

Heavy Metals in Urban Channel Sediments of Aveiro City, Portugal

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Abstract—The quantification of six metals: aluminum (Al), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb) and zinc (Zn), alongside with determination of organic carbon (OC) and calculations of C:N ratios was performed from surface sediments collected in urban channels of Aveiro City. The city is located along the shores of the Ria de Aveiro, a coastal lagoon, and until recently the city's channels and some of its oldest areas were tidally submerged by tidal floods. These events alongside with the impacts associated with urban development have contributed to create accumulation of metals in the sediments. Organic enrichment is generalized in the inner city channels whereas the opposite occurs in the outer channels. Significant correlations were established for the original dataset between Al and Cr > Zn > Cd ($R^2 = 0.79, 0.74, \text{ and } 0.69$, respectively), but not for Cu or Pb ($R^2 = 0.25, \text{ and } 0.005$, respectively), pointing to the prevalence of point sources of these two metals. Regressions of Metal/Al were used as the dataset normalizer allowing simultaneously the establishment of mathematical geochemical backgrounds and the consequent calculation of Enrichment Factors (EF). It was concluded that enrichment occurs in the inner city channels which export metals that are readily dispersed by tidal action.

Keywords: sediment, urban channels, metals, enrichment factors

INTRODUCTION

Estuaries serve as corridors for the transit of terrigenous metal-rich materials (originated from rock or mineral deposit weathering) to the sea, being the main contributor to coastal metal loads (Sharp *et al.*, 1984). The advent of the industrial era, with the associated demographic boom, caused anthropogenic sources to surpass loads created by the action of natural agents (Summers *et al.*, 1996; Rae, 1997). Since historically urbanization developed mainly in the vicinity of waterways, particularly near estuaries, these anthropogenic loads are higher in cities located in such geographic settings. Aquatic contamination from cities can occur from a wide range of sources. Atmospheric deposition, construction materials, road wear, tire wear, vehicle wear, soil, vegetation, and building wear (Taylor, 2007), just to cite a few, that despite its origin find a common fate—

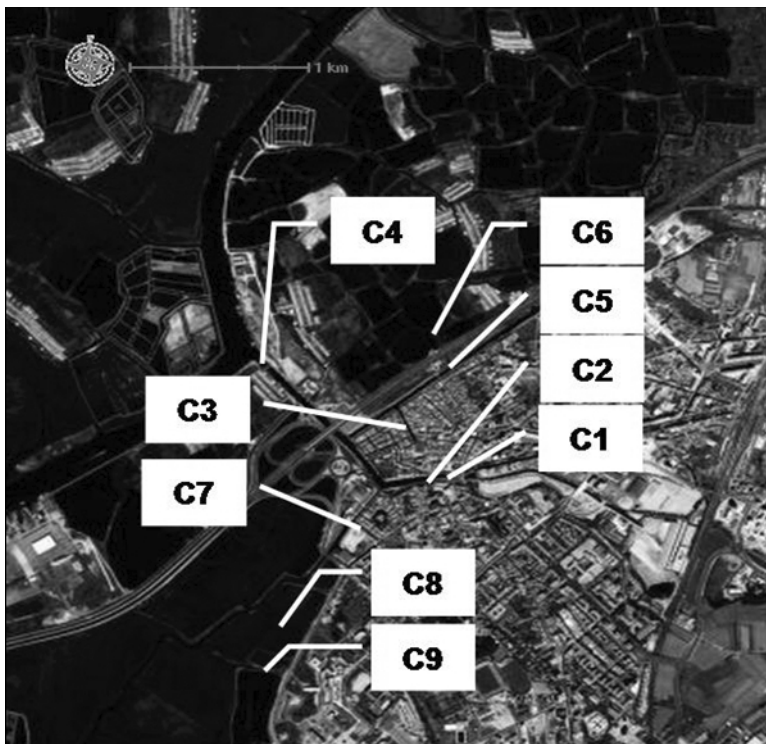


Fig. 1. Aerial view of the Aveiro City with location of sampling stations. Source: Instituto Geográfico Português (<http://www.igeo.pt/>).

deposition in sediments. Sediments in urban waterways, given their action as vectors of metal transfer and metal storage become thus a major factor on these ecosystems health (Taylor, 2007).

The city of Aveiro ($40^{\circ}38'9''$ N, $8^{\circ}40'29''$ W - Fig. 1) is situated on the shores of a coastal lagoon also mentioned as a “bar built estuary” (Ria de Aveiro, $40^{\circ}38'$ N, $8^{\circ}44'$ W) (Dias *et al.*, 2001). The oldest part of the city is inundated by this body of water through several channels, that according to the tidal phase can be totally dry or, until the recent past, flooding from its course invaded the streets. This peculiarity strengthens the normal impacts cities generate in urban water bodies, being these impacts often translated in added accumulation of metals in the bottom sediments (Cheung *et al.*, 2003). Given the variability of matrices usually present in natural sediments and consequently in the retention capability of contaminants, it becomes essential to apply a normalizing factor (dataset normalization) in order to allow comparisons between samples. In this study Aluminum was used as a geochemical-based grain-size proxy. Ratios of metal/Al are fairly constant in the earth’s crust (Kersten and Smedes, 2002), possessing

the added advantage over the more traditional granulometric approaches of helping identify technogenic enhancements (Kersten and Smedes, 2002).

The present work quantified concentrations of metals in bottom sediments from channels of Aveiro City, and attempts to identify probable sources of enrichment. In that sense sampling stations were established in inner city and outer perimeter channels in order to evaluate sediment contamination and fluxes of metals between them.

MATERIALS AND METHODS

Sediment collection

Sediments from the bottom of the channels were obtained using a Van Veen type grab sampler. The 5 top cm of each grab (3 grabs per site) were collected with a teflon scoop, stored in polyethylene bags and frozen at -20°C until analysis.

Sediment analysis

The method used for sediment metal analysis is fully described in Pastorinho *et al.* (2009). For the determination of carbon and nitrogen content, three replicate sub-samples of each sample were dried at 110°C for 48 hours and run in a Perkin Elmer series II 2400 HNS/O elemental analyzer. To correct for inorganic carbon, a different set of sub-samples were combusted at 550°C for four hours and then processed along with un-combusted samples.

Statistical analysis

Correlation coefficients

After verification of the normal distribution of the dataset by a Kolmogorov-Smirnov test, a Pearson correlation coefficient was used to determine the correlation between the analyzed elements, including organic carbon (OC). All necessary statistics were performed with SigmaStat 5.1 software package.

Normalization procedure

Regression analysis was used to geochemically normalize the dataset and simultaneously ascertain the “normal” or background relationship between Al and a target metal in order to analyse anthropogenic enrichment. Outliers were identified using regression analysis. Residuals of each regression (metal/aluminum and metal/OC) were analyzed for normality (Kolmogorov-Smirnov test). If a normal distribution was not achieved, sites with residuals greater than two standard deviations (positive or negative) were eliminated (following the method developed by Schiff and Weisberg (1999)). The process was repeated the necessary number of times until a normal distribution was achieved for each element (Schiff and Weisberg, 1999). Once the baseline regressions established, the formula

$$\text{EF} = (X_{\text{sample}}/\text{normalizing agent})/(X_{\text{predicted}}/\text{normalizing agent})$$

Table 1. Analytical data for sediment samples collected in Aveiro City channels. All metal values in ug/g, except Aluminium (%). Organic Carbon in %. ERL – Effects Range-Low, as adopted by US EPA (Long *et al.*, 1995).

Station	Zn	Pb	Cr	Cu	Cd	Al	Org C	C:N
C1	99.84	8.49	12.22	15.29	0.16	0.02	1.09	8.38
C2	322.80	42.15	25.78	41.17	0.81	0.17	3.16	11.29
C3	287.87	18.63	26.43	39.48	0.64	0.24	3.14	5.81
C4	332.88	15.73	17.98	33.41	0.47	2.46	3.28	2.45
C5	30.43	18.54	1.05	66.25	0.03	0.19	1.09	7.27
C6	143.81	3.94	13.37	6.10	0.16	1.30	1.93	9.65
C7	373.50	71.73	15.26	114.71	0.61	1.20	3.96	15.23
C8	166.60	14.71	10.15	16.75	0.26	1.45	1.64	2.69
C9	169.26	19.00	6.93	21.31	0.34	1.39	0.80	2.22
ERL	150.00	46.70	81.00	34.00	1.20	—	—	—

where X_{sample} is the element of interest concentration and $X_{\text{predicted}}$ is the predicted value for that element can be applied, leading to an indicative enrichment factor (EF) (Covelli and Fontolan, 1997). EFs are an estimation of the anthropogenic contribution of a given trace element to the sample.

RESULTS AND DISCUSSION

Effects Range Low (Long *et al.*, 1995), is among one of the most widely used sets of sediment quality guidelines (SQGs). Its predictive power has been tested since 1995 against large datasets obtained by US-EPA (United States Environmental Protection Agency) and NOAA (National Oceanic and Atmospheric Administration) monitoring programs containing simultaneously measured chemical and toxicological parameters (O'Connor, 2004). It indicates the probable occurrence of biological effects when metal concentrations in sediment transcend reference values. When compared with this SQG analytical results showed that 67, 11, and 33% of the stations present this possibility for Zn, Pb, and Cu, respectively. For the same metals, concentrations varied between 373.5–30.3, 71.7–3.9, and 114.7–6.1 ug/g, respectively (Table 1). Cr and Cd did not present values above the respective ERL, their variation being between 26.4–1.0, and 0.8–0 ug/g, respectively.

For the metals under appraisal correlation analysis indicated significant positive correlations between Zn and Cr being these metals independently correlated to Cd (Table 2). Cu and Pb are highly significantly correlated among themselves (Table 2) but not to any other of the studied metals. Regarding normalizers (Al and OC) we verified the existence of significant positive correlations with Zn, Cr, and Cd, but not with Pb and Cu. This clearly points to distinct sources for these two metals, whilst the remaining were associated with terrigenous inputs (significant correlations with Al) but mainly (due to the high significance of the correlations with OC) with diffuse anthropogenic sources.

The statistical methodology applied (see “Normalization procedure”) to the

Table 2. Pearson correlation matrix for metal concentrations and organic carbon (OC) of the entire dataset.

	Zn	Pb	Cr	Cu	Cd	Al	OC
Zn	1						
Pb	0.66	1					
Cr	0.76*	0.26	1				
Cu	0.43	0.87**	0.01	1			
Cd	0.91**	0.63	0.85**	0.34	1		
Al	0.74*	0.01	0.79*	-0.25	0.69*	1	
OC	0.92**	0.66	0.75*	0.55	0.80**	0.59	1

*Significance at the 0.05 level.

**Significance at the 0.01 level.

initial dataset gave rise to highly significant regressions of all metals with Al ($p < 0.001$) (Table 3). Despite the reduction of data caused by the statistical methodology applied (upon a *ab initio* a restricted dataset), the geochemical rationalization provided by the regressions metal/Al is highly robust—as documented by several studies (e.g. Schropp *et al.*, 1990; Summers, 1996; Trimble *et al.*, 1999; Wang and Chen, 2000; Armstrong *et al.*, 2005)—endowing relevance to the obtained models. The models showed good agreement between predictions and observations, with predictions generally falling well inside the 95% confidence interval. The exception was Pb which demonstrated a tendency for underpredicting those values.

These models allow the establishment of mathematical geochemical backgrounds which can be used to highlight the existence of man-caused sedimentary metal enhancements and the calculation of the corresponding Enrichment Factors. Metal concentrations are, in essence, site specific (Santchi *et al.*, 2001). One such coefficient constitutes a very useful, powerful and essential tool to assess the history and extension of a contaminated location (Borrego *et al.*, 2002). Due to natural mineralogical differences of the sediments and analytical uncertainty, only sediments with an EF greater than 2 were considered as enriched (Aloupi and Angelidis, 2001).

In general terms, the inner channels yield enriched zones, whereas the peripheral channels show no enrichment whatsoever (Table 4). Stations in the outer perimeter (C4, C6, C8, and C9) showed no evidence of enrichment by anthropogenic metals, together with low C:N ratios, indicated the strong tidal-based hydrodynamics and high microbial activity and/or very low primary production of these areas, respectively. All these stations are located in areas articulating city channels with the main body of the Ria where tidal hydrodynamics are stronger, promoting sediment export (particularly the fine fraction) (Dias *et al.*, 2001), thus leading to uncontaminated samples.

The metal/Al regression model shows (through the negative values of the EFs - Table 4) that in station C5 four metals were depleted (Zn, Cr, Cu, and Cd).

Table 3. Results of the regression applied to Al and the original data set (A) and data set when outliers and influential cases were withdrawn (B). Correlations between all metals and Al were significant (A: $p < 0.05$; B: $p < 0.001$).

Metal	N		R^2		Slope		Intercept	
	A	B	A	B	A	B	A	B
Zinc	9	8	0.55	0.912	0.014	0.015	17.541	-31.725
Lead	9	5	0.005	0.535	1.54E-05	0.001	23.433	-0.67
Chromium	9	6	0.631	0.979	0.001	0.001	-0.288	-2.498
Copper	9	5	0.063	0.708	-0.001	0.002	58.12	-5.899
Cadmium	9	5	0.478	0.95	2.78E-05	1.96E-05	-0.017	-0.04

A - Original data.

B - After removal of outliers.

Table 4. Enrichment Factors calculation for Aveiro City channels.

Station	Zn	Pb	Cr	Cu	Cd
C1	1	1	1	1	1
C2	1	2	2	1	2
C3	1	1	1	1	2
C4	1	1	1	1	1
C5	-11	15	-2	-32	-14
C6	1	0	1	0	1
C7	3	6	2	6	3
C8	1	1	1	1	1
C9	1	1	1	1	1

In this case calculated metal values are higher than the observed concentrations, which consistently points to a depletion of the used geochemical tracer (Al). The most likely explanation is that sediments are being dredged (despite no available records indicating so). Interestingly enough in this station there is a fifteen-fold enrichment of Pb, which directs us to believe that maybe a point source is in place or that amateur fishing activities in this channel are so intense that lead shot is being deposited in great quantities in bottom sediments.

Station C7 deserves special mention since all five metals analyzed registered values (moderately or notoriously) above those of the predicted background. Station C7 is under the direct influence of an urban wastewater outfall. The high C:N ratio (Table 1) indicates allochthonous metal rich organic matter being deposited and only partially degraded. This station is in direct connection with the area where stations C8 and C9 are located. It is again demonstrative of the strong hydrodynamics affecting the latter that metals transferred from the former are not causing perceptible enrichment. Remobilization from deposited sediments by bottom friction and erosion during flood tide (Dias *et al.*, 2001) and ready

transport by outflowing freshwater during ebb tides must be responsible for this outcome.

An interesting spatial variation occurred between neighboring stations C1 and C2. As mentioned, C2 showed metal enrichment in Pb, Cr, and Cd (Table 4), whereas station C1 does not register any enrichment of the analyzed metals. Yet these stations are only 50 m apart. The explanation for this discrepancy lies in the fact that sampling was performed in the opposite sides of the channel. In this area the channel is highly silted and the tide waves excavated a winding “V” shaped progression bed. Sediments representing C1 were collected in this bed while C2 sediments were collected in the soft muddy “bank” area above which several commercial boats are usually docked. This resulted in the observed discrepancy in metal concentrations and organic carbon contents (the latter reflected in markedly higher different C:N ratios) (Table 1).

In conclusion, Al showed significant correlations with the other metals (and organic carbon) demonstrating to be well suited as a normalizing agent for the data set. The area of the study possesses two very opposed situations. One, present in the upper reaches of the city channels with metals presenting enrichment (from diffuse and point sources) and high C:N ratios. The other developing in the outer perimeter, open to the main body of water (the Ria) and, as a consequence mainly of hydrodynamics, staying free from heavy metal concentration and demonstrating very low C:N ratios (averaging 1/3 of the Redfield Ratio). Evidence points towards metal transference from the former to the latter.

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REFERENCES

- Aloupi, M. and M. O. Angelidis (2001): Geochemistry of natural and anthropogenic metals in the coastal sediments of the island of Lesbos, Aegean Sea. *Environ. Pollut.*, **113**(2), 211–219.
- Armstrong, T. N., T. J. Ianuzzi, J. B. Thelen, D. F. Ludwig and C. E. Firstenberg (2005): Characterization of chemical contamination in shallow-water estuarine habitats of an industrialized river. Part II. *Metals, Soil & Sediment Contamination*, **14**, 35–52.
- Borrego, J., J. A. Morales, M. L. de la Torre and J. A. Grande (2002): Geochemical characteristics of heavy metal pollution in surface sediments of the Tinto and Odiel river estuary (southwestern Spain). *Environ. Geol.*, **41**, 785–796.
- Cheung, K. C., B. H. T. Poon, C. Y. Lan and M. H. Wong (2003): Assessment of metal and nutrient concentrations in river water and sediment collected from the cities in the Pearl River Delta, South China. *Chemosphere*, **52**, 1431–1440.
- Covelli, S. and G. Fontolan (1997): Application of a normalization procedure in determining regional geochemical baselines. *Environ. Geol.*, **30**(1/2), 34–45.
- Dias, J. M., J. F. Lopes and I. Dekeyser (2001): Lagrangian transport of particles in Ria de Aveiro lagoon, Portugal. *Phys. Chem. of Earth Pt. B*, **26**(9), 721–727.
- Kersten, M. and F. Smedes (2002): Normalization procedures for sediment contaminants in spatial and temporal trend monitoring. *J. Environ. Monitor.*, **4**, 109–115.
- Long, E. R., D. D. MacDonald, S. L. Smith and F. D. Calder (1995): Incidence of adverse biological effects within ranges of chemical concentrations in marine and estuarine sediments. *Environ. Manage.*, **19**, 81–97.
- O'Connor, T. P. (2004): The sediment quality guideline, ERL, is not a chemical concentration at the threshold of sediment toxicity. *Mar. Pollut. Bull.*, **49**(5–6), 383–385.

- Pastorinho, M. R., T. C. Telfer and A. M. V. M. Soares (2009): Amphipod susceptibility to metals: Cautionary tales. *Chemosphere*, **75**, 1423–1428.
- Rae, J. E. (1997): Trace metals in deposited intertidal sediments. p. 16–41. In *Biogeochemistry of Intertidal Sediments, Cambridge Environmental Chemistry Series 9*, ed. by T. D. Jickells and J. E. Rae, Cambridge University Press, Cambridge.
- Santchi, P. H., L. Guo, S. Asbill, M. Allison, A. B. Kepple and L. S. Wen (2001): Accumulation rates and sources of sediments and organic carbon on the Palos Verdes shelf based on radioisotopic tracers (^{137}Cs , $^{239,240}\text{Pu}$, ^{210}Pb , ^{234}Th , ^{238}U , and ^{14}C). *Mar. Chem.*, **73**, 125–152.
- Schiff, K. C. and S. B. Weisberg (1999): Iron as a reference element for determining trace metal enrichment in Southern California coastal shelf sediments. *Mar. Environ. Res.*, **48**, 161–176.
- Schropp, S. J., F. G. Lewis, H. L. Windom, J. D. Ryan, F. D. Calder and L. C. Burney (1990): Interpretation of metal concentrations in estuarine sediments of Florida using Aluminum as a reference element. *Estuaries*, **13**(3), 227–235.
- Sharp, J. H., J. R. Pennock, T. M. Church, J. M. Tramontano and L. A. Cifuentes (1984): The estuarine interaction of nutrients, organics and metals: a case study in the Delaware estuary. p. 241–257. In *The Estuary as a Filter*, ed. by V. S. Kennedy, Academic Press, New York.
- Summers, J. K., T. L. Wade, V. D. Engle and Z. A. Malaeb (1996): Normalization of metal concentrations in estuarine sediments from the Gulf of Mexico. *Estuaries*, **19**(3), 581–594.
- Taylor, K. G. (2007): Urban environments. p. 191–222. In *Environmental Sedimentology*, ed. by C. Perry and K. G. Taylor, Blackwell Scientific Publications, Oxford.
- Trimble, C. A., R. W. Hoenstine, A. B. Highley, J. F. Donoghue and P. C. Ragland (1999): Baseline sediment trace metals investigation: Steinhatchee river estuary, Florida, northeast Gulf of Mexico. *Marine Georesources and Geotechnology*, **17**, 187–197.
- Wang, F. and J. Chen (2000): Relation of sediment characteristics to trace metal concentrations: a statistical study. *Water Res.*, **34**(2), 694–698.

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