

## Full Length Research Paper

# Arsenic and fluoride in water in northwestern Buenos Aires: their association with natural landscape elements

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Numerous publications analyze the origin of Arsenic and Fluoride, their behavior and distribution in groundwater indicating the importance in understanding the relation between their occurrence with other physical and chemical properties. Here, such properties associated with elements of the landscape in the plain of the Chaco-Pampean region are discussed. The landscape is represented by hills, lagoons and plains used for agricultural purposes. Water was sampled in mills, piezometers and lagoons following sections with different topographic elevation, soil type and vegetation in nine field campaigns from 2011 to 2013. Results in Lincoln are compared to localities in Trenque Lauquen, Pehuajó and Carlos Casares. Hydro geochemical modeling assisted to define composition and origin of the water from local mineralogy in soil and subsoil. Three major water groups were defined HCO<sub>3</sub>-Na, HCO<sub>3</sub>>Cl-Na and HCO<sub>3</sub>>Cl>SO<sub>4</sub>-Na. Piezometers were located at the top and base of hills with the presence of *Acuic Hapludolls* – *Natric thapto Hapludolls*, and *Typic Natraqualfs* with halophytic vegetation, respectively. Arsenic and Fluoride presence was not fully explained by groundwater chemistry type and association with HCO<sub>3</sub><sup>-</sup>, Na<sup>+</sup>, salinity and pH, although generally were linked to alkaline soil and halophyte vegetation. High Arsenic and Fluoride presence in groundwater are explained by discharge flows travelling long distances through a thick sedimentary sequence; relative low concentration is referred to local travelling flows recharged in nearby high terrain. Groundwater origin and its relations with other elements of the landscape permitted an understanding of groundwater functioning and to anticipate a general situation with respect Arsenic and Fluoride contents. In the present study this criterion is applied to analyze the relation of the occurrence of Arsenic (as total Arsenic,  $\tau$ As) and Fluoride (F<sup>-</sup>) content in water of the Lincoln region in the Buenos Aires province of Argentina.

**Key words:** Arsenic, fluoride, discharge and recharge zone, groundwater flow system, soil, natural vegetation.

## INTRODUCTION

Physical geography considers the landscape as the unit of study. Landscape is a territory, whose character is the

result of the action and interaction of natural and/or human intervention, including i) physical elements

(landform, soil, water, and geological framework); ii) natural biodiversity elements (ecosystem, vegetation and animal community); iii) human elements including land use (agricultural land and infrastructure); and iv) climatic conditions. Various combinations of basic associations among climate, soil, and water may be established (Holdridge, 1978). Therefore, in this study physical elements and vegetation under the prevailing climatic conditions are considered and further incorporated into the groundwater flow systems theory by Tóth (2000). This theory focuses on those elements to define their systemic functioning, which represent the actual conceptual groundwater flow model of a particular region. This theory considers that under natural conditions there is a relation among elements of the landscape with groundwater movement in flows of different hierarchy. There are local, intermediate and regional systems each having three contrasting components: recharge, transit and discharge zones. Their potential recognition includes a harmonizing methodology that considers matching among the various components of natural elements such as climate, soil, landscape, vegetation, with the physical, and chemical of groundwater, as well as with the hydraulic response within the geological framework of the circulating path.

The presence of  $\text{As}^{\text{III}}$  in the water supply for human use is becoming an increasing worldwide concern because of their negative effects on human health. Depending on the dose, the effects of  $\text{As}^{\text{III}}$  range from gastrointestinal distress, severe dermatological effects, to death. Chronic  $\text{As}^{\text{III}}$  exposure may affect several major organ systems (primarily of skin, bladder, and lung cancer) (Hughes et al., 2011). Edmunds and Smedley (1996) among others have brought out the importance of the hydrogeological media in its occurrence. Localities with problems of  $\text{As}^{\text{III}}$  in their water tend to be found in environments with geologically young sediments with a flat topography, low-lying areas where groundwater flow is sluggish (Smedley and Kinniburgh, 2002). Several agencies that provide water services in the Province of Buenos Aires face serious legal problems linked to water with high levels of  $\text{As}^{\text{III}}$  (Minaverry and Cáceres, 2016). Similarly to  $\text{As}^{\text{III}}$ , fluoride ( $\text{F}^-$ ) in drinking water has been a major concern in many parts of the world as it diminishes the acceptable good quality of groundwater sources. Agüero (2015) analyzes problems linked to excess and deficit of  $\text{F}^-$  in drinking water for Argentina. Fluoride content in water is linked to problems with teeth, skeleton, kidney and hepatic ailments, as well as carcinogenic impacts to humans (Edmunds and Smedley, 2002; WHO, 2006; San-Xiang et al., 2007; Ozsvath, 2009). In Argentina, a large population group is susceptible to waterborne diseases because most of the extracted groundwater is

extracted from fine sediments which have a high content of  $\text{As}^{\text{III}}$  and  $\text{F}^-$ , among other elements (Auge, 2004, 2008).

However Lavado et al. (1983) in the western Buenos Aires emphasize that soluble  $\text{F}^-$  comes from groundwater and is not related to soil mineralogy. Espósito et al. (2013) in the southeast of the Pampean region, measured high concentrations of  $\text{As}^{\text{III}}$  and  $\text{F}^-$  that correlate with each other (principally at the water-table). These authors point the need to consider the concentrations of  $\text{As}^{\text{III}}$  and  $\text{F}^-$  for irrigation projects in horticulture, and cereal and forage production (for cattle breeding). The natural contamination investigated causes not only a potential reduction of crop yields, but also its transference to humans through drinking water and food consumption (Roseli et al., 2010; Puntoriero et al., 2014; Bastías and Beldarrain, 2016). Therefore, the main problem in being aware of the possible excessive presence of  $\text{As}^{\text{III}}$  and  $\text{F}^-$  in groundwater could be tackled by means of understanding groundwater flow functioning and its relation with the geomorphological expression which controls total circulation depth from local to regional scales.

### Arsenic

There have been attempts in defining the relation between the occurrence of  $\text{As}^{\text{III}}$  in surface water as well as in groundwater flows based on different physical and chemical variables which are associated with hydrogeological components as reported in López (2006), Ortega (2009) and Panagiotaras et al. (2012). A detailed analysis of the origin, behavior and distribution of  $\text{As}^{\text{III}}$  in soil, water and vegetation has been considered by Carbonell et al. (1995), and Litter et al. (2006). Specifically, for the Chaco-Pampean plain the reviews of Nicolli (2006), Nicolli et al. (2006), Ferpozzi (2006), and Schulz (2006) are considered instructive. Puntoriero et al. (2014) cited authors indicating the Chaco-Pampean plain being the world biggest region with high  $\text{As}^{\text{III}}$  concentration in groundwater; they study  $\text{As}^{\text{III}}$  in soft fish tissues of silverside (*Odontesthes bonariensis*) and could be shown transference of this element to different organs, making them harmful for human consumption. Schultz (2006) emphasizes anarchical distribution patterns of  $\text{As}^{\text{III}}$ , without a systematic behavior of distribution with respect to other ions in the water, lacking a consideration with the regional hydrogeological characteristics under the studied local conditions. On the other hand, Ferpozzi (2006) indicates some relation between  $\text{As}^{\text{III}}$  with water components under regional and local environmental factors in the Chaco-Pampean Plain; local sediment, and volcanic components (loess, volcanic glass, soluble

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sulfides and salts) determine its presence in the water (between  $5 \mu\text{g}\cdot\text{l}^{-1}$  to  $5,000\text{-}8,000 \mu\text{g}\cdot\text{l}^{-1}$ ). Nicolli et al. (2006) emphasize that although the hypothesis of volcanic glass as the source of  $\tau\text{As}$  to surface and groundwater of the Pampean region indicated in several publications, its origin and processes are still unclear, being argued to be derived from silicates.

Different proposals have been presented to explain the magnitude of the presence of  $\tau\text{As}$ , such as, residence time of interactions, and geochemical variables to include at local scale (pH-Eh, salinity-alkalinity, competition with other ions), as proposed by Smedley et al. (2005), or specifically being controlled by the pH of groundwater as found in northern Mexico by Mejía et al. (2014). Also in Mexico, Rodríguez et al. (2016) in a region located in an equivalent lithological environment (rhyolite - granite) although with contrasting aquifer units, variations in  $\tau\text{As}$ , F<sup>-</sup>, and other hazardous elements are explained in terms of potential contamination sources as anthropogenic and geogenic origin (mainly rhyolitic rocks bearing deep regional thermal flow as well as cold local flow), and migration mechanisms as interaction and exchange processes of thermal fluids with host-rock, progressive alteration processes and formation of new mineralogy. They found difficulty in defining which  $\tau\text{As}$  origin is most important in their region.

Litter et al. (2006) emphasizes the presence of high  $\tau\text{As}$  concentration in different water-bearing geological material presenting more than 200 minerals with  $\tau\text{As}$  content. Ruggieri et al. (2011) investigated volcanic ashes from Southern Andes and their potential contribution to local geochemical  $\tau\text{As}$  fluxes through water; major potential toxic trace element content was found to be corresponding to  $\tau\text{As}$ , Cu, F, Mo, Ni, Pb, and Zn, although with important differences in concentration levels among the studied volcanic ashes (eight eruptions along the 20th Century). Bundschuh et al. (2006a) describe that  $\tau\text{As}$  is contained in silicates as quartz, feldspar, plagioclase, biotite, amphibole, pyroxene, hypersthene and olivine, among others. These minerals supply  $\tau\text{As}$  in environments with high organic matter content through influencing changes in the redox potential according to particular water-rock interactions.

In areas of the Pampean region, Blanco et al. (2006), found a lack of direct association between volcanic glass contents in loess and  $\tau\text{As}$  in water. Results in agreement with Nicolli et al. (2006) regarding the noticeable heterogeneity in  $\tau\text{As}$  concentration in groundwater present in Buenos Aires Province (Puelche and Pampean aquifers) which circulates through geological material not necessarily enriched in  $\tau\text{As}$  (Pampean from  $1$  to  $400 \mu\text{g}\cdot\text{l}^{-1}$ , Puelche usually with  $\approx 10 \mu\text{g}\cdot\text{l}^{-1}$ , occasionally with sites reporting from  $37$  to  $200 \mu\text{g}\cdot\text{l}^{-1}$ ). Morrás (2003) reports  $\tau\text{As}$  heterogeneity in the composition and distribution of surface loess sediments from which Pampean soils are derived. Othax et al. (2014) also report varying amounts of  $\tau\text{As}$  ( $0.009$  to  $0.5 \text{mg}\cdot\text{l}^{-1}$ ) from different origin such as

weathering of silicates in primary loess as biotite as well as in volcanic glass (Limbozzi et al., 2005, cited in Othax et al., 2014). Blanco et al. (2006) indicate chemical water trends: an increase in  $\tau\text{As}$  in groundwater in the discharge zone as related to a negligible concentration in the recharge zone; they consider that its presence is associated to travel distance, water-rock interaction, and chemical water type ( $\text{HCO}_3^- \text{-Na}^+$ , and  $\text{Ca}^{+2}\text{-Mg}^{+2}$ ). Paoloni et al. (2005, cited in Nicolli et al., 2006) found a relation between groundwater flow type defining higher  $\tau\text{As}$  concentration in the lengthier path than in the shorter local path.

Bundschuh et al. (2006b) and Litter et al. (2006) agree to indicate that  $\tau\text{As}$  in groundwater is controlled by three main factors: i) primary source of  $\tau\text{As}$  (soil and air), ii) processes of mobilization-retention of  $\tau\text{As}$  in the solid-liquid phase, and iii)  $\tau\text{As}$  transport in water. They conclude that the main cause of the presence of  $\tau\text{As}$  in water is not the source but the interaction between phases and its mobilization control (reactions of sorption-desorption, precipitation-dissolution, co-precipitation and co-dissolution).

Litter et al. (2006) indicate that the chemical conditions due to redox potential, pH, presence of organic matter, competing ions (by sorption sites or those associated with oxi-hydroxides) Fe, Al, Mn,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^-$  or  $\text{HCO}_3^-$ , may indirectly control  $\tau\text{As}$  adsorption-desorption by their effects on the chemical speciation, emphasizing that the chemistry of  $\tau\text{As}$  follows closely that of S and Fe, with pyrite formation, mainly in reduced environments and integrating  $\tau\text{As}$  in the process;  $\tau\text{As}$  which is available to be released under different conditions.

In agreement with Mejía et al. (2014) which found  $\tau\text{As}$  concentration to be increased under alkaline conditions, Bundschuh et al. (2006b) indicate that the presence of  $\tau\text{As}$  in water is possible under neutral to alkaline conditions due to silicate hydrolysis, carbonate dissolution under the presence of volcanic glass, clay, organic matter, hydroxides, oxides and Fe through the interchange, in oxidation conditions with Arsenic (V) in remarkable variable concentration, where the slow transit (long residence time) of water in aquifer materials, diminish the opportunity to eliminate  $\tau\text{As}$  of the system. Therefore, intermediate and regional flow systems are more likely to bear  $\tau\text{As}$  and it is most likely that this situation to be observed in their discharge natural zones, and consequently,  $\tau\text{As}$  may be observed in shallow wells tapping discharge zones of that nature. Note that a discharge zone by definition has a shallow water-table distribution.

Regarding the physical and chemical characteristics of water related to the  $\tau\text{As}$  content, although some tendencies have been described they are not always coincident. Ortega (2009) finds  $\tau\text{As}$  to be associated to a  $\text{HCO}_3^- \text{-Na}^+$  chemical water group, and mainly due to silicate dissolution (feldspars and biotite), whereas the origin of F is related to fluorite dissolution as well as to

silicates (feldspar and mica). Nicolli (2006) indicates a strong correlation between  $\tau$ As and F, related to the physical and chemical conditions of the water that support the migration of both elements: high  $\text{HCO}_3^-$  with pH values of  $\geq 7.5$  for pH. Blanco et al. (2006) also found a relation between high  $\tau$ As content with salinity greater to  $1 \text{ dSm}^{-1}$ , alkaline conditions, and large residence time of groundwater. However, Litter et al. (2006) indicated that the role of  $\text{HCO}_3^-$  in relation to the desorption processes of  $\tau$ As has not been found to be clear.

The problem of  $\tau$ As and other hazardous elements in water for animal, vegetation and human utilization has determined the need to propose methodologies that provide a comprehensive framework for groundwater quality data analysis to implement agreeable planning and management tools of groundwater extraction (Grima et al., 2015; Rodríguez et al., 2016). These authors indicated that such implementation becomes vital in regions with potential sources of contamination processes in soil and groundwater.

Available bibliography suggests inconsistencies regarding the presence of  $\tau$ As in groundwater proposing a need to carry out studies on regional bases under similar physical and chemical (hydrogeological) conditions.

In regions like the northwest of the province of Buenos Aires, characterized by a cyclical presence of dry and humid periods (includes flooding), where the water-table is shallow (i.e., discharge conditions), the understanding on how the landscape functions becomes important for defining soil management and flooding control (Alconada-Magliano et al., 2011, 2014). The reaching of an understanding on how the environment could function may assist in finding control on obtained water quality, in particular for  $\tau$ As considering its high level of potential toxicity. It becomes central to define those environments that might supply  $\tau$ As to crops as in this studied territory which is controlled by shallow groundwater surfaces. Costa et al. (2016) finds that  $\tau$ As accumulates in different parts of the crop plants in a rate varying with the species; these authors also gives references to authors describing the translocation of  $\tau$ As in plant systems and how levels of  $\tau$ As in grain are due to several factors including the mobilization and bioavailability of  $\tau$ As in the soil. For example, Bastías and Beldarrain, (2016) review possible mechanisms involved in  $\tau$ As absorption that contaminate rice plant through soil and water. The root of rice is able to absorb and accumulate large amounts of  $\tau$ As, but only small amounts are transferred to the grain and tillers. However, some rice varieties have been developed to be resistant to high  $\tau$ As content. Recently, an increase interest has been reported in phyto-remediation species due the capability of a plant to absorb and accumulate  $\tau$ As. Roseli et al. (2010) confirmed *Eucalyptus grandis* as a species with potential for  $\tau$ As phyto-extraction, tending to accumulate it in the root system and stem. Note that *Eucalyptus sp* is used in bio-drainage technique where

evapotranspiration is useful to deepen shallow groundwater surfaces (Heuperman et al., 2002). This is promising for regions where there a possibility to have a *Eucalytus sp* plantation or in a silvopastoral system (plantation of forest species with bovine-cattle ranching) (Alconada-Magliano et al., 2009).

An understanding of the concentration of  $\tau$ As present in water, its chemical and physical controlling conditions as oxide-reduction, pH, and the role of the components of the landscape such as geomorphology, water-table position, vegetation, soil, would assist to achieve the required water management.

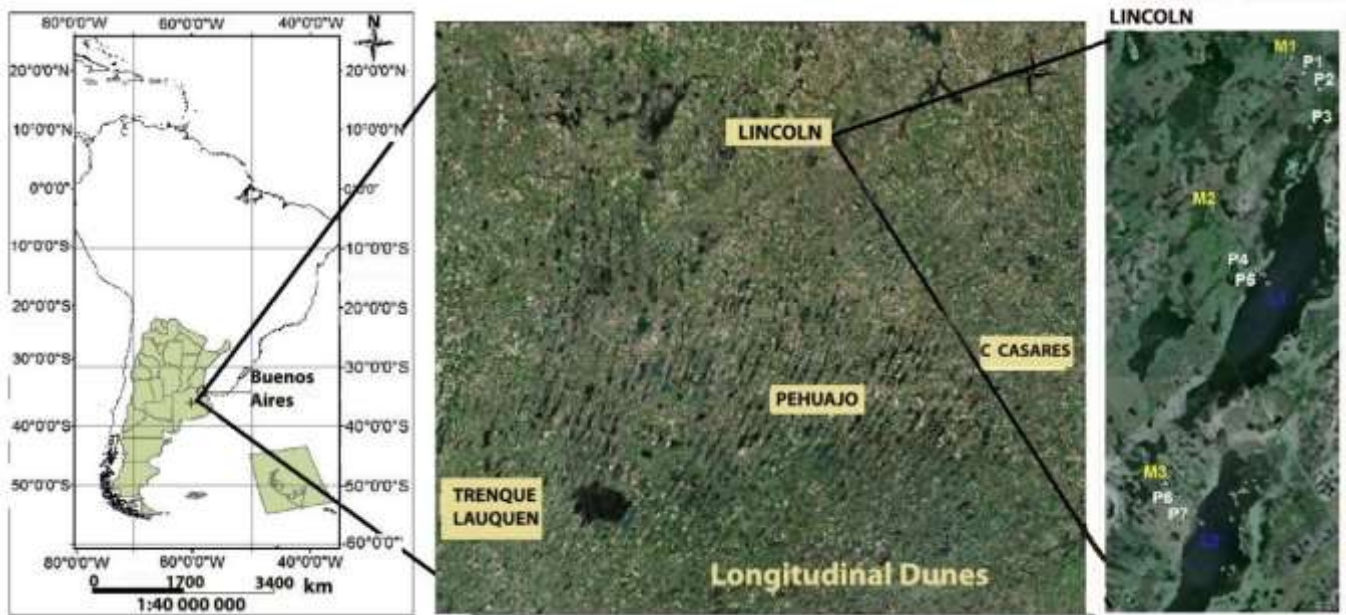
## Fluoride

A wide variety of studies is available on various concepts of  $\text{F}^-$  as related to groundwater dealing with water-rock interaction in various aquifers with different lithology among which Edmunds et al. (1984), Robertson (1986), Zhaoli et al. (1989), Travi and Faye (1992), Nordstrom et al. (1989) and Hitchon (1995) provide an adequate reference. From the groundwater quality point of view Nanyaro et al. (1984), Gaciri and Davies (1993), and Pekdeger et al. (1992) have found  $\text{F}^-$  to be a potential natural occurring contaminant due to its high observed concentration in ground water which is low in  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . Carrillo-Rivera et al. (2002) described proposals of various authors on complex and costly techniques to remove  $\text{F}^-$  from groundwater, and advise a procedure based on the knowledge of the hydrogeological conditions and the management of prevailing flow systems, controlling  $\text{F}^-$  concentration before groundwater is being abstracted in a well; technique that avoids the need of a water-treatment plant and the management of generated sludge.

The association between the occurrence of  $\tau$ As and  $\text{F}^-$  in obtained groundwater has been indicated in works as those of Nanyaro et al. (1984); Hitchon (1995); Edmunds and Smedley (2005); Galindo et al. (2005); Nicolli (2006); Ortega (2009); Panagiotaras et al. (2012); Mejía et al. (2014) and Othax et al. (2014). In general they indicate that their mobility is associated with the media conditions, mainly pH, salinity, and anaerobic conditions. The presence of both elements has been mentioned by various authors in sediments of the Chaco-Pampean plain (Morrás, 2003; Auge, 2004; 2008; Smedley et al., 2005).

## Research objective

The definition of the relation of groundwater functioning with other components of the environment becomes an important issue to achieve an eventual control  $\tau$ As and  $\text{F}^-$  in extracted ground water or being absorbed by vegetation. This may be achieved when the chemical



**Figure 1.** Location of the studied territory and referred sites related to the Sandy Pampa in Buenos Aires, Argentina.

S1, S3 and S3

relation of circulating groundwater in the region is understood from the perspective of the theory of the groundwater flow systems by Tóth (2000). Therefore the objective in the present study seeks to define the relation of  $\tau$ As and F<sup>-</sup>, with natural components of the landscape, and their relation with the groundwater flow systems under the flow system theory as a base to reach an understanding on how the landscape is an indirect means of groundwater functioning.

## MATERIALS AND METHODS

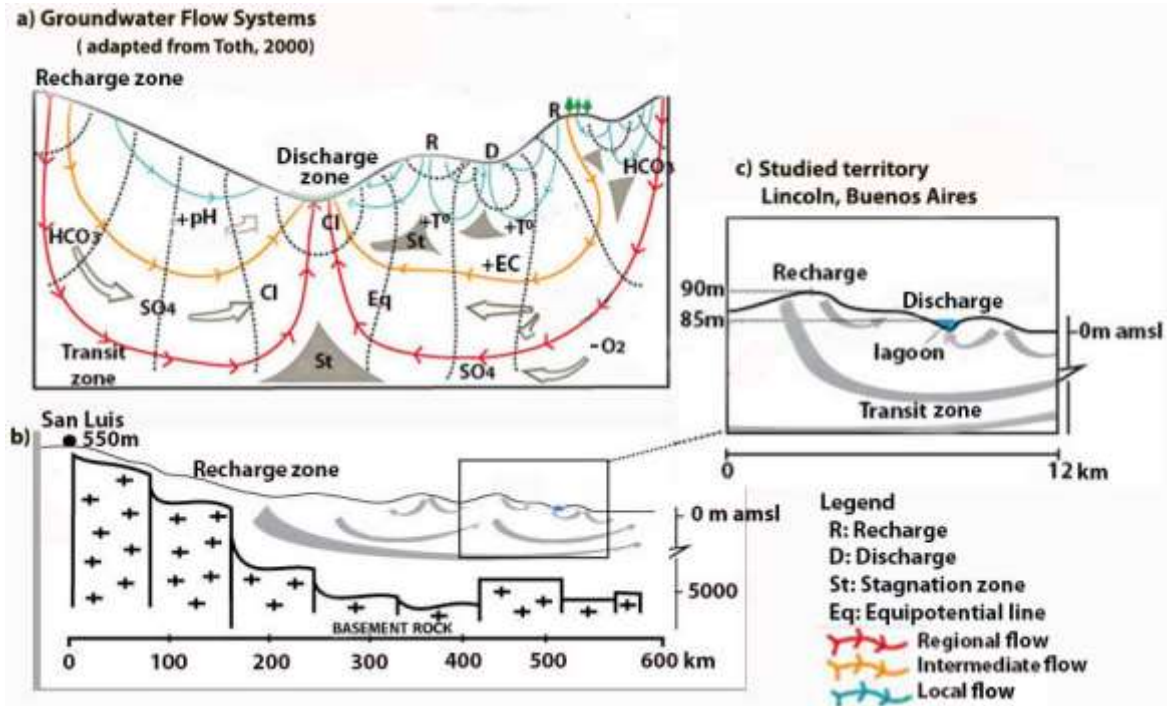
This study was carried out at the Lincoln (Li) region, which includes part of the Longitudinal Dunes Sector of the Sandy Pampa (some 5'500,000 ha) in the province of Buenos Aires, Argentina. Twelve sites were subject to soil and water sampling and included in three sections (S) (Figure 1); S1: Upper section, Mill 1 (M1), piezometers 1 (P1), 2(P2), and 3 (P3) (distance from M1 to P3 is 1,605 m, slope 0.16%). S2: Medium section, Mill 2 (M2), piezometers 4 (P4), and 5 (P5), and Lagoon 1 (L1) (distance from M2 to L1 is 1,815 m, slope 0.14%). S3: Lower section, Mill 3 (M3), piezometers 6 (P6) and 7 (P7), and Lagoon 2 (L2) (distance from M3 to L1, is 1,055 m, slope 0.12%).

When these three cross-sections are considered, the topographic difference between the lowest and the highest site, is of 3.65 m, with an overall sampling length of 9,935 m and a general slope of 0.037%; these sections are located in a larger region with a slope of 0.6% (NW-SE direction), and elevations from 90.0 to 82.5 m amsl (meters above mean sea level). The surface natural drainage lacks a definite pattern, surface water flows slowly among a micro-relief of crests and stabilized dunes. These landforms are defined as extended flat hills separated by small depressions. Results along these locations are compared with previous studies as in Pehuajó (Pe), Trenque Lauquen (TL), and Carlos Casares (CC) (Alconada-Magliano et al., 2011). Part of the challenge is to define the

groundwater control that permits the transport of  $\tau$ As and F<sup>-</sup> in the water.

## Groundwater flow systems

This is a relative modern methodology in hydrogeology (Tóth, 2000) that appears to be a feasible proposal to define groundwater and  $\tau$ As and F<sup>-</sup> functioning in the studied territory. This method considers that under natural conditions there is a relation among soil, vegetation, geomorphology, geological structure, and water related characteristics. Groundwater movement is acknowledged in 3-D and implying velocity and direction that becomes evident in three contrasting components: recharge, transit and discharge zones. Water quality recognizes the existence of different and contrasting flow systems coexisting in the vertical plane at the same site through different manifestations of contrasting nature and scale as local system, intermediate system and regional system. The local system travels short and shallow path as compared with the regional system being the deepest and lengthiest whose limit underneath is the basement rock; an intermediate system travels in between both. The components of these flows are complemented in their hydrological functioning by contrasting characteristics, mainly in geomorphology (recharge zone with deep water-table depth in an upper topographic level as compared to a discharge zone with shallow water table depth in the lowest one), water quality (salinity will increase with flow hierarchy, the prevailing Na<sup>+</sup> and Cl<sup>-</sup> increase in the discharge zone, oxygen will diminish with path length resulting also in a pH and temperature increase) and flow direction (vertical downwards for recharge, horizontal in transit, upward in the discharge zone). Discharge and recharge zones have contrasting physical and chemical characteristics to those of the discharge zones where soil and vegetation types will be coincident with such features and the nature of the present flows. In this work, the defined type of flow (local, intermediate or regional), and their respective recharge, transit and discharge zones were defined according to the flow systems theory (Tóth, 2000) portrayed in Figure 2(a), which appears with more detail in Alconada-Magliano



**Figure 2.** (a) Theoretical profile showing fundamental groundwater flow systems (adapted from Tóth, 2000); the vertical scale depends on the geological framework (i.e., Basement rock position). (b) Proposed flow systems in the region of reference; (c) Conceptual model of groundwater flow systems within San Luis and Lincoln in Buenos Aires, Argentina. (EC, electrical conductivity, T, temperature).

et al. (2014). The actual conceptual groundwater flow model could be represented as shown in Figure 2(b); a west-east vertical section is located in the vicinity of the city of San Luis (near the Andes Mountains) ending about 500 km away on the outskirts of the city of Lincoln. Note that the sand dunes are at the very top of 5,000 m of granular materials deposited on a Cambrian Granite formation (basement rock) (Etchichurry et al., 1988; PMI, 1999; Gonzalez, 2005). In part (c) of Figure 2 it shows more detailed outline of the proposed flow systems in the region (local and intermediate flows with recharge, transit and discharge zones), which is based on previous studies in the region (Alconada-Magliano et al., 2011).

### Water sampling and analytical procedures

A total of 108 water samples were collected at nine time intervals: D1, 12/05/2011; D2, 28/07/2011; D3, 28/09/2011; D4, 22/11/2011; D5, 29/02/2012; D6, 18/06/2012; D7, 19/09/2012; D8, 28/11/2012, and D9, 19/3/2013. Samples were collected at mills (M) with after cleaning extraction system. In Piezometer (P), water extracted with mechanical pump, after draining the extraction tube, and subsequent recovery of the water level. In lagoons (L) water was extracted from the center portion to 40 cm deep (average water deep in lagoon about 1 to 1.5 m). Water was collected in new (500 ml) bottles washed with a solution containing 10% nitric acid and rinsed with distilled water, on site these bottles were rinsed three times with the sample water. Samples for  $\text{As}$  were not filtered, no acid was included and daily were sent to the laboratory for processing. Samples for major anions and metals were filtered with a  $0.45 \mu\text{m}$  membrane and high purity  $\text{HNO}_3$  was added to reach a pH of  $\approx 2$  to keep metals in solution. Standard sampling procedures includes field measurements of temperature, pH, and electrical

conductivity (EC) (HANNA Model HI-8424). All used equipment was in situ calibrated with buffer solution for pH (4.7 and 10  $\pm$  0.01) and EC with solution  $12,880 \mu\text{Scm}^{-1}$  at 25  $^\circ\text{C}$ ) (APHA-AWWA-WPCF, 1989). Field measurement was used to check laboratory measurement (Table 1). All analytical determination was performed at the Tecnoagro S.R.L and Laboratorio Inagro (INTA: Red de Laboratorios de Suelos, Agua y Vegetales, RILSAV).  $\text{As}$ ,  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ , were determined by atomic absorption with generator of hydrides; F $^-$  was measured by selective electrode.  $\text{CO}_3^{2-}$  y  $\text{HCO}_3^-$  were determined by acid-base titration,  $\text{Cl}^-$  by titration with  $\text{AgNO}_3$  (Mohr's Method),  $\text{SO}_4^{2-}$  by turbidimetric method,  $\text{Na}^+$  and  $\text{K}^+$  by flame photometry, pH was determined by portable pH meter as well as salinity by electrical conductivity meter. All reported values have ionic balance error within 5% except some samples of highly mineralized water which show less than 10% error;

Obtained data were processed using HIDROGEOQUIM model (Fagundo et al, 2006), whereby it is obtained of FCCI, factor of  $\text{Cl}^-$  concentration with respect to rainwater; water type; average hydro geochemical pattern of Kurlov (Fagundo, 1998), which represents the relationship between anions and cations ( $\text{Na}+\text{K}:\text{Ca}:\text{Mg}:\text{Cl}:\text{HCO}_3:\text{SO}_4$ ) (detailed description may be obtained in Alconada-Magliano et al., 2014). Rainwater was collected in October 2012 from pluviometer type B installed next to the P4 sampling site.

The quality of data was validated comparing actual electrical conductivity (EC) with theoretical EC (Miller et al., 1988). The faces hydrogeochemical (diagrams of Stiff), hardness ( $\text{CaCO}_3$ ), total dissolved solids (TDS), and the geochemical processes suggesting the origin of the chemical composition of water were determined using the MODELAGUA model (Fagundo-Sierra et al., 2001; Fagundo et al., 2006). The selection of the geochemical processes that could explain the origin of the chemical composition of water was established based on the lithology constitution (Etchichurry et

**Table 1.** Average values for water of nine sampling dates of Lincoln.

S	T	pH	EC	SAR	FCIC	$\tau_{As}$	F <sup>-</sup>	Water type	AHP	
S1	M1	17.4	7.9	3.9	21	56	0.019	0.885	HCO <sub>3</sub> >Cl>SO <sub>4</sub> -Na	901-352
	P1	17.0	8.1	3.1	23	24	0.037	1.903	HCO <sub>3</sub> -Na	901-172
	P2	17.2	7.9	10.2	39	237	0.036	1.450	Cl>SO <sub>4</sub> -Na	901-514
	P3	17.4	7.7	19.5	45	555	0.087	2.191	Cl>SO <sub>4</sub> -Na	901-514
S2	M2	17.4	8.0	5.9	31	116	0.041	1.360	HCO <sub>3</sub> =Cl>SO <sub>4</sub> -Na	901-442
	P4	17.5	8.2	3.8	38	54	0.117	3.722	HCO <sub>3</sub> >Cl-Na	901-352
	P5	17.2	7.7	16.0	43	442	0.044	1.640	Cl>SO <sub>4</sub> -Na	901-514
	L1	18.7	8.4	8.6	35	262	0.035	0.376	Cl>SO <sub>4</sub> -Na	901-613
S3	M3	19.2	7.9	5.0	20	121	0.027	1.025	Cl>HCO <sub>3</sub> >SO <sub>4</sub> -Na	901-532
	P6	16.9	8.0	4.1	26	80	0.077	2.507	HCO <sub>3</sub> =Cl>SO <sub>4</sub> -Na	901-442
	P7	17.1	7.8	10.6	30	323	0.038	1.678	Cl>SO <sub>4</sub> -Na	901-613
	L2	17.0	8.3	15.1	35	502	0.032	0.449	Cl>SO <sub>4</sub> -Na	901-613

Explanation: pH, electrical conductivity (EC, dSm<sup>-1</sup>), temperature (T, °C), sodium absorption ratio (SAR), factor of chloride concentration (FCIC),  $\tau_{As}$  and F<sup>-</sup> (mgL<sup>-1</sup>), hydrogeochemical pattern (AHP: relation Na+K:Ca:Mg-Cl:HCO<sub>3</sub>:SO<sub>4</sub>) as obtained in cross-sections (S) S1 Upper (M1, P1, P2, P3), S2 Middle (M2, P4, P5, L1), and S3 Lower (M3, P6, P7, L2). P: piezometer, M: mill, L: lagoon.

al., 1988; PMI, 1999; González, 2005). Samples with low Na<sup>+</sup> and Cl<sup>-</sup> content (P1, P4 and mills) used in the model of mass balance were referred to rainwater. For sites with high content of Na<sup>+</sup> and Cl<sup>-</sup>, a model of water mixture was used with low saline reference, in this case the less saline water of the studied region was used (P1, D1). The reference of the water with highest mineralization, thermal water in nature where obtained from the mineral water catalogue by SEGEMAR, well BA73, was used as a reference (Pesce and Miranda, 2003) (data no presented).

### Soil sampling and analyses

In each sampling site soil was studied by standard procedures of analysis and characterization, using the classification by USA Soil Taxonomy (Soil Survey Staff, 2010) with the established adaptations for Argentina (SAGyP-INTA, 1989). The mineral composition was determined using an x-ray diffraction system; measurements were made in the Mineral Laboratory of the Soils Institute, INTA-CIRN. Soil types were also interpreted according to the expected recharge or discharge conditions.

### Aquifer material and main regional geomorphology

The studied region is an extensive plain developed on eolian sediments stabilized by vegetation. The stratigraphic sedimentary sequence includes: Invading Dunes Formation (thickness 0-30 m, E1); Pampean (loess, thickness 5-150 m, E3), Araucana, Puelche, Paraná, Olivos, Las Chilcas, and Belgrano formations (with a joint thickness from 1,000 to 6,000 m) (PMI, 1999; González, 2005). Pampeana, Araucana, Puelche formations (with a collective thickness of 500m) are the active groundwater system. The Pampeana Formation is considered in the region to be the top of the aquifer units in conjunction with the Invading Dunes Formation, which is described as the main aquifer unit in the Sandy Pampa (Figure 1). This formation shows sand dunes on its top and gives origin to the geo-morphological unit: named Longitudinal Dunes (Figure 1). These geo-forms are approximately 100 km in length, 2-5 km wide and 6 m height, spaced each by a 3-4 km inter-dune. The surfaces of inter-dunes have a flat to flat-concave shape, 0.5 to

5 km wide. The Parana Formation is the base of the local shallow system (aquiclude, or confined aquifer unit). All geological units are saturated with hydraulic continuity and may be considered, regionally, like an unconfined groundwater system; the water-table generally is <5 m in depth, producing a large number of wetlands and lagoons (PMI, 1999; González, 2005). These water bodies are the manifestation of discharge of groundwater flows of local and intermediate nature. The regional groundwater flows travel deep below above indicated formations from their recharge inland to their discharge zones in the Atlantic Ocean.

### Soils and local geomorphology

The soils are formed from sediments of the Invading Dunes (E1) and Pampean (E3) formations. They have been formed in two subsequent cycles, one older with an sandy loam and clayey silt texture (Pampean Formation) and more recently one of sandy fine to silty-clayey composition (Invading Dunes Formation) that outlines the Longitudinal Dunes (Figure 1) (SAGyP-INTA, 1989; Giménez et al., 1990; Cabral et al., 1996). Dillon et al. (1985) recognized inside those main geo-forms there are smaller geo-form units locally called: *small dunes, mantles, shallow mantles, inter-dune depressions, and deflation buckets*. This author also recognized a soil named "thapto" (buried) developed in both sediments with vertical lithologic discontinuity. Figure 3, shows examples in Trenque Lauquen, showing geo-forms of mantles, brief mantles, and inter-dunes depressions, as well as detail of the vegetation difference as the thickness of geo-form mantle, and the site to where water discharges from the inter-dune, and in Lincoln with different development of wheat for each particular thickness of upper deposit (E1). Thus the longitudinal dunes form a series of smooth hills and shallow plains that characterize the region, due to the perennial discharge condition the presence of lagoons between dunes is a common observed landscape feature.

### Mineralogy

Regarding the mineralogy of outcropping sediments (up to <12 m depth in Invading Dunes Formation (E1), Etchichurry et al. (1988)



**Figure 3.** Trenque Lauquen, geo-forms (upper left) and vegetation difference as the thickness of geo-form (upper right). Lincoln, difference in the development of wheat due to the thickness of the upper deposit (E1) bottom left and right).

report the following minerals: quartz (between 19 and 26%); plagioclase (between 15 and 40%); K-feldspars (between 6 and 8%); weathered rock (between 14 and 47%); augite, volcanic glass, biotite (between 0.6 and 1.71%); hypersthene, hornblende, lamprobolita (<0.4%); and rutile, zircon, and garnet (<0.10%). These mineralogy are coincident with PMI (1999) and Gonzalez (2005) for Invading Dunes (E1) (Holocene) and Pampean (Pampeana, E3) formations (Pleistocene). The proportions of these minerals and textures differ for both sediments because sedimentation occurred in several wind pulses (Nicolli et al., 2006). This sediment is primary loess (recent deposits are more sandy) and secondary loess (or loessoid, reworked loess) (old deposits are clayed and silty) (Rocca et al., 2006). These authors indicate that Pampean loess is generally characterized by abundance of plagioclase (20 to 60%), relatively little quartz (20 to 30%) and a considerable content of volcanic glass (15 to 30%).

#### Identification of groundwater flow systems

The different elements of the landscape (physical-chemical characteristics of water, springs and shallow water-table, soil, type and mineralogy, vegetation, as well as local and regional geomorphology) are analyzed and linked at each sampling site. Previous studies of other localities linked hydrogeologically from a regional perspective were also considered. The applied criterion as established by Toth (2000) which established the flow hierarchy each with its pertaining recharge or discharge zone was considered. Additional information is presented in Alconada-Magliano et al.

(2011, 2014). Groundwater flow system association is established among environmental variables and the physical and chemical characteristics of water where the presence of  $\tau$ As and  $F^-$  might be managed with simple but sound correlations.

## RESULTS AND DISCUSSION

### Lincoln, general environmental characterization

#### Water quality

Table 1 shows chemical characteristics of sampled water indicating values of pH, electrical conductivity, temperature, sodium absorption ratio, factor of chloride concentration,  $\tau$ As and  $F^-$  with average for 9 measurements made at different dates. Data is referred to cross-sections S1, S2 and S3 showing also the type of water and average hydrogeochemical pattern (AHP). The three water groups (G) to which they were found to belong are indicates in Table 2. Also, Table 2 indicates vegetation and depth to the water-table as recorded in the first sampling date (D1), landscape position, topographic elevation, soil type, flow hierarchy and the pertaining recharge or discharge zones. The groundwater component identified as recharge, transit or discharge



**Table 2.** Characteristics of the sampling sites in Lincoln.

S	Position	m amsl	Vegetation cover. D1	Soil	m WT	G	FH	Z
S1	M1 P- HH	90.62	Soybean. Corn stubble	TH	6.0	1	L	R-T
	P1 P- EFH	89.36	<i>Melilotus sp. Bromus unioides. Lotus sp</i>	AH	1.9	1	L	R-T
	P2 P- MLH	88.44	<i>Spergularia sp. Lotus sp. Distichlis sp. Salts</i>	NTH	1.2	3	I	D
	P3 P- L	88.00	<i>Distichlis sp. Spergularia sp. Salicicornia sp</i>	TNf	1.0	3	I	D
S2	M2 P- HH	89.48	Weath. Corn stubble. Flooded for water-table	ATH	6.0	1	L	R-T
	P4 P- EFH	88.44	Corn stubble	NTH	1.8	1	L	R-T
	P5 P- L	87.19	<i>Distichlis sp. Chloris berroi</i>	TNf	0.7	3	I	D
	L1 B	86.34	Lagoon with shore lacking vegetation		0.0	3	I	D
S3	M3 P- HH	88.02	Soybean. Corn stubble	TH	6.0	2	I	R-T
	P6 P- EFH	87.99	Soybean. Corn stubble	NTH	1.6	1	L-I	R-T
	P7 P- MLH	86.97	<i>Distichlis sp. Cynodon sp. Salt on surface</i>	TN	1.0	3	I	D
	L2 B	85.91	Lagoon with shore lacking vegetation		0.0	3	I	D

Explanation: landscape position (P, plain; HH high hill; EFH, extended flat hill; MLH, medium low hill; L, low; B, bucket); topographic elevation (m amsl); vegetation (in date D1); soil, *Typical Hapludolls* (TH), *Acuic Hapludolls* (AH); *Argic or Natric thapto Hapludolls* (ATH or NTH); *Typic Natracualls* (TNf); *Typic Natracualls* (TN), Water-table depth in m (WT in date D1); water group (G); hydrogeochemical pattern (AHP); Flow Hierarchy FH, (I) intermediate, local (L); zones (Z): recharge-transit (R-T); discharge (D). Cross-sections (S) S1 Upper (M1, P1, P2, P3), S2 Middle (M2, P4, P5, L1), and S3 Lower (M3, P6, P7, L2), of Lincoln (Li). P: piezometer, M: mill, L: lagoon.

zone as well as the nature if the flow hierarchy were obtained from the physical and chemical characterization of the water and landscape elements, all of which should be in agreement with the groundwater flow systems theory (Tóth, 2000; Alconada-Magliano et al., 2014).

The location characteristics of the three cross-sections (S1, S2, S3) are: distance between sampling site, topographic elevation difference, and depth to the water-table (mills 6m, P1, P4 and P6 between 1.6-1.9 m, and P3, P5, P7 between 0.7 and 1.0 m which would not suggest noticeable differences as those obtained in water quality. The identified water groups and flow systems to which they belong (Table 2) are as follows: *Group 1*,  $\text{HCO}_3\text{-Na}$ ,  $\text{HCO}_3\text{>Cl-Na}$  and  $\text{HCO}_3\text{>Cl>SO}_4\text{-Na}$  with average EC of  $4.16 \text{ dSm}^{-1}$  (M1, M2, P2, P4 and P6, all located in the highest position in cross-sections). *Group 2*,  $\text{Cl>HCO}_3\text{>SO}_4\text{-Na}$ , average EC of  $5.0 \text{ dSm}^{-1}$  (M3, highest elevated sector of S3, sampling to 6 m depth). *Group 3*,  $\text{Cl>SO}_4\text{-Na}$ , average EC of  $13.33 \text{ dSm}^{-1}$  (P2, P3, P5, P7, L1 and L2). Consequently, a water evolution from  $\text{HCO}_3\text{-Na}$  in P1, the highest elevated sector, with external environmental characteristics of recharge, to  $\text{Cl-SO}_4\text{-Na}$  in the lower sectors with discharge features in P2, P3, P5, P7, L1 and L2. In all the cases the salinity and alkalinity showed high  $\text{Na}^+$  which is the commonly found cation, therefore an AHP of 901 represents 90%  $\text{Na+K}$  and 10%  $\text{Mg}$  (Table 1).

### Identification of groundwater flow systems

In Lincoln, mills and piezometer P1, P4 and P6, are in

high position (on a hill), with typical soils of recharge conditions, the water mineralization (EC) is lower than in positions located in lower topographic sites (Table 1). This suggests that water of *Group 1* belongs to a local flow system. Although it has a high factor of  $\text{Cl}^-$  concentration with respect to rainwater (FCIC) and other values as indicated in Table 3. this table also includes the average values of nine sampling dates and extremes values (minimum and maximum) of the composition of water in piezometers (P) located on hills (P1, P4, and P6), of three sections (S, S2 and S3, respectively), respect to rainwater collected (October 2012) pluviometer type B installed next to the P4 sampling site.

The chemical quality (Table 1) of the water of *Group 3*, suggests conditions of an intermediate flow (Table 2). The chemical characteristics (Table 1) of *Group 2* propose the presence of a mixture of a shallow and an intermediate groundwater flow system (Table 2). In all cases, with the exception of  $\text{HCO}_3^-$ , the composition of anions of the extracted water in piezometer in the lower topographic positions (P2, P5 and P7) are higher than those presented in Table 3 for water from piezometers (P) located on hills, and corresponds to the type of water and other properties indicated for these waters at Table 2. Thereby the composition of anions was:  $\text{HCO}_3^-$  between  $16.7$  and  $22.5 \text{ meqL}^{-1}$ ;  $\text{Cl}^-$  between  $45.0$  and  $105.5 \text{ meqL}^{-1}$ ;  $\text{SO}_4^{2-}$  between  $43.3$  and  $81.2 \text{ meqL}^{-1}$  and without  $\text{CO}_3^{2-}$ . Regarding cations, all concentrations were high in the low positions, showing the very high  $\text{Na}^+$  content. The average composition was  $\text{Ca}^{+2}$  between  $3.3$  and  $7.0 \text{ meqL}^{-1}$ ;  $\text{Mg}^{+2}$  from  $8.3$  to  $21.1 \text{ meqL}^{-1}$ ;  $\text{Na}^+$  between  $92.6$  and  $171.8 \text{ meqL}^{-1}$ ; and  $\text{K}^+$  from  $1.3$  to  $2.2$

**Table 3.** Average values of nine sampling dates (Av) and values extremes (minimum and maximum composition of water (b) high position (on a hill)).

P		T	pH	EC	SAR	FCIC	HCO <sub>3</sub> <sup>-</sup>	CO <sub>3</sub>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-</sup>	Ca <sup>2+</sup>	Mg <sup>+</sup>	Na <sup>+</sup>	K <sup>+</sup>
P1	Av	17.0	8.1	3.1	23	24	20.3	0.2	4.6	5.3	0.7	2.1	27.2	0.7
	b	15.0-19.7	7.9- 8.7	2.6- 3.5	21.0-25.0	20.0-29.0	18.8-22.2	0.0-1.4	3.8-5.6	4.3-6.7	0.3-0.9	1.8-2.4	25.2-30.5	0.6-0.8
P4	Av	17.5	8.2	3.8	38	54	19.7	0.7	10.3	7.4	0.4	1.5	36.1	0.7
	b	15.2- 19.1	8.1- 8.4	3.4 - 4.5	34-40	44-69	18.5-21.3	0-1.9	8.4-12.5	6.3-9.5	0.4-0.5	1.2-2.0	33.1-41.5	0.7-0.8
P6	Av	16.9	8.0	4.1	26	80	16.0	0.3	15.2	8.6	1.0	3.1	36.3	0.9
	b	13.9-19.5	7.9-8.1	2.9-5.2	25-30	42-113	14.8-16.8	0-1.6	7.9-21.5	5.4-11.3	0.5-1.4	1.8-4.5	27.4-43.9	0.7-1.0
RW		*	7.2	0.063	1.4	*	0.3	0	0.2	0.31	0.20	0.05	0.10	0.03

Explanation: Piezometers (P) on hills (P1, P4, and P6) of three sections (S, S2 and S3 respectively), and with respect to rainwater (RW), collected on October 2012. pH, electrical conductivity (EC, dSm<sup>-1</sup>), temperature (T, °C), Sodium Absorption Ratio (SAR), factor of chloride concentration (FCIC), cations and anions (meqL<sup>-1</sup>); (\*) not measured.

meqL<sup>-1</sup>. Regarding the water of the lagoons, the concentration is also higher than in the piezometers located in high topographic position; however, it is more variable because it is influenced by the local rainfall (and groundwater flow). The composition averages were HCO<sub>3</sub><sup>-</sup> from 6.2 to 6.8 meqL<sup>-1</sup>; Cl<sup>-</sup> between 49.9 and 95.4 meqL<sup>-1</sup>; SO<sub>4</sub><sup>-2</sup> 30.3 to 51.8 meqL<sup>-1</sup>, and CO<sub>3</sub><sup>-2</sup> 0.6 and 1.6 meqL<sup>-1</sup>. The cation composition in the last piezometers markedly prevails with Na<sup>+</sup> between 46.6 and 127.7 meqL<sup>-1</sup>, Ca<sup>+2</sup> between 2.8 and 8.3 meqL<sup>-1</sup>, Mg<sup>+2</sup> between 7.0 and 17.0 meqL<sup>-1</sup>, and K<sup>+</sup> between 1.8 and 2.4 meqL<sup>-1</sup>. The FCIC is another variable that contribute to define the type of intermediate flow and discharge zone. The average values in piezometers (P2, P3, P5, P7) varies between 237 and 555, and in the lagoons between 262 and 502. These values are bigger than in piezometers in high topography position (Table 2).

This also agrees with salinity (EC), but not with SAR, possibly because they maintain a certain cationic relationship regardless of their particular

concentrations.

### Soils

The general characteristics of the soils in the region have been reported (SAGyP-INTA, 1989). However, for the objective of the present study these data are insufficient to characterize a soil in relation to its origin and link to groundwater flow. It is paramount to define how soils behave from a regional perspective (Alconada-Magliano et al., 2014). In this region, it is observed that the interaction of the water-table position and vegetation with the topography (landform) determine the soil type and its ability to develop contrasting recharge-discharge conditions and evapotranspiration processes which interact in what “*at priori*” could be inferred to as a position in the local topography (Figure 3). In Figure 3, as indicated above, the thickness of the surface deposit determines the nature of the soil and marks the difference in the development of a

particular vegetation due to the position of the water-table (depth) controlling the expected evapotranspiration rate.

Thus in Lincoln, differences in thickness of the upper deposit (E1) allows the presence of different soils. In elevated ground of Lincoln, mills (M1, M2 and M3) and piezometer P1, the upper deposit is of thick texture (geo-form of mantles, Figure 3), soils are *Typic Hapludolls* (HT), and *Acuic Hapludolls* (HA). In lower parts, or where the soil thickness diminishes even in high ground, a lithology discontinuity is recognized, and soils are *Argic thapto Hapludolls* and *Natric thapto Hapludolls*; where the upper deposit cover disappears or is insufficient, these soils being defined as *Typic Natracuolls* and *Typic Natracualfs* (Table 2). The water regime prevailing in these soils mainly in the lower positions is aquic conditions (soil moisture regime) (Soil Survey Staff, 2010) this suggests the presence of groundwater discharge zones. This corresponds with data obtained in Trenque Lauquen, Pehuajó and Carlos Casares (Alconada- Magliano et al.,

**Table 4.** Results for mineral analysis of soil samples in the area of piezometers P1, P6 and P7.

Soil profile	Depth (cm)	Minerals in silt-sand fractions					Total Clay (%)	Type of clay (%)		
								I/E+E	I	K
P1	0-26	Quartz	Plagioclase	Gypsum	Calcite		20.0	19	76	5
	26-44	Quartz	Plagioclase	Gypsum	Calcite	Halite	12.5	26	65	9
	44-74	Quartz	Plagioclase		Calcite	Halite	17.5	30	65	5
	74-93	Quartz	Plagioclase		Calcite	Halite	22.5	41	55	4
P6	0-30	Quartz	Plagioclase		Calcite	Halite	19.0	22	70	8
	30-45	Quartz	Plagioclase	Gypsum	Calcite	Halite	11.5	19	73	8
	45-61	Quartz	Plagioclase		Calcite	Halite	19.0	45	52	3
P7	0-29	Quartz	Plagioclase		Calcite	Halite	15.0	14	78	9
	29-49	Quartz	Plagioclase		Calcite	Halite	24.0	45	51	4
	49-59	Quartz	Plagioclase		Calcite	Halite	26.5	60	39	2

Explanation: I/E, Interbedded Illite-smectite; E, Smectite; I, Illite; K, Kaolinita. Plagioclase, includes albite and anorthite.

2011).

Defined water quality and the nature of the observed soil suggest small elevation differences lead to great contrast in the position at which intermediate and local type groundwater flows discharge; intermediate flows discharge from 87.0 to 88.4 m amsl and local flows from 88.0 to 90.6 m amsl, lagoons are present at the lowest level with 85.9 m amsl. Their location is further evident with high salinity and alkalinity, as appears to be additionally supported by water type, AHP (Table 1) and the presence of discharge zones of intermediate flows as suggested by P2, P3, P5 and P7 (Table 2). Local flows are sustained by on site rainfall which show direct influence in samples P1, P4, M1, and to some extent in P6, M3 and M2.

### Soil mineralogy composition

In Table 4 reports the mineralogy composition of soil profiles for three piezometers in the Sandy Pampa: P1 in the hill of S1; P6 in hill of S3, and P7 in lower ground of S3. The profile recognizes at depth the presence of quartz, plagioclase (anorthite and albite) and calcite. Gypsum is recognized only on the hills, in sites P1 and P6. Halite appears in all of the profiles occurring at different depths, mainly at shallow depth in P1, although never at surface. These minerals were found to be consistent with the origin of water salinity using MODELAGUA (see the following section). There is a clear association between the minerals of the original soils and minerals presented in the soils where water infiltrated (Table 4) and circulates through, resulting in the chemical quality of groundwater (Table 1). It is likely that residence time of the water, the rock-water interaction, and type of flow that is developed (Table 2) modify the degree of weathering of those minerals.

In all profiles the proportion of expansive clay is increased (I/E+E) with depth (45-60%) being large in proportion on the site of the piezometers located in low grounds where more alkaline conditions prevail (P7). At surface, expansive clays represent between 14 and 19%, illite (I) between 70 and 78%, and kaolinite (K) only 5 and 9% (Table 4). The increase of expansive clay correspond with the prevailing hydro-halomorphic setting confirming the presence of discharge conditions of an intermediate flow which favors the evolution to this type of clays (Zapata, 2004).

### Origin of water quality

The main mineral composition reported for the Sandy Pampa (Etchichurry et al., 1988; PMI, 1999; Gonzalez, 2005) was considered in hydrogeochemical MODELAGUA modeling (Fagundo-Sierra et al., 2001; Fagundo et al., 2006) as evidence to explain the nature of studied waters. This modeling was also used to understand main geochemical processes (algorithms of the model, no-presented), resulting in mineral weathering and their products of reaction. In all cases, the geochemical processes that explain the origin of the chemical composition of the water are similar. Modeling results indicate congruent dissolution of halite and gypsum; incongruent dissolution of plagioclase (89.6-98.8% albite and 1.2-10.4% anorthite), kaolinite, biotite and orthoclase, with calcite precipitation; results explain the presence of most of  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{HCO}_3^-$  in the sampled waters (Tables 1 and 3).

In P1 and P4 water has the lowest salinity; its composition defined by modeling suggests the dissolution of three minerals: albite (21-25%), halite (5-10%) and gypsum (3.5-5%). In P1 the contribution of halite and albite is lower than in respect to P4. Both samples are

**Table 5.** Content of Arsenic ( $\tau$ As,  $\text{mgL}^{-1}$ ) in cross-sections (S1, S2, S3), of nine dates (D1 to D9). Average values (Av) for all dates and variability coefficient (CV, in %).

S		D1	D2	D3	D4	D5	D6	D7	D8	D9	Av	CV
S1	M1	0.015	0.014	0.013	0.032	0.022	0.014	0.014	0.014	0.037	0.019	46.4
	P1	0.044	0.042	0.039	0.040	0.038	0.045	0.040	0.041	0.002	0.037	5.9
	P2	0.030	0.035	0.034	0.037	0.040	0.041	0.035	0.036	0.034	0.036	9.2
	P3	0.102	0.056	0.084	0.086	0.096	0.117	0.075	0.087	0.076	0.087	20.2
S2	M2	0.041	0.040	0.033	0.037	0.047	0.052	0.050	0.053	0.014	0.041	29.9
	P4	0.043	0.086	0.113	0.125	0.118	0.131	0.155	0.153	0.133	0.117	29.7
	P5	0.049	0.048	0.041	0.049	0.043	0.041	0.044	0.039	0.043	0.044	8.4
	L1	0.025	0.049	0.082	0.004	0.035	0.024	0.035	0.027	0.030	0.035	62.1
S3	M3	0.018	0.019	0.023	0.017	um*	um*	0.025	0.028	0.056	0.027	51.1
	P6	0.073	0.058	0.061	0.045	0.049	0.090	0.093	0.130	0.095	0.077	35.5
	P7	0.040	0.037	0.033	0.028	0.037	0.043	0.046	0.042	0.038	0.038	14.2
	L2	0.013	0.026	0.021	0.028	0.015	0.024	0.040	0.039	0.079	0.032	63.2

Explanation: Sections, S1 Upper (M1, P1, P2, P3), S2 Middle (M2, P4, P5, L1), and S3 Lower (M3, P6, P7, L2). P, piezometer, M, mill; L, lagoon. (\*) um, unmeasured.

located on hill tops, but P1 is in a location with higher elevation than P4 (Table 2). With respect to P6, located on a hill of a cross-section located at the lowest elevation (S3) differs from the previous ones in greater participation of halite (19%) and similar the participation of albite and gypsum (22% and 5%, respectively).

In piezometers P2, P3, P5, and P7, as well as in the lagoons L1 and L2, weathering processes are intense due to high prevailing hydromorphism resulting from the discharge of an intermediate flow with high salinity-alkalinity (Tables 1 and 2). Although, only in P2, P3 and P5 increased the participation of albite (27.4; 49.9 and 37.7% respectively), gypsum as a second mineral in importance and low participation of halite and biotite. In contrast piezometer P7, of the principal mineral was halite (76%) while participation of albite and gypsum were 18.5% and 19.5% respectively. In the lagoons, also prevalence halite (35.4-69.7%), albite as a second mineral in importance (36-35%), and calcite precipitation processes are also occasionally present (L1 and L2 respectively). In the mills, albite (19-32%), halite (11-20%) and gypsum (5-6%) prevail although differences in salinity and alkalinity were small (Table 1).

### Content of $\tau$ As and $F^-$ in water

Tables 5 and 6 show individual values for every sampling date and sampling site as well as average values of  $\tau$ As and  $F^-$ , respectively. The level of reference for human consumption for  $\tau$ As is  $0.01 \text{ mgL}^{-1}$  and for  $F^-$  varies according to the environmental temperature, between a minimum limit of 0.6 to  $0.96 \text{ mgL}^{-1}$ , to a maximum of  $1.7 \text{ mgL}^{-1}$  (WHO 2006).

Regarding  $\tau$ As concentrations in all of the collected samples surpasses this value; they increase more towards the sector under cross-section S1. Thus,  $\tau$ As content in the water of P1 for the nine sampling dates varies from 0.002 up to  $0.045 \text{ mgL}^{-1}$  and in P3 from 0.056 up to  $0.117 \text{ mgL}^{-1}$  (Table 5). But it happens to be the inverse in sections S2 and S3, despite being these sites topographically lower than the other sites (Table 5). It is remarkable the diminution of albite mentioned previously (MODELAGUA) in P6 and P7 respect other piezometers.

The variability of concentration reported for the sampling dates is high, only it is lower than 10% in P1, P2 and P5, which cannot be associated to their local position, soil type (Table 2), incident flow, nor water group (Table 1 and 2). It is noticeable the high variability of concentrations of  $\tau$ As in the mills being located in hills with *Typical Hapludolls* developed from the Invading dune (E1) that lies over loess (E3). As mentioned in the introduction, Nicolli et al. (2006) noted that both sedimentary deposits have a similar mineralogical composition but in different proportions. These authors also find that there is more  $\tau$ As in recent sediments (E1,  $22 \text{ mgL}^{-1}$ ) and a lower proportion in the oldest Pampean loess sediments (E3,  $6.4 \text{ mgL}^{-1}$ ). Espósito et al. (2013) in the southeast of the Pampean region found high  $\tau$ As and  $F^-$  content correlating with soil mineralogy at water-table level; groundwater found in fine sediments is used for human consumption (Auge, 2004, 2008) leading to serious health problems (Agüero, 2015) as well as legal demands of users to stakeholders (Minaverry and Cáceres, 2016).

Above mentioned authors as Blanco et al. (2006), Bundschuh et al. (2006b), Litter et al. (2006), Nicolli et al. (2006), Nicolli et al. (2006), Morrás (2003) and Othax et

**Table 6.** Content of Fluoride ( $F^-$ ,  $mgL^{-1}$ ) in cross-sections (S1, S2, S3), of nine dates (D1 to D9). Average values (Av) for all dates and variability coefficient (CV %).

S		D1	D2	D3	D 4	D5	D6	D7	D8	D9	Av	CV
S1	M1	0.460	0.480	0.480	1.487	1.540	0.490	0.538	0.550	1.940	0.885	66.9
	P1	2.050	1.980	1.890	1.900	2.060	2.390	2.108	2.180	0.570	1.903	7.9
	P2	1.270	1.390	1.340	1.560	1.700	1.520	1.431	1.450	1.390	1.450	8.8
	P3	2.170	2.240	2.140	2.130	2.360	2.410	2.108	2.140	2.020	2.191	5.7
S2	M2	1.130	1.370	1.240	1.274	1.680	1.660	1.452	1.910	0.520	1.360	29.5
	P4	3.440	3.800	3.550	3.480	3.660	4.010	3.720	4.030	3.810	3.722	5.7
	P5	1.720	1.620	1.540	1.801	1.990	1.470	1.542	1.490	1.590	1.640	10.3
	L1	0.190	0.330	0.460	0.287	0.190	0.260	0.434	0.490	0.740	0.376	46.9
S3	M3	0.760	0.840	0.870	0.835	um*	um*	0.940	0.780	2.150	1.025	48.7
	P6	2.170	2.050	2.100	1.863	2.200	3.030	2.809	3.330	3.010	2.507	21.4
	P7	1.570	1.570	1.390	1.487	1.870	2.040	1.636	1.770	1.770	1.678	12.1
	L2	0.180	0.340	0.520	0.319	0.260	0.360	0.570	0.570	0.920	0.449	49.9

Explanation: Sections, S1 Upper (M1, P1, P2, P3), S2 Middle (M2, P4, P5, L1), and S3 Lower (M3, P6, P7, L2). P, piezometer, M, mill; L, lagoon. (\*) um, unmeasured.

al. (2014) point noticeable heterogeneity in  $\tau As$  concentration in groundwater present in the Buenos Aires Province and lacking of direct association to minerals content in loess, suggesting the arrival of water with high  $\tau As$  content circulating through geological material not necessarily locally enriched in  $\tau As$ . Studies found different origin as weathering of silicates (biotite) in primary loess as well as from volcanic glass, suggesting the geological material is not the main cause of  $\tau As$  presence but the interaction between water phases and  $\tau As$  mobilization control. In this regard, Smedley et al. (2005) also explain the magnitude of the presence of  $\tau As$  on residence time of interactions, and geochemical variables included at locally (pH-Eh, salinity-alkalinity, competition with other ions). This is consistent with Ortega (2009) in Mexico and Mejía et al. (2014). Other authors (Blanco et al. 2006; Paoloni et al., 2005 (in Nicolli, et al., 2006)) indicate increase of  $\tau As$  in groundwater in discharge zones as related to a negligible concentration in the recharge zone, which is associated to travel and depth distance, water-rock interaction, and chemical water type evolution.

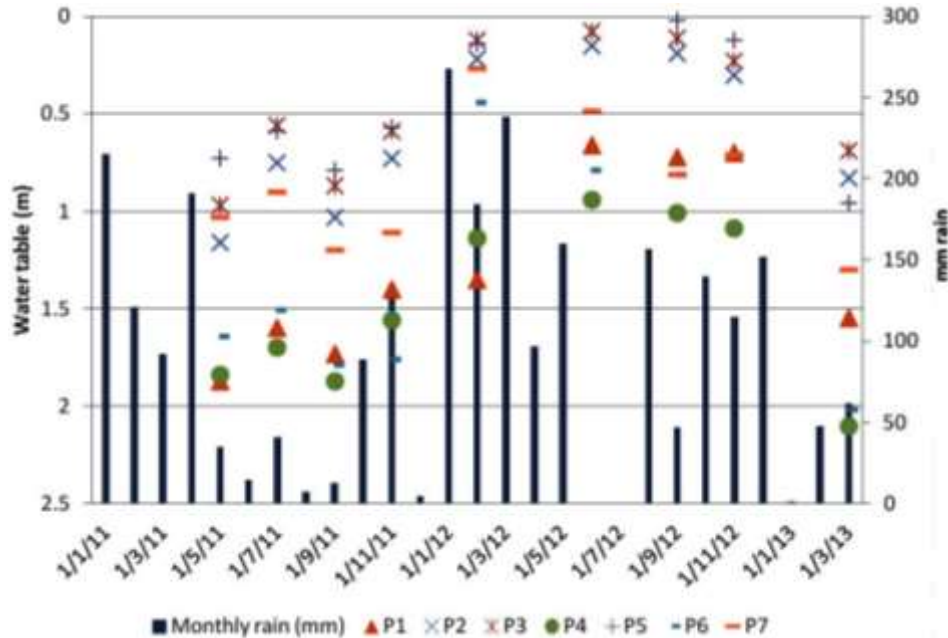
Consequently the variability mentioned in present study could be attributed to vertical components of flow from beneath, that influence the water regime and quality in different times, influence which effect is more noticed at shallow levels reflecting a more readily groundwater discharge. In lagoons the high variability in the concentration of  $\tau As$  are probably associate to dilution due to rainfall and prevailing the oldest sediments (E3). If the average of all measurements of  $\tau As$  in piezometers is considers its value is higher than in mills and lagoons (0.062, 0.029 and 0.033  $mgL^{-1}$ , respectively).

Regarding  $F^-$  concentrations (Table 6), they are high in all the piezometers, being highest in those located in the

elevated location of cross-sections as in P1, P4 and P6 (for all dates). The variability of results in time is smaller than 10% in the piezometers, except in P6 and P7 (>12%). Regarding the mills, their average in  $F^-$  content is lower in all of the cases than those obtained for the piezometers during the same sampling time showing high variability in  $F^-$  values of the nine dates (30 to 67%). In the lagoons the level of  $F^-$  was always very low although with high variability among dates (>45%) (Table 6). It is possible to relate evapotranspiration and/or precipitation in the lagoons and piezometers. The variability in the content of  $F^-$  in the mills is similar to that of  $\tau As$ , with similar magnitude to that in the lagoons. Such results in the mills could be associated to the entrance of recent rainfall water resulting in the presence of local flows. High values of  $F^-$  in the piezometers suggest the sampled water belonging to a deeper origin acknowledging the presence of an intermediate flow as compared to a recent flow; the nature of the older intermediate flow is in agreement with the obtained high  $Cl^-$  (and  $\tau As$ ) values (Table 3), such features could influence the hydro-halomorphic conditions shown in the soils (Table 2). If the average of all measurements of  $F^-$  in piezometers is considers it is higher than in mills and lagoons (2.156, 1.113 and 0.412  $mgL^{-1}$ , respectively). This is different from observed  $\tau As$ , although both are correlated, as discussed next. Lavado et al. (1983) for the same region, explain the presence of  $F^-$  due to the contribution of groundwater, while Espósito et al. (2013) suggest the same source mainly, but include the mineralogy of soil and subsoil.

#### Depth to water-table, precipitation and $\tau As$ and $F^-$ content

Figure 4 shows the water-table depth variation as related



**Figure 4.** Depth to the water-table in piezometers from P1 to P7, for the 9 dates in the studied site of Lincoln as related to local rainfall that occurred during the 2011 to 2013 period.

to the monthly precipitation. In all cases, a shallow water-table depth (that is, discharge conditions) affects agricultural practices (Figure 3). A shallow water-table is more than a potential reduction in crop yield, the transference of the particular chemistry in the water to humans through drinking water and food consumption is to be further understood (Roseli et al., 2010; Puntoriero et al., 2014; Bastías and Beldarrain, 2016).

The water-table depth was reported to be highly variable even in piezometers on the hills (CV 29.4% to 45.0%). In P1, P4 and P6, the depth to the water-table in the nine dates varied in 1.1 m at P1 and P4, and in 1.6 m in P6 (variation between maximum and minimum depth). In P7 located in the low part of S3 also varies markedly (45.5%) but always near the surface (between 0.2 to 1.3 m). Piezometers on middle part of all sections (P2, P3 and P5) show variation of water-table depth (CV 56 to 73%) between dates was even higher but like P7 always more near of surface than the other piezometers at the hills. In P2, P3 and P5, the variation between the deepest and shallowest was 1.01 m, 0.89 m and 0.84 m respectively. It has a remarkable shallow water-table in some dates for these piezometers (Figure 4). The water balance calculated from precipitation and evapotranspiration estimate suggests a deficit of 208 mm the water between May and September 2011 and an excess of 277 mm from January to May 2012. Consequently, it is observed that although in general there was correspondence between water balances and variations in water-table depth, this variation did not occur to the same extent in all piezometers. This could be explained by the discharge of flows of intermediate type.

Although depending on local conditions, there could be an expected relation between chemical compositions to water-table depth; however, as the analyzed flows are of different nature (local and intermediate) and the observation points under contrasting time and conditions (recharge and discharge), results may not be eligible for a basic geo-statistical analysis.

The correlation between depth to the water-table and  $\tau$ As content is not significant ( $r$  0.13), similar results are observed for  $F^-$  ( $r$  0.33). The variability of  $\tau$ As and  $F^-$  as related to the type of water, lacks a defined tendency, their presence may not be associated to changes in water-table depth. As expected, when the water-table response is analyzed with observed rainfall, there is lack of general agreement among rainfall, time, and EC, with  $\tau$ As and  $F^-$  data.

Under prevailing soil conditions (Table 2), with high content of expansive clays as in P7 (Table 4), water is expected to take an increasing long time before infiltrated water reaches the water-table of the local flow systems. However, this possible upward flow water in discharge zone. It is appropriate for this topic to consider the electrical conductivity of the analyzed water. In all sites measured electrical conductivity was high increasing in the lowest sites of the three sections with low variability in piezometers (CV<10%) (Table 7) suggests a lack of dilution-concentration response, thus confirming that studied sampling points receive a continuous groundwater flow from other regions. The nature of this flow being intermediate like in mills but the big variability in its chemical concentration, probably is due for position of its recharge and transit path and related effects (vertical

**Table 7.** Electrical conductivity ( $\text{dSm}^{-1}$ ) in cross-sections (S1, S2, S3), of nine dates (D1 to D9). Average values (Av) for all dates and variability coefficient (CV, in %).

S		D1	D2	D3	D4	D5	D6	D7	D8	D9	Av	CV
S1	M1	3.96	4.14	4.20	3.97	4.24	4.09	3.51	3.69	3.45	3.92	7.3
	P1	2.69	2.80	2.91	2.78	3.24	3.04	2.85	3.30	3.46	3.01	6.8
	P2	9.44	9.89	9.83	10.14	11.14	10.27	9.70	10.05	11.44	10.21	4.9
	P3	19.00	19.03	19.50	21.00	20.00	17.96	18.93	19.52	20.52	19.50	6.5
S2	M2	9.02	5.81	6.35	5.86	6.36	5.66	5.26	5.27	3.66	5.92	19.6
	P4	3.93	3.45	4.14	3.81	4.55	3.96	3.55	3.50	3.84	3.86	9.6
	P5	15.49	14.99	15.84	14.75	15.23	15.73	16.12	18.08	17.49	15.97	7.3
	L1	3.75	8.95	20.00	16.91	7.80	4.35	5.23	3.85	6.91	8.64	67.0
S3	M3	5.40	2.65	3.74	3.30	*	*	6.53	7.75	5.71	5.01	42.1
	P6	4.73	4.64	4.97	4.48	5.21	3.85	3.35	2.93	3.22	4.15	18.9
	P7	11.04	11.73	12.83	10.00	8.06	8.06	9.87	9.87	9.87	10.15	12.6
	L2	6.96	14.97	36.50	25.46	12.10	7.21	8.43	6.30	17.63	15.06	71.2

Explanation: Sections, S1 Upper (M1, P1, P2, P3), S2 Middle (M2, P4, P5, L1), and S3 Lower (M3, P6, P7, L2). P, piezometer; M, mill; L, lagoon; (\*), non-measurement

flow) with the overlaying local flow (Table 2). Water in the lagoons is modified by climatic conditions and discharge water from local and intermediate flows composition ( $\text{CV} > 67\%$ ) (Table 7). Similar results were obtained when comparing EC with  $\tau\text{As}$  and  $\text{F}^-$  content in the related waters, has also been observed by Blanco et al. (2006).

Available references on this topic indicate that local effects on the groundwater composition acquire more relevance than regional ones resulting in random distribution (Schulz, 2006) being rock-water interaction the main cause for the presence of  $\tau\text{As}$  in water (Litter et al., 2006), local effects which are taking place in the region seems to be influenced by intermediate (with long travel time) groundwater flows (Table 2), being the ones that define the salt groundwater content. Although available mineral content in rock and soil, like albite (Table 4 and results of MODELAGUA) is possible that play an important role in yielding  $\tau\text{As}$ , it is more likely that its content is more directly associated with the intermediate groundwater.

### Relationship among $\tau\text{As}$ , $\text{F}^-$ and other water characteristics

The linear coefficients of correlation between  $\tau\text{As}$  and  $\text{F}^-$  were highly significant ( $P < 0.01$ ) for all cases (9 dates, include mills, piezometers and lagoons, total  $n = 108$ ,  $r = 0.82$ ; mills  $n = 27$ ,  $r = 0.89$ ; piezometers  $n = 63$ ,  $r = 0.86$ ; and lagoons  $n = 18$ ,  $r = 0.57$ ). Nevertheless, the correlations are not always clear when  $\tau\text{As}$  and  $\text{F}^-$  associated with the concentration of cations, anions, pH, EC, SAR, and temperature. If all samples are considered ( $n = 108$ ) a significant correlation ( $P < 0.05$ ) was found between the

following variables:  $\tau\text{As}$ -RAS ( $r = 0.35$ ),  $\tau\text{As}$ - $\text{HCO}_3^-$  ( $r = 0.29$ ),  $\text{F}^-$ - $\text{HCO}_3^-$  ( $r = 0.55$ ),  $\text{F}^-$ -RAS ( $r = 0.21$ ). Mills show good correlation of  $\tau\text{As}$  with variables associated to alkalinity and salinity than  $\text{F}^-$ , for a  $P < 0.01$ , between:  $\tau\text{As}$ -RAS ( $r = 0.88$ );  $\text{As}$ - $\text{HCO}_3^-$  ( $r = 0.70$ );  $\tau\text{As}$ - $\text{Na}^+$  ( $r = 0.64$ );  $\tau\text{As}$ -EC ( $r = 0.51$ ); and  $P < 0.05$ , between:  $\tau\text{As}$ -pH ( $r = 0.37$ );  $\tau\text{As}$ - $\text{Cl}^-$  ( $r = 0.34$ );  $\tau\text{As}$ - $\text{SO}_4^{2-}$  ( $r = 0.34$ ). Piezometers had similar correlations than mills but less significant. There was a considerable correlation but with negative sign between  $\text{F}^-$  and  $\text{Na}^+$ , as with  $\text{Ca}^{+2}$  and EC ( $P < 0.01$ ,  $r = -0.44$ ;  $r = -0.73$ ;  $r = -0.46$ , respectively). Also a negative noteworthy correlation for  $\tau\text{As}$  and  $\text{Ca}^{+2}$  was obtained only in mills ( $r = -0.61$ ).

A lack of correlation was found between  $\tau\text{As}$  with temperature, whereas  $\text{F}^-$  was correlated to temperature for the mills ( $P < 0.01$ ,  $r = 0.43$ ). Regarding lagoons, a good relationship was found for  $\tau\text{As}$  and  $\text{F}^-$  ( $P < 0.01$ ,  $r = 0.89$ ) as well as with alkalinity and salinity ( $P < 0.01$ ,  $\text{F}^-$ -pH,  $r = 0.67$ ;  $\tau\text{As}$ - $\text{HCO}_3^-$ ,  $r = 0.79$ ;  $\text{F}^-$ -SAR,  $r = 0.49$ ; and  $P < 0.05$ ,  $\text{F}^-$ - $\text{HCO}_3^-$ ,  $r = 0.44$ ). Regarding the relation of  $\text{F}^-$  with  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{+2}$  and  $\text{K}^+$ , it is weak in all cases, except in mills.

Results obtained in the study are partially coincident with those by other authors. Smedley et al. (2005), Blanco et al. (2006), Litter et al. (2006), Nicolli et al. (2006), Bundschuh et al. (2006b), Ortega (2009), Panagiotaras et al. (2012), Mejía et al. (2014) indicate an association for the presence of  $\tau\text{As}$ , with  $\text{HCO}_3^-$  content,  $\text{Na}^+$ ,  $\text{F}^-$ , salinity, and pH. However, those results lack an attempt to be interpreted in regard of their association with the type of soil, topographic position, water-table fluctuation, and local rainfall. The outcome is associated in this study to the arrival of groundwater of long residence time under alkaline characteristics, and the outstanding presence of sodium in the samples. It has been argued a cation exchange between  $\text{Ca}^{+2}$  and  $\text{Na}^+$ ,

**Table 8.** Average values for physical and chemical characteristics of sampled water of the localities of Trenque Lauquen (TL), Pehuajó (Pe), Carlos Casares (CC) and Lincoln (Li).

Parameter		pH	EC	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>-2</sup>	Ca <sup>+2</sup>	Mg <sup>+2</sup>	Na <sup>+</sup>	K <sup>+</sup>	CaCO <sub>3</sub>	SAR	τAs	F <sup>-</sup>
P	TL	7.8	3.3	10.9	16.0	4.7	1.7	2.9	27.6	1.6	231	15	0.02	0.40
	Pe	7.3	3.8	5.7	27.0	4.5	4.2	5.9	25.0	1.0	505	11	0.01	0.26
	Li	7.9	9.6	17.7	46.6	33.1	3.2	9.3	84.4	1.4	621	35	0.10	2.20
M	TL	7.8	7.3	6.2	63.5	17.7	5.1	16.7	68.7	1.1	1095	17	0.07	1.14
	Pe	7.8	4.0	15.2	22.5	6.6	1.7	4.9	37.2	0.8	326	20	0.10	2.50
	CC	7.0	8.0	10.4	37.2	9.6	5.9	5.7	60.9	1.9	578	21	0.01	0.36
	Li	7.8	4.9	18.6	18.2	12.3	2.4	4.4	42.3	1.1	341	24	0.04	1.09
L	TL	7.5	17.4	4.92	139.5	52.3	8.1	21.9	165.2	2.8	1.501	38	0.02	0.26
	Pe	8.5	14.9	5.34	123.2	26.1	4.3	16.1	141.2	2.7	1.021	37	0.02	1.01
	Li	8.3	11.8	6.5	72.6	41.0	5.5	12.0	102.1	2.09	875	35	0.04	0.41

Explanation: pH, EC (dS m<sup>-1</sup>) cations and anions (meqL<sup>-1</sup>), CaCO<sub>3</sub> (meqL<sup>-1</sup>), SAR, τAs and F<sup>-</sup> (mg L<sup>-1</sup>) in piezometers (P), well-mills (M), and lagoons (L).

resulting in calcite dissolution.

### Regional analysis: Lincoln and other localities

For comparison purposes Table 8 shows average values for physical and chemical properties of the sampled water of Lincoln (Li) as to compare to similar data from Trenque Lauquen (TL), Pehuajó (Pe), and Carlos Casares (CC). Particular values could be found in Alconada-Magliano et al. (2011).

Regarding τAs and F<sup>-</sup> in the localities of TL and Pe, they show high concentrations in the mills, whereas in piezometers and lagoons, values are lower than those recommended as drinking water limit (WHO, 2006). On the contrary, in Lincoln a large concentration in the piezometers is found; although also they are high in mills and lagoons (Tables 1, 5, 6). In general, values with high concentration correspond with those having high salinity-alkalinity content in the region, showing lack of correspondence to differences in local topographic elevation. For example, in Pehuajó the elevation of piezometers varies between 86.0 and 87.5 m amsl, and in Lincoln, between 87.0 and 89.4 m amsl, in all cases, Li, TL, Pe, CC, with a water-table depth of less than 2.0 m, showing a plain with intermediate flow discharge conditions but interacting with recharge or discharge of flow of local nature, which confirm the type of the observed soils (*Typical Hapludolls* where the water-table is deep, and the presence of *Typical Natracuolls* and *Natracualls* where it is shallow (Alconada-Magliano et al., 2011).

On the question about how τAs content is linked to other variables of the water the samples of TL, Pe, and CC, it is observed that similarly to reported for the mills of Lincoln, a significant correlation is found (n: 18, P 0.01)

for τAs and F<sup>-</sup> (r 0.68) as well as for τAs and HCO<sub>3</sub><sup>-</sup> (r 0.76). However, the correlation between τAs and SAR, and of F<sup>-</sup> with SAR had little significance (r 0.25); for τAs and the EC (r -0.14). Regarding F<sup>-</sup>, it maintains a significant correlation in samples of other localities (n: 18, P 0.01) as with pH (r 0.53), temperature (r 0.52), and HCO<sub>3</sub><sup>-</sup> (r 0.78).

In the piezometers of other localities, the correlation for τAs and F<sup>-</sup> is significant (P 0.01) and improves for alkalinity related parameters τAs and HCO<sub>3</sub><sup>-</sup>, τAs and Na<sup>+</sup>, as well as with τAs and SAR (r 0.71; 0.80, and 0.89, respectively), and SO<sub>4</sub><sup>-</sup> should also be included (r 0.66, P 0.05). Regarding other variables, although there is a lack of significant number of samples (n: 9), available data shows a tendency suggesting τAs correlates with temperature, EC, and Cl<sup>-</sup>. With respect to F<sup>-</sup>, in the piezometers of other localities the correlation improves with the SAR (r 0.64, P 0.05) and diminishes with respect to pH. If all piezometers of Lincoln and other localities are considered the correlation for F<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> is highly significant (r 0.56, n: 72).

When the lagoons of other localities are considered, the correlation between τAs to F<sup>-</sup> and τAs to HCO<sub>3</sub><sup>-</sup> are maintained, and that of τAs to EC, and τAs to Na<sup>+</sup> improve (r 0.57, r 0.59 respectively (P 0.05); for τAs to SAR (r 0.80, P 0.01) and τAs to K<sup>+</sup> (r 0.80, P 0.01); being the only case in which both are related. If the lagoons of Lincoln and those of other localities are considered, the correlations lack any improvement, or even diminish. A tendency τAs to correlate with Cl<sup>-</sup> is observed. Regarding F<sup>-</sup>, it improves its correlation with Na<sup>+</sup> and the SAR (r 0.79, r 0.68 respectively, P 0.01). These results suggest the general tendency of F<sup>-</sup> and τAs to remain in solution disregarding local climate effects, due to a constant inflow of these elements in the intermediate groundwater flow systems discharging in the lagoons.



In the studied territory, it has also been observed that small differences in the thickness of the surface deposit (Invasion dune, E1, over loess, E3), modifies the way that the intermediate flow with  $\text{Na}^+$  related characteristics (Tables 2 and 3) affects the soil profile, and includes the coexistence of local flows (Alconada-Magliano et al., 2014).

Based on soil, geomorphology, and water quality it was defined at regional level that the Lincoln party behaves as a discharge zone of intermediate flows and local flows are coexisting. This is considered the most probable cause of the observed presence of  $\tau\text{As}$ . This is coincident with the regional association and types of flow suggested by Blanco et al. (2006) proposing an increase of  $\tau\text{As}$  towards the discharge zone.

The random distribution pattern of  $\tau\text{As}$  indicated by Schulz (2006), which could be explained by the high heterogeneity of  $\tau\text{As}$  in the water-bearing material (Nicolli et al., 2006), and soils (Morrás, 2003) as well as with the great amount of minerals which potentially contain  $\tau\text{As}$ , to be released by processes of mobilization-retention in the rock-water interaction phase; this could be the case even if the geological material is not necessarily enriched in  $\tau\text{As}$  (Litter et al., 2006). An understanding on how local flows are linked to the region in providing the observed consequences of human intervention in the landscape such as agricultural, forestry or groundwater extraction is required. Espósito et al. (2013), as discussed in the introduction, point to the need to consider the concentrations of  $\tau\text{As}$  and  $\text{F}^-$  in water in food production even livestock. This implies to recognize that local conditions are controlled, essentially, by the influence of regional conditions, as occurs in the Northwestern of Buenos Aires where local flows coexist with intermediates (Alconada-Magliano et al., 2011).

In environments as the studied region, although the dynamics of  $\tau\text{As}$  can be attributed to the alkalinity of groundwater, soils have potential to release  $\tau\text{As}$  (as from silicates in soil, Table 4) depending on oxide-reduction conditions changes at local level. This is consistent with results obtained by Ortega (2009), relating the presence of  $\tau\text{As}$  and  $\text{F}^-$  with Na-plagioclase, and alkaline conditions with high proportion of  $\text{HCO}_3^-$  and  $\text{Na}^+$ . Also is consistent with Nicolli et al. (2006) who also recognize silicates as  $\tau\text{As}$  source which is released to water from crystal structure by hydrolysis, dissolution and oxide-reduction, depending on the geo-availability occurring in sedimentary sequences (E1-E3). In this study the magnitude of the inducement of  $\tau\text{As}$  to the extraction level resulting from groundwater development must be attributed to the general position of the discharge zone of intermediate flow systems which have travelled hundreds of kilometers before their arrival to Lincoln, whose discharge conditions coexisting in lagoons with those of flows of smaller hierarchy (local).

Consequently, as indicated by Ferpozzi (2006) there are regional and local environmental factors that must be

considered in the hydrogeological functioning of any region, factors that are also suggested to necessarily considered by other authors (Lopez, 2006; Ortega, 2009; Panagiotaras et al., 2012). This may only be possible when the components of the landscape are integrated as in the conceptual model of Tóth (2000), which is considered to acknowledge the relation of groundwater setting (recharge, discharge and flow hierarchy) with the particular soil and (natural) vegetation; relation emphasizing the importance of recharge and discharge conditions resulting by the presence of hilly and flat terrain in any region (Alconada-Magliano et al., 2011, 2014).

## Conclusions

The concentration of  $\tau\text{As}$  in groundwater of Lincoln was found to be high at all the analyzed samples, being greater in piezometers than in mills or lagoons. Also  $\text{F}^-$  concentration was high in piezometers and low at mills and lagoons. The concentration of  $\text{F}^-$  correlates positively with  $\tau\text{As}$ , and in both the concentration was highly variable between dates being more marked that variability in the mills and lagoons than piezometers. Also, in localities as Trenque Lauquen, Carlos Casares and Pehuajo, high values are found for  $\tau\text{As}$  and  $\text{F}^-$  in the mills, whereas in piezometers and lagoons, values are lower.

The mineralogical composition of soils and parent material explains the presence of  $\tau\text{As}$  in the studied water samples; high concentration has been related to discharging conditions of intermediate flows. There is a lack of clear relationship among  $\tau\text{As}$  with other physical and chemical characteristics of the water; no defined patterns of its distribution are found for Lincoln and other localities, showing lack of correspondence to differences in local topographic elevation. Although a general relation with high salinity-alkalinity prevails, the best correlations for Lincoln are observed in mills and lagoons, being low in piezometers, and low in other localities. This phenomenon is postulated to be associated to the variable influence of recharge-discharge of local flows imposing a relative low salinity presence.

Observed concentrations of  $\tau\text{As}$  and  $\text{F}^-$  could be related to the general discharge condition evident at the plain (as opposite to hills) with alkaline soil environment and shallow water-table depth, where lithology discontinuities affect the movement of water through the soil, and specific local oxidation-reduction conditions and pH could favor the liberation of  $\tau\text{As}$  from the ample presence of Na-plagioclase, albite, in the studied territory. A correspondence for  $\tau\text{As}$  and  $\text{F}^-$  with elements as natural vegetation and soil needs to be given further interest as well as to the study of related trace elements and environmental isotopes in the water.

The presence of local flows coexisting with intermediate

flows is an acceptable and expected feature in the region resulting from the hilly environment produced by the dunes. Due to the prevailing geological framework, these local flows developed in the dunes are controlled by the intermediate flows travelling beneath in the thick sedimentary sequence containing some 5,000 m of deposits; the main recharge of the intermediate flow systems is postulated to take place at the western highlands some >280 km distance (and at >250 m amsl); several intermediate flow systems are likely to develop and have their discharge in the studied territory.

The understanding of water origin and its relations with other elements of the landscape opens a possibility in searching for a correct identification of groundwater functioning and to anticipate the general situation with regard of its  $\text{TAs}$  and  $\text{F}^-$  content. The definition of discharge conditions of intermediate flows (shallow water-table and permanent lagoons) is paramount where alkalinity and the presence of  $\text{HCO}_3^-$  and  $\text{Na}^+$  could be used as key factors to propose the presence of  $\text{TAs}$  and  $\text{F}^-$  in groundwater; conditions observed in low topographic sites. Local recharge conditions (high terrain) were low salinity water is found, usually excludes the presence of alkaline conditions and high pH and therefore of high  $\text{TAs}$ . Regarding the high concentration of  $\text{F}^-$  in groundwater it seems to be controlled by the restricted presence of  $\text{Ca}^{2+}$  in the sediments supported by a characteristic 901 value of the AHP description of water in the region.

## Conflict of Interests

The authors have not declared any conflict of interests.

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## REFERENCES

Agüero R (2015). Alerta por la fluoración del agua potable. Argentina. <https://dejendefluorarelaguapotable.wordpress.com/> (consulted in July 2016).

Alconada-Magliano MM, Bussoni A, Rosa R, Carrillo-Rivera JJ (2009). El bio-drenaje para el control del exceso hídrico en Pampa Arenosa, Buenos Aires, Argentina. *Investigaciones Geográficas*, Bulletin of the Institute of Geography, UNAM (Mexico) 68:50-72.

Alconada-Magliano MM, Fagundo-Castillo JR, Carrillo-Rivera JJ, Hernández PG (2011). Origin of flooding water through hydrogeochemical identification, the Buenos Aires plain, Argentina, *Environmental Earth Sciences* 64 (1):57-71.

Alconada-Magliano MM, Damiano F, Fagundo-Castillo JR (2014). El suelo en el funcionamiento hidrológico y manejo agropecuario-forestal. *Actas Congreso Latinoamericano Ciencia del Suelo*. Cusco, Perú.

APHA-AWWA-WPCF (1989). *Standard methods for the examination of water and wastewater*. Vol 17. Washington, DC.

Auge M (2004). Regiones hidrogeológicas de la República Argentina y provincias de Buenos Aires, Mendoza y Santa Fe. *Asociación Latinoamericana de Hidrología Subterránea* 111 p. [http://sedici.unlp.edu.ar/bitstream/handle/10915/15909/Documento\\_completo.pdf?sequence=1](http://sedici.unlp.edu.ar/bitstream/handle/10915/15909/Documento_completo.pdf?sequence=1)

Auge M (2008). *Hidrogeología Ambiental* 295 p. <http://tierra.rediris.es/hidrored/ebooks/indexm.htm>

Bastías JM, Beldarrain T (2016). Arsenic translocation in rice cultivation and its implication for human health. *Chilean J. Agric. Res.* 76(1):114-122.

Bundschuh J, Bhattacharya P, von Brömssen M, Jakariya M, García ME (2006a). Localización de acuíferos seguros en áreas rurales y de acuíferos con altos contenidos de arsénico. In *Taller de distribución del As en Iberoamérica*. Buenos Aires, Argentina. [http://www.cnea.gov.ar/pdfs/actividades\\_ambientales/libroresumenestaller-2006.pdf](http://www.cnea.gov.ar/pdfs/actividades_ambientales/libroresumenestaller-2006.pdf)

Bundschuh J, Giménez FE, Guerequiz R, Pérez CA, García ME, Deschamps J, Deschamps E (2006b). Fuentes geológicas de arsénico y su liberación al medio ambiente. Capítulo 7 In: *IBEROARSEN. Distribución del arsénico en las regiones Ibérica e Iberoamericana*. Ed. Bundschuh J, Pérez CA and Litter M. CYTED 241 p.

Blanco M del C, Paoloni JD, Morrás H, Fiorentino CE, Sequeira M (2006). Content and distribution of arsenic in soils, sediments and groundwater environments of the Southern Pampa region, Argentina. *J. Environ. Toxicol.* 21(6):561-574.

Cabral M, González N, Giménez J, Hernández M, Hurtado M (1996). Análisis geo-ambiental de la región semiárida del noroeste de la provincia de Buenos Aires. VI Congreso Nacional y Conferencia Internacional Geol. Ambiental y Ordenamiento del Territorio. VIII. pp 345-364.

Carbonell BA, Burló Carbonell FM, Mataix Beneyto JJ (1995). *Arsénico en el sistema suelo-planta. Significado ambiental*. España, Universidad de Alicante 129 p.

Carrillo-Rivera JJ, Cardona A, Edmunds WM (2002). Use of abstraction regime and knowledge of hydrogeological conditions to control high fluoride concentration in abstracted groundwater: basin of San Luis Potosí, Mexico. *J. Hydrol.* 261:24-47.

Costa BES, Coelho LM, Araújo CST, Rezende HC, Coelho NMM (2016). Review Article Analytical Strategies for the Determination of Arsenic in Rice. *J. Chem.* 11 p. <http://dx.doi.org/10.1155/2016/1427154>

Dillon AA, Hurtado M, Giménez J, Castillo RJ (1985). Consideraciones geomorfológicas y estratigráficas como base del carteo de suelos de un sector de la Pampa Arenosa (Pcia. Buenos Aires). *Actas Primeras Jornadas Geológicas Bonaerense, Tandil*. pp. 737-749.

Edmunds WM, Andrews JN, Burgess WG, Kay RLF and Lee DJ (1984). The evolution of saline and thermal groundwaters in the Cammenellis Granite. *Min. Mag.* 48:407-424.

Edmunds WM, Smedley PL (1996). Groundwater chemistry and health-an overview. *Environ. Geochem. and Health*. In Appleton JD, Fuge R., McCall GJH. (Ed) *Geol. Soc. Special Pub.* 113:91-105.

Edmunds WM, Smedley PL (2005). Fluoride in natural waters. In: Selinus O (Ed). *Essential of Medical Geology*. Elsevier. Academic Press, Burlington MA, *Essentials Med. Geol.* pp. 311-336.

Espósito ME, Sequeira ME, Paoloni JD, Blanco MC, Amiotti N (2013). High fluorine and other associated trace elements in waters from the south of the Pampean plain. *Phyton* 82:35-44. <http://www.revistaphyton.fundromuloraggio.org.ar/vol82/ESPOSITO.pdf>

Etchichurry MC, Tofalo OR, Forzinetti ME (1988) Composición de la fracción psamítica de sedimentos actuales de la provincia de Buenos Aires y su significado tectónico. *Actas Seg. Tour Geológico Bonaerense, Bahía Blanca*.

Fagundo JR (1998). Patrones hidrogeoquímicos y relaciones matemáticas en aguas naturales. *Ingeniería Hidráulica en México*, 19(2):62-78.

- Fagundo-Sierra J, Fagundo JR, González P, Suárez M (2001). Modelación de las aguas naturales. Contribución a la Educación y la Protección Ambiental. Habana. 959-7136/13-9.
- Fagundo JR, González P, Fagundo-Sierra J, Álvarez E, Suárez M, Melián C (2006). Application of hydrogeochemical modeling to characterization and water quality control of coastal karst aquifer. In Demuth S, Gustard A, Planos E, Scatena F, Servat E (Ed) Climate Variability and Change Hydrological impacts. Int. Assoc. Hydrolog. Sciences Public. Netherlands pp. 596-600.
- Ferpozzi LH (2006). Fuentes geogénicas de contaminación con arsénico de aguas naturales en Argentina: aspectos geoambientales e hidrogeoquímicos. Workshop of As distribution in Ibero-América. [http://www.cnea.gov.ar/pdfs/actividades\\_ambientales/libroresumenestaller-2006.pdf](http://www.cnea.gov.ar/pdfs/actividades_ambientales/libroresumenestaller-2006.pdf) Centro Atómico Constituyentes. Buenos Aires, Argentina
- Gaciri SJ, Davies TC (1993). The occurrence and geochemistry of fluoride in some natural waters of Kenya. *J. Hydrol.* 143:395-412.
- Galindo G, Fernández TJL, Parada MA, Torrente DG (2005). Arsénico en aguas: origen, movilidad y tratamiento. Taller II Seminario Hispano-Latinoamericano sobre temas actuales de hidrología subterránea. 192 p. [http://digital.csic.es/bitstream/10261/40191/Galindo\\_et\\_al-Arsenico-2005.pdf](http://digital.csic.es/bitstream/10261/40191/Galindo_et_al-Arsenico-2005.pdf)
- Giménez J, Dillon AA, Hurtado M (1990). Consecuencias de los anegamientos en centros urbanos del oeste de la provincia de Buenos Aires, Argentina. I Simposio Latinoamericano sobre Risco Geológico Urbano, Sao Paulo, Brasil. Actas pp. 42-54.
- González, N (2005). Los ambientes hidrogeológicos de la provincia de Buenos Aires. XVI Congreso Geológico Argentino, La Plata. Cap XXII: 359-374.
- Grima J, Luque EJA, Mejía JA, Rodríguez R (2015). Methodological approach for the analysis of groundwater quality in the framework of the Groundwater Directive. *Environ. Earth Sci.* 74(5):4039-4051.
- Heuperman AF, Kapoor AS, Denecke HW (2002). Biodrainage. Principles, experiences and applications. International Programme for Technology and Research in Irrigation and Drainage, Food and Agriculture Organization of United Nations-FAO. Synthesis Report 6. <http://www.iptrid.org>.
- Hitchon B (1995). Fluoride in formation waters. Alberta Basin, Canada. *Applied Geochem.* 10: 357-367.
- Holdridge LR (1978). Ecología basada en zonas de vida. Instituto Interamericano de Ciencias Agrícolas. Editorial IICA San José de Costa Rica 216 p.
- Hughes MF, Beck BD, Chen Y, Lewis AS, Thomas DJ (2011). Arsenic exposure and toxicology: A historical perspective. *Oxford J. Med. Health Science Mathe. Toxicological Sci.* 123(2):305-332. <http://toxsci.oxfordjournals.org/content/123/2/305>.
- Lavado RS, Reinaudi N, Vázquez JA (1983). Flúor en aguas, suelos y vegetación del oeste bonaerense. *Rev Ciencia del Suelo* 1(1):9-14.
- Litter M, Pérez Carrera A, Morgada ME, Ramos O, Quintanilla J, Fernández Cirelli A (2006). Formas presentes de arsénico en agua y suelo. Capítulo 2. In: IBEROARSEN. Distribución del arsénico en las regiones Ibérica e Iberoamericana. Bundschuh J, Pérez Carrera A y Litter M (Ed) CYTED. 241 p.
- López DL (2006). Fuentes naturales y transporte del arsénico en aguas superficiales y subterráneas. Taller de distribución del As en Iberoamérica Workshop of As distribution in Ibero-América Centro Atómico. Provincia de Buenos Aires, Argentina. [http://www.cnea.gov.ar/pdfs/actividades\\_ambientales/libroresumenestaller-2006.pdf](http://www.cnea.gov.ar/pdfs/actividades_ambientales/libroresumenestaller-2006.pdf)
- Mejía GMA, González Hita L, Briones Gallardo R, Cardona Benavides A, Soto Navarro P (2014). Mecanismos que liberan arsénico al agua subterránea de la Comarca Lagunera, estados de Coahuila y Durango, México. *Tecnología y Ciencias del Agua* 1:71-82.
- Miller RL, Bradford WL, Peters NE (1988). Specific Conductance: Theoretical Considerations and Application to Analytical Quantity Control. *U.S. Geological Survey Water-Supply* 2311:1-21.
- Minaverry C, Cáceres V (2016). La problemática del arsénico en el servicio de agua en la provincia de Buenos Aires, Argentina. Análisis de casos jurisprudenciales. *Revista Internacional de Contaminación Ambiental* 32(1):69-76.
- Morrás H (2003). Distribución y origen de sedimentos loésicos superficiales de la pampa norte en base a la mineralogía de arenas. Resultados preliminares. *Revista Asociación Argentina de Sedimentología* 10(1):53-64.
- Nanyaro JT, Aswathanarayana U, Mungore JS, Lahermo PW (1984). A geochemical model for the abnormal fluoride concentrations in waters in parts of northern Tanzania. *J. Afr. Earth Sci.* 2:129-140.
- Nicolli HB (2006). Fuentes y movilidad del arsénico en aguas subterráneas de la Llanura Chaco-Pampeana de la Argentina. Workshop of As distribution in Ibero-América. Centro Atómico, Provincia de Buenos Aires, Argentina. [http://www.cnea.gov.ar/pdfs/actividades\\_ambientales/libroresumenestaller-2006.pdf](http://www.cnea.gov.ar/pdfs/actividades_ambientales/libroresumenestaller-2006.pdf)
- Nicolli HB, Blanco MC, Paoloni JD, Fiorentino CE (2006). Ambientes afectados por el arsénico Capítulo 4. En: IBEROARSEN. Distribución del arsénico en las regiones Ibérica e Iberoamericana. Ed. Bundschuh J, Pérez-Carrera A y Litter M. CYTED. 241 p.
- Nordstrom DK, Ball JW, Donahoe RJ, Whittemore D (1989). Groundwater chemistry and water-rock interactions at Stripa. *Geochimica et Cosmochimica Acta* 53:1727-1740.
- Ortega GMA (2009). Presencia, distribución, hidrogeoquímica y origen de arsénico, fluoruro y otros elementos traza disueltos en agua subterránea, a escala de cuenca hidrológica tributaria de Lerma-Chapala, México. *Revista Mexicana de Ciencias Geológicas* 26(1):143-161.
- Othax N, Peluso F, González Castelain J (2014). Riesgo a la salud integrado por fluoruros, nitratos y arsénico en agua subterránea: Caso del partido de Tres Arroyos, Argentina. *Revista Internacional de Contaminación Ambiental* 30(1):27-41.
- Ozsvath DL (2009). Fluoride and environmental health: a review. *Review Environmental Science, Biotechnol* 8:59-79.
- Panagiotaras D, Panagopoulos G, Papoulis D, Avramidis P (2012). Arsenic Geochemistry in Groundwater System. In: *Geochemistry-Earth's System Processes*. Editor Panagiotaras D. INTECH. 500 p. <http://cdn.intechopen.com/pdfs-wm/36460.pdf>
- Puntonero M L, Volpedo AV, Fernández Cirelli A (2014). Riesgo para la población rural en zonas con alto contenido de arsénico en agua. *Acta toxicológica Argentina* 22(1):15-22.
- Pekdeger A, Özegür N, Schneider HJ (1992). Hydrochemistry of fluoride in shallow aqueous systems of the Gölcük area, SW Turkey. In: Kharaka YK. and Maest AS. (Eds.). *Proc. 7<sup>th</sup> International Conference on Water-Rock Interaction*, Utah, pp. 821-824.
- Pesce H, Miranda F (2003). Catálogo de manifestaciones termales de la República de Argentina. Vol I.- II Región Noroeste. SEGEMAR, Buenos Aires. pp. 1666-3462.
- PMI, Plan Maestro Integral Cuenca del Río Salado (1999). Argentina: Ministerio de Economía de la Provincia de Buenos Aires-Halcrow-Banco Mundial. Informe técnico 1300 p.
- Robertson FN (1986). Occurrence and solubility controls of trace elements in groundwater in alluvial basins. Regional aquifer systems in the U.S. *Amer. Water Res. Assoc.* pp. 69-80.
- Rocca RJ, Redolfi ER, Terzario IRE (2006). Características geotécnicas de los loess de Argentina. *Revista Internacional de Desastres Naturales, Accidentes e Infraestructura Civil* 6(2):149-166. [http://www.fceia.unr.edu.ar/geologiaygeotecnia/Loess%20Rocca\\_Redolfi\\_Terzariol.pdf](http://www.fceia.unr.edu.ar/geologiaygeotecnia/Loess%20Rocca_Redolfi_Terzariol.pdf)
- Rodríguez R, Morales AI, Rodríguez I. (2016). Geological Differentiation of Groundwater Threshold Concentrations of Arsenic, Vanadium and Fluorine in El Bajío Guanajuatense, Mexico. *Geofísica Internacional* 55(1):5-15.
- Roseli FM, Dias LE, Vargas de Mello J W, Oliveira JA (2010). Behavior of *Eucalyptus grandis* and *E. cloeziana* seedlings grown in arsenic-contaminated soil. *Revista Brasileira de Ciência do Solo* 34(3):985-992.
- Ruggieri F, Fernández Turiel JL, Saavedra J, Gimeno D, Polanco E, Naranjo JA (2011). Environmental geochemistry of recent volcanic ashes from the Southern Andes. *Environ. Chem.* 8:236-247.
- SAGyP-INTA (1989). Mapa de suelos, Provincia de Buenos Aires. Escala 1:500,000. Secretaría de Agricultura, Ganadería y Pesca e Instituto Nacional de Tecnología Agropecuaria. 525 p.
- San-Xiang W, Zheng-Hui W, Xiao-Tian C, Jun L, Zhi-Ping S, Xiang-Dong Z, Ling-Ling H, Xiao-Yan Q, Zhao-Ming W, Zhi-Quan W (2007). Arsenic and fluoride exposure in drinking water: children's IQ and growth in Shanyin County, Shanxi province, China. *Environ.*

- Health Perspect. 115(4):643-647.
- Schulz CJ (2006). Presencia y distribución del arsénico en aguas subterráneas de la Llanura Pampeana – Caso de estudio: provincia de La Pampa, Argentina. Workshop of As distribution in Ibero-América Centro Atómico. Provincia de Buenos Aires, Argentina.
- Smedley PL, Kinniburgh DG (2002). A review of the source, behavior and distribution of arsenic in natural waters. *Appl. Geochem.* 17(5):517-568.
- Smedley PL, Kinniburgh DG, Macdonald DJM, Nicolli HB, Barros AJ, Tullio JO, Pearce JM, Alonso MS (2005). Arsenic associations in sediments from the loess aquifer of La Pampa, Argentina. *Appl. Geochem.* 20(5):989-1016.
- Soil Survey Staff (2010). Claves para la Taxonomía de suelos. USDA, Departamento de Agricultura USA. Servicio de Conservación de Suelos. 11 Edición. Traducción Ortiz Solorio CA, Gutiérrez Castorena MC, Gutiérrez Castorena EV. [www.suelos.org.ar/adjuntos/claves\\_taxonomia\\_de\\_suelos\\_11th\\_ed\\_espaniol\\_2010.pdf](http://www.suelos.org.ar/adjuntos/claves_taxonomia_de_suelos_11th_ed_espaniol_2010.pdf)
- Travi Y, Faye A (1992). Fluoride in Paleocene aquifers in Senegal. An example of the contamination of a confined aquifer by its roof zone, aggravated by intensive exploitation. *I.A.H. Selected papers on aquifer over-exploitation* 3:145-154.
- Tóth J (2000). Las aguas subterráneas como agente geológico: causas procesos y manifestaciones. *Boletín Geológico y Minero, Instituto Tecnológico GeoMinero de España.* 8:49-26.
- WHO (2006). Guías para la calidad del agua potable. Primer apéndice a la tercera edición, Volumen 1. Recomendaciones. Organización Mundial de la Salud, 398 p. [http://www.who.int/water\\_sanitation\\_health/dwq/gdwq3\\_es\\_full\\_lowres.pdf](http://www.who.int/water_sanitation_health/dwq/gdwq3_es_full_lowres.pdf)
- Zapata HR (2004). Química de la acidez del suelo. Ed. Universidad Nacional de Colombia, Medellín. 197 p. <http://www.bdigital.unal.edu.co/1735/1/9583367125.1.pdf>.
- Zhaoli S, Mi Z, Minggao T (1989). The characteristics of fluoride in groundwater of north China and the significance of fluorite-water interaction to fluorine transportation. In: *Procc. 6<sup>th</sup> Int. Symp. Water Rock Interaction.* Malvern, U.K. Balkema, pp. 801-804.