

## **Hydrogeochemistry and pollution effects of an aquifer in Quaternary loess like sediments in the landfilling area of Mar del Plata, Argentina**

## **Hidrogeoquímica y efectos de la contaminación en un acuífero en sedimentos loésicos Cuaternarios en el área de rellenos sanitarios de Mar del Plata, Argentina**

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### **Abstract**

Loess like sediments cover an area of about 1.800.000 km<sup>2</sup> in the Pampa plain of Argentina, forming an aquifer system which is used for water supply for most of the cities and rural population in the region. This aquifer supplies water to agricultural productive activities that contribute to about a 60% of the national gross produce of the country. In this paper, detailed studies in a local sector of the aquifer near to Mar del Plata, in the landfilling area of the city, are performed. The main goal is to characterise the hydrogeochemical processes giving the chemical groundwater composition, and to analyze the impact of the infiltration of the leachate from a neighbouring landfill on some samples. Five wells were drilled to take sediments and water samples. The textural and mineralogical composition of the aquifer sediments was analysed and the chemical composition of groundwater was determined. The equilibrium relationship between the solid phase and groundwater was considered using specific computer codes. The achieved conclusions were that the chemical composition of groundwater is mainly due to calcite equilibrium and cationic exchange with calcium uptake and sodium release. The dissolution of amorphous silica minerals, and subordinate silicate hydrolysis, are responsible of the characteristic high dissolved silica concentrations. High chloride and nitrate contents result from leachate infiltration, but the main geochemical processes in the mix are the same.

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----- *Keywords:* hydrochemistry, Loess sediments, Argentina, mineral saturation, silica contents

### Resumen

Sedimentos de tipo loésico cubren una superficie aproximada de 1.800.000 km<sup>2</sup> en la llanura Pampeana de Argentina, formando un sistema acuífero que es utilizado para abastecimiento de agua a ciudades y la población rural en la región. Este sistema acuífero suministra el agua que sustenta las actividades productivas que contribuyen en un 60% al producto bruto nacional. Es este trabajo se realiza un estudio detallado en un sector del acuífero próximo a la ciudad de Mar del Plata, provincia de Buenos Aires, en el que se localizan tres rellenos sanitarios. El principal objetivo es caracterizar los procesos geoquímicos que dan origen a la composición observada del agua subterránea. Se perforaron cinco pozos para la toma de muestras de agua y sedimentos, y evaluar el impacto de la infiltración del lixiviado sobre esos procesos. Se determinó la composición textural y mineralógica de los sedimentos y la composición química del agua. Las relaciones de equilibrio entre la fase sólida y la solución se determinó utilizando programas específicos. Se concluye que la composición química observada en las aguas es consecuencia principalmente de procesos de equilibrio con calcita e intercambio catiónico con adsorción de calcio y liberación de sodio. La disolución de minerales de sílice amorfo, y la hidrólisis de silicatos en forma subordinada, da origen a altas concentraciones de sílice en las aguas. La mezcla con la infiltración del lixiviado incrementa las concentraciones de los iones conservativos cloruro y nitrato, pero no se modifican en general los procesos hidrogeoquímicos mayoritarios.

----- *Palabras clave:* hidrogeoquímica, sedimentos loésicos, Argentina, saturación de minerales, contenido de sílice

### Introduction

The so-called Pampean sediments [1] represent one of the largest geological formations in Argentina, covering approximately 1,800,000 km<sup>2</sup> (figure 1). These sediments, of silt and silty-sand composition, with interstratified silt-clay layers, are of eolic and fluvial-eolic origin, dating back to the middle to Upper Quaternary. They contain a lot of aquifers which, as a

whole, conform the aquifer system that provides one of the most densely populated and most economically active with a supply of fresh water. In fact, this area accounts for more than a 60% of the national gross product of the country [2]. The quality of the water obtained varies greatly along this system of aquifers, with some areas in the Pampean region evidencing problems related to high contents of arsenic and fluoride [3 - 9] or nitrate [10].



**Figure 1** Distribution of loess deposits in the Argentine Pampa Plain

In order to analyze a hydrogeological system like this, it is necessary to look into the interrelation among its three phases: a gas phase resulting from an exchange with the atmosphere or from biogeochemical processes in the unsaturated zone, a solid phase formed by the minerals that constitute the porous media, and a liquid phase, the aqueous solution that is groundwater. Chemical equilibrium as a way of understanding has been early developed in the work of Chebotarev [11], but especially the work of Garrels and Christ [12] highlighted the usefulness of this tool, leading it to be the most applied methods of analysis at present.

The main goal of this work is to increase the knowledge of the hydrogeochemistry of the aquifers formed by Pampean sediments by mean of a detailed study of the mineralogical

composition of the sediment matrix in contact with the analyzed groundwater samples and the complementary measurement of silica and aluminum in the solution, which allows the consideration of the equilibrium with silicate minerals. Some specific features of the restricted considered area are very locals, i.e. coastal location, marine aerosol contribution in recharge, small thickness of the aquifer, proximity of the hydrogeological basement, etc., and especially the fact that the wells are located very near to a landfill which is operating since 1995, occupying a surface of 40 ha. Previous studies have characterized the groundwater pollution in the area [13 - 15] at a descriptive level.

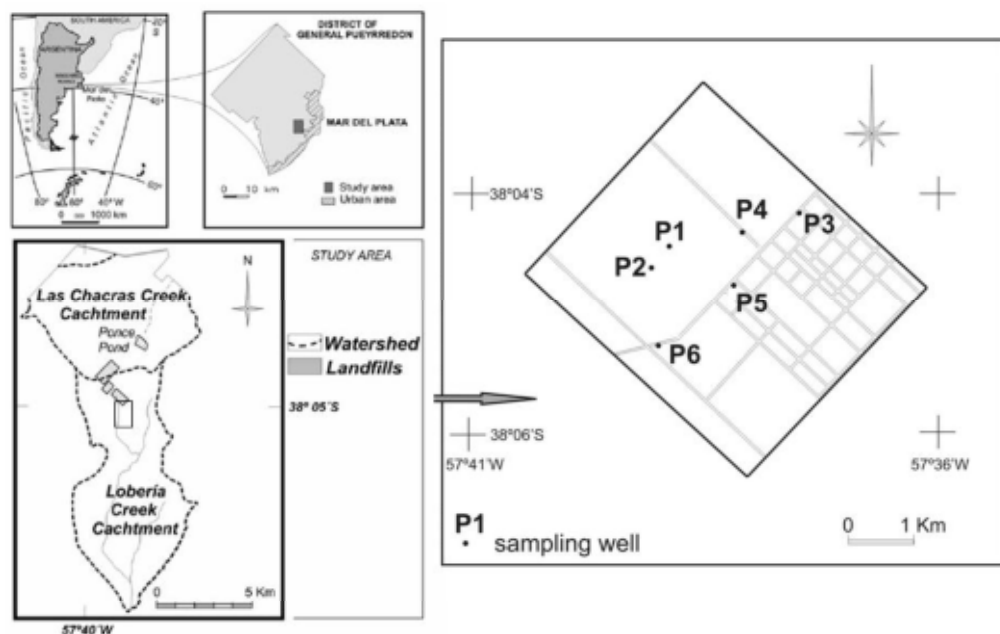
Nevertheless few previous contributions relate hydrochemistry with a detailed mineralogy of the sediments also including clay cristallinity and composition, and which specific processes take place if high recharge is partially affected by landfills leachate. This paper is focused in a single area of the Pampean Plain, but the application of a whole study involving mineralogy, chemistry of sediments, hydrochemistry and processes modeling under chemical equilibrium conditions make it a contribution that rises regional meaning in reference with the study methodology.

The mineralogical composition of the loess-like sediments was described in the study area in an important previous work on the Pampean Loess by Teruggi [16] analyzing samples taken near to Mar del Plata and La Plata, and describing a constant composition in all the considered samples. The content of calcite in this loess and loess-like sediments is about 2% and 4% [17]. A study carried on Pampean sediments in the southeast o the province of Córdoba [3] assign the major composition of sand and silt fractions to feldspars (40-75%) followed by volcanic glass (25-50%), and decreasing proportions of quartz, calcite, muscovite and rock debris. Illite is the dominant species in the clay fraction. Volcanic glass abundance is a distinctive feature of argentine loess, differentiating it from the loess in China that having a similar composition and also CaCO<sub>3</sub> content, doesn't include volcanic shards [18].

### Study area characterization

The study area is presented in figure 2, corresponding to the headwaters sector in the

basin of the Loberia creek (total area 15 km<sup>2</sup>), placed in the District of General Pueyrredón, near to the city of Mar del Plata, at 38°05' lat. S and 57°38' long. W.



**Figure 2** Location map of the study area

The climate is dry sub-humid mesothermal type “B2” [19]. Over the past 10 years, annual precipitation values have ranged from 703 to 1.400 mm/year, with an average of 943 mm/year.

The catchment of the Lobería Creek is characterised by a hilly relief, which is due to a shallow structural control. Blocks formed by orthoquartzites of Early Palaeozoic age corresponding to Balcarce Formation [20]. They are the southernmost spurs of the Tandilia Range [21], and a thickness of more than 400 m has been described in the area, overlying Precambrian metamorphic rocks. Three fault systems are recognized in the Paleozoic bedrock, with NW–SE, NE–SW, and E–W trends with which three joint systems are associated [21].

The orthoquartzites comprise the impermeable hydrogeological basement of the region [22]. They have been reached by the study wells at

depth between 4 and 50 m below the sedimentary cover of loess-like sediments. Though generally considered impermeable, the joints of these orthoquartzites produce a secondary porosity, which considered negligible as an aquifer with regard to the overlying clastic aquifer. The most common sequence presents orthoquartzites topped by loess-like Pleistocene-Holocene sediments and very thin sandy sediments. Hydrologically, these loess-like deposits represent the principal aquifer in the region. The clastic thickness of the analyzed basin was determined by means of drilling and geoelectrical prospecting [13].

The basement reaches a depth of more than 100 m in the distal zone of the basin. The aquifer of Mar del Plata is a Pleistocene sedimentary sequence (silt and silty-sand). The permeability varies from 10–15 m/day. Pumping tests show values for transmissivity of 500 m<sup>2</sup>/day in the southwestern zone of the district, between 500 and

700 m<sup>2</sup>/day in the urban zone, and between 1,000 and 1,200 m<sup>2</sup>/day in the northern and northwestern rural zones. The storage coefficient is in the order of 0.001. The recharge takes place in the upper part of the aquifer in practically the entire exposed area. The recharge reaches the highest levels of the aquifer and from there drains into deeper levels. Rainfall infiltration produces the recharge to the systems. The annual average rainfall for the period 1901–1987 was 851.6 mm. The losses produced by evapotranspiration have been calculated by the Thornthwaite method in 719.2 mm/year, leaving a surplus of 132.4 mm/year.

The underground flow direction is the same as the surface water flow direction on the northern slope, i.e., it is NW–SE. The average hydraulic gradient in the foothills is 0.015, whereas on the plains it is 0.008 [13, 15].

## Methods

Six boreholes of a 4” diameter were built using a rotary machine in a zone of low thickness of the sedimentary section (figure 2). The boreholes were drilled almost on the water divide, corresponding then to a recharge zone where groundwater starts the flow sense towards the SE. The final depth of each well was: P1: 12 m; P2: 6m; P3:11.5 m; P4:15 m; P5: 39.5 m; P6: 12 m, reaching the quartzitic bedrock the wells P1, P2, P3 and P5. A PVC casing was used in each of them. Debris samples were taken each meter of depth to be analyzed in laboratory.

Water samples were taken in each well, including an additional sampling of wells P4 and P5 using the pump at different depths. Water table depth was recorded by using a bipolar probe, and the values were between 2 m and 5 m. Physical-chemical parameters temperature, pH, electrical conductivity (EC) and alkalinity were measured “in situ” during sampling procedure. Partial pressure of CO<sub>2</sub> (P<sub>CO<sub>2</sub></sub>) is obtained if pH and alkalinity are measured as they are related according the expression [23]

$$[\text{HCO}_3^-] = 10^{-7.8} P_{\text{CO}_2} / [\text{H}^+] \quad (1)$$

Codes like NETPATH [24] or PHREEQC [25] compute P<sub>CO<sub>2</sub></sub> automatically from the input alkalinity and pH data.

Considering the well logs, six representative sediment samples were selected to perform detailed studies. The samples correspond to different wells and different depths. The studies include textural analysis by sieving and pipette techniques and mineralogical description of the sand fraction using binocular magnifying glass, X-ray diffraction analysis of the mineralogy of clay fraction using a cooper radiation Philips instrument. Cationic exchange capacity (CEC) and organic matter content were also measured. The content of organic matter was determined using the chromic acid titration method [26]. The chemical composition of the selected sediment samples were analysed by acid digestion spectrometry ICP in order to give a more complete characterisation.

Water sampling methods were according to Kent and Payne [27] suggestions, especially in relation to pumping time to take representative samples. United States Geological Survey (USGS) techniques [28] were applied for water samples conservation. Standard techniques were used to measure the major ion concentrations. Analytical results were processed using PHREEQC2.0 code [25] in order to study equilibrium processes. Saturation indexes (SI) of mineral species were obtained, and some reaction paths were simulated. Netpath code [24] was used to perform mass balances to quantify the identified processes.

## Results

### Solid phase

The textural analysis of the selected sediment samples shows that the material forming the Pampean aquifer present a normal distribution of its grain size, being comprise in the range between phi -0.5 and 11 (32 mm to 0.00005 mm). The modal fraction I in the range from 3.5 to 4.5 phi (0.088 mm to 0.044 mm), indicating that almost the 40% of the aquifer is formed by fine sand and coarse silt. The statistical parameters [29] of the analyzed samples are shown in table 1.

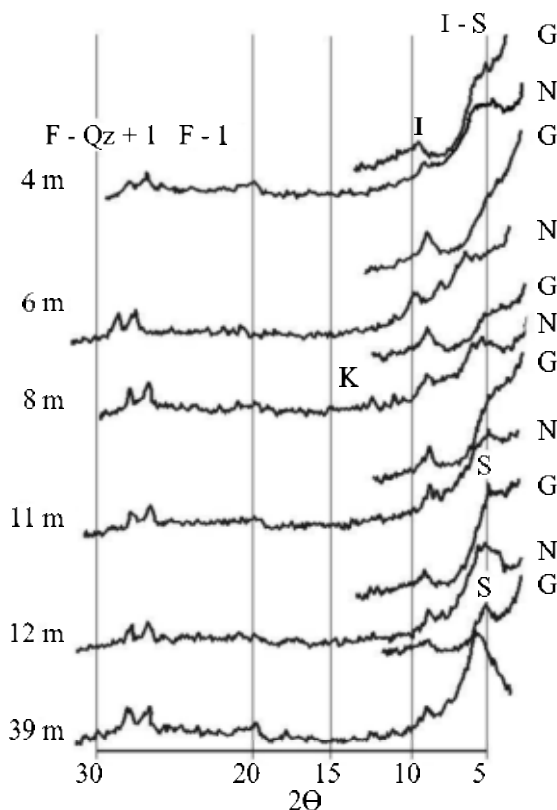


**Table 1** Sedimentary features of the aquifer expressed in weight percentage of each grain size fraction. Statistical parameters expressed in phi units according Folk and Ward [29] percentages, organic matter expressed in weight percentage and Cation Exchange Capacity in meq/100

<i>Well and sampling depth</i>	<i>% pefites</i>	<i>% psamites</i>	<i>% pelites</i>	<i>Media phi</i>	<i>Stand. Dev.</i>	<i>Asymmetry</i>	<i>% Organic matter</i>	<i>CEC</i>
P3-6m	0	39.85	60.15	4.47	1.85	0.255	0.482	19.8
P3-8m	0	53.69	46.31	4.00	2.30	0.115	0.772	35.2
P3-11m	0	57.29	42.71	4.00	2.56	0.059	0.431	-
P1-12m	0	58.10	41.90	3.70	2.79	0.086	0.772	38.8-
P4-4 m	0	56.34	43.66	4.23	1.95	0.313	0.784	-
P5-39m	0	44.00	56.00	4.43	2.54	0.174	0.703	34.4

Quartz is the dominant mineral in the very fine sand fraction, followed by plagioclases, rock debris, potassium feldspar, volcanic glass, mica, pyroxene, amphibole, magnetite, calcite, amorphous silica (mainly silicophytolites and sponge needles), olivine and sillimanite. In general, the weathering degree of the minerals is inversely related to the order of abundance. The most weathering affected minerals are: silicophytolites, rock debris, olivine, pyroxene, mica, potassium feldspar, plagioclases, and finally quartz and volcanic glass that appears with a low weathering degree.

The mineralogy of the clay fraction (figure 3) shows a dominance of expansive minerals, of the type of the smectites to the deeper levels. In the upper levels the interstratified minerals are dominant. They are of the type illite-smectite with poorly defined reflections, only expressed in an expansive zone between 3° and 7° (2θ). Illite is found with the typical reflection at 1.004 nÅ in the natural and glicolated samples, and at 1.765 nÅ in the natural samples. This mineral increases its crystallographic definition to the deeper levels.



**Figure 3** X-Ray diffractogram of the clay fraction at different depths. F: feldspar, Qz: quartz, I: illite, K: kaolinite, S: smectite, N: normal sample, G: glicolated sample

The definition of the reflection peaks of illite muscovite increases to the deeper levels, and more clear peaks of the reflection of calcium and magnesium smectites at 1.496 nÅ and calcium smectites in glicolated samples at 1.522/1.605 can be observed. Kaolinite is present as a trace in surface samples and increases lightly its

abundance to deeper levels. Quartz, potassium feldspars and plagioclases are common in the clay fraction of all the studied samples.

The chemical composition of two samples of sediments taken at 4 m and 6 m depth is shown in table 2.

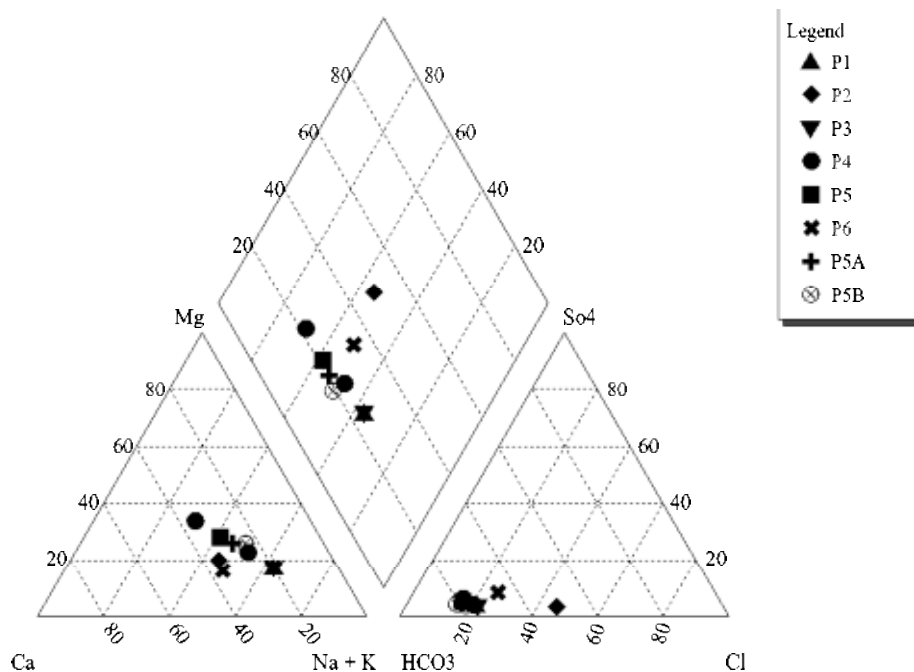
**Table 2** Chemical composition of sediment samples expressed in weight percentage

<i>Oxide g/100g</i>	<i>P 3 prof 6 m</i>	<i>P 4 prof 4 m</i>	<i>Oxide /100g</i>	<i>P 3 prof 6 m</i>	<i>P 4 prof 4 m</i>
SiO <sub>2</sub>	64.9	63.0	P <sub>2</sub> O <sub>5</sub>	0.22	0.19
Al <sub>2</sub> O <sub>3</sub>	16.3	16.6	MnO	0.13	0.11
Fe <sub>2</sub> O <sub>3</sub>	4.7	4.9	BaO	0.07	0.06
CaO	3.0	3.1	SO <sub>3</sub>	0.04	0.03
K <sub>2</sub> O	2.2	1.9	SrO	0.04	0.03
Na <sub>2</sub> O	1.8	1.2	ZrO <sub>2</sub>	0.03	0.03
MgO	1.6	1.8	Cr <sub>2</sub> O <sub>3</sub>	0.01	0.01
TiO <sub>2</sub>	0.68	0.71	PPC 1000°C	4.3	6.3

### **Hydrogeochemistry**

Reliability check of the analysis was done considering the electroneutrality balance. Most of the samples are below the 5% of difference, with the only exception of sample P4 which is about 16%. The results are used anyway considering that despite the analysis includes some non acceptable error; the main conclusions are not strongly affected because of that.

The water samples taken are bicarbonate waters, being sodium waters the samples from wells P1, P3, sodium being dominant cation the samples from wells P2, P4, P5, P5A, P5B, P6. Only the sample P4' presents HCO<sub>3</sub>-Ca/Mg composition. The hydrochemical water-types are represented in the Piper diagram of figure 4. The waters are low or medium salinity, with a salt content between 500 mg/L and 1.250 mg/L. The chemical composition of the samples and their pH and EC values are shown in table 3.



**Figure 4** Piper diagram representing the hydrochemical water-types of groundwater from the study wells

**Table 3** Composition of groundwater samples (Concentration values in mg/l, Specific Conductivity in  $\mu\text{S}/\text{cm}$ , - : no determined)

	<i>P1</i>	<i>P2</i>	<i>P3</i>	<i>P4</i>	<i>P5</i>	<i>P6</i>	<i>P4'</i>	<i>P5A</i>	<i>P5B</i>
pH	7.7	7.5	7.7	7.6	7.7	7.4	7.2	7.3	7.4
TDS	915	1242	1010	959	482	652	-	-	-
Conduct.	1315	1644	1370	1370	712	767	687	569	606
$\text{HCO}_3^-$	610	577	682	684	357	293	385	395	428
$\text{Cl}^-$	101	303	117	107	45	66	47	49	48
$\text{SO}_4^{2-}$	26	27	23	27	17	28	22	16	17
$\text{NO}_3^-$	83	85	89	86	16	83	61	13	16
$\text{NO}_2^-$	0.01	0.06	0.01	0.2	<0.01	0.5	-	-	-
$\text{Ca}^{2+}$	56	134	49	58	40	56	64	43.6	39.2
$\text{Mg}^{2+}$	30	45	20	32	22	15	37	24.3	26.0
$\text{Na}^+$	200	190	244	128	84	78	58	76.7	88.3
$\text{K}^+$	14	9	14	20	14	15	11	10.0	11.6
$\text{F}^-$	0.7	0.5	0.6	0.7	0.8	0.3	-	-	-
$\text{SiO}_2$	-	59	60	60	-	-	66.0	63.4	62.3
Al	-	-	-	-	-	-	0.98	0.80	1.98
Fe	-	-	-	-	-	-	1.02	0.57	0.94
Mn	-	-	-	-	-	-	0.05	0.02	0.03



A main differentiation can be made in water samples. One group is integrated by samples P1, P2, P3 and P4 is characterized by EC higher than 1,300  $\mu\text{S}/\text{cm}$ , chloride concentrations over 100 mg/l and nitrate concentrations exceeding 80 mg/l. On the other hand samples P4', P5, P5A and P5B are low salinity (EC < 750  $\mu\text{S}/\text{cm}$ ) and low chloride (< 70 mg/l) and nitrate (< 16 mg/l) excepting P6 which is 61 mg/l concentrations.

A preliminary explanation is that the first group, more saline and nitrate contaminated, correspond to the shallow boreholes which are closer to the landfill area. On the other side it is the well P5, which is farther from the landfill (about 500 m) and much deeper (39.5 m) because a higher aquifer thickness, and partially well P6 which is also farther. P1, P2, P3 and P4 are probably affected by a leachate infiltration enhanced by the low dilution in so slim saturated zone. P5, P5A and P5B samples, and sample P4' taken at the bottom of P4 seems not to be affected by leachate

infiltration. Also P6 is far enough to the landfill to be affected by leachate infiltration, and its nitrate concentration can be attributed to farming practices in the surroundings.

On the basis of the calculated concentrations as activities it is possible to obtain the saturation indexes (SI) of the solution respecting the minerals that can be formed with the measured components. The SI is

$$IS = \log (\text{Ionic Activity Product/Equilibrium constant})$$

Positive values of SI indicate over-saturated samples, and negative values indicate under-saturated samples. La IS values for some mineral species are shown in table 4.

Most of the samples are under-saturated in sulfate minerals or halogen salts, over-saturated in quartz, and near to equilibrium with carbonate minerals, being calcite the existing phase.

**Table 4** Saturation indexes of some mineral species

<i>Mineral</i>	<i>P1</i>	<i>P2</i>	<i>P3</i>	<i>P4</i>	<i>P5</i>	<i>P6</i>
Anhydrite	-2.626	-2.329	-2.735	-2.593	-2.846	-2.492
Aragonite	0.372	0.489	0.357	0.339	0.062	-0.179
Calcite	0.523	0.640	0.509	0.490	0.214	-0.028
Quartz	-	1.142	1.140	1.140	-	-
Diopside	-2.219	-2.509	-2.465	-2.577	-2.392	-3.615
Dolomite	0.384	0.416	0.236	0.330	-0.225	-1.021
Fluorite	-1.388	-	-1.577	-1.373	-1.332	-2.035
Gypsum	-2.377	-2.079	-2.485	-2.343	-2.596	-2.242
Halite	-6.275	-5.837	-6.127	-6.443	-6.979	-6.847
Magnesite	-0.910	-0.176	-0.223	-0.112	-0.390	-0.945
Amorphous silica		0.138	0.136	0.136		

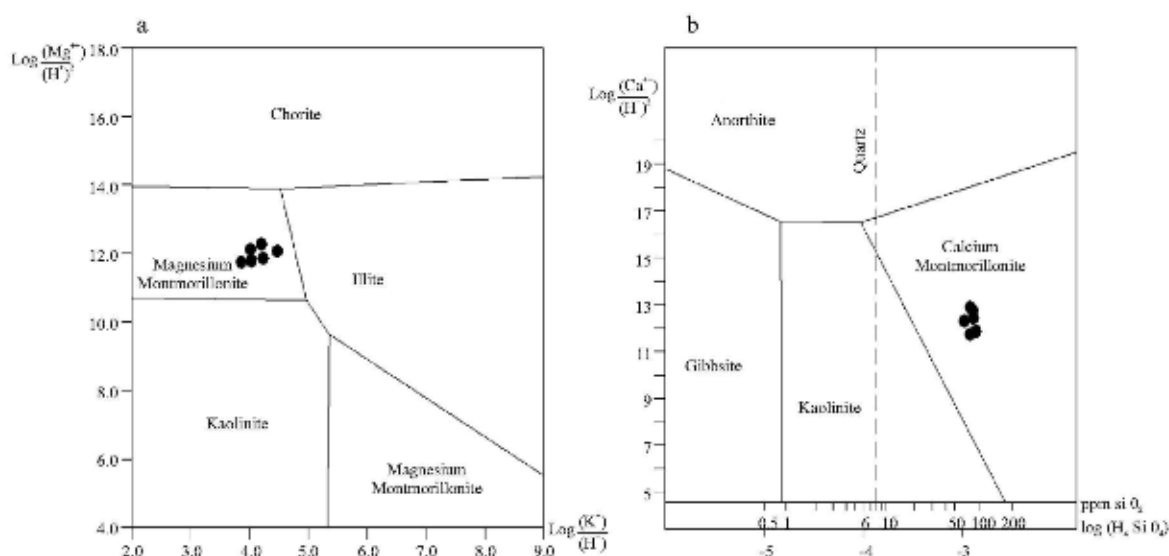
Aluminum was measured in the samples taken in the second sampling, allowing obtaining the SI

of some aluminum-silicate minerals, as shown in table 5.

**Table 5** Saturation indexes in some minerals species, corresponding to samples taken in the second campaign including aluminum data

Mineral	P4'	P5A	P5B
Albite	2.63	2.59	3.03
Anortite	2.06	1.70	2.43
Calcium Montmorillonite	10.18	9.65	10.43
Calcite	-0.04	-0.08	-0.04
CO2(g)	-1.74	-1.81	-1.85
Dolomite	-0.11	-0.20	-0.04
Fe(OH)3	2.39	2.38	2.75
Gypsum	-2.34	-2.60	-2.62
Illite	9.33	8.85	9.72
Potassium feldspar	4.37	4.16	4.61
Muscovite	16.55	15.95	17.08
Quartz	1.17	1.15	1.14
Amorphous SiO2	-0.16	-0.18	-0.19

Using the activity ratios it is possible to plot the observed compositions in equilibrium diagrams as showed in figure 5.a. (taken from [30]). The ionic ratios of the analyzed solutions are plotted in the field of the magnesium montmorillonite. Ionic ratios including calcium area shown in figure 5.b. (from [31]), where it is possible to see that the considered solutions are represented in the calcium-montmorillonite field. Using PHREEQC2.0 it is possible to simulate the reaction between anorthite and rainwater giving as product the neo-formation of calcium-montmorillonite. This reaction, forcing the previous calculated SI, gives as result that it is necessary to dissolve 2.53  $\mu\text{mol}$  of anorthite, resulting in the montmorillonite formation and the release of 3  $\mu\text{mol}$  of  $\text{Ca}^{2+}$  and 5  $\mu\text{mol}$  of Si.



**Figure 5** Stability mineral diagrams taken from: a. [30], b. [31], and plotting of groundwater composition from the study wells

Taking into account the observed equilibrium, and inverse modeling using NETPTAH [24] was performed in order to quantify the processes that

explain the observed compositions. One model was done to explain the non polluted composition model, and the initial solution used was the

average composition of the rain water of Mar del Plata. This average composition is: pH 6.54, Na<sup>+</sup> 18.33 ppm, K<sup>+</sup> 0.2 ppm, Mg<sup>2+</sup> 2.07 ppm, Ca<sup>2+</sup> 3.52 ppm, Cl<sup>-</sup> 16.67 ppm, SO<sub>4</sub><sup>2-</sup> 18.42 ppm and HCO<sub>3</sub><sup>-</sup> 13.10 ppm. The final composition is that of sample P5A.

The models devoted to explain groundwater composition of the polluted wells use as initials a mix between rain water and leachate average composition [13] to achieve the final composition of sample P2. This average leachate composition is: pH 8.21, Na<sup>+</sup> 426.5 ppm, K<sup>+</sup> 22.8 ppm, Mg<sup>2+</sup>

74.9 ppm, Ca<sup>2+</sup> 77.4 ppm, Cl<sup>-</sup> 665.7 ppm, SO<sub>4</sub><sup>2-</sup> 62.3 ppm and HCO<sub>3</sub><sup>-</sup> 587.2 ppm.

According the observed SI the considered processes were carbonate equilibrium, amorphous silica equilibrium, loss or dissolution of CO<sub>2</sub> and cationic exchange. The solid phase calcium montmorillonite was also included. The increase in chloride concentration was used to calculate the rain water evaporation factor. The obtained results were very similar for the three final solutions, showing below the model corresponding to sample P5A in table 6.

**Table 6** Results from the geochemical inverse modeling using NETPATH code. Initial solution is average rainfall composition and final solution the composition of sample P5A

<i>Phase</i>	<i>Process</i>	<i>Mass transference mmol/l</i>
cALCITE	Dissolution	2.07473
CO2 GAS	Dissolution	4.02387
EXCHANGE	Calcium uptake and sodium release	1.24604
Mg/Na EX	Sodium uptake and magnesium release	0.75009
SiO2 (amorphous)	Dissolution	1.00917
Ca-Montmorillonite	Dissolution	0.1273
Evaporation factor	Evaporation	2.943

On the other hand the results of modeling for polluted groundwater are shown in table 7, considering almost the same processes but considering rain water and leachate mixing

during recharge after reacting with the solid phase. The formation of iron monosulfides (Fe-S) was included to explain the sulfur decrease in the mass balance.

**Table 7** Results from the geochemical inverse modeling using NETPATH code. Initial solution is average rainfall mixed with leachate average composition, and final solution the composition of sample P2. (\* mixing proportion of each initial solution)

<i>Phase</i>	<i>Process</i>	<i>Mass transference mmol/l</i>
Mixing*		0.56 rain - 0.44 leachate
CALCITE	Dissolution	2.77620
CO2 GAS	Dissolution	2.86452
EXCHANGE	Calcium uptake and sodium release	0.26297
Mg/Na EX	Sodium release and magnesium uptake	-0.44508
Ca-Montmorillonite	Dissolution	0.26792
Fe-S	Precipitation	-0.11223

## Discussion

The chemical composition of groundwater is the result of the interaction with the minerals present in the flow path. The ratio  $\text{Ca}^{2+}/\text{Mg}^{2+}$  determines that calcite is the most stable carbonate mineral. The SI values for calcite are consistent with this sentence, being near to 0. SI of dolomite also is near to equilibrium, but this mineral has not been identified in the sediments of the aquifer, and its precipitation is not possible according to its diagenetic origin as determined by Berner [32]. Other minerals of fast reaction, like gypsum, halite or mirabilite are under-saturated, and then they must not be presents in the sediment in the study area.

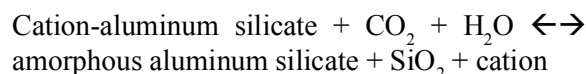
Calcite SI indicates equilibrium conditions in the samples showed in table 5, but oversaturation in the samples included in table 4. These oversaturation conditions correspond probably to sampling errors, being possible that the pH measurements in surface were affected by the sample aeration due to the pumping by a centrifugal pump.

The SI of the silicate minerals forming the aquifer matrix indicates oversaturation in all the cases. According the magnesium/potassium ratio represented in stability diagrams, magnesium montmorillonite is the stable clay mineral. Taking this into account it is possible that montmorillonite is a neoformation product mineral, while illite should be of detritic origin. Taking into account the ratio of calcium and proton activities, and the activity of silica in solution, calcium montmorillonite apperas as the stable phase against anortite, which unstable in this environment. Then it is again considered that anorthite is of detritic origin and calcium montmorillonite due to neoformation. The increase in the proportion of smectite toward deeper levels, together with the increase in its degree of crystallinity, supports the hypothesis of the neoformation of these minerals. Moreover, the modeling performed with PHREEQC demonstrated numerically the coherence of the reaction of incongruent dissolution of anorthite,

the montmorillonite neoformation and the addition to solution of calcium and silica. The incongruent dissolution of silicates produces an effect on groundwater that is the addition of cations and silica, and in a secondary way the bicarbonate formation [23].

The SI value of amorphous silica of 0.16 shows an equilibrium state. The high concentration of silica, which is a characteristic of the pampeano aquifer, can be explained by the dissolution of the amorphous silica minerals, and in a lower degree by the weathering of silicates. Among the amorphous silica minerals the more abundant are volcanic glass and silicophytolites. In spite of the alteration of volcanic glass has been observed in other areas of the Pampean Plain [3], in the studied sector the volcanic glass shards are observed in general with a low degree of weathering. The dissolution of biogenic silica minerals has been evidenced for their high degree of weathering, bringing silica to the solution. Taking into account the dominant water type existing in the area ( $\text{NaHCO}_3$ ) it should be important to mention that Marshall and Warakowski [33] demonstrated that the solubility of amorphous silica is higher in  $\text{NaHCO}_3$  solutions. The amorphous silica minerals present in the argentine loess are the reason of the high contents of dissolved silica. Groundwater in the loess form China, not containing important proportions of amorphous silica, has just about 10% to 20% [18] of the amounts of silica determinate in this study.

Moreover the incongruent dissolution of silicates and monmorillonite neoformation involves a reaction of the type:



The cation composition given to the solution by the silicate dissolution processes are later affected by exchange processes in adsorption surfaces. Cation exchange capacity (CEC) measurements in the sediments result in values in the order of 30-40 meq/100 g. The main exchange processes in this aquifer have been specifically studied [34], determining in the recharge areas like

that considered in this work the dominance of calcium uptake and sodium release. The cation adsorption selectivity determined for normal flow conditions from recharge to discharge zones is  $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$  and is responsible of the evolution from calcium waters to sodium waters.

Inverse hydrogeochemical modeling applied to non polluted (i.e. low chloride and low nitrate groundwater) indicates that, starting from rain water, to achieve the composition of the sample P5A, it is necessary: to dissolve 2.047 mol of calcite, 4.024 mol of  $\text{CO}_2$  and 1.009 mol of amorphous silica. In the cationic exchange process 0.49 mol of  $\text{Na}^+$  and 0.75 mol of  $\text{Mg}^{2+}$  are released and 1.246 mol of  $\text{Ca}^{2+}$  are uptake. A small quantity of calcium montmorillonite must be dissolved to explain the  $\text{Al}^{3+}$  in solution. Nevertheless, it should be noted that  $\text{Al}^{3+}$  was not measured in rain water, considering 0 its concentration.

Inverse modeling applied to a contaminated sample indicates approximately equal proportions of landfill leachate infiltrates mixed with precipitation recharge. This mixing contributes with most of the high salinity, i.e. dissolved chloride and sodium, while the other ions seem to be affected by the same processes than in normal evolution.

### Conclusions

The hydrochemistry of the Pampeano aquifer system is the result of the interaction of recharge water, mainly rain water, with the mineral phases forming the aquifer. Taking into account the mineralogical composition there are two main kind of processes: chemical equilibrium between the solution and some minerals, specially calcite and amorphous silica, and cationic exchange. Calcite is a mineral widely distributed in Pampean sediments present forming compact layers or disseminated as small concretions, and equilibrium condition can be assumed according the rapid reversible dissolution reaction. Amorphous silica is present as volcanic glass shards or silica minerals formed by biological

(vegetal) processes known as silicophytolites. As mentioned silicophytolites appears more weathered than volcanic glass in the study area. Amorphous silica minerals dissolution is responsible of one of the most noticeable features of groundwater from loess pampean aquifers, which the high dissolved silica contents, ranging usually in the order of 50-70 mg/L.

Groundwater in the area is in equilibrium respect to calcite and amorphous silica and oversaturated with respect to most of the silicate minerals forming the aquifer. The solution is subsaturated in sulfate and halogen salts, which explains the absence of gypsum or mirabilite in the sediment. The cation adsorption selectivity determined for normal flow conditions from recharge to discharge zones is  $\text{Ca} > \text{Mg} > \text{Na} > \text{K}$  and is responsible of the evolution from calcium waters to sodium waters, and the high CEC of the loess-like sediments in the Argentine Pampa enhance the importance of the process. Incongruent dissolution of silicates with montmorillonite neoformation is also partially responsible of silica and calcium content.

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