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Partition of arsenic in soils sediments and the origin of naturally elevated concentrations in groundwater of the southern pampa region (Argentina)

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Abstract Excessive arsenic concentrations above the Argentinean and WHO guidelines for drinking water $(10 \ \mu g \ L^{-1})$ affects shallow aquifers of the southern Pampean Plain (Argentina) hosted in the Pampean and the Post Pampean formations (loess and reworked loess; Plio-Pleistocene–Holocene). Health problems related to high As concentrations in drinking waters are known as Endemic Regional Chronic Hydroarsenicism. Hydrochemistry of shallow groundwaters and soil geochemistry were investigated aiming to (1) understand the partition of As in the solid phase and its relationship with unacceptable As concentrations in waters, (2) identify the provision source of As to groundwaters. Only 5% of the samples had As concentrations $<10 \ \mu g \ L^{-1}$; in 27% As concentrations ranged from 10 to 50 $\mu g \ L^{-1}$ and in

58% it reached 60–500 µg L⁻¹. The coarse fraction (50–2,000 µm) hosts about 27% of the total As in the solid phase, being positively correlated to Ba (p < 0.01; $r^2 = 0.93$). About 70% is included in the <2 µm fraction and had positive correlations of As–Fe (p < 0.05; $r^2 = 0.85$) and As–Cr (p < 0.05; $r^2 = 0.68$). Soils and sediment sand fractions of vadose zones are the primary sources of As in shallow groundwater while adsorption–desorption processes, codisolution–coprecipitation, and evaporation during the dry seasons raise As concentrations in waters exceeding the guideline value for drinking water.

Keywords Arsenic · Groundwater · Soil-sediment · Pampean plain · Argentina

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Introduction

Drinking water is probably the main arsenic input placing human health at risk. Populations where the only source of water has high (>10 μ g L⁻¹) arsenic concentrations have a 1% higher chance of developing some types of cancer (Morales et al. 2000). These effects may be apparently developed after 5–15 years consuming daily doses of As from 10 μ g kg⁻¹ per day and from 0.5 to 3 years at doses higher than 40 μ g kg⁻¹ per day (Batthacharya et al. 2003). However, not all persons consuming As-contaminated waters will suffer from arsenical pathologies; however, according to environmental characteristics they could potentially expose to develop arsenical diseases over time (>20 years; Chowdhury et al. 2000). In terms of the actual number of people at risk, this means a serious need to carry out basic research and more knowledge about the origin and mobility of this toxic trace element so that remedial actions could be taken. In recent years a considerable amount of literature has been published reporting new areas around the world with high As concentrations in groundwater used for human consumption (Welch and Stollenwerk 2003) and particularly in Argentina, where arsenical pathology was detected the first time early in the twentieth century, and in the neighboring Uruguay (Ayerza 1917a, b, 1918; Galindo et al. 2007; Manganelli et al. 2007; Francisca and Carro Perez 2009). Skin lesions, skin cancer, soft tissues cancer, neuropathy and vascular pathologies are strongly linked to As-water consumption for long periods (Ratnaike 2006). Many areas in Argentina are not investigated for As in their aquifers, and thus the people may not realize that they are consuming As-toxic waters. As more studies are developed, this contaminant is detected in increasing risk areas and revealing an important public health problem since development of As-symptoms may be delayed for more than 20 years.

Phreatic groundwaters are mostly utilized, being exploited by wells at a shallow depth that reach the upper section of the Pampean and the Post Pampean formations built up of aeolian loess (Plio-Pleistocene) or re-worked loess sediments (Holocene). The quality of drinking water pumped from shallow aquifers of the southern Pampean Plain (Argentina) is affected by natural arsenic concentrations higher than the limit laid down in the Argentine Food Standards Code (CAA 10 μ g L⁻¹) and by the guideline value of World Health Organization (1995) exposing a wide section of the rural population to health hazards. Industrial effluents and mining spills or any other anthropic activities do not provide As to aquifers of the SW pampean region; hence, excessive As is exclusively naturally originated. Health problems related to high As concentration in drinking water from the Chaco-Pampean Plain are known as Endemic Regional Chronic Hydroarsenicism (in Spanish: HACRE) acronym for HidroArsenicismo Crónico Regional Endémico (Tello 1951). Conceptual models proposed to analyze the arsenic path to groundwaters accounting for the health As-hazard in Bangladesh, West Bengal, India, certainly do not explain groundwater contamination in the Chacopampean region of Argentina in view of profound environmental differences and of their contrasting geopedogenetic evolution. In the south Asian region, the modes of As release from lithology to waters range from the oxidative or reductive degradation of As-bearing solids to competitive ligand displacement by phosphate, being reductive dissolution of Fe(III) (hydr)oxides, the most widely accepted explanation of arsenotoxicity (McArthur et al. 2001; Anawar et al. 2002; Polizotto et al. 2005).

The As concentrations in groundwater in the southern Pampean Plain are mainly related to the geology of saturated and vadose zones of aquifers, the latter including loess sediments, parent materials, and loess-derived soils. The regional evaluation of the arsenic content in soils and sediments and its spatial distribution contribute to understanding the geochemical background, the identification of sources, and its geoavailability. According to Gałuszka (2007), the geochemical background is a theoretical natural concentration of a substance in a specific environmental sample or medium considering the spatial and temporal variables. Knowledge on natural background indicates the base level of an element that permits to distinguish acceptable contents from those toxic either natural or anthropic origin in a given area.

The working hypothesis is that arsenic distribution in the studied region appears to be closely related to its partition in the different subfractions of the loess' solid and aqueous phases in every landscape position. In order to reach deeper insight into these relationships, a geochemical study was performed in Holocene soils developed in calcareous loess and in lacustrine sediments identified in different landscape segments of the southern Pampa where shallow groundwaters show high As concentrations.

Thus, this was developed to investigate the distribution of arsenic in the different particle size fractions making up the soils and sediments of the southern Pampa region with a view to understanding the soil–water relationship and its contribution to natural arsenic in the phreatic aquifers.

Antecedent studies and regional setting

The study region is situated in the south of the Pampean Plain and comprises a region settled in the southern section of Buenos Aires Province, Argentina, approximately 150 km NE of Bahía Blanca city. The area is part of the Positive Morphostructural Domain of Ventania. It is a typical plain landscape of the Western Subventanic Plain (WSP) of Buenos Aires that extends from the hilly area of Sierra de la Ventana towards the Atlantic coast (Gonzalez Uriarte 1984). This unit is dissected by several main rivers (Sauce Grande, Sauce Chico, Napostá Grande, Saladillo Dulce and Saladillo de García) and presents several depressions containing lakes that behave as local discharge areas during the rainy season and as evaporative surfaces in the dry season. The climate is temperate subhumid transitional to semiarid. Pedoclimate changes from udic to ustic to the south of the 600-mm mean annual rainfall isoline. Locally, the water table is very close to the surface contributing to the development of hydromorphic processes. The native vegetation cover includes mainly steppe and prairie species ("Pastizal pampeano", *Stipa, Piptochaetium, Aristida, Melica, Briza, Eragrostis* and *Po*; Cabrera 1976).

Very few studies have been carried out on sedimentgroundwater interaction in this region of Argentina (Blanco et al. 1999b; Morrás et al. 2002); natural concentrations including arsenic depend on the geology of sediments and soils. Downward movement of the aqueous phase may transport As through the vadose zone to groundwater accounting for the As-toxicity of waters (Blanco et al. 2006; Galindo et al. 2007; Heredia and Fernandez Cirelli 2009). A close relation of the environment to public health does exist, mainly in the wide rural and urban sectors of the population without access to uncontaminated drinking water.

Methods and materials

The study area is located in the Coronel Dorrego District (Buenos Aires Province, Argentina) between $38^{\circ}18'$, $38^{\circ}58'S$ and $61^{\circ}31'$, $61^{\circ}43'W$. Aiming to a hydrochemical characterization, to determine As concentrations (μ g L⁻¹) and to analyze their spatial distribution to detecting elevated As concentrations in groundwater samples (*n*:111) were collected from the phreatic aquifer during humid and

Fig. 1 Groundwater and soilssediments sampling sites dry seasons. Water was accessed by wells and perforations and three replicates were collected at every sampling site. The geographic distribution of sampling sites is shown in Fig. 1. As concentrations were determined by HG-ICP-OES (detection limit 0.33 ppb). A map of isolines was drawn (Surfer V. 8) to visualize the regional distribution of As in the phreatic aquifer. Groundwater in contact with the studied soils yielded high As-concentrations (LG_{water} 250 μ g L⁻¹ and SD_{water} 100 μ g L⁻¹); parent materials are Holocene aeolian loess in the plains and lacustrine sediments in the depressions. Disturbed soil samples (0-30 cm, LG1; 30-60 cm, LG2; 60-90 cm, LG3; 90-120 cm, LG4; 120-150 cm, LG5 and 0-30 cm, SD1; 30-60 cm, SD2) and three replicates were collected at every site. Texture was determined; the sand fraction (50-2,000 µm; wet sieving), the silt fraction (2–50 μ m) and <2 μ m clay fraction (Robinson pipette method) were collected separately. In the sand and in the clay particle size fractions, As and 29 trace elements were determined by INAA ACTLABS: Ontario-Canada, detection (in limit: 0.5 mg kg^{-1}). Simple linear correlations were performed among the variables studied at the 5 and 1% significance levels.

Results and discussion

Arsenic concentrations in shallow groundwater

Hydrochemistry and As concentrations in phreatic waters are shown in Table 1. Shallow aquifers host highly mineralized waters with As concentrations in the range of 50–500 μ g L⁻¹, which exceed the WHO guideline value (10 μ g L⁻¹; World Health Organization 1995). Rainfall recharges the aquifer at Sierra de la Ventana hilly system and is distributed into the extended WSP plain (1%



Tuble 1 Spatial and seasonal variability of hydroenemistry and his concentrations in shanow groundwaters								
	SEC (dS m^{-1})	pH	As $(\mu g \ L^{-1})$	F (ppm)	B (ppm)	PO ₄ ³⁻ (ppm)	DO (mg L^{-1})	
Recharge								
Humid season	0.12	7.5	-	0.10	0.14	_	13.0	
Dry season	0.40	7.9	-	0.10	0.10	0.10	9.0	
Discharge								
Humid season	0.80	7.9	30	0.91	0.85	_	13.0	
Dry season	0.87	8.4	180	1.60	1.00	0.10	14.0	

Table 1 Spatial and seasonal variability of hydrochemistry and As concentrations in shallow groundwaters

Total number of samples: n: 111. Figures are arithmetic means

SEC Specific Electric Conductance, As Arsenic, F Fluoride, B Boron, PO_4^{3-} Phosphate, DO Dissolved oxygen

gradient) S, SW, SE direction discharging at the Atlantic coast where high As-concentrations were determined in groundwater (Paoloni et al. 2005).

Groundwater in the recharge is Ca-bicarbonate type, has an almost neutral to slightly alkaline reaction either in the rainy and the dry season, and is devoid of As being acceptable as drinking water. At the aquifer discharge, the waters are Na bicarbonate type and As-enriched above the threshold (humid season: $30 \ \mu g \ L^{-1}$; dry season: 180 μ g L⁻¹) and are associated with an elevated pH, respectively, from 7.9 in the humid season up to 8.4 in the dry season. The general trend of groundwater shows As increments exceeding 10 μ g L⁻¹ from the recharge to the discharge in the Atlantic coast. However, the aquifer anisotropy conducted gradual and discrete local changes according to rainfall input, basin morphology, flow velocity, loess characteristics, soil type, and land use. In agreement, although groundwater is ever hosted in loess sedimentary sequences, the relationship between rainfall and As concentration was inverse in the same direction (Blanco et al. 2006). The most influencing environmental variables of As occurrences are soil pH, hydraulic conductivity, soil type, aquifer type, well depth, elevation, sand, silt and clay fractions, mean annual precipitation, temperature, and land use (Blanco et al. 2006; Camacho et al. 2011). Although phosphate concentration appears as a control factor of As in groundwaters, this component was not analyzed in this study.

At the recharge, despite the elevated rainfall, the high topographic gradient determined a slow weathering rate owing to a short period of contact between loess sediments and waters, yielding to acceptable As in groundwater. Here, the solid phase remains stable in a mild hydrochemical environment of neutral pH and oxidizing characteristics, silicate hydrolisis being the main mechanism of As release from the loess to the phreatic aquifer. The amount of released As is low and does not reach toxic levels.

Spatial predictions on As concentrations cannot be achieved; however, the plain landform towards the

aquifer's discharge causes a slow flow velocity and flushing, a more aggressive hydrochemistry, and a longer residence time of water that drives an increase up to excessive As towards the discharge zones, close to the coast. A similar variability was demonstrated too in both the humid and the dry seasons for surface waters (Table 1). The Asconcentration isolines are widely separated and show an almost parallel pattern (Fig. 2), indicative of gradual spatial changes in As concentrations. Nevertheless, patches with the highest As-concentrations that had no apparent relation to regional discharge flux are detected. Specific electrical conductance (SEC) varied between 0.9 and 5 dSm^{-1} and showed a comparable trend though with a more irregular distribution pattern. Water infiltration and vertical movements predominate as a consequence of the plain relief and the high evapotranspiration during the dry season. Evaporation rises As concentrations up to excessive levels. Only 15% of the analyzed samples have As concentrations $<10 \ \mu g \ L^{-1}$; in 27% of samples they range between 10 and 50 μ g L⁻¹, and in 58% of the samples between 60 and 500 μ g L⁻¹. As is positively correlated to high F, B, and V (Paoloni et al. 2005), though these ions do not exhibit an analogous spatial distribution pattern as described in other sectors of the Pampean region (Nicolli et al. 1989; Smedley et al. 2002, 2005; Galindo et al. 2007). A positive As and V correlation was already found in Coronel Dorrego district in 58.7% of water samples (Fiorentino et al. 2007). Sorption-desorption is influenced by changes in the pH of water, which may promote As attachment or detachment from clay particles; this last process caused high arsenic concentrations (USGS 2000; Partey et al. 2009).

Arsenic and associated elements in loess soils and sediments

Soils developed in loess parent materials of the distal interfluve plains and of the proximal extremes of the WSP include detrital grains of quartz (11–29%), feldspars (orthoclase 11–27%), plagioclase (7–12%), volcanic glass (9–19%), Fig. 2 As-isocentrations expressed in mg L^{-1} in phreatic waters of Coronel Dorrego District Buenos Aires province, Argentina



phytoliths (3–14%), biotite (1–5%), muscovite (1–2%), and lithic fragments (15–30%) in their light fractions. In the heavy mineral suite, frequent opaque minerals (20–30%), scarce tourmaline (1–3%), zircon (1–4%), rutile (1–4%), common olivine (5–7%), epidote (5–17%), augite (5–20%), hypersthene (1–9%), lithic fragments (12–28%), green hornblende (18–40%), a little brown hornblende (1–9%), biotite (2–13%) and scarce muscovite (1–5%) were identified (Blanco et al. 1997). Volcanic glass consists of small shards of acidic and basic composition, mostly fresh although there appear some particles with a linear, irregular and surface pattern of weathering with increased frequency towards the proximal sectors of Ventania Hills in accordance with the udic soil moisture regime.

Alteration developed 2:1 clays (Blanco and Sánchez 1995). Illite, illite/smectite, chlorite/smectite and amorphous are the most abundant clay minerals that may influence As behavior, coexisting with other silicate minerals such as quartz, microcline, orthoclase and plagioclases with pyroxene or amphibole, ilmenite, and apatite particle size <2 μ m (Blanco and Sánchez 1994; Blanco and Amiotti 2001; Blanco et al. 2003). No discrete As minerals were identified petrographically in any of the studied fractions, from which it may be surmised that arsenic is hosted in the crystalline structure of some primary minerals by isomorphic substitution.

The loam to heavy loam soil texture is uniform throughout, indicating a uniform lithologic source. The texture of soils is shown in Fig. 3. In general terms, sand



Fig. 3 Textures of the studied soils and sediments

content ranged from 41.9 to 58.9%; the fine fraction has 17.9–32.7% silt and 19.6–34.0% clay. The very fine sand particle size predominates in the sand fraction.

Contribution of Ventania System rocks to As-contamination through weathering of mainly quartzites is nil, but loess plays a role in regional arsenic distribution since the phreatic aquifer interacts with loess-derived soils and sediments containing from 4.3 to 7.8 mg kg⁻¹ of As in the sand fraction of LG soil, and slightly higher from 7.8 to

	LG1	LG2	LG3	LG4	LG5	SD1	SD2
As mg kg ⁻¹	4.3	4.9	5.1	7.3	7.8	7.8	8.3
Ba mg kg ⁻¹	510	490	535	640	640	625	625
Br mg kg ⁻¹	0.5	1.5	1.2	2.9	0.5	0.5	0.5
Ca (%)	3	2	3	6	3	2	3
Co mg kg ⁻¹	6	7	8	10	9	6	5
Cr mg kg ⁻¹	27	25	21	30	25	25	18
Cs mg kg ⁻¹	3	4	3	4	4	3	2
Fe (%)	2.43	2.30	2.69	2.96	2.84	2.15	1.75
Hf mg kg ⁻¹	3	4	4	4	4	4	3
Mo mg kg ⁻¹	4	2	1	2	1	1	2
Na (%)	3.03	2.98	3.03	2.80	3.01	3.02	2.91
Ni mg kg ⁻¹	30	94	31	34	35	30	29
Rb mg kg ⁻¹	64	75	66	58	93	44	43
Sb mg kg^{-1}	0.6	0.6		0.5	0.8	0.5	0.5
Sc mg kg^{-1}	7.3	7.7	9.4	10.0	11.1	7.6	6.6
Th mg kg ⁻¹	5.7	5.2	5.7	6.6	5.7	4.9	4.9
$\rm U \ mg \ kg^{-1}$	1.4	1.7	2.1	2.2	1.8	1.6	1.1
Zn mg kg ⁻¹	49	48	77	266	433	48	47

Table 2 Arsenic and other trace elements contents in the sand fraction (50–2,000 $\mu m)$

8.3 mg kg⁻¹ in that of SD soil (Table 2). Considering the 50- to 2,000- μ m fraction of LG soil, the top soil had the lowest arsenic content (LG1, 4.3 mg kg⁻¹) of all samples. The highest content was found in LG5 (7.8 mg kg⁻¹). Approximately 27% of arsenic in the solid phase occurs in the sand fraction.

Most (approximately 70%) of the arsenic occurs in the <2 µm fraction. The clay fraction contains 8.9-29.8 mg kg⁻¹ of As and shows a higher vertical heterogeneity than the sand fraction, which may be attributed to its reactive character and to the occurrence of adsorptiondesorption processes (Table 3). The $<2 \mu m$ fraction belonging to the SD1 top soil solid phase, affected by an oscillating water table, and subjected to periodic waterlogging, has a lower As content (SD1: 15.6 mg kg⁻¹) than the underlying horizon (SD2: 29.8 mg kg^{-1}). The latter content is the highest detected in the present study; however, all of them are normal values in soils and sediments. As enrichment in SD2 can be explained by the higher water-holding capacity of the pores owing to the higher 2:1 clays content than SD1 (SD1, 19.6%; SD2, 30.1%) and to the longer residence time of the water in the soil because of the flat-to-concave characteristics of the local geomorphic environment.

Other trace elements determined in high amounts in the solids although not evaluated in groundwater were Fe, Ba, Zn, Cr, Co, Br, Rb, and Ni (Tables 2, 3). The clay fraction of LG soil contains 165–400 mg kg⁻¹ of Ba, whereas the clay fraction of SD soil has significantly less (SD1 = SD2 49 mg kg⁻¹). Ba occurs in the structure of feldspars and

their weathering products; it can be recognized in the light subfraction of the loess mineral association.

Zinc content in the sand fraction of LG soil ranged from 48 to 441 mg kg⁻¹, the highest quantity being found at depth. In the SD sand fraction significant less Zn contents occur (47–48 mg kg⁻¹); however, the SD clay fraction had smaller Zn contents than LG (LG: 49–441 mg kg⁻¹; SD: 46–47 mg kg⁻¹).

Cobalt content amounted to 6–10 and 9–17 mg kg⁻¹ in the sand and clay fractions of LG soil, respectively. In SD soil, 5–6 mg kg⁻¹ was determined in the sand fraction and 12–13 mg kg⁻¹ in the fine fraction. The Cr content of the sand and clay fractions of LG soil and in the sand fraction of SD soil was found to be similar (LG sand 21–30 mg kg⁻¹, LG clay 22–32 mg kg⁻¹, SD sand 18–25 and 14–18 mg kg⁻¹); in the SD clay fraction Ni content was: LG sand 30–94 mg kg⁻¹, LG clay 45–54 mg kg⁻¹; SD sand 29–30 mg kg⁻¹, SD clay 42–45 mg kg⁻¹.

The source of Zn, Co, Cr, and Ni can be traced to sulfides and ferromagnesian silicates of the loess heavy mineral fraction (Rankama and Sahama 1962). Cr evolution follows Fe in the process of magmatic fractionated crystallization; Cr is also found in olivine and in the Fe oxide phases. Similarly, Ni can be incorporated into olivine crystalline structure through isomorphic substitution. Rb (LG soil sand 58–93 mg kg⁻¹, clay 14–113 mg kg⁻¹; SD soil sand 43–44 mg kg⁻¹, clay 14–54 mg kg⁻¹) is associated with the presence of K-feldspars and is found in both the sand and clay fractions.

Table 3 Arsenic and other trace elements content in the clay fraction ($<2 \mu m$)

	LG1	LG2	LG3	LG4	LG5	SD1	SD2
As mg kg ⁻¹	11.6	8.9	10.6	20.6	15.9	15.6	29.8
Ba mg kg ⁻¹	400	227	165	250	49	49	49
Br mg kg ⁻¹	24.9	42.3	13.5	9.4	6.3	4.0	12.3
Ca (%)	0.9	0.9	0.9	0.9	0.8	1.0	3.0
Co mg kg ⁻¹	17	17	14	13	9	12	13
Cr mg kg ⁻¹	32	32	28	25	22	18	14
Cs mg kg ⁻¹	7	7	8	7	6	4	4
Fe (%)	4.60	4.11	3.58	2.76	2.71	3.25	1.20
Hf mg kg ⁻¹	3	4	2	2	2	2	4
Mo mg kg ⁻¹	5	1	1	4		1	1
Na (%)	6.11	5.01	5.87	6.04	7.80	5.22	5.90
Ni mg kg ⁻¹	49	45	48	50	54	42	45
$Rb mg kg^{-1}$	43	84	73	113	14	55	14
Sb mg kg^{-1}	0.5	0.6	0.8	0.6	0.4	0.4	0.4
Sc mg kg^{-1}	18.2	22.1	20.2	15.5	13.6	10.3	12.7
Th mg kg ⁻¹	4.9	6.5	8.3	8.1	7.9	6.5	4.1
$\rm U~mg~kg^{-1}$	0.5	0.5	2.0	0.5	1.4	0.5	0.5
Zn mg kg ⁻¹	49	74	441	256	48	46	47

Both fractions of all the studied soils contain U (LG sand 1.4–2.2 mg kg⁻¹ and SD sand 1.1–1.6 mg kg⁻¹; LG clay 0.5–2.0 mg kg⁻¹ and SD1 = SD2 clay, 0.5 mg kg⁻¹). Such contents are lower than in Quaternary loess of north and northeastern Argentina (U: Esperanza 2.65 mg kg⁻¹; Villa Trinidad 2.79 mg kg⁻¹; Nicolli et al. 2001). U does not appear to fit well in any mineral structure due to its large size. It has been identified in low-temperature pressure minerals that are late in forming. The abundance of U tends to increase with silica content. U can also be abundant in certain accessory minerals (Bea 1999). In the present case, rock fragments and the accessory zircon, apatite, and titanium silicates found in loess materials could supply U to the sand and clay fractions.

A highly significant positive correlation was observed between As and Ba in the sand fraction (p < 0.01; $r^2 = 0.93$) and significant inverse correlations exist between As and Cr (p < 0.05; $r^2 = 0.68$) and between As and Fe (p < 0.05; $r^2 = 0.85$) in the $<2 \mu m$ fraction (Figs. 4, 5, 6). Comparable correlations were found by Nicolli et al. (2009). All these elements are found in the Holocene aeolian loess and/or loess-derived sediments reworked by fluvial or aeolian processes. Hence, they could be affected by precipitation–hydrolysis–dissolution reactions releasing As and Fe and introducing too minor amounts of these elements into mineral structures formed by coprecipitation (i.e., Fe-oxides) in the geochemical environment. On the other hand, codissolution controlled by mineral stability gives rise to As release from the



Fig. 4 Simple linear regression of As versus Ba in the sand fraction $(50-2,000 \ \mu\text{m}), (p < 0.01)$



Fig. 5 Simple linear regression of As versus Cr in the clay fraction (<2 μ m), (p < 0.05)

coprecipitated solid phase and mobilization into water leading to lower As contents in the mineral structure and, consequently, an increase of As in solution (Litter et al. 2008). Coprecipitation/codissolution mechanisms could be an argument in favor of the inverse correlation As–Fe found in the <2 μ m fraction.



Fig. 6 Simple linear regression of As versus Fe in the clay fraction (<2 $\mu {\rm m}$), (p < 0.05)

Spatial distribution of As in phreatic groundwaters

There is no apparent regional trend in the arsenic groundwater distribution in the Pampa region of Argentina (Paoloni et al. 2000; Smedley and Kininburgh 2002; Smedley et al. 2002; Bundschuh et al. 2004; Galindo et al. 2007). A similar highly irregular geographic configuration in the spatial distribution pattern of groundwater arsenic, generally found in patches, has been observed in a wide area in the extreme south of the Pampa region, comprising the SW-SE section of Buenos Aires Province (Paoloni et al. 2000, 2003). The detailed studies based on a higher density of sampling points also show variable distribution in more restricted areas of Buenos Aires Province such as the Coronel Dorrego district. The wide variation in As levels even within short distances as well as the concentration increases towards the discharge areas are likely to depend on local factors such as geomorphology and landscape position, relief and slope characteristics, texture and sedimentary sorting, the residence time of the water, and the aggressiveness of the microenvironment in the vicinity of the mineral grains (Blanco et al. 1999b; Nicolli et al. 2006).

Sources of As to groundwaters

It has been generally accepted that the high arsenic concentrations in water are related to the presence of volcanic glass, commonly making up between 15 and 30% of the mineral constituents of the sand fraction of the Quaternary loess sediments covering the Pampean plains. To date, the direct dissolution of volcanic glass has been considered the major source of arsenic in Pampean aquifers (Nicolli et al. 1989; USGS 2000; Smedley and Kininburgh 2002; Smedley et al. 2002; Galindo et al. 2007; Ruggieri et al. 2010). However, in addition to volcanic glass there are other sources in the loess sediments (Blanco et al. 1999a, b; Smedley et al. 2002; Bundschuh et al. 2004). The sand fraction of loess soils and sediments of the SW Pampean region contains between 6.4 and 22.0 mg kg⁻¹ of As (Blanco et al. 1999a). These amounts are similar to those determined in: (1) soil and sediments from different locations of the Pampean region known to receive sedimentary contributions from several sources $(3-27 \text{ mg kg}^{-1}; \text{Morrás})$ et al. 1998), (2) acidic volcanic ash (6 mg kg⁻¹; Bundschuh et al. 2004), and (3) volcanic glass (6 mg kg⁻¹ in average, range 2.2–12.2 mg kg⁻¹; Smedley and Kinniburgh 2000; Smedley et al. 2002, 2005). Furthermore, both the light and heavy sand sub-fractions belonging to soils developed in loess exhibit variable quantities of arsenic, ranging from 8.8 to 29.0 mg kg⁻¹ in the light and from 15.0 to 26.0 mg kg⁻¹ in the heavy fraction.

As a whole these data indicate a certain degree of ambiguity on the precise source of the As found in groundwater. It can, therefore, be held that (1) the high As concentrations in groundwater do not originate exclusively in the volcanic glass clasts found in the light sand separately, (2) other mineral constituents of both soil and sediment sub-fractions contribute to As concentrations, (3) adsorption–desorption processes onto the clay particles, (4) codissolution–coprecipitation largely control mobility and therefore As-concentrations in groundwater flux paths (Partey et al. 2009), and (5) evaporation during the dry seasons rises As concentrations in waters up to an excess.

The amount of arsenic in groundwater in the study region largely exceeds the WHO and the Argentinean guidelines for drinking water of 10 μ g L⁻¹ (LG_{water}, 250 μ g L⁻¹ and SD_{water}, 100 μ g L⁻¹; World Health Organization 1995). LG water samples were collected from a well located in a rural school with no access to public water supply, obviously constituting a high risk to children using the well water for drinking purposes. There is currently no monitoring mechanism in place to control water quality in the area. Previous studies showed a seasonal variation in the amount of As in surface water. During the humid season the As concentration is lower than the critical threshold in all sections of the studied basins, whereas during the dry season high As concentrations were observed mainly in the lower basins (Fiorentino 1999). Hence, the direct evaporation is another mechanism contributive to As concentration along the flow pathway (Gao et al. 2007).

Conclusions

The partition of arsenic in the soil coarse and fine grain size fractions and in water is critically related to its source and its capacity to be conserved in or driven from the aquifer. Arsenic is first removed from the minerals of the loess psammitic fraction (50–2,000 μ m) in view of the occurrence of mineral weathering reactions, mainly hydrolysis of silicates and carbonate dissolution controlled by the local geochemical factors: pH, Eh, alkalinity, salinity, predominant anions and cations, and competition with other ions. The subsequent complex behavior of arsenic is affected by processes occurring in the fine fraction as

adsorption-desorption, codisolution-coprecipitation, competition for adsorption sites, and oxide-reduction. Desorption processes and the increase of arsenic concentration in the aquifers are controlled by groundwater pH. Hydrogeochemical evolution to alkaline pH can favor As desorption. The ion exchange properties of the pelitic fraction $(<2 \mu m)$ provide the means to explore mechanisms of adsorption and desorption of arsenic ions in groundwater. The clay fraction can apparently behave either as a source or as a sink of arsenic. Evaporation is another mechanism that accounts to concentrate As in solution above the guide value. The population usually drinks As-affected phreatic waters and in most cases they are not aware of the consequences of long-term consumption of potentially toxic waters. In the future, a great impact may be expected in child population since seven of the eight schools of the studied area have high As-concentrations in their groundwater supply. Future research should focus on improving the systematic examination of the spatial variability of geological and edaphic materials and their linkage to hydrogeochemical characteristics with a view to filling the knowledge gap regarding arsenic speciation processes in the groundwater of the region.

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References

- Anawar HM, Komaki K, Akai J, Ishizuka T, Takahashi T, Yoshioka T (2002) Diagenetic control on arsenic partitioning in sediments of the Meghna River delta, Bangladesh. Environ Geol 41:816–825
- Ayerza A (1917a) Arsenicismo regional endémico (keratodermia y melanodermia combinadas). Bol Acad Medicina 2-3:11–24
- Ayerza A (1917b) Arsenicismo regional endémico (keratodermia y melanodermia combinadas) (continuación). Bol Acad Medicina 2–3:41–55
- Ayerza A (1918) Arsenicismo regional endémico (keratodermia y melanodermia combinadas) (continuación). Bol Acad Medicina 1–24
- Batthacharya R, Chatterjee D, Nath B, Jana J, Jacks G, Vahter M (2003) High arsenic groundwater: mobilization, metabolism and mitigation—an overview in the Bengal Delta Plain. Mol Cell Biochem 253(1–2):347–355
- Bea F (1999) Uranium. In: Marshall CP, Fairbridge RW (eds) Encyclopedia of geochemistry. Kluwer Academic Publisher, Dordrecht, pp 645–648
- Blanco Mdel C, Paoloni JD, Morrás HJM, Fiorentino CE, Sequeira M (2006) Content and distribution of arsenic in soils, sediments and groundwater environments of the Southern Pampa Region, Argentina. Environ Toxicol. doi:10.1002/tox20219, 561–574
- Blanco MdelC, Amiotti NM (2001) Excursion Guide Book. Semi-arid and humid soils of Buenos Aires province, 12 the International Clay Conference and 3rd. International Symposium on Activated Clays, July 22–28, B. Blanca, Argentina 71 pp

- Blanco MdelC, Sánchez L, Aguilar Ruiz J (1997) Mineralogía y micromorfología de suelos loessicos con desarrollo moderado en la Llanura Subventánica Occidental Bonaerense, Argentina. Edafologia., Rev Soc Española Cca. del Suelo (2):215–219
- Blanco MdelC, Paoloni JD, Morrás H, Fiorentino C, Sequeira M (1999a) Variabilidad espacial del paisaje Pampeano sudoccidental y su influencia en la distribución del ión arsénico en suelos y aguas, Actas. I Congr. Arg. de Cuaternario y Geomorfología. La Pampa, Argentina, pp 25–26
- Blanco MdelC, Paoloni JD, Morrás H, Fiorentino C, Sequeira M (1999b) Contenidos de arsénico en suelos-sedimentos y su correlación con la calidad del agua subterránea en el SW pampeano, Argentina, 14 Cong. Lat de la Cca. del Suelo. Pucón, Chile
- Blanco MdelC, Sánchez LF (1994) Mineralogía de arenas en suelos loessicos del sudoeste pampeano. Turrialba 4(3):147-159
- Blanco MdelC, Sánchez LF (1995) Caracterización de las fracciones limo y arcilla en suelos loessicos del suroeste pampeano en Argentina. Turrialba 45(1–2):76–84
- Bundschuh J, Farías B, Martín R, Storniolo A, Bhattacharya P, Cortés J, Bonorino G, Albouy R (2004) Groundwater arsenic in the Chaco-Pampean Plain, Argentina: case study from Robles County, Santiago del Estero Province. Appl Geochem 19(2):163–260
- Cabrera A (1976) Regiones fitogeográficas Argentinas. In: Kugler WF (ed) Enciclopedia Argentina de Agricultura y Jardinería, Tomo 2, Fasc. 1., 1–85, Buenos Aires, 1–1408 pp
- Camacho LM, Gutierrez M, Alarcón Herrera MT, Villalba L, Shuguang D (2011) Occurrence and treatment of arsenic in groundwater and soil in northern Mexico and southwestern USA. Chemosphere 33(3):211–225. doi:10.1016/j.chemosphere.2010. 12.067
- Chowdhury UK, Biswas BK, Chowdhury TR, Samanta G, Mandal BK, Basu GC, Chanda CR, Lodh D, Saha KC, Mukherjee SK, Roy S, Kabir S, Quamruzzaman QD (2000) Groundwater contamination in Bangladesh and West Bengal, India. Environ Health Perspect 108(5):393–397
- Fiorentino CE (1999) Evaluación y riesgo de la contaminación de los recursos hídricos superficiales en las vertientes del Sistema de Ventania. Tesis de Magister. Universidad Nacional del Sur, Bahía Blanca (Inédito)
- Fiorentino CE, Paoloni JD, Sequeira M, Arosteguy P (2007) The presence of vanadium in groundwaters of the southern extreme in the Pampean region, Argentina: relationship with other chemical elements. J Contam Hydrol 93(1–4):122–129
- Francisca FM, Carro Perez MEC (2009) Assessment of natural arsenic in groundwater in Córdoba Province, Argentina. Environ Geochem Health 31(6):673–682
- Galindo G, Sainato C, Dapeña C, Fernández-Turiel JL, Gimeno D, Pomposiello MC, Panarello HO (2007) Surface and groundwater quality in the northeastern region of Buenos Aires Province, Argentina. J South Am Earth Sci 23:336–345
- Gałuszka A (2007) A review of geochemical background concepts and an example using data from Poland. Env Geol 52:861–870. doi:10.1007/s00254-006-0528-2
- Gao SJ, Ryu KK, Tanji C, Herbel MJ (2007) Arsenic accumulation and speciation in evaporating waters of agricultural evaporation basins. Chemosphere 67:862–871
- Gonzalez Uriarte M (1984) Características geomorfológicas de la región continental que rodea la Bahía Blanca, provincia de Buenos Aires.Actas X Congr. Geol. Argentino, S. C. de Bariloche, Argentina, III:556–576
- Heredia OS, Fernandez Cirelli A (2009) Trace elements distribution in soils, pore water and groundwater in Buenos Aires, Argentina 409–414. doi:101016/j.Geoderma.2008.12020
- Litter M, Perez Carrera A, Morgada ME, Ramos O, Quintanilla J, Fernandez Cirelli A (2008) Formas presentes de As en agua y

suelo. En: Bundschuh J., Litter M. (Editores). Iberoarsen. Distribución del arsénico en las regiones Ibérica e Iberoamericana. 5–32 pp

- Manganelli A, Goso C, Guerequiz R, Fernández Turiel J, García Vallès M, Gimeno D, Pérez (2007) Groundwater arsenic distribution in South-western Uruguay. Env Geol 53(4):827–834
- McArthur JM, Ravenscroft P, Safiulla S, Thirwall MS (2001) Arsenic in groundwater: testing pollution mechanisms for sedimentary aquifers in Bangladesh. Water Resour Res 37:109–117
- MdelC Blanco, Amiotti N, Aguilar Ruiz J (2003) Reconstrucción de la evolución geo-pedogenética en una toposecuencia del sudoeste pampeano. Ciencia del Suelo 21(3):59–70
- Morales KH, Ryan L, Kuo TL, Wu MM, Chen CJ (2000) Risk of internal cancers from arsenic in drinking water. Environ Health Perspect 108:655–661
- Morrás H, Zech W, Nabel P (1998) Composición geoquímica de suelos y sedimentos loessicos de un sector de la Pampa Ondulada. 2das. Jornadas Geológicas y Geofísicas Bonaerenses, Mar del Plata, I:225–232
- Morrás H, Blanco Mdel C, Paoloni JD (2002) Algunas observaciones sobre el origen del arsénico en sedimentos, suelos y aguas de la región Chaco-pampeana, Argentina. II Taller sobre Sedimentología y Medio Ambiente, Resúmenes: 37–38, Buenos Aires, Argentina
- Nicolli J, Smedley P, Tullio J (1989) Aguas subterráneas con altos contenidos de flúor, arsénico y otros oligoelementos en el norte de la provincia de La Pampa: Estudio preliminar. Congreso Internacional sobre Aguas, Workshop sobre Química Ambiental y Salud, Libro de Resúmenes, III-3
- Nicolli H, Tineo A, García JW, Falcón C, Merino MH (2001) Traceelement quality problems in groundwater from Tucumán, Argentina. In: Cidu R (ed), Water–rock interaction 2:993–996
- Nicolli HB, Tineo A, Falcón CM, García JW (2006) Distribución del arsénico y otros elementos asociados en aguas subterráneas de la región de Los Pereyra, Provincia de Tucumán, Argentina En: Galindo G, Fernández Turiel JL, Parada MA, Gimeno Torrente D (eds), Arsénico en aguas: origen, movilidad y tratamiento. II Seminario Hispano-Latinoamericano sobre temas actuales de Hidrología Subterránea, IV Congreso Hidrogeológico Argentino, pp. 83–92
- Nicolli HB, Tujchneider O, Paris M, Blanco MdelC, Barros A (2009) Movilidad del arsénico y oligoelementos asociados en aguas subterráneas del centro-norte de la provincia de Santa Fe, Argentina. VI Congreso Argentino de Hidrogeología, IV Sem. Hispano-Latinoamericano sobre Temas Actuales de Hidrogeología Subterránea, Santa Rosa, La Pampa, 1–10 pp
- Paoloni JD, Fiorentino CE, Sequeira M, Echeverría N (2000) Spatial variability and concentration of arsenic in the groundwater of a

region in southwest Buenos Aires Province, Argentina. J Soil Water Conserv 55(4):436-438

- Paoloni JD, Sequeira M, Fiorentino CE, Amiotti N, Vazquez R (2003) Water resources in the semi-arid Pampa–Patagonia transitional region of Argentina. J Arid Environ 53:257–270
- Paoloni JD, Sequeira ME, Fiorentino CE (2005) Mapping of arsenic content and distribution in groundwater in the southeast Pampa, Argentina. Int Perspect J Environ Health 67(8):51–53
- Partey F, Daid N, Samuel N, Nartey R (2009) Mechanism of arsenic sorption onto laterite iron concretions. J Colloid Interf Sci 321(2):493–500. doi:10.1016/j.jcis.2008.02.034
- Polizotto M, Harrey Ch, Guauchau L, Badruzzman B, Ashraf L, Newville M, Sulton S, Fendorf S (2005) Solid-phase and desorption processes of arsenic within Bangladesh sediments. Chem Geol 228:97–111
- Rankama K, Sahama ThG (1962) Geoquímica. Ediciones Aguilar SA Seg. Edición. 250 pp
- Ratnaike R (2006) Arsenic in health and disease. In: Naidu R, Owens G, Bhattacharya P, Nadebaum P (eds) Managing arsenic in the environment: from soil to human health, CSIRO Publishing, Collingwood, Australia, 297–309
- Ruggieri F, Saavedra J, Fernandez Turiel JL, Gimeno D, García Vallés M (2010) Environmental geochemistry of ancient volcanic ashes. J Haz Mater 183:353–365
- Smedley P, Kininburgh DG (2002) A review of the source behavior and distribution of arsenic in natural waters. Appl Geochem 17(5):517–568
- Smedley P, Kinniburgh DG (2000) Source and behavior of arsenic in natural waters. http://www.who.int/water_sanitation_health/ dwq/en/arsenicum1.pdf. Accessed 23 October 2010
- Smedley P, Nicolli HB, Macdonald DM, Barros AJ, Tullio JO (2002) Hydrogeochemistry of arsenic and other inorganic constituents from La Pampa, Argentina. Appl Geochem 17(3):259–284
- Smedley P, Kinniburgh DG, Macdonald DM, Nicolli HB, Barros AJ, Tullio JO, Pearce JM, Alonso MS (2005) Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. Appl Geochem 20:989–1016
- USGS (United States Geological Survey) (2000) Geochemistry of Arsenic. http://www.or.water.usgs.gov.pubs/online/html/ WRI98-4205/as_repot6.html
- Tello E (1951) Hidroarsenicismo crónico regional endémico (HACRE), sus manifestaciones clínicas. (ed) Univ. Nac. de Córdoba, Argentina
- Welch AH, Stollenwerk KG (2003) Arsenic in groundwater: geochemistry and occurrence. Kluwer Academic Publisher, Borton, 475 pp
- World Health Organization (WHO) (1995) Guidelines for drinking water quality. 2nd Ed. I. pp 43–45