Research Articles

Copper, Lead and Zinc Distribution in Soils and Sediments of the South-Western Coast of the Río de la Plata Estuary

María C. Camilión[1], Marcelo J. Manassero[2], Martín A. Hurtado[1] and Alicia E. Ronco[3*]

[1] CISAUA-UNLP: Centro de Investigaciones de Suelos y Aguas de Uso Agropecuario, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Calle 3, Nº 584, 1900-La Plata, Argentina
[2] CIG-UNLP-CONICET: Centro de Investigaciones Geológicas, Facultad de Ciencias Naturales y Museo, Universidad Nacional de La Plata, Calle 1, Nº 644, 1900-La Plata, Argentina
[3] CIMA-UNLP-CONICET: Centro de Investigaciones del Medio Ambiente, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, Calle 47, esq 115, 1900-La Plata, Argentina

* **Corresponding author** (cima@dalton.quimica.unlp.edu.ar)

DOI: dx.doi.org/10.1065/jss2003.04.073

Abstract

Background, Aim and Scope. The compositional study of suspended matter in water from rivers of different latitudes and climates has revealed that the fine fraction reflects both substrate lithology from source areas or topsoil composition along the course. Metal distribution patterns are also strongly related to the clay mineral fate in fluvial aquatic systems. For the particular case of the coastal area of the Río de la Plata estuary in South America, previous studies have, on the one hand, focused on the analysis of distribution patterns of heavy metals in bottom river sediments and, on the other hand, on the assessment of metal contents in topsoils. The present study was conducted to evaluate the Cu, Pb and Zn distribution in soils and sediments from four drainage basins crossing two differentiated geomorphologic units composed of unconsolidated materials and to understand the metal behaviour.

Methods. Data used included the existent, self-produced soil and sediment data sets (grain size, organic matter and Cu, Pb and Zn contents from 124 samples). Analyses were performed by using standardised methods: grain size analysis by sieving and settling; organic matter content based on the reduction of dichromate ion followed by titration; metal content by atomic absorption spectrophotometry following acid digestion.

Results and Discussion. The average (% w/w) clay and organic matter content were 45.9 ± 17.1 and 1.5 ± 1.7 for sediments and 32.0 ± 19.8, and 7.5 ± 7.6 for soils, respectively. The raw mean metal concentrations ($mg \cdot kg^{-1}$ dry weight) for sediments and soils were: Cu: 28.02 ± 27.28, 32.08 ± 21.64; Pb: 32.08 ± 46.94, 68.44 ± 69.25 and Zn: 83.09 ± 150.33, 118.22 ± 74.20, respectively. A good correlation for each clay-normalised metal concentration was found between soil and sediments using regression analysis considering average data for each basin sampling site ($r > 0.89$, $p < 0.05$). A comparison between metal concentration levels taking into account geomorphologic units by a *t* independent sample test showed significant differences for the normalised soil-sediment metal data ($p < 0.001$), responding to differences in grain size, clay mineralogy, organic matter and neoformed Fe-Mn oxide composition.

Conclusion, Recommendation and Outlook. A clear parenthood between the topsoils and the bottom sediments in the study area was found. The Argiudolls from the inner zone are frequently affected by rainwater erosion, which washes the fine materials with sorbed metals and carries them to the streams. These watercourses reach the flat coastal plain, where soil flooding and bottom sediment depositional processes predominate. Here, both soils and bottom sediments are enriched in clay, organic matter and metals. The topography and lithology, under the environmental conditions of a temperate and humid climate control the fate of metals within these small basins. The influence of the physical media on the distribution and fate of pollutants should not be minimised in the understanding of the governing processes from natural systems.

Keywords: Argiudolls; drainage basins; Epiaquerts; heavy metals; Río de la Plata coast; run-off; soils; stream bottom sediments; topography

Introduction

Human activities are increasing the circulation of toxic metals through soils, waters and air (Nriagu and Pacyma 1988). As these environmental compartments act as inexhaustible sources of the biosphere (Tölgyessy 1993), their qualitative or quantitative changes at a global and regional scale must be studied to prevent long-term impacts on living organisms or human health. Sediments are important materials for retaining heavy elements in rivers, lakes and estuaries within the hydrological cycle (Fergusson 1991), and the finer mineral fractions and suspended matter from river sediments, unconsolidated surface sediments and soils of a given region are frequently similar in their composition (Chamley 1997). Published data have shown that clay minerals from the topsoils seem to determine the geochemical composition of the suspended matter in river basins from different latitudes and climates (Konta 1990). Metal distribution patterns are also strongly related to the clay mineral fate in surficial terrigenous and fluvial systems (Tarvenier 1995) and to hydrochemical properties (Kondhauser et al. 1994).

Only a few studies have been found in the literature in relation to the heavy metal distribution in soils and sediments from the humid Pampa-plains of Argentina. Previous research has focused on the analysis of heavy metals in bottom river sediments (Manassero et al. 1998, Ronco et al. 2001). Other studies are aimed at assessing the metal content in surface and ground water, soils and air particulate matter (Succar et al. 1985, Llosa et al. 1990, Camilión et al. 1996, Lavado et al. 1998, Gonzalez et al. 1999, Bilos et al. 2001, Galindo et al. 2002).

A local study case of metal distribution in four drainage basins crossing two differentiated geomorphologic units to understand the system behaviour is shown in this paper.

1 Study Area

The region belonging to the known Pampa plains, is located in the NE sector of the Buenos Aires Province comprising the districts of La Plata (942 km^2), Berisso (138 km^2) and Ensenada (100 km^2), with an approximate population of 700,000 inhabitants. Specifically, 550,000 people live in the urban area of La Plata. The sector of the region studied has been divided from a geomorphological point of view into an inner zone and a coastal plain (Fidalgo and Martinez 1983). The inner zone is a geological continental Pleistocene domain, composed of Pampa type loess (Iriondo 1997) derived from Terciary rocks from the Patagonian Cordillera. It is composed of eolian sandy silts and silty sands with intercalations of volcanic ash layers. It is displayed between the topographic curves of 5 to 28 metres (Martinez et al. 2000), and shows a parallel or dendritic pattern drainage system with a SW to NE trend (Fig. 1). Well-defined streams, with main collectors, receiving tributaries of different hierarchy, could be observed. The streams are fed by rainwater and groundwater, reaching a maximum of 4 metres water depth in the event of heavy rain storms. The longitudinal gradient slope varies from highest to lowest topographic level from 0.4 to 0.1%. Well-drained Mollisols and Vertisols (Soil Survey Staff 1999) are the soil covers of interfluves and slopes, while a complex of a great group of these taxa with aquic moisture regimes is restrained to floodplains. The soil profiles are well developed, enriched in illite and smectite clays (Bonorino 1966). The coastal plain is a marine Holocene domain developed under the topographic curve of 5 m. Its muddy plain, contiguous to the inner zone, is a plane-concave area with tidal flats, silted up old tidal channels and swamps. For the most part of the year it is covered by water. The longitudinal gradient decreases sharply with respect to the inner zone and the velocity of the streams slows down discharging directly into the depressions. The drainage pattern becomes chaotic and several channels had to be artificially dug to improve the drainage. Hydromorphic soils with high sodium content, mostly composed by smectitic clays, are typical here. The alluvial plain, developed parallel to the present Río de la Plata coastline, is the youngest landform, composed by poorly developed sandy soils.

The climate is mild and humid, type B1 B'2 according to Thornthwaite and Mather (1955), with an annual mean temperature of 16°C (mean and extreme temperatures for January until midsummer 24°C and 43°C, and July until midwinter 9°C and –5°C, respectively) and the mean annual rainfall is 1000 mm, with a fairly uniform distribution.

2 Methodology

Each of the streams and sediment sampling stations has been identified, as in previous contributions, with numbers, Del Gato (1), El Pescado (2), Carnaval (3), Martín (4) and Carnaval-Martín (5) and letters (A, B, C and D), respectively (Manassero et al. 1998; Ronco et al. 2001). The last publication contains the sediment data set used in the present comparative sediment-soil analysis. From semi-detailed, scale soil mapping, a total of 64 surficial horizon samples were selected for the study. Soil samples belong to the main geographical soil type located upland to the sediment sampling place or to the local soil types surrounding each stream sampling station. The same number and lettering identification was used for both sediments and soils (see Table 1).

The sieving and settling velocity technique, with previous cement removal (Day 1965), was performed for grain size analysis. Organic matter content was determined by the dichromate oxidation method followed by titration according to Walkey and Black (Allison 1965). Analysis of total metal content was done by atomic absorption spectophotometry (Varian Spectra AA, air-acetylene flame), following acid digestion of samples (HNO_3-HCl) (Kimbrough and Wakakuwa 1992, APHA 1998). All results refer to dry weight. Analytical controls included reagent blanks, duplicate samples and certified reference material analysis (Pond Sediment 2, National Institute for Environmental Studies, Yatabe, Tsukuba Ibaraki, Japan). Chemicals used were of analytical grade. Raw metal data were recalculated taking into account the grain-size differences by clay content normalisation (Horowitz 1985) in order to evaluate distribution patterns.

Statistical examination included descriptive parameters, regression analysis between metal contents and matrix components and a two-sample *t* test to evaluate differences between geomorphologic sectors. Box plots and scatter plot diagrams were performed to observe data distribution.

3 Results and Discussion

3.1 Soil matrix properties

In the inner zone, slightly acid vertic Argiudolls and typic Hapluderts have been developed, both in the highest topographic positions of the basins and in the slopes (**Fig. 1**). Argiudolls are the dominant soil type; its mollic epipedon, with a thickness from 25 to 35 cm, contains 3–4% organic matter and approximately 25% w/w clay (**Table 1**). Underlying this there is a thick Bt horizon (> 90 cm) with more than 45% clay. From the three metals studied, zinc is the most abundant. Its average content in acid digests from bulk soils at the surface is 35 $mg{\cdot}kg^{-1}$, while Cu and Pb levels are 13 and 16 $mg{\cdot}kg^{-1}$, respectively. At the sites where intensive agricultural practices have been performed, mainly Zn and Cu concentrations are increased (Table 1). At the NW area, in similar topographic positions, the topsoil has more than 30% w/w clay and the soils became typic Hapluderts. They – as all the Vertisols – are characterised by abundant slickensides and cracks wider than 1 cm in the surface and reaching 1 m depth in dry periods. The Hapludert epipedon is frequently richer in organic matter than the one from Argiudoll, but the thickness is depleted, probably due to runoff by erosion processes. The upper illuvial section underlying

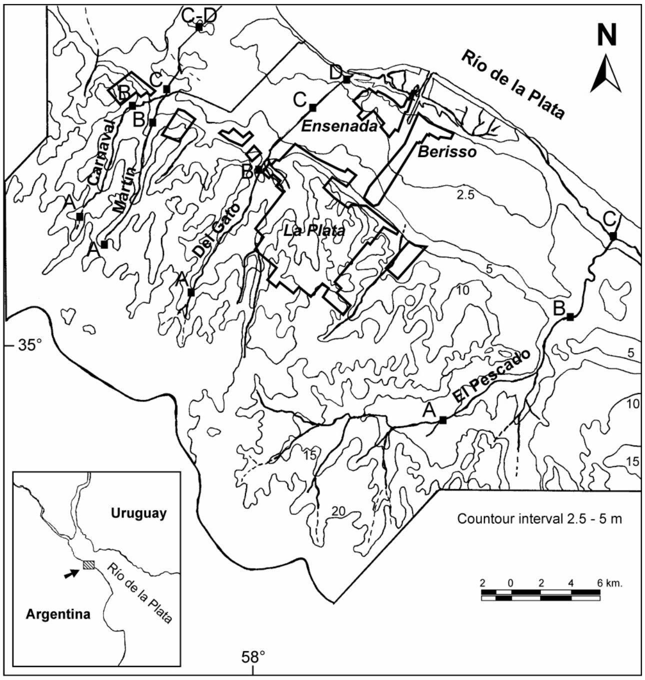

Fig. 1: Topographic map of the study area, streams and sediment sampling stations

it contains more than 55% w/w of clay. Its lower permeability, in relation to the eluvial section, generates a sub-superficial water flow, revealed by the presence of hydromorphic features (Fe-Mn concretions and mottles) at that depth with a pH decrease (Camilión, personal communication). In these soils, the three metals are present in higher concentration than in Argiudolls (Table 1). In the sector where the relief is locally low (Fig. 1), acid hydromorphic intrazonal soils were developed, like Argiaquolls and Argialbolls. Similar soils and alkaline Natraquolls and Natraqualfs have developed in the transition area between the inner zone and the coastal plain (**Fig. 2**) involving different types of parent material (clays, sands, shell-beds). Most of them show higher metal content than zonal soils, with the exceptions of Udipsamments and Rendolls, developed in marine sands and shell-beds, respectively. Frequently, the halomorphic soils have a superficial sealing crust (reaching 3 cm thick), indicating frequent sheet water erosion producing epipedons below 15 cm thick.

The Del Gato stream middle course, piped underground, runs across La Plata City towards the coastal plain. The soils from the urban and suburban area were related to sampling site 1C (Fig. 1) and were considered as Anthrosoils due to the fact that the surficial layer corresponds to a loessic type of filling material covering the natural soil in urban areas. Higher levels of Zn and Pb contents are observed in these Anthrosoils while Cu content, in most cases, remains within the background concentration (Table 1).

In the coastal plain, Vertisols like Epiaquerts and Natraquerts developed on the holocenic marine clays are dominant in the landscape (Fig. 1). They occasionally contain an organic horizon or, at least, an A horizon very enriched in organic matter. At the surface they have more than 50% of clay

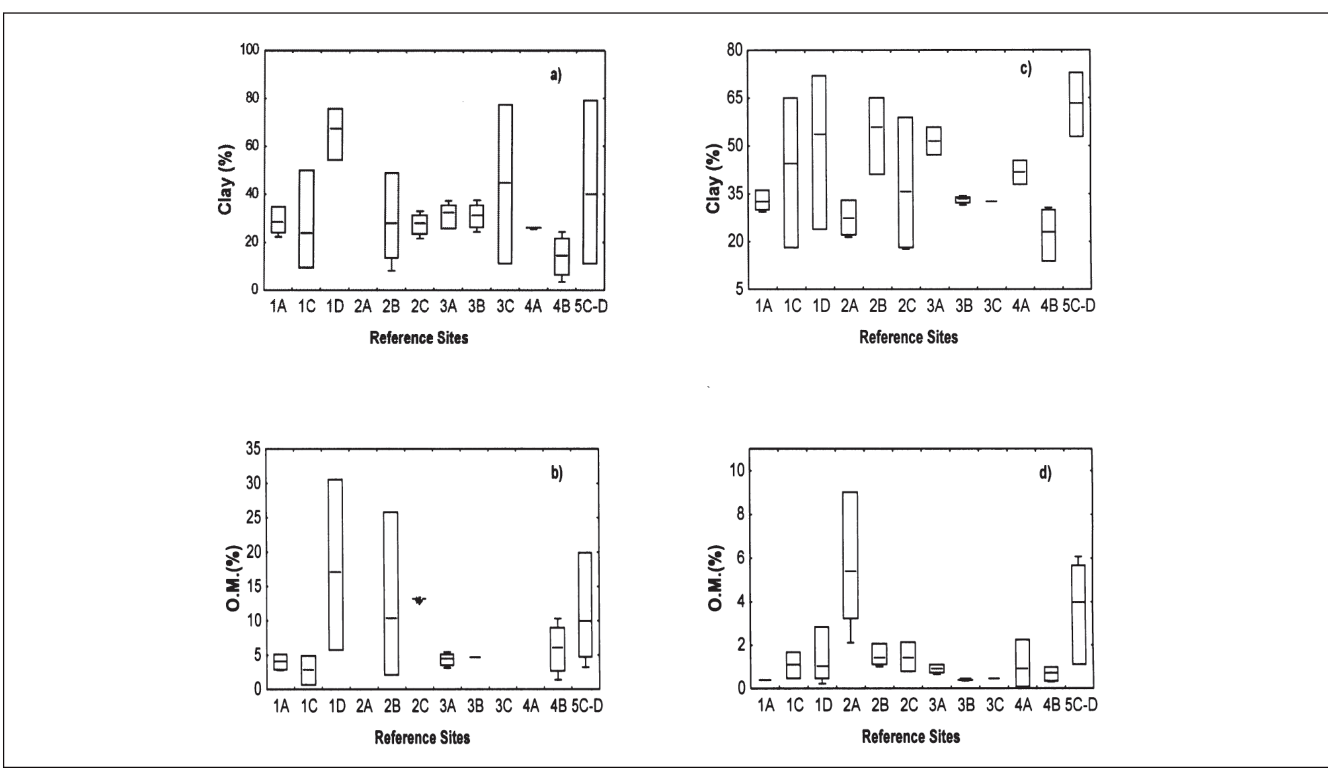

Fig. 2: Variability of clay and organic matter content (%) per sampling stream site of soil and sediment raw data : a) and b) soil clay and organic matter; c) and d) sediment clay and organic matter. Box values indicate standard deviation and the horizontal line in box mean value. Bars indicate maximum and minimum values, numbers and letters indicate stream and sampling station

Table 1: Soil sample location, soil type, land use, grain size and organic matter content and heavy metal concentrations

Ref. site	Soil type	Land use	Clay (% w/w)	Silt (% w/w)	Sand (% w/w)	O.M. (% w/w)	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
1A	Argiudoll	intensive	24.0	53.8	22.2	2.8	37.5	18.2	102.9
1A	Argiudoll	pastures	25.6	55.6	18.9	3.8	10.0	15.2	31.6
1A	Argiudoll	intensive	26.6	58.6	14.8	nd	18.4	18.2	33.9
1A	Argiudoll	intensive	nd			nd	50.5	17.4	47.7
1A	Hapludert	pastures	34.7	50.5	14.8	5.1	30.4	22.5	49.9
1C	Anthrosoil	urban	27.5	34.4	38.1	1.7	26.0	80.0	176.0
1C	Anthrosoil	suburban	12.0	26.6	61.3	3.5	52.0	130.0	213.0
1C	Anthrosoil	suburban	38.2	37.5	24.2	1.9	33.0	35.0	158.0
1C	Anthrosoil	suburban	23.8	55.0	21.2	4.2	21.0	58.0	138.0
1C	Anthrosoil	urban	18.3	21.0	60.7	1.7	37.0	191.0	227.0
1C	Anthrosoil	suburban	23.4	44.1	32.5	nd	41.0	122.0	197.0
1C	Anthrosoil	urban	17.4	39.0	43.6	2.3	60.0	136.0	345.0
1C	Anthrosoil	urban	20.9	25.4	53.7	0.7	28.0	34.0	83.0
1C	Anthrosoil	urban	16.1	21.7	62.2	2.1	39.0	311.0	254.0
1C	Anthrosoil	urban	35.3	36.0	38.9	3.7	41.0	197.0	262.0
1C	Anthrosoil	urban	34.8	49.7	15.5	5.0	25.0	154.0	171.0
1C	Anthrosoil	urban	12.6	54.2	33.2	nd	33.7	67.3	108.3
1C	Anthrosoil	urban	13.9	51.9	34.2	nd	23.9	40.2	65.8
1C	Anthrosoil	suburban	33.3	50.3	16.4	nd	32.5	65.0	86.3
1C	Anthrosoil	urban	28.1	34.5	37.0	nd	49.0	200.0	264.0
1C	Anthrosoil	urban	28.1	55.9	16.0	nd	35.0	130.0	138.0
1C	Natraquert	rangeland	46.7	48.7	4.6	nd	33.0	22.0	86.0
1C	Anthrosoil	urban	13.9	51.9	34.2	nd	32.0	111.0	102.0
1C	Anthrosoil	suburban	9.8	18.5	71.7	nd	90.0	162.0	123.0
1C	Anthrosoil	urban	9.7	23.9	66.4	1.6	42.0	143.0	212.0
1C	Anthrosoil	urban	9.3	53.7	37.0	nd	22.5	50.3	82.5
1C	Anthrosoil	suburban	nd	52.6	5.5	nd	28.0	23.0	79.0
1C	Hydraquent	recreative	50.3	27.0	22.7	nd	68.0	77.0	225.0
1C	Natraquert	rangeland	46.6	48.8	4.6	nd	37.5	18.2	102.9
1C	Hapludert	intensive	nd	nd	nd	nd	41.3	123.3	171.5
1C	Anthrosoil	urban	nd	nd	nd	nd	34.0	251.0	111.0
1D	Epiaquert	rangeland	71.6	25.2	3.2	24.9	37.2	52.1	140.5
1D	Epiaquert	rangeland	75.8	20.5	3.7	8.2	32.0	20.0	117.0
1D	Hydraquent	rangeland	67.1	30.2	2.0	30.6	155.0	134.0	283.0
1D	Epiaquert	rangeland	54.3	39.5	6.1	14.9	40.5	33.0	189.4
1D	Epiaquert	rangeland	64.5	23.9	11.6	5.8	31.5	25.0	127.5
2B	Argialboll	rangeland	48.6	46.0	5.4	25.9	16.4	20.0	36.0
2B	Argiaquoll	rangeland	19.6	39.4	41.0	2.7	12.8	10.1	39.0
2B	Natracuoll	rangeland	13.1	33.6	53.3	2.0	4.9	10.2	41.2
2C	Argiaquoll	rangeland	nd	nd	nd	13.0	18.0	12.0	47.0
2C	Argiaquoll	rangeland	23.2	43.0	33.8	13.0	18.4	12.2	46.7
3A	Argiudoll	field crops	25.4	55.5	18.9	nd	14.0	17.0	38.0
3A	Hapludert	pastures	35.2	55.6	9.1	3.4	23.0	24.0	55.0
3A	Hapludert	field crops	34.7	42.5	22.8	5.1	30.4	22.5	49.9
3B	Epiaquert	rangeland	26.2	55.2	18.5	4.6	24.0	20.0	119.7
3B	Hapludert	Cropland	35.7	21.7	20.6	nd	41.3	123.3	171.5
3C	Epiaquert	rangeland	77.3	18.9	3.8	6.0	41.0	21.0	106.0
3C	Natraqualf	rangeland	11.2	43.4	45.4	nd	46.3	129.4	123.7

Table 1: Soil sample location, soil type, land use, grain size and organic matter content and heavy metal concentrations (*cont'd*)

Ref. site	Soil type	Land use	Clay (% w/w)	Silt (% w/w)	Sand (% w/w)	O.M. (% w/w)	Cu (mg kg^{-1})	Pb (mg kg^{-1})	Zn (mg kg^{-1})
4A	Argiudoll	pastures	25.4	55.5	18.9	nd	14.0	17.0	38.0
4A	Argiudoll	field crops	25.6	55.6	18.9	nd	10.0	15.2	31.6
4B	Argiaquoll	rangeland	21.3	56.2	22.1	9.0	15.7	12.5	34.2
4B	Udipsamment	recreative	6.6	11.7	81.7	2.7	6.3	2.0	22.5
5C-D	Natraquert	rangeland	58.0	36.4	5.5	20.0	23.8	12.5	68.8
5C-D	Anthrosoil	suburban	15.8	21.7	62.4	nd	15.0	79.0	156.0
5C-D	Argiudoll	intensive	26.7	37.5	35.7	nd	22.0	59.0	163.0
5C-D	Anthrosoil	suburban	18.3	30.1	51.8	nd	22.0	98.0	185.0
5C-D	Argiaquoll	rangeland	31.9	49.8	18.3	13.0	24.0	214.0	104.0
5C-D	Natraquoll	rangeland	24.4	58.1	17.4	5.3	11.8	13.2	27.5
5C-D	Fluvaquent	recreative	21.9	26.8	51.3	nd	31.3	25.0	113.8
5C-D	Epiaquert	rangeland	50.0	27.9	22.1	nd	25.0	20.0	155.0
5C-D	Endoaquert	rangeland	78.8	19.4	1.8	1.8	23.8	30.0	75.0
5C-D	Epiaquert	rangeland	62.7	28.0	9.3	1.0	21.3	31.3	90.0
5C-D	Natraqualf	rangeland	11.2	68.9	19.8	4.7	7.5	22.3	17.6
5C-D	Epiaquert	rangeland	77.3	18.9	3.8	6.0	41.0	21.0	106.0

reaching up to 70% w/w, increasing with depth. These types of soils contain the highest metal levels of the studied region, with the exception of the Anthrosoils. Average concentrations for Zn, Pb and Cu are of 118, 26 and 31 mg·kg^{-1}, respectively. Hydraquents, developed in the modern fluvial sands of the estuary, located in the recent alluvial plain, also contain higher levels of metals (Table 1). All coastal plain soils show abundant hydromorphic features (gley colours and Fe-Mn nodules) as indicators of periodical flooding.

A sequential chemical extraction study (Camilión et al. 1998) performed on these Argiudolls and Hapluderts following the Tessier et al. (1979) method, showed that most of the Zn could be ascribed to the residual fraction (minerals, resistant sulfides and refractory organic material) while Cu is found almost in equivalent proportion between Fe-Mn oxides, organic matter and residual fractions. In Natraqualfs, Zn and Cu are mainly distributed between Fe-Mn oxides and residual forms. The behaviour of these soils before the addition of Cu(II) and Zn(II) salt enrichment experiments show that metals are mainly associated with exchangeable forms bound to carbonates or Fe-Mn oxides, with the exception of Cu(II) in the alkaline soil, which is mostly bound to the last two forms. Based on this study, it could be assumed that the digestion pretreatment method used here for metal analysis would yield at least 50% of the total metal content in the soil and most of the available metal (fractions 1 through 4 from Tessier et al. 1979). Only the Zn content in Argiudolls is mostly bound to the residual fraction (more than 70%). Therefore, we would expect that total Zn contents in zonal soils are higher than those reported in this contribution. As to Pb behaviour, taking into consideration the results reported in the literature (Fergusson 1991, Howard and Sledzinski 1996, Adamo et al. 2002), it could be inferred that Pb will be mostly associated to organic matter or oxide fractions in the system described. The change in the matrix composition and properties of soils from the coastal plain, with higher contents of colloids, allows us to assume the existence of higher available metal levels in accordance with the analytical techniques used in this contribution.

3.2 Sediment matrix properties

A data set with information on stream sediment composition and metal contents from the studied area has been previously reported (Ronco et al. 2001). Fine grain size components in sediments from all streams are over 80%. Most samples contain between 30 and 50% w/w of clay, with higher values in the Carnaval-Martín sector (see Fig. 2c). Organic matter content is variable (see Fig. 2d), with a clear tendency to increase within the coastal plain in the Carnaval-Martín basin, reaching values up to 5%. A high concentration value was also detected at the head of El Pescado stream, associated with low topographic areas. The streams showed higher metal concentrations within the upper layers of bottom sediments as well as downstream. The most abundant metal was Zn, followed by Pb in most cases. Copper concentration was frequently the lowest, remaining at similar levels in the high and middle stream sectors of the Del Pescado, Carnaval and Martin basins. Sites C and D of the Del Gato stream were exceptions. The general metal concentration trend along the basins showed an increasing concentration from the head to the middle course in each stream, decreasing again in a lower degree to the mouth, especially for Del Gato and Carnaval-Martín streams.

3.3 Comparative soil-sediment data analysis

The dispersion of raw data matrix parameters (clay, organic matter and metal content) for the region studied can be seen in Table 2. If we consider both soils and sediments, sediments show a higher variability of grain size distributions with a dominance of finer particles (see Fig. 2a, 2c; **Fig. 3**). As to organic matter, soils register higher and very variable con-

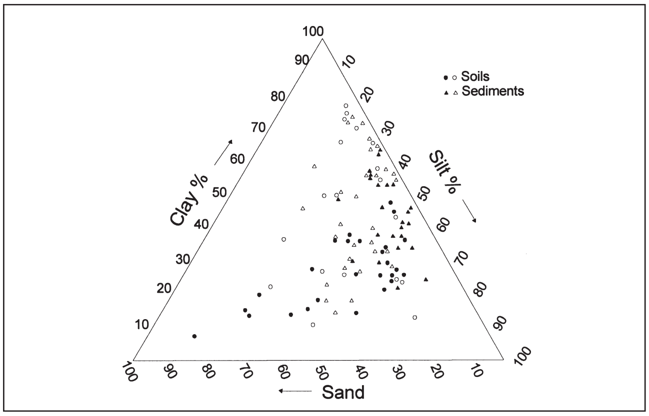

Fig. 3: Textural classes of soil-sediment data. Closed and open symbols represent inner zone and coastal plain samples, respectively

tents (see Fig. 2b, 2d). Raw metal contents also show variable concentration levels, with larger differences for Zn and Pb and higher levels in soils (**Table 2**). The soil-metal data base was used in a linear regression analysis with the clay and organic matter concentrations, showing maximum coefficient values for all soil data sets of r = 0.42 and of r = 0.58 in data without Anthrosoils. These results are similar to those obtained with stream bottom sediments for the studied metals, including Cr, Ni and Cd (Ronco et al. 2001).

When geomorphology and lithology were introduced in the comparative analysis with the raw data set, it could be observed that higher contents of clay fraction, organic matter and metal levels were generally associated with the coastal plain (see Table 1 and Fig. 2). Soils from the inner zone showed medium textures (silty clay loam, clay loam or silt loam classes), while those of the coastal plain predominately revealed finer textures (clay class) (Fig. 3). When introducing these variables, highly significant differences on raw soil trace metal contents were registered for Pb and Zn ($p < 0.01$) and significant ones for Cu ($p < 0.05$) between the two greater geomorphologic sectors, as seen in the previously published bottom sediment analysis (Ronco et al. 2001). Also, the linear regression analysis between metal contents from each geomorphological unit and clay or organic matter content showed an improvement with higher coefficients. The best correlations were found in the coastal plain for metal-organic matter (Cu: 0.71, Pb: 0.51, Zn: 0.69) and in the inner zone for metal-clay correlations (Cu: 0.56, Pb: 0.30, Zn: 0.45).

Considering the matrix spatial and grain size variability, all data was clay normalised (Horowith 1985). The normalised metal distribution (**Fig. 4**) shows a wider range of values when compared to the raw data set, more noticeable in the soils, especially those from the coastal plain. Soil normalised values are higher than those found for sediments from each sampling place. This fact shows the stream transport of materials towards the Río de la Plata estuary, which is acting as a dilution system of metal loads from soil. Only sites C and D of the del Gato stream showed higher Zn values in sediments, in agreement with previous observations of pollution in the area (Ronco et al. 1995, 1996).

In order to assess the material parenthood using raw metal and grain size normalised metal contents, a very good correlation ($r > 0.88$ for normalised data) between average mean metal concentrations in soils and sediments was found for each sampling site (**Fig. 5**). Results indicate a local soil provenance of metals to bottom sediments. Zonal soils like the Argiudolls from the highest topographic positions (inner zone sampling site) are the main source of detrital particles reaching the streams by runoff processes. The Hapluderts, with higher clay and organic matter contents, locally developed in the Carnaval basin, are associated with an intensive flower production area. Here, the distribution pattern of the normalised soil-sediment metal contents (Fig. 5) shows higher metal values in soils, diverting from the group trend. This is an example of the additional effect of both higher soil retention capacity and local anthropic metal sources. Site 1 C, located downland from the urban-industrial sector, splits from the grouping tendency, showing higher metal contents in both compartments, associated with pollution burdens, as explained previously.

The mineralogy of clay materials has shown that illite is the main clay component in all the bottom sediments of the streams (Ronco et al 2001). Higher contents of this clay mineral were detected towards the head of the basins, while smectite increases downstream. The soil clay mineralogy shows the same pattern (Bonorino 1966, Camilión 1993). This compositional difference, seen in the presence of neoformed Fe-Mn-like oxide nodules in low topographic areas of the coastal plain, must be considered as an additional cause of the metal behaviour observed.

Table 2: Mean, extreme values and standard deviation of soil and sediment data

Soil and Sediment Data	n	Mean	Maximum	Minimum	Standard Deviation
Soils					
Clay %	58	32.04	78.00	6.58	19.84
Organic matter %	34	7.49	30.60	0.70	7.64
Cu mg kg^{-1}	64	32.08	155.00	4.85	21.64
Pb mg kg^{-1}	64	68.44	311.00	2.03	69.25
Zn mg kg^{-1}	64	118.22	345.00	17.60	74.20
Sediments					
Clay %	58	45.53	73.00	14.00	15.47
Organic matter %	46	1.51	9.02	0.05	1.69
Cu mg kg^{-1}	61	28.02	133.00	4.00	27.28
Pb mg kg^{-1}	61	32.08	212.00	1.00	46.94
Zn mg kg^{-1}	61	83.09	703.00	0.50	150.33

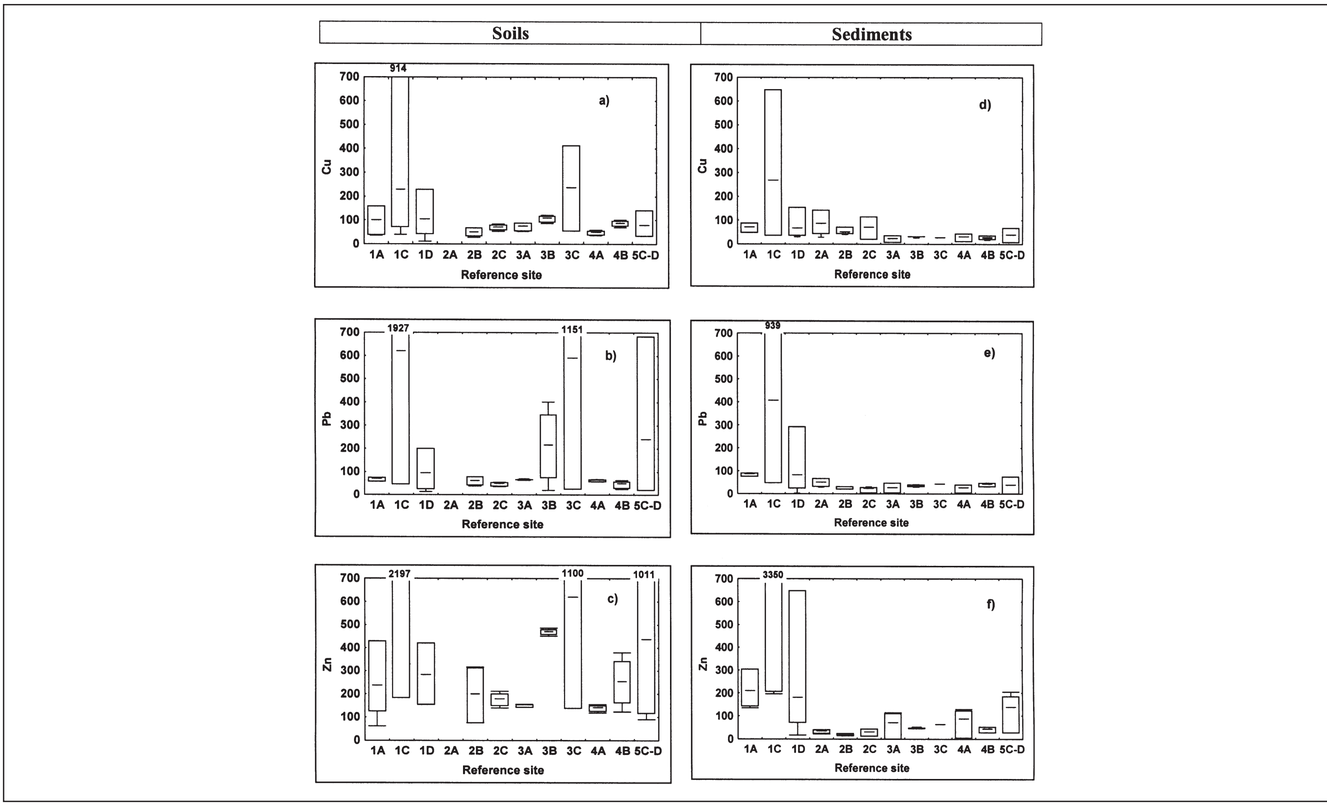

Fig .4: Variability of trace element content (mg·kg⁻¹) per stream sampling site of the 124 clay normalised data set: a, b and c) soils; d, e and f) sediments. Box values indicate standard deviation and horizontal line in box mean value. Bars indicate maximum and minimum values, numbers and letters indicate stream and sampling station

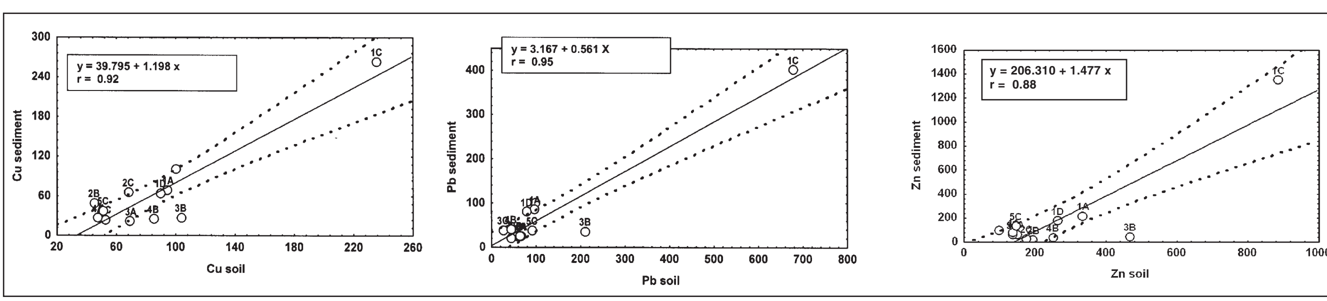

Fig. 5: Scatter diagram of trace element content between soils and sediments (average values) in mg·kg⁻¹ from 124 clay normalised data set. The solid line shows fitted regression and dotted bands indicate the 95% confidence limits

4 Conclusions

The stream bottom sediment metal concentrations are locally related to neighbouring metal topsoil contents within the basins. Topography and lithology landscape determine the water residence time on surface and in the subsurface, affecting in different forms the stability of the soil horizons. Runoff is particulary intense in slopes from the inner zone of all basins. Topsoils with 30 cm thickness in the highest positions decrease to near 10 cm in slopes and foot slopes. The illitic detrital material reaches the water streams, partly deposited as bedsediments or transported as suspended matter favouring the concentration of solutes in low lands. The change from erosional to depositional dominant processes is defined by the topographic step of the 5 metre contour line (boundary between both geomorphological units). These variables, together with Fe-Mn oxides and organic matter contents, explain most of the differences found between metal contents in soils and sediments from the inner zone and coastal plain.

The higher soil metal concentration indicates that an important fraction of the bottom sediments does not retain an important fraction of the removed solutes, which are following their way to the estuary in this non-conservative system (Fergusson 1991). Relative concentrations of the metals in the compartments studied show that Zn is the most abundant, followed by Pb. These two elements are the trace metals with more enrichment by anthropic actions, in agreement with reported data on their relative proportion in air particulate matter, as total suspended (Bilos et al. 2001) or settleable particles (Sinkec, Moschione, Ronco, unpublished results). According to a study published in the same area (Camilión et al. 1998) and our results, the inputs of metals into the solid phases of soils and sediments by pollution are mainly retained as available chemical forms.

The present contribution underlines the importance of geological parameters (topography, source materials, hydrologic action and drainage patterns) that may be taken in account for understanding metal distribution in polluted and non-polluted environments.

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Received: October 16th, 2002
Accepted: April 21st, 2003
OnlineFirst: April 23rd, 2003