
Mechanisms of arsenic and fluoride release from Chacopampean sediments (Argentina)

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Abstract: We have examined the sources and mechanisms that control the release of fluoride and arsenate from fluvial and loess sediments collected from the Chacopampean region, Argentina. The two types of sediment show slight differences regarding the mechanism of release. In fluvial sediments the release of fluoride seems to be controlled by the dissolution of primary F-bearing minerals, such as fluorapatite (FAP) and biotite. Much lower concentrations of As are also released from fluvial sediments under acidic conditions, owing to the dissolution of As-bearing igneous FAP. Under more alkaline conditions, the release of both anions is the result of desorption from Fe (hydr)oxide coats. In loess sediments, F and As are released by dissolution of FAP present either as detritic grains or forming thin coats onto the volcanic ash, while arsenate is preferentially desorbed from Fe (hydr)oxide coats under alkaline conditions or by competitive desorption at acidic pH.

Keywords: As-bearing fluorapatite; volcanic glass; loess; Pampean ranges; competitive desorption; alkaline waters; desorption from Fe (hydr)oxide coats; scanning electron microscopy/energy-dispersive X-ray spectrometry analysis; SEM/EDS analysis; F-rich granites; leaching experiments.

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1 Introduction

Argentina was the first country in Latin America where the presence of high concentrations of arsenic in groundwater was described, as well as its harmful effect on people's health (Bundschuh et al., 2012). Besides arsenic, some other potentially toxic elements occur in high concentrations in groundwater, such as fluoride, vanadium and uranium. Although major concerns are focused on groundwater quality, river waters draining granitic terrains in the Pampean ranges (central Argentina), also exhibit high concentrations of some of the above-mentioned elements. Weak to moderate dental fluorosis has been detected in the children population of this mountain region, where average fluoride concentrations in drinking water is about 2 mg l^{-1} (i.e., García et al., 2012).

The relevance of this environmental problem has motivated a number of studies, focused on the determination of the spatial distribution of soluble As (and also F) in deep and shallow groundwaters of the Chacopampean plain (i.e., Bundschuh et al., 2004; García et al., 2007, 2009; Nicolli et al., 2012 and references therein; Smedley et al., 2002, 2005; Warren et al., 2005). In general, all these studies described the presence of high concentrations of As associated with alkaline, NaHCO_3 -type waters, moderately reducing, where the As(V) predominates over As(III) species and where the concentration of As positively co-varies with other trace elements such as V, U, Mo and F. The aquatic geochemistry was analysed in most of these works and only a few include a complete chemical and mineralogical characterisation of the sediment (i.e., Nicolli et al., 2010; Smedley et al., 2005). There is a broad agreement among these authors that the contents of As and F (as well as V, Mo, U and B) in groundwater are mainly due to the alteration of volcanic glass and rock fragments present in loess, which may account for ~5–25% of the bulk mineral composition (Bundschuh et al., 2012). The mobility of As and F ions depends not only on the type of association in their primary source, but also on the chemical conditions predominant in the environment in which they were deposited.

Levels of As associated with volcanic glass has been already documented (i.e., Nicolli et al., 2012; Ruggeri et al., 2012), but little is known about the contents of F in samples of volcanic ash and loess of the Chacopampean region. Several factors may control the mobility of fluoride in natural waters. Many authors described the

dissolution of fluorite enhanced by calcite precipitation, as one important mechanism of fluoride release to waters in equilibrium with calcite (i.e., Currel et al., 2011; Desbarats, 2009; Genxu and Guodong, 2001). The dissolution of fluorite may also be enhanced by other mechanisms that result in Ca^{2+} scavenging, such as cation exchange or apatite precipitation. Besides, the dynamics of F and As may also be controlled by adsorption/desorption onto different mineral surfaces, mainly Fe or Al (hydr)oxides.

The aim of this paper is to analyse the possible sources of F and As and the mechanisms that control their release from sediments of two types of aquatic reservoirs, in the Chacopampean region:

- mountainous rivers draining crystalline rocks from the Sierras Pampeanas ranges
- shallow aquifers in loess-like sediments.

The assessment was performed on the basis of experimental work and the study of the chemical and mineralogical characteristics of sediments in contact with As/F-rich waters of the Chacopampean region.

2 Materials and methods

2.1 Sampling, chemical and mineralogical analyses

The studied sediments were collected from two aquatic reservoirs found in the Chacopampean region, where As- and F-rich waters were reported. Samples AR and AB correspond to river bed sediments collected in the upper and medium reaches of the Charbonier stream in the Sierras Chicas de Córdoba, Central Argentina (30°46'S; 64°32'W and 30°46'S; 64°34'W, respectively). Samples L1 and L10 correspond to loess-like sediments collected from two different sections in northern Chacopampean Plain. Sample L1 was taken from the bottom of a 9.3-m vertical section at Corralito (32°00'S; 64°09'W; 490 m a.s.l.) that is exposed along an abandoned road excavation, 35 km south of Córdoba city. Sample L10 was collected from a 5.0-m freaticum located in Lamadrid city (27°38'S; 65°14'W; 293 m a.s.l.), 90 km south of San Miguel de Tucumán city. At the moment of sampling, the sediment was completely saturated.

After collection, samples were air-dried and separated into two portions. One was sieved through <63 μm mesh, while the remaining was ground in agate mortar. Chemical analyses were performed on the ground total fraction by ICP/OES after a lithium metaborate/tetraborate fusion. Water, carbonate and organic matter were determined gravimetrically in a previously weighted portion of the total fraction. X-ray diffraction (XRD) analysis was performed in the <63 μm size-fraction.

Clay mineralogy was determined in the <2 μm size-fraction. Separation of this fraction was performed following the USGS open file report 01-041 guideline. Briefly, a portion of the sediment was suspended in 1:4 acetic acid overnight to remove carbonates. The procedure was repeated until suspension no longer effervesces. In a second step, organic matter was eliminated with 3% hydrogen peroxide until the addition of hydrogen peroxide to the samples no longer caused bubbling. After each step, the suspensions were allowed to settle and then washed with distilled water by centrifuging.

The mineralogy of both fractions (<63 μm and <2 μm) was determined by XRD analysis performed on a Philips X'Pert PRO X-ray diffractometer operating at 30 kV and 15 mA and using Cu-K α radiation. Measurements were performed on both, random (<63 μm) and oriented (<2 μm clay fraction) samples. Oriented slides were tested in preparations initially air-dried and then saturated with ethylene glycol. XRD data were obtained in the 2θ range from 4° to 65° (step size: 0.004; 3.5 seg/step) for random samples and from 2° to 30° (0.004/2 s) for oriented samples. The reflections assignments were done using the software X'Pert HighScore, installed on the X-ray diffractometer.

2.2 Scanning electron microscopy (SEM) and microprobe analysis of sediments

SEM/EDS studies were performed with a JEOL 35 JXA-8230 electron probe microanalyser coupled with an energy-dispersive X-ray spectrometry (EDS) analyser. The samples were prepared in graphite stubs and coated with carbon. In addition, SEM was coupled with focused energy dispersive X-Ray analyses (EDAX DX4 apparatus) to perform the elemental semi-quantification. The detection limit of these microprobe analyses was about 0.5% for fluorine and the spatial resolution was about 1 μm .

2.3 Fluorine and arsenic release experiments from sediments samples

Batch experiments were performed to determine the kinetics of the fluorine and arsenic release and to investigate the influence of pH and ionic composition (Na^+ or Ca^{2+}) on this process. Reactions were carried out in cylindrical, water-jacketed reaction vessels covered with a cap, to keep the temperature constant at $25.0 \pm 0.5^\circ\text{C}$. The suspensions were prepared using 100 ml of a 0.1, 0.01 and 0.001 M NaNO_3 solutions aiming to set the ionic strength values typically found in the studied environments. About 5 g of dry sediment was added to the corresponding NaNO_3 solution and the pH of the suspension was adjusted to 6.0 or 8.0 by the addition of either 0.1 M HNO_3 or NaOH . Suspensions were continuously stirred until the end of the experiments. Aliquots of the suspension were withdrawn after 1 h, and 2, 5 and 7 days from the moment of pH adjustment, and filtered through a 0.45 μm cellulose membrane filter. Fluoride, arsenate (as total As) and Ca^{2+} were measured in the separated supernatant. During the experiment, pH was continuously checked and kept constant by adding either 0.1 M HNO_3 or NaOH . The same procedure was followed in experiments conducted with Ca^{2+} electrolyte solutions (CaCl_2).

The total fluoride concentration was measured using a specific fluoride combination electrode (ISE 25) connected to an Orion pH meter. A total ionic strength adjustment TISAB buffer (TISAB: 58 g NaCl + 57 ml acetic acid + 10 Na-citrate, adjusted to pH 5.2 with 5M NaOH in a total volume of 1 l) was used to adjust pH before measurement, and to eliminate any interference from high levels of aluminum and iron that could be present in the solution (Shen et al., 2003). The calibration curve was constructed using NaF standard solutions that received the same treatment described previously. Total arsenic was analysed using a flow injection system (FIHG-AAS) coupled with a hydride generator-graphite furnace atomic absorption spectrometer. Ca was determined by atomic absorption spectroscopy. Detection limits were as follows: As: $0.6 \mu\text{g l}^{-1}$, F: 0.1 ppm and Ca: 0.25 mg l^{-1} .

All solutions were prepared from analytical reagent grade chemicals and purified water (Milli-Q system).

3 Results

3.1 Chemical and mineralogical characteristics of sediments

The bulk chemical composition of the studied sediments was rather similar, and only the organic matter and carbonate contents are the most conspicuous differences among them (Table 1).

Table 1 Chemical composition of studied sediments

Sample	<i>SiO₂ Al₂O₃ Fe₂O_{3(T)} MnO MgO CaO Na₂O K₂O TiO₂ P₂O₅</i>										LOI	Total	CaCO ₃
	(%)												
L1	58.6	15.0	4.90	0.10	1.65	4.51	2.23	2.76	0.71	0.23	6.90	97.6	1.8
L10	61.2	15.9	5.41	0.09	2.35	2.57	2.49	3.39	0.79	0.14	4.60	99.0	1.1
AR	52.3	12.6	4.51	0.10	2.04	4.86	2.58	2.67	0.63	0.21	13.80	96.4	1.9
AB	62.8	12.8	4.81	0.10	2.09	4.84	2.42	2.95	0.65	0.14	5.60	99.2	2.3

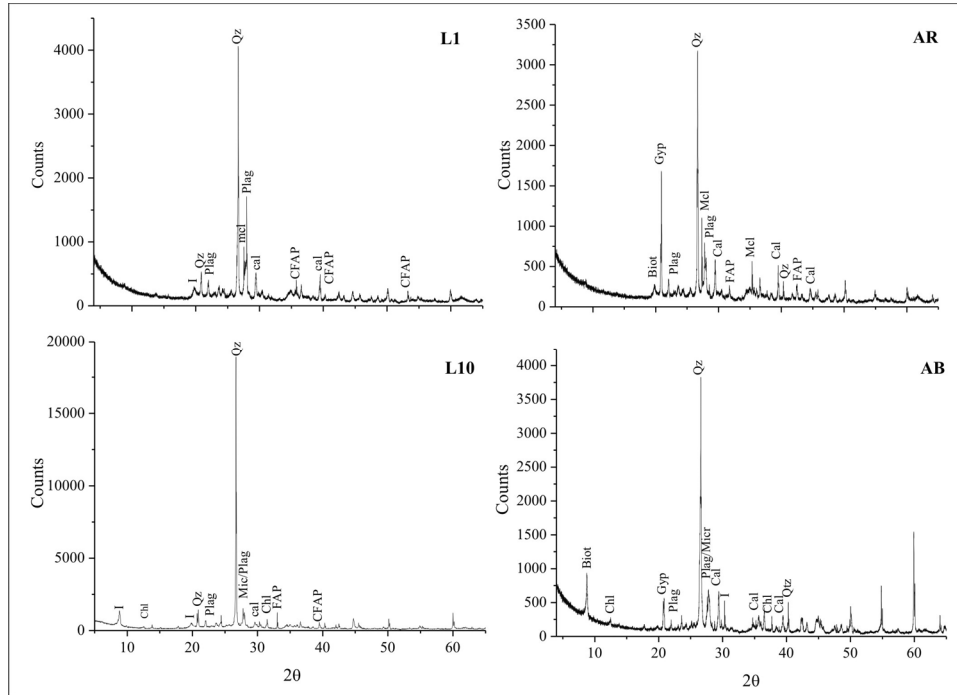
Dominant mineralogy in all studied sediments is also rather homogeneous. Primary minerals determined by XRD are quartz, K-feldspar and plagioclase (Figure 1). Biotite, chlorite and gypsum were only detected in fluvial samples. Calcite is also present in all samples. Illite and kaolinite are the predominant clay minerals in the <2 μm size fraction (Figure 2).

The heavy fraction, that was not visible in the X-ray diffractogram due to its restricted relative abundance (<5%), have been identified using SEM/EDS. Ti–Zr oxides, titanite, Fe and Mn (hydr)oxide coats, and fluorapatite (FAP) are frequently found in loess samples, as well as volcanic glass, autigenic barite and pyrite. Detritic grains of FAP (~10 μm) are highly altered and associated with autigenic calcite (Figure 3(a)).

In fluvial sediments the extent of mineral weathering is lower than those observed in loess samples (Figure 3(b)). Granate, biotite, ilmenite, anatase, zircon, amphiboles, piroxenes, calcite, FAP, and coatings of Ti and Fe (hydr)oxides (Figure 4) associated with altered aluminosilicates were observed. Microprobe analysis in FAP showed contents of F of ~2.8%, which are values typical for this mineral. In these sediments, detritic FAP is less altered and generally associated with clay minerals.

3.2 Batch kinetics experiments and As-F relationships

Figure 4 illustrates the results obtained in the kinetic experiments of fluoride and arsenate release, carried out at pH 6.0 and 8.0. In general, the kinetic process involved two stages: a first step, which occurs during the first hour, followed by a second much slower step, which involves a gradual release of both anions with time, until reaching equilibrium after 90 h.

Figure 1 XRD diagrams showing the mineralogical composition of loess (L1 and L10) and fluvial (AB and AR) sediments

QZ: quartz; Bt: biotite; Pl: plagioclase; Gp: gypsum; Mc: microcline; Cal: calcite; FAP: fluorapatite; Ill: illite; Chl: chlorite; CFAP: carbonate fluorapatite.

The experiment results indicate that the release is pH dependent. In most cases, lower pH lead to higher release of the analysed anions (Figure 5). The only exception was observed in the suspension of sample L10, where a slightly higher release of fluoride was measured at pH 8.0 in the first hour of reaction, and irrespective of the dominant cation in the solution. Besides this only exception, the general trend found at the end of the experiments (after 1 week of reaction) indicates that the concentrations of fluoride and arsenate carried out with NaCl suspensions and at pH 6.0 were higher than those measured at pH 8.0. Similar variability was observed in experiments carried out in CaCl₂ suspensions.

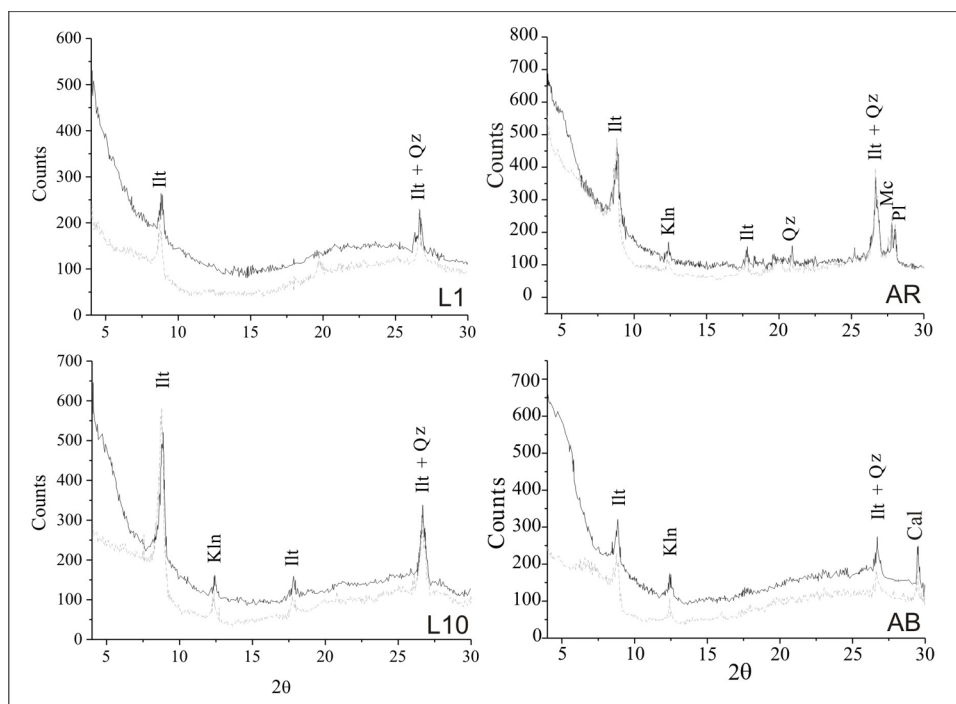
The replacement of Na⁺ for Ca²⁺ as the dominant ion in the solution at constant pH was also studied. Changes in the cation composition lead to the inhibition of both anions release in experiments performed at either pH 6.0 or pH 8.0 (Figure 5). River bed sediments collected at the Sierras Pampeanas Ranges were more sensible to both, pH, and dominant cation composition changes, while loess samples showed the lowest variations.

Figure 6 shows the relationship between As and F released from the studied sediments. Dashed lines indicate the As and F international guideline values for drinking water (WHO, 2004). The figure shows that there is a direct positive relationship between both anions, which suggests that:

- both anions are released from a common source, or
- the mechanisms of release are the same.

In spite of this common trend observed in the two types of analysed sediments, some differences may be distinguished. For example, in fluvial samples the ratio F/As is the same in each individual sample, whatever the pH of the suspension. Indeed, the release of fluoride from sample AB at pH 6.0 and 8.0 is higher than the corresponding release measured in suspensions of sample AR where, on the contrary, the release of arsenic was higher than in sample AB at both pH values. On the other hand, the F/As ratio in loess samples remained constant for the two samples but varied with pH, being higher at pH 8.0, i.e., F⁻ is preferentially released under more alkaline conditions.

Figure 2 XRD diagrams showing the mineralogical composition of the clay-size fraction (<2 µm) of loess (L1 and L10) and fluvial (AB and AR) sediments. Black lines correspond to air dried samples; Grey lines correspond to ethylene glycol solvated samples



QZ: quartz; Illt: illite; Pl: plagioclase; Mc: microcline; Cal: calcite; Kln: kaolinite.

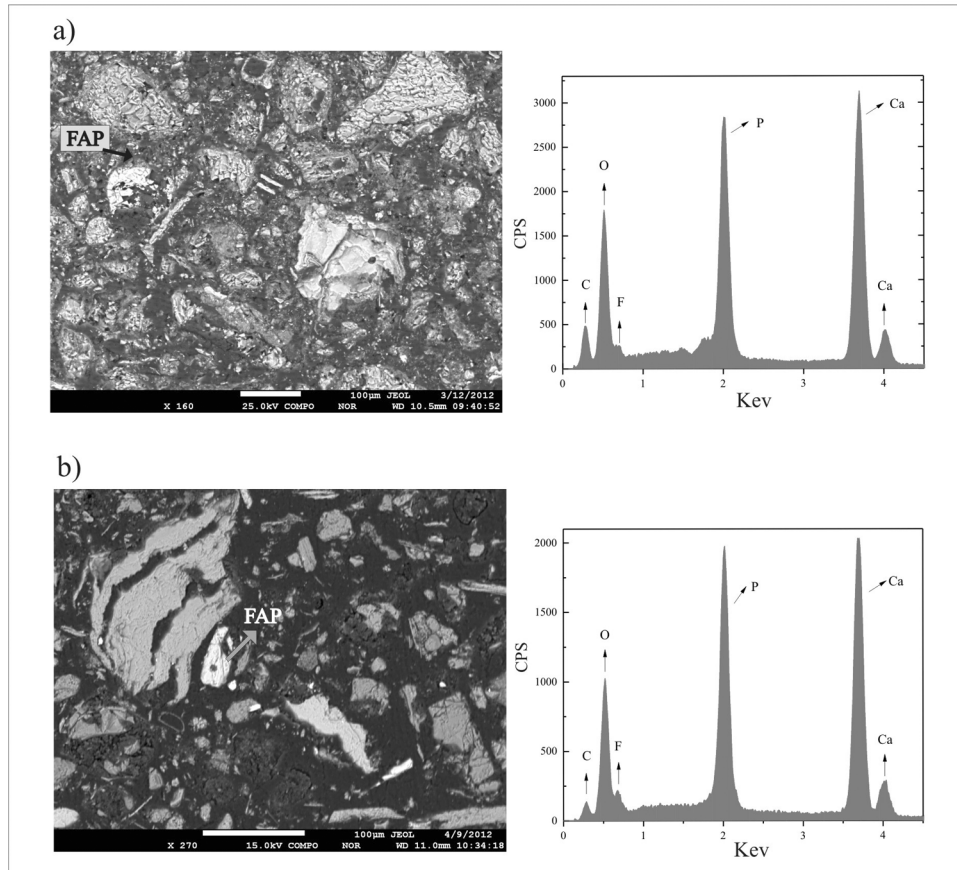
4 Discussion

4.1 Identification of F and As sources

SEM/EDS and DRX observations in both, fluvial and loessic samples revealed the occurrence of accessory detritic FAp and abundant altered biotite. No individual As

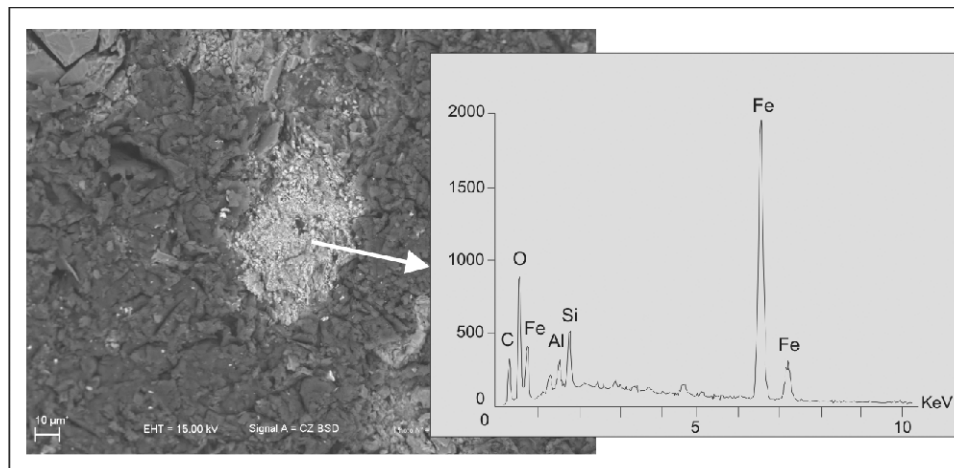
minerals (such as arsenopyrite) were detected by either XRD or SEM–EDS. The detection of low levels of As by this last method is not adequate when Mg-bearing minerals are also present, due to the overlap of peaks.

Figure 3 SEM images of (a) loess and (b) fluvial sediment samples. Insets on the right show the EDS analysis obtained for FAp grains identified in both samples



As mentioned before, the release of fluoride and arsenic from the studied sediments depends on pH and dominant cation in the solution. Higher values of pH and Ca^{2+} concentrations inhibit the release, whereas it is enhanced at acidic pH and Ca^{2+} deficiency. This behaviour could be the consequence of the dissolution of a Ca–As–F-bearing mineral. Several F-bearing phases have been detected in the analysed sediments, FAp, biotites, volcanic glass shards and Fe(hydr)oxides being the most relevant. From these four sources, FAp and biotite are primary sources of fluoride, as it is included into their lattices during magmatic crystallisation by substituting OH^- ions (Bailey et al., 1984). Arsenate and vanadate are commonly found in apatites, as they can also substitute for phosphate (Bhatnagar, 1969; Wilson et al., 1977). Sha and Chappel (1999) informed contents of As that may vary between <2 to >200 ppm depending on the predominating mafic or felsic composition of the host igneous rock.

Figure 4 SEM image of L10 sample showing the presence of Fe (hydr)oxide coats onto silicate grains. The inset shows the corresponding EDS diagram



Fe(hydr)oxides are considered as secondary sources as they clearly bind F^- and arsenate ions as a consequence of scavenging processes that occur during the transport of mineral particles from their sources to the final depositional environment or in their actual sedimentary environment itself.

Volcanic glass has been traditionally considered the main source of fluoride, As and some other trace elements such as V, U and Mo in groundwaters of the Chacopampean Plain (i.e., Nicolli et al., 2012 and references therein). Classical chemical procedures and neutron activation analysis performed on grains of volcanic glass separated from loess samples collected in Córdoba province, revealed a rhyolitic composition and contents of As, Mo, U and some other trace elements that were similar or even lower (in the case of As) than the corresponding concentrations measured in the total fraction of the sediments (Nicolli et al., 1989). No information about fluorine contents in glass grains was included in this work, but the occurrence of high levels of fluorine associated with volcanic ashes has been extensively reported worldwide (e.g., Delmelle et al., 2007; Jones and Gislason, 2008; Oskarsson, 1980; Ruggieri et al., 2010; Witham et al., 2005; Wolff-Boenisch et al., 2004). This association is related to the scavenging in the volcanic plumes of volatiles including sulphur, halogens, as well as metal and metalloid species. During the volcanic eruption, gaseous species of As and F would be adsorbed onto the ash surfaces, or precipitated forming coats of sparingly soluble compounds. Delmelle et al. (2007) demonstrated using AFM imaging and ash-leachate studies that extremely thin coats (<10 nm) form at the ash surfaces, probably throughout in-plume processes. This material is composed of soluble sulphate and halide salts mixed with fluoride compounds (CaF_2 , AlF_3 and $Ca_5(PO_4)_3F$). Experimental and theoretical work on the stoichiometry and stability of As gaseous complexes in the system $As-H_2O-NaCl-H_2S$ at temperatures higher than $500^\circ C$ demonstrated that $As(OH)_3(gas)$ is the predominant As complex in volcanic gases (Pokrovski et al., 2002). This species is proposed to be the responsible for the preferential partitioning of As into the vapour phase as observed in fluid inclusions from high-temperature magmatic-hydrothermal ore deposits (Pokrovski et al., 2002). Other studies show that toxic inorganic AsH_3 is the most volatile of the inorganic species in fumaroles systems. In consequence, it is possible to infer that volcanic shards spread in

loess sediments from the Chacopampean plain are likely carriers of F/As-bearing minerals that are precipitated or adsorbed onto thin coats at the tephra surfaces.

Figure 5 Kinetics curves showing the release of fluoride and arsenate with time. Full symbols: pH 6; open symbols: pH 8; circles: Na⁺-dominant suspensions; triangles: Ca²⁺-dominant suspensions

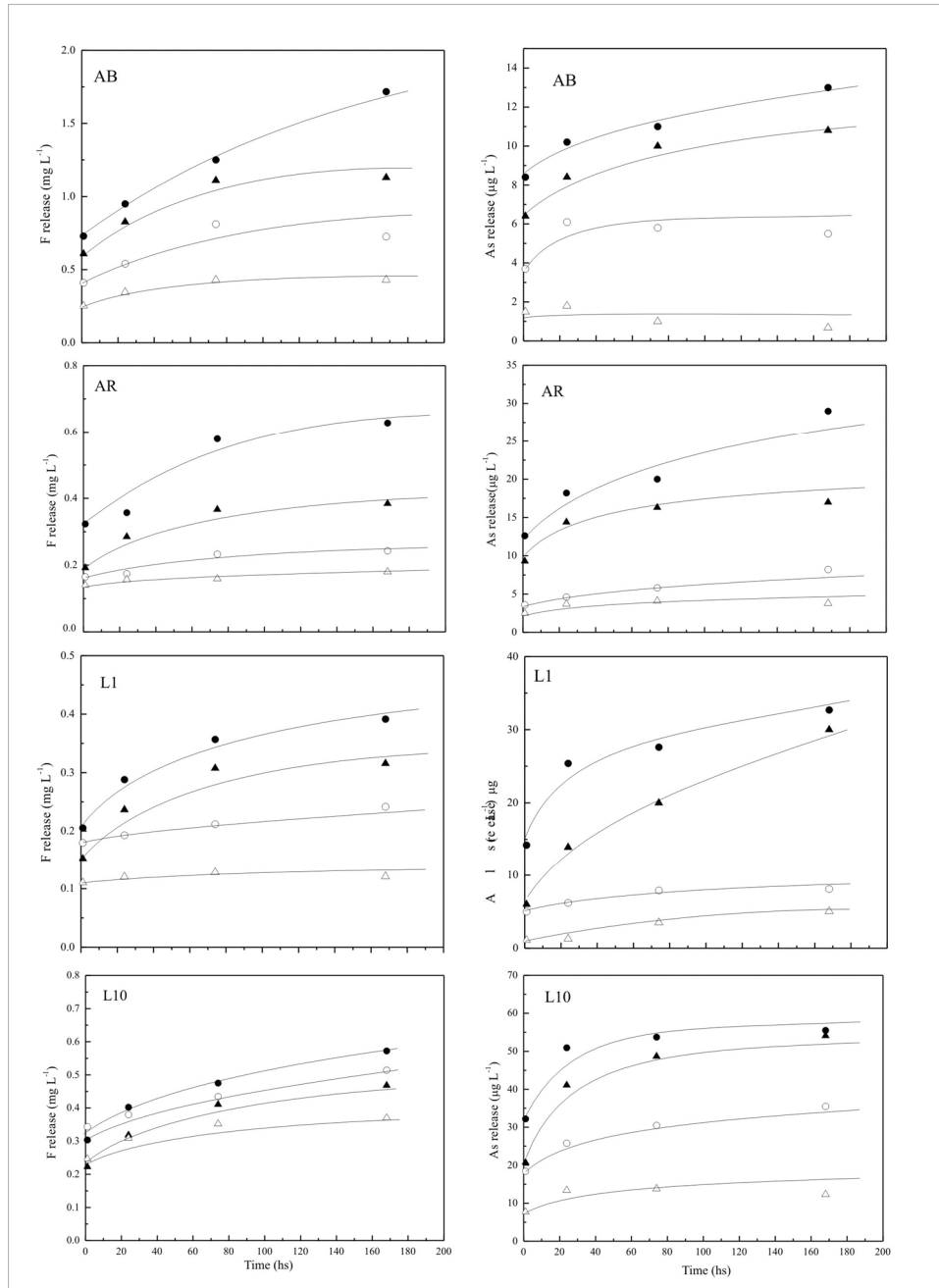
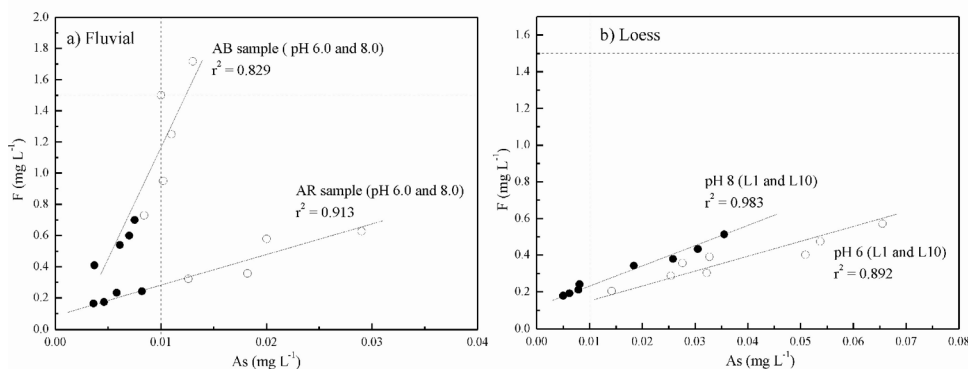
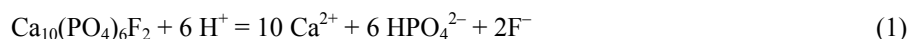


Figure 6 Relationship between As and F for the studied sediment: (a) fluvial sediments and (b) loess sediments. Solid circles: pH 8. Open circles: pH 6.0



4.2 As and F dynamics

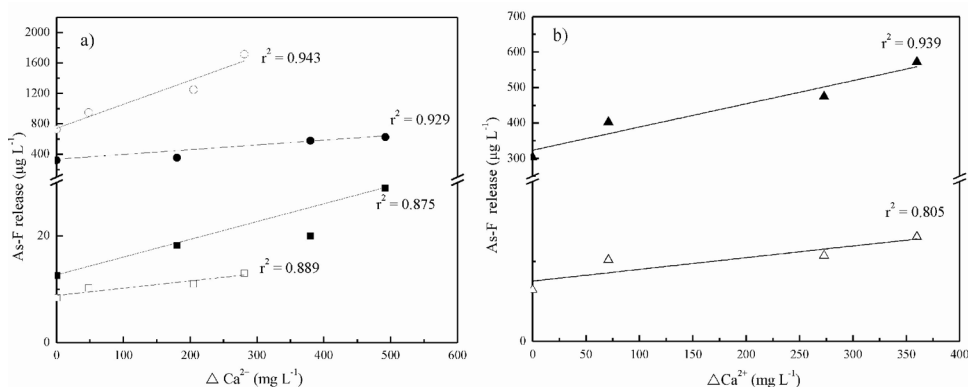
Results of the kinetics experiments suggest that both anions are probably released throughout a dissolution process that is enhanced at acidic pH and inhibited in presence of Ca^{2+} ions. This behaviour is consistent with the dissolution of FAp, represented in equation (1):



According with this equation, increasing dissolution of FAp will release increasing amounts of Ca^{2+} and F^- (and eventually As) to the solution. Figure 7 shows the relationship between Ca^{2+} and the ratio F/As measured in the leachates of fluvial and loess sediments at pH 6.0, in NaCl suspensions. Because Ca^{2+} may be released by the dissolution of some other minerals, the increment of Ca^{2+} concentrations was used. In all cases both, As and F^- show a positive linear trend with ΔCa^{2+} , suggesting that both elements are released by the dissolution of a Ca–F–As bearing mineral. Guidry and Mackenzie (2003) studied the dissolution kinetics of igneous and carbonate fluorapatite and they found that equilibrium was reached after 3 days, and that the concentration of fluoride, phosphate and calcium always increased as the dissolution took place. These authors also indicated that the fluoride concentration rapidly increased during the first day of reaction, and then dissolution became increasingly slower until equilibrium was reached. These results match with our observations performed in release experiments and suggest that dissolution of As bearing FAp present as detritic grains or as coatings onto volcanic glass particles may be responsible for the joint release of fluoride and arsenate at acidic pH.

Although dissolution seems to be the main mechanism of fluoride and arsenate release from both types of sediment samples, competition with HCO_3^- should also be considered as an important contribution at acidic pH. The hydrolysis of aluminosilicates and dissolution of calcite are one of the main sources of HCO_3^- in natural waters. These mechanisms predominate at acidic pH, as well as the adsorption of HCO_3^- onto Fe (hydr)oxide surfaces. As a consequence, calcite dissolution and subsequent HCO_3^- adsorption may lead to the release of fluoride and arsenate by competitive desorption, even under acidic pH.

Figure 7 F and As release vs. delta Ca for the studied sediments at pH 6.0: (a) solid circles: fluorine release for AB sample; solid square: arsenate release for AB sample; open circles: fluorine release for AR sample; open square: arsenate release for AR and (b) solid triangles: fluorine for L10 sample; open triangles: arsenate for L10 sample



Under more alkaline conditions these two anions are also released but to a much lower extent, which suggests that another mechanism of release predominates in such conditions. Desorption from Fe, Al and Mn (oxy)hydroxides has been mentioned as a secondary source of fluoride and arsenate in groundwaters in contact with the studied loess sediments (e.g., Smedley et al., 2005) and in some other parts of the world with similar geochemical characteristics, such as in the alkaline, Na-rich groundwaters from the Yuncheng basin, China (Currel et al., 2011). The adsorption of fluoride and arsenate onto Fe (oxy)hydroxides occurs via a ligand exchange process between the anion and the surface hydroxyls groups (Hiemstra and Van Riemsdijk, 2000). The adsorption occurs under neutral to acidic conditions; desorption, hence, is favoured at alkaline pH (i.e., Arnesen and Krogstad, 1998; Hiemstra and Van Riemsdijk, 2000; Omueti and Jones, 1977; Sparks, 1995; Sposito, 2008; Tang et al., 2009). Besides, competitive desorption took place, as indicated in the following equation:



To evaluate the extent of competition in the studied systems, the dissolution of calcite at pH 6.0 and 0.01 and 0.001 M ionic strengths was simulated, using PHREEQC 2.13 (Parkhurst and Appelo, 1999). Dashed lines in Figure 8 represent the concentrations of HCO_3^- released at pH 6.0 from this hypothetical system. Comparing the simulated concentration of HCO_3^- with the concentrations of fluoride measured in the leachates at the end of the experiments (and following the stoichiometric relation between HCO_3^- and F^- in equation (2)), it is found that F^- concentrations are significantly higher (89, 31, 21, 29 μM for AB, AR, L1 and L10 samples, respectively) than the values calculated for HCO_3^- (5 μM). Therefore, the amount of fluoride that may be released by competition with HCO_3^- at pH 6 is not significant. On the contrary, the concentrations of As measured at the end of the experiments are lower than the simulated concentrations of HCO_3^- (0.16, 0.33, 0.4 and 0.66 μM for AB, AR, L1 and L10 samples, respectively). This indicates that competition with HCO_3^- , could be the main mechanism controlling the arsenate release at acidic pH. This process would also explain the trend between ΔCa^{2+} and As shown in Figure 6, as increasing dissolution of calcite at acidic pH would release

increasing concentrations of HCO_3^- to water, and promote the competitive desorption of AsO_4^{3-} .

The mineralogical characteristics and the chemical composition of water in contact with sediments are key factors to understand and elucidate the mechanisms involved in the release process. Primary and secondary sources of As and F in the studied sediments seem to be the same, but the mechanisms of release are different. Table 2 summarises the possible sources and mechanisms that may control the release of arsenate and fluoride in the studied sediments. In the case of fluvial samples derived from the weathering of crystalline rocks, the dissolution of detritic FAp and/or biotite (this last source is only valid for F^-) is the main mechanism of release at acidic pH. Under alkaline conditions both, dissolution (to a much lower extent) and desorption may occur.

Figure 8 Diagram of distribution of H_2CO_3^- species: (a) fluvial samples and (b) loess samples. Dotted lines indicate the concentration of As-F at pH 6.0

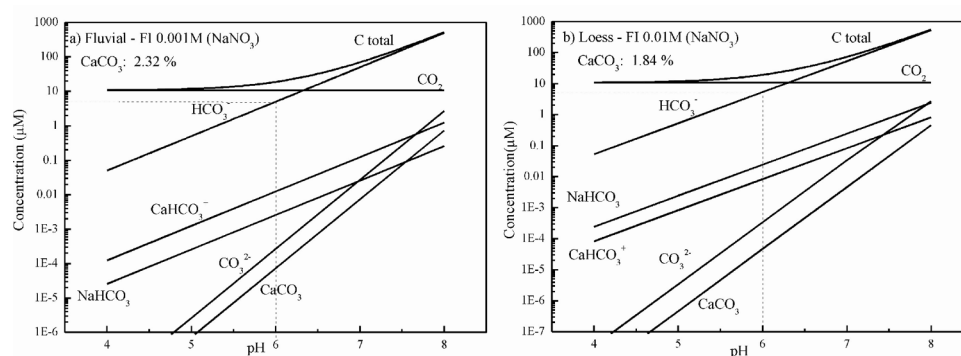


Table 2 Possible sources and mechanism involved fluoride and arsenate release

Fluoride		Arsenate			
Sediment	Source	Release mechanism	Sediment Source	Release mechanism	
Fluvial	Detritic igneous FAp	Dissolution at acidic pH; Ca inhibit the process	Fluvial	As-bearing detritic igneous FAp	Dissolution at acidic pH
	Biotite	Dissolution at acidic pH			
Loess	Volcanic ash (FAP coatings)	Dissolution at acidic pH; Ca inhibit the process	Loess	Volcanic ash (As-bearing FAP coatings)	Dissolution at acidic pH
	Sorbed onto Fe (hydr)oxides	Desorption at alkaline pH	Fe(hydro)oxides	Fe(hydro)oxides	Competitive desorption (HCO_3^-) at acidic pH
			Fe(hydro)oxides	Desorption at alkaline pH	

The mineralogical composition of loess samples is dominated by the presence of As and F bearing volcanic glass. The experimental evidence suggests that these two phases are associated with coats of FAp onto the glass surface that are more soluble under acidic pH. Competitive desorption with HCO_3^- may also explain the release of arsenate adsorbed

onto Fe (hydr)oxide coats at acidic pH. Under alkaline conditions, on the contrary, the release of both, fluoride and arsenate from loess sediments is dominated by a desorption mechanism.

5 Conclusions

This work examined the release behaviour of two typical contaminants found in rivers and aquifers of the Chacopampean region, Argentina. According to the experimental results, both types of sediments show a similar general behaviour regarding the release of fluoride and arsenate, but some slight differences may be distinguished. Mineralogical composition, the extent of alteration of sediments and the water geochemistry are the most conspicuous factors affecting the release process. Thus in fluvial sediments, mostly made of slightly altered minerals originated from the weathering of F-rich igneous and metamorphic rocks, the release of fluoride to the water seems to be controlled by the dissolution/alteration of primary fluoride bearing minerals, more likely FAp and biotite. Much lower concentrations of As are also released from fluvial sediments under acidic conditions, which likely originates from the dissolution of As-bearing igneous FAp. Under more alkaline conditions, the release of both anions is the result of desorption from Fe (hydr)oxide coats. Therefore the amount of fluoride and arsenate measured in natural waters from the Pampean ranges results from the balance between the concentration released by dissolution and the amount adsorbed onto particle surfaces.

In loess sediments, primary sources of fluoride such as detritic FAp and biotite are less frequent because of the higher alteration of the sediments. Therefore, the release of fluoride from these primary sources is considered to be less important. The widespread presence of volcanic glasses in loess has been traditionally considered the main responsible of the high levels of As and F measured in groundwaters of the Chacopampean Plain. In spite of this, the association of these two elements with the glass still remains unknown. Experimental and field observations, however, strongly suggest that these two anions could be associated in the volcanic glass forming thin coats of fluoride salts or adsorbed onto Fe/Mn (hydr)oxide coatings also described in these volcanic particles. The mechanisms of release of fluoride and arsenate are different in this kind of sediments. At acidic pH fluoride is likely released by the dissolution of FAp present either as detritic grains or forming thin coats onto the volcanic ash, while arsenate is preferentially desorbed by competitive desorption. At alkaline pH both anions are desorbed from Fe(hydr)oxide coats.

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