that slowly melt through the summer, liberating water to the environment. This snowpacks receive and concentrate dust deposited from the atmosphere, which is then transported to the environment when the snow melts.

This manuscript attempts to test the presence of As in the surface of summer snowpacks, extensively collected in the Glaciar Valley of Respomuso (Central Pyerenees, Spain). Large quantities of As have already been found in the reservoir that this valley holds by other estudies carried out by our team (Lavilla *et al*. 2006; Zaharescu *et al*. 2009a, 2009b). We based this study on the fact that the most important source for the As found in the surface of summer montane snowpacks is atmospheric deposition, and so the quantity of As measured would be a good indicator of the importance of the part that atmospheric transport plays in the pollution by As in the Respomuso water bodies.

2. Materials and methods

2.1 Sampling

Sampling of snow was made during summer 2008 at 42 snowpacks distributed across 4 main zones at altitudes ranging from 2200 to 3000 m in a number of 62 samples collected. This led to a remarkable dataset of trace element concentrations in surface snow from high altitudes. Each sample consisted on 3 replicas that were collected during summer 2008. More than one sample was taken from especially big snowpacks. All samples were taken randomly.

Figure 1

2.2. Study area

The Pyrenees lie on the transition zone between the Mediterranean and Atlantic climatic regimes. This borderline position, combined with the particular climatic features of mountains (Beniston 2005), makes the Pyrenees especially sensitive to global climate

effects in SW Europe, one of the areas in Europe where the largest rates of climatic change are expected (Intergovernmental Panel on Climate Change, 2007). Climate has an influence on the airborne element fluxes over this region through the atmospheric circulation patterns associated with different climatic situations. The dominant surface winds (under 500mbar) determine the spatial distribution of deposited elements. In this valley, the most frequent wind fluxes come from the West (28% of the days present wind coming from this direction), providing precipitations up to 67% of the time under cyclonic conditions. The second most frequent winds come from the North West (24% of the days), with up to a 62% of days with precipitation under cyclonic conditions (Creus-Novau 1983). It's worth noting that, due to the orografic configuration of the valley both dominant winds enter the valley roughly from the same direction, which means that 52% of the days present winds coming from the same direction, which will determine the distribution of As depositions between the different sampling sites.

2.3. Sample preparation

Snowpack samples were collected directly into sterilin sample bottles. All snow samples were prepared for analysis by filtering through 0.45 µm cellulose nitrate membrane. All chemicals used were of analytical-reagent grade. Ultrapure water was obtained from a Milli-Q™ water system (Millipore, Bedford, MA, USA). HNO3 (Merck) was used for extraction after suitable dilution. As stock standard solution (1000 mg/L) was prepared from As2O3 (Merck). The filtered and acidified samples were stored at <5 °C until their analysis.

2.4. Trace mineral analyses

All digested snow samples were analysed by inductively coupled plasma — mass spectrometry (ICP-MS). Snow samples were analysed for As using standard ICP-MS operating conditions. The analyses followed standard procedures and QA/QC protocols.

2.5. Quality assurance protocol

An analytical quality control program was applied throughout the study. Blank absorbance values were recorded and subtracted from the readings before the results were calculated. The limit of detection in the acid digest was set at 3 times the standard deviation of the reagent blanks (0.18 µg L-1 for As). The limits of quantification, expressed as concentration in the snow, were calculated on the basis of the mean sample weight and volume (0.45 µg L-1 for As).

2.6. Statistical analysis

The data from snow analyses were manipulated in SPSS 15 package for Windows for statistical analysis. Due to the relatively low number of samples, we chose to use a 90% confidence interval for our statistical analysis.

3. Results

The maximum and mean concentrations of the arsenic measured in the snowpacks from the various locations of the Glaciar Valley of Respomuso, is presented in Table 1.

Table 1. Figure 2. **Table 2.**

Our results show significantly higher quantities of As in snowpacks sampled in Tebarray than in La Facha, Formigal and Balaitous. Also, the maximum quantities of

dissolved As found in Tebarray and La Facha were higher than the limit values given by WHO guide value for drinking water (10 µg As L−1).

4. Discussion

Our results show the effect of the surface winds (Fig.1 and Table 2), which are the ones which modify their trajectory and behaviour according to the orography of the terrain. This gives place to dynamic and thermal phenomenons such the Föen effect (Whiteman 2000).

The arsenic concentrations displayed a wide range among sampling sites, being in Tebarray, exposed to the dominant surface winds, the highest (4.1145 µg L-1) with some values (13.0 µg L-1) over the limit values given by the WHO for drinking water. La Facha also showed some values over these guidelines (15.7 µg L-1), which might be explained by its partial exposition to the dominant winds. The mean results obtained at La Facha (2.77 µg L-1), though generally higher, with mean As concentrations almost doubling those found in Balaitous (1.11 µg L-1), were not significantly greater than them, statistically speaking. However, in Formigal and Balaitous, which present a SW exposition that gives them partial cover against dominant surface winds, the dissolved As values were significantly lower (1.11 µg L-1 and 0.46 µg L-1), with no values over the limit values given by the WHO. Therefore, the quantity of As found shows a positive correlation with exposition, being the highest in the locations with a direct exposition to the dominant winds, and diminishing in locations that show total or partial cover against it. This points to a long-range atmospheric transport by the dominant surface winds followed by a Föen effect-mediated deposition as the source of the high concentrations of dissolved As found.

Atmospheric fluxes affecting the sampling sites have caused high concentrations of several trace elements in Pyrenean snowpacks at a level which may be of ecotoxicological relevance to the nearest human populations. The highest metal contents of As was measured at La Facha snowpacks. The mean concentrations of As found in this study were higher than the values reported for other pristine sites in Europe, North and South America (Rognerud *et al.* 2000; Birch *et al*. 1996; Moiseenko & Gashkina 2007; Vazquez *et al*.,2004).

As snowpacks are making a scavenger function, snow melting water can make two different contributions to the surrounding ecosystems: (i) percolate into the ground reaching the freatic layer and bringing new pollution load to the ground waters; (ii) make a direct load to the superficial ecosystems due to runoff water directly from melting snow. Both contributions will directly affect to the Respomuso reservoir water body.

High concentrations of arsenic in snowpacks found in our study area have an atmospheric deposition origin, but large concentrations of arsenic present in Respomuso reservoir, both in water column and sediments, are related to at least another two potential mechanisms: (i) release of arsenic from oxidation of arsenic-rich pyrite; and (ii) desorption of arsenic from iron oxyhydroxide within sediments, especially under reducing conditions (Rumi *et al*. 2002). According to the geological pattern of our study site, characterized by Subías *et al*. 1997, with a ranging from monomineralic fluorite ores to polymetallic deposits with abundant fluorite containing dark-sphalerite+galena+ pyrite+chalcopyrite, we have found the expected high contents of trace elements in the sediments had relationship with their counterparts in water samples collected from the Glaciar Valley of Respomuso reservoir. As for the presence of relatively high arsenic

concentrations in water, it may have resulted from its higher mobility from the sediments or surrounding metal rich geology under the oxic condition of the streams (Lavilla *et al.* 2006; Zaharescu *et al*. 2009a) but the new finding in this study clearly points out to another source to the large concentration of arsenic by the overload due to the snowpacks melting contribution that make an scavenger role accumulating the atmospheric deposition pollution. The results of this new study modify our previous conclusions (Zaharescu *et al.* 2009b) and point at long-range transport as the main atmospheric source of As, opposed to the short range transport of As-rich dust from rock weathering. The summer snowpack melting addressed here is as a secondary effect of the global change in our montane environments and support the mobilization of the trace metals accumulated in these reservoirs into the water and sediments.

Therefore the double pollution origin, geological and atmospheric pollution deposition, states our study area as one of the most contaminated for arsenic. The relevance to human populations sited besides the Respomuso valley (Sallent de Gállego, Panticosa) is given by the use of Respomuso Valley springs as drinking water, and will have a higher concentration of arsenic during the melting snowpacks months (August and September). This finding is supported by the study made by Garrido *et al.* in 2001 where they detected concentration of arsenic in the spring waters coming from Tebarray zone, ranging from 13 to 26 µg/L, unusual values in High Mountain waters.

Severe health effects (Guha-Mazumder 2008) have been observed in populations drinking arsenic-rich water over long periods in countries world-wide. Arsenic is widely distributed throughout the earth's crust (Wedepohl 1995).

Industrial effluents also contribute arsenic to water. In some areas Arsenic is also used commercially e.g. in alloying agents and wood preservatives. Combustion of fossil fuels

is also a source of arsenic in the environment through atmospheric deposition. Arsenic pollution of drinking water poses a great risk for public health. We are aware of the presence of industrialized zones close to our study area and of health problems showed by the nearby population that might be caused by the high As concentrations in drinking water.

Future actions could be addressed by study the exposure effects that could be caused by arsenic contaminated water in local ecosystems where some anomalous and endemic behaviour in the *Rana temporaria* populations inhabiting our study area was found in previous work by our research team (Vieites *et al.* 2004). Also, the high concentrations of As found in the snowpacks could make advisable further studies in the area including a close control of nearby spring waters so that poisoning episodes can be prevented.

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Figure 1. Map showing the study area, main airflow trajectories from Western Atlantic regime in our study valley, and the main sampling zones. 1: Formigal (1550m); 2: Balaitous (3144m); 3: Tebarray (2956m); 4: La Facha (3005m).
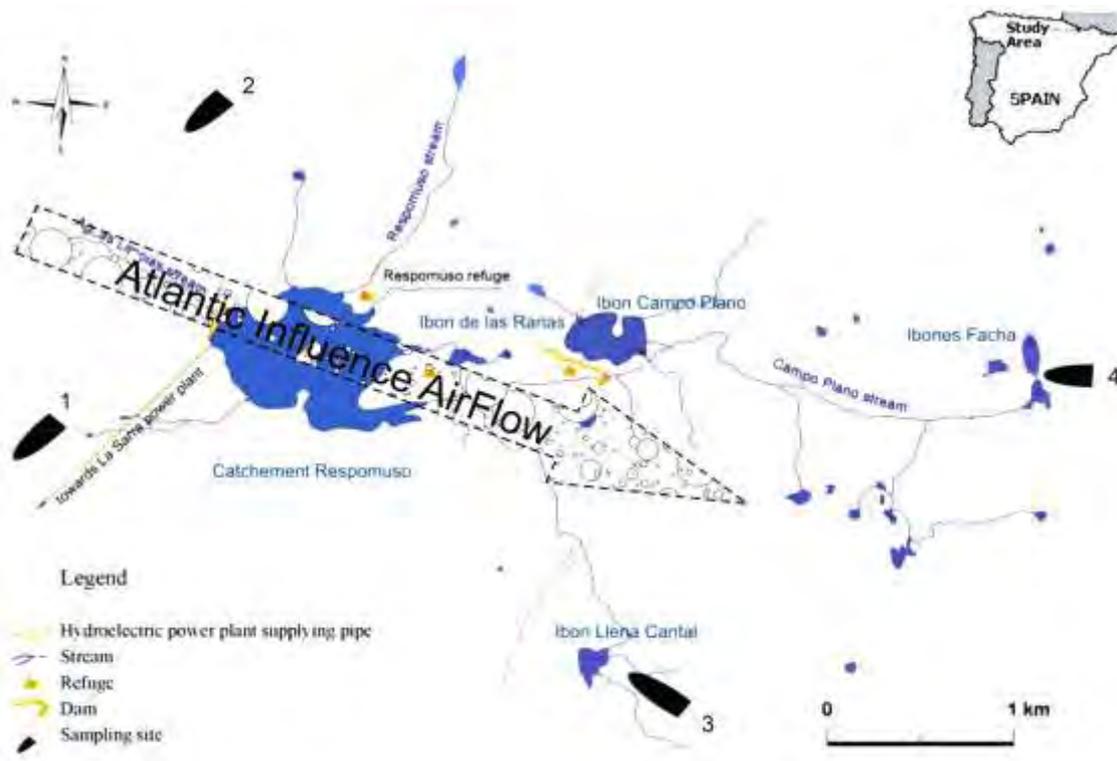
Figure 2. Mean concentrations of As found in sampling sites. 1: Formigal (1550m); 2: Balaitous (3144m); 3: Tebarray (2956m); 4: La Facha (3005m). Locations are arranged in base to their exposition to dominant surface winds.
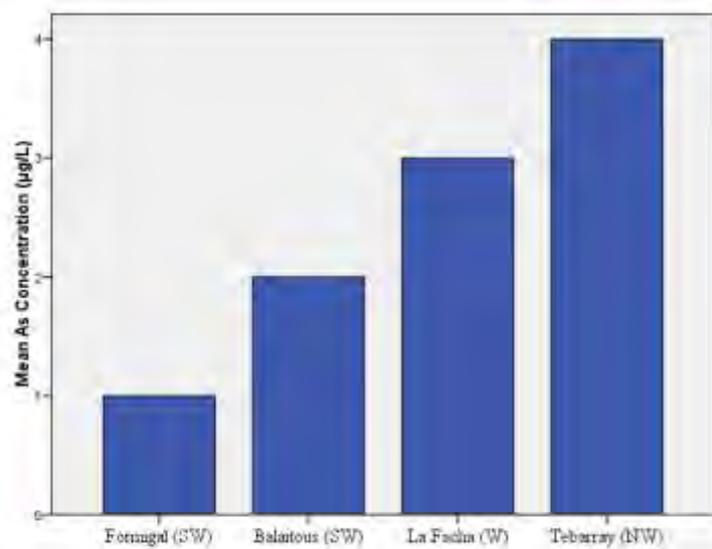
Table 1. Characteristics of the sampling locations and results from the statistical analysis from the Arsenic concentration data.

Snow pack locality	Latitude	Longitude	Altitude (m)	Exposure and orientation to the dominant wind (NW)	Peak	Peak Altitude (m)	As N	As Concentration			
								Mean	SE	Variance	Maximum
Formigal	42°46'43''	0°21'26''	1624	SW (45°)	Foratata	2341	6	4550	173	181	1 13
Balaitous	42°50'09''	0°17'37''	2727	SW (45°)	Balaitous	3144	12	1 1083	291	1 021	3 40
Tebarray	42°47'43''	0°15'38''	2776	NW(90°)	Tebarray	2916	8	4 1125	1 354	14 667	13 00
Facha	42°48'44''	0°14'23''	2695	W (60°)	La Gran Facha	3005	16	2 7688	1 022	16 730	15 70

Table 2: Mean comparison between the different sampling sites. showing the significancy of the differences in [As] (T-test). Significant difference is given by values below 0.1. Significant values are marked with *.

	Formigal	Balaitous	Tebarray	La Facha
Formigal	------------------	0.133	0.021*	0.151
Balaitous	0.133	------------------	0.017*	0.183
Tebarray	0.021*	0.017*	------------------	0.447
La Facha	0.151	0.183	0.447	------------------