Groundwater arsenic in the Chaco-Pampean Plain, Argentina: case study from Robles county, Santiago del Estero Province

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Abstract

In large parts of rural Argentina people depend on groundwater whose As content exceeds the Argentine drinking water standards (0.05 mg l^{-1}). The most affected areas are located in the Chaco-Pampean Plain, where aquifers comprise Tertiary loess deposits (in the Pampean Plain) and Tertiary and Quaternary fluvial and aeolian sediments (in the Chaco Plain). Robles county is located in the alluvial cone of the Dulce River consisting of loess (aeolian), and gravel, silt, sand and clay (alluvial) deposits. In the shallow aquifers, more than 48% of the 63 studied wells show As at toxic levels (maximum 4.8 mg l^{-1}), while in the deep groundwater the concentration is below 0.05 mg l^{-1}. The pH of the shallow groundwaters range between 6.5 and 9 and generally have high electrical conductivity with mean values of 2072 and 1693 µS/cm^{-1} in the years 1998 and 1999, respectively. Arsenic concentrations are high in the alkaline Na–HCO$_3$ type groundwaters, where As correlates positively with Na$^+$ and HCO$_3^-$. Moreover, As correlates positively with Mo, U, and V, while a negative correlation was observed with Ca^{2+} and Mg^{2+}. The potential sources of groundwater As are: (i) layers of volcanic ash with 90% of rhyolitic glass; (ii) volcanic glass dispersed in the sediments; and (iii) clastic sediments of metamorphic and igneous origin. Great lateral variability in the concentration of groundwater As is caused by several hydrogeological and hydrogeochemical factors.
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1. Introduction

In Argentina, at least 1.2 million people, predominantly from rural areas depend on groundwater whose As concentration exceeds 0.05 mg l^{-1} (Martin, 1999; Bundschuh et al., 2000). The most affected areas are extended parts of the Chaco-Pampean Plain (Fig. 1a and b) where nearly 18% of the inhabitants have unsatisfied basic necessities (INDEC, 1994; CEPA, 1993). In general, poverty is much higher in the plains of the Chaco region as compared to the Pampean plain (Fig. 1c). About 17% of the total population lives in rural communities with less than 2000 inhabitants, while nearly 12% live in dispersed settlements with less than 50 inhabitants (Bundschuh et al., 2000; Fig. 1d). The shallow aquifers with high As concentrations are the only affordable drinking water resource available during the whole year for most of the rural population.

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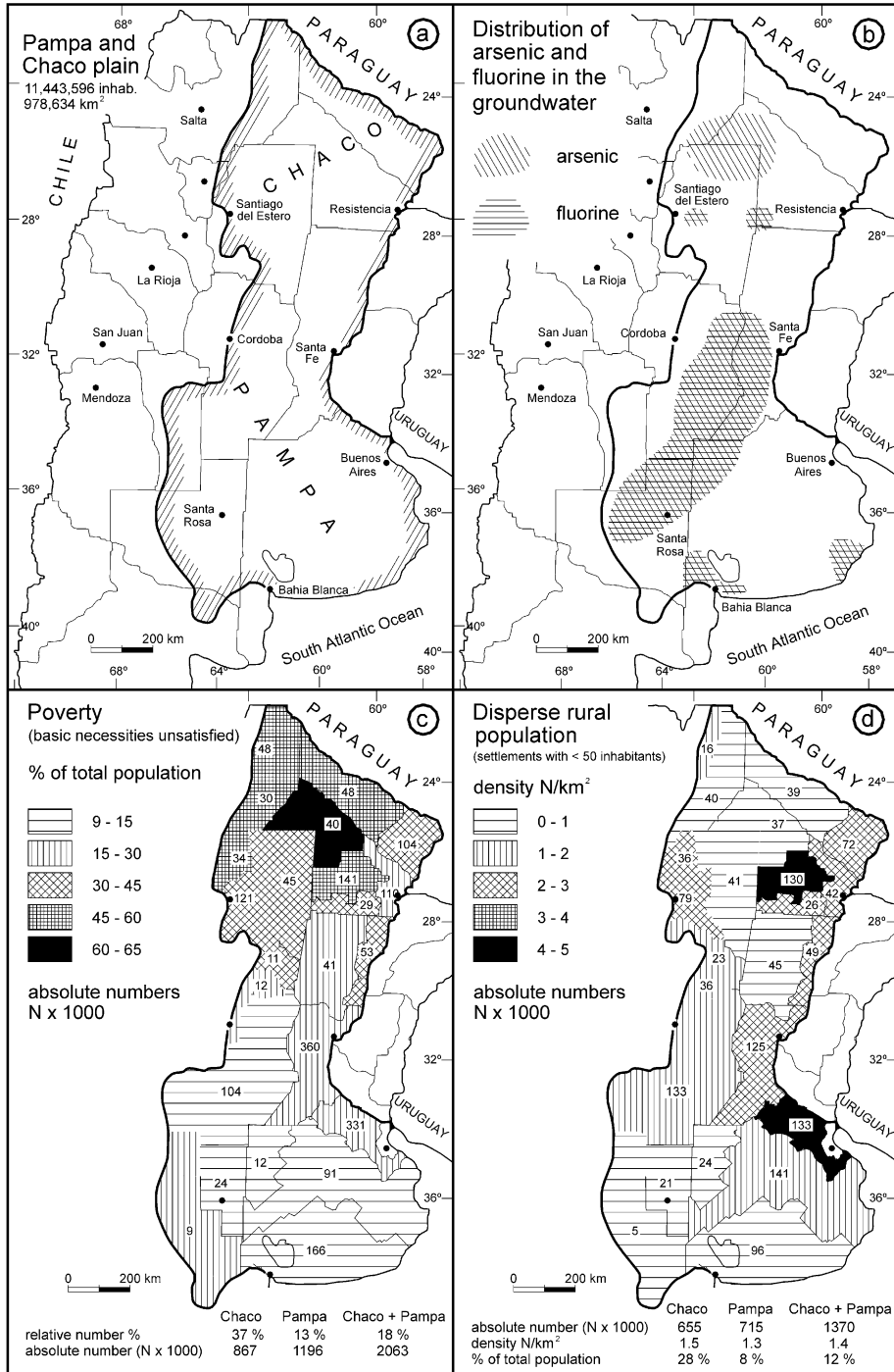*E-mail address:* jochenbundschuh@yahoo.com
(J. Bundschuh).

Fig. 1. Map of Argentina showing: (a) limits of the Pampa and the Argentinian part of the Chaco plain; (b) areas with occurrences of groundwater with high concentrations of As and F; (c) status of poverty represented as a function of unsatisfied basic necessities; and (d) density and absolute numbers of the dispersed rural population. Both (c) and (d) were compiled using statistical data from CEPA (1993) and INDEC (1994).

The sedimentary aquifers consist of Tertiary aeolian loess-type deposits in the Pampean plain and of predominantly fluvial sediments of Tertiary and Quaternary age in the plains of the Chaco region. Loess-type sediments in Chaco-Pampean plain contain 10–25% volcanic ash in dispersed form, while additionally in the Chaco plain volcanic ash beds are intercalated with the predominantly fluvial sediments. It is considered that the volcanic ash, which contains over 90% rhyolitic glass has As concentrations in the range 6–10 mg kg^{-1} (Rossi, 1996; Nicolli et al., 1989; Castro et al., 1998; DYMAS, 1975; Smedley et al., 1998). According to Henriquez (1978), loess originated not only from the andesites and basalts of the Andes, but also from the rocks of the peri-Pampean mountains consisting of Precambrian crystalline rocks (gneiss with intercalations of crystalline limestones and amphibolites and mica schists and phyllites) and huge masses of plutonic rocks, mainly granites, which act as additional sources for As in groundwater. Since loess and volcanic glass have similar concentrations of As, there are some ambiguities concerning the source of As in groundwater of the Chaco-Pampean aquifers.

First symptoms of chronic endemic regional hydro-arsenicism were detected among the rural population in the counties of Robles and La Banda of Santiago del Estero province during 1983. Although water from the Dulce River is widely used for irrigation in the region, due to contamination this surface water source is unsuitable for drinking. Consequently, the rural population in the region use shallow groundwater for drinking purposes. Monitoring of groundwater by the provincial government in 1984 indicated great irregular spatial variability in As concentration. Within extended zones, As concentrations exceeded 0.4 mg l^{-1}, about 8 and 40 times higher than the permissible limits of As in drinking water in Argentina (0.05 mg l^{-1}; Fiorentino et al., 1998; CAA, 1994) and the WHO guideline value (0.01 mg l^{-1}; WHO, 1999) respectively. In the following period only groundwater level changes were monitored within the irrigated area and no further actions and investigations were undertaken. The As concentration was however below the national limit in the deeper groundwater of the area.

The present study was carried out during 1998–1999, with the aim of investigating the possible sources of As in groundwater in the county of Robles, and to explain the possible reasons for its lateral variability. Attempts were made to correlate the distribution of As in groundwater with other hydrogeological and hydrogeochemical parameters together with the sedimentological and mineralogical characteristics of the unsaturated zone.

2. Location and geology

The area of the present study covers approximately 200 km^2, located within the alluvial basin of the Dulce river (2000 km^2) in the county of Robles, about 40 km SE of the city of Santiago del Estero (Fig. 2). The climate is characterised by hot rainy summers (November–March) and cold dry winters (April–October). The average annual precipitation (1938–1990) amounts to 532 mm (maximum 1072, minimum 260 mm) measured at the National Institute for Agriculture (INTA) climate station at La Banda. The area is intensively used for agriculture with numerous small sized irrigated farms.

The alluvial basin is limited to the west by the Huyamampa fault. A sequence of 30 m Pampean loess of Pleistocene age is found to the west of this fault comprising dispersed volcanic ash and calcareous crusts. It is underlain by a sequence of lower Pliocene and green Miocene clays with a total thickness of 70 m. Holocene to recent sediments of the Dulce river basin (Post-Pampean formation) occur to the east of the fault. These fluvial and aeolian sediments comprise alternating layers of gravel, sand, silt and clay and exhibit discordance with the underlying Pliocene sediments. The coarser sediments represent the deposits of the palaeo-channels of the Dulce river system. The thickness of this alluvial fill is nearly 150 m at the fault margin and pinches out about 50 km towards the east. The post-Pampean loess caps the entire alluvial basin.

3. Materials and methods

The topographic height of the piezometers (Fig. 3a), were determined by GPS during 1998 and 1999, and the depth to the groundwater table was determined (one measurement each series). Groundwater samples were collected during the dry season in May and August 1998 from 63 shallow wells equipped with hand pumps (Fig. 3b). These wells correspond to the previous sampling locations for the Arsenic Monitoring Programme during 1984 where only the As concentration and the electrical conductivity (EC) were determined. Additionally water samples were taken from 8 deeper wells. The pH and EC were measured in the field using Luton-pH-2062, and Altronix CT-1 instruments, respectively. Two sets of samples were collected from each sites: (i) filtered using a Sartorius 0.45 μm online filter for anion analyses; and (ii) filtered and acidified samples with 0.2% (2 mL l^{-1}) of concentrated ultrapure HNO_3 for major cations and As (1998 series). Fluoride was analysed in 30 samples. Sampling of groundwater was repeated for 28 sites during July 1999 (dry season) for the wells that indicated high As concentrations during the 1984 investigations. Samples were preserved with acetic acid for the determination of major cations and trace elements including As. Analyses were performed on a Perkin Elmer ELAN 6000 ICP-MS at the Activation Laboratories Limited (Actlabs), Ontario in Canada. Silicon was analysed at Actlabs by a Perkin Elmer Optima 3000 ICP-OES instrument.
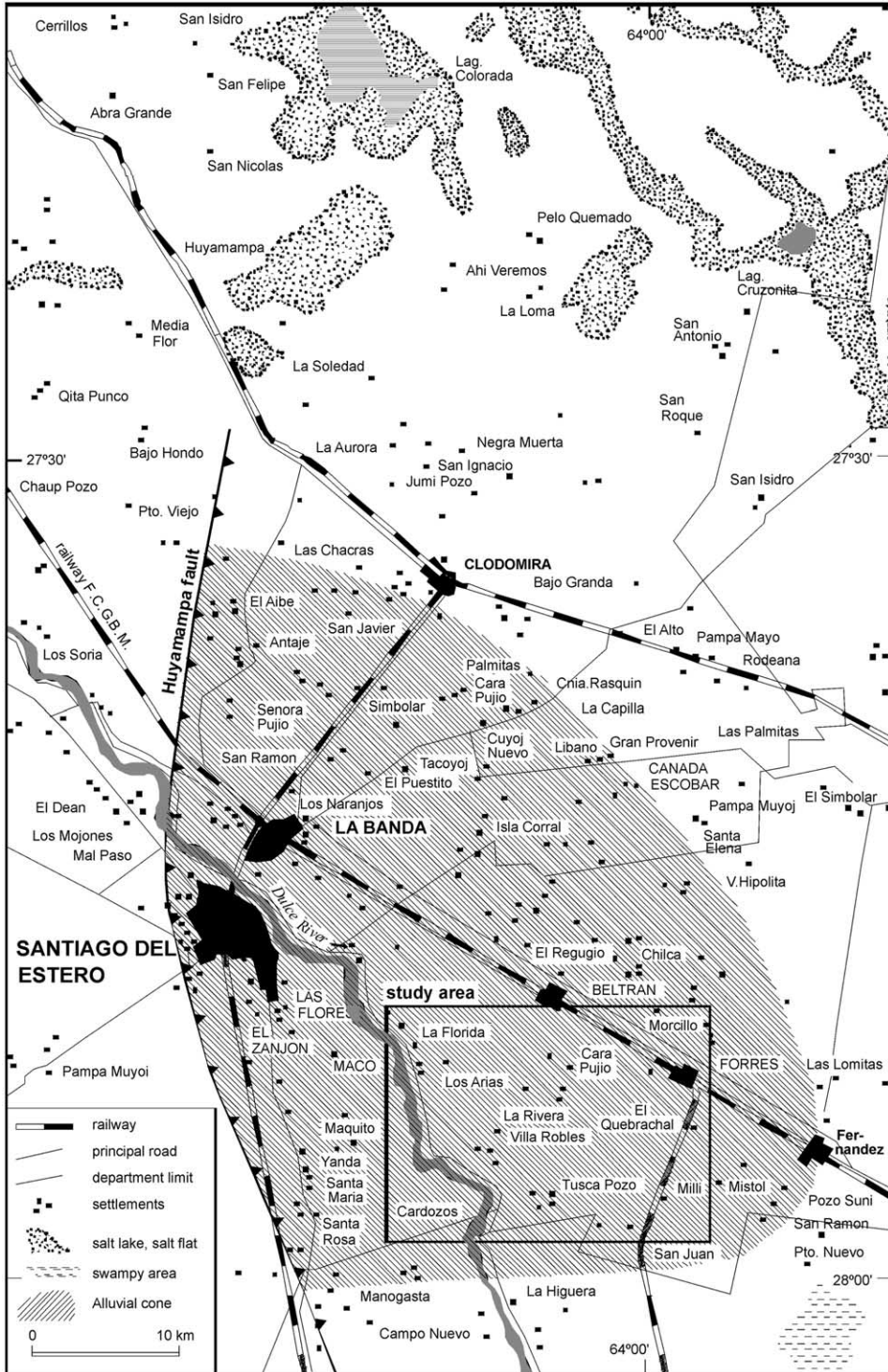
Fig. 2. Map of the Santiago del Estero province showing the geological and geomorphological characteristics and location of the area of the present study in Robles county.

Sediment samples were collected from 24 sites in the unsaturated zone. At each site 10–12 samples were taken at different depths. Piezometers (P1-P24) were pre-installed for groundwater level monitoring at each of the selected sites (Fig. 3a). All sediment samples were analysed by sieving and pipetting to determine their grain size distribution. The mineralogical composition of the sand fraction was determined by thin section petrography. For selected representative samples, the light and heavy mineral fractions were separated and the subsamples were studied by petrographic microscopy, using a minimum of 500 grains of each subsample. Samples from the volcanic ash layer were analysed for their textural characteristics while the mineralogical composition of the layer was determined by microscopy for the fraction between 0.05 and 0.2 mm. One representative sample of volcanic ash was analysed at Actlabs, Canada for major and trace elements following lithium metaborate/tetraborate fusion and subsequent

digestion in weak HNO_3 solution by ICP-MS (Actlabs, 2002).

4. Results

4.1. Characterisation of the unsaturated zone

The unsaturated zone with a thickness of 1–6 m, comprises terrigeneous fine clastic eolian and fluviatile sediments, represented predominantly by silt and fine sand fractions. A layer of volcanic ash is present in a major part of the area, which is considered as a possible source of As and other trace elements in groundwater.

4.1.1. Sand fraction

The grain size of the sand ranges generally between 0.124 and 0.061 mm (fine sand). Coarser sand was found towards the east, in the zone of the palaeo-meander segments of the river (P6 and P7). The mineralogical composition of the sand fraction (Table 1) indicated abundance of micas, mostly biotite and muscovite. Biotite showed a low grade of alteration, whereas heavy minerals such as hornblende and hypersthene indicated a high grade of alteration. The most important light minerals were quartz and plagioclase, predominantly albite and oligoclase.

Amorphous volcanic ash was found in significant amounts ($\sim25\%$). From the mineralogical composition a mesobasic origin can be concluded for the sand fraction. Lithic fragments of metamorphic rocks and to a lesser extent of acid plutonics were identified in the coarse sand fractions in specific layers of the sediments of the palaeochannels.
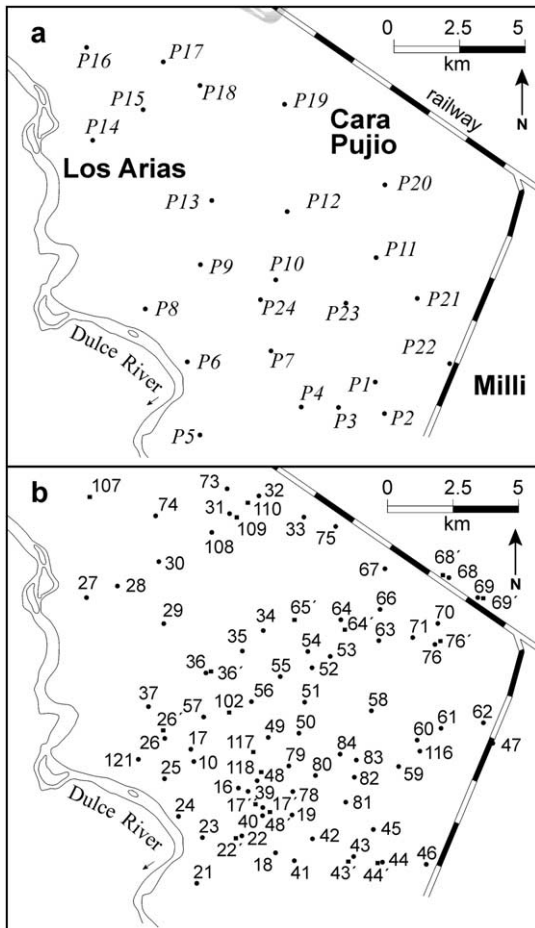

Fig. 3. Map of the study area in Robles county, Santiago del Estero with the locations of: (a) sediment sampling and piezometers (P1-P24); and (b) groundwater sampling (all years).

Table 1
Mineralogical composition of the sand fraction of the sediment

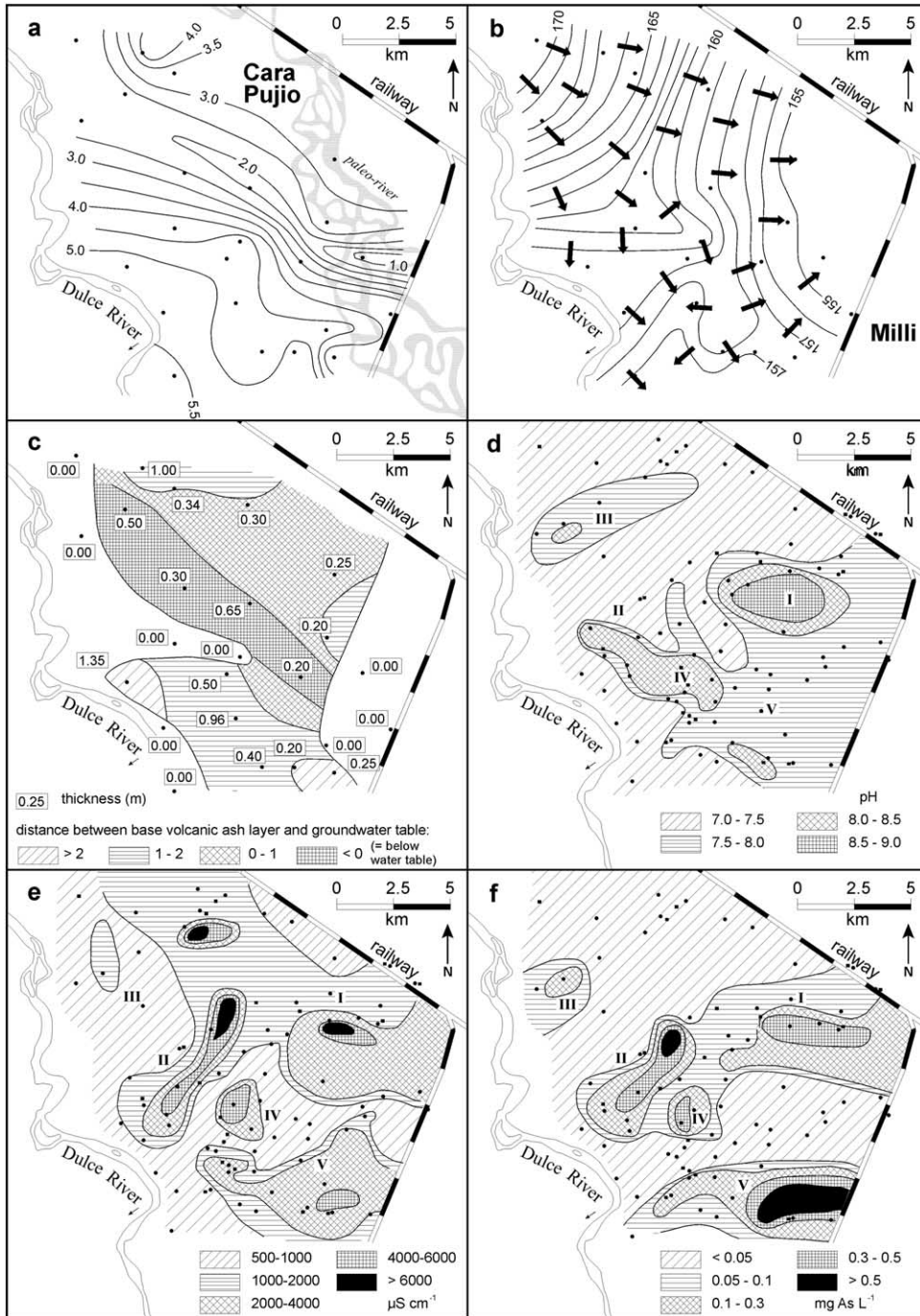| Mineral	%
Opaque matter	1.0
Hornblende	2.0
Augite	0.3
Biotite	4.2
Muscovite	2.8
Diopside	0.3
Hypersthene	1.3
Chlorite	0.7
Zircon	–
Garnet	0.2
Tourmaline	0.5
Rutile	–
Orthoclase	5.6
Quartz	34.9
Plagioclase	19.4
Glass	25.1
Lithic fragments	0.9

Fig. 4. Geological, hydrogeological and hydrochemical characterisatics of the study area in Robles county, Santiago del Estero. (a) depth to groundwater table (m); (b) groundwater level contour lines (m above mean sea level); (c) thickness of volcanic ash layer (m) and the distance between the base of the volcanic ash layer and groundwater table; (d) groundwater pH variation; (e) variation of electrical conductivity; and (f) distribution of As in groundwater.

4.1.2. Volcanic ash layer

The volcanic ash layer was detected in 14 out of 24 sampling sites (P1 to P24) corresponding to 53% of the studied profiles. The spatial distribution of the volcanic ash is plotted in Fig. 4c. The maximum thickness of the volcanic ash layer, 1.35 m, is in the proximity of the Dulce River, while the mean thickness is 0.53 m. The volcanic ash layer was found to dwindle away towards the west and east. The reason for this thinning could be due to the erosion of the ash layer by the Dulce River in the west and by its palaeochannels in the east. However, it is possible that the volcanic ash layer may be located entirely in the saturated zone where the sediments were not investigated and hence remained undetected.

Most of the volcanic ash is isotropic volcanic glass (refractive index from 1.50 to 1.52). Effects of devitrification are widely observed, along with weathering which results in the formation of different clay minerals. However, these clay minerals were not identified during this study. The predominant mineralogy of the volcanic ash was quartz and orthoclase along with smaller amounts hornblende, hypersthene, augite, epidote and zircon. Iron oxides were found as coatings on the grains. Grain size distribution curves show a maximum in the coarse silt fraction. The grain size analysis of the volcanic ash samples (Table 2) reveals predominant silt-sized detritus along with subordinate clay and fine sand.

Geochemical analysis of the volcanic ash sample (Table 3) indicates a composition similar to pyroclastic acid eruption of rhyolitic to rhyodacitic magma as the source of the volcanic ash deposits. Among the trace elements Ba (139 mg kg^{-1}) and Zr (106 mg kg^{-1}) revealed remarkably high concentrations. The most important heavy elements were V (21 mg kg^{-1}), U (20 mg kg^{-1}), As (6 mg kg^{-1}) and Mo (3 mg kg^{-1}).

4.2. Hydrogeology

Fig. 4a shows that in most of the area the depth of the water table ranges between 2 and 5 m. Together with the topographic heights of the groundwater levels in the piezometers, these data were used to construct a contour map of the groundwater table and to determine the

Table 2
Grain size analysis of the volcanic ash samples

	Textural attributes		
	Fine sand 0.063 mm	Coarse silt 0.02 mm	Middle silt fine silt clay
Sample number 0.1 mm 0.061 mm	0.053 mm		
	%	%	%
2	9	54	37
3	25	28	47
4	14	52	34
7	30	45	25
	22	43	33
11	16	52	32
12	19	55	26
	19	58	23
13	20	45	35
15	19	47	34
	19	42	38
17	30	34	35
	28	38	33
18	25	39	35
19	21	47	31
20	28	44	27
23	30	37	33
24	26	39	33
	27	37	35
Mean	20	42	26

Table 3
Major and trace element distribution in the volcanic ash layer

Major elements	Wt.%	Trace elements	mg kg^{-1}	Trace elements	mg kg^{-1}	Trace elements	mg kg^{-1}
SiO_2	70.05	Ba	139	Sn	3.0	Tm	0.38
Al_2O_3	13.33	Co	3	Sb	1.8	Yb	2.6
Fe_2O_3[a]	1.54	Ni	bdl	Cs	26.8	Lu	0.39
MnO	0.09	Cu	bdl	La	24.0	Hf	3.9
MgO	0.56	Zn	39	Ce	48.0	Ta	4.6
CaO	0.91	Ga	20	Pr	4.9	W	5.9
Na_2O	3.25	Ge	2	Nd	17.7	Ti	1.4
K_2O	5.11	Rb	335	Sm	3.7	Pb	27
TiO_2	0.191	Sr	60	Eu	0.4	Bi	1.1
P_2O_5	0.07	Y	21	Gd	3.1	Th	27.8
LOI	3.94	Zr	106	Tb	0.6	V	21
		Nb	38	Dy	3.2	U	20
		Ag	bdl	Ho	0.7	As	6
				Er	2.1	Mo	3

[a] Total Fe as Fe_2O_3.; LOI: Loss on Ignition; bdl: below detection limit.

groundwater flow field (Fig. 4b). The hydraulic gradient decreases from an average value of 0.0013 in the northern and north-western part of the study area to 0.0004 in the central and southern part. No data on the hydraulic conductivity is available. Based on the grain size characteristics of the aquifers, hydraulic conductivity was calculated using the formula of Hazen to range between 10^{-4} to 10^{-6} m s^{-1}. Groundwater flow velocities were estimated to range between 1.3 and 40 m/a, assuming an effective porosity of 0.1.

4.3. Hydrogeochemistry

Table 4 gives an overview of the ranges of values, their means, maxima, minima and standard derivation (σ). In Fig. 4f, the As concentrations obtained from the sampling series of 1999 are plotted and compared with those from 1998 and 1984. The correlation between various parameters is difficult to interpret due to the inadequate data sets for groundwater composition.

5. Discussion and conclusion

5.1. Lateral variability in the distribution of As in groundwater and correlation with other parameters

Aresnic occurs at toxic levels (>0.05 mg/l) in the groundwaters of shallow aquifers within about 50% of the present study area (Fig. 4f). Both lateral as well as temporal variability is noted for the distribution of As in these shallow groundwaters (Figs. 4f and 5). Lateral variations in the concentrations of As for the 1984, 1998 and 1999 sampling seasons (Fig. 4f), indicated similar high-As zones where concentrations exceeded 0.3 mg l^{-1} (depicted as zones I–V). High-As groundwaters in zones I, II and IV are separated from zones III and V by an intervening zone, where groundwater contains low As (<0.05 mg l^{-1}). Based on the comparisons of the data on As distribution in groundwater and its relationship with other hydrogeochemical and hydrogeological parameters it can be summarised that:

- *Depth to groundwater table (Fig. 4a)*: no relation between the depth to water table, and the groundwater As distribution could be recognised.
- *Groundwater flow pattern (Fig. 4b)*: high concentrations of As were found in zones with low hydraulic gradients, which correspond to low groundwater flow velocities and hence high groundwater residence times.
- *Presence and position of the volcanic ash layer (Fig. 4c):* comparing the occurrence of the high groundwater As zones with the distribution and position of the volcanic ash layer with respect to

the water table shows no dependency. It must be considered also that high concentrations of As were found in areas where no volcanic ash layer was observed. These observations suggest that the volcanic ash layer is not the only source of As in groundwater, but other volcanic ash lenses or volcanic glass dispersed in the sediments be considered.

- *Groundwater pH (Fig. 4d)*: a clear correlation between the distributions of high groundwater As zones and zones with high pH-values exists.
- *Electrical conductivity (Fig. 4e)*: zones with high concentrations of groundwater As correlate with zones of high electrical conductivity, which are due to high Na$^+$ and HCO$_3^-$ concentrations. However, Na–Cl water types persist in zones with salinization.

5.2. Temporal variations of groundwater As concentrations

Although the data set is limited, considerable temporal variability was observed for the concentration of As in 28 wells, which were sampled during 1984, 1998 and 1999 (Fig. 5). Reasons for the variability are manifold and could be related to: (i) local influences of groundwater recharge either by irrigation or rainfall, (ii) inflow of water from the Dulce river into the aquifers, locally; (iii) changing hydrogeochemical conditions which may affect the concentration of dissolved As; and (iv) inaccuracies and use of different analytical methods.

5.3. Correlation of groundwater As with other hydrochemical parameters

The highest As concentration in groundwater is related to alkaline Na–HCO$_3$ type water prevalent in nearly 73% of the investigated wells. This is also indicated by a moderate positive correlation of groundwater As with Na$^+$ ($R = 0.44$; $n = 92$) and HCO$_3^-$ ($R = 0.33$; $n = 65$) and by a moderate negative correlation with Ca^{2+} ($R = 0.36$; $n = 73$) and with less significance with Mg^{2+} ($R = 0.18$; $n = 92$) (Fig. 6). Since Na$^+$ and HCO$_3^-$ are the principal major ions, a positive correlation is found between the As concentration and the electrical conductivity ($R = 0.26$; $n = 92$). However, there are some exceptions in areas with high salinity (characterized by Na–SO$_4$ and Na–Cl type waters). A moderate positive correlation was observed between As and SO$_4^{2-}$ ($R = 0.39$; $n = 65$). However, no correlation was noted between As and Cl$^-$ ($R = 0.06$; $n = 65$).

A positive correlation between pH ($7.0 <$ pH < 9.5) and As ($R = 0.41$; $n = 92$) has been observed for most groundwaters in the investigated region. Similar positive
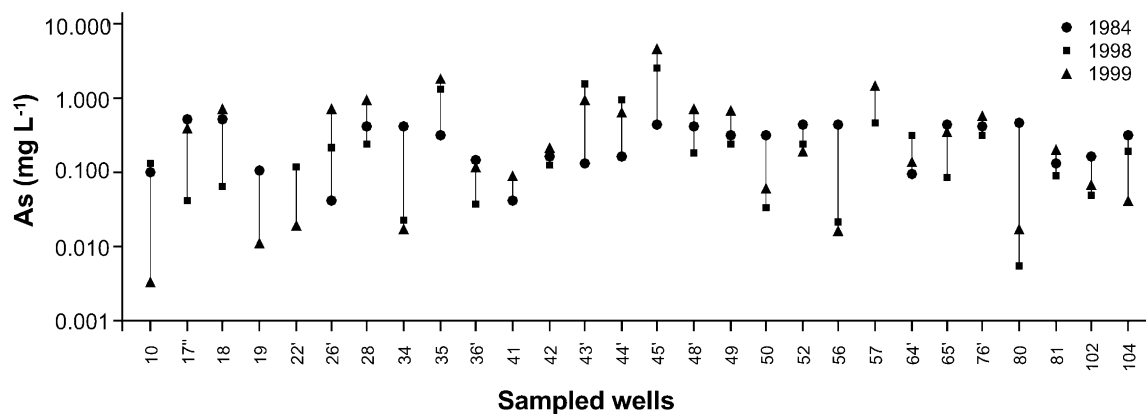
Fig. 5. Comparison of the concentrations of As in groundwater during the years 1984, 1998 and 1999. Refer to Fig. 3b for the reference number of the wells.

Table 4
Results of the analyses of groundwater samples from Robles county collected during the field seasons 1998 and 1999

Parameters/year	1998 ($n = 65$)			Parameters/year	1999 ($n = 27$)		
	Range	Mean	σ		Range	Mean	σ
pH	6.9–8.8	7.63	0.46	pH	6.9–8.6	7.8	0.42
EC ($\mu S\ cm^{-1}$)	650–12285	2072	1948	EC ($\mu S\ cm^{-1}$)	450–3800	1693	932
Ca^{2+} ($mg\ l^{-1}$)	2–149	43.5	33.3	Mg^{2+} ($mg\ l^{-1}$)	0.3–44.3	9.2	10.8
Mg^{2+} ($mg\ l^{-1}$)	1–150	13.1	18.8	Na^+ ($mg\ l^{-1}$)	715–1640	440	390
Na^+ ($mg\ l^{-1}$)	56–1564	373	341	K^+ ($mg\ l^{-1}$)	3.5–26.7	9.2	5.4
HCO_3^- ($mg\ l^{-1}$)	12–1893	540	313	V ($mg\ l^{-1}$)	0.02–3.55	0.42	0.76
SO_4^{2-} ($mg\ l^{-1}$)	19–1368	288	322	Mo ($mg\ l^{-1}$)	0–0.37	0.07	0.89
Cl^- ($mg\ l^{-1}$)	1.3–2716	231	374	U ($mg\ l^{-1}$)	0.002–0.52	0.08	0.1
F^- ($mg\ l^{-1}$)	0.1–4.7	1.43	1.29	Zn ($mg\ l^{-1}$)	0.06–0.54	0.17	0.11
As ($mg\ l^{-1}$)	0.002–2.4	0.17	0.391	As ($mg\ l^{-1}$)	0.01–4.78	0.56	0.93

correlations are also noted between pH and V, Mo, U as well as F levels. This may be explained by the fact that at higher pH, hydroxyl ions compete increasingly for the adsorption sites on Fe and Mn oxides and clay minerals, resulting in a positive correlation of As, V, Mo, U and F concentrations with groundwater pH. The increase in pH may be explained by exchange of cations such as Ca^{2+} and Mg^{2+} for Na^+ on clay minerals coupled with dissolution of carbonates, which occurs with increasing residence time along the groundwater flowpath. This exchange explains the negative correlation between As and Ca^{2+} and Mg^{2+} concentrations as a secondary effect.

Concentrations of Si in groundwater ranged between 19 and 42 l^{-1} (corresponding to 40–90 mg l^{-1} SiO_2). These high levels of Si indicate the presence of a highly soluble source of silica, such as volcanic glass. Since high Si concentrations are also found in groundwater in areas upstream of the zone with a predominant volcanic ash layer, it can be assumed that more lenses of Holocene volcanic ash may be present over a wider area. It is

also possible that the high Si concentrations originate from volcanic glass, which is dispersed in the sandy sediment in the unsaturated zone. A moderate correlation was found between As and Si ($R = 0.49$; $n = 27$). Assuming that As and Si are predominantly mobilized by the dissolution of volcanic ash, concentrations of As, V, Mo, U and F should be uniformly distributed in the groundwaters. In contrast, concentrations of As, and other trace elements such as V, Mo, U and F show a great deal of variability in their concentrations, while the levels of Si are more or less uniform. This indicates that the mobility of As and other trace elements is strongly influenced by the local geochemical environment.

Arsenic shows fairly strong correlation with V ($R = 0.9$; $n = 28$) and Mo ($R = 0.83$; $n = 28$) and fair correlation with U ($R = 0.45$; $n = 28$) (Fig. 7). The relation As:V:Mo:U in the groundwater is 1:0.74:0.31:0.23 (mean values). The corresponding ratio for the volcanic ash was 1:2.8:3.3:0.5. The differences observed in the trace element ratios in groundwater and the volcanic ash
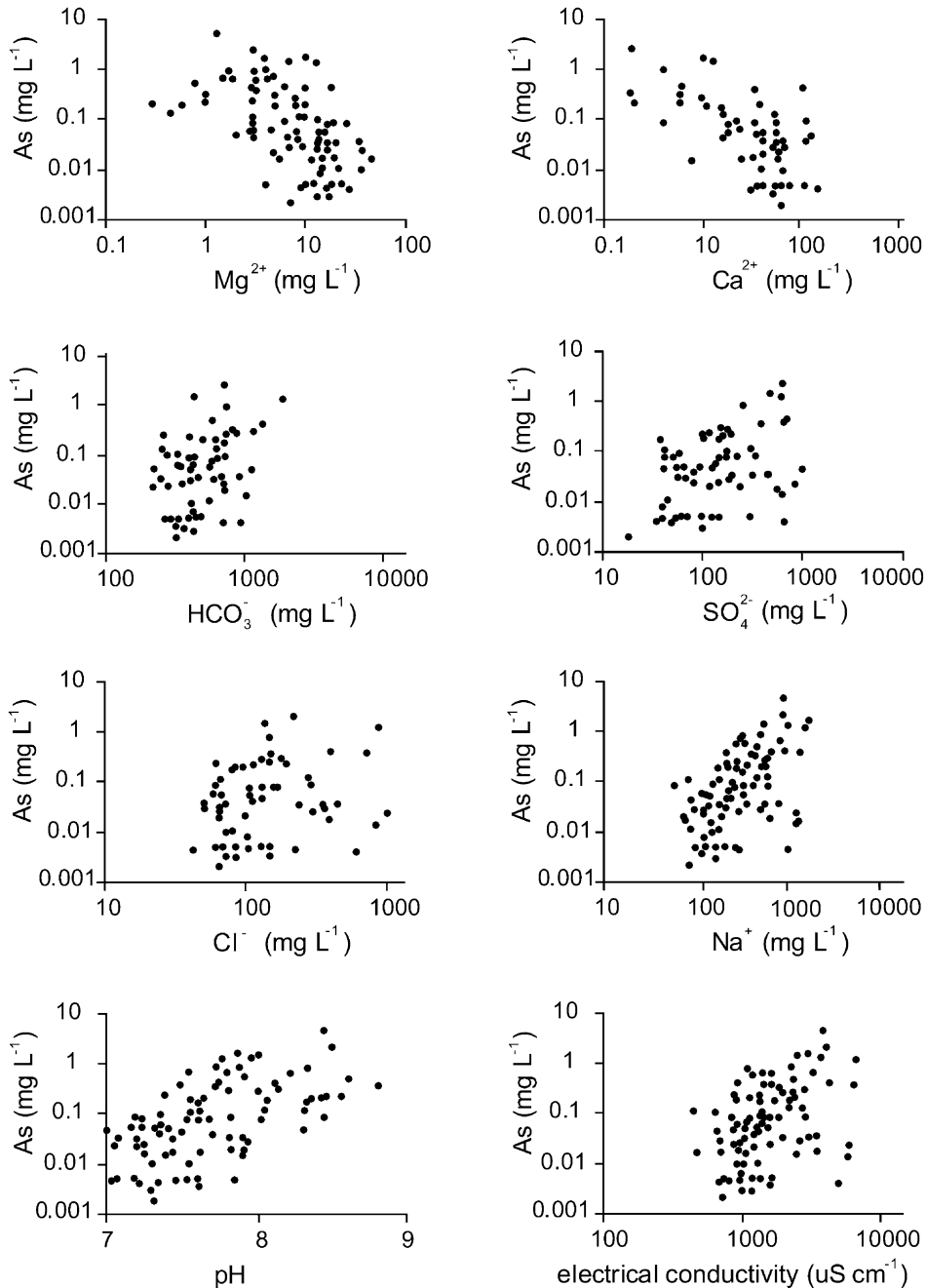
Fig. 6. Relationship of As with major ions, pH and electrical conductivity in shallow groundwaters in Robles county.

sample indicate that the elements V, Mo and U are less mobile than As. Arsenic is 4, 11 and 2 times more mobile than V, Mo and U respectively. Except for a sample with exceptionally high As (1.3 mg l^{-1}), the plot between As and F reveals moderate positive correlation ($n = 29$, $R = 0.32$) for aquifers beneath the volcanic ash layer.

5.4. Mobility controls of As in groundwater

Arsenic may be leached from the volcanic glass and transported into the aquifer:

- Due to infiltration of rain and irrigation water through the unsaturated zone. Assuming an
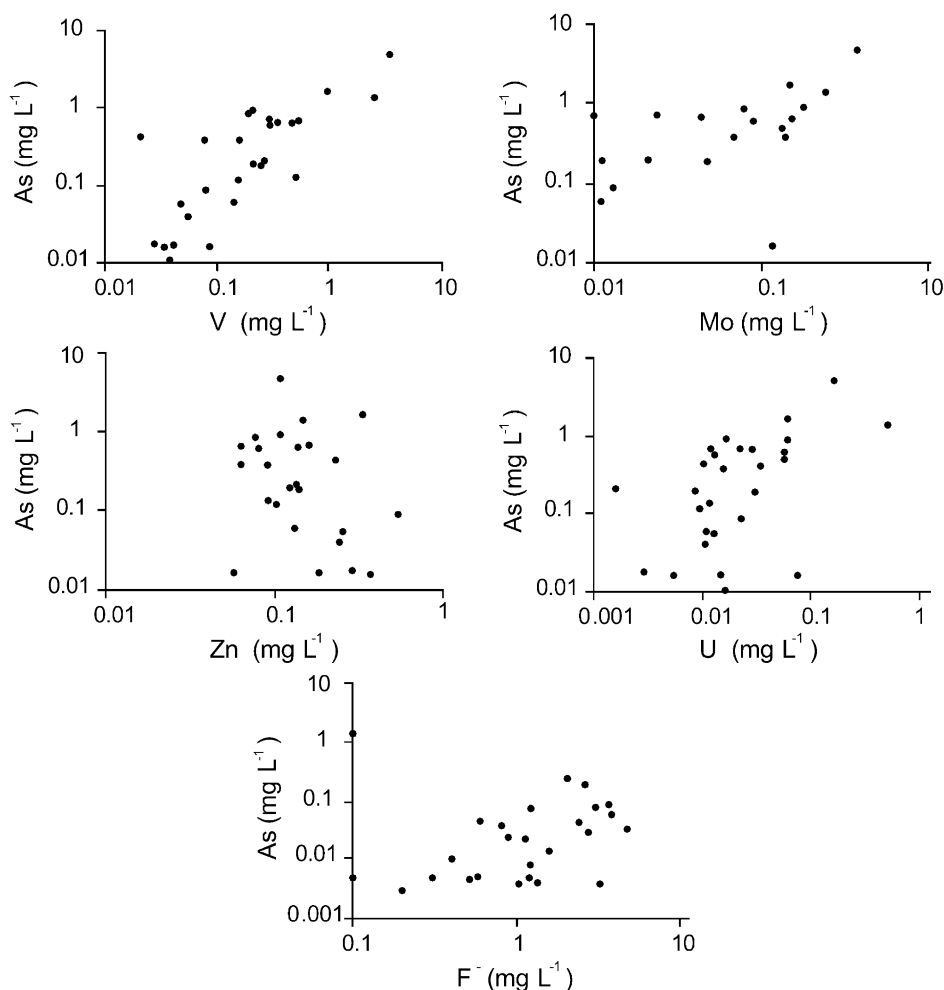
Fig. 7. Relationship between As and other trace elements in groundwater.

average infiltration rate of 0.5 m a^{-1} (Martin, 1999), an average effective porosity of 0.1, and a depth to water table between 3 and 4 m, groundwater recharge time can be estimated to be in the order of 0.6–0.8 a, indicating that the leaching rate may be quite high.

- By groundwater if the volcanic ash layer is at least temporarily located below the groundwater table.
- By capillary fringe movement when water extends up to 0.9–1.0 m in fine sand and up to 1.75–2.0 m in the sandy silt above the groundwater table, and comes into contact with the volcanic ash layer in most of the study area (Fig. 4c).

Under oxidising conditions in the study area, it can be conjectured that most of the As-oxyanions are present as As(V) species, preferably sorbed on e.g. Al, Mn and

Fe oxides. Since no data on the content of dissolved organic C (DOC) exists, it is unknown whether methylation of As occurs. In addition, the concentration of dissolved As may show temporal variability locally, in response to the changes in the hydrogeochemical conditions. Additionally, dissolved As-F complexes may be present in the groundwater (Bundschuh et al., 2000), which needs further study.

Transport and mobility of As and other trace elements, such as V, Mo and F in the shallow groundwaters in Robles county, Santiago del Estero are governed by factors such as: (i) the availability of leachable As in the sediment which depends on its total concentration in the solid phase and especially on its form which determines its leachability; (ii) groundwater recharge; (iii) depth to water table; (iv) groundwater flow pattern/residence time; (v) systems of mineral equilibria and the distribution of aqueous species which are functions of ionic strength, temperature, pH and Eh-value,

pCO_2, pO_2; and (vi) ion exchange and surface complexation/sorption processes (e.g. on clay minerals, Fe and Mn oxides). Sorption processes are more important to govern the mobility of heavy metals, as compared to the mineral equilibria. Mobility of As and other oxyanionic elements in these shallow groundwaters, seem to be controlled by sorption processes, particularly on Al- and Mn-oxides and to a limited extent on Fe-oxides (M. Claesson and J. Fagerberg, pers. comm., 2003).

5.5. Sources of groundwater As

Since deeper groundwaters do not contain As in significant amounts, it is evident that the sources for As are within the uppermost 20 m. Three possible sources for As have been considered:

- The Holocene volcanic ash layer, containing about 6 mg kg^{-1} As, identified in the unsaturated zone within 53% of the study area (Fig. 4c). In the rest of the area, this layer is either eroded or is completely located within the saturated zone.
- The volcanic glass dispersed in the sediments, due to reworked Pleistocene Pampean loess which was identified at different sites in the Chaco-Pampean Plain.
- The sediments derived from metamorphic and acid magmatic rocks.

Since deeper layers of the Quaternary fill do not contain As in significant concentrations, and because these sediments have the same origin (metamorphic and plutonic rocks), it can be concluded that sediments of this origin contribute little or no As to groundwater. It is therefore probable that volcanic glass is the principal source of As, V, Mo, U and F in the shallow groundwaters of Robles county. Since no geochemical information is available on the volcanic glass present in the fine sand and silt sediments of the unsaturated zone, it cannot be ascertained whether and to what extent this glass contributes to the concentrations of As, V, Mo, U and F in groundwater. Further studies are currently in progress to understand the factors that govern the spatial variation and mobilization of As in groundwater and to identify the aquifers that would yield water for safe drinking in the affected regions.

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