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Regional geochemical baselines for sedimentary metals of the tropical São Francisco estuary, NE-Brazil

Elisamara Sabadini-Santos^{a,*}, Bastiaan Adriaan Knoppers^{a,1}, Eliane Padua Oliveira^{a,1}, Thomas Leipe^{b,2}, Ricardo Erthal Santelli^{a,1}

^a Department of Geochemistry, Fluminense Federal University-UFF, Outeiro Sao João Baptista s/n, Niteroi/RJ 24020-015, Brazil

^b Leibniz Institute for Baltic Sea Research Warnemünde-IOW, Seestrasse 15, D-18119 Rostock, Germany

River catchments of the humid tropics deliver a large amount of the world's particulate suspended matter and associated elements to the coastal zone (Hay, 1998; Meybeck, 1993). The estuaries and mangrove habitats set along this transport pathway transform, retain and accumulate a fraction of the river-borne particulates and metals in their sediments (Lee, 1995; Jennerjahn and Ittekkot, 2002; Machado and Lacerda, 2004). The metals are preferentially buried with fine-grained sediments and also affected by the mineralogy and content of organic matter (Hornberger et al., 1999). Many metal accumulation studies in coastal systems focused on the establishment of geochemical baselines for the evaluation of the degree of natural and/or anthropogenic metal loadings in the system. The tropical and sub-tropical coastal zone of Brazil has been subject to manifold metal contamination studies of its embayments, estuaries, coastal lagoons and mangrove habitats embedded in these systems affected by a varying degree of multiple human impacts, such as urbanization, industrialization, deforestation, land erosion and agricultural practices (Patchineelam et al., 1988; Lacerda et al., 1992, 1999, 2006; Marins et al., 2004). However, consistent geochemical baselines are still relatively scant and in practice may also only be established on a regional basis, as the grain size, mineralogical and chemical composition of suspended matter of Brazil's tropical rivers varies greatly in accor-

dance to the regional climate, geological relief and matrix, sedimentology, vegetation cover and human land-uses of the drainage basins (Tintelnot, 1995; Knoppers et al., 1999; Leipe et al., 1999; Leão and Dominguez, 2000; Souza and Knoppers, 2003; Jennerjahn et al., 2006).

This study establishes a regional geochemical baseline for the metals Fe, Mn, Cr, Cu, Ni, Pb and Zn from surface samples and cores taken in several sedimentary environments of the São Francisco river estuary, NE-Brazil. It adopts the normalization procedure of metal concentrations against the dominant conservative grain size proxy of the region and the calculation of enrichment factors with display of concentration scatterplots (Loring, 1991; Schropp et al., 1990; Loring and Rantala, 1992; Covelli and Fontolan, 1997; Abraham, 1998; Covelli et al., 2006; Mil-Homens et al., 2007).

The findings are regarded as a unique example of a tropical humid estuary near to solely impacted by river dams constructed since the late seventies in the middle-lower semi-arid reaches of the São Francisco (SF) river basin (Lat. 10°36'S, Long. 36°23'W; $A_b = 634 \times 10^3 \text{ km}^2$, $L = 2840 \text{ km}$). The dam cascade regulated river flow to a constant Q_r of $2060 \text{ m}^3 \text{ s}^{-1}$ and retained over 94% of the suspended sediments in their reservoirs. The estuaries turbid waters have become transparent and oligotrophic. Material replenishment downstream of the dams is near to negligible and human activities are restricted to rice field agriculture and local diffuse inputs of effluents from small urban settlements. The middle-lower SF river basin is embedded in the morphological unit denominated as the "Late Tertiary Barreiras Formation" comprised of unconsolidated iron-rich alluvial sediments, which borders the entire Brazilian eastern and northeastern shoreline. The Quarternary river delta ($A = 800 \text{ km}^2$, width = 50 km) of the SF estuary is comprised

* Corresponding author. Tel.: +55 21 2629 2210; fax: +55 21 2629 2234.

E-mail addresses: esabadini@gmail.com (E. Sabadini-Santos), bastiaan.knoppers@pq.cnpq.br (B.A. Knoppers), eliane.padua@gmail.com (E. Padua Oliveira), thomas.leipe@io-warnemuende.de (T. Leipe), santelli@geoq.uff.br (R.E. Santelli).

¹ Tel.: +55 21 2629 2210; fax: +55 21 2629 2234.

² Tel.: +49 381 5197 381; fax: +49 381 5197 352.

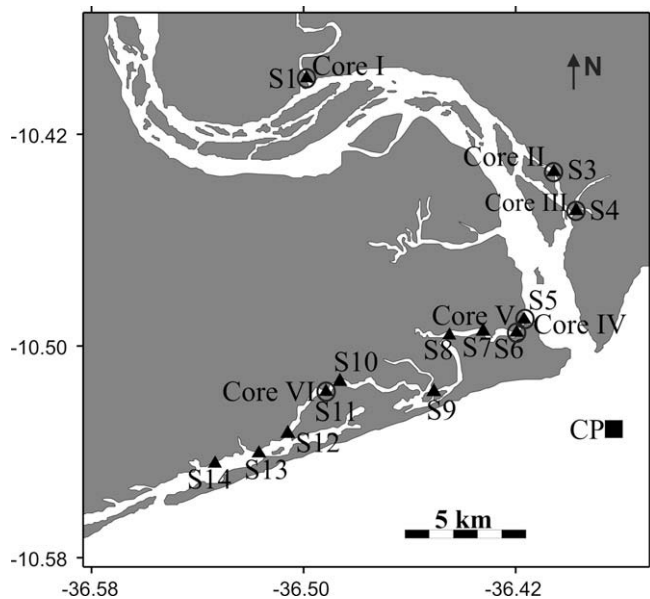


Fig. 1. Location of surface sediments (\blacktriangle) and cores (\circ) collected in the São Francisco estuary. The square symbol (\blacksquare) represents a muddy deposit sampled at the pro-delta (St. CP) off the river mouth. Note: circle with triangles (\triangle) correspond to sites where surface and cores sediments were collected simultaneously.

of alluvial sediments, sand dunes along its northern shoreline, and a main river channel reaching 12 m depth and a smaller and shallower mangrove dominated secondary channel (Fig. 1; Tintelnot, 1995; Leão and Dominguez, 2000; Marques et al., 2004; Knoppers et al., 2006; Medeiros et al., 2007).

A total of 127 sediment samples, including 15 from the surface (S) and 122 from 06 short cores (C I to C VI, $L < 45$ cm), were collected at depositional river banks along the main and secondary channels of the estuary (Fig. 1). Surface samples were taken with a Van Veen Type grab and the cores with a manual piston type corer and acrylic tubes. One surface sample was obtained from the pro-delta muddy deposits off the river mouth (St. CP, Fig. 1), two cores (C I and C II) from the fluvial end-member, three (C III, C IV and C V) along the estuarine gradient and one (C VI) from a small embayment bordered by mangroves. The cores were split at 2 cm intervals. Prior to storage, sub-samples were taken for grain size analyses and the remainder kept frozen in Zipp-Loc[®] plastic sachets prior to processing.

Grain size was analyzed with a laser optical particle size analyzer CILAS 1180L. Dried sub-samples (0.2 g) were prepared by adding H_2O_2 to remove organic matter, followed by a treatment in an ultrasonic bath and addition of potassium polyphosphate to avoid re-coagulation (Ziervogel and Bohling, 2003). The metals (Fe, Ti, Mn, Cr, Cu, Ni, Pb and Zn) were determined after acid digestion with an Ultima 2 sequential inductively coupled plasma optical emission spectrometer (ICP-OES, Jobin-Yvon, France). Total digestion of sediment samples (0.5 g) was performed in Teflon beakers using a mixture of concentrated HNO_3 , HF and HCl (3:2:2 v/v/v) at 100 °C until dryness (Fizman et al., 1984). The variation coefficient for triplicates of the same sample was lower than 10%. Standard reference material (NIST-1646a), supplied by the National Institute of Standards and Technology (USA), was used to estimate the accuracy of the method; recovery rates for the metals were 93% for Fe; 99% for Ti; 78% for Mn; 77% for Cr; 81% for Cu; 82% for Ni; 76% for Pb and 85% for Zn. Statistical procedures involved the establishment of normality with the Shapiro-Wilk test and Pearson correlation and linear regressions with the software package STATISTICA[®] (StatSoft Inc., Tulsa, OK, USA). Sample station locations

were positioned by GPS (Garmin II) and plotted with the Surfer Version 8.00 software (Golden Software, Inc., USA).

The surface and core sediments exhibited a marked heterogeneity in grain size composition brought about by the different hydrodynamic conditions which operate in the main and secondary channels of the estuary, as well as, the depositional changes induced by the dams since the 70s. The contribution of the clay fraction ($< 2 \mu m$) was in all low, varying from 1% to 17% and of silt from 1% to 93% (Table 1). Sandy sediments were dominant at the inner portion of the SF river mouth (St. S4, S5 and S6, top of C III, C IV and C V) and at the seaward end of the secondary SF channel (St. S12, S13 and S14), all exposed to the interaction between river flow and mesotidal action. The deposition of finer sediments was encountered at the fluvial end-member of the estuary (St. S2, C I), the choked central part of the secondary SF mangrove channel (St.'s S9, S11 and C VI) and the pro-delta (St. CP, i.e., 89% silt and 9% clay). Station CP reflects a relict deposit from pre-dam conditions being eroded by wave and tidal action and is regarded as a reference for the bottom core inventories (Knoppers et al., 2006; Santos, 2007). All cores contained a sandy top varying from 0 to about 12 cm depths and finer sediments down core (Table 1). The sandy top layers suggest that sand shoaling, river bank erosion and gradual insilting have been taking place by hydrographical changes induced by the dams (ANA, 2003; Marques et al., 2004). However, the mangrove environment represented by Core VI with its highest concentrations of fine sediments still served as an efficient trap for fine materials, being most similar to the conditions of St. CP of the pro-delta.

Total metal concentration ranges of the surface samples and the cores were (Table 1): 0.35–4.30% for Fe; 187–257 $mg\ kg^{-1}$ for Mn; 10–82 $mg\ kg^{-1}$ for Cr; 1–26 $mg\ kg^{-1}$ for Cu; 2–27 $mg\ kg^{-1}$ for Ni; 4–16 $mg\ kg^{-1}$ for Pb; and 1–57 $mg\ kg^{-1}$ for Zn. The inter- and intra-specific variability of metal core inventories oscillated within a factor of 3–6, depending on the metal. Highest metal concentrations associated to finest sediments were found at the fluvial end-member (C I and C II), the mangrove embayment (C VI), the marine pro-delta (CP) and also at mid-core depths of the remainder (C III, C IV and C V) set within the more hydrodynamic portion of the estuary.

Concentration levels of all metals are within the same order of magnitude and range as sediments from the Capivari river, located on a high-relief forest-covered pristine island off Rio de Janeiro state, considered a reference site for the SE Brazilian coast (DePaula and Mozeto, 2001). Similar low metal levels have also been reported from mangroves in Singapore (Cuong et al., 2005), the Gomti river, India (Singh et al., 2005) and the Brisbane river, Australia (Mackey et al., 1992). The moderately impacted organic-rich and enclosed coastal lagoons of Rio de Janeiro (Lacerda et al., 1992, 1999) and the Chinese mangroves of western Xiamen Bay (Zhang et al., 2007) and the Pearl river estuary (Liu et al., 2002) harbor metal concentrations 2–5 times higher than the SF estuary. Highly impacted systems such as Guanabara Bay, Rio de Janeiro (Kehrig et al., 2003), and Mai Po, Hong Kong (Ong Che, 1999) present sedimentary metal contents several orders of magnitude higher. Unfortunately, Brazil still lacks a regional reference guideline for sedimentary environments. However, by adopting NOAA's screening reference guideline (Buchman, 1999), the SF sedimentary metal concentrations fall close to or below the category of the threshold effects level (TEL). Only for a small number of surface and core samples with the highest fractions of fine sediments, Cr and Ni concentrations reached the category of the effect range-low (ERL). In comparison to the Chinese sediment quality guideline cited in Zhang et al. (2007), all metals met the primary quality standard criteria.

Positive significant correlations between all metals and the fine sediment fraction $< 63 \mu m$ (Table 2) indicated that they are locked

Table 1Grain size and geochemical data of sediment samples from the SF river estuary, 15 from the surface (S) and 122 from 06 cores (C I to C VI). Metal concentrations in mg kg⁻¹.

Sample	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Fe	Mn	Cr	Cu	Ni	Pb	Zn
S1	0–5	5	59	35	2.09	91	38	8	10	12	17
S2	0–5	9	91	0	3.58	141	66	26	27	16	48
S3	0–5	7	59	34	1.63	136	41	9	10	11	16
S4	0–5	3	17	81	0.74	66	19	2	3	5	1
S5	0–5	5	36	59	1.27	101	45	6	8	8	18
S6	0–5	3	24	73	1.21	67	40	5	6	8	5
S7	0–5	6	40	54	2.03	91	40	8	8	11	11
S8	0–5	4	27	70	1.07	98	35	4	4	7	3
S9	0–5	17	82	1	3.28	239	69	17	20	15	35
S10	0–5	3	17	80	0.70	45	20	3	3	6	1
S11	0–5	14	73	13	2.16	82	59	12	13	11	8
S12	0–5	4	23	73	0.59	27	15	2	3	5	10
S13	0–5	3	19	73	0.71	38	33	5	4	5	1
S14	0–5	4	29	67	1.84	73	53	9	13	9	14
CP	0–5	9	89	1	3.28	196	82	15	21	12	35
Core I-1	0–2	6	57	38	2.10	71	34	9	12	5	16
Core I-2	2–4	6	63	31	2.43	85	38	10	14	7	20
Core I-3	4–6	6	69	25	2.24	68	38	9	13	6	19
Core I-4	6–8	6	65	29	2.48	108	40	10	14	8	23
Core I-6	10–12	6	65	29	2.00	59	39	10	13	6	17
Core I-7	12–14	6	61	33	2.05	84	38	9	13	8	21
Core I-8	14–16	6	66	28	1.55	91	35	8	12	9	17
Core I-9	16–18	6	68	26	1.93	123	39	10	14	9	22
Core I-10	18–20	6	63	31	1.87	139	38	9	13	12	21
Core I-11	20–22	5	65	29	1.84	102	39	10	14	8	20
Core I-12	22–24	7	69	25	2.00	118	43	11	14	8	20
Core I-13	24–26	7	68	25	1.92	117	41	11	15	9	21
Core I-14	26–28	8	78	14	2.60	179	51	14	19	13	30
Core I-15	28–30	7	74	19	2.34	128	44	11	16	11	26
Core I-16	30–32	7	69	24	2.04	105	44	12	17	10	23
Core I-17	32–34	8	69	23	1.89	131	41	10	14	10	23
Core I-18	34–36	9	79	12	2.81	78	53	17	22	9	31
Core I-19	36–38	6	68	26	1.64	94	37	9	13	7	17
Core I-20	38–40	8	73	19	2.22	162	45	11	16	9	23
Core I-21	40–42	6	64	30	1.93	131	39	9	13	10	22
Core II-1	0–2	7	67	27	2.50	162	50	15	16	12	30
Core II-2	2–4	8	81	11	1.65	192	42	11	12	11	24
Core II-3	4–6	9	86	6	3.43	194	64	22	24	14	45
Core II-4	6–8	8	77	15	2.62	140	52	15	17	12	30
Core II-5	8–10	9	83	8	3.40	180	61	18	20	14	37
Core II-6	10–12	9	76	16	2.80	130	51	14	16	12	28
Core II-7	12–14	8	71	21	1.19	121	43	12	14	11	27
Core II-8	14–16	8	67	24	0.66	106	40	11	12	10	23
Core II-9	16–18	11	78	11	3.05	117	54	16	18	10	34
Core II-10	18–20	10	80	10	3.00	119	56	16	18	12	33
Core II-11	20–22	10	86	4	3.14	194	55	18	20	13	39
Core II-12	22–24	9	83	8	2.60	188	55	17	19	13	36
Core II-13	24–26	11	75	14	2.37	153	49	14	16	13	32
Core II-14	26–28	10	74	17	1.77	161	50	17	17	13	33
Core II-15	28–30	6	45	49	2.18	153	47	11	12	11	25
Core II-16	30–32	10	77	13	3.13	192	41	15	17	12	33
Core II-17	32–34	9	73	18	1.85	153	51	13	15	13	32
Core II-18	34–36	8	70	22	2.08	127	46	17	13	11	25
Core III-1	0–2	3	21	75	0.86	152	19	3	5	6	9
Core III-2	2–4	5	34	61	1.19	72	24	5	7	6	12
Core III-3	4–6	4	26	70	1.03	84	23	4	6	6	10
Core III-4	6–8	2	14	83	0.65	38	22	3	4	4	6
Core III-5	8–10	2	17	81	0.53	39	13	3	4	5	7
Core III-6	10–12	3	20	77	0.76	45	19	3	4	4	7
Core III-7	12–14	6	43	50	1.23	76	29	6	8	5	13
Core III-8	14–16	5	34	61	1.01	48	21	5	7	4	9
Core III-9	16–18	9	56	35	1.47	72	36	9	11	5	15
Core III-10	18–20	7	44	49	1.00	50	24	5	7	4	10
Core III-11	20–22	8	58	34	1.27	46	27	7	9	4	11
Core III-12	22–24	9	65	26	1.57	69	35	10	12	6	17
Core III-13	24–26	9	52	39	1.30	60	28	8	10	5	13
Core III-14	26–28	7	47	46	1.07	41	25	6	8	4	11
Core III-15	28–30	8	56	36	1.37	61	28	8	9	5	13
Core III-16	30–32	9	68	23	1.51	67	33	9	11	5	15
Core IV-1	0–2	4	25	72	1.12	76	23	5	7	6	57
Core IV-2	2–4	5	29	67	0.91	71	19	3	5	7	10
Core IV-3	4–6	1	6	93	0.43	44	12	1	2	5	5

(continued on next page)

Table 1 (continued)

Sample	Depth (cm)	Clay (%)	Silt (%)	Sand (%)	Fe	Mn	Cr	Cu	Ni	Pb	Zn
Core IV-4	6–8	2	10	88	0.55	54	15	2	3	6	8
Core IV-5	8–10	7	54	39	2.26	134	38	10	12	12	21
Core IV-6	10–12	9	66	25	3.01	184	45	12	15	12	28
Core IV-7	12–14	8	68	24	3.11	175	52	14	17	10	34
Core IV-8	14–16	6	55	38	1.86	74	33	8	11	7	23
Core IV-9	16–18	5	43	52	1.97	85	33	7	11	9	27
Core IV-10	18–20	7	53	40	2.57	139	39	10	13	9	29
Core IV-11	20–22	9	76	15	3.50	234	56	15	22	12	45
Core IV-13	24–26	8	73	20	4.31	257	59	16	20	15	46
Core IV-15	28–30	3	20	78	0.84	68	17	2	5	7	20
Core IV-16	30–32	3	19	78	0.60	18	14	2	4	6	14
Core IV-17	32–34	2	15	83	0.98	76	17	3	6	7	24
Core IV-18	34–36	3	21	76	0.99	36	20	3	6	6	16
Core IV-19	36–38	4	30	66	1.38	100	27	5	8	8	15
Core IV-20	38–40	2	13	85	0.64	50	16	2	3	7	8
Core V-1	0–2	3	19	78	0.81	91	20	3	5	6	8
Core V-2	2–4	4	25	71	0.95	81	23	4	6	7	12
Core V-3	4–6	4	30	66	1.20	130	31	6	8	8	31
Core V-4	6–8	8	66	26	2.30	115	46	10	16	10	25
Core V-5	8–10	6	57	37	1.71	117	34	7	12	9	20
Core V-6	10–12	6	47	47	1.33	107	34	6	9	7	16
Core V-7	12–14	5	46	48	1.23	91	28	5	9	7	16
Core V-8	14–16	4	34	61	1.04	89	24	4	7	7	12
Core V-9	16–18	3	24	73	0.89	81	28	4	6	6	10
Core V-10	18–20	2	8	91	0.54	62	14	3	4	5	16
Core V-12	22–24	2	14	84	0.60	55	15	2	4	6	7
Core V-13	24–26	5	40	55	1.33	91	30	7	9	8	16
Core V-14	26–28	3	21	76	0.69	81	19	3	5	6	8
Core V-15	28–30	2	9	89	0.39	59	14	2	2	4	5
Core V-16	30–32	2	8	90	0.35	49	10	1	2	5	4
Core V-17	32–34	2	11	87	0.46	60	15	2	3	5	6
Core V-18	34–36	3	20	78	0.64	61	20	3	5	6	8
Core VI-1	0–2	4	24	72	1.05	71	42	4	5	8	11
Core VI-2	2–4	7	39	54	1.23	72	31	6	7	9	26
Core VI-3	4–6	11	73	16	2.51	76	31	12	14	11	29
Core VI-4	6–8	12	73	15	2.34	59	50	12	8	12	28
Core VI-5	8–10	12	68	20	2.23	75	53	10	12	11	25
Core VI-6	10–12	13	79	8	3.00	85	46	15	17	11	42
Core VI-7	12–14	13	80	7	2.80	68	55	14	17	13	42
Core VI-8	14–16	10	66	24	1.96	71	58	9	10	10	21
Core VI-9	16–18	13	75	12	2.54	82	37	13	16	12	34
Core VI-10	18–20	13	77	10	2.74	76	55	14	16	11	32
Core VI-11	20–22	12	77	11	2.66	89	59	13	14	12	30
Core VI-12	22–24	13	76	11	2.79	86	54	14	17	13	31
Core VI-13	24–26	13	81	6	2.82	94	59	16	18	12	43
Core VI-14	26–28	14	81	5	2.73	83	64	15	18	13	42
Core VI-15	28–30	15	84	1	3.50	103	66	19	23	14	50
Core VI-16	30–32	14	84	2	2.97	86	68	17	17	13	34
Core VI-17	32–34	14	84	2	2.88	73	67	16	15	15	33
Core VI-18	34–36	14	86	1	3.18	83	75	19	22	14	39
Core VI-19	36–38	13	84	3	3.35	99	72	18	22	14	37
Core VI-20	38–40	13	85	2	3.41	97	81	19	18	14	40
Core VI-21	40–42	13	84	3	2.97	71	62	16	19	12	43
Core VI-22	42–44	14	83	3	3.24	88	71	18	23	14	38
Core VI-23	44–46	13	80	8	3.19	80	72	18	21	13	47

Table 2

Correlation matrix of grain size and geochemical data. All coefficients were significant ($p < 0.0001$, $n = 127$).

	Clay	Silt	Sand	Fe	Mn	Cr	Cu	Ni	Pb	Zn
Clay										
Silt	0.87									
Sand	−0.90	−1.00								
Fe	0.80	0.88	−0.88							
Mn	0.32	0.55	−0.53	0.61						
Cr	0.84	0.86	−0.87	0.89	0.52					
Cu	0.83	0.92	−0.93	0.92	0.58	0.91				
Ni	0.79	0.93	−0.92	0.93	0.62	0.89	0.96			
Pb	0.75	0.79	−0.79	0.85	0.65	0.86	0.86	0.83		
Zn	0.73	0.77	−0.77	0.84	0.55	0.77	0.84	0.85	0.81	

up physically and/or chemically in detrital particles and minerals originating from a single Fe-rich lithogenic source (i.e., latosols) of the Tertiary basin. The correlations revealed that Fe is the most suitable conservative element for metal normalization procedures in the region. In general, the rivers of E- and NE-Brazil are the main source of smectite and illite particles largely coated with iron oxyhydroxides to the estuarine and nearshore coastal sediments (Tintelnot, 1995; Leipe et al., 1999; Souza and Knoppers, 2003). Iron has also been successfully used as a normalizer in other studies (Sinex and Wright, 1988; Szefer, 1990; Herut et al., 1993; Morse et al., 1993; Kennicutt et al., 1994; Covelli and Fontolan, 1997; Tam and Yao, 1998).

Metal scatter plots depicted in Fig. 2 for all surface and core samples normalized against the Fe grain size proxy exhibited sig-

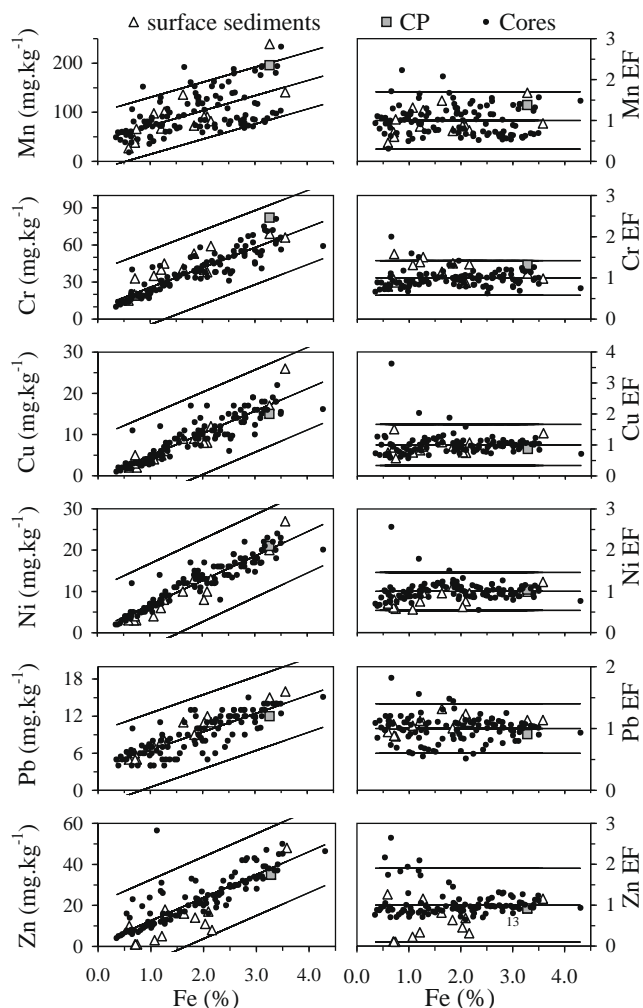


Fig. 2. Relationship between Fe and Mn, Cr, Cu, Ni, Pb and Zn concentrations (left column) and their enrichment factors (EF; right column) in surface sediments (Δ), the pro-delta sediment (\square) and core samples (\bullet) from the São Francisco river estuary. Middle lines represent the regression equation (left column) and EF equal to one (right column). Potentially anomalous concentrations and EFs lying outside the upper and lower lines, defined as $\pm 2\sigma$ range (σ = standard deviation).

Table 3

Regression results ($y = a + bx$) of metal concentrations (y) against Fe (x) for the São Francisco estuarine system.

	a	b	r	p	n
Mn	45.02	26.27	0.60	<0.0001	120
Cr	9.41	16.14	0.89	<0.0001	127
Cu	-0.52	5.40	0.92	<0.0001	127
Ni	0.79	5.91	0.93	<0.0001	127
Pb	3.56	2.94	0.85	<0.0001	127
Zn	0.38	11.54	0.89	<0.0001	126

nificant linear relationships of each metal against Fe and the 95% prediction limits and enrichment factors oscillating close to 1, reflecting baseline conditions throughout the pre- and post-dam periods and the range of regional natural variability. In spite of the large variations in grain size and environmental conditions within the SF estuary, the similar scatter plot patterns show that all metals behaved according to the variability of the Fe grain size proxy, suggesting that it is a suitable reference tool for the recog-

nition of anthropogenic inputs. The large data set of this study posed a favorable setting for the application of this tool. The usefulness of scatter plots of element concentrations against grain size or the Fe grain size proxy for normalizing geochemical data, as well as to discern between natural and anthropogenic enrichments, has been discussed extensively by Loring (1991), Loring and Rantala (1992) and Covelli and Fontolan (1997).

A negligible amount of outliers falling slightly beyond these limits was removed from the original data matrix for the recalculation of linear regressions (Table 3), herewith defined as the regional normalization functions useful for future environmental assessments of sediment quality. Results of the enrichment factors (i.e., the ratio between real and predicted values) lying outside the range $1 \pm 2\sigma$ (σ = standard deviation) are considered as being potentially anomalous, such as the concentrations of Mn, Zn, Cu and Ni at mid-core depths of Core II at the middle portion of the estuary (Table 2; Fig. 2).

It seems that metal concentrations between the pre- and post-dam periods maintained themselves within similar and even pristine levels. The top sandy layers down to 0–12 cm depths of the cores reflect the period affected by the dams which reduced water flow and the load of suspended matter to the estuary and enhanced sediment shoaling (Knoppers et al., 2006), and the bottom of the cores the pre-dam conditions, coinciding with the lowest metal concentrations. However, concern is on the increase due to the expansion of shrimp farming and the introduction of some trace metals, mainly Cu, from aquafeeds within the secondary channel bordered by mangroves. This activity has already affected other mangrove estuaries along the NE-Brazilian coastline (Silva et al., 2003; Madrid, 2004; Lacerda et al., 2006) and other regions of the world (Boyd and Massaut, 1999; Chou et al., 2002; Tacon and Forster, 2003). Furthermore, sugar-cane monoculture is now being implemented within the middle-lower SF basin, suggesting that metal emissions from land erosion could gradually affect the estuary. The present case study may be useful for future comparisons of metal related impacts.

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