GEOCHEMISTRY OF HEAVY METALS IN BOTTOM SEDIMENTS FROM STREAMS OF THE WESTERN COAST OF THE RIO DE LA PLATA ESTUARY, ARGENTINA

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Abstract. The fluvial system within the southwestern coastal sector of the Río de la Plata interacts with a very large and efficient mixing basin known as the Río de la Plata estuary. The region is a densely populated and productive sector of Argentina and is characterised by a temperate humid climate. The streams Carnaval, Martín, Del Gato and El Pescado of the study area drain two main geomorphologic units: a higher inner zone and the low lands of the coastal plain. In particular, the Del Gato stream receives heavily polluted discharges from agricultural, urban and industrial point and non-point sources of pollution, while the other streams collect a lower and variable discharge input. As a part of an initial assessment of the role of fluvial bottom sediments in the fate of metals through the stream ecosystems, the spatial distribution of trace and major elements related to particles in the accumulation areas was examined. Concentration of Cr, Ni, Cu, Zn, Cd, Hg, Pb, Fe and Mn, grain size, mineralogy (clay-X ray diffraction) and organic matter content were analysed in the four streams considering both geomorphologic units at different depositional time. Untreated and iron-normalised trace metal concentrations in the most polluted streams show higher levels in the upper layers of most contaminated sectors and accumulation areas associated to topographic low lands. The coastal plain sector behaves as a regional sink between the upstream area and the estuary.

Key words: anthropic pollution, clay mineralogy, heavy metal distribution, Río de la Plata western coast, sediment-phase contaminants

1. Introduction

The Río de la Plata basin is a complex water system connecting the ‘del Plata basin’, one of the world largest basins, with the Atlantic Ocean. Very large amounts of water, organic matter and sediments from the Paraná and Uruguay rivers enter the mixing zone, sedimenting and controlling the distribution of suspended and sediment-phase contaminants. The area is densely populated. This study provides information needed for more effective pollution control in the basin.

The study area comprises a fluvial system (Carnaval, Martín, Del Gato and El Pescado streams) of the southwestern coastal sector of the Río de la Plata, within

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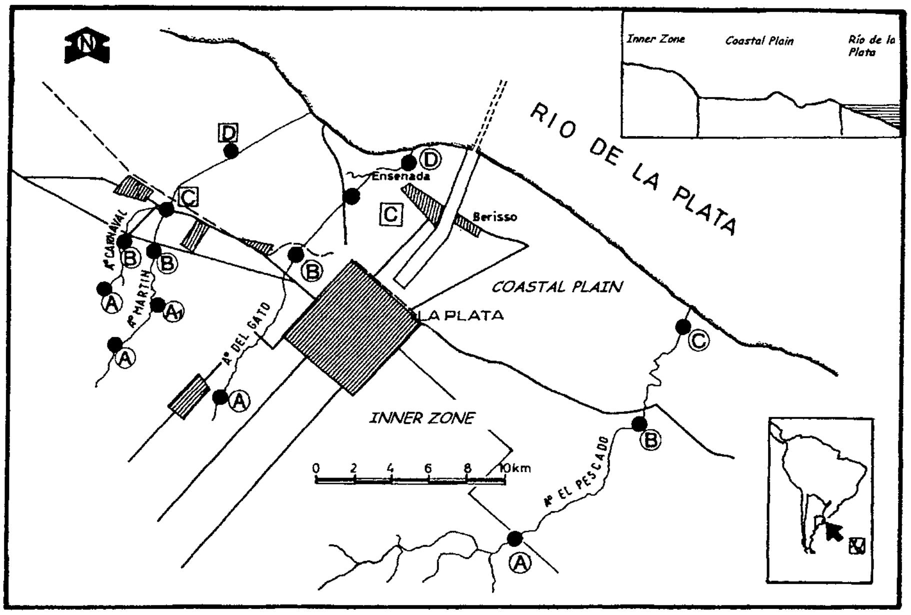

Figure 1. Study area, sampling site locations and geomorphologic scheme (modified from Giménez *et al.*, 1991).

the range of influence of the La Plata City. All the streams in the Pampa Ondulada (Frenguelli, 1957) flow from west to east, with their mouths in the coastal area of Río de la Plata and the Samborombón Bay (Figure 1). The highest topographic areas reach up to 30 m and the regional slope is around 0.2%. Mainly silts and sands of Pleistocene age, known as the Pampiano Fm over aolian sands and La Postrera Fm (Fidalgo y Martínez, 1983), comprise the upper and middle sectors of these basins. Infiltration processes predominate in these areas of poorly developed drainage patterns, while in the middle sectors, the slope tends to increase and the drainage systems show fluvial terraces reaching to 1 m. Fluvial silts of the Luján Fm outcrop within these valleys. On the other hand, mainly marine clays and silts of Holocene age known as Las Escobas Fm comprise the lower sectors, within the coastal plain, developing to the east from a slope break at the topographic curve of 5 m. This coastal plain comprises the estuarine fine sediments from the Holocene transgression, generally salt-rich due to present day intense evapotranspiration. Also, within the study area, several marine and continental units associated with different palaeosols, have been defined on the basis of their palaeogeography and stratigraphy.

All the basins show a rectangular shape. The Carnaval–Martín basin with a drainage surface of 9.1 km^2 is 16 km long. The Del Gato stream, 48 km^2 with 30 km of length, has similar characteristics; the El Pescado displays a drainage surface of nearly 80 km^2 and 36 km at its longest is an extensive low land area where infiltration processes dominate.

The available information on the area comprises aspects of geomorphology (Cavallotto, 1995), soils (Gimenez *et al.*, 1991), environmental chemistry (Colombo *et al.*, 1990; Serra *et al.*, 1992; AA-AGOSBA-ILPLA-SHN, 1997; Manassero *et al.*, 1998), ecotoxicology (Ronco *et al.*, 1995; Alzuet *et al.*, 1996; Scarlato *et al.*, 1997) and dredging and dumping practice (Kreimer *et al.*, 1996). Human activity within the area is the cause of serious pollution of surface waters, sediments and soils due to the direct industrial discharges. There are more than 300 point sources of pollution associated with chemical industries, metallurgy, wood and paper mills plus non-treated urban sewage (Ronco *et al.*, 1995; Alzuet *et al.*, 1996). As a consequence there is an important heavy metal burden in the environment.

The problem of the accumulation of heavy metals in sediments from different types of aquatic environments has been intensively studied since the 1970s. It is well known that an important proportion of metals are associated with suspended or bottom sediments regulated by sorption processes (Salomons and Förstner, 1984; Irion, 1991; Wang *et al.*, 1997). The retention capacity of metals by the bottom sediments is controlled by their composition, specific surface area of clays, organic matter content and by the hydraulic processes within the stream (Axtmann and Luoma, 1991; Sondi *et al.*, 1994).

This study reports data on Cr, Ni, Cu, Zn, Cd, Hg and Pb levels and their vertical and longitudinal distribution in bottom sediments from the aquatic systems. Results are analysed in terms of sedimentological and geomorphological parameters (grain size, class mineralogy, environments of deposition, stratigraphy), Fe and Mn and organic matter. The pattern of distribution of pollutants within the basins and the location of critical sites could provide the means to prevent further damage and help to plan remedial strategies.

2. Methodology

Sampling sites are located within the inner zone and the coastal plain as seen in Figure 1. Each one of the streams has been identified with a number for an easier graphic display as follows: Del Gato (1), El Pescado (2), Carnaval (3), Martín (4), and the common canalised sector Carnaval–Martín (5). Samples were obtained with 4 cm diameter plastic tubes on both margins of the stream with a core recovery up to 60 cm. Most of the sampling points were sampled twice. The cores were dried, divided and described on the basis of the macroscopic characteristics (colour, grain size, lamination, stratification).

Sieving and settling velocity technique, with previous cement removal (Black, 1965) was performed for grain size analysis. Organic matter content was determined according to Walkey and Black (Allison, 1965). The clay fraction was analysed by X ray diffraction (Bish and Reynolds, 1989). Semi-quantitative analyses were performed according to Moore and Reynolds (1989) on normal, glycolated and calcinated samples, in order to recognise the clay mineral associations. Analysis of total metal content was done by atomic absorption spectophotometry following acid digestion of samples (USEPA, 1986; APHA, 1998). Quality controls included reagent blanks, duplicate samples (APHA, 1998) and certified reference material analysis (Pond Sediment 2, National Institute for Environmental Studies, Yatabe, Tsukuba Ibaraki, Japan). All chemicals used were analytical grade.

The original data set of 62 samples and 16 parameters (Table Ia and b) was screened, removing a sample (site 1B), which consisted of gravel with anthropogenic construction material unrepresentative of modern fluvial deposition. Statistical examination included regression analysis between metal contents and matrix components, ANOVA-LSD to assess trace metal concentration differences between streams and a two-sample t test to evaluate differences between geomorphologic sectors and of depositional levels (Zar, 1999). Box plot and scatter plot diagrams were done to observe data distribution and trends of metal contents. Mercury content levels were not analysed since data values were too close or below the detection limit.

3. Results and discussion

3.1. MATRIX COMPOSITION

Variability of parameters controlling the metal distribution trends in the sediment phase of the studied streams is shown in Figure 2. Average clay plus silt contents are over 80% in all streams (Figure 2a). Most samples contain between 30 and 50% of clay (Figure 2b). All the streams show a similar range of differences, with higher clay proportion in the Carnaval–Martín sector (Table Ia and Figure 2b).

Illite is the main clay component in all the streams (Figure 2c). Higher contents were detected towards the head of the basins, while smectite increases downstream (Table Ia and Figure 2d). The main components of this clay mineral association are tied to different source areas. Illite is associated with the aeolic materials of Pampiano and La Postrera Fms (González Bonorino, 1966) and smectite is the typical parental material of the coastal plain (Holocene marine transgression). The minor clay mineral, kaolinite (Table Ia), is one of the characteristic minerals of the del Plata Basin (Gimenez *et al.*, 1991).

The concentrations of the major metals (Fe and Mn) show a high dispersion. The Fe content is very variable in most streams with ranges of variation from 2 to 3 orders of magnitude, except for El Pescado, where it is reasonably constant (Figure 2e). In the case of the Carnaval and Martín streams Fe mean concentration is one order of magnitude lower than the average level in the Del Gato stream. Manganese contents show slightly lower variability (Figure 2f)

TABLE Ia

Sample location, depth in core, grain size, clay mineralogy and organic matter content

Sample	Stream-site	Depth (cm)	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)	Illite (%)	Kaolinite (%)	Smectite (%)
g-A1-1	1A	19.00	–	–	–	–	–	–	–
g-A1-2	1A	6.00	0.35	30.0	50.00	20.00	–	–	–
g-A2-1	1A	15.00	–	33.05	55.33	11.60	26.44	0.99	5.62
g-A2-2	1A	5.00	–	36.39	51.17	12.50	–	–	–
g-B1-1	1B	10.00	0.55	10.90	21.90	67.20	5.45	0.90	4.58
g-C1-1	1C	17.00	1.70	41.37	34.80	24.00	27.59	9.17	4.54
g-C1-2	1C	4.00	–	18.19	40.67	41.10	10.39	5.20	2.55
g-C2-1	1C	14.00	0.43	64.55	31.49	4.00	32.27	10.07	21.94
g-C2-2	1C	3.00	0.46	52.03	42.95	5.00	17.33	5.78	29.14
g-C3-1	1C	12.00	1.16	49.05	34.32	16.60	23.94	4.91	20.12
g-C3-2	1C	2.00	1.36	40.37	44.29	15.30	23.01	11.71	17.42
g-D1-1	1D	46.00	–	65.90	30.80	3.30	37.56	18.45	9.89
g-D1-2	1D	36.00	0.58	51.50	28.10	20.40	28.33	14.42	8.76
g-D1-3	1D	30.00	–	72.30	20.40	7.30	41.21	14.46	16.63
g-D1-4	1D	20.00	0.71	26.50	40.80	32.70	13.25	8.08	5.17
g-D1-5	1D	10.00	1.27	45.00	22.30	32.70	28.80	10.35	6.30
g-D2-1	1D	37.00	0.57	58.00	38.30	3.80	–	–	–
g-D2-2	1D	21.00	–	58.00	36.00	6.50	41.18	6.35	10.39
g-D2-3	1D	11.00	2.82	56.10	37.20	6.70	42.08	7.01	7.01
g-D3-1	1D	53.00	–	72.30	27.10	10.60	40.48	16.43	12.49
g-D3-2	1D	43.00	0.48	23.70	40.00	36.60	12.80	4.73	6.14
g-D3-3	1D	31.00	–	71.10	18.30	10.60	–	–	–
g-D3-4	1D	16.00	0.70	55.20	35.80	8.90	30.91	15.47	8.84
g-D3-5	1D	9.00	0.48	37.50	35.00	27.40	19.88	9.38	4.58
p-A1-1	2A	19.00	–	–	–	–	–	–	–
p-A2-1	2A	9.00	9.02	21.59	59.97	11.43	17.70	2.09	3.25
p-A3-1	2A	17.00	3.79	25.97	65.14	8.86	20.52	2.60	2.60
p-A4-2	2A	15.00	3.20	33.42	58.73	7.84	27.40	2.01	4.01
p-B1-1	2B	24.00	–	61.00	36.00	8.00	–	–	–
p-B1-2	2B	16.00	–	54.00	36.00	6.00	–	–	–
p-B1-3	2B	6.00	–	56.00	37.00	6.00	–	–	–
p-B2-1	2B	28.00	1.17	61.46	36.54	8.17	28.27	10.42	20.84
p-B2-2	2B	22.00	1.10	54.95	36.34	6.56	26.38	6.18	23.02
p-B2-3	2B	6.00	1.29	56.14	37.33	6.53	23.02	10.11	23.02
p-B3-1	2B	36.00	2.03	64.98	34.01	1.01	28.59	11.70	24.69
p-B3-2	2B	24.00	1.47	41.05	54.62	4.33	15.60	7.80	17.65

TABLE Ia
continued

Sample	Stream-site	Depth (cm)	Organic matter (%)	Clay (%)	Silt (%)	Sand (%)	Illite (%)	Kaolinite (%)	Smectite (%)
p-B3-3	2B	7.00	1.07	56.32	36.18	7.49	25.91	11.83	18.59
p-C1-1	2C	18.00	2.14	28.81	51.94	27.26	14.98	5.60	7.20
p-C1-2	2C	12.00	1.57	34.37	45.29	20.34	20.28	5.16	8.94
p-C3-1	2C	22.00	0.79	59.10	19.18	22.30	36.64	4.70	17.63
p-C3-2	2C	16.00	1.02	17.68	47.62	34.70	9.72	3.71	4.24
c-A1-1	3A	23.00	0.72	53.30	39.50	7.20	32.51	2.67	18.12
c-A1-2	3A	8.00	0.76	55.60	34.60	10.00	40.59	1.66	13.32
c-A3-1	3A	26.00	0.74	49.00	27.90	23.10	38.22	4.41	6.37
c-A3-2	3A	8.00	1.12	47.00	45.80	7.20	40.42	2.38	4.20
c-B2-1	3B	19.00	0.37	33.99	40.30	25.79	29.57	0	4.39
c-B2-2	3B	5.00	0.35	32.02	41.68	26.30	29.14	0	2.88
c-C1-1	3C	18.00	0.41	32.07	50.40	17.57	21.17	1.28	9.62
c-C1-2	3C	7.00	–	–	–	–	–	–	–
m-A1-1	4A	19.00	0.05	42.20	53.00	4.70	25.74	2.11	14.36
m-A1-2	4A	16.00	2.24	40.00	51.50	8.50	28.80	1.60	9.60
m-A1-3	4A	5.00	1.66	41.30	50.50	8.20	–	–	–
m-A′1-1	4A	10.00	0.12	37.70	47.30	15.00	31.67	2.26	3.77
m-A′1-2	4A	5.00	0.09	45.50	52.20	2.20	30.03	2.73	12.75
m-B1-1	4B	15.00	0.33	30.36	41.8	27.84	19.73	0.61	10.02
m-B1-2	4B	12.00	0.60	14.11	46.29	39.64	–	–	–
m-B1-3	4B	4.00	0.98	24.36	47.14	28.52	20.71	0	3.65
cm-C1-1	5C	14.00	4.12	–	–	–	–	–	–
cm-C1-2	5C	5.00	5.50	68.00	28.70	3.30	31.28	15.64	21.08
cm-D1-1	5D	15.00	3.47	56.70	41.00	2.40	25.51	8.50	19.26
cm-D1-2	5D	4.00	5.67	72.60	24.20	3.20	34.85	13.07	24.68
cm-D2-1	5D	10.00	1.10	53.30	43.00	3.50	–	–	–

than Fe. A highly significant correlation between the two elements was found (Figure 3). The relationships between these two major elements and the clay minerals can be seen in Figure 4. Highly significant correlations between each metal with kaolinite and smectite were found. It can be observed that the majority of samples from sites C and D of the Del Gato stream depart from the central tendency. A similar behaviour can also be seen for site B of the El Pescado stream. For the case of Fe, the very high levels in the first stream are associated with lower contents of smectite and kaolinite. High Mn content variability detaches some samples above

TABLE Ib

Concentration of metals in mg/kg of dry sample

Stream-site	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Hg (mg/kg)
1A	12.50	12.70	26.10	91.00	1.25	25.70	3120.00	325.00	–
1A	7.50	8.70	18.80	49.00	< 0.50	22.80	20000.00	250.00	–
1A	15.00	12.50	25.00	70.00	0.72	29.20	29400.00	350.00	–
1A	7.50	8.70	17.70	51.80	< 0.50	32.50	19400.00	225.00	< 0.50
1B	12.50	10.80	71.00	315.00	0.50	175.00	22000.00	275.00	< 0.50
1C	82.50	35.20	133.00	547.00	1.70	192.00	64000.00	575.00	–
1C	85.00	26.90	117.00	603.00	1.50	169.00	51000.00	350.00	–
1C	20.00	19.10	24.00	135.00	0.50	32.00	48000.00	475.00	–
1C	22.50	20.30	33.00	155.00	0.50	55.00	55000.00	525.00	–
1C	60.00	25.90	100.00	557.00	1.20	212.00	51000.00	475.00	< 0.50
1C	47.50	24.90	121.00	703.00	1.50	167.00	44000.00	375.00	1.08
1D	21.43	1.50	23.80	47.78	< 0.50	16.00	–	–	–
1D	22.41	1.50	18.54	45.07	< 0.50	17.50	63000.00	1000.00	–
1D	28.89	2.25	31.15	58.04	< 0.50	19.30	–	–	–
1D	23.87	–	19.94	51.51	< 0.50	19.60	–	–	–
1D	35.75	2.25	33.03	103.25	0.50	41.50	–	–	–
1D	27.89	2.00	27.96	60.30	0.50	19.30	88000.00	1000.00	–
1D	25.74	1.75	27.47	55.44	< 0.50	20.30	72000.00	900.00	–
1D	86.25	3.00	86.05	364.25	2.25	164.20	–	–	–
1D	31.50	–	35.62	63.00	< 0.50	22.20	–	–	–
1D	23.88	1.75	21.64	48.01	< 0.50	19.90	47000.00	600.00	–
1D	28.20	2.25	27.46	56.67	0.77	56.70	122000.00	1300.00	–
1D	26.52	2.00	25.76	56.82	0.50	27.50	50000.00	800.00	–
1D	30.81	2.00	34.39	124.49	0.50	65.10	–	–	0.88
2A	9.55	7.64	21.49	7.38	0.72	4.06	14040.11	52.29	< 0.50
2A	10.56	9.56	31.44	9.05	0.78	14.84	14109.66	170.02	< 0.50
2A	8.28	7.79	15.10	7.48	< 0.50	8.04	15635.66	114.22	< 0.50
2A	10.14	9.15	14.84	7.62	< 0.50	14.59	18199.80	121.17	< 0.50
2B	22.25	20.50	25.75	9.28	< 0.50	18.25	32250.00	769.75	< 0.50
2B	23.38	22.10	28.26	9.58	< 0.50	16.96	39671.12	880.52	0.51
2B	21.81	21.32	28.51	9.25	< 0.50	16.36	36836.89	1541.15	< 0.50
2B	23.75	22.25	26.25	9.38	< 0.50	15.20	36875.00	846.50	< 0.50
2B	23.26	22.28	26.44	9.18	< 0.50	14.20	45176.30	834.48	< 0.50
2B	20.40	21.14	25.12	9.10	< 0.50	12.44	33457.71	873.13	< 0.50
2B	29.35	21.71	30.34	9.35	< 0.50	14.55	38135.18	1237.79	< 0.50
2B	24.56	20.14	28.49	9.09	< 0.50	12.03	34602.16	927.80	< 0.50
2B	20.31	16.80	24.82	9.05	< 0.50	11.79	36258.78	910.48	< 0.50

TABLE Ib
continued

Stream-site	Cr (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Mn (mg/kg)	Hg (mg/kg)
2C	14.78	12.53	19.79	8.87	< 0.50	7.52	26477.96	659.07	< 0.50
2C	14.68	12.69	19.90	8.38	< 0.50	9.95	25845.77	915.17	< 0.50
2C	8.25	8.25	11.51	7.00	< 0.50	3.25	25237.62	706.35	< 0.50
2C	12.26	10.76	20.76	7.58	< 0.50	3.50	17458.73	537.52	< 0.50
3A	6.50	7.00	12.50	36.25	< 0.50	16.00	15247.50	90.00	< 0.50
3A	2.00	7.75	10.00	49.25	< 0.50	11.25	192.50	210.00	< 0.50
3A	9.50	10.00	17.50	54.25	< 0.50	22.50	18622.50	452.50	< 0.50
3A	1.00	0.50	4.00	0.50	< 0.50	1.00	97.50	10.00	< 0.50
3B	42.50	24.00	9.50	16.00	< 0.50	10.75	9050.00	182.50	0.95
3B	7.50	6.25	8.50	14.50	< 0.50	12.75	9025.00	162.50	< 0.50
3C	5.00	6.00	7.75	18.75	< 0.50	12.25	8275.00	105.00	< 0.50
3C	12.50	9.75	9.75	15.25	< 0.50	19.75	5175.00	107.50	< 0.50
4A	1.00	6.00	7.50	36.00	< 0.50	7.00	50.00	87.50	< 0.50
4A	1.00	0.50	4.00	2.25	< 0.50	1.00	50.00	52.50	< 0.50
4A	4.25	12.75	17.50	49.00	< 0.50	13.50	310.00	662.50	< 0.50
4A	1.75	8.25	12.50	46.75	< 0.50	11.75	135.00	132.50	< 0.50
4A	7.50	8.75	12.50	34.00	< 0.50	18.00	21372.50	247.50	< 0.50
4B	10.00	8.75	6.25	12.75	< 0.50	12.25	5950.00	75.00	< 0.50
4B	5.00	3.25	4.75	7.00	< 0.50	6.75	6025.00	127.50	< 0.50
4B	20.00	11.50	5.00	6.75	< 0.50	7.50	5050.00	75.00	< 0.50
5C	50.50	18.00	35.00	74.50	1.00	33.75	27997.50	500.00	1.20
5C	14.00	18.25	15.00	105.75	0.75	20.00	50.00	870.00	< 0.50
5D	47.50	24.75	37.50	93.25	1.00	42.75	49622.50	655.00	1.08
5D	41.00	23.00	40.00	137.00	1.00	31.75	997.50	775.00	< 0.50
5D	1.00	2.50	4.00	15.75	< 0.50	1.00	50.00	170.00	< 0.50

and below the central tendency. On the other hand, illite shows negative and no significant correlation with both elements.

Organic matter content is also variable, with lower concentrations in the Del Gato and Carnaval streams and very variable within the course of El Pescado, reaching up to 9%. Average content of organic matter in the streams is within 2% (Figure 2g).

3.2. CORRELATION BETWEEN TRACE METALS AND MATRIX COMPONENTS

Trace elements were tested against Fe, Mn and organic matter contents. Correlation plots between iron versus Cr, Ni, Cu, Zn and Pb contents are shown in Figure 5.

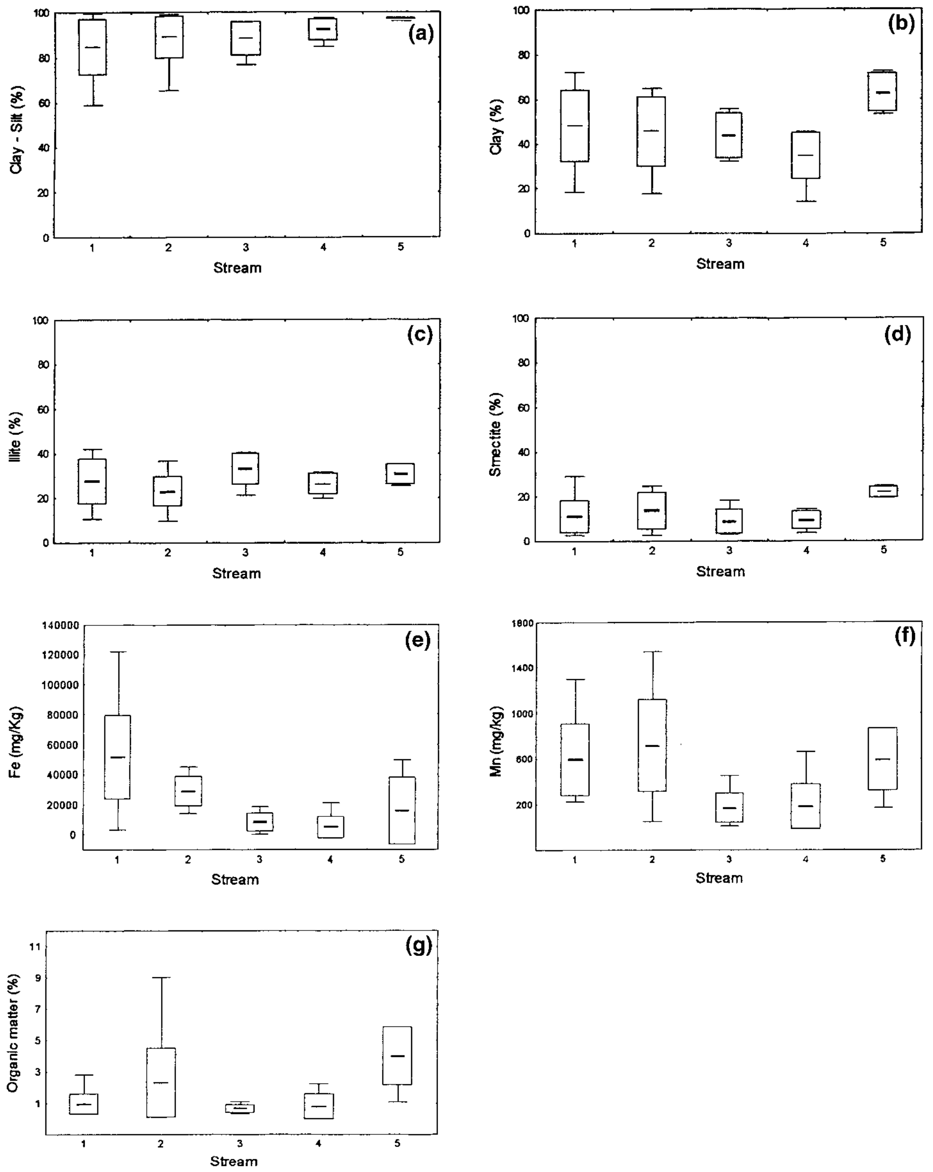

Figure 2. Variability of matrix components in the sediment phase of the studied streams. Box values indicate standard deviation and horizontal line in box mean value. Bars indicate maximum and minimum values. The numbers for the streams refer to the identification name found in text.

The data show a general grouping trend for all streams except for sampling sites C and D of the Del Gato. Particularly, Cr, Cu, Zn and Pb display a group of data with high ratios of trace metal: Fe contents (Figures 5a, c, d and f) in site C. With respect to the grouping tendency in site D of this stream, some samples show low ratios of Cr, Cu and Pb. All trace elements have significant correlation with Fe

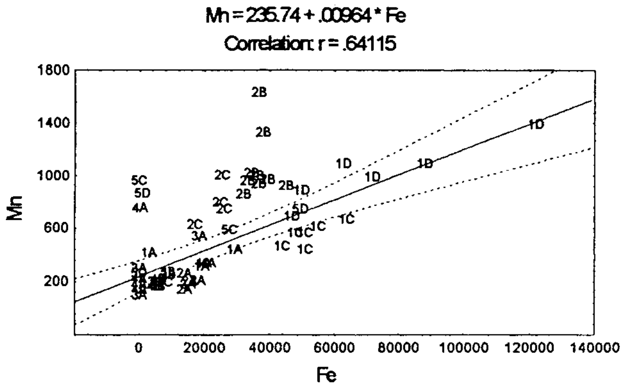

Figure 3. Relationship between Mn and Fe in mg/kg of 54 sample data set. Number and letter of data indicate stream and sampling station, respectively. The solid line shows fitted regression and broken bands indicate the 95% confidence limits.

($\alpha = 0.01$) except for Ni. The sectors of the Del Gato stream exhibiting this different pattern in the plots correspond to a highly polluted area in the coastal plain. On the other hand, the organic matter and Mn plots prove very low correlation factors ($r < 0.2$).

3.3. TRACE ELEMENTS SPATIAL AND VERTICAL DISTRIBUTION

Figure 6 shows the spatial distribution of raw concentrations of trace elements in all streams. Mean values per site per stream increase from the head to the middle sectors, decreasing again in a lower degree to the mouth. Chromium, Cu, Zn, Cd and Pb have a variable range of concentrations with the highest levels in site C of the Del Gato Stream. The El Pescado stream shows low concentrations along its course with a slight increase in the middle site. Nickel distribution (Figure 6b) is slightly different for the other elements, with a large decrease in the concentration in the mouth of Del Gato stream and high levels in the middle sector of Carnaval stream. All the analysed trace metals in the Carnaval and Martín streams reach the maximum values in the common sector downstream. Mercury concentration levels (Table Ib) are below the quantification limits in all the streams except for sites C and D of the Del Gato and Carnaval–Martín streams. Those sites also contain the highest concentrations of the other trace metals.

Inter-comparisons of the streams by ANOVA-LSD analysis indicate significant differences between them. The El Gato stream shows highly significant differences ($\alpha = 0.01$) with the others for Cu, Zn and Pb. Cadmium is also significantly different with respect to Carnaval and Martín streams ($\alpha = 0.05$). For the case of Ni, significant differences were found between the courses of the Del Gato and El Pescado, and also between El Pescado and Martín ($\alpha = 0.05$).

Highly significant differences between the two geomorphologic sectors (inner zone and coastal plain) were also found for Cr, Cu, Zn and Cd and significant

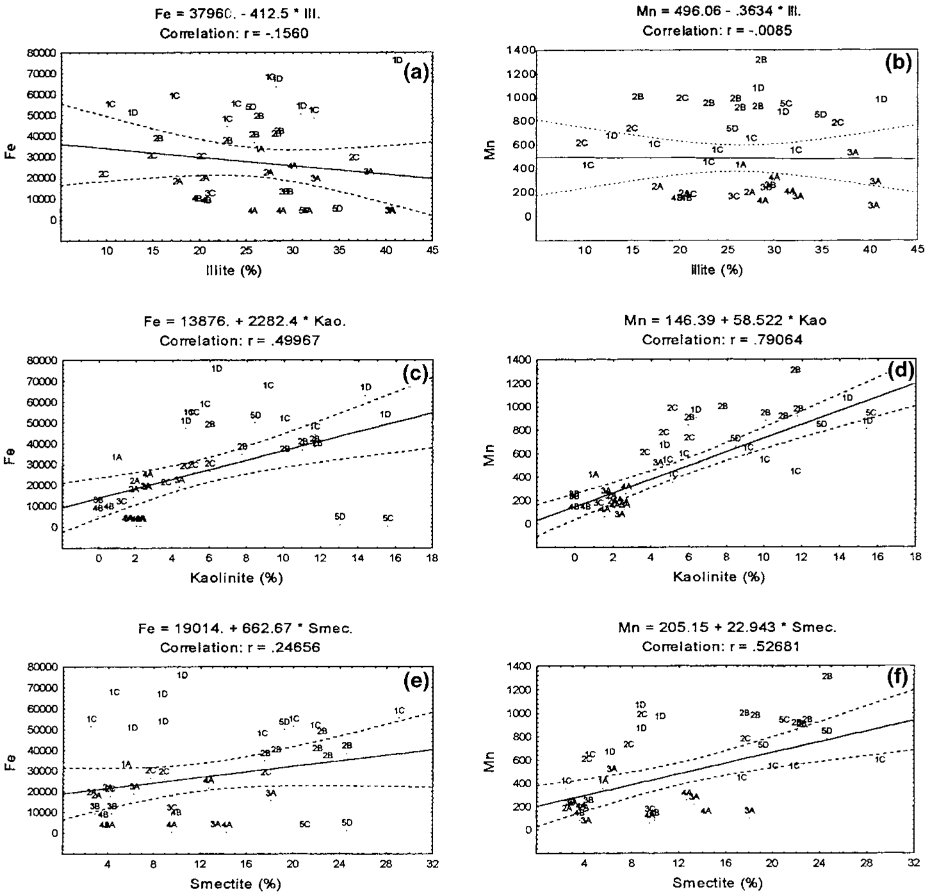

Figure 4. Relationship between concentration of Mn and Fe (mg/kg) and proportion of clay mineral group (%) of selected data. Number and letter of data indicate stream and sampling station, respectively. The solid line shows fitted regression and broken bands indicate the 95% confidence limits.

differences for Pb. The assessment of the vertical distribution considering more recent depositional levels (top 15 cm layer) with respect to deeper layers (over 15 cm), indicate no significant differences ($\alpha = 0.05$) for all the streams. The exception was the middle and lower sector of the Del Gato stream were highly significant differences were observed for Cr, Ni, Cu, Zn and Pb.

Trace metal: Fe normalisations (Horowitz, 1985; Coakley *et al.*, 1993; Acero Salazar *et al.*, 1999) supported the findings mentioned above. Consistent differences between streams, geomorphologic sectors and depositional level in the Del Gato stream were detected, increasing the significance level ($\alpha = 0.01$) for the last case. The Carnaval–Martín common sector also shows highly significant differences for Cr, Cu, Zn and Ni with El Pescado and Del Gato streams.

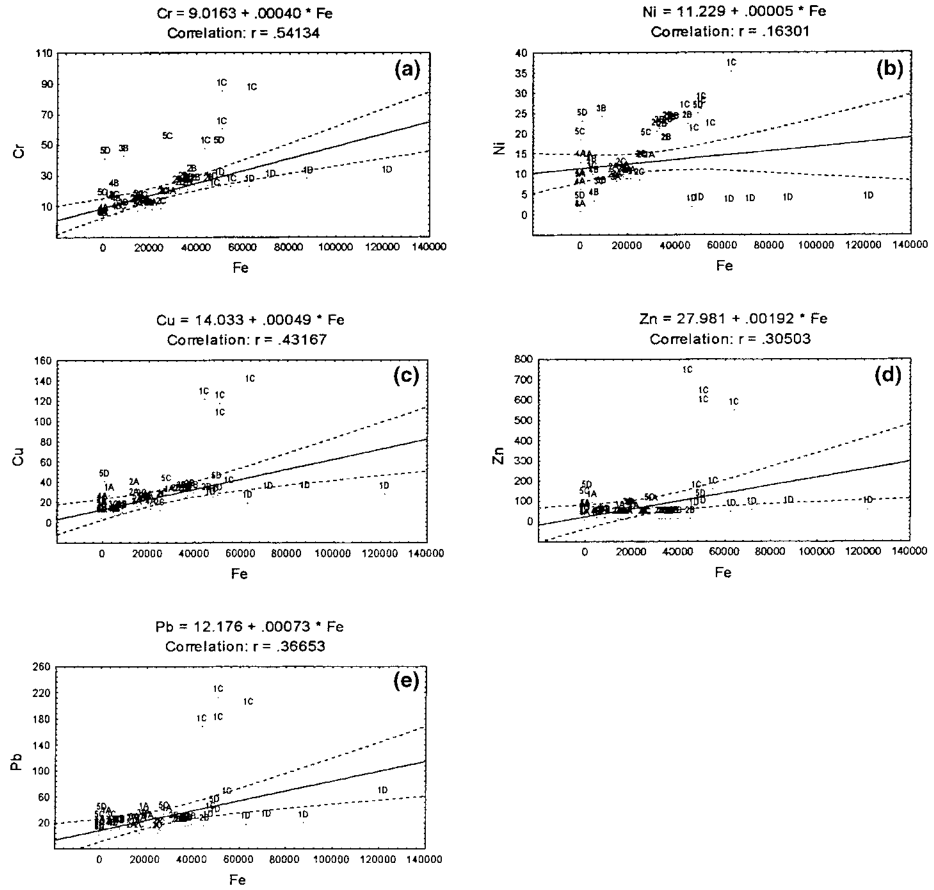

Figure 5. Relationship between trace element and Fe concentration in mg/kg of 54 sample data set. Number and letter of data indicate stream and sampling station, respectively. The solid line shows fitted regression and broken bands indicate the 95% confidence limits.

4. Conclusions

The Fe and Mn distribution in all streams show lower contents in the head and higher towards the mouth. The behaviour could be related to the two different geomorphologic units (inner zone and coastal plain) that the streams cross. In the coastal plain dominant chemical and biochemical redox processes associated to this type of environment produce Fe and Mn neoformations (Schwertmann and Fitzpatrick, 1992). The dominating hydromorphic conditions in the local depression of site B of del Pescado stream, accounts for a similar behaviour in this place.

Iron not only can associate to clay minerals by sorption process, but also is one of the components of smectitic clays. This is in agreement with the significant correlation found between Fe and smectite. For the case of kaolinite the correlation can be associated to the Fe neoformed minerals that usually cover the clay crystals

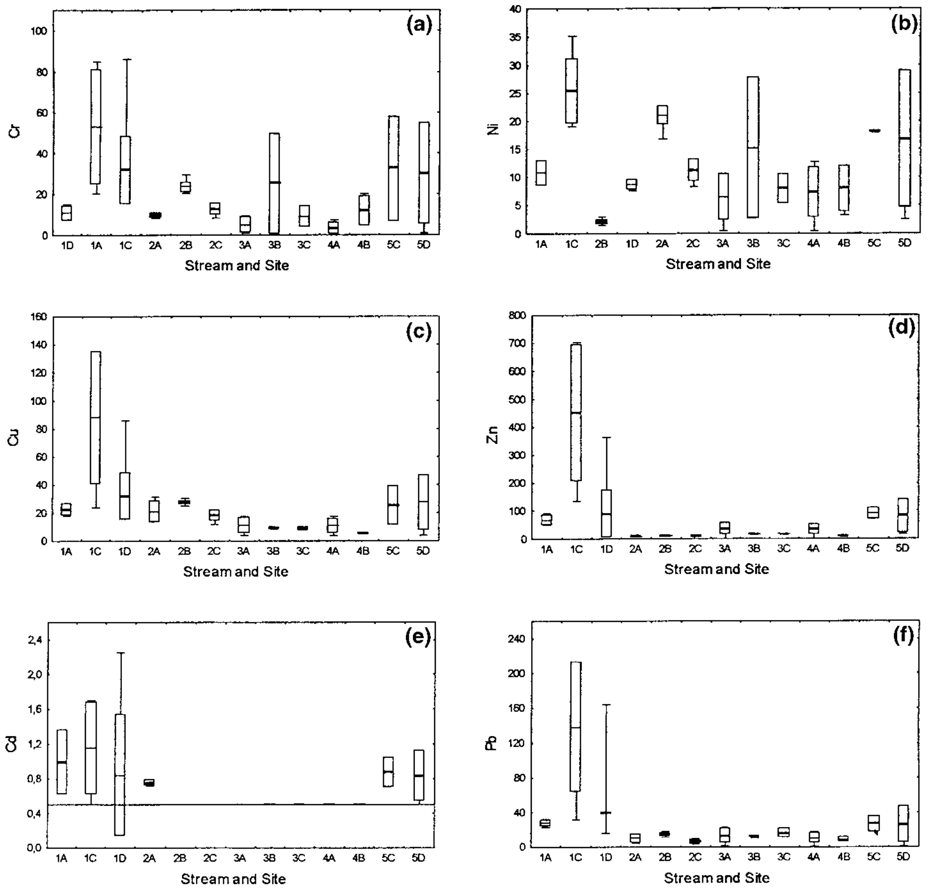

Figure 6. Variability of trace element contents (mg/kg) per sampling site and stream of the 61 data set. Box values indicate standard deviation and horizontal line in box mean value. Bars indicate maximum and minimum values. Number and letter indicate stream and sampling station, respectively. Line at 0.5 mg/kg of Cd plot indicates the detection limit.

(Yong and Ohtsubo, 1987). Although illite is the main clay mineral in the studied area, no correlation was found with Fe. Manganese shows a similar behaviour as the one found for Fe.

It can be observed from Figure 5 that most trace elements have significant correlation with iron content. Since Fe has a good affinity to clays and the concentration is several times higher than the trace elements, we can consider that iron saturates the binding capacity of clays. Since the coastal plain seems to act as the trace elements regional sink, iron neoformed minerals could be an important control factor involved in the sediment retention processes. Trace elements: Fe normalizations support this behaviour. It is also important to point out that for the polluted sector of Del Gato stream (site C) serious effects on the biota had been reported (Ronco *et al.*, 1995; Alzuet *et al.*, 1996).

When comparing the highest pollution levels in the studied streams to other water bodies of the region, we find that Cu, Pb and Zn content levels are in the same order of magnitude as those found for the Matanza-Riachuelo basin (Kreimer *et al.*, 1996). On the other hand, the detected levels of Cd and Cr are considerable lower in the study area. The trends along the basins show an increasing concentration of metals from the head to the middle sector of the coastal plain (riverine sediments) in each polluted stream. Lower trace metal contents in the mouth of the streams (estuarine sediments) may respond to a natural phenomenon of dilution due to the action of tides and waves within the Río de la Plata estuary.

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