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Multivariate Exploratory Analysis of Metals and Phosphorus Concentrations of Leachates Collected Monthly from a Municipal Sanitary Landfill

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Abstract Concentrations of 11 elements (P, Cu, Ni, Co, Pb, Ca, Mn, Fe, Zn, Cr and Al) were measured in leachate samples collected monthly from the municipal landfill in Jequié, Bahia, Brazil. P (0.943–23.8 mg L^{-1}), Ca (19.90–129 mg L^{-1}) and Fe (0.115–2.87 mg L^{-1}) were found in the highest levels, while Cu (<LOQ–0.230 mg L^{-1}), Ni (<LOQ–0.540 mg L^{-1}), Co (<LOQ–0.268 mg L^{-1}), Pb (<LOQ–0.563 mg L^{-1}), Mn (<LOQ–3.40 mg L^{-1}), Zn (<LOQ–0.594 mg L^{-1}), Cr (<LOQ–0.163 mg L^{-1}) and Al (<LOQ–2.27 mg L^{-1}) were found in lower concentrations. Principal components analysis and hierarchical clustering analysis revealed two distinct groups associated with dry and rainy periods. Overall, this study revealed that concentrations of elements in landfill leachate vary temporally, and rainfall strongly influences their levels.

Keywords Landfill leachate · Phosphorus · Metals · Multivariate analysis · Inductively coupled plasma optical emission spectrometry

Municipal sanitary landfills consist of land designed to receive and to treat the waste that is isolated from the environment by an impermeable layer in the ground and covered with a layer of soil (Kjeldsen et al. 2002). Leachate is a dark fluid with a strong odor produced by the storage and decomposition of waste (Filho et al. 2004). Leachate poses a potential risk to the environment and human health because it contains a wide range of pathogenic microorganisms, as well as toxic metals and other dangerous chemicals (Kjeldsen et al. 2002; Mor et al. 2006).

The amount of leachate produced by a landfill depends on its unique conditions, especially the topography, geology, rainfall intensity and regime (Filho and Von 2001; Samaras and Samara 2011). Leachate composition is influenced by the composition, quantity and types of waste in the landfill, crushing and compacting of the waste, local weather, season, and the stage of decomposition of the waste (Silva-Filho et al. 2006; Wang et al. 2008; Lee et al. 2010).

One problem with the production of landfill leachate is its possible infiltration into the soil, and subsequent contamination of groundwater underlying the landfill (Sisinno and Moreira 1996). As a result, environmental agencies have begun to characterize leachate to enable decision making regarding its appropriate treatment (Kumar 2005).

Toxicity studies of leachates from 14 landfills using Cu(II), Hg(II) and Zn(II) as test metals indicated low toxicity, despite the presence of these metals (Claret et al. 2011). This can be explained by the high relative concentration of organic and inorganic ligands present, which react with metallic ions, reducing their bioavailability and solubility. However, these concentrations can increase in the biota through bioaccumulation and biomagnification processes (Mannarino and Moreira 2011; Baun and Christensen 2004).

In this study, multivariate analysis techniques [principal component analysis (PCA) and hierarchical clustering analysis (HCA)] were employed to evaluate data from 11 elements generated by the analysis of leachate samples collected monthly from a municipal landfill in Jequié,

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Bahia, Brazil, by inductively coupled plasma optical emission spectrometry. The principal goals of this study were to characterize concentrations of metals and phosphorus in leachate produced by a landfill located in an arid region over the course of a year.

Materials and Methods

Instrumentation

An Optima 7000 inductively coupled plasma optical emission spectrometer (ICP OES; Perkin Elmer, Norwalk, CT, USA) with a charge-coupled device (CCD) as a detector was used to determine the concentrations of P, Cu, Ni, Co, Pb, Ca, Mn, Fe, Zn, Cr and Al. Data were stored and processed using the WinLab32 software. Argon (Itaox, Itabuna) was used for generation and maintenance of plasma, while nitrogen (N_2) was used as the purge gas for the optical system. The elements were measured under the conditions shown in Table 1.

A heating plate (Marconi 085) was used for digestion of the samples. An Elga (Purelab Classic) system was used to obtain ultrapure water (conductivity 18 MΩ cm^{-1}).

Table 1 Instrumental parameters used for analysis of phosphorus and metals in landfill leachate samples by ICP OES

Parameter		Value
Radio frequency generator power (kW)		1.3
Nebulizer gas flow rate (L min^{-1})		0.8
Plasma gas flow rate (L min^{-1})		15
Auxiliary gas flow rate (L min^{-1})		0.2
Nebulizer pressure (kPa)		620
Integration time (s)		5
Stabilization time (s)		15
Sampling flow rate (mL min^{-1})		1.5
View		Axial
Element	λ (nm)	LOQ
Cu	327.393	0.020
Zn	206.200	0.086
Fe	238.204	0.035
Mn	257.610	0.026
Ni	231.604	0.055
Cr	267.716	0.025
Al	396.153	0.12
Pb	220.353	0.025
P	213.617	0.011
Co	228.616	0.010
Ca	317.933	0.12

LOQ limit of quantification (mg L^{-1})

Conventional glassware (flasks, beakers, pipettes) was maintained in a 10 % v/v HNO_3 solution for about 24 h for decontamination, then rinsed with deionized water and kept in a dust free environment until use.

Sample Collection

Leachate samples were collected from a landfill in Jequié, which is located in the southwest portion of Bahia State (40.08°E and −13.85°S). The municipality is in the border zone between a savanna and forest area, with a population of 151,895 inhabitants, an area of 3227 km^2 and an average annual temperature of 24°C. The maximum temperature of 40°C occurs during summer, which is characterized by a semiarid tropical rainy climate, while the minimum temperature of 14°C occurs in winter, which is characterized as the dry season. According to the landfill administrators, the city produces about 39,000 tons of solid waste per year. For this study, about 500 mL of leachate samples were collected from the landfill collection lagoon on the last week of every month from December 2010 to November 2011.

Sample Digestion

About 20.0 mL of freshly collected leachate was transferred to a 50 mL Erlenmeyer flask, after which 5 mL of concentrated nitric acid and 5 mL of hydrogen peroxide 30 % (v/v) were added. This mixture was heated to about 100°C for 2 h, during which time a funnel was placed on the flask to work as a cold finger and prevent loss of volatile elements. Finally, the samples were cooled to room temperature and placed in 25.00 mL volumetric flasks. Three replicates of each sample were made. After digestion, the samples were packed in polyethylene bottles and stored under refrigeration (6°C) until analysis by ICP OES. Sample digestion was evaluated by addition/recovery tests using metals standards added at the same order of magnitude as the metal concentrations prior to the sample acid decomposition.

Statistical Software

Statistica for Windows® was used for PCA and HCA treatments.

Results and Discussion

To assess the accuracy of the method applied to the metals determination, addition/recovery tests in some landfill leachate samples were carried out. Metals were added before the digestion process for evaluation of losses by volatilization. The metals were added to give twice the concentration as originally found in the sample. The recoveries were as follows: 94 %–99 % (P), 98 %–107 % (Cu), 94 %–99 % (Ni), 94 %–102 % (Co), 93 %–95 % (Pb), 95 %–106 % (Ca), 99 %–104 % (Mn), 102 %–108 % (Fe), 94 %–103 % (Zn), 99 %–107 % (Cr) and 96 %–105 % (Al).

The average, standard deviation and range of observed values of the samples are presented in Table 2. P and Ca were present in the greatest concentrations in the samples. These results were expected because the leachate is derived from the decomposition of household waste, which comprises a considerable percentage of organic material (food scraps and other biodegradable materials of organic nature).

Aluminum, Mn and Fe were present in considerable amounts, which was likely due to the type of soil used to cover the layers of garbage in the landfill. Aluminum is the most abundant metallic element in the earth's crust and is present in the oxide of minerals. The rocks and soils of the region in which the municipality is located are also rich in Fe and associated metals.

Other elements (Cu, Ni, Co, Pb, Zn, and Cr) were present at concentrations below 0.2 mg L^{-1}. Analysis of the coefficients of variation revealed that Mn had the highest dispersion (134 %), while Co had the lowest (27.2 %).

The 12 leachate samples from the municipal landfill of Jequié had alkaline pH values of 9.6 ± 0.4. Alkaline pH favors the precipitation and removal of trace metals from leachate, making it stationary on the soil. Accordingly, it can be assumed that the analyzed leachate is produced from methanogenic decomposition of the waste mass. Since the landfill has been in operation for more than 10 years, the pH values corroborate the findings of previous studies and indicate low concentrations of potentially toxic metals (Kjeldsen et al. 2002). Based on the decreased levels of dissolved metals in leachate, the organic matter in the soil is capable of attenuating the migration of various metals into the leachate (Celere et al. 2007). Christensen et al. (2001) reported that the main processes of metals attenuation in leachate are dilution, complexation, sorption and precipitation. Precipitation is favored by alkaline pHs, such as those found in the leachate produced by the Jequié landfill.

PCA and HCA (Otto 2007) were applied to evaluate whether there were defined groups among the collected samples.

Much of the behavior of the data could be explained by the first two principal components (PCs), which accounted for 73.17 % of the variance of the data. Figure 1a shows the plot of the scores for both PCs. The results revealed a temporal separation of the two groups. Specifically, samples tended to separate into those collected in dry and rainy periods. The rainfall in the area covered by the landfill may cause increase metals leaching as well as their dilution. However, data from samples collected in October and November, which were relatively rainy, showed the same behavior as samples from dry periods. The long period of low heavy rainfall (May to September) that preceded these months likely contributed to this phenomenon.

Table 2 Leachate metal concentrations (mg L^{-1}) and rainfall (mm) for the Jequié municipal landfill

	P	Cu	Ni	Co	Pb	Ca	Mn	Fe	Zn	Cr	Al	Rf
Dec/10	0.943	0.159	0.216	0.138	<LOQ	125	3.28	0.324	<LOQ	0.115	0.112	112.5
Jan/11	18.8	0.169	0.238	0.148	<LOQ	129	3.40	0.264	<LOQ	0.101	0.500	55.0
Feb/11	22.3	<LOQ	0.158	<LOQ	<LOQ	24.5	0.046	0.148	<LOQ	0.036	0.846	20.0
Mar/11	23.8	0.230	0.340	0.198	<LOQ	85.5	1.54	0.394	<LOQ	0.156	1.03	94.0
Apr/11	8.53	0.154	0.540	0.268	0.025	88.0	2.17	2.87	0.098	0.163	2.27	87.1
May/11	11.4	0.028	0.099	0.197	0.212	21.2	0.036	0.086	<LOQ	0.025	0.389	17.2
Jun/11	3.97	0.135	0.168	<LOQ	0.563	33.7	0.056	0.345	0.594	0.040	0.355	5.5
Jul/11	4.52	0.030	0.104	<LOQ	0.308	28.9	0.036	0.311	0.246	0.025	0.254	25.5
Aug/11	3.90	<LOQ	0.145	<LOQ	<LOQ	26.9	0.029	0.143	0.145	0.025	0.240	9.0
Sep/11	3.51	<LOQ	0.158	<LOQ	<LOQ	26.1	0.026	0.125	0.118	0.025	0.164	12.5
Oct/11	2.52	<LOQ	<LOQ	<LOQ	<LOQ	19.9	<LOQ	0.169	0.145	<LOQ	0.336	44.5
Nov/11	6.84	<LOQ	0.080	<LOQ	<LOQ	22.8	<LOQ	0.115	0.088	<LOQ	0.253	50.0
Average	9.25	0.129	0.204	0.190	0.277	52.6	1.06	0.441	0.205	0.0712	0.562	
s	8.04	0.0745	0.133	0.0516	0.224	42.0	1.42	0.772	0.179	0.0569	0.603	
VC	86.8	57.7	65.3	27.2	80.9	79.9	134	175	87.5	80.0	107	

Relative standard deviations (n = 3) for these concentrations are better than 4.8 %

Rf rainfall (mm), *s* standard deviation, *VC* variation coefficient

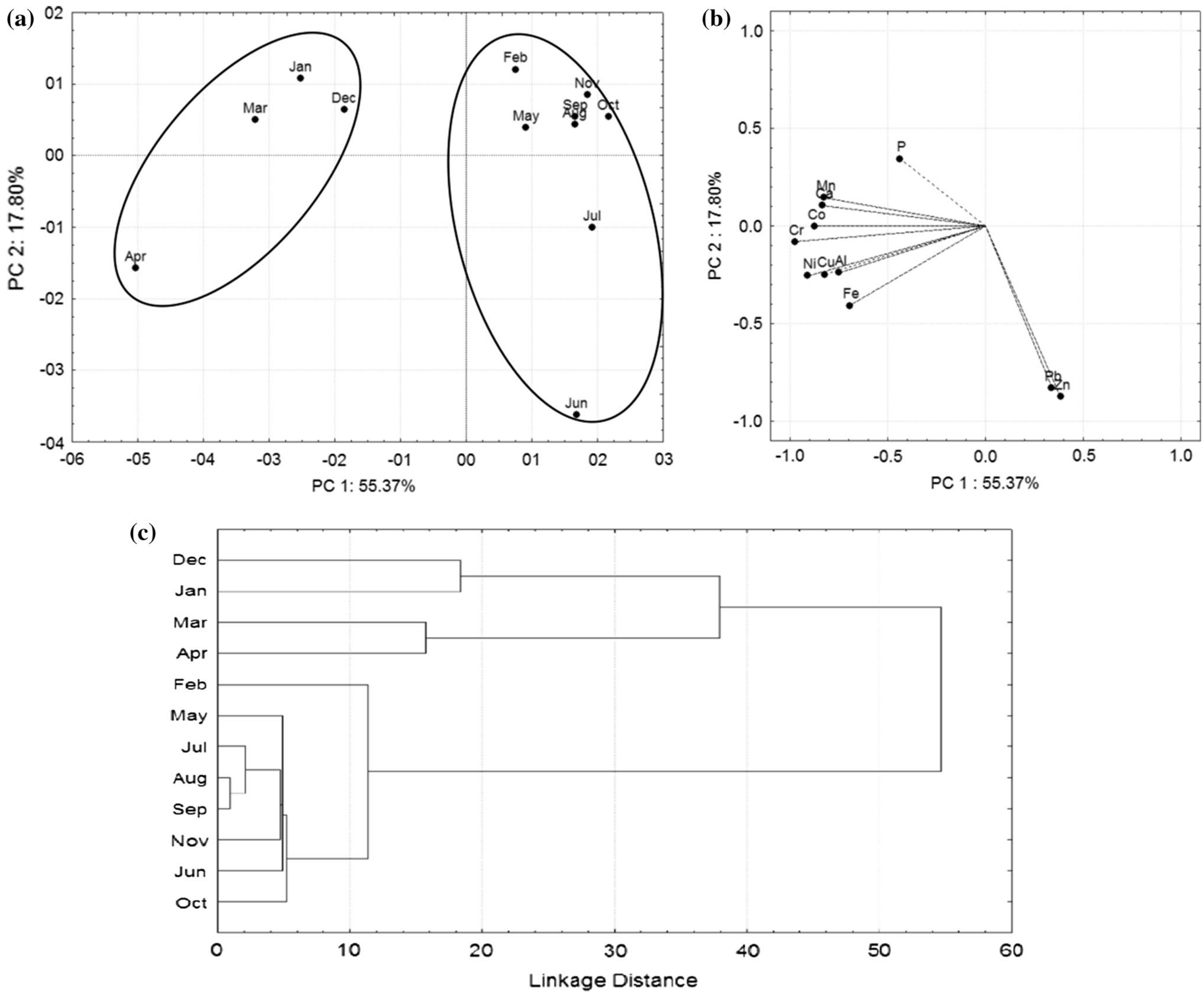

Fig. 1 Graphs of multivariate analysis of data describing leachate samples. **a** Score graph and **b** loading graph obtained by PCA and **c** dendrogram obtained by HCA

The loading graph (Fig. 1b) showed that Pb and Zn were the main variables responsible by the group composed by the majority of samples collected in the dry period, principally July and June. The samples from dry periods were influenced by P, Mg and Ca in addition to Pb and Zn. P, Mg, Ca, Co, Cr, Ni, Al and Fe formed a group of samples collected in rainy months. To the sample collected in April, Ni, Al, Fe, Pb and Zn contributed for its differentiation in relation to the others samples.

Cluster analysis was applied to the auto-scaled data that originated from elemental concentrations in the samples of leachate. The Euclidean distance was used to calculate sample similarities and a hierarchical agglomerative procedure was employed to establish clusters. The results obtained are shown as a dendrogram in Fig. 1c.

Two clusters corresponding to each rainy and dry period were found at a linkage distance level of 40. The first cluster (from the top of the dendrogram top) comprised samples collected in the rainy months. The other cluster was formed by samples collected in the dry months, as well as those from October to November. These findings correspond to the results of PCA.

As shown in Fig. 2, the average concentrations of Cu, Ni, Mn, Fe, P, Cr, Al and Ca were higher during the wet season. This was likely because of dissolution and leaching of compounds and soil components containing these elements during decomposition of the landfill mass and as a result of rainfall infiltration. Conversely, the average concentrations for Co, Pb and Zn were greater in dry months. It is believed that this was a result of higher evaporation,

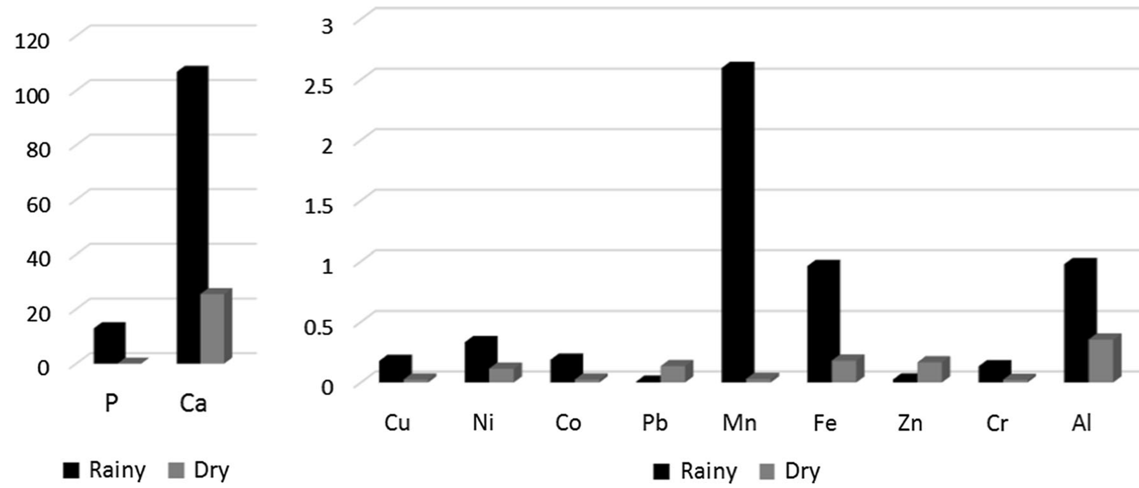

Fig. 2 Comparison of average metals and phosphorus concentrations from leachate collected during rainy and dry months

lower dilution and lower percolation water from the landfill during these months.

The results of this study indicated that the rainfall regime of the month in which the leachate was collected influences the concentration of metals in the samples. The rainy season promoted the dissolution of Cu, Ni, Mn, Fe, Cr, Al, P and Ca and consequently increased their concentrations in leachate. However, the levels of Co, Pb and Zn were higher during dry months, which was likely a result of concentration by evaporation of the liquid phase.

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