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Baseline Levels of Potentially Toxic Elements in Pampas Soils

RAÚL S. LAVADO
MARTA S. ZUBILLAGA
ROBERTO ALVAREZ
MIGUEL A. TABOADA

Facultad de Agronomía
Universidad de Buenos Aires
Buenos Aires, Argentina

The soils of the Pampas are thought to be generally non-contaminated but there is growing evidence of trace element accumulation at some specific sites. The goal of this study was to measure the current levels of the main Potentially Toxic Elements (PTE) in the top horizon and in specific soil profiles so that we would establish the baseline concentrations of these elements. Eighty-eight top soils and three soil profiles were sampled. The samples were acid digested. Arsenic, boron, barium, cadmium, cobalt, chromium, copper, lead, manganese, mercury, molybdenum, nickel, silver, selenium and zinc were determined with inductively coupled argon plasma emission spectrometry (ICPES).

All of the values found are within the normal range for uncontaminated soils as reported from several continents. Elements with high environmental risk potential are lower than the admissible range of the European Union and some of them are orders of magnitude lower than those of the United States Environmental Protection Agency (US-EPA) 501 levels. Potentially Toxic Elements contents increased with depth or showed a maximum concentration at the B2 horizon. This is related to the parent material and the pedogenetic processes but not to recent contamination. Soil profiles showed higher concentrations of PTE in clayey horizons. However, these relationships did not appear in top soil samples in any soil Great Group studied. The shown data establishes a baseline for PTE concentrations for Pampas soils.

Keywords Heavy metals, soil contamination, trace elements.

Introduction

The Pampas is one of the largest temperate cropland areas in the Southern Hemisphere. It has been subjected to a great intensification of agriculture production in the last decade. The present content of Potentially Toxic Elements (PTE) in the soils of the area has not been fully studied. It is believed that Pampas soils have a non-contaminated status at present, even though this idea is not widely supported by research. Lavado *et al.* (1998) showed that PTE content differed clearly from urban soils of Buenos Aires and its outskirts as compared to surrounding agricultural soils. In urban soils the concentration of cadmium, copper, lead

Address correspondence to Raúl S. Lavado, Facultad de Agronomía, Universidad de Buenos Aires, Av. San Martín 4453, C1417DSE Buenos Aires, Argentina. E-mail: lavado@agro.uba.ar

and zinc was much higher than the thresholds proposed by several international standards. In agricultural or grazed soils the concentrations of these elements were significantly lower and fell within the values found worldwide in non-contaminated areas. Soils recently started to receive an increased amount of chemical fertilizers and to a lesser extent other chemicals (lime, biosolids, etc.). Recently, indications of accumulation of PTE have been found in experimental plots that have received several years of phosphorus fertilization (Lavado *et al.*, 1999). This data supports the increasing concern for protecting the environmental quality of soils, similar to other parts of the world (Allaway, 1995).

A detailed review showed that PTE concentration varies according to the position of the soils within Soil Taxonomy (Frink, 1996). This survey included different parent material, soil-forming processes and different degrees of weathering. In those soils, type and content of clays play an important role in adsorption, accumulation or translocation of PTE. In contrast, soils of the Eastern part of the region, mainly Mollisols and to a lesser extent Alfisols, are derived only from loess-like materials. In order to establish the impact of agriculture intensification on soil contamination in the area, we need to know baseline levels of the main PTE in soils. Our objective was to determine the concentration of PTE and their variability in both the top soil and in soil profiles. We also studied the relationship between PTE content and selected soil properties including Taxonomical Units, and land use.

Materials and Methods

Soil of the area: Soil Taxonomic Units were characterized by their clay and organic matter content, and pH. Most soils are slightly acidic with a silty loam Mollic (A) horizon and a argilic (clayey B) horizon (Typic Argiudolls). Toward the east of the Pampas, soils are more clayey (Vertic Argiudolls and Vertisols), and towards the west they become sandier (Typic Hapludolls and Entisols). There are large areas affected by water excesses that are characterized by hydromorphic soils (Aquic Argiudolls). They are mixed with soils with a Natric B horizon (Typic Natraquolls and Typic Natrudolls) and soils alkaline in the whole profile with an ochric A horizon (Typic Natraqualfs and Typic Natrudalfs) (Soriano *et al.*, 1991). The pampean loess, like other loessic sediments in the world, was subjected to several cycles of sediment deposition, pedogenesis and erosion. In accordance with such a process, we find continuous buried paleosols and sediment remnants making up the local subsoils. Present soils and underlying materials show a close uniformity in mineralogical composition in both clay and sand fractions (Teruggi and Imbellone, 1987).

The area varies from intensive cropped lands to unplowed light grazed natural grassland: Argiudolls and Hapludolls are cropped, Natric soils are mainly devoted to animal husbandry. Aquic Argiudolls are seldom cropped (Soriano *et al.*, 1991). Contamination sources, like factories, are located along the Paraná and La Plata rivers. There are no mining operations or oil wells in the area.

Sampling and analysis: Eighty-eight plots from 20 farms located far from cities or roads were sampled. In each plot, 3 subsamples of the top horizon were taken and subsequently mixed. The area covered for the soil sample collection was around 10,000,000 ha and ranged from 33° 40′ S to 36° 0′ S and from 57° 35′ W to 61° 22′ W. The soils, locations and number of sampled plots are shown in Table 1 and sampling sites are shown in Figure 1.

Representatives of soils from east to west within the studied area were sampled in layers of 0.20 m up to a 1-m depth. The soils and locations were: Vertic Argiudoll (Vieytes), Typic Argiudoll (Solís) and Typic Hapludoll (25 de Mayo). In each case, 3 profiles were sampled. A deep sample (2.00–2.50 m depth) was also taken from each soil profile.

Table 1
Studied soils, location and sampling

Soils	Locations	Number of sampled plots
Typic Argiudolls	Solís (1), Villa Lía (2), Areco (3), Jauregui (4), Chacabuco (5), Pergamino (6), Salto (7)	38
Vertic Argiudolls	Vieytes (8), Baradero (9), San Pedro (10)	10
Aquic Argiudolls	Chascomús (11), Cañuelas (12)	6
Typic Hapludolls	Alberti (13), Bragado (14), 25 de Mayo (15), Casares (16)	14
Typic Natraqualfs/Mollic Natrudalf	Uribelarrea (17), Udaondo (18)	10
Typic Natraquolls/Typic Natrudolls	Uribelarrea (17), Libres del Sur (19), Pila (20)	10

All samples were acid digested (hydrochloric, sulfuric and nitric acids) (McGrath and Cunliffe, 1985). Arsenic (As), boron (B), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), molybdenum (Mo), nickel (Ni), silver (Ag), selenium (Se) and zinc (Zn) were determined on top soil of Typic Argiudolls, whereas in the remaining soils some elements were not determined. The PTE determination was performed with inductively coupled argon plasma emission spectrometry (ICPES). Cd, Cr, Cu, Pb, Ni and Zn were determined in the soil profiles samples using the same procedure. All analyses were checked against standard reference materials from NIST. The recovery of all PTE varied between 0.91 and 0.80, with the

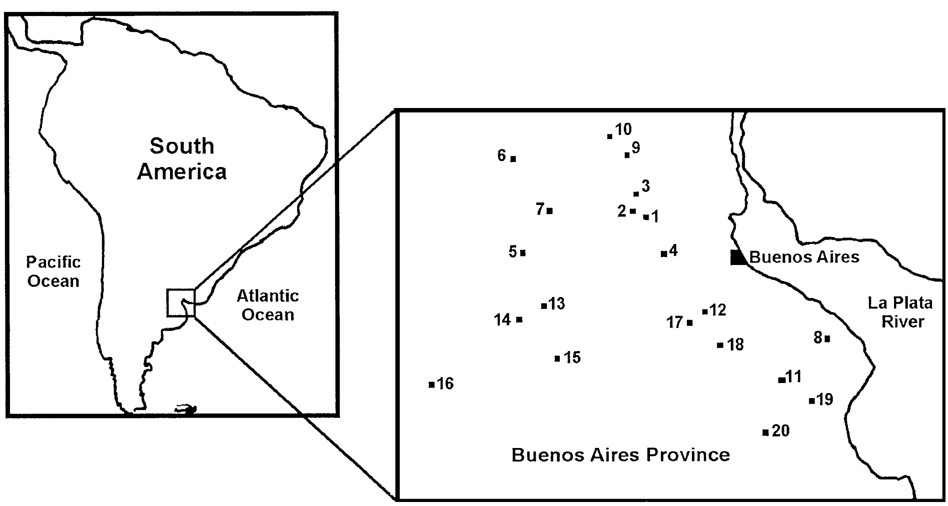

Figure 1. Map of the studied area. Geographical locations of sampling sites are indicated by numbers (see Table 1).

exception of Cr (0.54). Soil samples were also measured for pH, organic matter and clay content (data not shown) using standard techniques (Sparks *et al.*, 1996). All data were analyzed by simple statistical techniques.

Results and Discussion

Mean data of PTE are shown in Tables 2 to 7. All values are within the normal range found in several continents. However, concentrations of Ba, Cr, Hg and Ni were located in the lower segment as compared with average values from several parts of the world (Frinck, 1996; Berrow and Reaves, 1984). Some of the considered elements (As, Cr and Ni) were found in the same range as in sandy soils; that is to say, soils with low natural concentrations of PTE (Dudka, 1993). All elements with high environmental risk potential are lower than the admissible range of the EU (Berrow and Reaves, 1984). The concentration of As and Pb are orders of magnitude lower than the limits of the American US-EPA 501 permissible concentrations (Dudka and Miller, 1998). Tables 2 to 7 also showed some dispersion values. Variability reached a peak of 162.3% for Ba in the Typic Hapludoll but there is not a regular pattern of variability among elements or among soils. Related to variability, the median values are similar to mean values in most cases, with the exception of a few; i.e., Ba in the Typic Hapludoll. Figure 2 shows the mean concentration of all PTE. There were differences according to the type of soil, particularly with B, Cr, Ni, Pb, Se and others. However, the dispersion values were very high and it is not possible to clearly separate soils by concentrations, their taxonomy, position, or usage. The mean values of the Vertic Argiudoll, a clayey soil, showed a tendency of higher concentrations for several of the PTE.

Figures 3 to 5 show the concentrations of six PTE in the three soil profiles studied. The distribution of PTE shows either a pattern of maximum concentration in the B2 horizon

Table 2
PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Typic Argiudolls

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	2.97	1.33	44.92	3.00
As	3.07	1.61	52.34	2.90
B	14.41	12.89	89.45	22.00
Ba	134.72	66.00	48.99	120.00
Cd	0.75	0.46	61.16	0.78
Co	29.76	8.77	29.46	33.80
Cu	18.02	8.29	46.02	18.50
Cr	13.21	10.66	80.73	11.70
Hg	0.05	0.02	44.23	0.05
Mn	589.84	173.18	29.36	543.67
Mo	1.80	0.90	50.00	1.80
Ni	7.29	4.30	59.00	7.60
Pb	17.68	5.97	33.75	18.35
Se	0.54	0.45	84.20	0.30
Zn	48.00	24.14	50.29	46.30

Table 3
PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Vertic Argiudolls

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	3.00	0.00	0.00	3.00
As	2.27	0.06	2.55	2.30
B	26.33	5.51	20.91	26.00
Ba	108.33	12.58	11.62	110.00
Cd	0.69	0.38	55.41	0.79
Co	37.33	8.24	22.07	35.80
Cu	22.74	6.26	27.52	21.50
Cr	24.61	10.09	41.00	28.10
Hg	0.05	0.00	0.00	0.05
Mn	584.33	133.94	22.92	549.50
Mo	—	—	—	—
Ni	10.60	3.57	33.71	10.00
Pb	37.45	30.71	82.00	19.86
Se	0.30	0.00	0.00	0.30
Zn	59.05	21.36	36.17	55.50

depth or a pattern of increase in concentration with increasing soil depth of some PTE. The pattern depends on the particular PTE and the soil type. As found in other regions (Berrow and Reaves, 1984), this pattern of concentration of PTE in relationship to soil depth is mainly related to parent material and pedogenetic processes but not to anthropic

Table 4
PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Aquic Argiudolls

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	3.00	0.00	0.00	3.00
As	2.60	0.70	26.92	2.60
B	—	—	—	—
Ba	116.67	20.82	17.84	110.00
Cd	0.76	0.54	71.58	0.79
Co	—	—	—	—
Cu	11.44	8.44	73.72	11.30
Cr	11.40	6.25	54.81	11.20
Hg	0.05	0.00	0.00	0.05
Mn	660.00	36.06	5.46	650.00
Mo	—	—	—	—
Ni	3.80	3.59	94.57	3.82
Pb	20.93	4.59	21.94	20.35
Se	1.00	0.66	65.57	1.10
Zn	38.50	16.69	43.35	35.50

Table 5
PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Typic Hapludolls

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	2.50	0.00	0.00	2.50
As	2.63	0.10	3.92	2.60
B	—	—	—	—
Ba	209.83	340.54	162.29	88.50
Cd	1.02	0.50	49.16	1.25
Co	27.20	—	—	27.20
Cu	11.91	7.78	65.36	9.85
Cr	5.95	2.63	44.23	5.00
Hg	0.04	0.02	58.69	0.05
Mn	456.67	23.38	5.12	460.00
Mo	—	—	—	—
Ni	4.56	1.75	38.41	5.00
Pb	20.74	15.62	75.35	21.50
Se	0.51	0.38	75.02	0.28
Zn	42.13	15.59	37.01	47.00

contamination. This is in agreement with a previous finding in Argiudolls located in the north section of the study area (Lavado and Porcelli, 2000), where B, Cr, Cu, Pb and Zn were found mainly in insoluble fractions, again an indication of not contamination origin. PTE concentrations in the deep layers of the soils are shown in Table 8. Although the low

Table 6
PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Typic Natraquolls/Typic Natrudolls

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	—	—	—	—
As	—	—	—	—
B	25.67	6.43	25.05	23.00
Ba	—	—	—	—
Cd	1.25	0.63	50.00	1.25
Co	—	—	—	—
Cu	12.80	2.51	19.63	13.00
Cr	13.78	8.07	58.59	10.90
Hg	—	—	—	—
Mn	449.00	30.81	6.86	454.00
Mo	2.00	0.00	0.00	2.00
Ni	4.87	0.94	19.33	5.00
Pb	15.98	3.30	20.67	15.80
Se	—	—	—	—
Zn	38.03	6.51	17.11	42.80

Table 7

PTE mean values (mg kg^{-1}), standard deviation, variability coefficient (%) and median values (mg kg^{-1}). Typic Natraqualfs/Mollic Natraqualfs

Element	Mean	Standard deviation	Variability coefficient (%)	Median
Ag	—	—	—	—
As	—	—	—	—
B	25.67	6.43	25.05	23.00
Ba	—	—	—	—
Cd	0.92	0.59	64.33	1.25
Co	—	—	—	—
Cu	10.54	4.62	43.88	12.50
Cr	13.78	9.29	67.40	10.90
Hg	—	—	—	—
Mn	449.00	30.81	6.86	454.00
Mo	2.00	0.00	0.00	2.00
Ni	3.78	2.12	56.17	4.05
Pb	16.37	3.08	18.82	16.80
Se	—	—	—	—
Zn	35.03	7.87	22.48	37.50

number of samples hinders a statistical approach, these data show concentrations of PTE in the 2.00–2.50 m depth layers (former loessic material deposition) did not differ from those found in the 0.00–1.00 m depth. This is a direct evidence of absence of anthropic soil contamination. These data are consistent with results obtained by Camilión et al. (1996) in a previous local work: concentration of Cu, Pb and Zn in a Vertic Argiudoll subsoil (including two paleosols) were similar to that in the overlying present soil profile.

Several PTE showed a clear trend of concentration closely linked to clay content of soil horizons: the highest concentration of PTE was found in the clayey soil and the lowest concentration in the sandy one. In the Vertic Argiudoll profile the six PTE showed highly

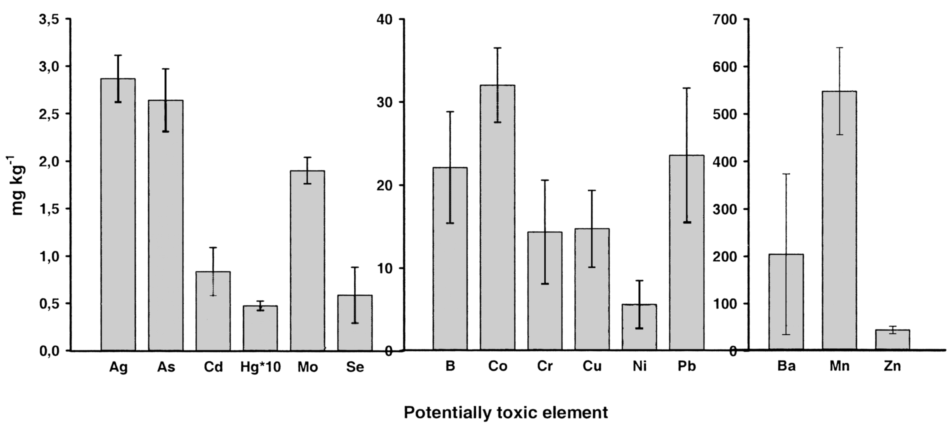

Figure 2. Average content of 15 PTE in all top soils sampled (mg kg^{-1}) and standard error.

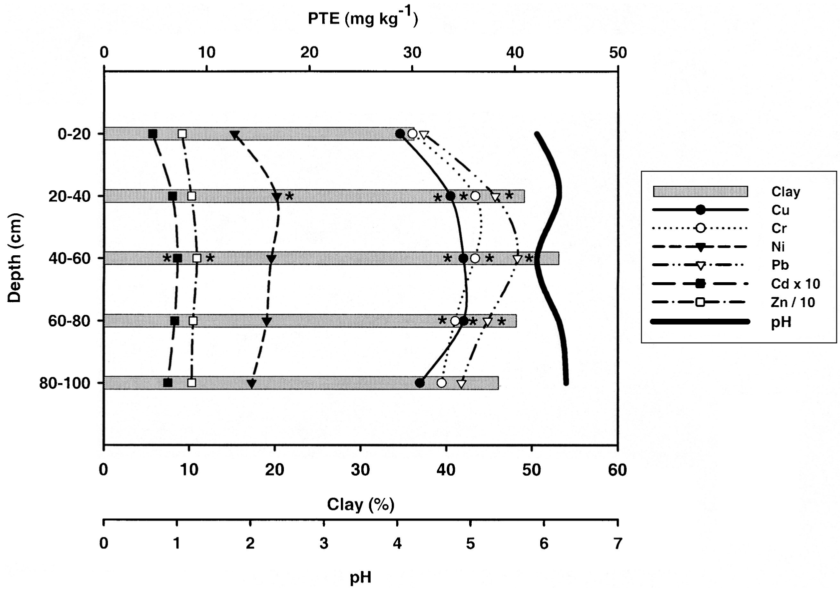

Figure 3. Contents of cadmium, chromium, copper, lead, nickel and zinc (mg kg^{-1}), clay percentage and pH in depth ranges. Vertic Argiudoll. Asterisks denote statistically significant (p: 0.05) higher values.

significant ($p = 0.001$) correlations with clay content (Cd: r^2 0.96; Cr: r^2 0.90; Cu: r^2 0.80; Ni: r^2 0.84; Pb: r^2: 0.96 and Zn: r^2 0.95); in the Typic Argiudoll only Cu (r^2 0.75) and Pb (r^2 0.79) showed significant ($p = 0.05$) correlations. No correlations were found in the Typic Hapludoll. This relationship between clay content and concentration of several PTE,

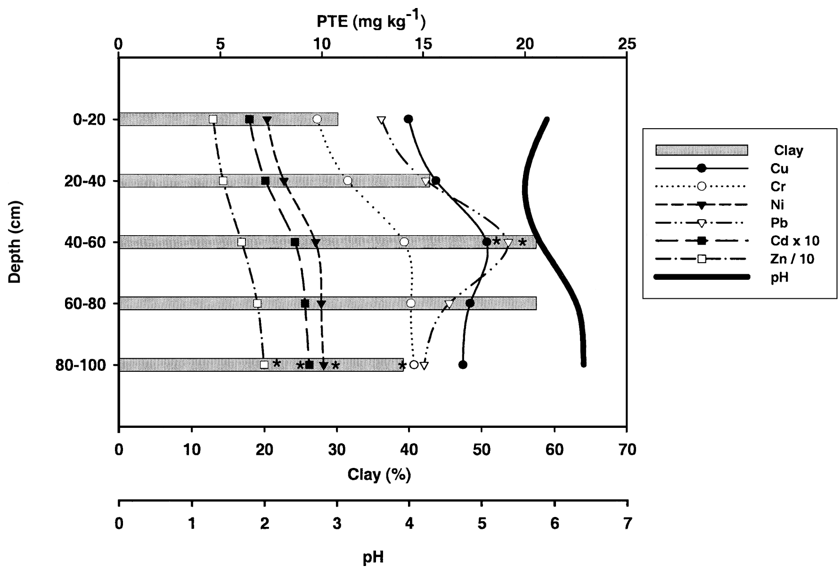

Figure 4. Contents of cadmium, chromium, copper, lead, nickel and zinc (mg kg^{-1}), clay percentage and pH in depth ranges. Typic Argiudoll. Asterisks denote statistically significant (p: 0.05) higher values.

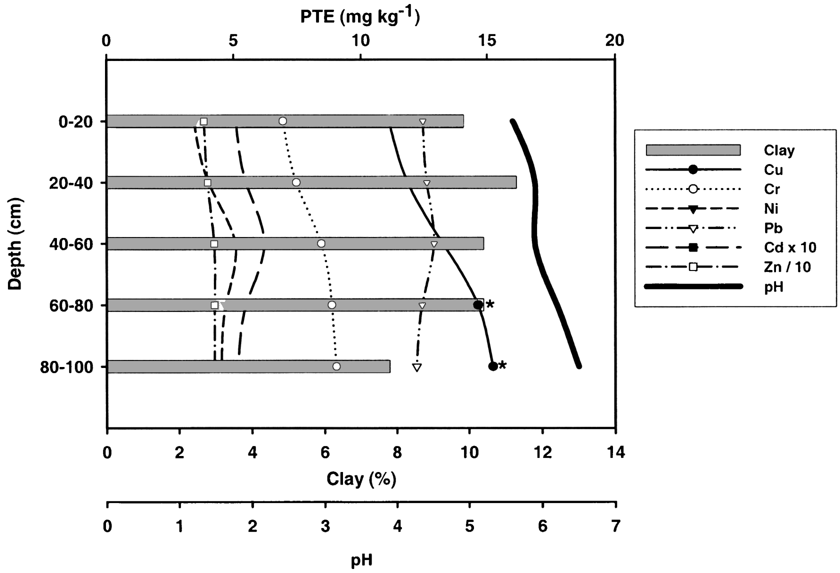

Figure 5. Contents of cadmium, chromium, copper, lead, nickel and zinc (mg kg^{-1}), clay percentage and pH in depth ranges. Typic Hapludoll. Asterisks denote statistically significant (p: 0.05) higher values.

which is usually found elsewhere (Dudka, 1993; Frink, 1996), was not detected when all top soils were compared: significant correlations ($p = 0.005$) were found only with Ag (r^2: 0.98),Ba (r^2: 0.99), Hg (r^2: 0.97), Mo (0.99) and Mn (r^2: 0.85). The clay content in top soils ranged from 6% to 42%; meanwhile, in the soil profiles, clay content varied from 4% to 65%. In topsoil the PTE-clay relationship is also affected by the natural variation in different properties and components, the overlapping effect of each soil history of crop management, input addition, the different element extraction by crops and so on. In contrast to clay content, soil pH showed highly significant ($p = 0.001$) correlations with Cr (r^2 0.98), Cu (r^2 0.95), Ni (r^2 0.88) and Zn (r^2 0.98) only in the Typic Hapludoll (Figure 4). The pH of the sandy soil clearly followed this tendency to increase with depth, showing a significant relationship with PTE concentrations. It is difficult to ascertain the cause,

Table 8
Average PTE concentration at 2.00–2.50 m depth and average PTE at 0.00–1.00 m depth (mg kg^{-1})

	Vertic Argiudoll		Typic Argiudoll		Typic Hapludoll	
PTE	2.00–2.50 m depth	0.00–1.00 m depth	2.00–2.50 m depth	0.00–1.00 m depth	2.00–2.50 m depth	0.00–1.00 m depth
Cd	0.90	0.64	0.84	0.82	0.44	0.55
Cr	34.27	33.88	ND	12.81	ND	8.14
Cu	33.93	32.67	22.10	16.45	12.30	13.22
Ni	18.60	15.23	ND	9.03	ND	4.35
Pb	65.73	36.34	21.07	15.71	19.05	12.53
Zn	83.50	85.05	56.06	59.57	32,60	41.11

but these relationships could be an indication of PTE movement toward depth over time, favored by high solubility due to acidity and higher leaching due to soil texture. There was not a significant correlation between pH or organic matter or a multiple correlation of pH, clay and organic matter contents, and PTE concentration in the top soils.

Conclusion

The top soils of the eastern pampas have concentrations and dispersion values of PTE (As, B, Ba, Cd, Co, Cr, Cu, Pb, Mn, Hg, Mo, Ni, Ag, Se and Zn) similar to non-contaminated soils in other parts of the world. This is irrespective of their taxonomical position and land uses. PTE concentrations increased with depth or showed a maximum concentration at the B2 horizon. This is related to the parent material and the pedogenetic processes but not to recent contamination. In addition, data of PTE from subsoil samples showed no sign of soil contamination. From this information it can be deduced that the obtained data are the baseline of PTE concentrations in those soils. PTE concentrations are related to clay content or pH in the clayey or sandy soil profiles, respectively.

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