# Evaluation of the retention of heavy metals in the soil of the Ilhabela, Brazil waste landfill

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**Abstract:** The appropriate disposal of solid domestic wastes is one of the most challenging problems facing society since the infrastructure for waste treatment has not been integral with urban growth. Several studies have shown that inadequate disposal of waste may generate leachate, through waste decomposition, that contaminates soil and groundwater. This leachate contains heavy metals, as well as the usual organic compounds. In the Ilhabela municipality (São Paulo state, Brazil) a landfill has been operating for more than 5 years without any foundation treatment. Chemical analysis and laboratory tests have verified the adsorption of heavy metals in the soil that is used as foundation and to cover the waste. These tests were carried out to help understand the geochemical behaviour of the metals Ba, Pb, Mn, Ni and Zn when they come into contact with the local soil. Laboratory tests show that the soil used to cover the waste tends to release Ba and Mn to the groundwater but is able to adsorb part of the Pb, Ni and Zn present in the leachate. However, the ions held in the soil may subsequently be re-mobilized as a result of variation in natural conditions. These include aspects such as acid rain, and changes in the physico-chemical characteristics of the leachate. If this happens, they become a risk to the groundwater of the region.. Therefore, the installation of a monitoring program is necessary to evaluate the potential impact on groundwater.

Résumé: Le rejet des déchets domestiques constitue un des problèmes cruciaux pour la société et les pouvoirs publiques, depuis que la technologie de traitement des déchets n ont pas été mises en place lors de l'urbanisation des villes. Plusieurs études ont montré qu'un dépot non adequat des déchets peut entrainer la contamination des sols et de la nappe phréatique a travers des lixiviats génères par la décomposition des déchets. Ces lixiviats sont riches en produits organiques et en métaux lourds. Dans la municipalite de Ilhabela (Etat de Sao Paulo, Brésil), une décharge a fonctionnée pour plus de 5 ans sans aucune étude préliminaire pour son installation. Les analyses chimiques et les tests de laboratoire ont prouvé l'adsorption des métaux lourds dans le sol (celui-ci est utilisé comme matériau pour couvrir les déchets). Ces tests ont été effectués dans le but de comprendre le comportement géochimique des métaux lourds. Ba, Pb, Mn, Ni et Zn une fois se trouvant en contact avec le sol. Les tests de laboratoire, montrent que le sol utilisé pour couvrir les déchets tend a relarguer Ba et Mn en direction de la nappe, mais il peut retenir une partie du Pb, Ni et Zn présents dans le lixiviat. Autrement, les ions du sol peuvent étre mobilisés par la variation des conditions naturelles telles que. pluies acides, les propriétés physico-chimiques du lixiviat et donc constitue un risque majeur pour la nappe phréatique.

**Keywords:** Contaminated land; geochemistry; geology of cities; groundwater contamination; landfill; leachate

## INTRODUCTION

Several anthropic activities have impacted the environment due to the disposal of different chemical compounds in the air, water and soil. Depending on their concentration, such compounds may affect the flora, fauna and/or the population that lives close to the disposal area. One of these activities is the disposal of solid domestic waste.

One of the major problems caused by an inadequate solid domestic waste disposal is caused by the leachate generated. It is formed from the decomposition of the waste material and also from the percolation of rainwater through the material (IPT/CEMPE 2000).

According to Alloway (1995) several mechanisms may be involved in the adsorption of metallic ions present in the leachate by the covering soil such as cathionic (specific adsorption), co-precipitation and organic complexation.

Ilhabela (Figure 1) is a city located in an island in the North seashore of São Paulo state, 220 km far from the capital (São Paulo). About 83% of this municipality is in a State Park (conservation park) created in 1977. The resident population is about 21000 inhabitants, however this raises to 150,000 inhabitants during the summer due the tourism. Most of the island is protected as conservation park without possibility to install a sanitary landfill. However, since there is no other area available to receive such residues, the area becomes the focus of study for health, environmental and economical reasons.

Ilhabela has a solid domestic disposal dump, which has been in operation since 1987. The dump operation is characterized by the simple disposal of the waste in a landfill without any foundation treatment or any system to prevent pollution of the area or the groundwater. The garbage is dumped by the collecting trucks, compacted by a tractor and, eventually, revolved with the local soil, exposing the area to the contamination.

 

Ilhabela waste landfill is divided in two deposits. The first received domestic wastes from 1987 to 1998 with the newer deposit in operation since. The leachate, produced by decomposition of the waste, drains into an infiltration pond, located downstream of the waste deposit, where it accumulates until it soaks away (Figure 2).

The objective of this study was to verify an eventual modification of the soil characteristics where the landfill is installed. Several soil samples were taken and analysed, with emphasis on heavy metals content.

# METHODOLOGY

The soil sampling was carried out in the older deposit where the waste had been for more than 4 years. A non-impacted soil sample was taken from the region where the covering soil is taken. This sample was used as reference for comparison with the other samples. The soil samples were stored in plastic bags and then in the laboratory, dried at environmental temperature, disaggregated and sieved.

The fraction smaller than 2 mm was separated and reserved for grain size analysis and chemical analysis. The chemical analysis was performed, by the Inductively Coupled Plasma-Atomic Emission Spectrometry method (ICP-AES), with emphasis on heavy metals.

pH and ΔpH of the soil samples were determined in the laboratory using the methodology proposed by Camargo *et al* (1986); 10 mL of soil are mixed with 25 mL of deionised water, the mixture is shaken for 15 minutes and then left to rest for 30 minutes. After this period, the pH is measured using a pH-meter previously calibrated with controlled solutions of pH 4.00 and 7.00. The procedure was repeated using KCl solution 1N instead of deionised water. The ΔpH was obtained by subtracting the $pH_{KCl}$ value from the $pH_{H2O}$.

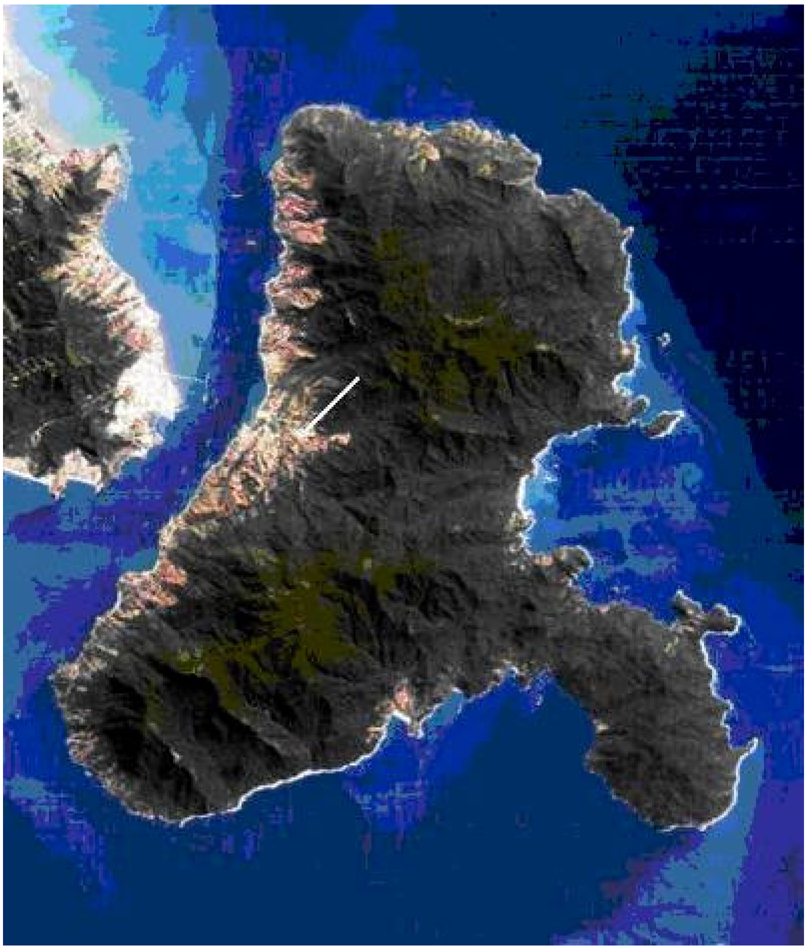

**Figure 1.** Ilhabela island – the arrow points out the landfill and study area.

The leachate used in the experiments of attacking the soil was collected from the infiltration pond. Temperature, pH, and electrical conductivity were measured at the time of sampling. Samples were preserved with $HNO_3$ (pH<2) and sent to the laboratory where metal concentrations were determined using the Atomic Absorption method.

The samples designated to attack the soil were preserved at temperature lower than 4°C until the beginning of the experiment, when 15g of the non-impacted soil was placed in a becker and mixed with 50 mL of the collected leachate

The soil samples were left in contact with the leachate for 1, 5, 7, 10, 15, 20 and 30 days with eventual mixing. After these periods the mixtures were filtered using slow filtration paper and the resulting solutions were analysed through Atomic Absorption method to determine the metals concentrations.

Another portion of the non-impacted soil was used to determine its retention capacity for the metals Pb, Ni e Zn.

Solutions of 0,1; 0,3; 0,5; 1,0; 2,0; 5,0; 10,0, e 20,0 mg.$L^{-1}$ of the ions $Pb^{2+}$, $Ni^{2+}$ e $Zn^{2+}$, were prepared and left in contact with 15.0 g of the soil by 7 days with eventual mixing. After that period, the solution was filtered, acidified with $HNO_3$ and sent to the chemical laboratory.

**Figure 2.** Infiltration pond.

## RESULTS

The results of the grain-size analysis and pH measurements are presented in Table 1. The projection of the grain size data in the Shepard (1954) diagram shows that soil from both the older deposit as well the soil used to cover the dump are predominantly sandy and not appropriate to receive the waste material.

All soil samples did however, reveal positive pH values that indicate predominance of negative surface charges, which favours the adsorption of metallic ions.

**Table 1.** Soil physical-chemical results

| **Samples** | **pH** $_{H2O}$ | **pH** $_{KCl}$ | **pH** | **Grain-size analysis** | | |
|---|---|---|---|---|---|---|
| | | | | **Sand** (%) | **Silt** (%) | **Clay** (%) |
| 1 * | 4,56 | 3,35 | 1,21 | 72,47 | 20,39 | 7,14 |
| 2 | 7,80 | 6,83 | 0,97 | 79,72 | 14,19 | 6,63 |
| 3 | 7,43 | 6,62 | 0,81 | 72,84 | 19,36 | 9,38 |
| 4 | 7,82 | 7,55 | 0,27 | 64,33 | 14,75 | 20,60 |
| 5 | 7,73 | 7,38 | 0,35 | 56,06 | 14,93 | 29,58 |
| 6 | 8,17 | 7,70 | 0,47 | 60,15 | 18,55 | 20,29 |
| 7 | 8,29 | 7,99 | 0,30 | 63,43 | 15,75 | 20,73 |
| 8 | 8,14 | 7,75 | 0,39 | 64,33 | 14,75 | 20,60 |
| 9 | 7,81 | 7,15 | 0,66 | 67,04 | 18,34 | 14,68 |
| 10 | - | - | - | 51,21 | 28,07 | 20,91 |

* non-impacted sample

Table 2 presents the results of chemical analysis of soil collected from the waste dump and of the reference sample.

**Table 2.** Results of the chemical analysis of the soil

| Samples | Ba (mg.kg$^{-1}$) | $Mn_{(t)}$ (mg.kg$^{-1}$) | Ni (mg.kg$^{-1}$) | Pb (mg.kg$^{-1}$) | Zn (mg.kg$^{-1}$) |
|---|---|---|---|---|---|
| 1* | 534 | 833 | 6 | 8 | 47 |
| 2 | 663 | 466 | 4 | 31 | 95 |
| 3 | 650 | 405 | 7 | 30 | 86 |
| 4 | 256 | 451 | 16 | 126 | 251 |
| 5 | 243 | 290 | 5 | 24 | 152 |
| 6 | 413 | 397 | 8 | 28 | 91 |
| 7 | 397 | 382 | 7 | 28 | 82 |
| 8 | 441 | 451 | 9 | 24 | 77 |
| 9 | 444 | 435 | 5 | 24 | 78 |
| 10 | 434 | 550 | 9 | 40 | 86 |

* non-impacted sample

The results of the chemical analysis of the samples that had contact with the leachate suggest an enrichment in the content of the metals analyzed such as Pb and Zn when compared with the chemical content of the non-impacted samples.

It is also possible to observe that the Mn and Ba presented lower concentration while Ni stays close to the values of the reference sample.

Tthe sample that was collected from the older damp (#4) however, presents higher values when compared with the other samples. It is important to notice that the Pb concentration is higher than the limit of the regulation agency (Cetesb 2001) and consequently requires monitoring.

The results of the physical-chemical analysis of the leachate collected in the infiltration pond and the results obtained from the chemical analysis of the solutions generated from the attack are presented in the Tables 3 and 4.

**Table 3.** Results of the physical-chemical analysis of the leachate collected in the infiltration pond

| | pH | E. C. (mS/cm) | Eh (mV) | DO (mg.L$^{-1}$) | T (°C) | Ba (mg.L$^{-1}$) | $Mn_{(t)}$ (mg.L$^{-1}$) | Ni (mg.L$^{-1}$) | Pb (mg.L$^{-1}$) | Zn (mg.L$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| Leachate | 7,95 | 31,10 | -224 | 0,10 | 36,5 | 0,134 | 0,188 | 0,536 | 0,568 | 1,010 |

**Table 4.** Results of the physical-chemical analysis of the solutions generated from the soil attack with leachate

| Time (days) | Weight (g) | Ba (mg.L$^{-1}$) | $Mn_{(t)}$ (mg.L$^{-1}$) | Ni (mg.L$^{-1}$) | Pb (mg.L$^{-1}$) | Zn (mg.L$^{-1}$) |
|---|---|---|---|---|---|---|
| **00** | - | 0,134 | 0,188 | 0,536 | 0,568 | 1,010 |
| **01** | 15,604 | 0,200 | 0,889 | 0,222 | 0,289 | 0,258 |
| **05** | 15,828 | 0,140 | 0,565 | 0,267 | 0,440 | 0,268 |
| **07** | 16,090 | 0,140 | 0,505 | 0,267 | 0,525 | 0,286 |
| **10** | 15,834 | 0,102 | 0,538 | 0,246 | 0,515 | 0,231 |
| **15** | 15,556 | 0,140 | 0,412 | 0,255 | 0,529 | 0,195 |
| **20** | 15,202 | 0,132 | 0,347 | 0,245 | 0,504 | 0,293 |
| **30** | 16,123 | 0,350 | 0,306 | 0,246 | 0,461 | 0,195 |

The adsorption tests allowed a better understanding of the mechanisms of adsorption of the metals in the soil. After 7 days of contact between the soil and the leachate the concentration values of the metals adsorbed tend to stabilize.

The concentration of the ions $Ba^{2+}$ and $Mn^{2+}$ in the analyzed solution increased, suggesting a deliver of these ions to the liquid medium. The other metals studied ($Pb^{2+}$, $Ni^{2+}$and $Zn^{2+}$) presented a decrease in the concentration of the solution analyzed after a period in contact with the soil suggesting that the soil adsorbed part of those ions.

The adsorption tests using pre-defined concentrations allowed verification of the retaining capacity of the soil. Figures 3, 4 and 5 present the percentage of Pb, Zn and Ni adsorbed by the soil in those adsorption tests.

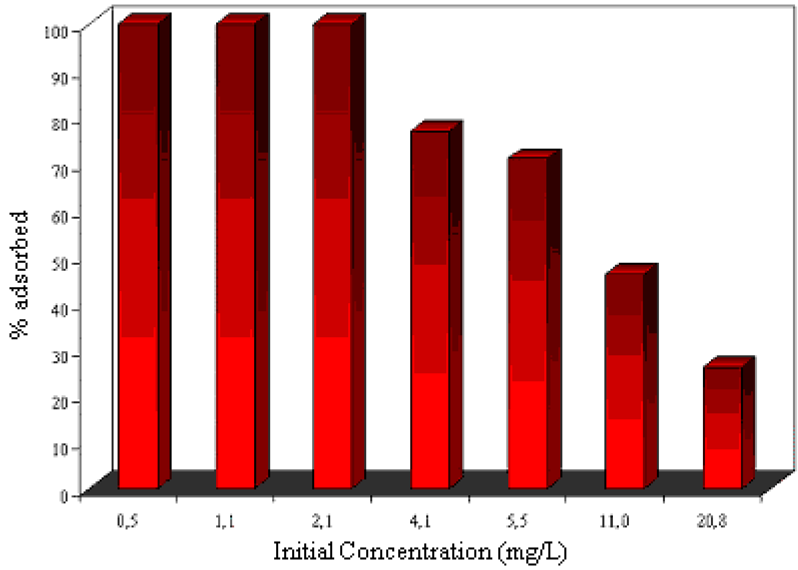


**Figure 3.** Percentage of Pb adsorbed in the soil as function of the initial concentration.

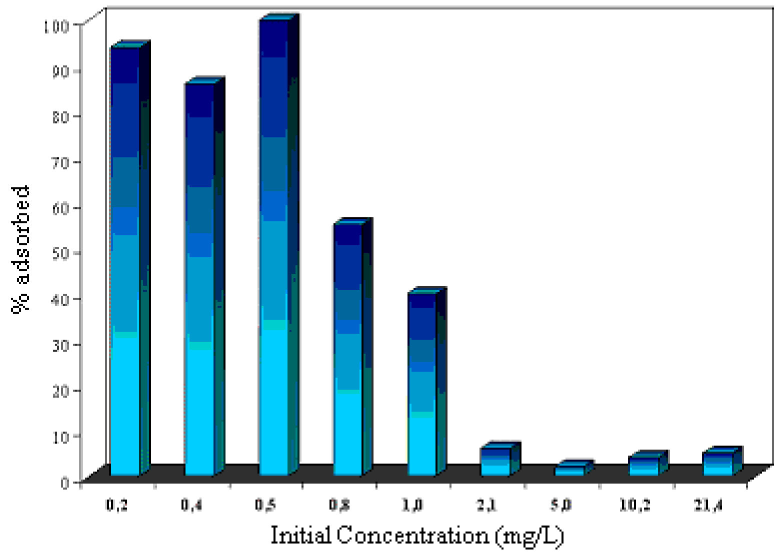


**Figure 4.** Percentage of Zn adsorbed in the soil as function of the initial concentration

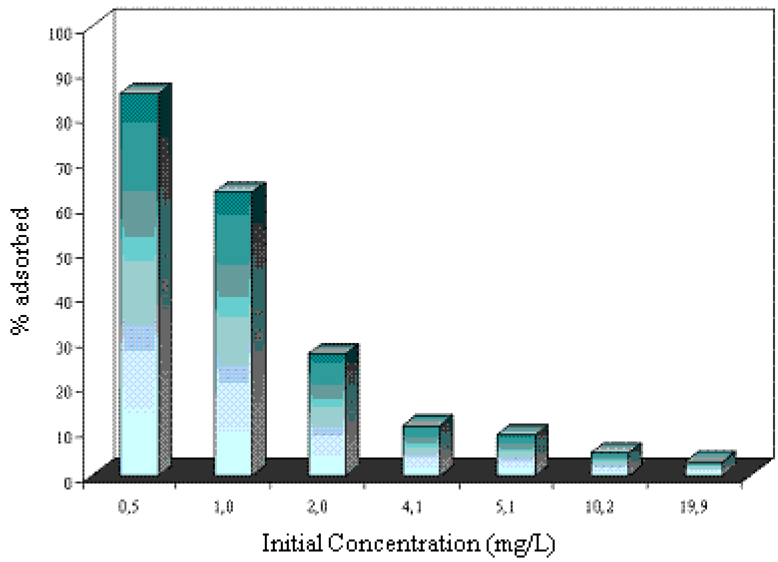


**Figure 5.** Percentage of Ni adsorbed in the soil as function of the initial concentration.

The soil has a good retention capacity for Pb (100%) when in contact with solutions with concentrations lower than 4,0 $mg.L^{-1}$ but for higher concentrations the retention capacity decreases.

Solutions with concentrations of Zn and Ni close to those of the leachate were well adsorbed (close to 100%) but for concentrations higher than 1,0 $mg.L^{-1}$ the retention was lower than 50%. It is important to point out that the regulatory standards in Brazil (Resolution CONAMA 20) allows infiltration of leachate with concentrations of Zn and Ni up to 5,0 $mg.L^{-1}$ and 2,0 $mg.L^{-1}$ respectively.

# CONCLUSIONS

The soil used as foundation and covering material is composed mainly of sand, with low retention capacity for metallic ions.

The soil samples that had contact with the leachate produced in the Ilhabela waste landfill presented enrichment of Pb, Ni and Zn. At the same time these samples presented lower Ba and Mn concentrations when compared with the original soil.

In the older deposit where the waste has been placed for more than five years the metallic ions concentrations are higher than the limits imposed by the environmental agency (CETESB) thus requiring an immediate monitoring program.

It is important to highlight that the metals that are adsorbed in the soil may be mobilized due to potential climatic changes such as acid rain and even changes in the physical-chemical characteristics of the leachate generated. Therefore, these could become factors in determining to the quality of the groundwater in the region.

The retention of metals Pb, Zn and Ni by the covering soil is satisfactory for the concentrations present in the leachate produced in the Ilhabela landfill. However, the soil presents retention capacity lower than 50% if the concentrations increase up to 4,0 $mg.L^{-1}$ (Pb) and 1,0 $mg.L^{-1}$ (Zn e Ni).

Considering the fact that most of the municipality territory is in an environmental reserve park and there is no other area available to install a sanitary landfill, it is important to regulate the landfill using soil brought from some other area . Therefore, the installation of a monitoring program is necessary to evaluate the potential impact on the groundwater.

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