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Hydrogeochemistry and sustainability of freshwater lenses in the Samborombón Bay wetland, Argentina

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ABSTRACT

Freshwater lenses constitute one of the most vulnerable aquifer systems in the world, especially in coastal wetland areas. The objectives of this work are to determine the hydrogeochemical processes that regulate the quality of the freshwater lenses in a sector of the Samborombón Bay wetland, and to assess their sustainability as regards the development of mining activities. A hydrochemical evaluation of groundwater was undertaken on the basis of major ion, trace and environmental isotope data. The deterioration in time of the freshwater lenses in relation to mining was studied on the basis of the analysis of topographic charts, aerial photography and satellite imaging. The results obtained show that the $CO_{2(g)}$ that dissolves in the rainwater infiltrating and recharging the lenses is converted to HCO_3^-, which dissolves the carbonate facies of the sediment. The exchange of Ca^{2+} for Na^+, the incongruent dissolution of basic plagioclase and the reprecipitation of carbonate produce a change of the Ca–HCO_3 facies to Na–HCO_3. In depth, the pH increases with the groundwater flow, and the volcanic glassis dissolved, releasing $F^-$and As. Besides, the evapotranspiration processes cause the saline content to increase slightly. As the only sources of drinking water in the region are the freshwater lenses occurring in the shell ridges, mining operations have deteriorated this resource and decreased the freshwater reserves in the lenses. The study undertaken made it possible to develop some preservation, remediation and management guidelines aimed at the sustainability of the water resources in the region.

1. Introduction

In many deltaic areas and coastal plains, groundwater is saline due to the Quaternary marine transgressions that originated them or to seawater intrusion (Custodio and Bruggeman, 1987; Stuyfzand and Stuurman, 1994; Logan et al., 1999; Carol et al., 2009; Weert et al., 2009; Post and Abarca, 2010; De Louw et al., 2011). In these environments, the presence of sand dunes, littoral shell ridges or palaeochannels may lead to the formation of freshwater lenses from rainwater infiltration (Wallis et al., 1991; Collins and Easley, 1999; Mass, 2007; Carol et al., 2009; De Louw et al., 2011).

Freshwater lenses constitute one of the most vulnerable aquifer systems in the world (Morgan and Werner, 2014), mainly in coastal wetland areas (Odum and Harvey, 1988; Rheinhardt and Faser, 2001; Carol et al., 2014). The deterioration of such lenses is associated with (1) the low relief (natural or lowered by anthropogenic action), which leads to flat hydraulic gradients and high susceptibility to land surface inundation by saline water; (2) the fact that these areas are generally limited in extension, a characteristic which makes them sensitive to dry periods; and (3) the fact that there is a great dependence of the local communities on the limited alternative freshwater supply sources, which causes the lenses to be overexploited (White et al., 2007; White and Falkland, 2010; Carol et al., 2014).

The Samborombón Bay wetland comprises an extensive coastal plain associated with an ancient tidal plain, shell ridges and marsh environments (Fig. 1), all of which were deposited during the Holocene as a consequence of the successive displacements of the shoreline caused by the sea level oscillations (Richiano et al., 2012). In the littoral sector, the coastal plain overlies a volcanic loess substrate that crops out in the more continental sectors. It is a topographically low area, with heights usually below 7 m.a.s.l. and a slope close to 10^{-4}, with a predominance of saline surface and

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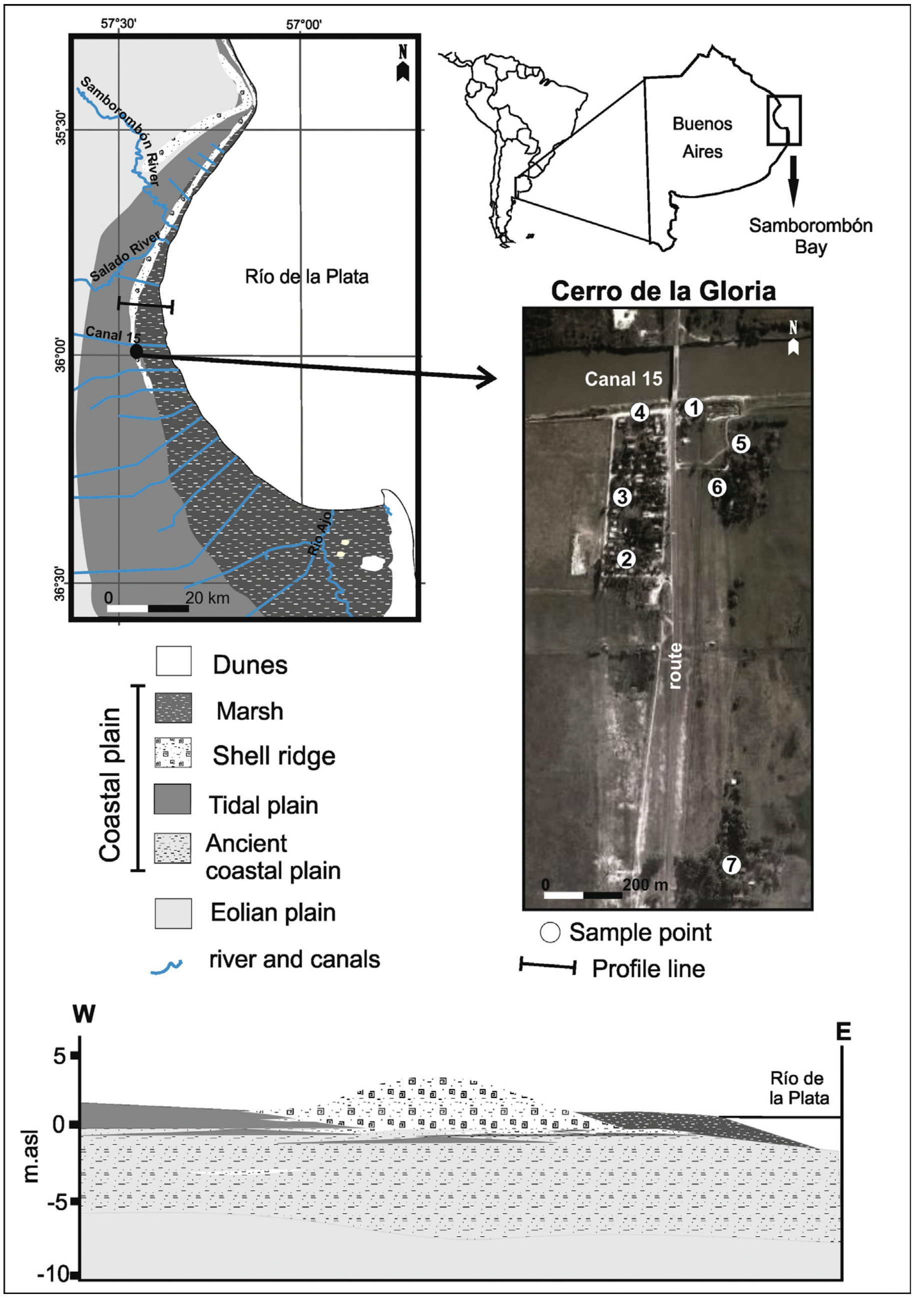

Fig. 1. Location of the study area: geomorphological map, geological profile and sampling points.

groundwater. The only source of water fit for human consumption in the region is associated with the presence of freshwater lenses within the shell ridges (Sala et al., 1978; Carol et al., 2010; Carol and Kruse, 2012). These lenses have a limited extension and are laterally limited and underlain by the saline groundwater occurring in the sediments of the coastal plain (Carol and Kruse, 2012; Carol et al., 2013). The humid temperate climate, the high permeability of the shell ridges and annual precipitations close to 1000 mm feed these freshwater lenses despite the fact that evaporation is close to 770 mm a year (Carol et al., 2014). The scarce number of villages and farms in the central and northern sectors of the wetland depends on these lenses for water supply.

The shell ridges occur parallel to the coastline from the centre of the bay towards the north. They are positive relief landforms with heights ranging between 6 and 17 m.a.s.l., composed of loose seashell debris alternating in sectors with sand and clay layers. The mineralogy of these sediments is mainly dominated by carbonates (shells and concretions), quartz, basic plagioclase and volcanic glass, the latter originating from the reworking of the underlying loess substrate during deposition. Clay and interchangeable sodium intercalations, as well as the presence of kaolinite and montmorillonite, have also been identified (Carol et al., 2013).

The mining operations associated with the extraction of shells cause the decrease and deterioration of the freshwater lenses (Tejada et al., 2011). The scarcity of freshwater in the region is one of the main limitations to population development, with the locality of Cerro de la Gloria (approximately 200 permanent inhabitants) being the only urban centre that develops on the littoral of the bay (Fig. 1).

These freshwater lenses are fragile, dynamic reserves exposed to the influence of natural and human factors and they must be protected. Their preservation, remediation and management require the understanding of the processes regulating the quality and quantity of freshwater, both in natural conditions and when affected by anthropogenic activity. Understanding the evolution and current state of the freshwater lenses will make it possible to coordinate government policies, plans and actions to achieve the sustainability of the water resource and ensure the wellbeing of the inhabitants in the region.

The objectives of this work are to determine the hydrogeochemical processes regulating the quality of the freshwater lenses occurring in the Samborombón Bay wetland in the vicinity of Cerro de la Gloria, as well as to assess the current state of the freshwater reserves in the context of the development of mining operations. The results obtained will help develop management guidelines for the hydrological sustainability of the lenses.

2. Methodology

A hydrogeomorphological characterisation of the shell ridges and the adjacent coastal plain was undertaken on the basis of data from lithological profiles obtained from water wells and field surveys. Besides, a characterization of the water type occurring in the shell ridges was carried out on the basis of major ion data obtained from shallow exploration wells. The groundwater chemistry (i.e., major anions, TDS, pH, hardness, fluorides and arsenic) of the freshwater lenses located in the locality of Cerro de la Gloria was evaluated on the basis of samples collected from water supply wells (Fig. 1 and Table 1). The collection, preservation and chemical analysis of the water samples were carried out according to the methods established by the American Public Health Association (APHA, 1998). Sodium (Na^+) and potassium (K^+) were determined by flame photometry. Hardness as calcium carbonate ($CaCO_3$), calcium (Ca^{2+}), carbonate ($CO_3{}^{2-}$), bicarbonate ($HCO_3{}^-$) and chloride (Cl^-) were determined by volumetric methods. Magnesium (Mg^{2+}) was calculated on the basis of the data on total hardness and calcium. Sulphate ($SO_4{}^{2-}$) was measured by nephelometry, nitrates ($NO_3{}^-$) by spectrophotometry, fluorides (F^-) by ion-selective electrode, arsenic (As) by silver diethyldithiocarbamate and the amount of total dissolved solids (TDS) or salinity was determined by gravimetry. Electrical conductivity and pH were measured in the field immediately after the collection of the samples, using portable equipment. In certain sampling points, a subsequent sampling was undertaken in which determinations of environmental isotopes and TDS were carried out. Isotopic ratios, $\delta^{18}O$ and δ^2H were measured by laser spectroscopy with equipment manufactured by Los Gatos Research (Lis et al., 2008). Results are reported in the usual δ notation in (‰) relative to V-SMOW (Gonfiantini, 1978). Analytical uncertainties were ±0.3‰ for ^{18}O and ±1‰ for ^2H.

Table 1
Chemical data for the supply wells of the locality of Cerro de la Gloria. The location of the samples is shown in Fig. 1.

Sample	TDS	pH	$SO_4{}^{2-}$	Cl^-	$NO_3{}^-$	As	F^-	Hardness
1	570	8.3	50	58	1	0.04	1.3	144
2	1414	7.6	343	322	2	0.04	1.1	590
3	2400	7.4	800	535	2	0.01	0.5	728
4	820	7.8	132	143	3	0.01	0.8	367
5	834	8.1	132	90	5	0.03	0.8	277
6	900	8.2	110	130	2	0.07	1.9	89
7	1140	8.6	66	47	1	0.08	1.8	37

By means of topographic charts, aerial photography and satellite imaging, the mining exploitation areas in the shell ridges were analysed. The 1:50.000-scale topographic charts drawn in 1965 were used to obtain the morphology and height of the shell ridges before they were exploited. The evolution in time of the extension and deepening of the exploitation area was carried out on the basis of the interpretation of aerial photographs from 1984 (scale 1:20,000), satellite images from 2013 acquired by the QuickBird satellite downloaded from Google Earth and field surveys. The photographs and images were georeferenced and digitised to estimate the mining exploitation surface and the volume of shell and sand extracted. An estimation of the decrease in water reserves was also undertaken, considering a mean effective porosity of 0.3 (Sala et al., 1978) and an average unsaturated zone (UZ) thickness of 1 m (Carol et al., 2014).

3. Results

3.1. Hydrogeochemistry of freshwater lenses

Water in these lenses is predominantly of the sodium bicarbonate type, with only one sample of magnesium bicarbonate type (Fig. 2). These samples show Na^+ excesses (positive values of $Na^+ - Cl^-$) and Ca^{2+} and Mg^{2+}deficiencies (positive values of $(CO_3H^- + SO_4{}^{2-}) - (Ca^{2+} + Mg^{2+})$) with a ratio close to 1:1 (Fig. 2).

In the supply wells, the salinity expressed as TDS is low (below 1500 mg/L), except for a sample that shows values of 2400 mg/L (Table 1). The samples as a whole display a tendency towards an increase in salinity, mainly associated with an increase in the concentration of chlorides and sulphides (Fig. 3a and b). Alkalinity values range between 265 and 840 mg/L, with most of the samples showing values below 450 mg/L. Hardness reaches values of up to 728 mg/L that decrease as pH increases from 7.4 to 8.6 (Fig. 3c). Nitrate concentrations are low in all cases, with values varying between 1 and 6 mg/L.

The content of arsenic shows a strong positive correlation with fluoride ($r^2 = 0.91$; Fig. 4a). Regarding these ions, and taking into consideration that the guideline value for arsenic is 0.01 mg/L (WHO, 2004), the water is in most of the samples unfit for human consumption, as 70% of them are above this value. In the case of fluorides, the maximum limit is 1.5 mg/L, with 28% of the samples from the phreatic aquifer being above such a limit. As regards pH, it can be observed that the concentrations of both fluoride and arsenic tend to increase towards more alkaline pH values (Fig. 4b and c).

As for isotope content, the samples are aligned along the local meteoric water line (Dapeña and Panarello, 2004) with $\delta^{18}O$ values between −4.3 and −6.2, and δ^2H values between −22 and −39 (Fig. 5a). However, isotopic enrichment associated with a slight increase in salinity (Fig. 5b) indicates, together with the deviation of some samples from the local meteoric water line, processes of water evaporation. It should be noted that in the graph representing δ^2H as a function of the TDS, two samples show a tendency towards a salinity increase without isotopic enrichment (Fig. 5b).

3.2. Characterisation of freshwater lenses in relation to mining

The study area comprises a shell ridge that, according to the topographic charts, has a length of 14 km, a width close to 400 m and topographic heights reaching 7.7 m.a.s.l. Towards the east, it borders with the marsh, which comprises a littoral fringe with an average width of 5.2 km where the topography does not rise above 1.7 m.a.s.l. and which is flooded periodically by the Río de la Plata tide. To the west, it borders with the tidal plain, where the former tidal channels constitute frequently waterlogged depressed areas.

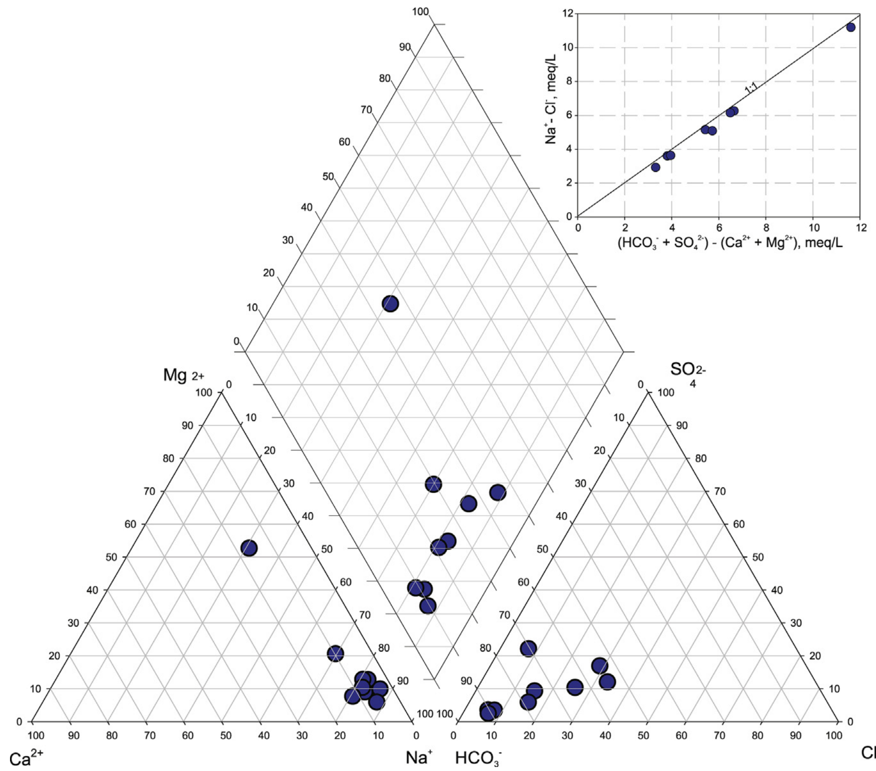

Fig. 2. Water classification diagram (Piper, 1944), and relation between $Na^{+}-Cl^{-}$ and $(CO_3H^{-} + SO_4^{2-}) - (Ca^{2+} + Mg^{2+})$.

The shell ridge is intersected by the Canal 15, which drains the water surplus of the Salado River, with the locality of Cerro de la Gloria situated on the right bank of the canal (Fig. 1).

At the bay, the shell ridges have been exploited as building material since the early 20th century. The main environmental problems related to mining are the degradation of the freshwater lenses and the depletion of the native *Celtis tala* forest, which only occurs in the shell-ridge areas of the wetland (Fig. 6).

The analysis of aerial photography from 1984 and satellite images from 2013 allowed the documentation of the temporal evolution of the mining operations. These can be identified by the presence of excavations intersecting the water table and forming ponds, or of areas with remobilised material, where the calcareous sediment can be observed on the surface (Fig. 7). When comparing the surface occupied by the shell ridges in the topographic chart and in the aerial photographs from 1984, it can be observed that by that time nearly 35% of the shell-ridge area (corresponding to 2.42 km^2) had been exploited by mining. Out of this surface, 0.48 km^2 (7%) correspond to exploitations below the water table and 1.94 km^2 (28%), to exploitations at the same topographic level as the tidal plain (2.5 m.a.s.l.). Taking into consideration that mining exploitations generally have a depth of 1.5 m below such a level when forming pits or are at the same height as the tidal plain or the adjacent marsh, the volume of material removed by that time was 3.76 hm^3. Considering the effective porosity and the average thickness of the UZ, it can be estimated that such a volume of removed material reduced the groundwater reserves in the freshwater lens 0.52 hm^3.

By the year 2013, several of the abandoned quarries were being exploited once again, deepening the excavations or broadening the extraction area. However, it can also be observed that some quarries with lakes were refilled with sandy reject material and taken to the same topographic level as the adjacent coastal plain (Fig. 7). By that time, the total surface exploited reached 3.72 km^2 (54% of the shell-ridge area), out of which 1.06 km^2 (16%) correspond to excavations below the water table and 2.66 km^2 (38%), to exploitations at the same height as the topographic level of the tidal plain, increasing the estimated volume of extracted material to 6.63 hm^3. Taking into consideration these calculations, it can be estimated that the subsurface freshwater reserves decreased 0.97 hm^3.

When the mining exploitations from 1984 and 2013 are compared, four sectors in which the mining activity caused major modifications can be recognised (Fig. 7). Sector *a* shows a 100% increase of the surface affected by mining, with a reduction of the *C. tala* forest of almost 50% (Fig. 7a). In Sector *b*, there are no significant changes, showing pits in the same sectors in both periods (Fig. 7b). In Sector *c*, the surface of mining exploitation increased almost 100%, with a larger number of pits and an almost complete depletion of the *C. tala* vegetation (Fig. 7c). Finally, in Sector *d* the situation is similar on both dates, showing a large number of pits (Fig. 7d).

4. Discussion

The hydrogeochemical studies based on the ion relations make it possible to determine the processes conditioning water quality, such as water/sediment interaction, saline intrusion, contamination, etc. (Gimenez and Morrel, 1997; Jorgensen, 2002; Marimuthu et al., 2005; de Montety et al., 2008; Silva-Filho et al., 2009).

In the phreatic aquifers with limited areal extension, such as the case studied, most of the ions dissolved in water are acquired during rainwater infiltration in the unsaturated zone (UZ). This is mainly due to the fact that rainwater reacts with the $CO_{2(g)}$ in the atmosphere and in the sediment pores, generating HCO_3^{-} and H^{+}. The latter imparts acidity to water, which attacks the minerals, especially the carbonate phases. The dissolution of carbonates decreases acidity, which in the UZ is recovered by the dissolution of more $CO_{2(g)}$, mainly generated by the roots and the decomposition

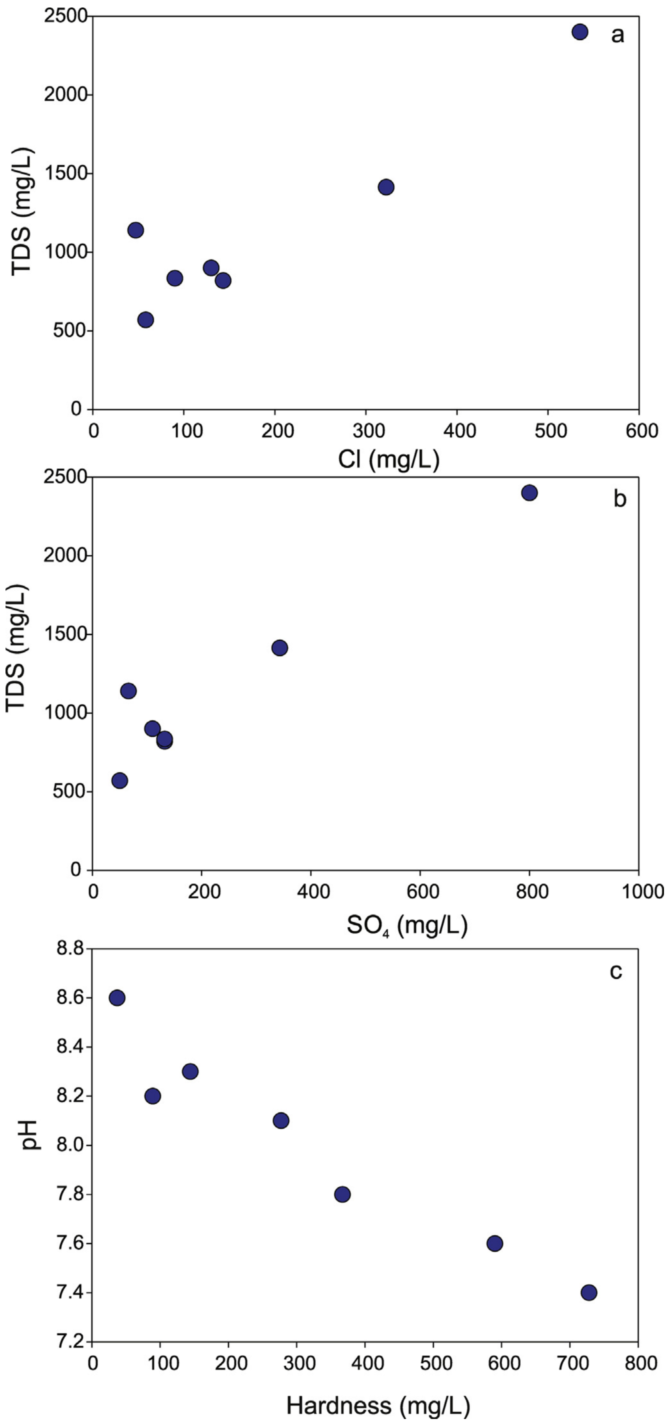

Fig. 3. Relation between salinity content, pH and anions in the shell-ridge groundwater.

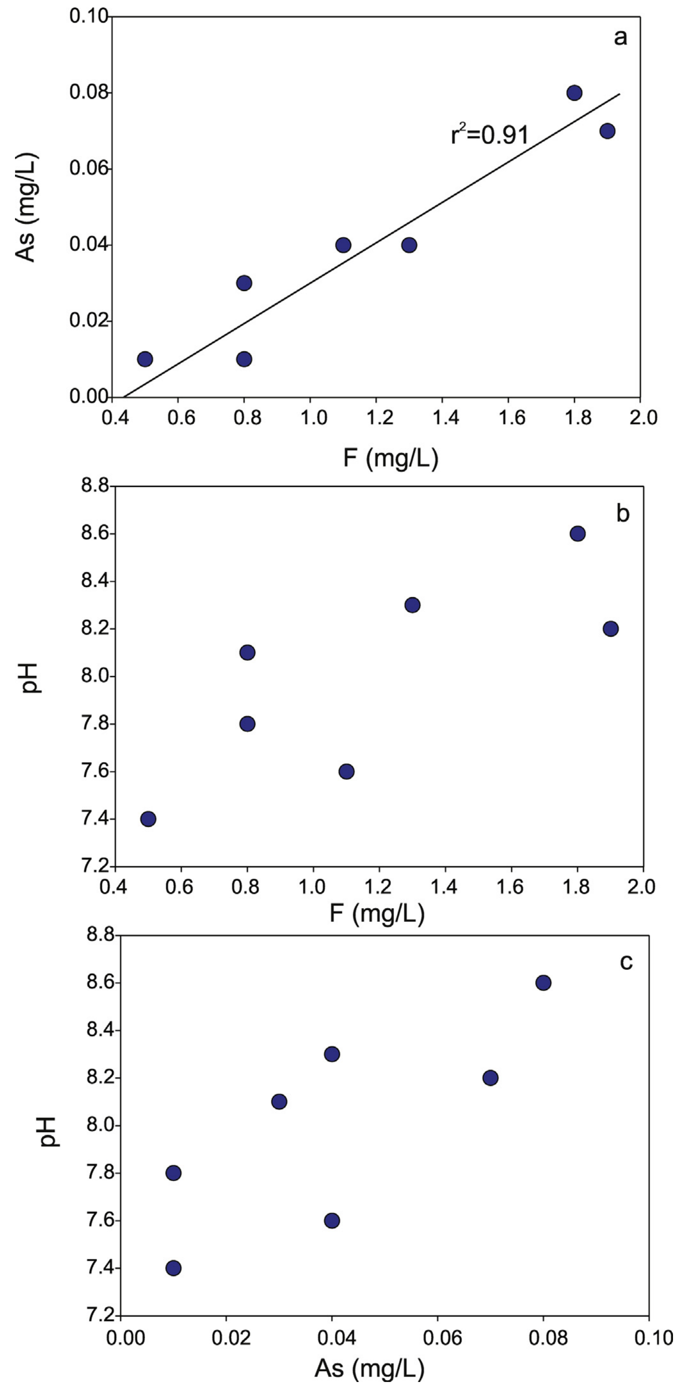

Fig. 4. Relation between (a) arsenic and fluoride content; relation between pH with respect to fluoride and arsenic (b and c, respectively) in the shell-ridge groundwater.

of organic matter in the soil, and secondarily by the atmosphere. These reactions occurring in the UZ and more superficial sectors of the aquifer create a buffer system that maintains the pH values. When water reaches the water table and it mixes with the groundwater flow as the dissolution of carbonates consumes H^+ and $CO_{2(g)}$, it loses acidity as it is unable to incorporate $CO_{2(g)}$ to the system, decreasing its capacity to dissolve and alter minerals (Hem, 1985; Appelo and Postma, 2005). In this way, when rainwater infiltrates, it dissolves the shells and the carbonate concretions, generating increased water hardness values. With the groundwater flow, the pH in the water tends to increase and, therefore, the reprecipitation of carbonates occurs, forming aggregates in the matrix or concretions in the sediments. Soil studies undertaken in the shell ridges show that the reprecipitation of carbonates is a common process in this environment in the areas affected by the oscillation of the water table (Imbellone and Giménez, 1997).

The 1:1 ratio observed between the Na^+ excesses and the Ca^{2+} deficiencies show that the Ca^{2+} released by the dissolution of carbonates is exchanged by Na^+ adsorbed in the clayey fractions intercalated in the ridges. Besides, the incongruent dissolution of albite to kaolinite and/or montmorillonite, identified by

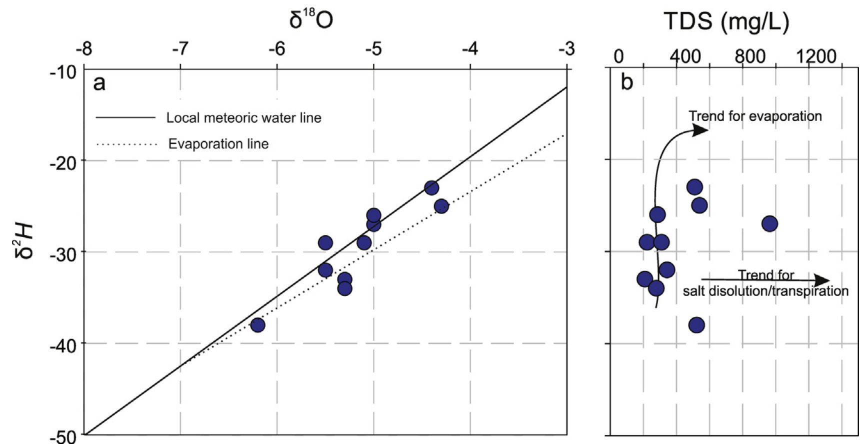

Fig. 5. Relation between (a) δ^2H as a function of δ^{18}O and (b) δ^2H as a function of salinity.

Fig. 6. (a) Shell ridge with *Celtis tala* vegetation; (b) and (c) mining exploitation where the land clearance can be observed.

mineralogical analysis, may potentially contribute to the groundwater Na^+ and bicarbonate content (Kortatsi, 2006). The Ca^{2+}/Na^+ cation exchange processes, the alteration of albite and the reprecipitation of carbonates contribute to Na^+ becoming the dominant cation, which leads to the predominance of Na–HCO_3 facies.

The contents of fluoride and arsenic in groundwater originate from the alteration of the volcanic glass occurring both in the volcanic sediments underlying the shell ridges (Tricart, 1973) and in the reworked loess material present in the shell ridges. The silica, which constitutes the volcanic glass, begins to dissolve as groundwater reaches slightly alkaline pH values (Appelo and Postma, 2005), increasing the concentrations of F^- and As (Viswanathan et al., 2009). It should be noted that slightly alkaline pH conditions occur in the middle and deep sectors of the water lens, where no buffer conditions occur associated to the dissolution of $CO_{2(g)}$ and the pH is above 8. This behaviour explains the positive correlation observed between the pH and the concentrations of arsenic and fluoride.

In turn, nitrate is a very scarce ion, appearing in all of the analysed samples in concentrations lower than 6 mg/L. Given the presence of organic soils in the shell ridges (Giménez et al., 2008), the scarce nitrate content may be explained as a consequence of the decomposition of the soil organic matter (Canter, 1996).

Finally, the evapotranspiration processes are also relevant in phreatic aquifers, given their connection with the atmosphere through the UZ and plant roots, mainly in the shallower ones, and also because rainwater may evaporate before it infiltrates. In the δ^2H vs δ^{18}O relations, a slight isotopic enrichment can be observed, caused by the evaporation of the rainwater recharging the aquifer. It is also as a consequence of such evaporation that a slight increase in water salinity occurs. However, in two of the samples an increase in salinity without isotopic enrichment was registered, a characteristic which indicates the occurrence of salt dissolution or transpiration (Fass et al., 2007; Carol et al., 2009). In turn, given the absence of mineral facies of the halite or anhydrite type in the ridges, the low Cl^- and SO_4^{2-} contents may be mainly related to a concentration due to rainwater evaporation and transpiration, with the possible occurrence of contributions from the aerosol originating in the saline water of the estuary. A particular case can be observed in a supply well that reaches salinities of 2400 mg/L and whose well design draws water close to the freshwater/saline water interface. All of the geochemical processes recognised are shown in the conceptual model in Fig. 8.

As regards the sustainability of the freshwater lenses, it is essential to preserve the natural conditions of the shell ridges. In natural conditions, the high permeability of the shells and sand that compose them (200 m/d; Sala et al., 1978) favours rainwater recharge. Besides, their positive morphology causes the elevation of the water table, which prevents the saline groundwater occurring in the adjacent coastal plain and marsh (Sala et al., 1978; Carol and

Fig. 7. Identification of mining exploitations in the shell ridges for 1984 and 2013.

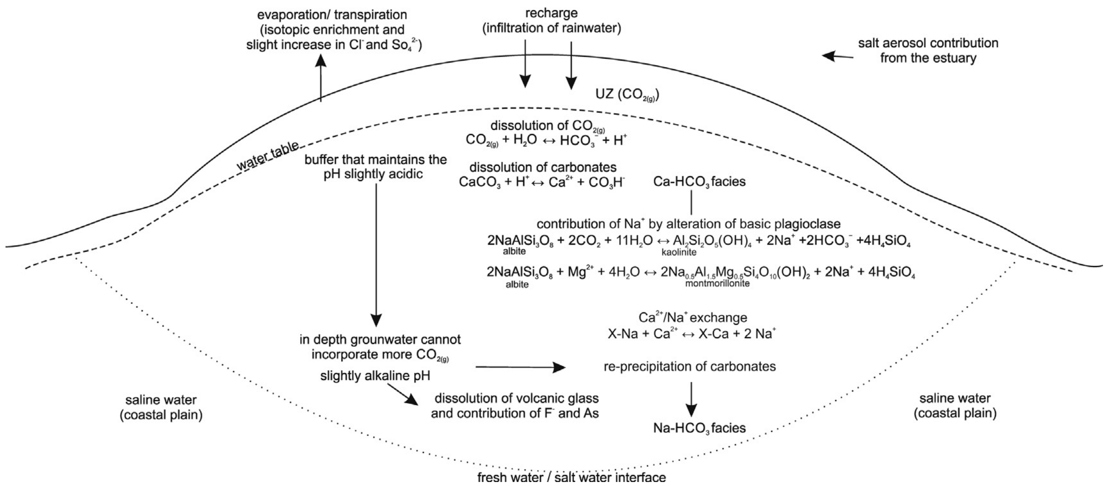

Fig. 8. Conceptual model of geochemical processes in freshwater lenses.

Kruse, 2012; Carol et al., 2013) from flowing towards the lens (Fig. 9a). The mining exploitations below the water table form lakes in which saline water may enter laterally from the coastal plain and the marsh, decreasing the quality of the freshwater lenses (Fig. 9b). Besides, the evaporation processes also contribute to the salinization, as well as exposing these areas to the direct entry of contaminants from the surface. When the mining exploitations are at the same height as the adjacent coastal plain and marsh, and even though the sandy sediments used to refill the quarries are permeable, the infiltration of rainwater is lower and, therefore, the lens is less thick. This, in addition to the loss of the positive morphology that determines the existence of the freshwater lens as a recharge zone, leads to the salinization of water in periods of scarce precipitations (Fig. 9c).

In the vicinity of the locality of Cerro de la Gloria, few shell-ridge sectors still preserve the original morphology and maintain the natural hydrological behaviour of freshwater lenses. Even though at present some quarry sectors collect freshwater, these reserves are limited and can only supply the homesteads in neighbouring farms. It should be highlighted that in the vicinity of the village, mainly to the south, there are numerous pits with exploitations below the water table, which not only deteriorate the water resource but also stop urban development.

5. Conclusions

The economic and population development of any region is strongly dependent on water sources. In the case studied, the water

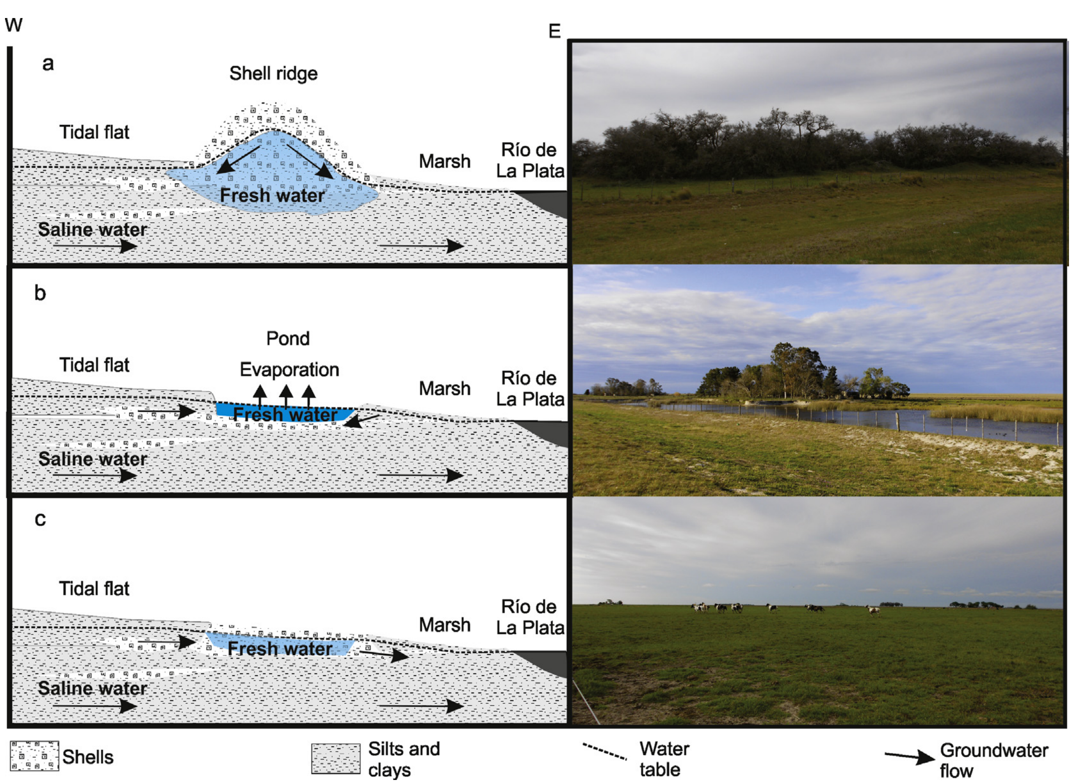

Fig. 9. Diagram showing the hydrodynamic behaviour and the occurrence of freshwater lenses (a) in natural conditions, and (b) and (c) subsequent to mining exploitation.

stored in the lenses of the shell ridges is the only possibility for the supply of fresh groundwater, which is why understanding the hydrogeochemical processes and the state of the reserves is vital in order to develop sustainable management plans.

The hydrogeochemical processes regulating the quality of the groundwater in the freshwater lenses occurring in the shell ridges largely depend on the water/sediment interaction. Among the geochemical processes identified, the contribution of F^- and As by dissolution of volcanic glass is the only process that supplies ions that may limit water potability. Such ions require further monitoring by health and management organizations.

As regards the state of the reserves, mining operations have eliminated the shell ridges and caused the deterioration or loss of such water reserves. The magnitude of the water reserves depleted, according to the estimation carried out (0.97 hm^3), is of no significance for the environmental conditions of the region where drinking water is scarce. Besides, it should be taken into consideration that these estimated values may be higher at present, since mining operations in the ridges continues to be authorised with very lenient environmental legal requirements as regards the preservation of the freshwater lenses.

The exploitation of the shell ridges should be undertaken in a rational manner, considering the sustainability of the freshwater reserves and seeking a balance between the social and economic development, and the preservation of the biological environments of the wetland. In the case of the areas already exploited, refilling them with sandy reject material, levelling the existing pits and revegetating them with native species (*C. tala*) would be measures to be taken so as to minimise the impact on the environment. Even though such mitigating measures would not make it possible to recover the natural hydrological conditions, a UZ would be generated, impeding the contact with the contaminants on the surface and favouring the infiltration of rainwater, as well as the formation of small freshwater lenses. It should be noted that these lenses would only be functional during periods of water surpluses, in which there is higher infiltration of rainwater. In turn, as almost all of the calcareous material has been extracted, the geochemical processes related to the water/sediment interaction shall change. As the locality of Cerro de la Gloria is limited by mining excavations, the refilling of the quarries would also allow urban expansion and eliminate the deep excavations, which are dangerous areas for the inhabitants. Concerning the areas that still remain unexploited, it is essential to develop guidelines aimed at their preservation, in order to ensure the supply of freshwater reserves for the inhabitants of the region.

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