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Assessment of toxic metal contamination using a regional lithogenic geochemical background, Pampean area river basin, Argentina

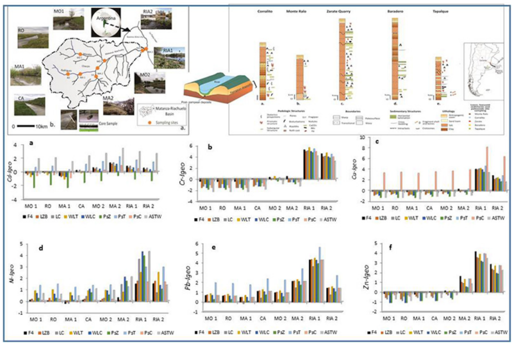
Liliana Norma Castro [a,b,*], Alicia Elena Rendina [c], Maria Julia Orgeira [a,d]

[a] Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Ciencias Geológicas-IGEBA (Instituto de Geociencias Básicas, Aplicadas y Ambientales de Buenos Aires), Ciudad Universitaria, Pabellón II, C1428EHA, Buenos Aires, Argentina
[b] Universidad de Buenos Aires, Facultad de Agronomía, Departamento de Ingeniería Agrícola y Uso de la Tierra, Av. San Martín 4453, C1417DSE, Buenos Aires, Argentina
[c] Universidad de Buenos Aires, Facultad de Agronomía, Departamento de Recursos Naturales y Ambiente, Cátedra de Química Analítica, Av. San Martín 4453, C1417DSE, Buenos Aires, Argentina
[d] Consejo Nacional de Investigaciones Científicas y Técnicas de Argentina, CONICET, Argentina

HIGHLIGHTS

- Regional lithogenic metals backgrounds for evaluating heavy metal geo-accumulation index.
- Pristine pampean loess revealed similar results compared to residual fraction metal concentrations
- World average shale is not adequated for applying in the case of Riachuelo-Matanza Basin
- Pristine pampean loess is less time-consuming, more economical, and an adequate method to verify the contamination level in the area of influence.

GRAPHICAL ABSTRACT



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ABSTRACT

Contamination assessment in riverbed sediments depends on the accurate determination of the background values. The aim of this study is to assess the degree of contamination and to evaluate the most adequate background for the determination of anthropogenic contamination in Cd, Cr, Cu, Ni, Pb and Zn in bed sediments of the Pampean area river basin (Matanza-Riachuelo River and tributary streams), Argentina. The geo-accumulation index (Igeo) values were calculated using selected lithogenic backgrounds (loess, loessoid sediments and paleosoils), the metal concentrations in the residual fraction (F4) in riverbed sediments and a global average shale often applied in the estimation of toxic metal Igeo. The IgeoF4, IgeoLZB and most of the others Igeos, indicated that in land areas used mainly for agriculture and cattle grazing, the superficial sediments were uncontaminated with Cd, Cr, Cu and Zn, and slightly contaminated with Ni and Pb. Conversely, in those areas dedicated to urban and industrial use, the metal contamination was greater. Overall, the relatively significant anthropogenic contamination of Cr > Pb ≥ Cu > Zn > Ni > Cd in the Riachuelo River area was associated with metallurgic activities, tanning and industrial waste. The comparative analysis of different values suggested that Buenos Aires' "pristine" loess could be recommended to evaluate the Igeo index of riverbed sediments in the Pampean area. To enhance the use of the selected background, the normalized enrichment factor using Al. In this study case, the Igeo and the EF using LZB background display the same trend, showing the greatest degree of contamination, as would be expected, in Riachuelo samples (RIA 1 and RIA 2) located in the urban/industrial area.

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* Corresponding author at: Universidad de Buenos Aires, Facultad de Ciencias Exactas y Naturales, Departamento de Ciencias Geológicas-IGEBA (Instituto de Geociencias Básicas, Aplicadas y Ambientales de Buenos Aires), Ciudad Universitaria, Pabellón II, C1428EHA, Buenos Aires, Argentina.
E-mail address: lil@gl.fcen.uba.ar (L.N. Castro).

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1. Introduction

Both industrial activities and urbanization can lead to high levels of contamination and pollution of water bodies. Bed sediments represent the main sink for toxic metals, with subsequent potential toxicity and risks to aquatic ecosystems and human health (Wan et al., 2016). Toxic Metals (TMs) pollution is currently of major environmental concern.

The Matanza-Riachuelo River in the Pampean region, Argentina, is one of the most polluted rivers in Latin America (Olson et al., 1998; Rendina, 2015). This river is the main collector of a 2300 km^2 basin, and drains directly into the River Plate, a huge binational estuary, which is the main source of drinking water for the city of Buenos Aires and its suburbs (Magdaleno et al., 2008; Rendina, 2015). Urban runoff, waste leachates, and communal and industrial wastewater effluents transport contaminants that are dumped into the river or its tributaries. In view of this situation, the evaluation of the environmental impact resulting from anthropogenic activities is high priority. However, very few studies (Rendida and Iorio, 2012) investigate the background level of metals in these sedimentary environments. The Matanza-Riachuelo Basin is formed in Pampean and Postpampean sediments after Frenguelli (1957) and Fidalgo et al. (1975), and currently covers the Ensenada, Buenos Aires (Riggi et al., 1986) and the Rio Lujan Formations (Fidalgo et al., 1973). These formations are composed of loess and loessoid sediments (reworked loess). Loess and loessoids sediments cover a wide Pampean area in Argentina, particularly in Buenos Aires Province. The Pampean loess is considered to be the most representative of South American Eolian sediments of the late Pleistocene and Holocene ages. Its genesis and evolution have been related to the last glacial events in Patagonia (Gallet et al., 1998).

It is well known that many approaches have been applied to assess the grade of sediment contamination and to understand the natural and anthropogenic inputs in aquatic sediments. The most common is the geo-accumulation index (Igeo), introduced by Müller (1969). The Igeo is used to assess toxic metal contamination of fluvial, estuarine, and marine sediments by making comparisons with the background level of natural fluctuations, including a very low anthropogenic input. These values are associated with a qualitative scale of contamination (Farkas et al., 2007). Samples may be classified as uncontaminated (Igeo ≤ 0, Class 0), uncontaminated to moderately contaminated (0≤Igeo≤1, Class 1), moderately contaminated (1 ≤ Igeo ≤ 2, Class 3), moderate to strongly contaminated (2 ≤ Igeo ≤ 3, Class 4), strongly contaminated (3 ≤ Igeo ≤ 4, Class 5), strongly to extremely contaminated (4 ≤ Igeo ≤ 5, Class 5), and extremely contaminated (Igeo ≥ 5, Class 6). There are various criteria for estimating the background concentration of metals in sediments:

a. Using an average elementary composition of the earth's crust. However, there are certain objections to the use of these values. Reimann and de Caritat (2005) considered that normalized with this global average might lead to errors due to the variable composition of natural rock.
b. Using an average shale composition unaffected by human activities as global reference. The most common average shale used is that calculated by Turekian and Wedepohl (1961). Müller (1969) used these values for developing the geo-accumulation index (Igeo).
c. Using element concentrations from presumably local uncontaminated sediments or using the metals present in the residual fraction as local baseline data for the assessment the anthropogenic contamination (Sharmin et al., 2010). The toxic metals concentration in the residual fraction (mainly primary and secondary minerals) is estimated by applying sequential extraction procedures (SEP). Conceptually, the solid material can be divided into specific fractions, which can be extracted selectively using appropriate reagents. According to the SEP protocol designed by Tessier et al. (1979), the metals present in the residual fraction are used as baseline data to assess the degree of contamination of soil and sediments. The strong association between metals and the residual fraction of uncontaminated soils can be used as an indicator of anthropogenic enrichment (Zakir et al., 2008). However, the background estimation of a metal base concentration in the residual fraction is time-consuming and SEP are not procedures routinely used in the laboratory.

The aim of this paper is to evaluate the degree of contamination and to evaluate the most adequate background to determine anthropogenic Cd, Cr, Cu, Ni, Pb and Zn contamination in bed sediments of the Pampean area river basin (Matanza-Riachuelo River and tributary streams), Argentina (Fig. 1). This includes use of loess, loessoid sediments (reworked loess) and paleosoils, which are contrasted with other commonly used backgrounds. After determining the geo-accumulation index (Igeo), the normalized enrichment factor using Al (EF) is calculated to enhance the effectiveness of the chosen background.

2. Geological framework

The Matanza-Riachuelo river Basin in the Pampas region is a vast plain, covered by Quaternary aeolian sediments and partly reworked loessoid sediments by fluvial action. It covers more than 500,000 km^2 with a thickness of 40–50 m^2, located in the eastern and central regions of Argentina (between 32° and 38°S, and 58° and 63°W). The surface is flat to slightly undulating and reflects the wind deflation and loess accumulation during the late Cenozoic and Pleistocene (Zárate, 2003; Tofalo et al., 2011). A relatively homogeneous sedimentary succession representing the late Cenozoic continental record comprises clayey silt and sandy-loam colors volcaniclastic deposits, loess and loessoid sediments, (reworked loess linked to fluvial action, Teruggi, 1957). Loessoid sediments are much more abundant than primary loess (Zárate, 2003). This cycle began in the late Miocene (ca. 12–11 Ma), after the withdrawal of the Paranaense sea (Zárate, 2003). The Pampas region is the only Quaternary sedimentary basin in the Southern hemisphere. The composition of the loess deposits differs from those in China, Siberia, and the United States (Gallet et al., 1998). Local deposits are volcanic-pyroclastic, derived from the magmatic arc of the Andes, and the volcanic dust was deposited on the continental plains distally, on limnic environments and on the continental shelf. These deposits are divided in Pampean and post-Pampean.

The Late Pleistocene/Holocene loess deposition is associated with a multistage transport mechanism, involving fluvial and aeolian processes. Inferred westerly and southwesterly winds, as dominant carriers of the aeolian deposits, match the westerly paleo-wind simulations using climate models (Zárate, 2003).

3. Materials and Methods

3.1. Fluvial sediments sampling and metal concentration analysis

Bed sediments were sampled in eight sites in the Matanza-Riachuelo Basin (see Fig. 1). Three sites were in the Upper Basin (MO1, RO and MA1), three in the Middle Basin (CA, MO2 and MA2) and two in the Lower Basin (RIA1 and RIA2).

The land use in the upper basin is predominantly rural (cattle grazing, poultry and porcine production, and bovine feedlots) and agricultural, with some urban settlements. The middle basin is the periphery of a very industrialized and urban area. The lower basin is the most polluted area of Buenos Aires province due to industrial waste discharge.

The sampling of sediments was performed manually by pushing down into the bed sediment a PVC tube (50 cm long and 4 cm bore). Twelve core samples were collected from each of the eight sites. The upper sections (0–2 cm, the sections closest to the sediment-water interface) and the deepest sections of the cores (20–24 cm to 28–32 cm depth) were used in this study Fig. 1b). Sections from three cores were combined into each of four composite samples for each site and depth.

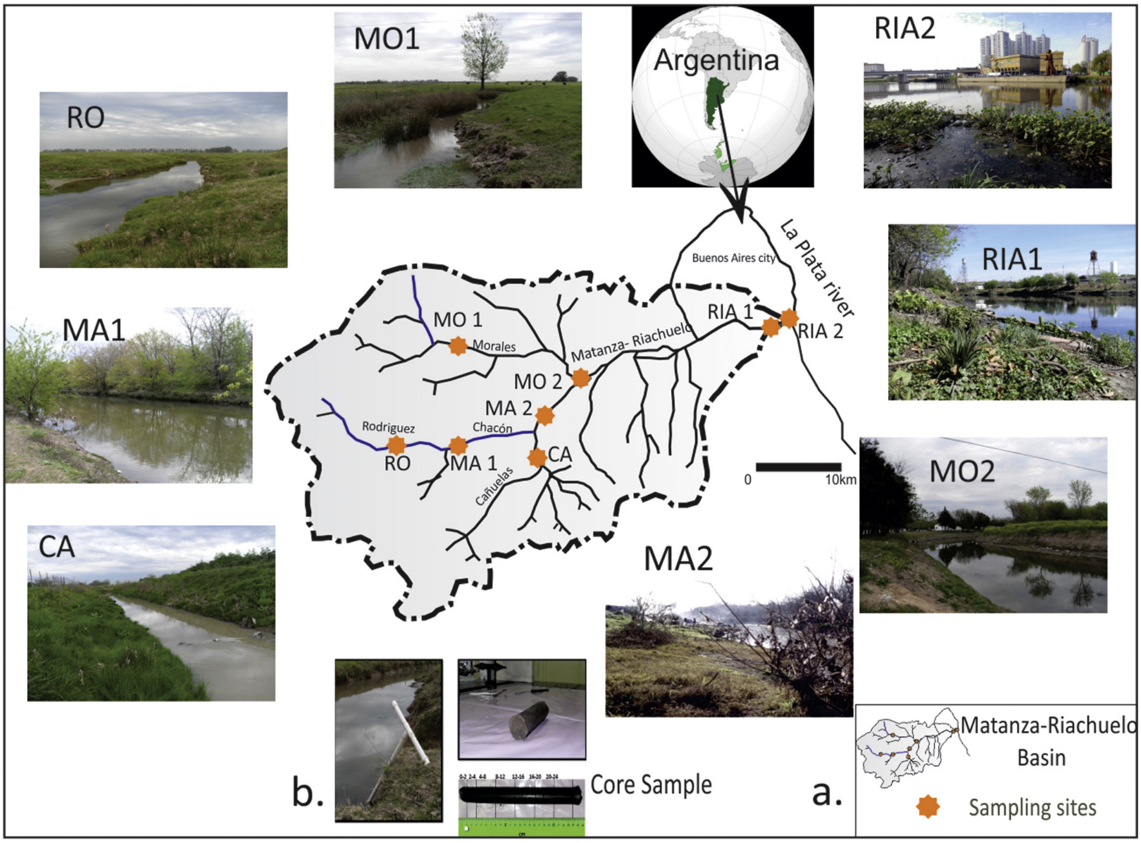

Fig. 1. Sampling sites.

To perform the SEP procedure modified from Tessier et al. (1979), sediment samples were weighed and dried at 103 °C for 24 h following the protocol of Rendina et al. (2001), Rendida and Iorio (2012) and Rendina (2015). The metals were separated into four fractions: F1 (exchangeable metals and metals associated with amorphous sulfides and carbonates), F2 (metals associated with oxides Fe/Mn), F3 (metals associated with organic matter) and F4 (residual fraction of metals). The total concentration of each metal in the sediment was calculated by adding the concentrations of that metal in F1, F2, F3, and F4, and this was calculated and analyzed in triplicate.

The average coefficient variations obtained (less than 8%) were considered adequate for the environmental analysis. A standard reference material CRM320 (river sediment) was used to verify the accuracy of metal determination in the sequential extraction analysis. The recovery rates for toxic metals in the standard reference material ranged from 89% to 106%. Metal concentrations in all the extracts were measured by atomic absorption spectrometry with air/acetylene flame (Perkin Elmer Model AAnalyst 200), using external reference standards prepared from stock solution of the metals (1,000 mg/kg, Merck). Sample analysis results were reported as dry weight of sediment.

Data was analyzed using one-way analysis of variance (ANOVA). The Bartlett´s test was used to verify the homogeneity of variances, and means were compared using the Tukey range test at the 0.05 level of significance. The Cd, Cr, Cu, Ni, Pb and Zn geoaccumulation index (Igeo) values were calculated as: $\text{Igeo} = \log_2 (\text{Cn}/1.5 \times \text{Bn})$. The total concentration of each metal (Cn) in the sediment was calculated by adding the concentrations of the metal in the F1, F2, F3, and F4 fraction of SEP used in the upper section of the core, and Bn was the geochemical background for the same metal. The factor 1.5 was introduced to correct possible variations of the background values linked to lithologic variations (Rendina, 2015). Values and Igeo classes were calculated using the baseline level (Bn) concentrations of metals in the residual fraction (F4) as reference, and were compared with the values obtained using the metal concentrations in loess, reworked loess, paleosoils and global reference shale of Turekian and Wedepohl (1961). To enhance the use of the selected background, the normalized enrichment factor using Al is calculated with the following equation:

$$\text{EF} = \text{M}_{\text{sample}} \times \text{Al}_{\text{loess}}/\text{M}_{\text{loess}} \times \text{Al}_{\text{sample}}$$

where M_{sample} and $\text{Al}_{\text{sample}}$ are the sediment sample concentrations of the heavy metal and Al, while M_{loess} and Al_{loess} are the concentrations in the selected background, following Simex and Helz (1981). The EF < 1 indicates no enrichment (Level I), EF < 3 is minor enrichment (Level II), EF = 3–5 is moderate enrichment (Level III), EF = 5–10, is moderately severe enrichment (Level IV), EF = 10–25 is severe enrichment (Level V), EF = 25–50 is very severe enrichment (Level VI) and EF > 50 is extremely severe enrichment (Level VII).

3.2. Selected samples for evaluating lithogenic regional backgrounds

Seven representative samples from outcrops of loess (LZB y LC), loessoids (reworked loess sediments WLT and WLC) and paleosoils (PsZ, PsT, PsC) from Corralito, Monte Ralo (Córdoba area), Zarate, Baradero and Tapalque (Buenos Aires area) were taken and assessed as selected regional lithogenic backgrounds (Fig. 2). The samples were air-dried, with approximately 15 g further ground with an agate mortar to obtain a homogenous powder of >100 μm grain. Metal concentrations (Cd, Cr, Cu, Ni, Pb and Zn) were analyzed by ICP-MS at the Argentine Geological Mining Survey (SEGEMAR), after wet mineralization with HNO_3-HClO_4-HF. An Igeo index for each material was calculated and assessed.

3.2.1. Corralito Loess and Monte Ralo Loess, Cordoba Province

The Corralito and Monte Ralo profiles (Fig. 2a and b) are located in the Pampean plain, Cordoba, at 32°11′S; 64 °11.13′W, and 31° 54′S and 64°10′W, respectively. The sediments in this area are windblown

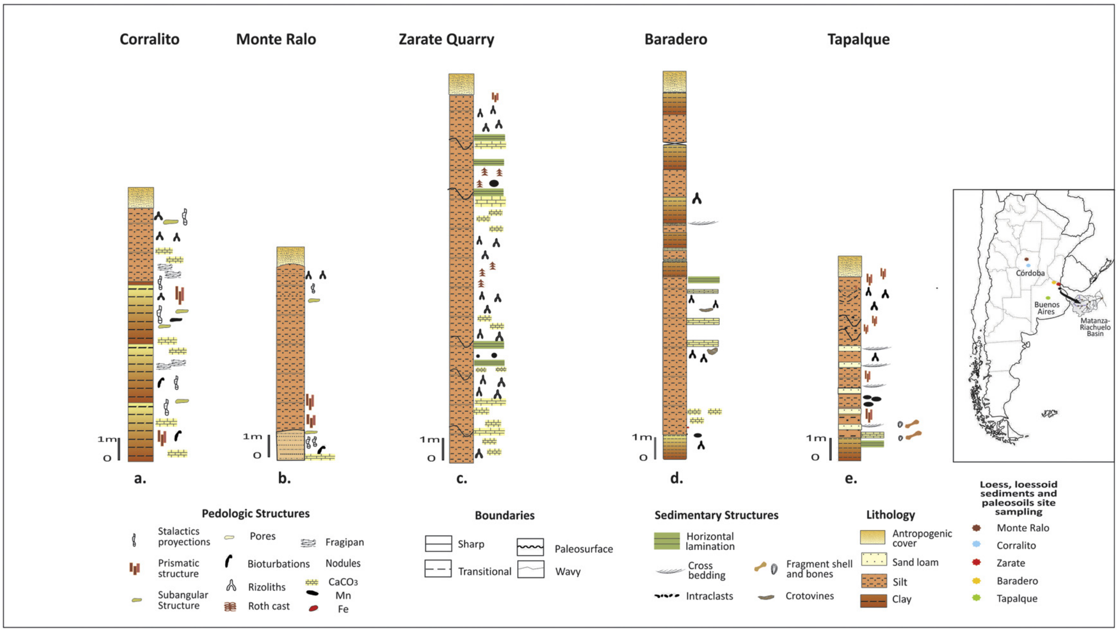

Fig. 2. Stratigraphic sections: Corralito (a), Monte Ralo (b), Cordoba Province, modified from Rouzaut and Orgeira (2016) and, Zarate Quarry (c) modified from Tofalo et al. (2011), Baradero (d) modified from Nabel et al. (1993), and Tapalque (e) modified from Orgeira et al. (2003), Buenos Aires province.

sediments (loess) which have been partially reworked by water; the estimated age for these sediments being Pleistocene–Late Holocene. In contrast with Monte Ralo's, Corralito's sediments do not show evidence of being fluvial reworked. Interdigitated paleosoils can be observed in both profiles (Fig. 2a and b); consequently, pedological features are present (Rouzaut and Orgeira, 2016). Mineralogically, the material contains abundant volcanic glass, quartz, K feldspar, illite, smectite and plagioclase, amongst other minerals.

3.2.2. Zarate Loess quarry

Samples were taken from a quarry located (Fig. 2c) near to the town of Zarate, Buenos Aires Province, (34°09′S, 59°04′W). The 9m thick sequence section of loess and paleosoils forming outcrops across a wide bank, dates from the late Pleistocene (Tofalo et al., 2011). The sequence includes loess sediments affected by strong pedogenesis, creating a complex and cyclic sedimentary-pedogenetic sequence. The mineralogical composition of sand and coarse silt fractions indicates an unequivocal volcano-pyroclastic provenance. Calcrete observed at various levels is related to phreatic layer oscillations.

3.2.3. Baradero Loess

Middle and Upper Pleistocene sediments were reported as part of the Pampean sediments (Fig. 2d) near Baradero town (59°30′W, 33°49′S, Buenos Aires Province, Nabel et al., 1993). The 15 m of profile is formed by sand and coarse silt fractions compose. The mineralogy, mainly quartz, feldspars, clays such as illite and smectite, and volcanic glass, indicates a volcano-pyroclastic source.

3.2.4. Tapalqué

The Arroyo Tapalque section (Fig. 2e) is 7 m thick and it is formed of four successive sedimentary units covered by modern soil (Orgeira et al., 2003). The profile of Postpampean sediments consists of polimictic material and medium grain-sized silt, with variable amounts of interlayered and very fine sand affected by pedoturbation. Irregular dusty calcite patches are also common. Glass fragments characteristic of a direct pyroclastic source, as well as minor from metamorphites, plutonites and sedimentites represent the main mineralogy. In general, the mineralogy of these post-Pampean formations resembles other loessic units (Orgeira et al., 2003).

4. Results

4.1. Sources of lithogenic regional backgrounds

The probable source areas of the Pampean loess are located in SW flood plains and fluvial fans of rivers which drain the Andean glaciers (Iriondo and Kröhling, 1995; Zárate, 2003, amongst others). For the Cordoba loess (LC), in particular, an additional source from Pampean Ranges and direct volcanic emissions from the west Andean sector is considered (Iriondo, 1997). Although aeolian transport from Patagonia is often used to explain the accumulation of the Pampean loess, there is another more complex hypothesis. Chemical and isotopic fingerprinting methods have led to the acceptance that Patagonian sediments can explain only part but not the entire range of compositions found in

Table 1
Metal concentrations in loess (L), loessoid sediments (WL) and paleosoils (PS) from various provenances and average shale (ASTW) of Turekian and Wedepohl (1961).

Sample	Type	Province	Location	Cd	Cr	Cu	Ni	Pb	Zn
LZB	Loess	Buenos Aires	Zarate-Baradero	1.5	53.1	32.2	16.1	28.8	88.2
LC	Loess	Córdoba	Monte Ralo-Corralito	1.3	49.0	28.0	14.9	18.6	94.4
WLT	Loessoids sed	Buenos Aires	Tapalqué	1.9	32.8	26.4	9.6	13.7	70.4
WLC	Loessoids sed	Córdoba	Monte Ralo-Corralito	1.5	53.0	31.4	17.0	19.5	116.1
PsZ	Paleosoil	Buenos Aires	Zarate	4.9	60.9	43.8	27.4	21.0	122.8
PsT	Paleosoil	Buenos Aires	Tapalqué	0.7	38.4	19.8	6.9	16.9	67.9
PsC	Paleosoil	Córdoba	Monte Ralo-Corralito	1.7	53.2	28.9	16.7	19.5	80.8
ASTW	*Global average shale* (Turekian and Wedepohl, 1961)			0.3	90	45	68	20	95

Table 2
Mean concentration (mg/kg DW) of total metals in upper section (0–2 cm, **Up**) and deepest section (**Dp**) of core sediments.

Site	Cd		Cr		Cu		Ni		Pb		Zn	
	Up	Dp	Up	Dp	Up	Dp	Up	Dp	Up	Dp	Up	Dp
MO 1	1.7	1.3	27.2	25.1	26.0	21.8	26.9	22.4	48.1	27.4	86.7	73.8
RO	1.9	1.3	26.5	24.9	28.1	21.8	28.7	25.3	46.3	34.4	79.9	67.9
MA 1	1.3	1.3	25.8	25.3	24.7	21.7	24.1	21.6	41.9	35.3	95.6	68.2
CA	2.3	1.6	33.7	28.3	29.6	22.0	26.6	24.0	64.0	31.8	94.6	72.2
MO 2	3.0	1.6	68.4	30.7	32.2	22.1	27.7	22.6	58.0	35.1	114	70.7
MA 2	4.9	1.4	51.3	32.2	37.9	22.7	25.1	26.7	130	34.2	261	77.0
RIA 1	3.5	1.7	2400	490	715	123	80.4	47.7	594	142	1528	616
RIA 2	2.9	2.3	1240	990	210	144	80.6	47.4	80.2	73.4	665	543

those archives. Based on rare earth elements (REEs) analyses, it is possible to single out four main source areas for Pampean loess: Patagonia, Southern Central West Argentina, Northern Central West Argentina and Puna (Gili and Gaiero, 2014). Despite these differences over the source areas, everyone agrees that W and SW winds were responsible for transporting the material.

4.2. Variation of metal concentrations in loess, loessoids and paleosoils

While determined metal concentrations in loess samples show no substantial differences, loessoids sediments and paleosoils exhibit major variations (Table 1). Additional consideration must be given to pedogenic processes. The paleosoils (PsZ, PsT and PsC) show a slightly higher concentration of Cu (43.8 mg kg^{-1}), Ni and Cr (27.4 and 60.9 mg kg^{-}1), respectively compared to their parental material (LZB and LC), particularly in Zarate. This behavior is similar to that in the Cordoba area (LC versus PsC). The results could be explained by different paleoclimate in both areas. Zarate quarry has had a warm to subtropical wet climate which allowed extensive pedocomplex development (Tofalo et al., 2011); while in Cordoba the paleosoil development was more limited due to a drier climate. So, areas with higher precipitation had reinforced lixiviation processes and consequently, concentration of toxic metals must be expected. Higher concentrations of Cd, Cr, Ni, Pb and Zn were related to clay content (Lavado et al., 1998; Lavado et al., 2004). Therefore, for example, the lower Cu, Cd, Ni content in Tapalque (WLT) can be attributed to higher soil porosity (<clay content), which allows higher mobility of this elements. These metal concentrations not only reflect climatic variations but also multi-recycled processes.

Chromium, Ni and Cu concentrations in loess and loessoid sediments (Table 1) are lower than the average shale (ASTW) of Turekian and Wedepohl (1961). This can be attributed to the fact that these elements cannot withstand prolonged aeolian transport, and therefore they are not concentrated because they do not travel a long distance from the source. Nevertheless, the low concentration of Ni and Cr (LZB and LC samples), should be attributed to a mesosilicic Andean rocks source, with scarce occurrence of basic rocks. Even Gallet et al. (1998) showed lower Cr, Cu and Ni values for loess and reworked loess in Pampean and Postpampean sediments compared to those in this paper.

Cadmium shows a great variability between the various local sites analyzed (between 0.7 and 4.9 mg kg^{-1}), and higher than ASWT (0.3 mg kg^{-1}). This could be related to the capacity of the loess clay component to adsorb cadmium (Yang et al., 2012). Particularly, a PsZ sample could reflect a greater clay and organic matter content in soil, which favors the increase of Cd adsorption.

4.3. Total concentration and residual fraction of metals

Total metal concentrations in bed sediments for both upper and deepest sections for each site are shown in Table 2. In most sites, a reduction is observed in the total metal concentrations in the deepest section of the sediment. On the other hand, RIA1 and RIA2 sites (Lower Basin) show higher content of Cr, Cu, Ni, Pb and Zn in the deepest section than the other sites, indicating a large accumulation of these metals in the profile.

The concentrations of six metals in F4 do not show substantial differences between the upper and deepest section for all sites (Table 3). However, it appears that for RIA1 and RIA2 (Lower Basin), Cd, Cu and Zn concentrations in F4 are markedly higher than in the Upper and Middle basin. This result suggests that in areas of high contamination the residual fraction may not be recommended as base level. Therefore, the mean concentrations of metals in F4, in the deepest section of the sediments from the Upper Basin sites (MO1, RO and MA1), were used to calculate the Igeo.

5. Discussion

The Igeo is used as a criterion to assess the anthropogenic contamination of metals in bed sediments of the study area. In this paper, the total toxic metal concentrations in superficial sediments (Cn) and mean metal concentrations in the residual fraction of SEP from the deepest section of the corer (Bn) are interpreted. In general, there is an increase in metal enrichment downstream, from the Upper Basin (mainly rural area) to Riachuelo (RIA1-urban and industrial area). At the same time, at the Riachuelo mouth (RIA2), a significant decrease in Igeo F4 occurs (Bn: Cu, Cr, Pb and Zn concentration in F4 is shown).

Based on the Cd, Cu, Cr, Ni and Zn Igeos (Table 4), the Upper basin (MO1, RO and MA1) is classified between "uncontaminated" (Igeo < 0, Class 0) and "uncontaminated-moderately contaminated" (0 < Igeo < 1, Class 1). The highest IgeoF4 values in Pb, amongst other metals, are shown in rural (MO1, MA1 and RO sites) as well as in peri-urban environment (CA, MO2 and MA2 sites). The Pb atmospheric pathway is probably one of the main reasons for Pb spread into rural environments. Lead may be found in small particles and aerosols (Komárek et al., 2008), which might fall on the earth's surface very far from their emission source. Also, brick manufacturing is widely present in both rural

Table 3
Mean concentration (mg/kg DW) of metals in F4 in upper section (0–2 cm, **Up**) and deepest section (**Dp**) of core sediments.

Site	Cd		Cr		Cu		Ni		Pb		Zn	
	Upper	Deep	Upper	Deep	Upper	Deep	Upper	Deep	Upper	Deep	Upper	Deep
MO 1	1.3	1.3	24.3	24.1	18.4	19.3	20.0	19.3	17.5	16.8	46.4	61.8
RO	1.2	1.3	23.6	24.0	19.5	18.5	21.4	19.0	24.0	24.3	55.5	54.3
MA 1	1.3	1.3	24.0	23.7	18.6	19.6	18.0	18.2	22.5	23.3	54.7	55.2
Mean upper basin	1.3	1.3	24.0	23.9	18.8	19.1	19.8	18.8	21.3	21.5	52.2	57.1
CA	1.3	1.5	24.0	24.0	19.9	19.2	20.0	19.7	23.4	18.6	63.6	53.5
MO 2	1.6	1.5	24.7	24.2	21.0	19.5	20.0	18.3	24.9	22.7	62.8	57.1
MA 2	1.3	1.3	25.5	24.6	19.5	20.1	22.0	20.0	22.5	20.5	62.8	62.8
Mean middle basin	1.4	1.4	24.7	24.3	20.1	19.6	20.7	19.3	23.6	20.6	63.1	57.8
RIA 1	1.2	1.3	53.7	53.9	32.6	34.2	26.0	25.8	23.4	23.1	72.0	62.8
RIA 2	1.3	1.3	54.9	53.7	32.8	32.9	26.1	24.8	25.2	22.9	72.0	62.8
Mean low basin	1.3	1.3	54.3	53.8	32.7	33.6	26.1	25.3	24.3	23.0	72.0	62.8

and peri-urban areas of the Matanza-Riachuelo basin. Ashes generated in the combustion of coal, oils, tires and other wastes are a potential source of metals, dioxins and other pollutants generally released into the atmosphere. In the Lower Basin, RIA1 exhibits the highest IgeoF4 for Cr (6.03), Cu (4.6), Pb (4.3) and Zn (4.1); therefore, sediments were categorized as strongly contaminated with Cu, Pb and Zn (Class 5), and extremely contaminated with Cr (Class 6).

On the other hand, the effect of reference material in the assessment of metal contamination shows interesting results. The geoaccumulation index (Igeo) values, obtained using the lithogenic background (metal concentrations in loess, loessoids sediments and paleosoils) from different localities, the residual fraction (F4) of each metal and their comparison with ASTW, are shown in Fig. 3a, b, c, d, e and f.

The Cd-Igeo (Fig. 3a) shows similar results ($p > 0.05$) for F4, LZB and LC (loess), WLT and WLC (loessoids sediments) and PsC (Cordoba paleosoil). Instead, the Cd-Igeo calculated on Buenos Aires paleosoils (PsZ and PsT) and ASTW showed significant differences ($p < 0.05$) compared with F4-Cd-Igeo. In particular, the use of ASTW overestimated (2 classes) the level of sediment pollution in all sites, due to Cd low concentration in ASTW (0.3 mg kg^{-1}) compared to Cd-F4 (1.3 mg kg^{-1}). Abrahim and Parker (2008) quantified the degree of contamination in the Tamaki estuary (New Zealand) using various methods for calculating

Table 4

Sediment geoaccumulation index (Igeo): Residual (F4); Loess Zarate-Baradero (LZB); Loess Corralito–Monte Ralo, Córdoba (LC); Loessoid sediments -reworked loess Tapalque (WLT); Loessoid sediments -reworked loess Cordoba (WLC); paleosoil Zarate (PsZ); paleosoils Tapalque (PsT); paleosoils of Cordoba (PsCba) and ASTW: average shale Turekian and Wedepohl (1961). Geo-accumulation index classification: uncontaminated (**U:** geo ≤ 0, Class 0), uncontaminated to moderately contaminated (**U-MC:** 0 ≤ Igeo ≤ 1, Class 1), moderately contaminated (**MC**: 1 ≤ Igeo ≤ 2, Class 3), moderate to strongly contaminated (**M-SC**: 2 ≤ Igeo ≤ 3, Class 4), strongly contaminated (**SC:** 3 ≤ Igeo ≤ 4, Class 5), strongly to extremely contaminated (**SC-E**: 4 ≤ Igeo ≤ 5, Class 5), and extremely contaminated (**EC**: Igeo ≥ 5, Class 6).

Site	F4	LZB	LC	WLT	WLC	PsZ	PsT	PsC	ASTW
Cd									
MO 1	U	U	U	U	U	U	U-MC	U	MC
RO	U	U	U	U	U	U	U-MC	U	MC-SC
MA 1	U	U	U	U	U	U	U-MC	U	MC
CA	U-MC	U-MC	U-MC	U	U	U	MC	U	MC-SC
MO 2	U-MC	U-MC	U-MC	U-MC	U-MC	U	MC	U-MC	MC-SC
MA 2	MC	MC	MC	U-MC	MC	U	MC-SC	U-MC	SC
RIA 1	U-MC	U-MC	U-MC	U-MC	U-MC	U	MC	U-MC	SC
RIA 2	U-MC	U-MC	U-MC	U-MC	U-MC	U	MC	U-MC	MC-SC
Cr									
MO 1	U	U	U	U	U	U	U	U	U
RO	U	U	U	U	U	U	U	U	U
MA 1	U	U	U	U	U	U	U	U	U
CA	U	U	U	U	U	U	U	U	U
MO 2	U	U	U	U	U	U	U	U	U
MA 2	U-MC	U	U	U-MC	U	U	U	U	U
RIA 1	EC	SC-EC	SC-EC	EC	SC-EC	SC-EC	EC	SC-EC	SC-EC
RIA 2	SC-EC	SC	SC-EC	SC-EC	SC	SC	SC-EC	SC	SC
Cu									
MO 1	U	U	U	U	U	U	U	SC	U
RO	U	U	U	U	U	U	U	SC	U
MA 1	U	U	U	U	U	U	U	SC	U
CA	U	U	U	U	U	U	U	SC	U
MO 2	U-MC	U	U	U	U	U	U	SC	U
MA 2	U-MC	U	U	U	U	U	U-MC	SC	U
RIA 1	SC	SC	SC-EC	SC-EC	SC	SC	SC-EC	EC	SC
RIA 2	MC	MC	MC	MC	MC	MC	MC	EC	MC
Ni									
MO 1	U-MC	U-MC	U	U-MC	U-MC	U-MC	MC	U-MC	U-MC
RO	U	U-MC	U	U-MC	U-MC	U-MC	MC	U-MC	U-MC
MA 1	U	U	U	U-MC	U-MC	U-MC	MC	U	U-MC
CA	U-MC	U-MC	U-MC	U-MC	U-MC	U-MC	MC	U-MC	MC
MO 2	U	U-MC	U-MC	U-MC	U-MC	U-MC	MC	U-MC	U-MC
MA 2	U-MC	U-MC	MC	U-MC	MC-EC	MC	MC	U	MC
RIA 1	MC	MC	SC	MC-EC	SC-EC	SC	MC-EC	MC	SC-EC
RIA 2	MC	MC	U-MC	MC-EC	MC	U	MC-EC	MC	MC
Pb									
MO 1	U-MC	U-MC	U	U-MC	U-MC	U-MC	MC	U-MC	U-MC
RO	U-MC	U-MC	U	U-MC	U-MC	U-MC	MC	U-MC	U-MC
MA 1	U-MC	U-MC	U	U-MC	U-MC	U-MC	MC	U-MC	U-MC
CA	MC	MC	U-MC	MC	U-MC	U-MC	MC-SC	MC	MC
MO 2	U-MC	U-MC	U-MC	MC	U-MC	U-MC	MC-SC	U-MC	U-MC
MA 2	MC-SC	MC-SC	MC	MC-SC	MC-SC	MC	SC	MC-SC	MC-SC
RIA 1	SC-EC	SC-EC	SC	SC-EC	SC-EC	SC	EC	SC-EC	SC-EC
RIA 2	MC	MC	U-MC	MC	MC	U-MC	MC-SC	MC	MC
Zn									
MO 1	U	U	U	U	U	U	U	U	U
RO	U	U	U	U	U	U	U	U	U
MA 1	U	U	U	U	U	U	U	U	U
CA	U	U	U	U	U	U	U	U	U
MO 2	U-MC	U	U	U-MC	U	U	U-MC	U-MC	U
MA 2	MC	U-MC	U-MC	MC	U-MC	U-MC	MC	MC	U-MC
RIA 1	SC-EC	SC	SC	SC	SC	MC-SC	SC	SC	SC
RIA 2	MC-SC	MC-SC	MC-SC	MC-SC	MC	MC	MC-SC	MC-SC	MC-SC

Fig. 3. Comparison of Sediment geoacumulation values (Igeo) Residual (F4); Loess Zarate-Baradero (LZB); Loess Corralito–Monte Ralo, Córdoba (LC); Loessoid sediments -reworked loess Tapalque (WLT); Loessoid sediments -reworked loess Cordoba (WLC); paleosoil Zarate (PsZ); paleosoils Tapalque (PsT); paleosoils of Cordoba (PsCba) and ASTW: average shale Turekian and Wedepohl (1961, see also Table 4).

toxic metal enrichment. They observed that the use of ASTW as reference gives higher concentration values compared to those in the deeper section. Conversely, Irabien and Yusta (1999) showed that the ASTW underestimated the metals enrichment of the sediments in the Bay of Santander (Spain), suggesting that the use of local metals background levels is a more suitable methodology for calculating metals enrichment. On the other hand, Rubio et al. (2000) concluded that the interpretation of the pollution status in Ria of Vigo (Spain) is more dependent on the background values than on the index or contamination factor used. Nowrouzi and Pourkhabbaz (2014) prefer to use grain fraction <0.063 mm instead of ASTW to calculate metal contamination in the sediments of the Hara Biosphere Reserve, Iran.

Cr-Igeo (Fig. 3b) values obtained by all the Pampean region lithogenic backgrounds (loess, loessoids sediments and paleosoils) were similar ($p > 0.05$) to those obtained by F4. Instead, the Cr-Igeo values using ASTW were significantly lower ($p < 0.05$). However, for each site, the level of Cr contamination was similar for all materials used (Table 3). Cu-Igeo values (Fig. 3c) based on lithogenic backgrounds were analogous to Cu-IgeoF4 ($p > 0.05$). PsC showed an exception, probably attributable to Cu anomalous behavior linked to pedogenic process. Ni-Igeo values (Fig. 3d) calculated with the Buenos Aires loess (LZ) were similar to Ni-IgeoF4 in all sample sites. In general, the rest of the materials overestimated the Ni enrichment at most sites. The *Pb*-Igeo (Fig. 3e) calculated on LZB (loess), WLT and WLC (loessoids sediments), PsC and ASTW, in all sites, showed insignificant differences ($p > 0.05$) compared to *Pb*-Igeo F4. In addition, with the exception of PsT, the Pb contamination level is similar for all background materials used. Zn-Igeo (Fig. 3f) calculated LZ and LC (loess), WT (loessoid sediments) and paleosoil, and ASTW give similar values ($p > 0.05$) compare to Zn-IgeoF4. For all Zn backgrounds, the level for the agricultural sites (MA1, MO1 and RO) and CA is Class 0 (uncontaminated); in contrast, the rest of the sites in the Medium and Lower Basin present slight differences in the allocated class, depending on the backgrounds used.

Based on all the toxic metals analyzed (Cd, Cr, Cu, Ni, Pb and Zn) and the Igeo comparisons between residual fraction (F4) and natural backgrounds, it is noticeable that the greatest similarities occur between F4 and "pristine loess", and in particular, with Buenos Aires's loess (LZB). It can be observed that almost all toxic metals, in all land sites used, fall within the same geoaccumulation class. On the other hand, ASTW is not recommended to calculate Cd-Igeo, since in most sites, it differed by two classes of geoaccumulation level compared to the other backgrounds. Also, PsT (paleosoil) shows substantially higher Cd, Ni and Pb concentrations than F4 (Fig. 3b, d, e), so it overestimates the contamination level of these metals, and therefore it is not recommended as

Table 5
Normalized enrichment factor, using Al. The $EF < 1$ indicates no enrichment (**Level I**), $EF<3$ is minor enrichment (**Level II**), $EF = 3–5$ is moderate enrichment (**Level III**), $EF = 5–10$, is moderately severe enrichment (**Level IV**), $EF=10-25$ is severe enrichment (**Level V**), $EF=25-50$ is very severe enrichment (**Level VI**) and $EF>50$ is extremely severe enrichment (**Level VII**).

Site	Use of the land	Cd	Cr	Cu	Ni	Pb	Zn
MO 1	Rural	I	I	I	II	II	I
RO	Rural	II	I	I	II	II	I
MA 1	Rural	I	I	I	II	II	I
CA	Peri-urban	II	I	I	II	III	I
MO 2	Peri-urban/ industrial	II	I	I	II	II	II
MA 2	Peri-urban/industrial	II	I	I	II	IV	II
RIA 1	Urban/industrial	II	VI	V	III	VI	V
RIA 2	urban/industrial	II	V	IV	III	III	IV

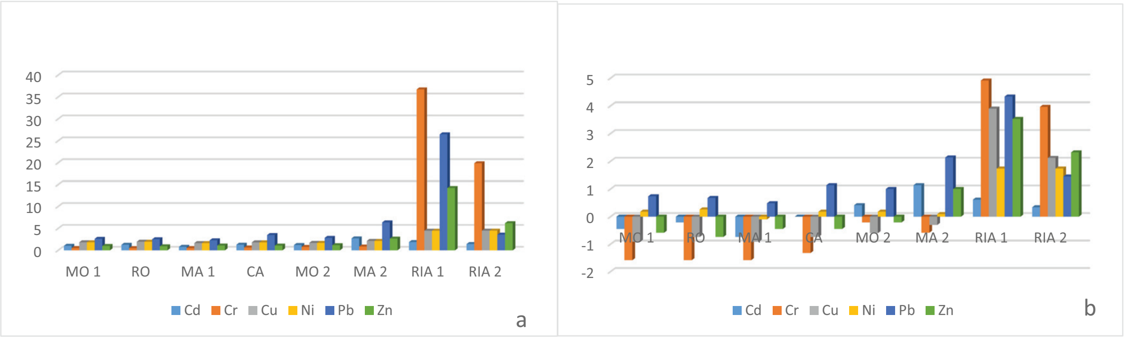

Fig. 4. a. Normalized enrichment factor, using Al, and b. sediment geoaccumulation values (Igeo) using Loess Zarate-Baradero background (LZB) for Cd, Cr, Cu, Ni, Pb and Zn.

reference background material to estimate the contamination of this Pampean Basin.

Finally, the pristine loess used as lithogenic background, supports previous results using the residual fraction of sediments. The appropriate background level choice is crucial for the interpretation of metal pollution in the riverbed sediments, especially in one of the most polluted rivers in Latin America.

Additionally, the normalized EF using LZB background indicates that in rural areas the EF levels for all the elements varies from no enrichment (Level I) to minor enrichment (Level II). In peri-urban and peri-urban/industrial areas, EFs remain at the same levels except for Pb that reaches moderate to moderately severe enrichment (Level III and IV). In urban/industrial areas, Cd $_{EF}$ displays minor enrichment (Level II), while other elements (Cr, Cu, Ni, Pb and Zn) $_{EF}$ vary between moderate and very severe enrichment (Level III to VI, Table 5).

In this study case, the Igeo and the EF using LZB background display the same trend, showing the greatest degree of contamination, as would be expected, in Riachuelo samples (RIA 1 and RIA 2) located in the urban/industrial area (Fig. 4a and b).

Furthermore, the use of the global average shale as reference material was not appropriate in this case, especially in Cd concentrations backgrounds, where all results were overestimated compared with regional backgrounds.

6. Conclusions

According to the geoaccumulation index (Igeo) classification, the toxic metals contamination of the bed sediment in the Pampean region (Matanza-Riachuelo River Basin) indicates that in areas where the land is used mainly for agriculture and cattle grazing, the surficial sediments should be considered uncontaminated with Cd, Cr and Cu, and slightly contaminated with Ni and Pb in most sites. Conversely, in those areas where the land use is both urban and industrial, the metal contamination levels were greater. Historically, the Riachuelo river has been affected by urban and industrial development, carried out without proper land use planning. Overall, the relative significance of antrophogenic contamination in the Riachuelo river area, particularly in RIA 1, showed the following order: Cr > Pb ≥ Cu > Zn > Ni > Cd. The Riachuelo sediments should be considered as strongly to extremity contaminated with Cr, moderately to extremely contaminated with Pb, moderate to strongly contaminated with Zn and Cu, moderately contaminated with Ni and uncontaminated to moderately contaminated with Cd. The high contamination in the Riachuelo river sediments is associated with industrial waste, and metallurgic and tanning activities.

The comparative analysis in the Matanza-Riachuelo Basin of Igeo values based on average shale (Turekian and Wedepohl, 1961), residual fraction and selected natural geochemical backgrounds (lithogenic backgrounds) suggests that "pristine" loess (LZB) coming from the Buenos Aires area can be recommended to evaluate the contamination index (Igeo) of Cd, Cr, Cu, Ni, Pb and Zn in bed sediments. The Igeo and EF using LZB background present the same trend, showing the degree of contamination that would be expected in Riachuelo samples (RIA 1 and RIA 2). The possible use of background metals concentrations of "pristine" sediments of an area, such as loess in our study case, is less time-consuming, more economical, and an adequate method to verify the contamination level in the area of influence. Furthermore, the use of global average shale as reference material was not appropriate in this case, especially in Cd concentrations backgrounds, where all results were overestimated compared with regional backgrounds. The appropriate background level choice is crucial for the interpretation of metal pollution in the riverbed sediments.

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