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Mercury, zinc, manganese, and iron accumulation in leachate pond sediments from a refuse tip in Southeastern Brazil

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Abstract

This work evaluates Hg, Zn, Fe and Mn transfer from the leachate of a refuse tip based on their accumulation in a sediment core of 17 cm collected in a leachate pond of a small refuse tip ageing approximately 10 years. Sediment samples were digested with an acid mixture (50% *acqua regia* solution), heated at 70 °C during 1 h, in a thermal-kinetic reactor "cold finger". The extract was analysed to obtain Hg content by cold vapour absorption atomic spectrometry (CVAAS). Fe, Mn and Zn contents were obtained by flame atomic absorption spectrometry (FAAS) after total decomposition of the samples. Concentration ranges along the core varied from 0.16 to 0.58 μg g^{-1}; 7.3 to 145 μg g^{-1}; 11.7 to 116 μg g^{-1} and 0.21% to 1.82% for Hg, Zn, Mn and Fe, respectively. All metals showed enrichment in the upper layers (above 6 cm) which probably correspond to the year 1996. Results indicated that Hg transfer is one order of magnitude higher than Zn and suggest that metals accumulation in sediments probably reduce their migration to groundwater.

Keywords: Refuse tip; Leachate; Metals; Sediments

1. Introduction

According to a national survey conducted by the Brazilian Institute of Geography and Statistics (IBGE), 55% of solid waste in Brazil is disposed in open dumps, 22% in controlled landfills and only 13% goes to sanitary landfills. In the last years, waste production in Brazil has increased from 0.5 to 1.2 kg per person per day and food bags usage has increased more than 100%. Waste disposition in areas without any management as well as in controlled landfills contributes for environmental contamination and for human health risks. The most important sources of heavy metals in landfills are industrial waste co-deposition, hospital and household waste which may contain products such as paint, garden pesticides, pharmaceuticals, photographic chemicals, certain detergents, personal care products, fluorescent tubes, waste oil, batteries, plastics, etc. [1–3].

Leachate pond is produced when rainfall percolates through refuses that contain significant amounts of metals and other contaminants [4]. The chemical composition of leachate is directly related to solid waste composition, which depends on social–economic, political and climate conditions. The more developed is a country, the more solid waste is generated, especially petroleum derivatives such as plastics and nylon. According to Vadillo et al. [5], rainfall amount has strong influence on leachate composition, since rainwater infiltration produces a decrease in conductivity and in all the chemical components due to mixing within the landfill.

São Pedro da Aldeia City is located 136 km far away from Rio de Janeiro City, in the lake region of the Rio de Janeiro State, with 358 km^2 of total area and 61,335 inhabitants [6]. The population can rise 3 times during summer season. This region is characterised by beautiful beaches and its economy is based on tourism. The climate is dry with maximum annual precipitation reaching 800 mm. The most significant environmental concern related to waste landfilling is the risk of groundwater contamination caused by leachate infiltration. The aim of this work is

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to evaluate metal transfer from the landfill to the environment by analysing their contents in a sediment core from leachate pond.

2. Materials and methods

The sediment core was collected in a leachate pond originated from the leachate drainage from a refuse tip located at São Pedro da Aldeia city (22°49′37″S; 42°03′01″W), which occupies an area of 22,000 m^2 (Fig. 1). São Pedro da Aldeia refuse tip receives garbage from different origins, being deposited in an inappropriate way and without control. The garbage is disposed over soil without any kind of treatment in an open dump. According to Santos [6], the refuse tip has received about 40 ton/day of solid waste since 1990.

Leachate samples were collected once a month, from November 2000 to June 2001, in Teflon flasks. Conductivity (Schott-Geräte, Model CG 859) and pH (Digimed Model DMPH-3) measurements were performed in situ.

For sulphide determinations the samples were stored after mixing with zinc acetate. Sulphide concentrations were determined by spectrophotometry, using the flow injection system described by Cassella et al. [7].

Mercury determination in leachate was performed in samples not filtered neither acidified, by cold vapour atomic fluorescence spectrometry (CVAFS, Tekran 2500), after oxidation with BrCl in situ.

Leachate samples were filtered (0.45 μm) and acidified (pH = 1) prior to Fe and Mn determinations. These determinations were performed by flame absorption atomic spectrometry (FAAS) using a SpectrAA 300 (Varian).

The studied sediment core was collected with an acrylic tube, in a leachate pond in November 2000. The core was sliced in seventeen segments of 1 cm depth intervals, lyophilised, grounded and stored in plastic bags until analysis. Organic matter (OM) content was obtained by loss of ignition using 1.000 g of sediment, which was ignited to 450 °C, during 6 h. The bulk density of each layer was obtained by taking out 8 cm^3 of a wet sediment section and drying it at 60 °C until constant weight.

For Hg determination, core samples (1.000 g) were digested with an acid mixture (50% *acqua regia* solution), heated at 70 °C during 1 h, in a thermal-kinetic reactor "cold finger" [8,9]. The extract was analysed to obtain Hg content by cold vapour absorption atomic spectrometry (CVAAS), using a Bacharach Coleman (50D-model) equipment.

For the determination of other metals, total decomposition of the samples (1.000 g) was obtained after digestion with an acid mixture (6 mL HCl + 4 mL HNO_3 + 2 mL HF) in closed Teflon tubes, at 90 °C for 12 h. Fe, Mn and Zn contents were obtained by flame atomic absorption spectrometry (FAAS), using a spectrometer SpectrAA 300 (Varian).

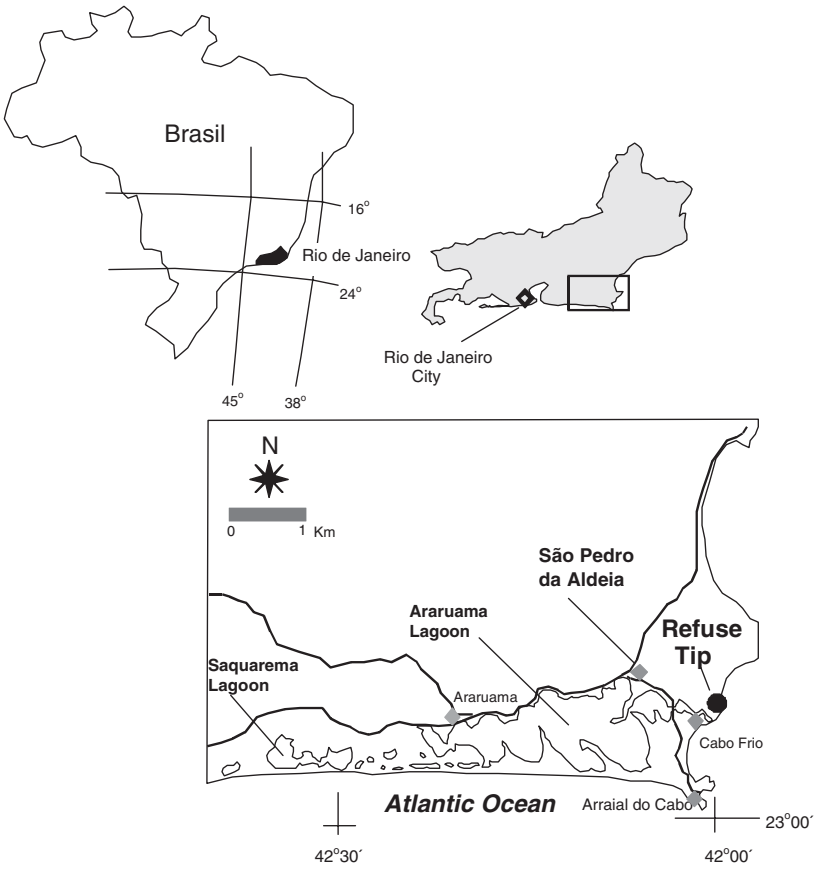

Fig. 1. Sampling site location in the refuse tip of São Pedro da Aldeia, Rio de Janeiro State, Brazil.

Buffalo River standard reference material (SRM 2704, NIST-USA) was analysed in parallel with metal determinations for quality assurance.

3. Results and discussion

The accuracy of the methodology was evaluated through the analysis of Buffalo River standard reference material SRM 2704 (NIST). Good to excellent recoveries ranging from 85% to 109% (Table 1) were obtained for Fe, Hg, Mn and Zn indicating a good overall accuracy of the methodology. The standard deviations were also consisted with those reported to SRM 2704.

Table 2 shows physical and chemical characteristics of the leachate formed by refuse percolation. Wide fluctuations of heavy metal concentrations were observed in the leachate during the monitoring period. These fluctuations have been reported by other authors and may be due to the sensitivity of the oxidation state and solubility to pH values as well as Fe and Al oxy-hydroxides concentrations [10]. Moreover leachate composition depends on rainfall [5].

Compared to the literature [10] electrical conductivity values obtained in this study are at the same order of magnitude. However higher conductivity and Fe content obtained by Oygard et al. [11] may be related to wrecked cars deposited in the landfill. According to Flyhammar [12], heavy metal concentrations in leachate are generally low due to their affinity with various waste materials. However, these concentrations are only a fraction of the metal associated with solid waste. Metal leacheability may increase over time as waste becomes more acidic and in oxidising conditions [13].

Fig. 2 shows the distribution profile of organic matter (OM), density, water content, Hg, Zn, Mn, and Fe within the sediment core collected from the leachate pond. OM and water distribution patterns clearly show two phases in the core. Higher water and lower OM contents were observed in the deepest layers. Below 13 cm layer water content average is 1.5 times higher than the ones observed in the upper layers while OM content decreases almost ten times with depth. These two phases are perfectly identified by density distribution along the core (Fig. 2).

The distribution pattern in the two phases is probably reflecting garbage accumulation phases, since there is some time between accumulation/degradation processes and leachate formation. The increase of OM values in the upper 10 cm layers may correspond to the beginning of maturation/degradation process in the refuse. According to Östman et al. [14] the ageing of a landfill can be divided into two phases: during the first one (aerobic phase) high microbial activity and OM content occur, followed by oxygen and nitrate-reducing step; during the second one (anaerobic phase) metal release is high due to low pH. Bozkurt et al. [15] and Kjeldsen et al. [13] described a humic phase, formed during landfill maturity, which is dependent on organic matter microbial degradation. As landfill reaches maturity, oxygen and oxygen-rich rainwater penetrates the landfill, oxidising OM and increasing heavy metal mobility.

Table 1
Mean concentrations ($n=6$) and standard deviations of Fe, Hg, Mn and Zn found in SRM 2704 Buffalo River sediment

Metal	Measured value	Certified value	Recovery (%)
Fe (%)	4.21±0.01	4.11±0.10	102
Hg (ng g^{-1})	58±3	60 [a]	97
Mn (μg g^{-1})	462±15	544±21	85
Zn (μg g^{-1})	476±5	438±12	109

[a] Information value only.

Table 2
Range of leachate physical–chemical parameters ($n=12$) compared with data from literature

Parameter	São Pedro da Aldeia [a]	Norway [b]	Nothern Italy [c]
pH	7.8–10	6.5–7.0	8.4
Conductivity (mS cm^{-1})	6.0–21	130–630	21
Hg (μg L^{-1})	0.002–1.03	0.013–0.027	–
S (mg L^{-1})	2.1–38	–	–
Mn (mg L^{-1})	0.07–0.55	–	0.38
Fe (mg L^{-1})	0.11–0.27	25.0–180	4.9

[a] This study.
[b] Oygard et al. [11].
[c] Frascari et al. [10].

The vertical distribution (Fig. 2) of the metals studied along the core was similar, with surface layers (above 6 cm) showing higher, and deeper layers (6–17 cm) showing lower and relatively constant concentrations. Similarly to OM and water content, two distinct phases can be seen in metal distribution. However, higher metal concentrations are observed (Fig. 2) above 6 cm depth.

Trace metal concentration ranges along the core are showed in Table 3. The wide ranges observed may be due to the fact that the material from the refuse is heterogeneous and variable over time [14]. The build-up of the refuse tip began in 1990 mostly containing household waste. In the early 90s improvements in Brazilian economy have changed population social–economic conditions. As a consequence, household product (such as paint, photographic chemicals, waste electronic and electrical equipment, etc.) consumption increased generating more waste.

Considering the landfill age (around 10 years before sediment sampling) and the core depth (17 cm) formed in the leachate pond coming from refuse percolation we may suggest that the 6 cm depth corresponds to an age of approximately 4 years. Taking into account that the core in the leachate pond was sampled in 2000, metal enrichment in the core probably began around 1996.

Provided that below the 6 cm layer all metals showed constant concentration, it is possible to suggest that those values correspond to background levels. Then maximum enrichment factors (EFs) were calculated by the ratio between maximum concentration values in the top of the core and minimum concentration values [16] at 14 cm layer, in order to avoid any interference from groundwater. The EFs obtained were 3.5, 20.0, 7.0, and 8.7 for Hg, Zn, Mn and Fe, respectively. These results show an evident enrichment in the surface layers. On the basis of EFs values, the studied core is enriched in metals in the following order: Zn>Fe>Mn>Hg. This enrichment is caused

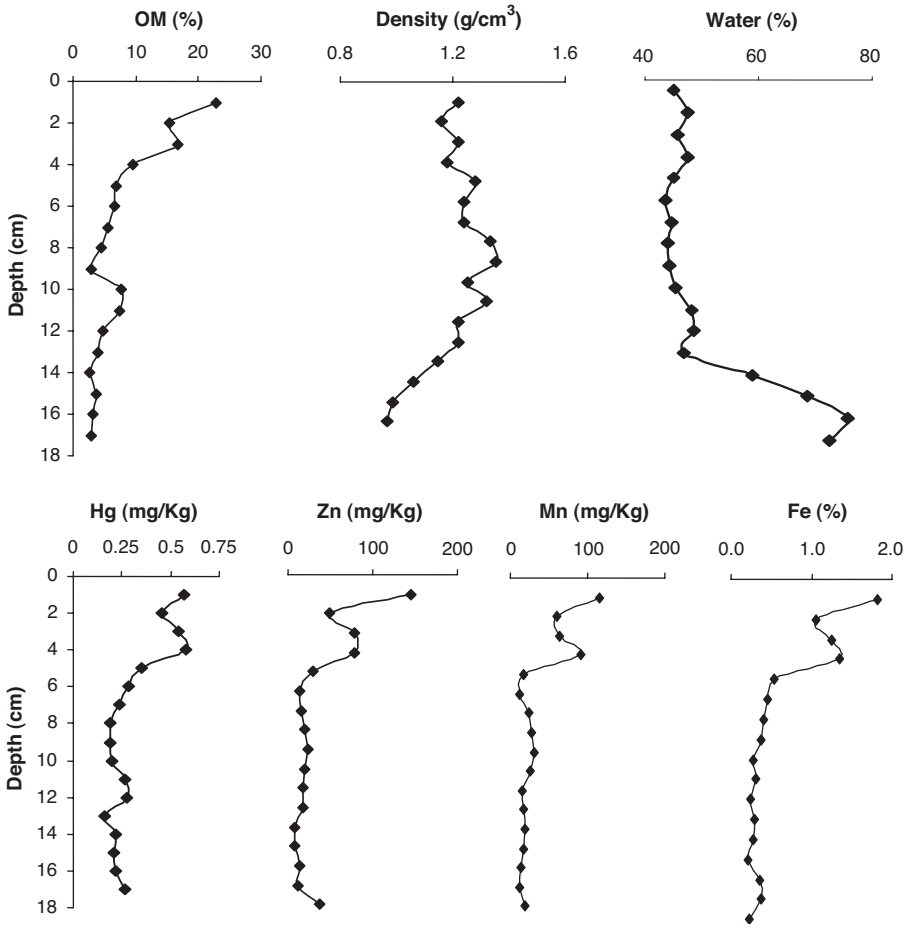

Fig. 2. Distribution profile of OM, density, water content, Hg, Zn, Mn and Fe concentrations in a core from a leachate pond of a São Pedro da Aldeia refuse tip.

by metals coming from refuse percolation, since the leachate pond is located downstream from refuse tip.

Correlation between all variables was significant ($n=17$, $p<0.05$) which was expected due to similar core distribution. This implies that all metals in leachate pond have the same origin, possibly coming from refuse tip percolation. Additionally, these strong correlations suggest the organic matter and/or Fe and Mn oxy-hydroxides as the main geochemical support for Zn and Hg. Organic matter is a typical support in reducing environments, while Fe is important in oxidant conditions.

Table 3 also shows average concentration ($n=17$) for Hg, Zn, Mn, and Fe obtained in the leachate pond core compared to data from the literature. Studies regarding to heavy metals contamination in environments submitted to landfill influence are scarce in Brazil. Zn, Mn, and Fe concentrations found in this work are lower than the ones obtained by Sissino and Moreira [17] in a study of a leachate stream sediment core from Morro do Céu landfill, located in Niterói, Rio Janeiro. Compared to Machado et al. [16] in a study of metal content in coastal sediments around the Gramacho landfill, Rio de Janeiro City, Hg and Zn concentrations are also lower. Both landfills receive garbage from cities that have a much higher population than São Pedro da Aldeia City. Moreover Gramacho landfill is located in

Table 3
Comparison of Hg, Zn, Mn, and Fe concentrations in the São Pedro da Aldeia (SPA) leachate pond core with data from literature for Rio de Janeiro State

Location	Hg (mg kg^{-1})	Zn (mg kg^{-1})	Mn (mg kg^{-1})	Fe (%)	Reference
SPA (average)	0.31	34.5	34.3	0.58	This study
SPA (range)	0.16–0.58	7.3–145	11.7–116	0.21–1.8	This study
Morro do Céu	–	270	216	3.5	[17]
Gramacho	0.76	820	–	–	[16]
Coastal Lagoons	0.12–0.44	–	–	–	[18]
Lake Region soils			4.58	5.9	[19][a]

[a] Unpublished data.

Table 4
Concentration inventories in São Pedro da Aldeia leachate pond core

	Entire core	0–6 cm	6–17 cm
Hg (μg m^{-2})	13.7	7.42	6.33
Zn (μg m^{-2})	1549	1052	497
Mn (μg m^{-2})	1550	954	596
Fe (mg m^{-2})	260	172	88

a mangrove area, at Guanabara Bay edge, influenced by industrial and household waste.

In the São Pedro da Aldeia leachate pond area, metals may come from two sources: from soil, which is poor in metals; and from refuse tip. As it can be seen by EFs calculation, Hg background value used in this study is half of maximum values obtained in bottom sediments of coastal lagoons in Rio de Janeiro State [18]. Mn background value is one order of magnitude higher than average values obtained in soils from that region [19]. On the other hand, Fe background value is one order of magnitude lower than the average values obtained by Silva-Filho [19] in soils from that region. Therefore, metals in the core are probably associated with their presence in the refuse tip rather than soil weathering.

Table 4 shows the results from concentration inventories which were calculated considering metal concentration ($\mu g\ m^{-2}$ for Hg, Zn and Mn; $mg\ m^{-2}$ for Fe), density ($g\ cm^{-3}$) and thickness (cm) of sediment-depth for each depth layer. Taking into account values from the entire core it is possible to notice that approximately 50% of metals were accumulated in the period of 1996 to 2000. Considering that Hg and Zn concentrations in urban refuse are 0.6–1.8 [20,21] and 80–220 $g\ ton^{-1}$ [22], respectively, the input of garbage to the tip is around 40 $ton\ day^{-1}$ and a tip area of around 22,000 m^2, the estimated Hg and Zn emissions from São Pedro da Aldeia refuse tip to sediments of leachate pond are 4.0–12 and 531–1460 $g\ m^{-2}$, respectively.

According to Slack et al. [3] less than 0.02% of heavy metals disposed in landfills are leached within the first 30 years. Considering refuse tip age and metal concentrations in the entire core (Table 4), estimated Hg and Zn inputs to core from refuse tip correspond to 0.005–0.0001% and 0.0003–0.0001%, respectively. In spite of lower Hg concentration in the core compared to other metals, results indicated that Hg estimated transfer is one order of magnitude higher than that of Zn. Considering higher Hg mobility we may suppose that sulphate-reduction process is less significant than the methanogenic one. The low sulphide concentration found in the leachate corroborates this hypothesis. On the other hand it should be taken into account that landfills are potential sources of Hg to the atmosphere [23].

4. Conclusions

Leachate pond sediments from São Pedro da Aldeia refuse tip retain elevated metal concentrations. Significant correlation between all metals and very low iron concentrations in this core (in comparison with soil concentrations) suggest that all metals studied come primarily from refuse degradation, rather than from surrounding soils.

Increasing consumption due to improvements in Brazilian economy in the early 90s coincides with an increasing metal accumulation, as showed in sediment upper layers collected in leachate pond of São Pedro da Aldeia refuse tip.

Higher mercury transfer from the refuse tip (e.g. in comparison with Zn) to pond sediment demands better strategies from authorities regarding refuse tip management. Future research needs to account mercury volatilisation to estimate its transfer from refuse tips, as an additional impact of unplanned solid waste disposal.

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