HYDROGEOCHEMISTRY AND STABLE ISOTOPES OF A SOLID WASTE DISPOSAL AREA FROM GUALEGUAYCHÚ, ENTRE RÍOS, ARGENTINA

Romina Sanci[1]*, Héctor Osvaldo Panarello*, Fernanda Cravero+

*Instituto de Geocronología y Geología Isotópica
Universidad Buenos Aires - Consejo Nacional de Investigaciones Científicas y Técnicas, Pabellón INGEIS, Ciudad Universitaria, C1428EHA, Ciudad Autónoma de Buenos Aires, Argentina

+CETMIC (Centro de Tecnología de Recursos Minerales y Cerámica)
Camino Centenario y 506, Gonnet, La Plata, B1897ZCA, Argentina

Tel: +54 1147833021/3022/3023; Fax: +54 1147833024
rominasanci@hotmail.com; romina@ingeis.uba.ar

ABSTRACT

Major and trace elements, pH, electrical conductivity and organic matter were determined in groundwater and subsoil samples collected from an urban solid waste final disposal site (Gualeguaychú city, Argentina) in order to quantify leachate impact on the quality of these resources. Geochemical modeling results showed mixing process of pristine water and leachate in different proportions which promote, in turn, other processes in the free aquifer such as cation exchange, outgassing of carbon dioxide, precipitation and dissolution of minerals. Anomalous electrical conductivity values of subsoil samples confirmed the leachate impact too. Soil-water interaction allowed the development of natural attenuation processes in water: low dissolved organic carbon (DOC), iron and aluminum concentrations were associated with high amounts in subsoil. High clay content (smectites) and high cation exchange capacity, organic matter and metals analysis suggesting that the exchange and or sorption process were effective. δ^{13}C-DOC constant values ratified the DOC sorption in sediments rather than oxidation. Other natural processes such evaporation and marine ingressions were detected through geochemical models. δ^{18}O y δ^2H values suggested not only a meteoric origin for the groundwater but also evaporation and mix process of waters. δ^{13}C-DIC demonstrated that CO_2 outgassing could have happened during the mixing.

Keywords: leachate; contamination; environmental isotopes; geochemical processes

INTRODUCTION

The urban solid waste (USW) final disposal sites are characterized for presenting different environmental problems related with pollutants that result from the physical, chemical and biological processes that act upon the waste. Leachate formation is one of the problems associated with these sites, since water percolation through the deposited waste extracts both organic and inorganic materials that dissolve and infiltrate into the porous media and could deteriorate soil and

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[1]*Corresponding author*

groundwater quality of the area and surrounding areas due to migration. This leachate composition will depend on initial humidity and waste composition, the amount of water that infiltrates by rain or that could enter the landfill as groundwater, on cover material permeability, the reactions associated with the degradation of the materials which form the cover and age of USW (Bocanegra et al., 2001). Pollutants from these leachates usually correspond to three great groups: dissolved organic matter, inorganic elements (Ca^{2+}, Mg^{2+}, Na^+, K^+, NH_4^+, Fe, Mn, Al, Cl^-, SO_4^{2-} and HCO_3^-) and heavy metals (Cd, Cr, Cu, Pb, Ni and Zn) (Christensen et al., 2001; Kjeldsen et al., 2002). Once these compounds are incorporated into the subsoil, in places where there are no environmental practices as to how to collect and treat them, different mobilization pathways are presented: compounds are either trapped in the soil because they are either dissolved in the aqueous phase or occupying exchange places, adsorbed on inorganic constituents (clays or Fe, Mn and Al oxides), associated with organic matter and/or precipitated as pure or mixed solids, or they can move to surface or ground waters (García and Dorronsoro, 2005). The polluting nature of this antropic source results in the emission of pollutants even after its closure and for a time span that can involve years. Therefore, in the areas where this kind of activities takes place, without control of contaminants, it is imperative to evaluate the processes that influence the generation, transport and destination of the pollutants. In order to explain and predict changes in groundwater composition near and away from contaminant source, the hydrogeochemical data sets contain the information on governing geochemical processes (cation exchange, proton buffering, mineral precipitation, degassing, redox as degradation of DOC inside the plume). Modeling is essential to deduce and quantify these processes in order to demonstrate and understand these mechanisms. Also, it is not only necessary to have hydrochemistry and mineralogical data from a sector of free aquifer of Cura Stream Basin but also information about the unsaturated zone affected by the disposal of waste. It is known that most processes that cause attenuation or remove pollutants from the subsoil are much more important in the soil profile as a result of its huge content of organic matter and clays and its great bacterial population. For example, heavy metals (Hg, Pb, Zn, Ag, etc.) are not always able to reach groundwater because processes like adsorption on clay surfaces or on organic matter or the formation of insoluble complexes may fix or delay their movement (Ogundilan and Afolabi, 2008). The same effect is achieved by the cation exchange capacity of the soil that plays an important role in the retention of metal cations generated through natural or anthropic processes. Therefore, and in order to be able to detect possible natural attenuation of contamination , it is important to know the cation exchange capacity of the soil in the study area (emphasizing the detection of organic matter and clays) and evaluate the precipitation and/or buffering processes (e.g. van Breukelen et al., 2003; Berj et al., 2005). Also, the use of environmental isotopes in water (hydrogen, oxygen and carbon) in conjunction with major ions contributes to detect contamination by leachate (e.g. North et al., 2004; Castañeda et al., 2012).

For this research, we first checked if there were mixing processes between leachate and groundwater that could affect the quality of this resource, quantifying its impact. In order to do this, a geochemical model was elaborated with data from major elements, temperature, pH, electrical conductivity, dissolved organic carbon and some metals from the unconfined aquifer by means of the NetPath program (Plummer et al., 1991; Plummer et al., 1994) which enabled to identify the reactions that help to explain the physico-chemical characteristics observed to explain along the groundwater flow. These same reactions were validated in turn, by field observations and mineralogical data of subsoil samples and the use of isotopes in groundwater. Besides, in order to evaluate the impact of leachate in the unsaturated zone, subsoil samples were taken from up to 2 m deep both in pristine and USW affected areas taking into account that electrical conductivity is an indicator of soil pollution. Thus, this parameter was quantified as well as some of the elements that may contribute to generate it e.g. some cations -Ca, Mg, Na, K- and heavy metals, together with cation exchange capacity, organic matter, carbonates and texture.

Area Descriptions

The study area is the Municipal USW final disposal site of Gualeguaychú, Entre Ríos, Argentina. The zones filled with USW cover approximately 34 ha and do not have subsoil gas extraction systems or leachate collection systems. This site is confined to the low area of El Cura Stream Basin, towards the south of the cited city, in the vicinity of the confluence of El Cura Stream and the Gualeguaychú River (Figure 1). Two geomorphological units are widely distributed in the basin: the loessic plain (LP) and the alluvial plain (AP) formed chiefly by two reddish-brown loessic levels (called "Pampean sediments) and silty to silty-clayey materials, respectively. These two levels are recognized within LP as Hernandarias Formation (Middle Pleistocene) and Tezanos Pinto Formation (Upper Pleistocene), and they have large lithological and hydrogeological similarities. Materials conforming these formations are silts and silty clays of aeolic origin (loess) with variable proportions of fine to very fine sand and different degrees of carbonate cementation and disseminated calcium carbonate concretions of approximately 2 cm long (Iriondo, 1980). Regarding the mineralogy, both levels contain in their sand fraction mainly plagioclase, quartz, volcanic glass, microcline and lithic fragments; in their pelitic fraction, quartz, phyllosilicates, plagioclase, amorphous minerals and in a smaller proportion, potassium feldspar; in their clay fraction, in a major proportion, smectites, with micas and illites (Boujon and Sanci, 2014). Between both loessic levels, discontinuous deposits of greenish silt with a high content of marine fossils were observed (Boujon et al., 2011; Boujon and Sanci, 2014), in coincidence with the levels described by Guida and González (1984) referred as the "Belgranense" marine ingression of the Late Pleistocene. The Hernandarias Formation presents numerous interbedded fluvial sediments in its interior, which confer it a marked heterogeneity, and gypsum accumulations towards its base and calcareous concretions or discontinued levels of tosca towards its top (Iriondo, 1996).
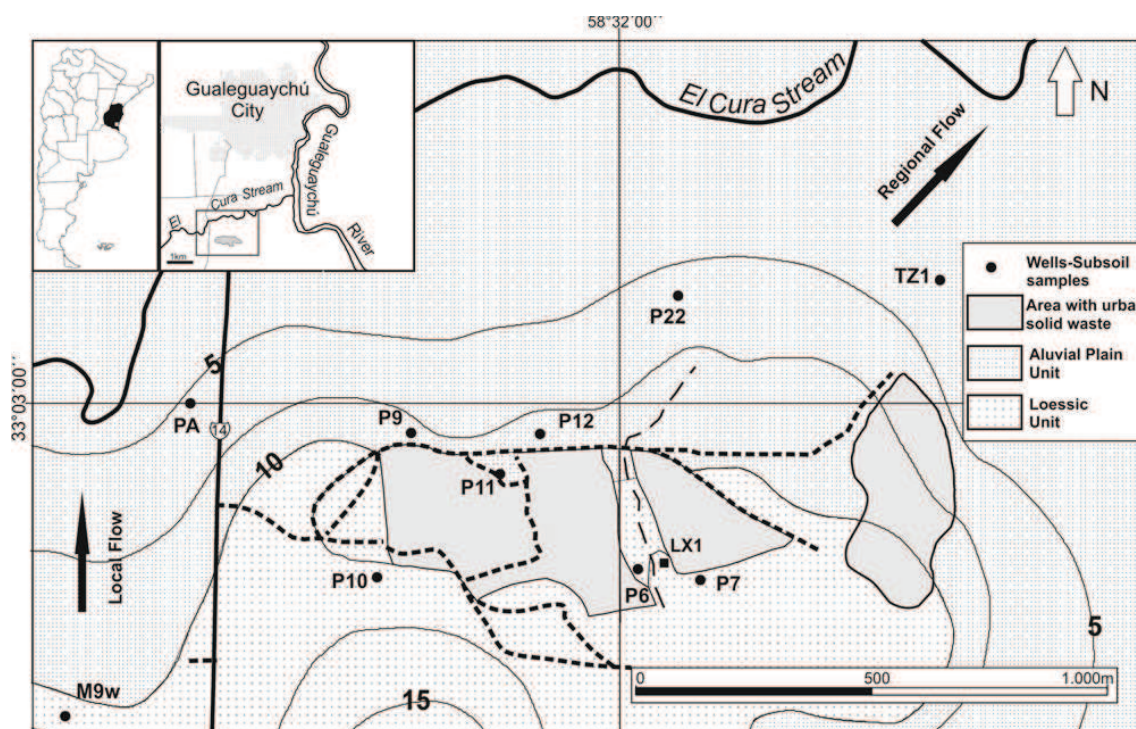
FIGURE 1
The study area (urban solid wastes final disposal site) showing the sampling locations, the predominant direction of groundwater regional (SW to NE) and local flow (S to N), and geomorphological units (loessic plain and alluvial plain). Right upper quadrant indicates the geographic location and confluence of El Cura Stream and Gualeguaychú River.

In El Cura stream basin, the "Pampeano" or "Pampean sediments" are located below the soil cover on sites topographically high and intermediate (between 50 m and 10 m contour lines) (Boujon and Sanci, 2014). It is a really continuous and its thickness ranges between 10 m and 45 m. Its hydrogeological importance is given because it behaves as free aquifer and contains the water table. The regional flow network obtained from water levels measured in the free aquifer within the basin showed that groundwater moves predominantly from SW to NE, in coincidence with the regional topographic slope of El Cura stream basin and the increase of salinity (from about 90 mg/L to 859 mg/L) in the same direction (Boujon y Sanci, 2014). Water from the free aquifer is for human and animal use and irrigation purposes. Locally, the USW final disposal site has 10 piezometers placed up and down stream (M9w, P10, P6, P7, P5, P11, P9, P12, P22, TZ1) whose depths never exceeds 4 meters. The local conceptual model for this area shows that groundwater, collected by piezometers P (Figure 1), corresponds to shallower flow lines (S-N oriented) and less influenced by the regional flow system (Boujon et al., 2011; Boujon, 2014).

The predominant soils within the LP geomorphological unit were the Vertic Argiudolls, subgroup of soils classified according to the Soil Taxonomy (Soil Survey Staff, 2014). They are characterized by a powerful mollic epipedon and a thick well-structured argillic horizon underneath, with these typical horizons: A1 A2 BA Bt1 Bt2 BCk and Ck (Boujon and Sanci, 2014). In general, "A" denomination relates to a mineral horizon obscured by organic matter, "Bt o Bk" to mineral horizon formed by accumulation of clays or calcium carbonate respectively, and "C" to mineral horizon little affected by pedogenic processes. On the other hand, in the AP unit, soils are poorly developed; there is a wide predominance of acquic moisture regime soils, simple profiles and evidences of repeated and continuous soil rejuvenation. Typic Endoaquols are the predominant ones (A-AC-C horizons).

Methods

A physico-chemical analysis of the unconfined aquifer was performed from 10 samples from piezometers located inside the Municipal USW disposal ground (Figure 1). The following parameters were determined: temperature, pH, electrical conductivity (E.C.) carbonates (CO_3^{2-}), bicarbonates (HCO_3^-), sulfates (SO_4^{2-}), chlorides (Cl^-), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+) and dissolved organic carbon (DOC). pH, E.C. and temperature were measured *in situ* and samples were taken and kept refrigerated until their analysis in the laboratory. CO_3^{2-} and HCO_3^- determinations were carried out 24 hours after receiving the samples by titration with sulfuric acid (H_2SO_4). Magnesium (Mg^{2+}), calcium (Ca^{2+}), sodium (Na^+) and potassium (K^+) were determined by atomic absorption spectrometry (Buck Scientific 200A), sulfate (SO_4^{2-}) by inductively coupled plasma atomic emission spectrometry (BAIRD-ICP 2070) and chloride (Cl^-) by titration with silver nitrate

(AgNO$_3$). Dissolved organic carbon (DOC) was determined by the SM (Standard Methods) 5310B analytical technique. Samples for dissolved methane analysis were taken and analyzed following Lomond and Tong (2011) procedure. For analysis of heavy metals in water, samples were filtered through Whatman G / F of 0.45μm pore size that were stored in 100 ml sterilized flasks and acidified and sterilized acidified with nitric acid to pH less than 2. The quantification of metals was performed by atomic emission spectrometry inductively coupled plasma (ICP).

Isotopic ratios of hydrogen (δ^2H), oxygen (δ^{18}O) and carbon (δ^{13}C) were measured in well pristine water (M9W), the leachate (LX1), P samples and PP sample. During 4 months prior to the survey, monthly integrated samples were collected in an ad hoc container placed at the landfill surveillance building in order to verify isotopic values (^{18}O and ^{2}H) of study area (sample PP). Carbon inorganic dissolved (DIC) from water was precipitated as BaCO$_3$ adding BaCl2 to 100 mL of sample previously adjusted to pH 11 (Valencio et al., 2003). The precipitates underwent *in vacuo* heat treatment at 350°C to remove organic matter interferences and then they were directly introduced into the extraction system. Carbon isotopic ratios ^{13}C/^{12}C were measured on CO$_2$ extracted from carbonates with phosphoric acid 100% according to McCrea's (1950) method modified by Panarello et al. (1982). The cryogenically purified CO$_2$ was contrasted with an internal reference (Carrara marble). Data was informed as isotopic deviations (δ ‰) relative to the international reference standard V-PDB, with an analytical uncertainty of ±0.1‰. Isotopic analyses (^{2}H and ^{18}O) were made by laser spectroscopy in a Los Gatos Research (LGR) Liquid Water Isotope Analyzer (OA-ICOS: Off-Axis Integrated Cavity Output Spectroscopy) at the Stable Isotopes Laboratory at the INGEIS. The reference standard used is the Vienna Standard Mean Ocean Water (V-SMOW). Isotopic results are expressed as δ, defined as δ= 1000(RS - RP)/ RP ‰, where δ is the isotopic deviation in ‰; S: sample; P: International reference; R: isotopic ratio (^{2}H/^{1}H, ^{18}O/^{16}O, ^{13}C/^{12}C).

DOC samples were prepared based on the technique described in Gandhi *et al*. (2004). A sample volume containing about 50 umol C was transferred to 50mL beakers (that were previously decontaminated with 50% nitric acid) and placed in an oven at ca.50°C, till dryness. 1mL of ultra-pure water was then added to the sample together with 85% phosphoric acid (ca. 100-300 uL) and agitated to remove DIC. More ultra-pure water was added to reach 2mL. 150uL of the concentrated sample were then transferred to tin capsules for liquids in several aliquots. The samples were dried in an oven (ca.50ºC) after each transfer. The closed capsules were then measured in a Carlo Erba Elemental Analyzer 1180, coupled to a continuous flow Thermo Scientific Delta V mass spectrometer through a Thermo ConFlo IV interface.

The hydrogeochemical data were subjected to hydrogeochemical modeling. Inverse mass-balance models were performed using NETPATH (Plummer et al., 1991). In order to determine if the quality of groundwater has been affected by leachate, ion Cl- was used in calculations as it is a conservative ion. Piezometer M9w (pristine) and sample LX1 were taken as initial water and P6, P11, P9,P 12 and P22 as

final water due to their geographical location (downstream) from USW and LX1. Since the plot does not have a leachate collection system from which pure leachate could be extracted, a "most possible representative" sample, named LX1 was taken from a small depression next to the waste heap from where that effluent (very dark in color) could be captured before its infiltration. In TZ1, due to its high chloride content (higher than LX1), a typical marine ingression water was added to the mixing (Plummer et al., 1994). The chemical and sedimentary characteristics of the study area, with the presence of discontinuous levels of marine ingressions, could support this assumption. The program required for its operation that there is at least one phase for each of the incorporated ion (constraints). Therefore the minerals for modeling were chosen from background data and identifications performed by X-ray diffraction.

The analysis of the soil samples from each site included pH (soil-water ratio 1:2.5; Peech 1965), electrical conductivity of the saturated paste extract (soil-water ratio 1:2.5) (Bower & Wilcox 1965), total carbon (Richter & Wistinghausen 1981), cation exchange capacity (CEC), exchangeable Ca, Mg, Na and K (Chapman 1965) and calcium carbonate equivalent. The texture of the samples from each site was determined using the gravimetric method. Subsoil samples were dried at 40 °C, filtered by 2 mm, homogenized and stored in plastic bags before analysis. The total content of metals (Fe, Mn, Al, Zn, Cu, Cr) in higher EC levels (25-50 cm) was also determined. XRD was performed using a Rigaku D-Max III, with Cu-Ka radiation and a graphite monochromator operated at 35 kV and 15 mA. XRD patterns were recorded on whole rock from 2º to 60º 2Θ and on the fraction <2 μm from 2 º to 30 º 2Θ to check for impurities. Once carbonates were eliminated, the fraction < 2 μm was obtained by centrifuging a suspension at 750 rpm for 3.3 min. In order to check for the presence of expandable clay minerals, samples were intercalated with ethylene glycol.

Results

Physico-chemical and isotopic data (δ^{13}C-DIC, δ^{13}C-DOC, δ^{18}O and δ^2H) from the samples taken in September, 2012, are shown on Table 1. As it can be seen in Figure 2, the influence of USW on the free aquifer resulted in a rise in Cl$^-$, SO$_4^{2-}$, Na$^+$, HCO$_3^-$, Ca^{2+}, Mg^{2+} and K$^+$ compared to the values from the reference water for this study, M9w. Some exceptions to the rule are the Ca^{2+}, Mg^{2+}, Na$^+$ and HCO$_3^-$ concentrations from P10, the Mg^{2+} and Na$^+$ from P7 and the SO$_4^{2-}$ from P9. Even if the differences are small, it is worth pointing out that Cl$^-$ (conservative element and leachate indicator) concentrations increase considerably in all cases in waters from the piezometers located downstream of the USW disposal area. At TZ1, the chloride ratio was much higher than at the other sampling sites (a 34:1 ratio), thus, the influence of another process other than mixing was considered. The existence of leachate is not only confirmed by the presence of chlorides but also by an increase in the electrical conductivity in water, an increase in DOC and a decrease in dissolved oxygen when compared with values from M9w. pH from M9w and LX1 are slightly alkaline whereas those from

TABLE 1

Physico-chemical and isotopic data (δ^{13}C-DIC, δ^{13}C-DOC, δ^{18}O and δ^{2}H) from water samples taken in September 2012.
M9w: pristine water; LX1: leachate. ND: not determinated

| Sample	pH	CE µS/cm	T °C	O2 mg/L	HCO3- mg/L	Cl- mg/L	SO42- mg/L	Ca2+ mg/L	Mg2+ mg/L	Na+ mg/L	K+ mg/L	NO3- mg/L	CH4 mg/L	DOC mg/L	δ13C-DOC ‰	δ13C-DIC ‰	δ18O ‰	δ2H ‰
P10	7.08	810	17.6	3.5	265	71	66.8	20.7	5.2	135.8	10.5	2.8	0	37.8	-24	-12.6	-1.8	1
P7	6.96	920	17.6	3.2	477.3	35.5	45.7	55.7	12.7	112.6	16.3	0.9	0	31.2	-25.9	-11.8	-3.1	-10
P6	7.01	3340	17.5	2.8	1794	177.5	62	50.7	19.4	795.4	3.1	1.1	0	16.7	-23.9	-6.7	-5.2	-25
P11	7.39	1840	18.6	4.3	1004	35.5	61.5	47	11.3	382.6	2.1	2.1	0	6.5	-25	1.3	-5.7	-27
P9	6.96	1730	17.4	2.8	1034.4	89	16.9	87	25.6	322	3.5	3.2	0	8.2	-24.7	6.1	-6.0	-29
P12	6.91	2020	17.4	2.9	1074	159.2	31.4	89.5	39.9	266.2	4.3	1.6	0	6.3	-25.7	2.5	-5.3	-26
P22	7.01	1480	16.3	4.3	730.5	88.8	63.6	90.8	28.1	205.4	5.8	4.1	0	3.1	-24.8	-5.6	-4.9	-24
M9w	7.4	757	18.5	6.2	417	13	25	51	13	146	2.4	3.28	nd	1.5	nd	-12.6	-4.8	-27
LX1	8.17	3207	22	0.2	1394	195	37.2	106	33.7	262.5	170	10.5	0	243	-25.4	9.1	-2.4	-4
TZ1	7.96	2710	18.1	3.2	710.3	443.8	157	53.2	60.5	500.8	0.8	3.9	0	4.4	-24.2	-12.5	nd	nd
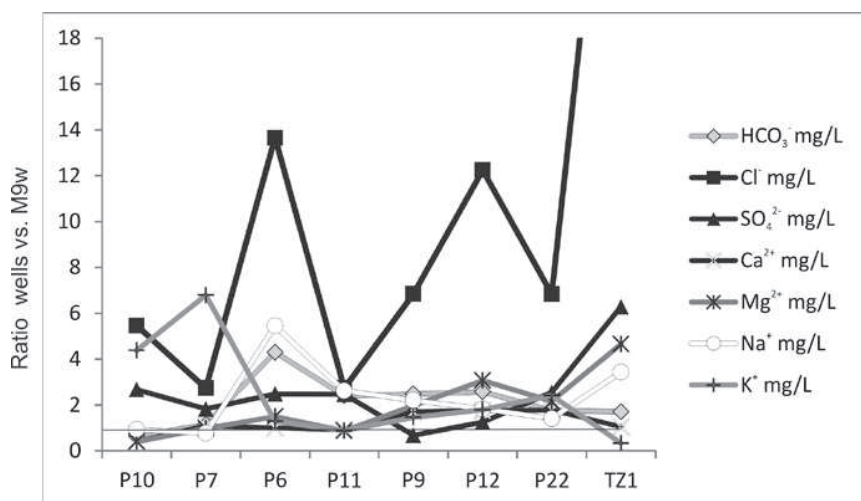
FIGURE 2
Concentrations of major elements compared to the values from de reference water (M9w).

P samples are neutral. On the other hand, data represented on a Piper diagram (Figure 3) show that the water samples, with the exception of TZ1, fall into the HCO_3- Na^+ water type, pointing out that the prevailing process has presumably been cation exchange. TZ1 is sodium chloride-bicarbonate water that would indicate the mixing of waters from the first type with another source with a higher chloride content, compatible with a marine ingression. Metallic trace elements are found in low concentrations (Table 2) and below the levels allowed for human consumption according to the Argentine Food Law, except for Mn that exceeds 0.10 mg/L in P7 P6 P9 P12 and P22. In all cases, the highest content of dissolved metals was found in LX1, where Fe, Mn, Al, Zn, Cu and Cr were present, with the exception of As, which presented the highest concentration in piezometers P. Cd, Cr and Pb were not found in those piezometers and Fe was only found in P10, P7 and P6, whereas Al was found in P10 and P7 and Cu, in P10, P11 and TZ1. Arsenic anomaly in samples P (higher values than LX1) probably corresponds to background values in the Chaco-Pampa Plain (Nicolli et al., 2012).

For the geochemical modeling, the following phases were considered: Calcite ($CaCO_3$), due to its abundance in the aquifer either in nodules, continuous levels or cementation; (H-exchange) to represent the exchange of Ca^{2+} by Na^+ and H^+ through clays (mainly montmorillonite-smectite), due to the nature sodium bicarbonate water and neutral pHs; CO_2 phase as exchange with the atmosphere since it is an open system; K-montmorillonite as capable mineral phase of incorporating K^+ excess of the mixing; and Gypsum as source of sulfate, characteristic of arid environments such as loess.
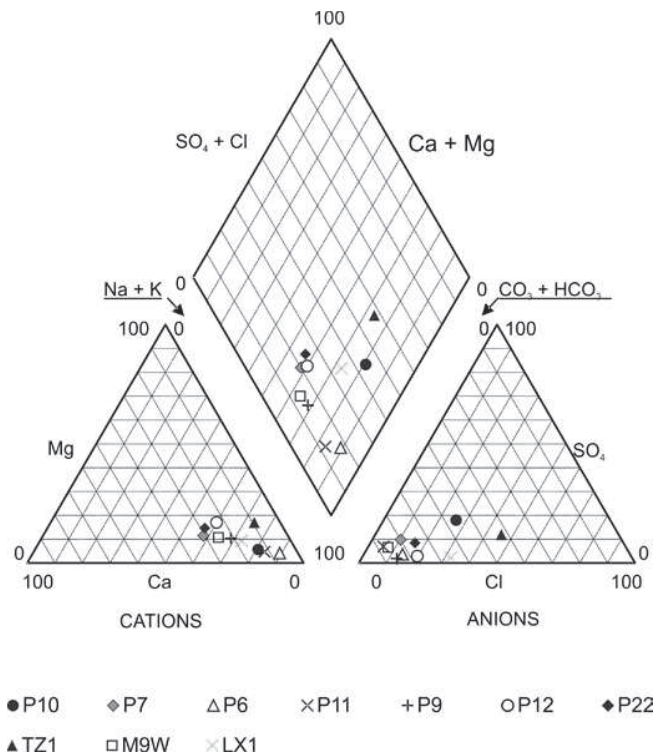
FIGURE 3
Piper diagram showing the chemical composition of groundwater from wells.

The models selected to explain groundwater composition (Table 3) show that the main operating processes are the mixing with leachate, water evaporation, outgassing of CO_2, cation exchange, gypsum salts dissolution or precipitation and K_+ adsorption in the interlayer (exchangeable cation) of soil montmorillonites already formed. The mixing percent-

ages found in the models reflect the influence of leachate on water in all the samples, with percentages that vary according to the analyzed piezometer. P22 and P12 are the most affected samples (35-66% of LX1). Since most piezometers' chemical composition can be interpreted as mixtures between M9W and LX1, taking into account that M9W (pH = 7.4), and LX1 (pH =8.3) the mixture would result a water with increased pH. Since the pH of such solutions are neutral and lower than M9W, an additional source of H^+ must be considered. The increment of H^+ (and Na^+) in the solutions can thus be explained by positive transport of these ions that are interchanged by Ca^{2+} in active clays. These exchange processes that take place in the free aquifer are held by the presence of exchanging clays such as smectite, which are characteristic of loess and alluvial plain. Also, Figures 3 shows the sodium character of the waters. In the case of Mg^{2+}/ Na^+ exchange, the transfer process (with positive and negative values) is more variable. The geochemical modeling for TZ1 (Table 3) gave similar processes with 2.4% leachate and 1.3% saline water typical of a marine ingression.

The mixing percentages thrown by geochemical modeling would indicate the presence of DOC in final water (1.5mg/L for M9w and 243 mg/L for LX1). However, in Figure 4a, it can be observed that DOC measured along a regional flow line (P10 P11 P12 P22 TZ1) is not constant and decreases downstream. Therefore, the possibility of an aerobic oxidation of organic matter due to O_2 availability in water (replacing the CO_2 phase with CH_2O and O_2 and the constraint redox) was considered without obtaining valid results. On the other hand, when results from δ^{13}C-DOC and δ^{13}C-DIC (presented in Table 1) are spatially linked along the regional flow line (Figure 4.A), little variations can be observed for the first parameter (between -25.7 ‰ and -24‰) and an enrichment in δ^{13}C-DIC from P10 onwards (from -12.6‰ to 2.5‰). This same trend can be observed if the results from a local flow line (P7 P6 P12 P22, Figure 4.B) are analyzed, with a decrease in DOC from P7 onwards, almost

TABLE 2
Concentrations of trace metallic elements in piezometers and leachate expressed in mg/L, and levels (*) allowed for human consumption to the Argentine Food Low (ANMAT, 2007).

| Sample	Fe	Mn	Al	As	Cd	Zn	Cu	Cr	Pb
P10	0.221	0.022	0.125	0.019	0	0.031	0.018	0	0
P7	0.138	0.818	0.014	0.013	0	0.011	0	0	0
P6	0.058	0.719	0	0.03	0	0.009	0	0	0
P11	0	0.05	0	0	0	0	0.004	0	0
P9	0	0.274	0	0.021	0	0.007	0	0	0
P12	0	0.376	0	0.02	0	0.007	0	0	0
P22	0	0.121	0	0.018	0	0.022	0	0	0
TZ1	0	0.003	0	0.039	0	0.025	0.003	0	0
LX1	2,297	2,176	10.48	0.022	0	0.177	0.045	0.057	0
Límit*	0.30	0.10	----	0.01	0.005	5	1	0.005	0.005

TABLE 3

Results of geochemical processes in groundwater from wells P6, P11, P9, P12, P22, using NETPATH. Processes refer to mixing between M9w and LX1; evaporation (positive sign); dissolution (positive sign) or outgassing (negative sign) of CO_2 in an open system; Ca^{2+}/Na^+-H^+ exchange (positive sign indicates the Ca^{2+} adsorption and the release of Na^+ and H^+ with molar ratio 1:1.6 Na^+ and 0.4H^+; Mg^{2+}/Na^+ exchange (positive sign indicates the Mg^{2+} adsorption and the release of Na^+ with molar ratio of 1:2); dissolution (positive sign) or precipitation (negative sign) of gypsum; precipitation of K-montmorillonite (negative sign).* Only Exchange (Ca^{2+} adsorption and the release of Na^+).

	Mixing process (%)		Evaporation Factor	Dissolution or precipitation of calcite	Dissolution or outgassing of CO_2	$Ca2+/Na+$ and $H+$ Exchange	$Mg2+/Na+$ Exchange	Dissolution or precipitation of gypsum	Precipitation of K-mont
Final water	Initial water M9w	Initial water LX1		(mmol/L)	(mmol/L)	(mmol/L)	(mmol/L)	(mmol/L)	(mmol/L)
P6	79	21	3,461	0	-5,662	1,107	0.483	-0.1	-2,859
P11	97	3	1,920	0	0.812	0.771*	0.317	0.069	-0.495
P9	80	20	1,789	0	-4,395	0.148	0.118	-0.187	-2,656
P12	34	66	1,223	0	-15,498	0.254	-0.258	-0.078	-8,327
P22	65	35	1,136	0	-9,129	0.045	-0.178	0.277	-4,445

TABLE 4

Results of geochemical processes in groundwater from wells TZ1 using NETPATH. Processes refer to mixing between M9w, LX1 and typical marine ingression (Plummer et al., 1991).

					Processes					
	Mixing process (%)			Evaporation factor	Dissolution of calcite	Dissolution of CO_2	$Ca2+/Na+$ Exchange	$Mg2+/Na+$ Exchange	Dissolution of gypsum	k-mont
Final water	Initial water M9w	Initial water LX1	Initial water Ingresion		(mmol/L)		(mmol/L)	(mmol/L)	(mmol/L)	(mmol/L)
TZ1	96	2.7	1.3	1,523	0	0	0.980	-0.333	0.415	-0.941
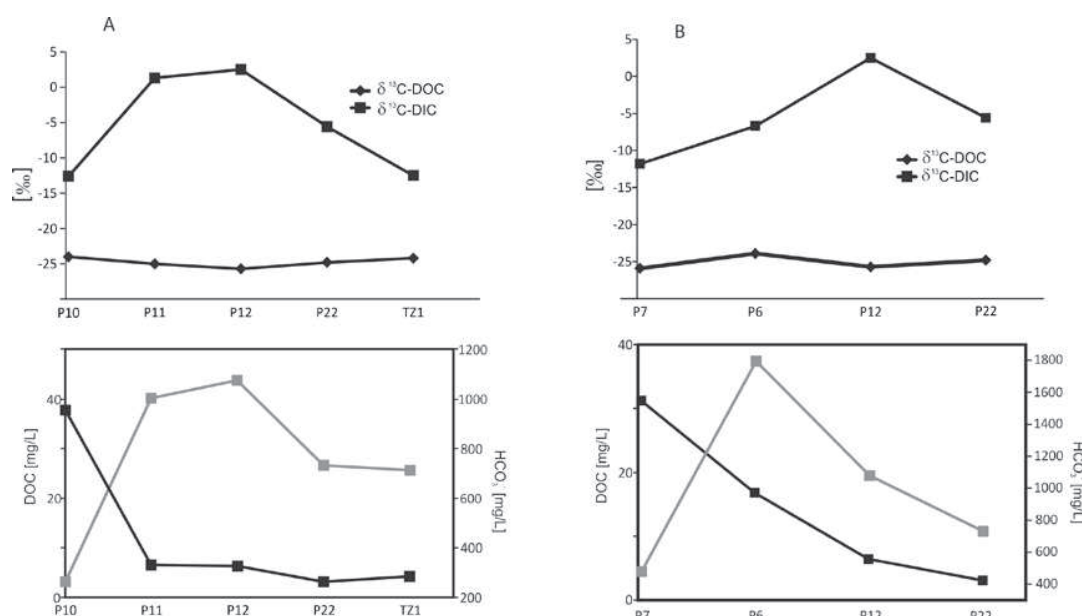
FIGURE 4

DOC (mg/L), δ^{13}C-DOC, HCO_3^- (mg/L) and δ^{13}C-DIC measured along a regional (A) and local (B) flow line.

constant δ^{13}C-DOC values between 25.9‰ and -23.9‰ and enrichment in δ^{13}C-DIC (from -11.8‰ to 1.3‰).

The width of the unsaturated zone at some points of the municipal site was minimal, with water depths that ranged from 0.90 m to 0.20 m at P10, P7, P6, P9, P11, P12 and P22. Thus, subsoil samples obtained from those piezometers (up to

2 m) would correspond to the unsaturated zone as well as part of the saturated zone. Table 5 shows the results of sand, silt and clay percentages, pH, CO_3 %, OM %, EC, CEC y exchangeable cations, taking as a reference the values from SP10 for the loessic plain and from AP for the alluvial plain. Regarding soil texture, SP10 has a greater content of sand than AP (21- 47% vs. 1-9%), and the latter shows a clay content (36-61% vs. 16-41%). Silt percentages are variable and this fraction is present in both soundings (between 5 and 53%). pH ranges from 6.9 to 10.3 with prevailing values from 8 to 10, which indicate alkaline conditions in the subsoil. CO_3^{2-} and CEC values from both units are similar to the reference values, but anomalies are found in %OM and EC. In the case of %OM, anomalies can be observed in almost all the levels of SP12 and SP22. In the case of EC, anomalies are found at SP9, SP12 and SP22, mainly at levels 25-50 cm. At these 25-50 cm levels with high EC, Al, Cr, Cu, Fe, Mn and Zn concentrations were measured (Table 6). When these values are compared with the values from alluvial plain pristine sites (AP), metallic anomalies are observed, SP9 shows

higher concentrations of Al, Cu, Fe, Mn and Zn, SP12 of Cu, Fe, Mn and Zn and SP22 shows higher concentrations of Al, Cr, Cu, Fe and Zn. SP7 (located upstream of USW and in the loessic plain) shows values even lower than AP (in the alluvial plain). Although CEC varies from level to level since it depends on the content and type of clay minerals and organic compounds, it could be said that the analyzed data, as a whole, show that CEC values are naturally greater in AP (between 31-56 cmolc/kg) than in SP10 (between 14-31 cmolc/kg) and that, in these samples, CEC values are mainly correlated with clay content in a 66% (Figure 5). When comparing the sum of exchangeable bases ($S = Ca^{2+} + Mg^{2+} + K^+ + Na^+$) with CEC, it can be observed that S is greater at some levels, mainly at SP12 and SP22, that would indicate that apart from exchangeable cations, soluble salts are also present. When this relation is analyzed in terms of % of base saturation ($V=(Ca+Mg+K+Na/CIC)x100$)), V is over 50% in many levels, which indicates a saturation of the adsorbent compound regarding these cations.

The X-ray diffraction mineral analysis (Figure 6) of the

TABLE 5

Results of sand, silt and clay percentages, pH, CO_3 %, OM %, EC, CEC y exchangeable cations, taking as a reference the values from SP10 for the loessic plain and from AP for the alluvial plain.

	Deep level (cm)	SP10	SP7	PA	SP9	SP12	SP22	TZ1
Sand/Silt/Clay	0-25	47.8/5.5/16.8	52.2/34.4/13.4	9.9/48.4/41.8	10.7/52.6/36.8	22.4/60.9/16.8	4.2/47.5/48.4	52.8/32.9/14.3
(%)	25-50	42.8/30.5/26.8	51.1/30.5/18.4	9.4/53.8/36.8	7.2/36.1/56.8	19.7/38.6/41.8	4.1/41.2/54.7	45.3/28/26.8
	75-100	30.3/27.9/41.8	45.8/42.1/12.2	4.2/34/61.8	6.4/31.9/61.8	12.1/26.1/61.8	6.3/47.8/45.9	37.6/33.2/29.3
	125-150	21.6/51.6/26.8	39.8/31.9/28.4	1/37.2/61.8	35.3/27.9/36.8	49.8/23.4/26.8	1.2/55.4/43.4	27.1/38.7/34.3
	175-200	40.6/32.7/26.8	53.3/23.3/23.4				1/50.6/48.4	37.6/30.6/31.8
pH	0-25	6.9	10.3	7.8	8.6	8.4	7.3	8.5
	25-50	8.5	10.1	8.1	8.2	8.5	7.5	9.1
	75-100	9.5	9.3	8.2	SD	SD	8.2	8.7
	125-150	9.7	9.3	7.8	9.2	9.1	8	9.8
	175-200	9.5	9.5				7.9	9.7
CO_3 (%)	0-25	1.4	2.8	2.3	2	1.3	1.9	2.1
	25-50	1.4	3.1	4.7	5.9	4.9	3.5	1.8
	75-100	7.6	3.3	8.6	1.7	14.1	2.3	1
	125-150	1.5	2.7	5	1.9	1.7	1.9	5.8
	175-200	2.4	2.2				2	3.5
OM (%)	0-25	3.63	0.20	1.41	1.93	1.45	4.67	1.71
	25-50	0.99	0.19	1.06	0.84	1.92	2.39	0.34
	75-100	0.33	nd	0.88	0.98	1.32	1.08	0.67
	125-150	0.29	nd	0.35	0.35	0.26	0.90	nd
	175-200	0.21	0.17				0.89	0.33
EC (dS/m)	0-25	0.27	1.56	0.21	1.26	2.77	0.62	0.12
	25-50	0.55	1.16	0.19	4.86	5.88	4.29	0.86
	75-100	2.19	0.67	0.66	nd	nd	1.07	0.64
	125-150	2.03	0.81	1.76	0.65	0.66	0.34	1.24
	175-200	1.04	0.65				0.23	1.2
CEC (cmolc/kg)	0-25	14.8	9.6	31.8	35.1	18.3	27.8	13.9
	25-50	20.3	12.1	26	41	32	29.3	16.9
	75-100	29.4	11.6	43.4	43	49.4	29.1	19.3
	125-150	22.1	18.7	56.5	30.3	18.7	27.2	25.2
	175-200	31.2	15.9				26.8	23
Ca^{2+} (cmolc/kg)	0-25	6.4	2.6	23.2	13.2	6.4	17.1	6.8
	25-50	6.3	2.8	29.6	20.3	14.6	13.2	12.5
	75-100	6.6	6.2	36.4	7.8	20.8	13.2	13.2
	125-150	2.9	5	25.8	7.3	8.8	15.7	15.2
	175-200	4.8	4.2				16.5	16
Mg^{2+} (cmolc/kg)	0-25	1.7	0.4	2.5	4.9	3.8	6.7	1.6
	25-50	2.4	0.8	2.8	7.8	6.7	7.7	2.8
	75-100	4.2	4.8	8	7.1	8.3	7.3	2.4
	125-150	2.2	5.3	8.7	3.9	3.3	7.3	3.1
	175-200	3.4	2.7				6.4	3.4
Na^+ (cmolc/kg)	0-25	2.1	15.7	0.5	10.1	9.6	7.2	0.8
	25-50	2.4	16.1	0.6	19	19	17.4	11.1
	75-100	17.8	13.3	5.4	20.2	23.3	16.2	6.5
	125-150	17.6	15.4	11.2	7.2	4.8	8.9	23.6
	175-200	14.5	9.9				3.4	17
K^+ (cmolc/kg)	0-25	1.4	0.4	0.5	0.4	0.7	0.7	0.3
	25-50	3.6	0.3	0.4	0.8	0.7	0.5	0.4
	75-100	0.9	0.5	0.7	0.7	0.9	0.6	0.5
	125-150	0.8	0.7	0.8	0.4	0.4	0.7	1.2
	175-200	0.4	0.4				0.8	1

TABLE 6
Concentrations of trace metallic elements in sediments (level 25-50 cm).

Sample	Al	Cr	Cu	Fe	Mn	Zn
	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
PA	4272	2.6	6.4	2601	241	9.2
SP9	6631	4	12.8	4070	511	19.1
SP12	4321	3	8.4	2813	474	10.5
SP22	9722	5.9	19.2	7104	52	18.8
SP7	2548	1.9	5.2	1647	313	5.3
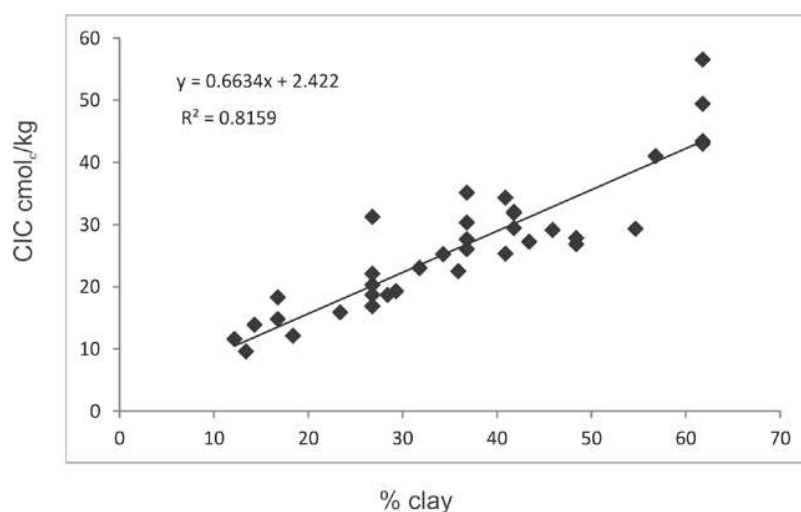
FIGURE 5
CEC values correlated with clay content from subsoil samples.

loessic plain (LP), represented by P10, indicates the presence of quartz, potassium feldspars-plagioclase and clays with variable proportions of tridymite-cristobalite in all levels and of calcite from 50cm onwards. In the alluvial plain sediments (AP), the same minerals were identified in all the levels with the exception of cristobalite, which was only found in the first 25 cm. In both cores, clay content increased towards the deeper levels. The fraction smaller than 63 microns from levels 25-50 cm at AP and V10 coincides with whole sample analysis for this level, regarding its mineralogy. Clay fraction analysis for levels 25-50 at AP and VZ2 indicate the presence, in decreasing order, of smectites, illites and kaolinites, with a prevalence of the first one (Figure 7). When discontinuous levels SP9, SP12 and SP22 were compared with PA, it was found the same mineralogy, as in TZ1.

DISCUSSION

Figure 8a (δ^2H vs. δ^{18}O cross plot) show the isotope composition of a mill network producing for the water table and surface waters sampled during March, 2010 (Boujon, 2014) together with the local meteoric water line (LML) from the station INGEIS Ciudad Universitaria, Buenos Aires (INGEIS-CU), the closest to the study area (180 km southwards), whose parameters do not differ significantly from that of Santa Fe (260 km NW) (Dapeña and Panarello, 2004-2007). Therefore, as there is no LML from Gualeguaychú, the LML from Ciudad Universitaria can be used without generating important errors. In addition the piezometer series was also plotted. Free aquifer isotope data, as indicated by the mill network, fall in a cloud around the average weighted value of INGEIS-CU station $i.e.$ δ^{18}O ~ -5‰ and δ^2H~ -26‰. On the other hand water from the Arroyo El Cura and tributaries and the Gualeguaychú River exhibit more depleted δ^2H and δ^{18}O values. Piezometers' values distribute along the MWL showing rapid response to the rain. As established by Gat (2010) this picture is related to a Rayleigh fractionation process produced by the so called "amount effect" in which the isotopic composition of a precipitation event become more depleted as the rain out proceed. The mills respond to whole precipitation whereas piezometers infiltrate only during a period of time and become saturated leaving to the
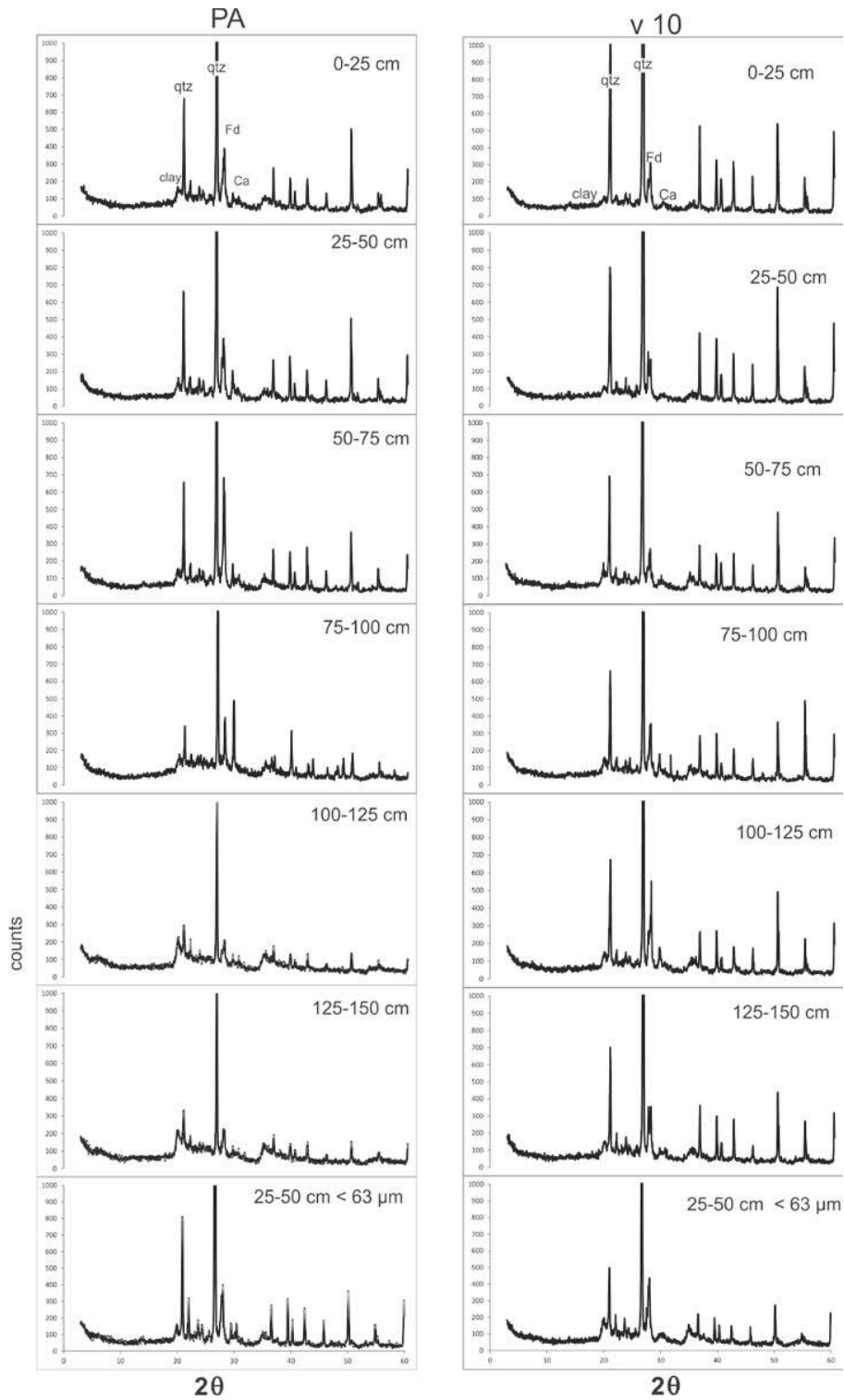
FIGURE 6
Identification of minerales by x-ray diffraction (XDR) of SP10 y AP (whole sample and fraction smaller than 63 µm).
Clay, Qtz (quartz), Fd and Ca (potassium feldspars-plagioclase).

runoff the remaining, more negative fraction of rain. This runoff reaches the creeks and rivers which discharge these depleted water that can be mixed with the base flow (free aquifer).

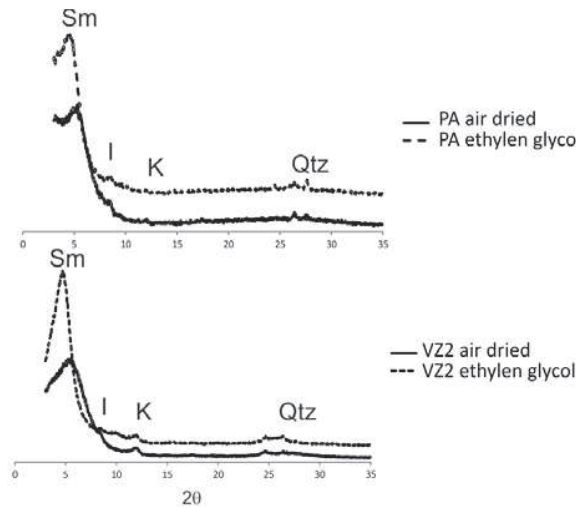Figure 8b present a detail the isotopic composition of the piezometers, together with a sample of the leachate (LX1)

FIGURE 7
Identification of minerales by x-ray diffraction (XDR) of SP22 y AP (clay fraction).
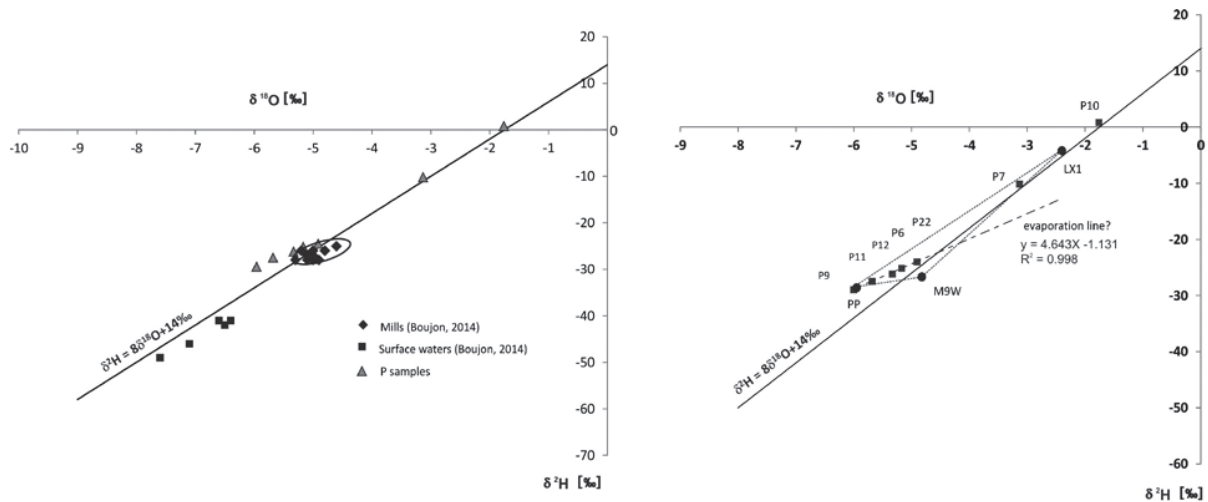Sm (smectite), I (illite), K (kaolinite), Qtz (quartz).

FIGURE 8
δ^2H vs. δ^{18}O cross plot showing the isotope composition of a mill network producing for the water table and surface waters
sampled during March, 2010 (Boujon, 2014)) (a) together with the local meteoric water line (LML)
and piezometer series (September 2012) (b).

and M9W corresponding to the average value of pristine water. PP represents the water input as precipitation. Isotopic composition of these rains is compatible with the prevalence of recycled rains (Gat, 2010), characterized by a high deuterium excess, and that statistically occur during May-June months in that region (Dapeña, 2007). In Figure 8b, it can be seen that the isotopic composition of the waters - with the exception of P10 - can be explained as a ternary mixing with variable proportions from samples M9W, LX1 and PP. In turn, P9, P12, P11, P22 and P6 line up along a line with a slope of 4.64, which can be interpreted as the result of an evaporation line with a greater gradient (in accordance with the meteorological conditions of the area) with varying contributions of water isotopically similar to that from M9w. It is worth mentioning that, given its position on the LML, P7

could be the result of the above-mentioned mixing, but this is not supported by the hydrochemical characteristics or by the geographical location of the piezometers with respect to the USW location. Isotopic differences between P7-P10 (upstream from the USW) and the other P piezometers (P9, P12, P11, P22 and P6 from downstream) could be explained by the incidence of the materials that were removed to cover the SIW (heterogeneous and non-compact), fact that affects the last group of piezometers and not P7-P10. This situation probably generates a differential vertical infiltration of rain in the ground and thus the seepage of volume elements with different isotopic composition due, as mentioned, to the amount effect.

Leachate chemical composition significantly varies according to the nature of waste, its age and the practices asso-

ciated to the USW burial. In general, all species concentrations are much higher in a young leachate than in an old one. In the former case, dissolved salts and heavy metals contents are much higher than the permissible limits for drinking water (Ogundilan and Afolabi, 2008). In this case, even though LX1 falls within the ranges proposed for this type of effluents (Table 7), the major and trace elements concentrations measured exceed the permissible limits for drinking water of the Argentine Food Law only in Cl^-, higher than 350 mg/L at TZ1, total hardness (as $CaCO_3$), higher than 400 mg/L at LX1 and Mn, higher than 0.10 mg/L at P7, P6, P9, P12 and P22. This situation can occur either because LX1 type water leached as a result of the action of groundwater coming from precipitations (LX1 does not differ significantly from the P waters, although it is more concentrated- Figure 3 and it falls on the meteoric line-Figure 5), or it is linked to the age of USW burial and its relation with the state of degradation. There is a strong relationship between the state of refuse decomposition and its associated leachate characteristics (Farquhar and Rovers, 1973). Generally, it is accepted that landfills undergo at least four phases of decomposition, (1) an initial aerobic phase, (2) an anaerobic acid phase, (3) an initial methanogen phase, and (4) a stable methanogen phase and an additional aerobic or humic phase of decomposition has been proposed (Bozkurt et al., 2000). Geochemical study of gases made on site (concentrations of CO_2, CH_4, N_2 and O_2 as well as carbon isotope composition of the CO_2) showed that the process underway is an aerobic phase of biodegradation (Sanci et al., 2012). Lack of methane and other evidence allowed to conclude that the time since the end of operations in the MSWFDS (14 years) makes it possible to assume that we are in the presence of a posthumous stage of biodegradation or postmethanogen phase. Sampling 2012 is also not found CH_4 dissolved in water.

Several authors (Christensen et al. 2001; Kjeldsen et al., 2002; Bjerg et al., 2005) refer to an acid phase and a methanogenic phase when talking about leachate, distinguishing how the concentration of several parameters vary in each phase. Although it is true that LX1 could be a postmethanogenic leachate, since the presence of CH_4 in water could not be corroborated (Table 1), it was observed that it affects the quality of the pristine water far beyond the evaporation indicated by geochemical models. DOC, EC and concentrations

at P and TZ1 piezometers are higher than at M9w, especially in Cl^-, HCO_3^-, SO_4^{2-} and Na^+ (Figure 2). These parameters are all indicative of leachate. TZ1 is also influenced by the marine ingression, whose field evidences were also seen in a sounding near TZ1 and within the municipal site (Boujon and Sanci, 2014). Moreover, there are EC and OM anomalies in subsoil samples from P12 and P22 (with higher concentrations than the reference values), as well as in the water from them, which showed the highest mixing ratios (35% and 65%, Table 3).

pH values are variable if we consider the mixing ratio indicated by the geochemical models (Table 3) and the pH value of the initial waters (M9w with 7.4 and LX1 with 8.17). The exception is P11 that only has a 3% of LX1 and the same pH as M9w. P12, P9 and P22 show more acid pHs, even more than pristine water, which lead to think that besides the exchange of Ca^{2+} for Na^+ (sodium bicarbonate waters) there was an exchange with H^+ according to the following reaction:

$$Na^+H^+X + Ca^{2+} \longleftrightarrow CaX + Na^+ + H^+$$

When there are acid inputs, pH decreases but, since bicarbonates are present, this excess is released as CO_2 and pH remains near neutrality ($HCO_3^- + H^+ \longleftrightarrow CO_2 + H_2O$). The process is, in short, a neutralization that justifies the pH obtained. In the case of our study, ground materials act mostly as aquifer sediments since groundwater depths are shallow. Therefore, ion exchange and cation retention can occur either from clays or from organic matter in the subsoil (both present in the site). The results of geochemical models show a positive transfer of Na^+ and H^+ to the water with Ca^{2+} adsorption and, in Figure 2, Ca^{2+} does not seem to increase in a significant way when compared to M9w. Since organic matter also exchanges and subsoil data indicate that there is base saturation (Table 5), it is possible to think that the acidity is provided by the organic acids present in the subsoil. OM anomalies detected at P12 and P22 are possibly due to the presence of leachate acids. Organic acids provide H^+ to the soil solution at a variable pH (Conti, 2007).

On the other hand, $\delta^{13}C$-DIC in wells P6 P9 P11 P12 P22 is enriched with respect to $\delta^{13}C$-DIC background (-12.6 ‰). High δ^{13}-DIC values are generally observed for landfill

TABLE 7
Typical range of concentrations of major and trace elements concentrations proposed by
Kjeldsen et al. (2002) and Christensen et al. (2001).

Sample	pH	CE	Cl^-	$SO4^{2-}$	Ca^{2+}	Mg^{2+}	Na^+	K^+	$HCO3^-$
LX1	8.1	2940	195	37.2	106	33.7	262.5	170	1394.12
Typical Range	4.5-9	2500-35000	150-4500	Aug-50	Oct-00	30-15000	70-7700	50-3700	610-7320

Sample	Cd	Cu	Cr	Pb	Zn	Fe	Mn	As	
LX1	0	0.045	0.057	0	0.177	2,297	2,176	0.022	
Typical Range	0.0001-0.4	0.005-10	0.02-1.5	0.001-5	0.03-1000	Mar-00	0.03-1400	0.01-1	

leachate and are thought to be related to production of isotopically positive CO_2 by methanogenesis (Hackley et al., 1996), and a lesser extent by outgassing of CO_2 (Baedecker and Back, 1979; Hornibrook et al., 2000). Since no CH_4 was found in water (consistent with the presence of dissolved O_2), the isotopic enrichment would be due to CO_2 degassing (as indicated by geochemical models, Table 3), which must have taken place in the final waters to compensate the carbon excess produced by mixing and evaporation. Moreover, $\delta^{13}C$ values of final waters are also influenced by the M9w and LX1 mixing ratio. M9w and LX1 water types have their own isotopic signatures: M9w $\delta^{13}C$, -12.6 ‰ and LX1 $\delta^{13}C$, +9.1‰. It is worth mentioning that if we calculate $\delta^{13}C$ values of final waters from the mixing percentage and the $\delta^{13}C$ values of each initial water, estimated $\delta^{13}C$ values of final waters show less enrichment, that is why it is supposed that there is fractionation through degassing. Evaporation does not generate isotopic fractionation in ^{13}C (Mook, 2000). P11 only has 3% of LX1 (it could be said that it has no leachate mixing) and it is the only that shows CO_2 dissolution, thus a $\delta^{13}C$ value of +1.3 ‰ is probably the result of intake of heavy subsoil CO_2 generated during the USW degradation (Sanci et al., 2012).

DOC decreases from 16 to 3.1 mg/l in downstream direction, while no dilution appears to take place. On the contrary, the isotopes ^{18}O and ^2H contribute to validate the evaporation process indicated by the models. The deuterium excess value of the samples (located over the local meteoric water line, Figure 8) may indicate exchange between H from water with that from the dissolved CH_4 (Clark and Fritz, 1997), but we found no CH_4 that would justify this. It is believed that the evaporation could be due to a process occurring prior to infiltration and/or evaporation in the aquifer consistent with the rise of the up-going flow at a discharge area, as in this case. $\delta^{13}C$-DOC showed a tendency to stay constant with distance from the landfill and an inverse correlation with DOC concentration was not found. Degradation of certain organic compounds favors the ^{12}C with respect to the ^{13}C isotopes, which results in enrichment for $\delta^{13}C$ in the residual fraction (Rayleigh process, van Breukelen et al., 2003). Therefore, the no observed correlation between increasing $\delta^{13}C$-DOC and decreasing DOC concentrations. It is more likely to have occurred DOC sorption in sediments rather than oxidation. Evidence could be that the DOC in P12 and P22 decreases and in those wells (with LX1 higher percentage) increases organic matter (Figure 4). Besides the DOC in the final water should be more concentrated when taking into account the mixing ratios between M9W (1.5 mg / l) and LX1 (243 mg / l), and that does not happen.

According to Kawahigashi et al. (2006) sorption of dissolved organic matter (DOM) on mineral phases is an important geochemical process for carbon preservation and element cycling in soils and aquatic systems. Sorption is more rapid than microbial degradation (Qualls & Haines, 1992; Kalbitz et al., 2003) and, therefore, is more efficient in removing DOM from water percolating through soil. Also, Kjeldsen et al. (2002) say that the acid phase, the leachate may show low pH values and high concentrations of many compounds, in particular high concentrations of easily de-

gradable organic compounds as volatile fatty acids. But in the later stable methanogen phase, the pH increases and the degradability of the organic carbon is lowered dramatically. The acids that accumulated in the acid phase are converted to gases and cellulose and hemicellulose decomposition also begins. The pH increases as acids are consumed. In the stable methanogenic phase, the methane production rate will reach its maximum, and decrease thereafter as the pool of soluble substrate (carboxylic acids) decreases. In this phase, the rate of CH_4 production is dependent on the rate of cellulose and hemicellulose hydrolysis. The pH continues to increase to steady state pool concentrations that are on the order of a few mg/L. Some COD is present in the leachate, but it is mostly recalcitrant compounds such as humic and fulvic acids (Barlaz and Ham, 1993; Christensen et al., 1994). In this way compounds of high molecular weight and rich in acidic functional groups and aromatic moieties sorb most strongly (Kawahigashi et al. 2006).

Total soil contents of Fe, Mn and Al at P9, P12 and P22 increase with respect to AP (Table 6) and in those piezometers, Fe and Al are not detected in the water and water Mn content decreases. It cannot be ascertained that those soil anomalies are only the result of the presence of oxides, since they were not detected by X-ray diffraction, but there is a possibility, since metals tend to fix in the soil at basic pHs and thus its leaching rate is low (Stumm and Morgan, 1996). Therefore in P9 P12 and P22 (where water and sediment was measured) could be said that the precipitation of trace element (as oxides) would control the concentration of Fe and Al in water and that both contribute to the adsorption of organic matter (the sorption depends much on the contents of Al and Fe oxides and carbon in soils, Kahle et al, 2004). Metals that are added due to leachate input can be captured by the formation of secondary minerals such as montmorillonite, illite, kaolinite, trace metals precipitation and adsorption (McLean and Bledsoe, 1992). These processes are the ones that control the concentration of many metallic elements in water.

CONCLUSIONS

The results obtained from physico-chemical and isotopic data provided useful evidence of leachate migration in the groundwater. The presence of leachate is indicated by anomalies in the content of the inorganic conservative element in waters from well P (located downward the USW disposal site) in relation to the content of those elements in M9w (non contaminated water). High values in major elements in the water are produced not only by antropic processes but also by other natural ones such as evaporation in P6, P11, P12 y P22 and marine ingression in TZ1. When all these processes are put together, the quality of water change mainly due to presence of those elements which are in concentrations unfit for human consumption. What is clear is that the soil EC increases in wells affected by USW what would indicate the presence of soluble salts coming from the leachate.

Environmental isotopes (carbon, oxygen and hydrogen) were a useful tool in validating the geochemical models. $\delta^{18}O$

y δ^2H values suggest not only a meteoric origin for the ground waters but also that samples P6 P11 P9 P12 y P22 have undergone a evaporation and mix process of waters of the type PP, M9w y LX1. Moreover, C isotopes, particularly those values enriched in $\delta^{13}C$-DIC, demonstrated that CO_2 outgassing could have happened during the mixing. No evidences were found (such as CH_4 dissolved in water) that could identified another process, such as metanogenesis, that could have been responsible for the $\delta^{13}C$ enrichment.

Soil-water interaction allow the existence in the area of natural attenuation processes in the water such as organic matter sorption in the subsoil, as shown by the lowering in the concentration of DOC in water, the rising of OM in the subsoil (mainly in those samples affected by mix of waters such as P12 y P22) and the constant values of δ^{13}-DOC in water. Furthermore, precipitation and/or adsorption of trace elements like Fe and Al, control the concentration of these elements in water, since they are not present in wells P11 P12 P22 P9 and TZ1 but are found in higher amounts in the subsoil. Those wells are located in the alluvial plain (higher clay, CEC and OM content), suggesting that the exchange and/or sorption processes were effective. Smectite was identified as the main clay mineral. This mineral not only exchange Ca^{2+} and/or Mg^{2+} for Na^+, but also could neutralize water, exchanging metals and H^+ and incorporated excess K^+ from leachate.

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