Trace elements distribution in soil, pore water and groundwater in Buenos Aires, Argentina

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ABSTRACT

The concentration of trace elements in soils, pore water and groundwater was determined in order to evaluate their distribution in the different environmental matrices and their transport through the unsaturated zone to groundwater in an area near Buenos Aires, Argentina. Exchangeable forms of trace elements are more useful than total element concentration in soils as indicative of groundwater pollution risk. Although the analysis of pore water is of utmost importance for the study of the vertical mobility of major ions as well as phosphate, occurrence of trace elements in pore water was not correlated with their presence either as exchangeable forms in soil profiles or in groundwater. Soil profiles of exchangeable Mn, Zn and Ni were determined in the different localities of Escobar county. For Mn, the general trend is to diminish with depth with a slight increase at 60 cm depth. Nevertheless, this element was detected in groundwater but not in pore water. Exchangeable Ni ranged from 0.085 to 0.16 $\mu g\ g^{-1}$, with an increase in depth for the three evaluated soils. Zn was detected in all systems: soil, pore water and groundwater. Arsenic is of natural occurrence in groundwater. The concentration of the trace elements found in groundwater (Cu, Fe, Mn, Zn, V) are much higher in the shallow aquifer, which is more polluted due to anthropic activities.

1. Introduction

The concentration of metals in uncontaminated soil is primarily related to the geology of the parent material of the soils. Metals associated with aqueous phase of soils are subject to soil water movement, and may be transported through the vadose zone to groundwater (McLean and Bledsoe, 1992). Metal concentration in soil profiles depends on the soil origin and the pedogenetic processes involved in its formation. Normal soil values as well as phytotoxicity have been reported for some elements (Adriano, 2001). Awareness of content of metals in soils is important for understanding the evolution and prediction of possible processes of soil and water contamination. Enrichment in certain elements is a result of anthropogenic activity, such as industrial activities or agriculture through the addition of fertilizers and pesticides.

Many places of disposal of dangerous residues contaminate their surrounding soils with heavy metals. The contamination of these soils represents a great concern due to its toxicity and risk for the health and the environment, since they can affect the soil ecology, the agricultural production, and food and water quality.

The factors that influence trace metals mobility are the metal properties, the quantity and type of adsorption places, pH, concentration of complexing anions (organic and inorganic), and cations in the soil solution (Alloway, 1995). The total trace metal concentration in soils is not indicative of the availability of these metals for plants and of their potential risk of soil and water contamination. Therefore, chemical methods to determine trace metal concentration in soils have been based on the measurement of extractable or labile fractions of these elements (De Siervi et al., 2004).

Immobilization of metals by sorption and precipitation mechanisms will prevent the metals from moving to groundwater. When metals are introduced into the soil surface, downward transportation does not occur to any great extent unless the metal retention capacity of the soil is overloaded, or unless metal interaction with the associated organic matter enhances mobility (McLean and Bledsoe, 1992).

In soil, metals may be found in different way such as dissolved in the soil solution, occupying exchange sites on inorganic soil constituents, specifically adsorbed on inorganic soil constituents, associated with insoluble soil organic matter, precipitated as pure or mixed solids; present in the structure of secondary minerals, or present in the structure of primary minerals (Shuman,1991). Once metals have been introduced into the environment through human activity, metals are more often associated with one of the first five above mentioned pools. The aqueous fraction, and those fractions in equilibrium with it, such as the exchangeable fraction, is important

when considering the potential migration of metals associated with soils to groundwater (Lindroos et al., 2007). Geochemical correlations of trace elements with major elements, such as Fe and Al, may be useful to discriminate contaminated samples from those that contain naturally occurring levels of inorganic constituents (Thorbjornsen and Myers, 2004). There are also health risks associated with the reuse of urban wastes and residual waters, with agrochemicals use and with soil contamination and heavy metals in waters ((Komatina and Komatina, 2002; Khalequzzaman et al., 2005).

In Argentina, there are few studies on the content of trace elements in agricultural areas. In the Rolling Pampas soils, Lavado et al. (2004) determined the concentration and dispersion of potentially toxic elements in the superficial horizon of soils that present similar values to those reported in unpolluted soils of other parts of the world. On the other hand, it was found that intrazonals soils have higher values of Cd, Pb, Cu, Zn and Cr than those registered in the zonal soils of the area of La Plata city, indicating that changes in metallic proportion in relation to landscape geoforms and parental material exist (Camilión et al., 2004).

In a previous study, in Belen de Escobar, Buenos Aires, Argentina, total metal concentration was determined for Cr, Ni, Pb, and Zn in Typic Argiudolls (Silva Busso et al., 2004). In the same area, we have also evaluated the groundwater chemical pollution risk taking into account the different land uses. The environmental risk of increasing P addition was analyzed in relation to soil sorption capacity (Heredia and Fernández Cirelli, 2007). Parameters such as clay content, organic carbon, CEC, soil pH, landscape position and phreatic depth were taken into account to propose a soil attenuation index (Heredia and Fernández Cirelli, 2008). The aim of this study is the determination of the content of heavy metals and trace metals in soils, pore water and groundwater to evaluate their distribution in the different environmental matrices and their potential retention in the unsaturated zone.

2. Materials and methods

2.1. Study area

The soil profiles, pore water and groundwater under study are located between 34° 18'S and 58° 51' W to 34° 24'S and 58° 44'W, in the county of Escobar, located in the geomorphologic unit called Rolling Pampas (Pampa ondulada) in Buenos Aires, Argentina (Fig. 1). The study area has wet climate and a mean temperature of 16 °C. The mean annual precipitation is 900 mm. Although precipitation is higher in the summer, the precipitation balance is negative in this season.

The Escobar county is near the city of Buenos Aires (ca. 50 km), and it has a population of 178,155 inhabitants with a density of 643 inhabitants km^{-2}. Only 13% of the population is connected to the sewerage system. Total surface (including the insular area of Delta del Paraná) is 304 km^2 (INDEC, 2001). The county is composed by 6 localities: Belen de Escobar, Ingeniero Maschwitz, Garin, Matheu, Loma Verde and Maquinista Savio. It belongs to the Lujan River basin (de la Plata River basin). Groundwater from Pampeano (shallow aquifer) and Puelches (semi-confined aquifer, 40–50 m depth) is the main water source in the study area (Santa Cruz, 1994).

Both aquifers are in the Epiparaniana section and form a series of unconfined or semi-confined aquifers, located in the Puelches sands and the Pampeanos sediments. The recharge of the system takes place from the rain precipitations, especially in the interfluvials areas and the main discharge takes place in the course of Luján River. The Pampeanos sediments offer lower flows when compared with the flows obtained in the Puelches aquifer.

The urban area accounts for 7486 ha, while the rural areas account for 15,114 ha. Industrial activity is important — so far, 233 industries have been reported. According to the last Agricultural National Census (INDEC, 2002), in the Escobar county there are 152 agricultural exploitations with defined limits, whose total surface is of 2873 ha
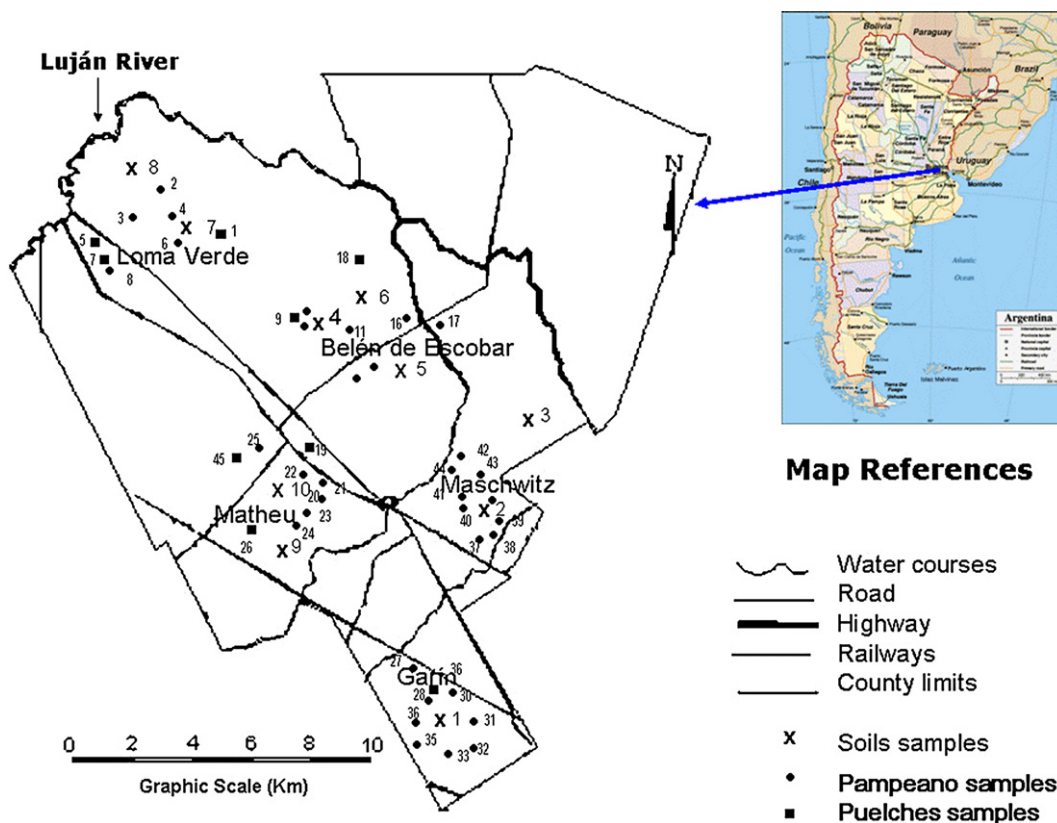

Fig. 1. Soil, and groundwater samples in Escobar county (Argentina).

with 148.5 ha dedicated to nurseries with aromatic, ornamental and forest plants.

2.2. Trace metals in soils

Soil samples location and classification is shown in Table 1. Composition of soils has already been described in a previous works (Heredia and Fernández Cirelli, 2007, 2008). Exchangeable trace elements were extracted with ammonium acetate 1N pH 7.0 (Tessier et al., 1979). This extractant is usually used to obtain exchangeable cations of soils and may be useful for trace metals. However, there is no universal extractant for phytoavailability determinations.

Trace elements were determined by ICP-OES (Inductively Coupled Plasm-Optical Emission Spectroscopy), with Perkin Good Elmer 2000 DV. For calibration reference materials with trazability certificate (Merck) were used. Metal contents were expressed in $\mu g\ g^{-1}$ soil (or ppm).

2.3. Trace metals in pore water and groundwater

Pore water was collected by means of a suction lysimeter, type vaccum-pressure suction cup sampler installed in a nursery in Matheu (soil 10) each two weeks during six month. Groundwater samples (Fig. 1 and Table 2) were collected from pre-existent wells both in Pampeano (34 wells) and Puelches aquifer (9 wells) in May 2004 (autumn). Sampling and analytical techniques followed the suggestions by APHA (1993) and groundwater samples were collected in 500 mL clean plastic bottles. Both pore and groundwater were acidified to pH <2 using ultrapure nitric acid and then, were refrigerated at 4 °C before chemical analysis. Heavy metals and trace elements were determined by ICP-OES using Perkin Good Elmer 2000 DV. For calibration reference materials with trazability certificate (Merck) were used. Metal contents in water were expressed in $\mu g\ L^{-1}$ (or ppb).

The ICP-OES detection limits for the elements analyzed were for As: 12 $\mu g\ L^{-1}$, Cd: 2 $\mu g\ L^{-1}$, Cr: 4 $\mu g\ L^{-1}$, Cu: 5 $\mu g\ L^{-1}$, Mn: 4 $\mu g\ L^{-1}$, Fe: 8 $\mu g\ L^{-1}$, Ni: 5 $\mu g\ L^{-1}$, Pb: 14 $\mu g\ L^{-1}$, Zn: 10 $\mu g\ L^{-1}$, Tl: 15 $\mu g\ L^{-1}$ and V: 12 $\mu g\ L^{-1}$.

2.4. Statistic analysis

Descriptive statistical analysis (mean, minimum and maximum value, standard deviation (SD) and Coefficient of Variation (C.V.) were analyzed), correlation and simple regression analysis for groundwater samples were carried out with the InfoStat version 1.1 program (2002).

3. Results and discussion

3.1. Trace metals in soils

Soil profiles of exchangeable Mn, Zn and Ni that were determined in the different localities of the Escobar county are shown in Fig. 2. Mn

Table 1
Ubication and identification of Escobar soil

Soil identification	Location	Taxonomic classification
1	Garin	Typic Argiudoll
2	Maschwitz	Entic Hapludoll
3	Maschwitz	Aquic Hapludoll
4	Belén de Escobar	Typic Argiudoll
5	Belén de Escobar	Typic Argiudoll
6	Belén de Escobar	Udarent
7	Loma Verde	Typic Argiudoll
8	Loma Verde	Typic Natraquoll
9	Matheu	Mollic Fluvaquent
10	Matheu	Typic Argiudoll

Table 2
Chemical characterization of groundwater samples

Element	Samples	Mean	C.V.	Minimum	Maximum	Median
Pampeano aquifer	30					
CE		1067.9	28.6	683.6	1860.4	1006.6
pH		7.18	3.90	6.81	8.14	7.15
Ca^{2+}		3.1	58.9	0.3	6.7	2.6
Mg^{2+}		3.3	62.8	0.2	8.8	3.2
Na^+		5.2	41.9	2.2	9.1	4.8
K^+		0.5	52.6	0.2	1.2	0.4
CO_3H^-		8.2	24.1	4.8	12.6	8.1
SO_4^{2-}		1.9	38.5	1.0	3.9	1.6
Cl^-		2.1	58.1	0.3	5.5	1.8
Puelches aquifer	9					
CE		948.2	21.5	732.0	1361.1	869.0
pH		7.22	2.80	6.90	7.51	7.25
Ca^{2+}		3.6	68.5	0.6	7.0	3.0
Mg^{2+}		2.6	70.7	0.4	5.0	2.6
Na^+		4.9	51.2	1.4	7.9	4.9
K^+		0.3	41.8	0.2	0.6	0.3
CO_3H^-		6.9	16.3	5.3	9.0	7.0
SO_4^{2-}		1.4	20.8	1.0	1.9	1.4
Cl^-		2.0	38.5	1.0	3.2	2.0

Cations and anions in $mmol_c\ L^{-1}$.

varied between 2.08 to 50.60 $\mu g\ g^{-1}$ in soil 1 (Garín), 8.0 to 41.3 $\mu g\ g^{-1}$ in soil 5 (Belen de Escobar), and 0.47 to 6.55 $\mu g\ g^{-1}$ in soil 10 (Matheu). Exchangeable Zn content varied between 3.0 and 1.1 $\mu g\ g^{-1}$ and Ni between 0.087 to 0.130 $\mu g\ g^{-1}$. The highest concentrations are always in the surface horizon, diminishing in depth (Fig. 2).

Mn concentration in soils is very variable and is mainly governed by physicochemical soil characteristics like pH and Eh that govern the oxidation state of the metal (Adriano, 2001). Morphological observations suggest that in the soil samples studied, Mn must be mainly in non reduced forms, which is also expectable taking into account the values of pH determined. Exchangeable Mn values in surface varied among 6.55 (in Matheu) to 50.60 $\mu g\ g^{-1}$ (in Garín). The general trend is to diminish in value according to the depth, with a slight increase at 60 cm depth for soils 5 and 10. The soil 1 had the highest value in the surface horizon, reaching a minimum in the B horizon, and then increasing in the C horizons. As the pH soils increase, all the soils had minimum concentration in depth. Mn is more soluble at lower pH values (Adriano, 2001). In contrast with Safo and Lowe (1973), Mn showed high variation with depth in the soil profile. Nevertheless, this element was detected in groundwater but not in pore water (Table 3).

Exchangeable Zn concentration in surface soil ranged from 0.8 (soil 10, Matheu) to 4.52 $\mu g\ g^{-1}$ (soil 1, Garín). Both soils have exchangeable Zn uniformly distributed in the soil profiles. Similar results were found in Colorado and California soils (Adriano, 2001). This element was also detected in the pore water in soil 10. In this soil amended with organic residues, the solubility of Zn may increase and for that reason it was possible to detect it in the pore water. Total Ni concentration in soils is quite variable, with an average of 20 $\mu g\ g^{-1}$, phytotoxic starting from 15–25 $\mu g\ g^{-1}$ for a wide range of agronomic and horticultural crops (Adriano, 2001). Ni enters the soil either through deposition of particulate material coming from emissions of industry and use of fossil fuels, and through the application of industrial sewage sludge compost. Davis et al. (1988) found Ni vertical displacement within 7.5 cm depth. In our soils, exchangeable Ni oscillated among 0.085 to 0.160 $\mu g\ g^{-1}$, with an increase in depth for the three evaluated soils. These values are very low and represent no ecophytotoxicity risk. The occurrence of Ni is related to the parent material and the pedogenetic processes but not to recent contamination. In California, reports on the Ni distribution in the soil profile have been in conflicting because of the lack of the uniform pattern. In 49 soil profiles analyzed, exchangeable Ni presented a normal distribution throughout the profile (16 profiles), increasing concentration with depth (20 profiles), decreasing concentration with depth (6 profiles) and increasing
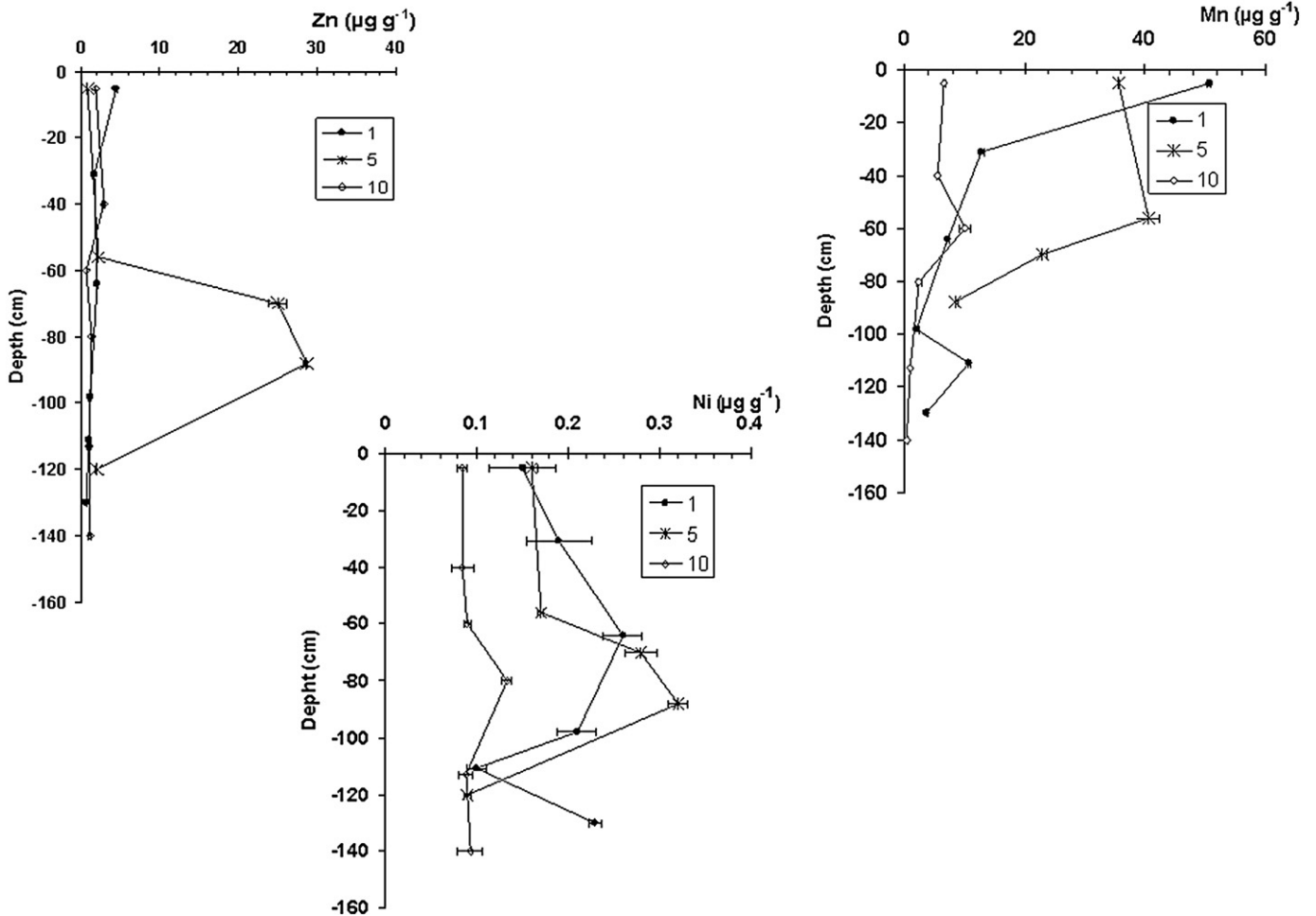
Fig. 2. Exchangeable Zn, Mn and Ni in soil profiles.

concentrations followed by a decreasing pattern (7 profiles) (Bradford et al., 1967, 1996). Our soils profiles coincide with the last pattern of Ni profiles.

We had found a significant and positive correlation between Ni and Zn ($r = 0.6839$ $p < 0.001$) and that the concentration of both metals tended to increase with depth and show a maximum concentration in the argillic horizon. Ni, Fe and Mn have been reported to accumulate in the same horizon (McGrath, 1995). Distribution of Zn and Ni in soil profiles is similar to that found by Lavado et al. (2004) in another region of Buenos Aires province.

Exchangeable Cu was only detected in surface horizon in soils 1 (Garin) and 10 (Matheu), being its value of 0.68 and 1.21 $\mu g\ g^{-1}$, respectively. Despite the occurrence of Cr and Pb when total concentration was determined in soils of Belen de Escobar, exchangeable Cr, Cd, Pb and Fe were not detected. Trace metals concentrations in soil, pore water and groundwater are shown in Table 3.

3.2. Trace metals in pore water and groundwater

During the sampling period only Zn was detected in pore water, however, it was not found regularly (Fig. 3).

In soil 10, exchangeable Zn concentration was in average 2 $\mu g\ g^{-1}$, whereas in the soil solution the Zn content was much lower, ranging among 0.14 to 0.1 $\mu g\ mL^{-1}$ an order of magnitude less than the one found in the argillic horizon. In groundwater, Zn concentration in the nursery was 35.8 $\mu g\ L^{-1}$. This value is 3.9 times lower than that found

Table 3
Trace metals concentration in soils, pore water and groundwater

	Zn	Mn	Ni	Cu
Soil exchangeable ($\mu g\ g^{-1}$)[a]	0.8–4.52	6.55–50.6	0.16–0.085	0.68–1.21
Soil water pore ($\mu g\ L^{-1}$)[b]	10–143	–	–	–
Pampeano groundwater ($\mu g\ L^{-1}$)[c]	298	95	5.5–8.9	15.8
Puelches groundwater ($\mu g\ L^{-1}$)[c]	105.4	–	–	11.38

[a] In surface horizon.
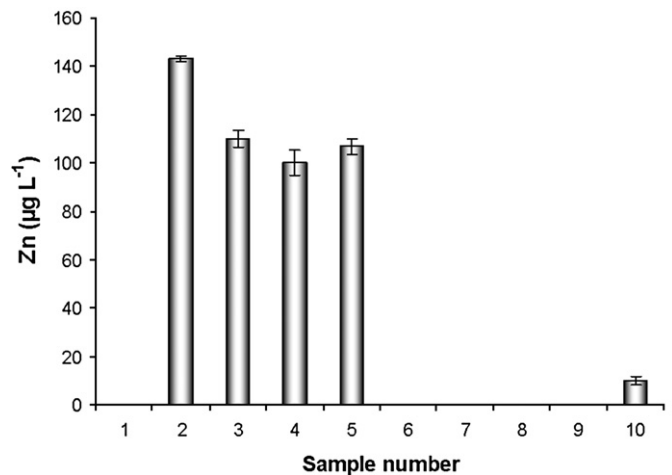[b] At 0.60 m depth.
[c] Average value.

Fig. 3. Zinc in pore water.

for Zn in pore water, in accordance with the high soil attenuation capacity of soil 10 (Heredia and Fernández Cirelli, 2008).

3.3. Pampeano aquifer

The concentrations of trace elements in Pampeano aquifer is shown in Table 4. All the concentrations of the analyzed metals presented high variability. Ni was found only in 5 samples, concentrations ranging between 5.5 and 8.9 µg L^{-1}. In all the studied samples, Cd, Cr, Pb and Tl were below the detection limit: for this reason, these elements are not considered in the descriptive statistic. In general, the median value was always lower than the mean value, and analysis of the element concentration of water samples would be more appropriate.

Zn was the element that showed the higher concentration, although the allowed limits for drinking water were far below. Maximum values were observed in Loma Verde (Fig. 5), associated to industrial activities, since a chlorine facility and a meat factory are placed near the wells where the samples were taken. Animal wastes may be an important source of Zn (Moscuzza et al., 2005). It is interesting to point out that one sample from Belen de Escobar (not included in Table 2, Table 4 and Fig. 5) accounted for 4095.5 µg L^{-1}. This sample was taken from a handpump (9 m depth) located in the neighborhood of a factory that almost ten years ago had a spill of toxic products.

Manganese showed the greatest variability, finding the higher values in Maschwitz, one of them associated with industrial activities (1781.1 µg L^{-1}).

The mean value of Fe was of 88.16 µg L^{-1}, with a maximum of 649.4 µg L^{-1} the minimum was below the detection limit. The highest value corresponds to Belen de Escobar, where high concentrations of Mn and Zn were also detected and are associated with industrial activities in the neighborhood.

The mean Cu value in groundwater samples was of 15.89 µg L^{-1} with a maximum of 101.7 µg L^{-1}, and the minimum below the detection limit. The highest value is in the proximity of the surrounding of meat factory in Loma Verde (101.7 µg L^{-1}). Apart from Zn, Cu is the other element that Moscuzza et al. (2005) have suggested as of great superficial accumulation in the places with high animal concentration. In relation to soil and pore water taken from a nursery, groundwater (Matheu) Cu concentration was 56 µg L^{-1}.

Arsenic is an element of natural occurrence in groundwater in Argentina, being the pampa plains one of the most extensive areas affected in the world (Nicolli et al., 1989; Pérez Carrera and Fernández Cirelli, 2004) and it is associated to the presence of volcanic ash. The mean value determined in the study area was 24.89 µg L^{-1}, and the
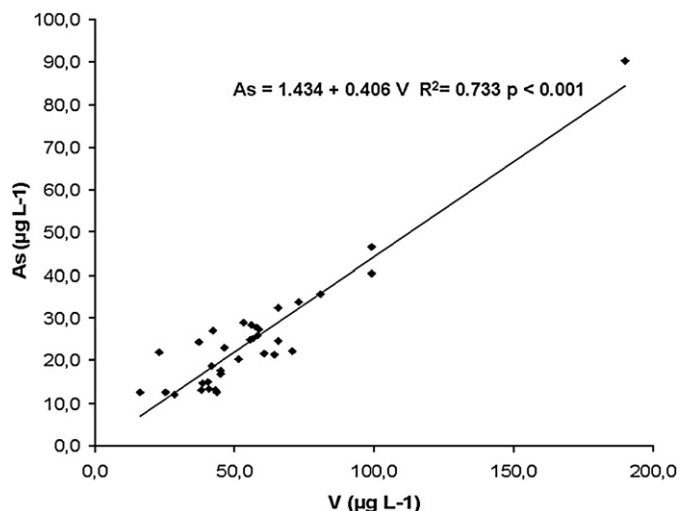

Fig. 4. Zinc and vanadium relationship in groundwater.

maximum 90.3 µg L^{-1}. All the samples were above the allowed concentration for drinking water in Argentina (10 µg L^{-1}, CAA, 2007).

Values of As and V are statistically associated since both elements have the same origin (Nicolli et al., 2001). The regression equation among them is shown in Fig. 4 in addition Zn presented a negative correlation with V ($r=-0.4919$ $p<0.01$).

3.4. Puelches aquifer

Concentration of trace elements in Puelches aquifer is shown in Table 4. Samples were taken from pre-existent wells and only 9 of the analyzed wells corresponded to Puelches aquifer. This aquifer presents mean and maximum values lower than those found in the Pampeano aquifer, because it is less impacted by anthropic activities than the shallow aquifer. Unlike Pampeano aquifer, Mn and Ni were not found in Puelches, Cd, Cr, Pb and Tl were in all the water samples below the detection limit. In general, coefficients of variation values are smaller than in the Pampeano, and the median continue being smaller than the mean values.

The maximum Zn concentration was 220.3 µg L^{-1} (Matheu), corresponding to a sample that also shows high Fe concentration. The minimum Zn concentration (16.8 µg L^{-1}) was also determined in the same locality, in an area of low population density. As shown in Table 4, Zn concentrations are variable. Fe concentrations show a higher variability than Zn, and only 3 samples were above the detection limit. Only 4 Cu samples have concentrations above the detection limit. The variability for this metal was the highest. As and V

Table 4
Concentrations of trace elements in Pampeano and Puelches aquifer, descriptive statistics

Trace elements	Samples number	Mean	CV	Minimum	Maximum	Median
Pampeano aquifer						
As	34	24.89	57.52	10.70	90.30	22.65
Cu	34	15.82	142.55	<dl	101.70	6.85
Mn	34	95.09	375.57	<dl	1781.10	2.34
Fe	34	88.16	167.82	<dl	649.40	15.50
Zn	34	298.04	155.83	3.14	1849.10	102.85
V	34	56.14	53.67	15.9	189.70	52.35
Puelches aquifer						
As	9	24.69	34.36	13.80	34.70	24.10
Cu	9	11.38	149.75	<dl	54.90	7.70
Fe	9	18.90	141.45	<dl	71.90	2.92
Zn	9	105.41	68.76	16.80	220.30	98.10
V	9	51.89	29.58	38.20	79.30	48.80

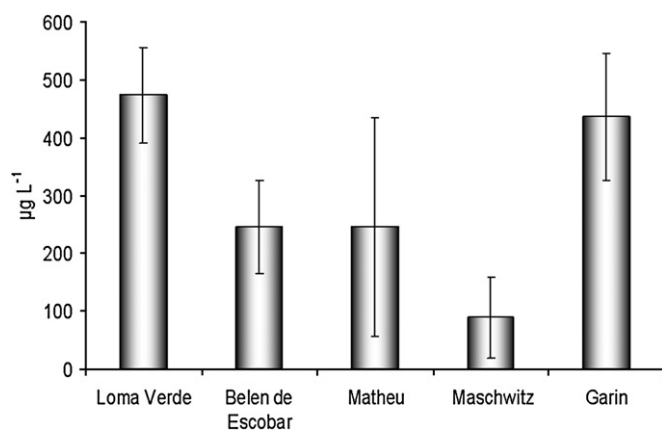Trace elements concentration: µg L^{-1}, dl: detection limit.

Fig. 5. Mean Zn concentration in groundwater.

show the lower variability. All As samples are above the allowed concentration for drinking water in Argentina. The As correlated in a positive and highly significant way with the V ($r=0.8774$ $p<0.001$) with a linear regression relationship ($r^2=0.77$, $p<0.05$).

3.5. Relationship among metals in soils, pore water and groundwater

Exchangeable trace elements were determined in soils, considering that they are more representative of their bioavailability and in consequence of the risk of groundwater contamination. Mn, Zn and Ni were determined in all the analyzed soil profiles. In a previous study (Silva Busso et al., 2004), total concentrations of Cr, Ni, Pb and Zn were determined in Belen de Escobar. Nevertheless, only Zn and Ni appear as exchangeable forms. Moreover, Cr and Pb concentrations were under the detection limit both in pore water and groundwater, reinforcing the fact that the determination of the total element concentration in soils is not indicative of their potential risk of water and/or food contamination. As expected, the concentration of the exchangeable forms of Ni and Zn are lower than the total concentrations. For Zn, the concentration of exchangeable form was 7.6 to 116 times lower than the total concentration, while for exchangeable Ni it was 63 to 104 times lower.

Zn was the only element found in all the studied compartments. The values in the pore water taken from the argillic horizon are 10 times smaller than those found as exchangeable Zn (1.1 µg g^{-1}) in soil 10. Although this exchangeable concentration in soil is higher than Zn found in groundwater in the study area (4.9–1193.5 µg L^{-1}), the exchangeable form is representative of the transference of the element from soil to water. Zn in the pore water gives an idea of Zn vertical movement, but the concentrations determined varied with time (Fig. 3) and determination is more complex than that of exchangeable forms.

Fe was detected in groundwater even though its concentration as exchangeable form was under the detection limit. It may be suggested that the extraction method used for the determination of exchangeable forms may not be appropriate for Fe.

Ni was only detected in 5 samples of the Pampeano located in Loma Verde, Garin and Maschwitz, but not in Matheu or in Belen de Escobar, where total and exchangeable forms of this element have been detected. Soils from the previously mentioned places show moderate soil attenuation index, and appear to be effective in the retention of this element (Heredia and Fernández Cirelli, 2008). On the other hand, in the soils of low soil attenuation index of the locality of Maschwitz, high concentrations of Cu, Zn, Fe and even V, were determined in groundwater. In the locality of Garín, in spite of the soil attenuation index (low to moderate), high concentrations of Zn and Fe were punctually determined in groundwater due to the presence of an industrial park.

4. Conclusions

Exchangeable forms of elements are more useful than total element concentration in soils as indicative of groundwater pollution risk. Nevertheless, the extraction procedure used in the present study may not be suitable for the determination of exchangeable Fe.

Although the analysis of pore water is of utmost importance for the study of the vertical mobility of major ions as well as phosphate, occurrence of trace elements in pore water was not correlated with their presence either as exchangeable forms in soil profiles or in groundwater.

In the evaluated soils, although the concentration of Mn diminished with depth, it was detected in groundwater. On the other hand, the concentration of exchangeable Ni increased with depth. Metal speciation studies in soil should be performed to explain this different behaviour. Only Zn was detected in soil, pore water and groundwater, as well.

Arsenic is of natural occurrence and its concentration is similar both in Pampeano (shallow aquifer) and Puelches aquifer. The same trend is observed for vanadium, whose origin is the same as for the former element and there is a good correlation between both of them. The other trace elements found in groundwater are not correlated, and their concentrations are much higher in the shallow aquifer which is more polluted due to anthropic activities.

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