Bull Environ Contam Toxicol (2013) 90:318–322
DOI 10.1007/s00128-012-0914-2

Trace Metals in Settling Particles from the Sewage Impacted Buenos Aires Coastal Area in the Río de la Plata Estuary, Argentina

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Received: 10 August 2012 / Accepted: 28 November 2012 / Published online: 11 December 2012

Abstract Sediment traps deployed in Buenos Aires sewage outfall area collected a substantial amount of material (average mass flux 22 ± 12 g cm ^{2} year^{-1}) with very high metal concentrations, mostly in the range of hazardous exposition for organisms (Zn: 138–671, Cu: 41–273, Cr: 44–255 and Pb: 26–260 μg g^{-1}). The combination of high mass fluxes and concentrations results in huge metal fluxes (0.005–0.7 to 3.6–31 g m^{-2} day^{-1} for minor elements and Fe, respectively). Metal concentrations were correlated to the total mass flux and total organic carbon but with different trends for redox-sensitive Fe and Mn (negative) and anthropogenic elements (positive). This reflects the key role of organic discharges promoting anoxia with Fe and Mn evasion, and also contributing toxic metals.

Keywords Metals · Sewage outfall · Settling particles · Río de la Plata

Disposal of sewage effluents to coastal and estuarine waters is a common practice in many large coastal cities worldwide representing a significant source of metals, nutrients, microorganisms, and persistent organic contaminants (Chambers et al. 1997). The Río de la Plata, a coastal plain turbid estuary with an average fresh water flow of 22,000 m^3 s^{-1} (Fig. 1), is not an exemption and Buenos Aires coastal area receives ~2 million m^3 per day of untreated effluents from the most populated and industrialized area of Argentina. This heavy anthropogenic input results in large vertical fluxes of organic carbon, aliphatic hydrocarbons, and polychlorinated biphenyls (Colombo et al. 2005a, b, 2007). In addition, the Riachuelo's Port and several polluted channels discharge an unknown amount of chemicals to the coastal area. A previous work in the area (Tatone et al. 2009) indicated exponentially decreasing gradients of trace metals with distance offshore in surface sediments and highest concentrations of anthropogenic metals in the sewer area. In this paper we report a detailed evaluation of trace metal concentrations, vertical fluxes, and temporal variability in settling material collected in the Buenos Aires sewer area.

Materials and Methods

Settling particles were collected 1.5 m below the surface during 23 trap deployments covering spring, summer, autumn and winter during 2004–2011. The settling material was collected with two fixed 10 cm-diameter bi and tricylindrical traps (total surface: 157–235 cm^2) deployed 100–200 m from the sewer for <1–8 days. The material collected by the traps was immediately centrifuged and split for total organic carbon analysis (TOC; catalytic combustion with a Thermo Finnnigan, CE FlashEA 1112

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elemental analyzer) and trace metal determination (Tatone et al. 2009). Briefly, after digestion at 100°C with aqua regia, trace metals were determined by flame atomic absorption spectrophotometry (Thermo Elemental Solaar M5). The quantification limits ranged from 0.38 μg g^{-1} for Zn to 2.00 μg g^{-1} for Pb. Analytical blanks were negligible, the variability in the precision was below 10 % and the analysis of certified reference materials (soil: CRM020-050 RTC; sewage sludge: CRM005-050 RTC) indicated recoveries of 68 %–135 % for Ni and Cr in soil and of 74 %–98 % for Cr and Zn, in sewage sludge. Pearson correlation analyses were performed among metals, TOC, total mass flux, and river flux. A Student t test ($p < 0.05$) was used to compare warm-rainy months with cold-dry periods.

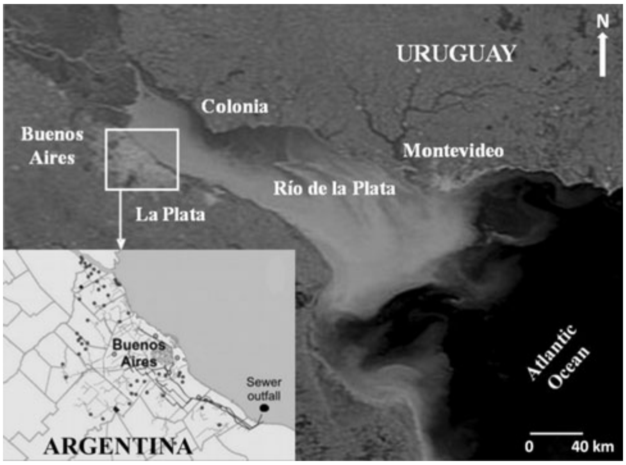


Fig. 1 Study area in the Río de la Plata estuary showing the sewer outflow of the metropolitan Buenos Aires area

Results and Discussion

The trap collected a substantial amount of material (Table 1) with average total mass flux of 21.8 ± 11.8 g cm^2 $year^{-1}$ (sedimentation rate: 8.2 ± 4.4 cm $year^{-1}$, density 2.65 g cm^{-3}) reflecting anthropogenic discharges but also the natural high turbidity of the estuary. The settling material contained higher TOC content relative to bottom sediments (9.0 % ± 5.4 % vs. 1.9 %, Tatone et al. 2009), pointing to an enrichment in the finer material

Table 1 Total organic carbon (TOC) and trace metal contents of settling particles

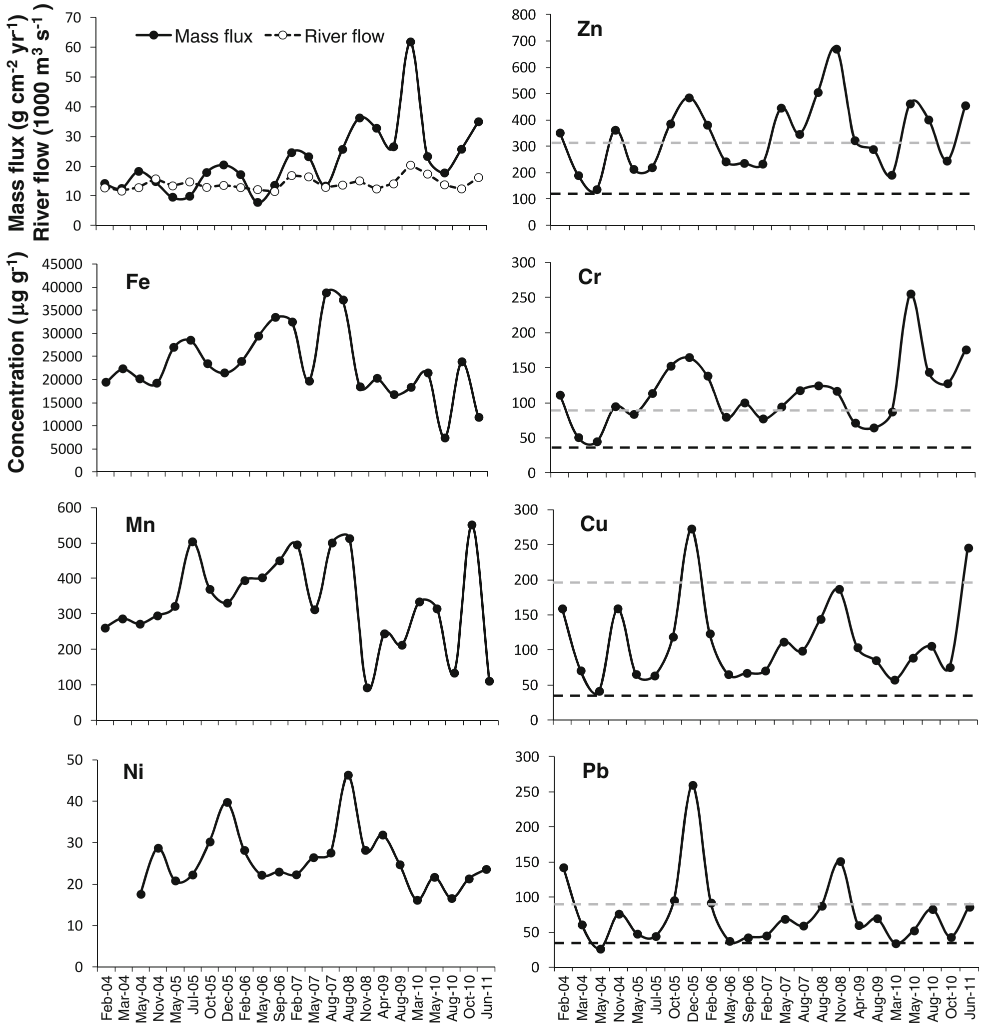
Date	Hours	Mass flux	TOC	Fe	Mn	Zn	Cu	Cr	Pb	Ni
		g cm^{-2} yr^{-1}	(%)				μg g^{-1}			
February 04	36	14.2	10.6	19421	261	353	159	111	142	–
March 04	20	12.5	4.7	22333	287	191	70	50	61	–
May 04	45	18.3	2.2	20156	272	138	41	44	26	18
November 04	24	14.8	12.4	19219	295	363	159	94	76	29
May 05	34	9.6	3.2	26968	322	215	65	83	48	21
July 05	25	9.9	3.3	28506	504	221	63	113	44	22
October 05	48	17.9	12.1	23429	370	387	119	152	95	30
December 05	35	20.4	14.4	21439	331	486	273	164	260	40
February 06	28	17.2	9.2	23921	395	382	123	138	92	28
May 06	192	7.8	4.8	29396	403	243	65	79	37	22
September 06	29	13.6	4.5	33454	451	237	67	100	42	23
February 07	25	24.6	4.2	32440	495	235	70	77	45	22
May 07	43	23.2	14.1	19655	313	447	111	94	69	26
August 07	36	13.3	7.7	38748	501	347	98	117	59	28
August 08	25	25.7	–	37199	513	506	144	124	87	46
November 08	26	36.2	21.3	18424	92	671	187	116	151	28
April 09	17	32.8	5.1	20269	245	324	103	71	60	32
August 09	48	26.6	8.5	16745	213	290	85	64	70	25
March 10	25	61.8	–	18311	335	192	57	87	34	16
May 10	48	23.3	–	21426	315	463	88	255	52	22
August 10	23	17.8	17.3	7370	134	402	105	143	83	17
October 10	26	25.7	4.8	23845	552	246	75	127	43	21
June 11	36	35.0	14.72	11822	111	456	245	175	86	24
Grand mean		21.8	9.0	23239	335	339	112	112	77	26
SD		11.8	5.4	7525	130	129	60	47	51	7.3

collected by the traps and a strong decay of organic matter at the sediment–water interface.

Trace metal concentrations in settling particles are very high, 1–2 times higher than values previously reported for underlying sediments (Tatone et al. 2009), reflecting a metal enrichment in the fine and organic rich material captured by the traps. The enrichment is selective for anthropogenic elements with average trap/sediment metal ratios decreasing from Cr (2.1) > Zn (1.7) > Ni (1.6) ~ Cu (1.6) > Pb (1.3) ~ Mn (1.3) > Fe (1.2). Río de la Plata metal concentrations are comparable with those reported for settling particles from sewage impacted areas in Massachusetts Bay, EEUU (Bothner et al. 2002), Sydney, Australia (Matthai et al. 2002) and Seine River, France (Gasperi et al. 2009). In order to evaluate the possible risks associated with trace metals, sediment trap concentrations are compared with Canadian sediment quality guidelines for the protection of aquatic life (CCME 2001). Concentrations of Zn, Cu, Cr, and Pb in settling particles are mostly in the SQG-PEL range suggesting that occasional adverse effects could exist for aquatic biota (Fig. 2). In contrast to surface sediments of the Río de la Plata which did not exceed PEL levels (Tatone et al. 2009) several trap values are higher than PEL suggesting frequent biological effects (i.e. Cr: 15 samples > 90 μg g^{-1}; Zn: 13 > 315 μg g^{-1}; Pb: 5 > 91.3 μg g^{-1}; Cu: 2 > 197 μg g^{-1}).

Trace metal average concentrations discussed above present high variability (RSD: 28 %–66 %) mainly related to the total mass flux and the river flow. Figure 2 presents the temporal variability of the total mass flux, Paraná River flow, and trace metal contents of settling particles. Total mass fluxes ranged between 7.8 and 61.8 g cm^2 $year^{-1}$ with minimum values usually corresponding to winter months (May, July, August), and most peaks in the warm season (November, December, February, March). The total mass flux is significantly correlated ($R^2 = 0.46$, $p < 0.05$) with the Paraná River flow (SRH, 2011) whose turbid waters form a distinct water corridor along the Río de la Plata's Argentinean coast (Piedra-Cueva and Fossati 2007). The increase of water flow during rainy warm periods

Fig. 2 Temporal variability of the total mass flux, Paraná River flow (*upper left*) and trace metal concentrations of settling particles. The *horizontal lines* show guidelines of sediment quality for protection of aquatic life, in black the SQG and in gray the PEL



favors the erosion and transport of material into the river mainstream and secondary affluents. Metal concentration in the settling material do not show significant differences ($p < 0.05$) between warm-rainy months (October and March) compared with cold-dry periods (April and September) as observed for organic pollutants (Colombo et al. 2007). However, two consistent peaks were observed for Zn, Cu, and Pb in December 2005 and November 2008 possibly reflecting the wash out and a more efficient transport of metals from polluted channels and ports during the wet summer.

Trace metal concentrations are correlated to the total mass flux and TOC but with different patterns for major, redox-sensitive and anthropogenic elements. Figure 3 presents the correlation of Mn (redox-sensitive), Zn (anthropogenic), and TOC (mostly anthropogenic) with the total mass flux. Mn presents a significant decreasing trend with the total mass flux whereas both TOC and Zn show an opposite increasing pattern. A similar contrasting behavior with the total mass flux is observed for Fe (negative), and Cu, Cr, Ni, and Pb (positive). The different pattern of redox-sensitive and anthropogenic metals with TOC is reflected by the opposing regressions. Whereas both Mn and Fe show an inverse relationship with TOC ($R^2 = 0.41$–0.36, respectively; $p < 0.05$), the other metals show a direct increasing pattern ($R^2 = 0.88$, 0.56, 0.43, 0.36 for Zn, Cu, Pb, and Cr, respectively; $p < 0.05$). The decrease of both Fe and Mn with increasing TOC average 13 %–15 % when TOC increase from <5% to 5 %–15 % and reach 52 %–71 % when TOC is higher than 15 %. Anthropogenic metals increase ∼400 %–800 % when TOC rises about 10 times between the extreme regression values. This confirms the interpretation of the different anthropogenic discharge role controlling the dynamic of redox-sensitive elements which are lost through under sub-oxic or anoxic conditions (evasion as dissolved Fe^{+2} and Mn^{+2}) promoted by the higher organic discharges, and anthropogenic metals which increase proportionally with the organic load.

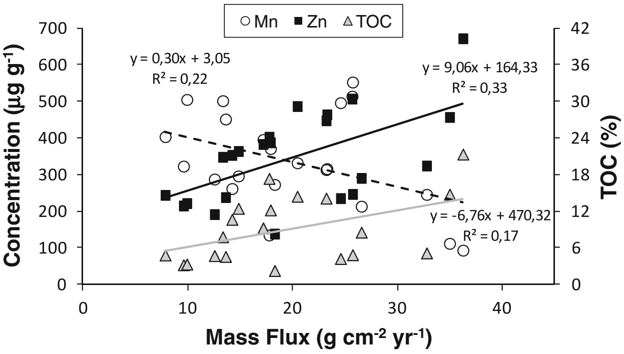


Fig. 3 Regression of Mn, Zn and TOC versus mass flux

The high total sedimentation rates recorded coupled with the high concentrations of metals in the particles resulting in huge vertical fluxes of metals (Ni: 16 ± 8.3, Pb: 46 ± 37, Cr: 68 ± 45; Cu: 70 ± 56, Mn: 189 ± 120, Zn: 210 ± 146, Fe: 13,096 ± 6,560 mg m^{-2} day^{-1}). As observed for organic components (Colombo et al. 2007), these fluxes are among the highest reported in the literature, i.e. they are 10–300 times higher than those observed in coastal marine areas adjacent to Sydney, Australia (0.16–123 mg m^{-2} day^{-1}; Matthai et al. 2002) and eastern Turkish coast of the Black Sea (0.50–120 mg m^{-2} day^{-1}; Ergül et al. 2008). Due to the covariation of metal concentrations in the settling material and the mass flux mentioned above, the variability of the vertical flux of metals results amplified (RSD: 50 %–81 %) in relation to trace metal concentrations (RSD: 28 %–66 %) or mass fluxes (54 %). There are basically two major pulses of anthropogenic metals in December 2005 and November 2008, more evident for Cu (153–185 mg m^{-2} day^{-1}) and Pb (145–150 mg m^{-2} day^{-1}). These pulses are ∼2–3 times higher than average fluxes indicating that discrete pulses represent a major pathway of metal transfer to the bottom increasing the potential risks for benthic organisms.

Acknowledgments Financial support was provided by the National Research Council (CONICET) and the Research Commission from Buenos Aires State (CIC).

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