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Occurrence of Fluoride in Arsenic-Rich Surface Waters: A Case Study in the Pampa Plain, Argentina

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Abstract High levels of fluoride in freshwater ecosystems are harmful for humans and animals, particularly, aquatic biota. In this paper, the concentrations of fluoride in arsenic-rich lotic ecosystems of the Pampa Plain, Argentina, were recorded. The relationship of fluoride with the concentration of arsenic was explored. Our results show that fluoride in these freshwater ecosystems ranged from 0.15 to 1.65 mg L^{-1}. Concentrations of fluoride were highly and significantly (r = 0.71; $p = 0.001$) correlated with arsenic.

Keywords Fluoride · Surface waters · Arsenic · Argentina

Fluorine is commonly found in aquatic ecosystems as fluoride (F). Natural sources of F include weathering of fluoride minerals, volcanoes gases and marine aerosols (Camargo 2003).

Fluoride is more often found in groundwater (Tekle-Haimanot et al. 2006). This element originates from weathering of inorganic fluoride minerals as fluorapatite ($Ca_5(PO_4)_3F$), fluorite (CaF_2) and cryolite (Na_3AlF_6). Concentration of F in groundwater usually ranges from 0.3 to 0.95 mg L^{-1} (Hem 1985). However, in some geographic areas, where high levels of arsenic (As) were reported, the actual values of F may be rather higher (up to 10 mg L^{-1}) (Franco and Carro Pérez 2009). The study of the relationship between As and F in surface waters has received less attention. Fluoride may reach freshwater ecosystems from both natural and anthropogenic sources. The concentration of F in unpolluted freshwaters ecosystems ranges from 0.01 to 0.3 mg L^{-1} (Camargo 1996, 2003; Datta et al. 2000). Nevertheless, F may largely exceed this range in those regions where geothermal and volcanic activity is present (Tekle-Haimanot et al. 2006).

High levels of F in freshwater ecosystems are harmful for humans and animals, particularly, aquatic biota. Among the aquatic biota, freshwater animals are, in general, more sensitive to fluoride toxicity than freshwater algae and macrophytes (Camargo 2003). Negative effects of high levels of F on fish include growth inhibition, behavioral changes, alteration of enzymatic metabolism, bones abnormalities and delayed hatching of fertilized eggs (CCME 2002; Camargo 2003; Moren et al. 2007; Shi et al. 2008). Arsenic, a very toxic element, is commonly found in association with F. In fishes, arsenic was related with skin discoloration, histological changes in gills and liver, growth retard and low efficiency in food conversion (Russell et al. 2010). In human health, high levels of F are related with bone and teeth diseases as well as with negative effects on the reproductive and nervous systems (Edmunds and Smedley 1996). Arsenic, in turn, is related with skin cancer and several disorders in different organs and systems of the body. The synergism of As and F on fish and human health has not been explored yet.

The Chaco-Pampa Plain is one of the largest regions in the world (ca. 1 million km^2) with the presence of As in groundwater (Smedley and Kinniburgh 2002). Recently, Rosso et al. (2011) reported the level of natural

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contamination with As (<0.01–0.198 mg L^{-1}) and other trace metals in 39 lotic ecosystems (streams and low order rivers) of this region. Whether these high levels of As in surface waters are associated with high levels of F is the main objective of the present study. The knowledge of F concentrations in surface waters of the Pampa Plain with high levels of As will allow us to explore the relationship between these two elements and discuss about the possible origin of F and its potential ecological risk.

Materials and Methods

The Pampa Plain is a vast region of central Argentina characterized by gentle slopes (0.1–0.3 m km^{-1}). Hydrography is dominated by a large number of shallow lakes and low order rivers and streams (Frenguelli 1956).

Just recently, Rosso et al. (2011) revealed the presence of arsenic-rich surface waters in lotic ecosystems of a wide geographic region in central Argentina. Following these results, we decided to further examine a group of selected water samples containing high levels of As. Particularly, we aimed to explore the presence of F in these samples. For this purpose, 17 water samples collected by Rosso et al. (2011) were selected and the concentration of F was quantified by triplicate (Fig. 1). These authors collected samples during average flow conditions and measured pH and water conductivity in situ. Total dissolved solids in water samples was estimated by multiplying water conductivity by a standard correction factor (0.7) (Walton 1989).

For the purposes of this paper, As, pH and water conductivity data was gathered from Rosso et al. (2011). We additionally measured the concentration of calcium (Ca), which was quantified by means of a colorimetric technique (HACH, Colorimeter DR/890). Fluoride was quantified using a selective electrode along with a reference electrode of standard calomel both connected to a pH meter with a expanded mV scale (THERMO ORION/model 96-09). This method is adequate to measure F concentrations ranging from 0.1 to 10 mg L^{-1} (APHA 1995).

The saturation index (SI) for fluorite was calculated as $SI = (Ca{\cdot}(F)^2) \cdot Ksp^{-1}$, where Ca = molar concentration of calcium, F = molar concentration of fluoride and Ksp = equilibrium solubility constant (3.45×10^{-11}, 25°C) (Han 2007). SI < 1 indicates that the water is undersatured with respect to that particular mineral. SI > 1 specifies that water is oversaturated with respect to the particular mineral and therefore incapable of dissolving more.

Fig. 1 Locations of sampling sites along 17 lotic ecosystems in the Pampa Plain. *Dashed circle* and *triangle* represent the low and high risk zones respectively

Clusters analysis was performed using data of As and F. We used a space-conserving fusion technique (average linkage) in order to better portray the original structure of the data (Jongman et al. 2004). The coefficient of Pearson was used as the resemblance measure and the cluster solution was evaluated using the cophenetic correlation. Several statistics as the median, percentiles, minimum and maximum were calculated for As and F data. This information was depicted in box plots. A Mann–Whitney test was performed to test for significance in the differences of As and F concentrations between groups identified by the cluster analysis. The relationship between As and F in surface waters of the study region was explored using the Spearman rank correlation analysis. The empirical relationships between F concentration, water hardness, conductivity and pH were explored. The softwares used in the statistical analysis were Statistica 6 (Statsoft) and NCSS 2000 statistical software (Hintze 1998).

Results and Discussion

Lotic ecosystems explored in this study were characterized by a wide range of physical and chemical conditions (Table 1). Correlation analysis showed that several variables were highly interrelated. For instance, F concentration in these environments significantly ($r = 0.71$; $p = 0.001$) increased as arsenic increased (Fig. 2). The fluoride solubility is favoured by high pH values.

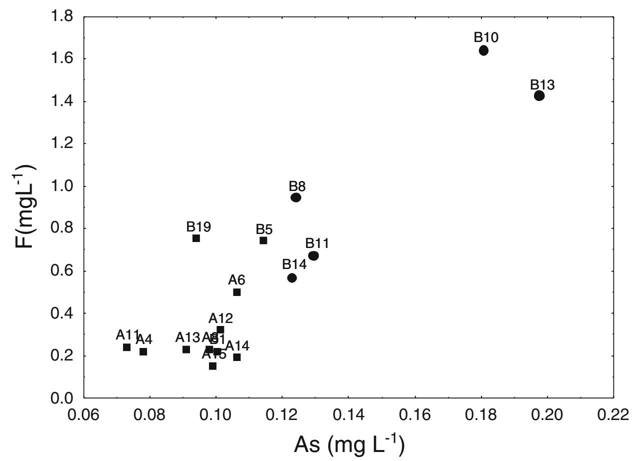

Fig. 2 Correlation between F and As concentrations (mg L^{-1}) in the study ecosystems ($r = 0.71$, $p < 0.01$). Graph is labeled by site code. *Circle*: G1 area, *square*: G2 area

All samples displayed concentrations of F over the limit suggested (0.12 mg L^{-1} F) by the Canadian Council of Ministers of Environment (CCME 2002) for the protection of the aquatic biota in freshwater ecosystems. Moreover, the concentrations of F recorded in almost 65% of the streams were above the double of the guide level suggested by the CCME. Only 3 streams (de las Mostazas, Chasicó and Indio Rico) exceeded the guide level (1.4 mg L^{-1}) proposed by local government agencies (Law 24051 1993). The scenario for the As is not better. All selected samples displayed concentrations larger than upper limits suggested

Table 1 Geographic location of study sites and measured values of pH, total dissolved solids (TDS, g L^{-1}), water specific conductivity (Cond, µS cm^{-1}), calcium carbonate ($CaCO_3$, mg L^{-1}), arsenic (As, mg L^{-1}), fluoride (F, mg L^{-1}) and saturation index (SI)

Study sites	Location	Code	pH*	TDS	Cond*	$CaCO_3$	As*	F	SI
de las Mostazas	38°45.703′S; 61°20.537′W	B10	8.96	1.53	2190	76	0.181	1.64	164.065
Chasicó	38°23.635′S; 62°50.63′W	B13	9.11	2.29	3270	21.5	0.198	1.42	34.774
Indio Rico	38°36.182′S; 60°38.840′W	B9	9.22	1.17	1669	54	1.134	1.37	81.366
Claromecó	38°42.169′S; 60°10.126′W	B8	9.02	1.34	1919	66	0.124	0.94	46.685
Napostá Grande	38°46.228′S; 62°14.024′W	B11	8.89	1.11	1594	72	0.130	0.67	25.858
Pigüé	37°12.575′S; 62°38.897′W	B14	8.58	0.51	733	79	0.123	0.57	20.609
Mendoza	38°33.229′S; 59°18.925′W	B5	9.02	1.05	1496	53.5	0.114	0.74	23.466
Quequén	38°15.102′S; 60°44.490′W	B19	8.84	0.34	486	18	0.094	0.75	8.099
Canal 5	37°12.967′S; 57°47.685′W	A14	9.26	0.54	771	8.4	0.106	0.19	0.243
Grande	37°31.462′S; 57°42.449′W	A12	9.23	0.70	1004	8	0.101	0.32	0.654
Vallimanca-Saladillo	35°27.612′S; 59°34.548′W	A8	9.81	5.03	7180	36	0.098	0.23	1.528
El Pescado	38°17.871′S; 58°14.758′W	B1	8.71	0.62	885	61	0.100	0.22	2.238
Chico	37°15.574′S; 57°46.947′W	A13	9.38	0.50	720	24.8	0.091	0.23	1.052
Canal 2	36°45.153′S; 57°48.145′W	A15	9.78	0.59	851	1.4	0.099	0.15	0.025
Tapalqué	36°16.052′S; 59°58.667′W	A6	10.33	0.63	908	40.5	0.106	0.50	8.120
Vivoratá	37°44.100′S; 57°38.873′W	A11	8.91	0.77	1096	52.5	0.073	0.24	2.416
de los huesos	37°4.875′S; 59°32.333′W	A4	8.67	0.48	690	6.3	0.078	0.22	0.242

* Data gathered from Rosso et al. (2011)

by both, international (0.005 mg L^{-1} in Canada) and national (0.015 mg L^{-1}) authorities.

Cluster solution reflected a marked structure in the data. The cluster analysis (cophenetic correlation = 0.93) distinctively grouped together lotic ecosystems of different hydrological regions within two groups with large dissimilarities in their level of contamination with As and F (Fig. 3). The Mann–Whitney test showed that both groups differed significantly in their concentration of As ($Z = 3.31$; $p < 0.001$) and F ($Z = 2.78$; $p < 0.001$). The first cluster (G1) grouped six streams (de las Mostazas, Chasicó, Indio Rico, Claromecó, Napostá Grande and Pigüe). This cluster could be regarded as the As-F rich group demarcating a high risk zone within the study area (Fig. 1). The second cluster (G2) grouped 11 ecosystems containing significantly lower concentrations of As and F delineating a low risk zone within the study area (Fig. 1).

The widespread geographic distribution of As and F in surface waters of the Pampa Plain (Rosso et al. 2011, this paper) could be associated to high levels of these elements in groundwater (Paoloni et al. 2003). High As and F contents in groundwater may be associated with loessic sediments (Smedley et al. 2002). On the other hand, anthropogenic sources of these elements in the study area may be discarded since most of the land is devoted to agriculture practices.

The saturation index calculated with molar concentrations of Ca and F in relation to the Ksp of fluorite (3.45×10^{-11}), revealed that lotic ecosystems of G1 have over saturated waters ($SI > 20$). The results showed an inverse relationship between the concentrations of F and Ca in G1 (Table 1). Oversaturation can be produced by

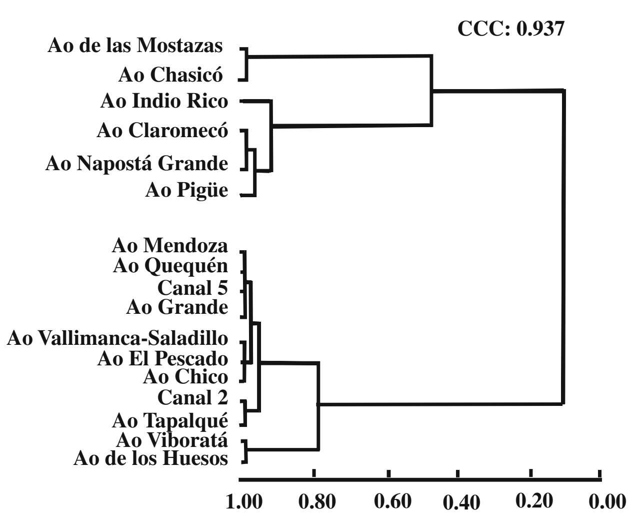

Fig. 3 Dendrogram of UPGMA cluster analysis of sampling sites by measures of As and F concentrations. *CCC* cophenetic correlation coefficient

different factors that include incongruent dissolution, common ion effect, and evaporation (Singh et al. 2011). These authors found in groundwater of Rajasthan (India) that high concentrations of sodium increase the solubility of fluoride. In this sense, the water bodies of G1 are brackish and present relatively high concentrations of total dissolved solids (1.11–2.29 g L^{-1}). The relationship between sodium and fluoride will be the object of future studies. On the other hand, lotic ecosystems in G2 are unsaturated or slightly oversaturated in fluorite (Table 1). No clear relationship between F and Ca could be observed.

High levels of F would pose a potential risk to the aquatic biota. Hence, as a precautionary approach, it should be recommended to carefully evaluate the health condition of freshwater biota in these F-rich ecosystems. Particularly, subsequent investigations should focus in detail on those lotic ecosystems of southeast Pampa Plain (G1 area) where the highest fluoride concentrations were observed. This will help to understand the relationship between groundwater and surface water, and to analyze the effect of the presence of two hazardous elements, as arsenic and fluoride, on fishery resources.

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