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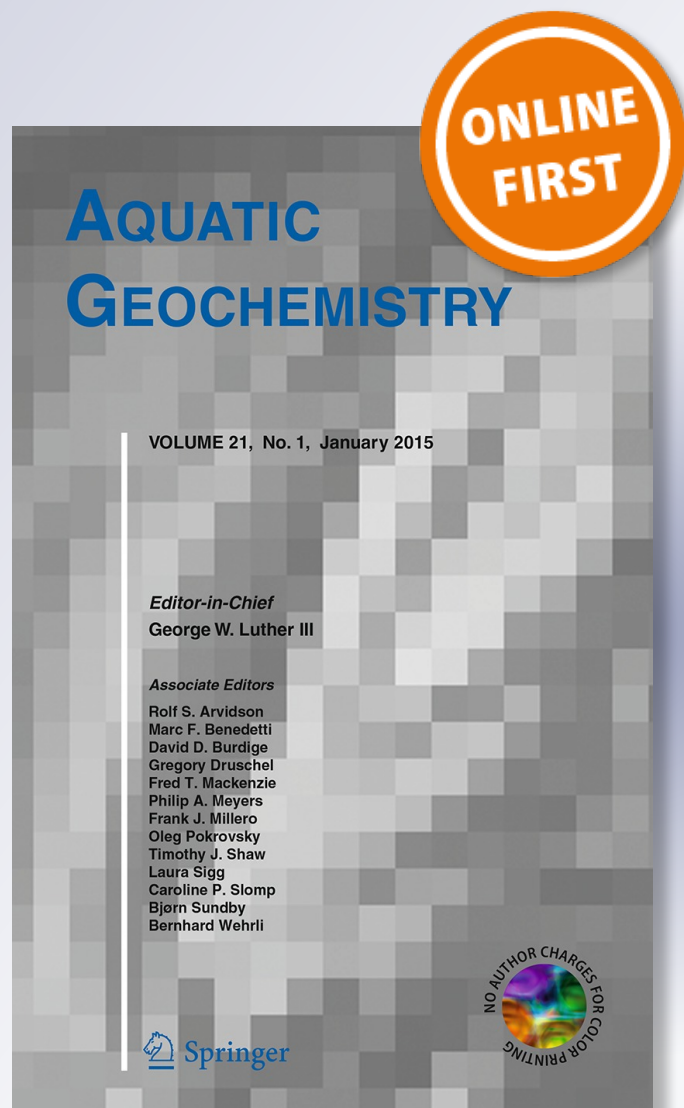
Virginia Puccia, Fabiana Limbozzi & Marcelo Avena

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Arsenic in Porewaters of the Unsaturated Zone of an Argentinean Watershed: Adsorption and Competition with Carbonate as Important Processes that Regulate its Concentration

Virginia Puccia¹ · Fabiana Limbozzi² ·
Marcelo Avena¹

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Abstract The arsenic (As) concentration in porewaters of the unsaturated (vadose) zone of a watershed located in the Chaco-Pampean Plain of Argentina was investigated. A water displacement method using carbon tetrachloride was applied to the sediments in order to obtain the water samples, which could not be obtained by a simple high-speed centrifugation method. The CD-MUSIC surface complexation model was applied to calculate arsenate adsorption on sediments, arsenate concentration in porewaters in contact with the sediments and effects of carbonate. Ferrihydrite was considered to represent the active adsorbing material in the sediments. Therefore, proton adsorption (surface charge) data and arsenate adsorption isotherms obtained with a synthetic ferrihydrite were used to calibrate the CD-MUSIC model. Arsenate and carbonate concentrations in the studied porewaters were positively correlated. The model was able to predict As concentration within a factor of two in most samples. Carbonate affects As concentration by competing with arsenate species for adsorption sites on the mineral surface. As it occurs with groundwater samples of the saturated zone in many aquifers, this article shows for the first time that adsorption–desorption processes also seem to control As concentration in oxic porewaters of the unsaturated zone.

Keywords Arsenate · Aquifer · Surface complexation model · Arsenic control · Vadose zone

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✉ Marcelo Avena
mavena@uns.edu.ar

¹ Departamento de Química, INQUISUR-CONICET, Universidad Nacional del Sur, Av. Alem 1253, 8000 Bahía Blanca, Argentina

² Departamento de Ciencias Agronómicas, CERZOS-CONICET, Universidad Nacional del Sur, Bahía Blanca, Argentina

1 Introduction

Occurrence, origin and mobility of arsenic (As) in groundwater are topics that have received much attention in the last decades, as a consequence of the health problems associated with consumption of As-containing water. Despite the large number of investigations that have been conducted thus far, the mechanisms controlling the concentration of As in groundwater in many regions of our planet are not yet well established. Several theories have been proposed to explain the As concentration in groundwater, and it is now well accepted that there is no a single mechanism or process that controls it. Each geographic region has its own particular characteristics regarding source of As, chemical and mineralogical composition of sediments, hydrological properties, temperature, the presence of oxidizing or reducing environments, etc., and thus, the controlling mechanism may vary from one region to other. For example, it is known that mining areas of high sulfide content generally have high As concentrations in groundwater as a result of oxidation and subsequent dissolution of As-containing sulfide minerals after coming in contact with oxidizing environments (Smedley and Kinniburgh 2002). Geothermal environments are also known to have high As concentrations (Nimick et al. 1998; Robinson et al. 1995; McLaren and Kim 1995). Since thermal waters are normally under reducing conditions at great depths, high As concentrations in most geothermal environments are the consequence of reductive dissolution of minerals (such as iron oxides) that release their arsenic contents into water (Hammarlund and Piñones 2009). There are also regions with high As contents that are not associated with mining processes or geothermal activity. If sediments are subject to reducing conditions, As occurrence in groundwater is normally due to reductive dissolution of Fe (oxy)hydroxides (Nickson et al. 2000); if they are subject to oxidizing conditions, where Fe (oxy)hydroxides do not dissolve appreciably, the control of As concentration is usually attributed to adsorption–desorption processes on mineral surfaces (Stachowicz et al. 2007; Biswas et al. 2014). In cases where the environment is not iron rich, but other metal cations (e.g., Ca^{2+} , Mg^{2+} , Pb^{2+}) are present in sufficiently high concentrations, the formation of the corresponding arsenate salt will form and control As concentration. Martínez-Villegas et al. (2013), for example, have shown that the precipitation of calcium arsenates controls the As mobility in a contaminated soil of Mexico.

As reviewed by Smedley and Kinniburgh (2002), the Chaco-Pampean Plain of central Argentina constitutes perhaps one of the largest regions of high As groundwaters known, covering around 10^6 km^2 . The As concentration in groundwaters ranges from $<1 \mu\text{g L}^{-1}$ to values as high as $5300 \mu\text{g L}^{-1}$ ($7500 \mu\text{g L}^{-1}$ in some groundwaters), with predominantly oxidizing conditions and neutral to alkaline pH. Sediments of the region are Quaternary deposits of loess, containing a significant amount of calcium carbonate in the form of calcretes. The characteristics of the sediments, groundwaters and redox conditions of the region have led Smedley et al. (2002) to suggest that As concentration in groundwaters is controlled by adsorption–desorption processes. Indeed, in a later study, Smedley et al. (2005) analyzed the chemical composition of water and sediments from the saturated zone of a loess aquifer in the province of La Pampa, Argentina, which is part of the Chaco-Pampean Plain, and concluded that high As concentrations in groundwaters are mainly due to the weak binding of As to the sediments. They gave good evidences to support the hypothesis that this weak binding is a consequence of high pHs and relatively high concentrations of As competitors, which suppress As adsorption. The need to carry out further investigations into this weakly bound As was also highlighted (Smedley et al. 2005).

A helpful approach to gain insights into the behavior of natural systems is to explore adsorption processes using surface complexation models. With these models, adsorption at the mineral surface is considered to be in equilibrium and thus the concentration of different adsorbing species can be calculated and compared to experimental data in order to draw conclusions about the system. Most of the investigations conducted with surface complexation models were applied to laboratory experiments using synthetic solids as adsorbents. The synthetic solids are usually ferrihydrite or goethite, which are some of the most reactive minerals in soils and sediments regarding As adsorption (Stachowicz et al. 2007; Hiemstra and Van Riemsdijk 2009). Working with synthetic solids has produced very important information about the processes that control the partitioning of As between the solid and solution phases. It is now clear from these models that As adsorption on ferrihydrite, goethite and other oxides is influenced by the presence and concentration of competing ions for adsorption sites (Stollenwerk 2002). High concentrations of competing anions such as carbonate or phosphate inhibit As adsorption increasing its concentration in solution (Appelo et al. 2002; Charlet et al. 2007; Stachowicz et al. 2007). This competition can explain, at least qualitatively, the positive correlation between As and carbonate concentrations that is often found in groundwaters (Anawar et al. 2004; Frau et al. 2008). There are also some publications where surface complexation models were applied directly to natural systems. Stollenwerk et al. (2007), for example, used the diffuse layer surface complexation model (Dzombak and Morel 1990) to describe As(III) and As(V) concentrations in groundwaters of Dhaka, Bangladesh. The model was able to simulate As adsorption by oxidized sediments in the presence of competing anions, such as phosphate, bicarbonate and silicate. Postma et al. (2007) could predict dissolved and adsorbed As contents in anoxic groundwaters and sediments of a flood plain near Hanoi, Vietnam, with the same type of model. They found that only 3 % of As, which was mostly As(III), occupied adsorption sites, while the remainder were occupied by competing anions, mainly carbonate and silicate species. Smedley et al. (2005) used also the diffuse layer surface complexation model to calculate distribution coefficients (K_d) of As in the presence and the absence of competitors and could observe low K_d values (weak binding) in the second case. More recently, Biswas et al. (2014) explored the ability of two different surface complexation models, the mentioned diffuse layer model and the 3-plane CD-MUSIC model (Hiemstra and van Riemsdijk 1996, 2006), to describe As adsorption and competition on groundwaters and sediments of the Bengal Basin. They found that reductive dissolution of Fe oxyhydroxides and competitive adsorption reactions are responsible for As enrichment in groundwaters.

As far as we know, in all cases where surface complexation models were applied to investigate As adsorption–desorption processes in groundwater, samples were obtained from the saturated zone. There is no information on the adsorption–desorption processes in porewaters belonging to the unsaturated zone. This water is in intimate contact with the surface of mineral particles in sediments, and thus, dissolved species can be considered in equilibrium with adsorbed species, allowing the use of surface complexation models to analyze factors that may control As concentration.

The aim of this paper is to investigate the As concentrations in porewaters from the unsaturated zone of the watershed of the Napostá Grande Brook, which is part of the Chaco-Pampean Plain of Argentina. A surface complexation model is applied to describe As concentrations and to investigate the effects of carbonate on these concentrations. Since many regions around the world can have similar characteristic to the studied watershed, the results could be qualitatively extrapolated to explain the behavior of loessic sediments not only in Argentina but also in other places of our planet.

2 Materials and Methods

2.1 Study Area and Samples

The study area is the watershed of the Napostá Grande Brook, located in the province of Buenos Aires, Argentina (Fig. 1). The brook flows along 105 km from the hills of Sierra de la Ventana (Sistema Ventania) to the Estuary of Bahía Blanca. The morphology of the watershed is typical of a plain environment with a smooth slope toward the south and a total surface of 1237 km². Besides the quartzite outcrops from Paleozoic, the loessic sediments (up to 200 m thick) from the Tertiary and Quaternary periods are the ones outcropping mostly in the study area. The presence of calcretes, as nodules and layers with variable thickness between 0.2 and 3 m, is very characteristic in these sediments (Fig. 1). According to the hydrodynamic conceptual model of the regional phreatic aquifer, the recharge is done with the precipitation surplus in the entire watershed, being the most important sector the hill area. Therefore, the regional circulation scheme considers one preferential area of recharge close to the hills, one circulation area in the plains and a discharge area in the coast.

Sediment samples were collected from ten wells denoted from I to X (Fig. 1) and ordered from the hill area to the coastal area. Samples correspond to subsurface sediments obtained at depths ranging from 3 m below the surface to 4 m above the phreatic level of the saturated zone. They correspond to sediment samples since soils of the region have a depth of <1 m (Bravo et al. 2007). Once in the laboratory, a fraction of the sediment samples was air-dried and conditioned for As quantification in the solid phase, and the remaining fraction was used to obtain porewater samples for chemical analyses. Since water from sediments of the unsaturated zone cannot be easily obtained by high-speed centrifugation as it is done with sediments of the saturated zone (Smedley et al. 2005), the water displacement method by Mubarak and Olsen (1976) had to be applied to our samples. The method comprises the treatment of the sediment with CCl₄ (0.8 L of CCl₄ per kg of sediment) and centrifugation during 90 min, so that water is displaced from pores generating a water layer on top of the centrifugate. Displaced water was gently withdrawn and reserved for the analyses. Water could not be obtained from all studied samples with this method. Sediments usually needed a gravimetric moisture content above 17 % to obtain enough porewater (approximately 30 mL) for analyses. A few special sediments containing around 10 % moisture produced some water and could also be studied.

Chemical analyses of sediment samples were performed by inductively coupled plasma emission spectrometry (ICP/ES) and inductively coupled plasma mass spectrometry (ICP/MS) after LiBO₂ fusion and dissolution with aqua regia. ICP/ES was used for the quantification of Si, Al and Fe, and ICP/MS was used for the quantification of As. For porewater samples, As was quantified by ICP/MS, and carbonate concentrations were obtained from alkalinity measurements. All quantifications were performed at ACTLABS (Activation Laboratories Ltd, Ancaster, ON, Canada).

Although the redox potential (Eh) of the porewaters could not be measured because sediment samples had to be taken to the laboratory in order to apply the water displacement method, measurements to groundwaters of the saturated zone in the sampling sites gave Eh values with an average of 332 mV, indicating oxidizing environments. This is in line with the well-known oxidizing conditions of groundwaters from the Chaco-Pampean Plain of Argentina (Smedley et al. 2002, 2005).

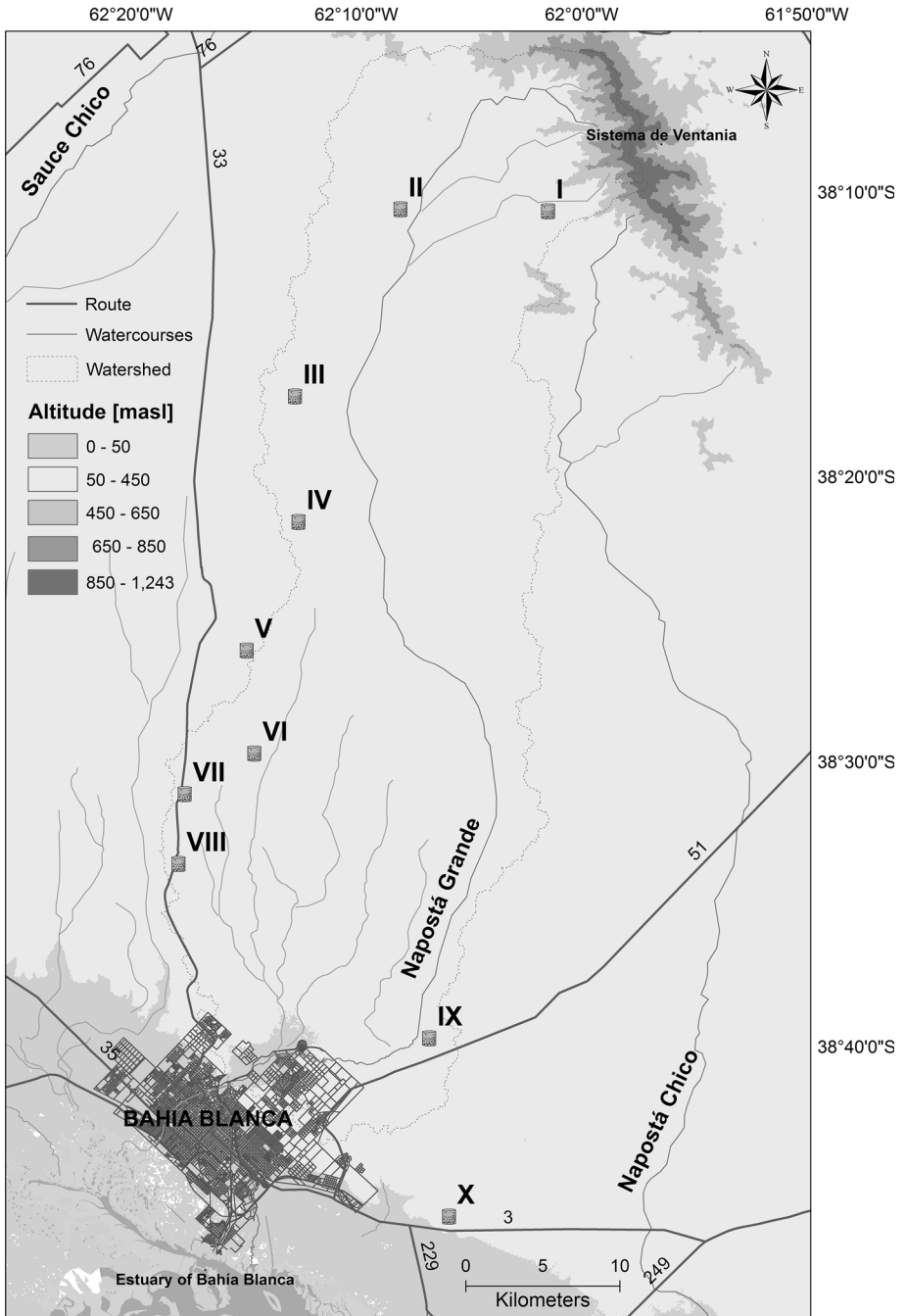


Fig. 1 Map of the watershed showing the different studied wells (roman numerals)

2.2 Synthesis and Characterization of Ferrihydrite

A 2-line ferrihydrite was synthesized following Schwertmann and Cornell (2000). Briefly, a freshly prepared 0.1 M $\text{Fe}(\text{NO}_3)_3$ solution was brought to pH 7.0–8.0 by dropwise addition of a 1 M NaOH solution. The resulting dispersion was aged for 16 h at 20 °C, and then, it was washed with doubly distilled water until the conductivity was lower than $10 \mu\text{Scm}^{-1}$. The product was freeze-dried, and a dry powder was obtained. Powder X-ray diffraction (measured with a Rigaku Geigerflex diffractometer between 20° and 80° 2 θ using CuK_α radiation) showed two broad peaks centered at 0.257 and 0.147 nm, confirming the presence of 2-line ferrihydrite particles (Cornell and Schwertmann 1996). Transmission FTIR spectrum (obtained with a Nexus 470 spectrophotometer) was also typical of 2-line ferrihydrite (Hausner et al. 2009). X-ray diffraction pattern and FTIR spectra are given as Supplementary Material.

Potentiometric titrations were performed to the ferrihydrite sample in order to quantify the surface charge as a function of pH and supporting electrolyte concentration. In total, 50 mL of a ferrihydrite suspension (9.5 g L^{-1}) was adjusted to pH 4 and placed in a cylindrical, water-jacketed reaction vessel covered with a glass cap at 25 °C. Mixing was done with a magnetic stirrer, and carbon dioxide contamination was avoided by bubbling N_2 . The ferrihydrite suspension was titrated up to pH close to 10 by successive additions of 0.1 M KOH and subsequently backtitrated to pH 4 by additions of 0.1 M HNO_3 . The titrations were performed at three ionic strengths: 0.01, 0.1 and 0.5 KNO_3 . Blank titrations were performed to KNO_3 solutions. The method described is similar to that reported by Antelo et al. (2005) to quantify the surface charge of goethite.

2.3 Arsenate Adsorption on Ferrihydrite

Arsenate adsorption isotherms on ferrihydrite were obtained at three different pHs (4.5, 7.0 and 9.5) in 0.1 M KNO_3 and at three different ionic strengths (0.01, 0.1 and 0.5 KNO_3) at pH 7. For each point of the isotherm, the desired volume of a 1.61×10^{-3} M stock arsenate solution in 0.1 M KNO_3 was mixed in a 10-mL polypropylene tube with 0.09 mL of a 9.5 g/L ferrihydrite dispersion and the corresponding volume of 0.1 M KNO_3 so that the final volume was 10 mL. The pH was then adjusted to the desired value by adding HNO_3 or KOH solutions. After 16-h equilibration, the suspension was centrifuged and the supernatant withdrawn to quantify the remaining As(V) in solution using the molybdene blue method by Murphy and Riley (1962). This method was initially developed for phosphate quantification, but it can be also used for arsenate (Lenoble et al. 2003) provided there is no phosphate in the sample. The method is simple, fast and sensitive and uses ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, antimony potassium tartrate, $\text{K}(\text{SbO})\text{C}_4\text{H}_4\text{O}_6\cdot 1/2\text{H}_2\text{O}$, and ascorbic acid in an aqueous acidic (H_2SO_4) media giving a blue-colored arsenomolybdate complex (maximum absorbance: 870 nm) when mixed with As(V) solutions (Lenoble et al. 2003). Absorbance readings were performed with an Agilent 8453 UV–Vis diode-array spectrophotometer equipped with a 1-cm quartz cell.

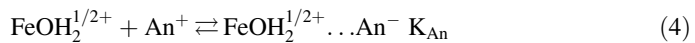
Adsorbed As(V) was calculated from the difference between initial arsenate concentration and final equilibrium concentration in the supernatant. All isotherms were performed at room temperature, and pH was checked and kept constant by adding minimum volumes of concentrated KOH or HNO_3 solutions if necessary.

2.4 Surface Complexation Model

The model used to describe the reactivity of the ferrihydrite surface was the CD-MUSIC model. Calculations were performed with the ECOSAT software, version 4.8 2004 (Keizer and Van Riemsdijk 1998). A full description of the model including different surface reactions and equations that describe the development of charges at the surface and the electric potential drop within the solid–water interface is given in Hiemstra and van Riemsdijk (1996, 2006). Only the adsorption reactions of protons, supporting electrolyte ions, arsenate and carbonate, are given below for a better understanding. In the CD-MUSIC model, it is assumed that singly coordinated ($\text{FeOH}^{1/2-}$) and triply coordinated ($\text{Fe}_3\text{O}^{1/2-}$) groups are the reactive surface groups for proton binding. The proton-binding reactions on these groups are:

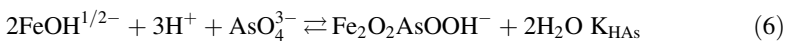
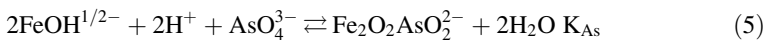


where K_{H1} and K_{H2} are the respective intrinsic equilibrium constants of the previous reactions. The ion-pair-formation reactions between charged surface groups and ions from the supporting electrolyte are:



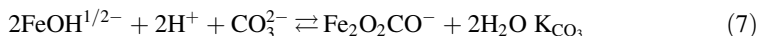
where K_{Cat} and K_{An} are the intrinsic equilibrium constants of the reactions. Two equivalent reactions were also used for ion-pair formation with $\text{Fe}_3\text{O}^{1/2-}$ and $\text{Fe}_3\text{OH}^{1/2+}$ groups.

Arsenic was assumed to be present as As(V) species because of the oxidizing conditions of the studied sediments. Arsenate adsorption reactions are based on EXAFS and IR spectroscopic studies, which suggest that arsenate ions adsorb mainly as bidentate complexes on ferrihydrite (Waychunas et al. 2005; Muller et al. 2010). This is also supported by MO/DFT calculations on adsorbed arsenic species by Kubicki (2005), who concluded that the bidentate configuration is most consistent with spectroscopic data. In addition, a complementary study of arsenate sorption on ferrihydrite, based on differential pair distribution function (d-PDF) analyses of high energy powder X-ray, confirms a bidentate binuclear binding mechanism (Harrington et al. 2010). A different conclusion was obtained by Loring et al. (2009) for arsenate adsorption on goethite. Using a combination of X-ray diffraction, EXAFS and IR spectroscopies, these authors conclude that arsenate coordinates at the goethite–water interface in a predominately monodentate fashion. However, we kept to the bidentate coordination, which is the coordination mode described for the case of ferrihydrite. Therefore, two bidentate surface complexes were considered in the modeling: a protonated bidentate complex and a non-protonated bidentate complex. The reactions leading to the formation of these complexes are, respectively:



where K_{As} and K_{HAs} are the intrinsic constants of the formation of the non-protonated complex and the protonated complex, respectively.

In order to consider effects of carbonate on arsenate adsorption, the following carbonate adsorption reaction was included:



where K_{CO_3} is the intrinsic constant of the reaction, which represents the formation of a bidentate binuclear surface complex. The presence of this complex at the surface was confirmed with MO/DFT calculations and IR spectroscopy (Hiemstra et al. 2004; Bargar et al. 2005).

3 Results and Discussion

3.1 Arsenic Content in the Studied Sediments and Porewaters

Table 1 shows the content of the major components Si, Al and Fe together with the content of As and the humidity of the studied sediments. The values are similar to those found by Smedley et al. (2005) for sediments of other Argentinean provinces belonging to the Chaco-Pampean Plain. Table 1 also shows the pH of the different porewaters, and arsenic and carbonate concentrations. The relationship between the concentration of these two substances is shown in Fig. 2. It is clear that arsenic and carbonate in porewaters are positively correlated. A positive correlation was also reported for the saturated zone of the Bangladesh groundwater system by Anawar et al. (2003), who concluded that the combined effect of the presence of carbonate and high pH is important in the mobilization of arsenic from iron oxides surface and subsurface sediments. The effect of carbonate is generally attributed to the adsorption of its species on mineral surfaces, mainly on iron oxides or other metal oxides, resulting in arsenate desorption (Anawar et al. 2003; Stachowicz et al. 2007). This hypothesis is tested below applying the CD-MUSIC model.

3.2 Ferrihydrite Surface Charge and Arsenate Adsorption

Figure 3 shows the surface charge versus pH curves of ferrihydrite. Curves obtained at different ionic strengths show a common intersection point at pH 8.3. This pH value is the point of zero charge (PZC) of the ferrihydrite sample and is in agreement with the PZC reported by many other authors (Kosmulski 2011a, b). There are some studies that informed a slightly higher value of 8.7 for the PZC (Antelo et al. 2010; Hofmann et al. 2005), which is obtained when all impurities and CO_2 are efficiently removed. The value 8.7 seems to be the most accurate value for the PZC for pure ferrihydrite, free of carbonate and other impurities, whereas the most commonly found value of 8.3 appears to be the result of minimum surface impurities, which are very difficult to remove in experiments. Predictions with the CD-MUSIC model are shown in Fig. 3 with lines, calculated with parameters listed in Table 2. The values of $\text{Log}K_{\text{H1}}$ and $\text{log}K_{\text{H2}}$ were set equal to the PZC (Hiemstra and Van Riemsdijk 1996; Hiemstra et al. 2004), whereas the values of $\text{Log}K_{\text{Cat}} = \text{Log}K_{\text{An}}$, C_1 and C_2 were used as fitting parameters. The surface site density was set to $N_{\text{s,FeOH}} = 6.0 \text{ nm}^{-2}$ for $\text{FeOH}^{1/2-}$ groups and $N_{\text{s,Fe}_3\text{O}} = 1.2 \text{ nm}^{-2}$ for $\text{Fe}_3\text{O}^{1/2-}$ groups (Hiemstra and van Riemsdijk 2009). A specific surface area of $700 \text{ m}^2 \text{ g}^{-1}$ was used, which is a value in the range typically used for ferrihydrite modeling, $650\text{--}750 \text{ m}^2 \text{ g}^{-1}$ (Dzombak and Morel 1990; Hiemstra and Van Riemsdijk 2009; Gustafsson 2001). The good fitting shown in Fig. 3 indicates that the model provides a

Table 1 Content of arsenic and major components in the solid phase and arsenic and total carbonate concentrations in porewaters of the unsaturated zone

Sample	As (mg Kg ⁻¹)	SiO ₂ (%)	Al ₂ O ₃ (%)	Fe ₂ O ₃ (%)	Others (%)	Gravimetric humidity %
<i>Sediments (solid phase)</i>						
I	3.0	59.83	15.77	5.76	18.64	29.20
III 1*	6.0	57.92	15.98	6.26	19.84	27.95
III 2	6.0	58.34	15.68	5.43	20.55	22.61
V	4.6	56.72	15.71	5.87	21.70	27.51
VI	4.3	59.71	16.07	5.77	18.45	24.65
VIII 1	10	54.42	13.49	4.59	27.50	20.11
VIII 2	9.0	59.95	16.06	5.69	18.30	17.54
VIII 3	8.0	58.76	15.62	5.57	20.05	23.33
IX 1	3.7	61.00	15.23	5.01	18.76	19.00
IX 2	6.5	56.59	14.92	5.77	22.72	28.56
X 1	4.8	56.43	13.22	4.14	26.21	10.67
X 2	3.3	65.07	14.91	4.84	15.18	11.40
X 3	6.0	57.46	15.70	6.43	20.41	33.82
Sample	Depth (m)	pH	C _{As} (M)	C _{carbonate} (M)		
<i>Porewater (aqueous phase)</i>						
I	13.3	7.9**	1.47 × 10 ⁻⁷	1.39 × 10 ⁻³		
III 1	11.0	8.3**	4.67 × 10 ⁻⁷	1.86 × 10 ⁻³		
III 2	18.0	8.3**	3.74 × 10 ⁻⁷	1.59 × 10 ⁻³		
V	36.0	8.2	1.95 × 10 ⁻⁶	2.94 × 10 ⁻³		
VI	12.0	8.6	2.54 × 10 ⁻⁶	4.25 × 10 ⁻³		
VIII 1	4.5	8.4	2.39 × 10 ⁻⁶	3.35 × 10 ⁻³		
VIII 2	10.5	8.7	5.01 × 10 ⁻⁶	6.13 × 10 ⁻³		
VIII 3	15.0	8.6	3.20 × 10 ⁻⁶	4.85 × 10 ⁻³		
IX 1	12.0	8.2	2.11 × 10 ⁻⁶	1.99 × 10 ⁻³		
IX 2	20.0	8.1	2.87 × 10 ⁻⁶	2.58 × 10 ⁻³		
X 1	3.0	8.7	2.56 × 10 ⁻⁶	3.55 × 10 ⁻³		
X 2	15.0	8.6	3.56 × 10 ⁻⁶	3.38 × 10 ⁻³		
X 3	26.0	8.7	3.51 × 10 ⁻⁶	3.73 × 10 ⁻³		

* Roman numerals denote the well. Arabic numerals denote samples obtained at different depths in the same well

** The pH values of these waters could not be measured. They were assumed to be the same pH as those of the saturated zone in the corresponding well

good description of the primary charging behavior of ferrihydrite at the different ionic strengths studied.

Figure 4 shows the arsenate adsorption isotherms in 0.1 M KNO₃ at different pH and the adsorption isotherms at pH 7 and different ionic strengths. The parameters listed in Table 2 were used in calculations with the model. The values of LogK_{H1}, logK_{H2}, LogK_{Cat}, LogK_{An}, C₁ and C₂ were those obtained during the fitting of surface charge data. The interfacial CD coefficients Δz₀ and Δz₁ used were taken from Stachowicz et al. (2006),

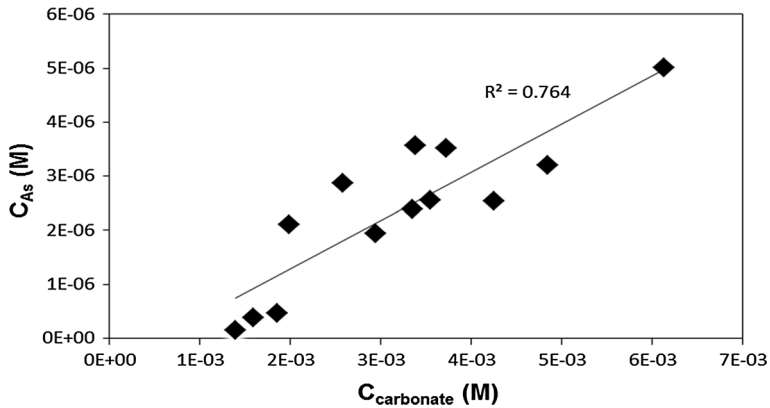


Fig. 2 Arsenic concentration (C_{As}) versus carbonate concentration ($C_{carbonate}$) in porewaters of the unsaturated zone of the watershed of the Napostá Grande Brook, Argentina. Carbonate concentration represents the sum of the concentrations of carbonate and bicarbonate

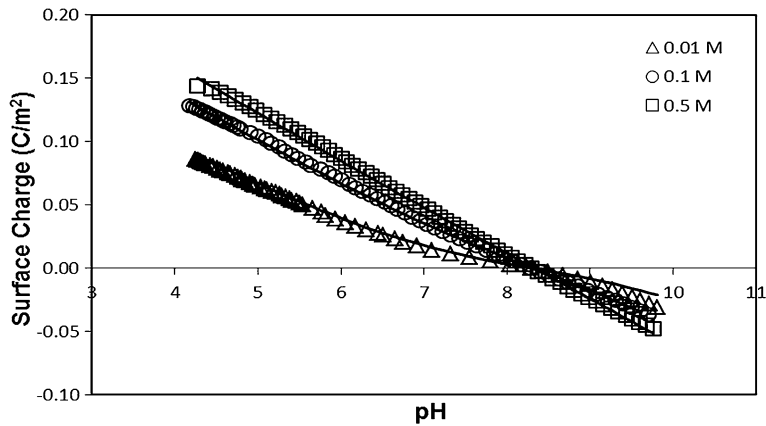


Fig. 3 Surface-charging behavior of the studied ferrihydrite sample at different supporting electrolyte concentrations (given in the figure). Symbols are experimental data, and lines are model predictions with parameters listed in Table 2

which are based on calculated ion charge distributions derived from the MO/DFT optimized geometries. Only $\text{Log}K_{As}$ and $\text{Log}K_{HAS}$ values were used as fitting parameters. A relatively good prediction of arsenate adsorption was obtained. Although several authors considered also the presence of a protonated monodentate species in their calculations (Gustafsson 2001, 2006; Stachowicz et al. 2006), including a reaction that leads to the formation of this surface species did not improve the fit in our case.

Figure 4 shows that arsenate adsorption on ferrihydrite increases as pH decreases and ionic strength increases. This is a typical behavior for arsenate, whose adsorption on iron oxides was studied by several authors (Zeng et al. 2008; Hiemstra and Van Riemsdijk 1996; Antelo et al. 2005, 2010). The increase in surface charge and surface potential as pH decreases favors the adsorption of anionic ligands and the formation of inner-sphere surface complexes with metal ions forming part of the oxide surface. The effect of ionic strength, at low arsenate adsorption and where the surface charge and surface potential are

Table 2 Definition of surface species according to the CD-MUSIC model and other parameters of the model

Surface species	FeOH ^{-1/2}	Fe ₃ O ^{-1/2}	Δz ₀	Δz ₁	log K
FeOH ^{-1/2}	1	0	0	0	0.00
FeOH ₂ ^{+1/2}	1	0	1	0	8.30
Fe ₃ O ^{-1/2}	0	1	0	0	0.00
Fe ₃ OH ^{+1/2}	0	1	1	0	8.30
FeOH ^{-1/2}K ⁺	1	0	0	1	-0.76
FeOH ₂ ^{+1/2}NO ₃ ⁻	1	0	1	-1	8.3-0.7 = 7.60
Fe ₃ O ^{-1/2}K ⁺	0	1	0	1	-0.76
Fe ₃ OH ^{+1/2}NO ₃ ⁻	0	1	1	-1	8.3-0.7 = 7.60
Fe ₂ O ₂ AsO ₂	2	0	0.47	-1.47	26.65
Fe ₂ O ₂ AsOOH	2	0	0.58	-0.58	30.64
Fe ₂ O ₂ CO	2	0	0.68	-0.68	22.33*
Other parameters					
N _{s,FeOH} (nm ⁻²)	6.0				
N _{s,Fe3O} (nm ⁻²)	1.2				
C ₁ (F m ⁻²)	0.76				
C ₂ (F m ⁻²)	0.90				

* Obtained from Stachowicz et al. (2007)

positive because $\text{pH} < \text{PZC}$, must be due to the fact that the positive charge of the surface increases by increasing ionic strength, leading to an increased adsorption. At high arsenate adsorption, where the electric potential becomes negative, the effect of ionic strength is usually attributed to changes in the electric potential in the interface, which decreases the electrostatic repulsion between the charged surface and the ligand, favoring the formation of inner-sphere surface complexes (Hiemstra and van Riemsdijk 1999). It can be also interpreted as an effect of the co-adsorption of cations from the electrolyte, which reduces the repulsion between the negatively charged surface and the adsorbing anion increasing the adsorption (Arai and Sparks 2001).

3.3 Calculation of Arsenate and Carbonate Content in Porewaters

Application of a surface complexation model to calculate arsenate adsorption on sediments, arsenate concentration in porewaters in contact with these sediments and effects of carbonate concentration requires to define the active (the adsorbing) material in sediments, proton, arsenate and carbonate adsorption reactions, the solid/solution ratio of the sediment and the type of system (close or open system, see below). Under oxidizing conditions, the iron “oxides” group (including ferrihydrite, goethite, nanogoethite, hematite, Fe(III) hydroxides coating clay surfaces) is believed to be the main responsible in regulating arsenic concentration in groundwaters through adsorption–desorption process (Smedley and Kinniburgh 2002; Swartz et al. 2004; Biswas et al. 2014). The most reactive oxide fraction is generally assumed to be ferrihydrite, because of its high specific surface area and high adsorption capacity (Antelo et al. 2010; Biswas et al. 2014). In fact, the arsenate adsorption capacity of ferrihydrite (about 700 $\mu\text{mol g}^{-1}$) is much higher than that of clay minerals such as kaolinite, montmorillonite and illite (<10 $\mu\text{mol g}^{-1}$ in both cases) (Luengo et al. 2011), meaning that minimum contents of ferrihydrite or similar hydrous

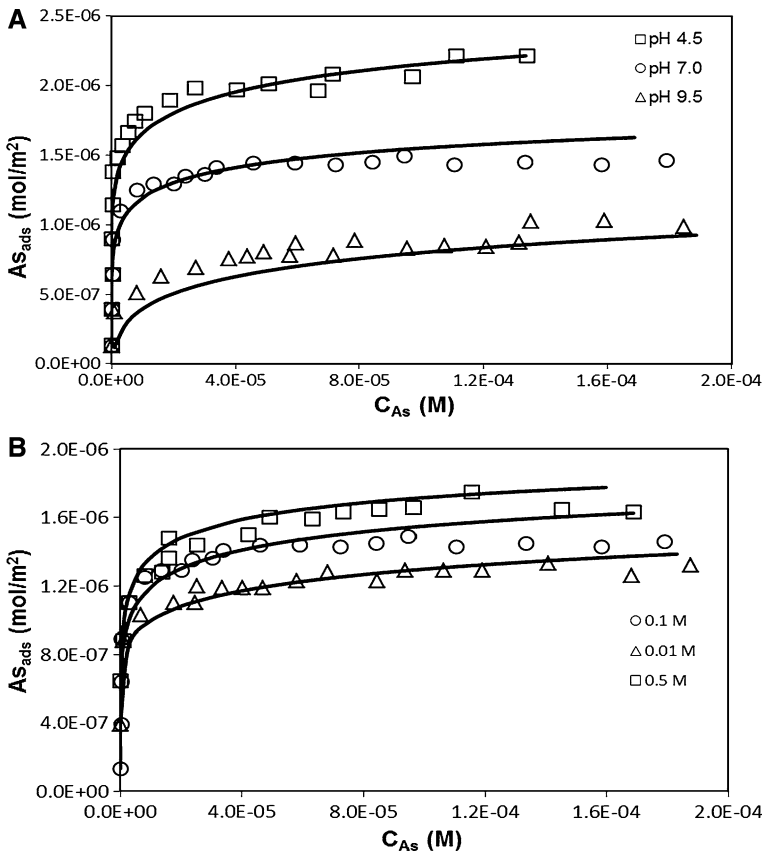


Fig. 4 Arsenate adsorption (As_{ads}) isotherms at different pH in $0.1 M KNO_3$ (a) and at different supporting electrolyte concentrations at pH 7 (b). Symbols are experimental data, and lines are model predictions with parameters listed in Table 2

ferric oxides will strongly affect or even control arsenate adsorption. Hiemstra et al. (2010), for example, studying a series of soils from the Netherlands showed that the specific surface area of the active material varied between 200 and $1200 m^2 g^{-1}$, concluding that the material was formed by nanosized particles with an equivalent diameter in the order of $1-10$ nm if considered as non-porous spheres and indicating that these surface areas and diameters are typical of ferrihydrite. To model the behavior of the studied soils, they have chosen goethite as the representative material because an extensive database is available for ion adsorption on goethite derived for the MUSIC model. However, they stated that ferrihydrite can be considered as a good or even better alternative, but a corresponding database is not available yet. In our calculations, and considering that the active material must have a high surface area, we have assumed that ferrihydrite was the active material in the studied sediments. It must be emphasized that other metal oxides and mineral surfaces may be also reactive in loessic sediments. Ferrihydrite was used here as representative of all these materials.

Proton, arsenate and carbonate adsorption reactions were those already described in Sect. 2.4, with parameters listed in Table 2. The value used for K_{CO_3} was the one reported by Stachowicz et al. (2007) for carbonate adsorption on goethite because no complexation

constant was found in the literature for the case of ferrihydrite in calculations with the CD-MUSIC model. Biswas et al. (2014), Jessen et al. (2012) and Charlet et al. (2007), for example, used the carbonate adsorption constants on ferrihydrite informed by Appelo et al. (2002), but they correspond to the 2-pK diffuse layer model; thus, they cannot be applied here. Since the intrinsic reactivity of ferrihydrite surface groups may differ from that of goethite, the value of K_{CO_3} reported by Stachowicz et al. (2007) was initially intended to be used as an adjustable parameter. However, model predictions worked well from the beginning so it was not adjusted. The solid/solution ratio was 4 kg L^{-1} , obtained from the average gravimetric humidity ($\sim 23 \%$) data informed in Table 1. This is a typical value of porous media (Stachowicz et al. 2007). The content of active material was set equal to 0.14% , in order to have an effective reactive surface area of $1 \text{ m}^2 \text{ g}^{-1}$ for the solid phase if ferrihydrite is assumed to be the only active material. This value was selected because it resulted in consistent calculations. Natural sediment samples generally have an active surface area of only a few $\text{m}^2 \text{ g}^{-1}$. Stollenwerk et al. (2007), for example, used $2.89 \text{ m}^2 \text{ g}^{-1}$ in calculations, value that was measured using the BET gas adsorption method. This method, however, is believed to overestimate the actual surface area that must be used because part of the measured surface area is not reactive in the adsorption process that is considered, arsenate adsorption in this case. Stachowicz (2007), on the other hand, used a surface area of $2 \text{ m}^2 \text{ g}^{-1}$ to calculate the average behavior of 227 sediment samples. Regarding the type of system, a closed system (Villalobos and Leckie 2000) was assumed, where the exchange of CO_2 gas with atmosphere may be considered null, and thus, total carbonate concentration remains constant. This type of system is typical of aquifers and sediments.

For general calculations, and in order to explore the effects of carbonate and pH on arsenate adsorption, the total As concentration (sum of all As species, adsorbed and in solution) was kept constant and equal to $3 \times 10^{-4} \text{ M}$. This is the value obtained from the average As content in the solid phase of the studied sediments (5.78 mg kg^{-1}) plus the As content in the porewaters (Table 1), although this last contribution to the total As concentration was not important. On the other hand, when the total carbonate concentration (sum of all species: adsorbed and in solution) was needed to be constant in calculations, it was kept equal to 0.01 M , which, according to calculations, is approximately the total carbonate average concentration in the studied systems (see below).

Figure 5 shows the general trend of the effects of pH on As concentration in the porewater of the studied system, in the presence and absence of carbonate. Calculations have not the intention of making a detailed fit of experimental data; they were only done to show how the presence of carbonate can modify arsenate concentrations in the studied porewaters at different pHs. Arsenic concentration data from Table 1 are also plotted in the figure for a quick comparison. The curve As concentration versus pH in the absence of carbonate is characteristic of a system with constant total arsenate concentration and an adsorbent such as ferrihydrite. Since arsenate adsorption decreases by increasing pH (Fig. 4), arsenate concentration in solution must increase, as it is observed in Fig. 5. When carbonate is considered to be present in the system, As concentration in solution increases considerably at pH below 11 due to carbonate–arsenate competition for adsorption sites. The fact that carbonate effect is weak at pH above 11 is due to the low adsorption of carbonate in strong alkaline media; the pH range 6–8 is where adsorption of carbonate species reaches its maximum in closed systems (Appelo et al. 2002; Hiemstra et al. 2004). A comparison of model predictions and experimental data shows that in the absence of carbonate, the model underestimates by around two orders of magnitude the arsenic concentration in porewaters. In the presence of carbonate, the model improves significantly

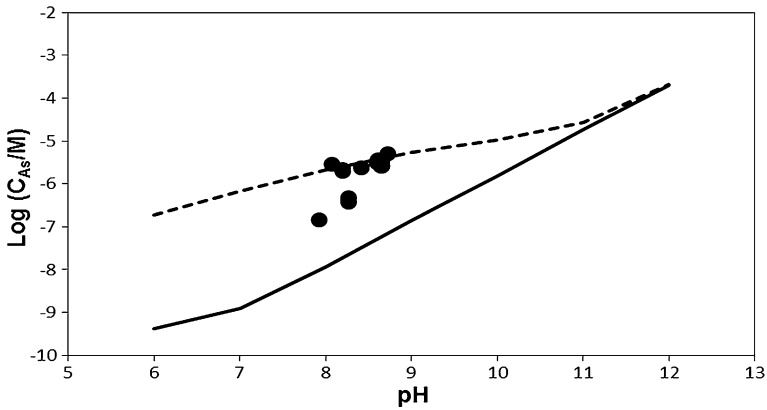


Fig. 5 Arsenic concentration in porewater as a function of pH as calculated with the model. Total As concentration: 3×10^{-4} M. *Solid line*: in the absence of carbonate; *dashed line*: in the presence of 0.01 M total carbonate concentration (adsorbed carbonate plus carbonate in solution). Symbols correspond to C_{As} values of the porewater samples (Table 1)

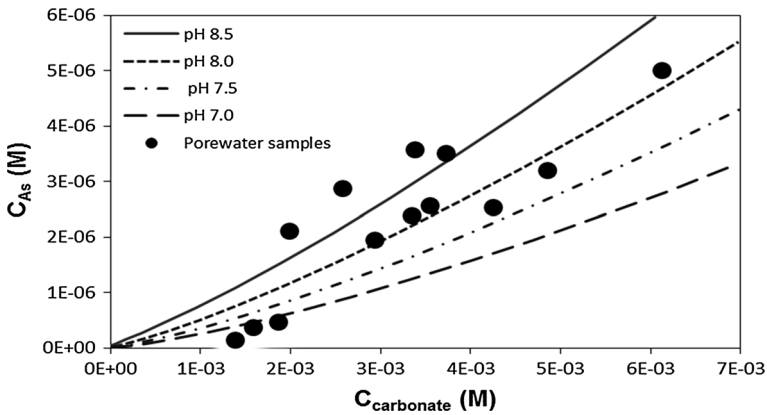


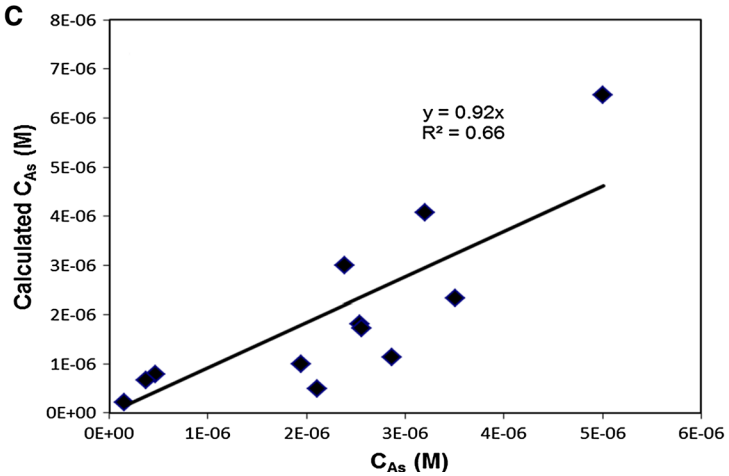
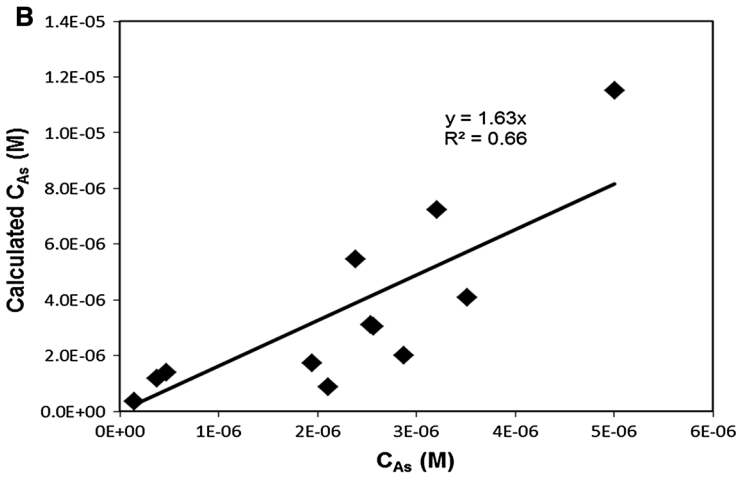
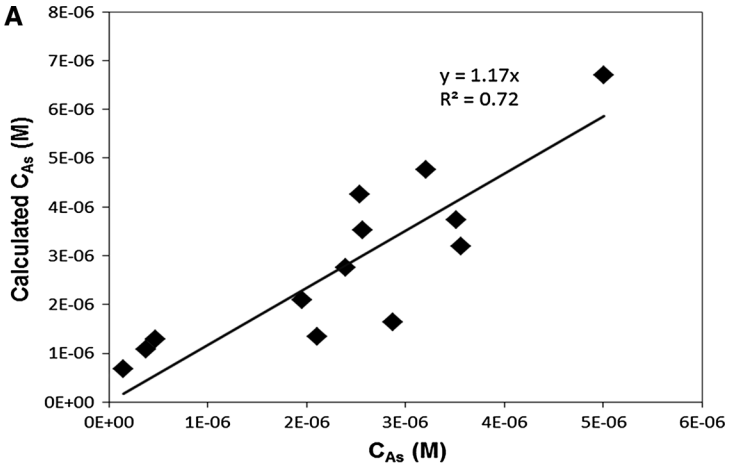
Fig. 6 Arsenic concentration in porewater as a function of carbonate concentration in solution at different pH as calculated with the model. Total As concentration: 3×10^{-4} M

the predictions, even though there are some experimental points that fall below the curve. It must be remarked, however, that this curve was obtained assuming a 0.01 M total carbonate concentration, which is not strictly the case for all those data points. They could be adjusted using smaller total carbonate concentrations in calculations.

Since total carbonate concentration may vary from sample to sample, another way of evaluating model predictions is by analyzing the effect of changing carbonate concentration on arsenic concentration at constant pH. With this aim, calculations were performed keeping as before the total As concentration at 3×10^{-4} M, but increasing gradually the concentration of dissolved carbonate, so that adsorbed carbonate and total carbonate also changed gradually. The general trends that resulted from these calculations are shown in Fig. 6, where calculated As concentration versus carbonate concentration in solution curves is shown, each curve representing the prediction at a given pH. The competitive effect of carbonate results in an increase in As concentration in solution as carbonate concentration increases. The same general trend is observed with experimental data,

having in mind that these data should not follow a unique line because each data point has its own pH and total As concentration. For a given pH, calculated As versus carbonate concentration curves is not straight lines. The shape of the curves results from the combined effect of competing adsorption equilibria and electrostatics in the double layer. Therefore, plots such as that shown in Fig. 2, where As and carbonate concentration are compared, should not necessarily be straight lines, as they are usually forced to in order to show the correlation between both species. It is necessary to make clear here that for a range of carbonate concentrations in solution from around 1×10^{-3} to 7×10^{-3} M, as shown in Fig. 6, calculated total carbonate concentration varied from around 5×10^{-3} to 1.7×10^{-2} M, with an average value of 1.1×10^{-2} M in the pH range 7.0–8.5. This is why a constant 0.01 M total carbonate concentration was used to evaluate general trends in Fig. 5.

General trends in Figs. 5 and 6 clearly show that As concentration in solution increases as pH and carbonate concentration increase. Although the model predicts concentrations that are in the order of the measured values in the studied porewaters, a precise comparison with experimental data is not possible because pH and carbonate concentration change from sample to sample. A best evaluation of the model prediction can be done, therefore, by performing calculations “point by point.” This means that for each sample, a calculation of As in solution is made using the pH and carbonate concentration that correspond to that sample, and the calculated value is compared to the experimental one. Figure 7 shows the results of these calculations. As a first approach, the point by point calculation was performed by keeping the constant average value of 3×10^{-4} M for total As concentration and using the pH and carbonate concentration of each sample (Fig. 7a). A positive correlation is observed between calculated and experimental data, and a straight line with a slope = 1.17 and $R^2 = 0.72$ is found. This indicates that the model predicts fairly well the As concentration in porewaters. Calculations show that As concentration can be predicted usually within a factor of 2, which may be considered good for natural systems. A more strict approach, however, requires the use of the total As concentration, pH and carbonate concentration corresponding to each sample. In such calculations, the predictions were surprisingly poorer (slope = 1.48, $R^2 = 0.55$, not shown). Even after discarding one data point (sample X2), whose inclusion resulted in low R^2 value, the predictions did not improve (slope = 1.63, $R^2 = 0.66$, Fig. 7b). The fairly high slope indicates that calculations overestimate As concentration in solution. There are several reasons that can explain it. One of them is related to the effective reactive surface area of $1 \text{ m}^2 \text{ g}^{-1}$ assumed in calculations: If the content of active material is set equal to 0.21 %, in order to have an effective reactive surface area of $1.5 \text{ m}^2 \text{ g}^{-1}$, the predictions improve significantly (slope = 1.10, $R^2 = 0.65$, not shown). The effect of increasing the surface area is to increase adsorbed As with the corresponding decrease in the calculated As concentration in solution. A second reason is related to the fact that the whole As content in sediments was assumed to participate in the adsorption–desorption reactions. A fraction of the total As may be buried within the structure of several minerals, and thus, it is inhibited from becoming adsorbed or desorbed according to reactions (5) and (6). In fact, calculations with an effective reactive surface area of $1 \text{ m}^2 \text{ g}^{-1}$ but assuming that only 60 % of the total As of each sample can participate in adsorption–desorption reactions improve also the predictions (slope = 0.92, $R^2 = 0.66$, Fig. 7c). There are other modeling assumptions that could still improve predictions (decreasing somewhat K_{CO_3} , for instance), but the intention is not to achieve the best fitting. It is only to show that arsenate adsorption–desorption reactions and competition with carbonate are important processes that influence As concentration in waters of the unsaturated zone.



◀ **Fig. 7** Comparison between calculated and experimental As concentration in the studied porewaters with “point by point” calculations. **a** Total As concentration: 3×10^{-4} M for all points; pH and carbonate concentration of each sample (see Table 1); specific surface area: $1 \text{ m}^2 \text{ g}^{-1}$. **b** Total As concentration, pH and carbonate concentration of each sample; specific surface area: $1 \text{ m}^2 \text{ g}^{-1}$. **c** Total As concentration, pH and carbonate concentration of each sample; specific surface area: $1 \text{ m}^2 \text{ g}^{-1}$, only 60 % of total As is allowed to participate in the reactions. In figures **b** and **c** the data point of sample X2 was not considered

The fact that a surface complexation model can describe satisfactorily the As concentration in porewaters of the studied watershed strongly suggests that adsorption–desorption reactions on mineral surfaces are playing a key role in controlling these concentrations. Since the mentioned porewaters belong to the unsaturated zone of the watershed, they are in intimate contact with the surface of sediment particles, and thus, it is reasonable that adsorption–desorption equilibria regulate the chemical composition of the aqueous phase. Even though this article points to the effects of carbonate and explains As data mainly as a result of competition between arsenate and carbonate species for surface sites, it is necessary to have in mind that other substances may be affecting As concentration in this and other systems. Phosphate, silicate, humic substances and other ligands that are able to form inner-sphere complexes at the mineral surfaces are good competitors for arsenate, and they should also affect As concentrations in water if present at significant concentrations. Dissolved cations, as Ca^{2+} , would also affect As concentration because they usually promote arsenate adsorption (Stachowicz et al. 2008). In the special case of sediments of the Chaco-Pampean Plain of Argentina, Smedley et al. (2005) also concluded that adsorption–desorption processes are important in regulating As concentrations in groundwaters of the Province of La Pampa, Argentina, where not only carbonate but also phosphate and perhaps vanadium species are competing for arsenate. Although the studied groundwaters in La Pampa belong to the saturated zone and are located at more than 300 km from the Napostá Grande Brook, it seems that adsorption–desorption processes are in general controlling the chemical speciation in porewaters of the Chaco-Pampean Plain.

4 Conclusions

The As concentrations in porewaters of the unsaturated zone of the studied watershed correlate well with carbonate concentrations. Calculations performed with the CD-MUSIC surface complexation model indicate that variations in As concentrations can be explained by adsorption–desorption process occurring at the mineral–water interface. Increasing carbonate concentrations and increasing pH result in an increased As concentration in the aqueous phase. Carbonate affects As concentration by competing with arsenate species for adsorption sites on the mineral surface. The effect of pH can be understood (a) considering the equilibria represented by Eqs. (5) and (6), which show that increasing pH favors arsenate desorption and (b) because increasing pH increases the negative charge (or decreases the positive charge, depending on the pH) facilitating the desorption.

Even though several dissolved species can modify arsenate adsorption, calculations with the model suggest that carbonate is an important arsenate competitor for adsorption sites.

As it occurs with groundwater samples of the saturated zone in many aquifers, adsorption–desorption processes also seem to control As concentration in porewaters of the unsaturated zone.

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Appendix

[Hexahidrita170910.MDI]

SCAN: 20.079.976(0.024/1(sec), Cu, I(max) = 41.0, 09/17/10 12:18p

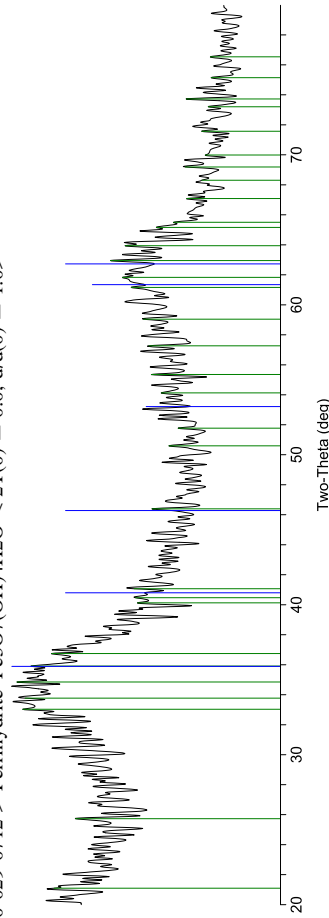
PEAK: 27-pts/Parabolic filter, Threshold = 3.0, Cutoff = 0.1 %, BG = 3/1.0, Peak-top = Summit

Intensity = Counts, 2T(0) = 0.0(deg), Wavelength to computed-spacing = 1.54059A (Cu/K-alpha 1)

#	2-Theta	d(Å)	Height	Height %	Phase ID	d(Å)	I %	(hkl)	2-Theta	Delta
<i>Peak ID report</i>										
1	21.104	4.2063	34.5	85.9						
2	25.737	3.4587	31.3	77.8						
3	33.032	2.7096	39.3	97.8						
4	33.776	2.6516	39.0	96.9						
5	34.856	2.5719	40.2	100.0						
6	35.912	2.4986	38.1	94.7	Fe5O7(OH)4H2...	2.5000	100.0	(110)	35.892	-0.020
7	36.752	2.4434	34.9	86.9						
8	40.136	2.2449	21.8	54.2						
9	40.474	2.2269	22.1	55.0						
10	41.072	2.1958	22.3	55.5	Fe5O7(OH)4H2...	2.2100	80.0	(200)	40.797	-0.275
11	46.399	1.9554	19.6	48.7	Fe5O7(OH)4H2...	1.9600	80.0	(113)	46.284	-0.115
12	50.600	1.8025	17.0	42.3						
13	51.776	1.7642	15.6	38.8						
14	54.128	1.6930	18.2	45.2						
15	55.353	1.6584	19.7	49.0						
16	57.268	1.6074	20.0	49.8						
17	59.048	1.5631	20.9	52.0						
18	61.160	1.5141	22.8	56.6	Fe5O7(OH)4H2...	1.5100	70.0	(115)	61.345	0.185
19	61.832	1.4993	24.1	60.0						
20	62.959	1.4751	25.9	64.5	Fe5O7(OH)4H2...	1.4800	80.0	(106)	62.728	-0.231

#	2-Theta	d(Å)	Height	Height %	Phase ID	d(Å)	I %	(hkl)	2-Theta	Delta
21	63.945	1.4547	23.7	58.9						
22	65.168	1.4304	18.9	47.1						
23	65.504	1.4238	16.3	40.6						
24	67.088	1.3940	14.3	35.5						
25	68.312	1.3720	12.0	29.9						
26	69.200	1.3565	14.5	36.1						
27	69.992	1.3431	11.5	28.5						
28	71.576	1.3172	12.0	29.9						
29	73.208	1.2918	11.0	27.4						
30	73.734	1.2839	14.4	35.8						
31	75.152	1.2632	10.6	26.3						
32	76.544	1.2436	10.7	26.6						

Line shifts of individual phases:
 00-029-0712 > Ferritohydrate-Fe5O7(OH)4H2O < 2T(0) = 0.0, d/d(0) = 1.0 >



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