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Raquel Souza Teixeira, Philippe Cambier, Regina Davison Dias, José Paulo Peccinini Pinese, Anne Jaulin. Mobility of potentially harmful metals in latosols impacted by the municipal solid waste deposit of Londrina, Brazil. *Applied Geochemistry*, 2010, 25 (1), pp.1-15. 10.1016/j.apgeochem.2009.09.022 . hal-01192085

HAL Id: hal-01192085

<https://hal.science/hal-01192085>

Submitted on 31 May 2020

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Mobility of potentially harmful metals in latosols impacted by the municipal solid waste deposit of Londrina, Brazil

Raquel Souza Teixeira^{a,*}, Philippe Cambier^b, Regina Davison Dias^c,
José Paulo Peccinini Pinese^d, Anne Jaulin-Soubelet^e

^a Universidade Estadual de Londrina, Departamento de Construção Civil, C.P.6001, 86055-900, Londrina/PR, Brazil

^b INRA – AgroParisTech, UMR, Environnement et Grandes Cultures, 78850, Thiverval-Grignon, France

^c Universidade Federal de Santa Catarina, Pós-Graduação-ECV, Rua. João Pio Duarte s/n, Bairro Córrego Grande, 88040-970, Florianópolis/SC, Brazil

^d Universidade Estadual de Londrina, Departamento de Geociências, C.P.6001, 86055-900, Londrina/PR, Brazil

^e INRA, UR251-PESSAC, Physicochimie et Ecotoxicologie des sols d'agrosystèmes contaminés, RD 10, 78000 Versailles, France

ARTICLE INFO

Article history:

Received 30 April 2009

Accepted 17 September 2009

Available online 24 September 2009

Editorial handling by R. Fuge

ABSTRACT

The contamination of soils by metals issuing from municipal solid waste (MSW) disposal in tropical environments has hardly been studied with regard to the particular problems associated with them, i.e., generally a high permeability of soils despite the abundance of clay, and the role of reactive Fe compounds. From a previous geotechnical and chemical survey, three latosol profiles differently affected by MSW leachates in the region of Londrina (Paraná, Brazil) were selected. The aims were to evaluate the extent of their contamination, to better understand the fate of potentially harmful metals in tropical soils and rank the determining factors. Samples between 0.5 and 7 m depth were analyzed for their physical, mineralogical and chemical properties, and their micro-morphology was described by optical and transmission electron microscopy. Two steps of a sequential extraction procedure helped to assess the mobility of elements and to better discriminate between metals originating from pedogenesis and issued from MSW. These combined approaches showed that exposed soil profiles have been impacted at various depths, down to 7 m, through increased metal content, especially enhanced mobility of Zn, Co, Mn, Cu and Fe, and through increased salinity and organic matter. The mobility of potentially harmful metals should decrease with pH, which significantly increased in some impacted horizons, but other factors can reverse this trend.

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1. Introduction

The diagnosis of soil contamination by potentially harmful metals has been the subject of public interest since the 1970s and of countless studies reported by many researchers, among them: Yong et al. (1996), Alloway and Ayres (1997), Sígolo (1998) and Jucá et al. (1999). This is due to the environmental and health problems caused by high metal contents in soils which can affect microorganisms, plants, animals and human beings through contamination of water and crops. High potentially harmful metal contents in soils may come from the bedrock itself, and in some cases through natural transport, but are more often due to anthropogenic sources like solid or liquid waste deposits, agricultural inputs, and fallout of industrial and urban emissions.

The most common destination of wastes generated by urban society in Brazil is a municipal solid waste (MSW) deposit. The characterization and evaluation of the contamination of soils by

MSW leachates caused by the degradation of residues since their deposition are essential for environmental control because they are usually close to areas with agricultural activities and human settlements (Heitzmann, 1999; Mwiganga and Kansiime, 2005; Baba et al., 2004). Among the most common contaminants are organic matter and metals like Cd, Cr, Cu, Mn, Pb, Hg, Zn and Fe (Barazani et al., 2004; Roy et al., 2004).

The mechanisms responsible for the retention or mobilization of metals in soils are physical (filtration, diffusion, dispersion, dilution and absorption), chemical (precipitation/dissolution, adsorption/desorption, complexation, cation exchange and redox reactions), and biological (aerobic and anaerobic transformations) (Sposito, 1989). The understanding of the speciation of metals in soils is essential to discuss and interpret their toxicity and bioavailability (Alloway, 1995). The term speciation refers to the chemical forms of elements in solution; however, it is also used to define the forms of elements linked to different solid mineral or organic phases, resulting from interactions between dissolved species and reactive solids, forming surface complexes, isolated precipitates or even the metabolites in living organisms (Alloway, 1995;

* Corresponding author. Tel.: +55 43 3371 4441; fax: +55 43 3371 4455.

E-mail address: raquel@uel.br (R.S. Teixeira).

Meurer, 2004). Metallic species and other contaminants in soils and water caused by the degradation of solid waste have been studied by Banat et al. (2005), Chen et al. (2005), Shukurov et al. (2005), Piantone et al. (2004), Segura-Muñoz et al. (2004) and Gonçalves et al. (2004).

This work presents the results of a geotechnical and geochemical study of different soil profiles impacted by the MSW deposit of the city of Londrina (Paraná, Brazil). The soil permeability, together with the continuous emission of leachates and the inadequate protection conditions operating, make this area a threat for surrounding soils and waters. The research is focused on the contaminants Co, Cu and Zn, which had been previously detected in leachates collected from the deposit, and on some other elements, highlighting the impact of the deposit. The aim is to evaluate the extent of this contamination and to identify its determining factors in relation to geochemical and physical characteristics of soils commonly found under a humid subtropical climate.

2. Materials and methods

2.1. Local characteristics

The city of Londrina is in the north of the state of Paraná (Fig. 1), and its MSW deposit is located in the SE, 7 km from the center, at 51°06' West longitude and 23°20' South latitude. Urban solid residues were simply deposited on the land from 1977 until 1993 (Fernandes et al., 1995). After this date and up to the present, the landfill has become a compacted deposit which has been covered daily. Nowadays, the municipal district of Londrina produces every day 348 tons domestic residues on average, that are deposited together with 68 tons of commercial residues and 0.9 tons hospital residues. The nearby vegetation is made up of pasture, some crops, such as corn and banana, and a small forest area. The climate is humid subtropical, where the summers are hot and humid (mean of 23.8 °C and 600 mm rainfall) and the winters cool and dry (mean of 16.8 °C and 200 mm rainfall), with an annual mean temperature of 22.5 °C.

The predominant geology in the area is the Serra Geral formation, belonging to the sedimentary basin of Paraná, and whose main lithology is basic volcanic rock. According to Teixeira et al. (2004), the weathering of basalt has resulted in a dark-red Latosol, following the Brazilian Soil Classification System (EMBRAPA, 1999). This soil type has a well drained deep B horizon with high clay content, overlying a C horizon made up of alterite, or residual soil, that maintains the basalt structure.

As reported by Teixeira et al. (2006), a monitoring project of the MSW disposal area began in 2003 with a topographical survey of the area. Then, investigations based on an electroresistivity meth-

od were carried out along the surrounding area of the sanitary landfill to detect anomalies possibly due to MSW leachates. The topographic map with the limit of the impacted area presented in Teixeira et al. (2006) is schematized in Fig. 2, which shows the line going away from the landfill boundary and further down in the direction of the Periquitos stream, linking points P4, P11, P5 and P6. Such points were submitted to mechanical probing with the standard penetration test (SPT) and sampled at different depths for laboratory investigation (see Section 2.2). The same authors described the stratigraphical profile, based on the SPT at points P2, P4 and P7. It is made up of three strata, whose characteristics vary from lateritic, dark red and particularly soft porous silty clay to very compact variegated sandy silt in the lower stratum. A silty clay texture is predominant in the profile. The water table was found at a depth of 8.10 m in P2. The hydraulic conductivity of the B horizon was evaluated in situ, by means of four permeability tests, and found to be in the range 10^{-4} – 10^{-6} cm s⁻¹ (Teixeira et al., 2006).

2.2. Soil sample collection

2.2.1. Choice of study profiles and sampling depths

Based on the results of the monitoring, three nearby locations were chosen for further investigation: P4 and P11, which are considered to be affected by MSW leachates, and P3 which appears unaffected, in relation to its slightly elevated position (Fig. 2). The exact locations and elevations are given in Table 1, together with a schematic pedological classification according to EMBRAPA (1999), and the encoding of the different profiles and samples.

2.2.2. Undisturbed and representative sampling of the soil

Pits, approximately 80 cm in diameter, were dug manually at the three locations. At each depth defined previously, two samples were collected: an undisturbed sample, approximately 20 × 20 × 20 cm, was cut, wrapped in paraffin and removed; then a representative sample of about 1 kg, was collected from multiple subsamples.

2.3. Characterization of soil samples

2.3.1. Geotechnical characterization

The analyses were carried out based on the Brazilian Standard methods – NBR (Vargas, 1978). All samples were submitted to grain size analysis according to NBR 7181/84 and solid specific gravity, natural specific weight and water content were determined according to NBR 6508/84; NBR 10838/88 and NBR 6504/84, respectively.

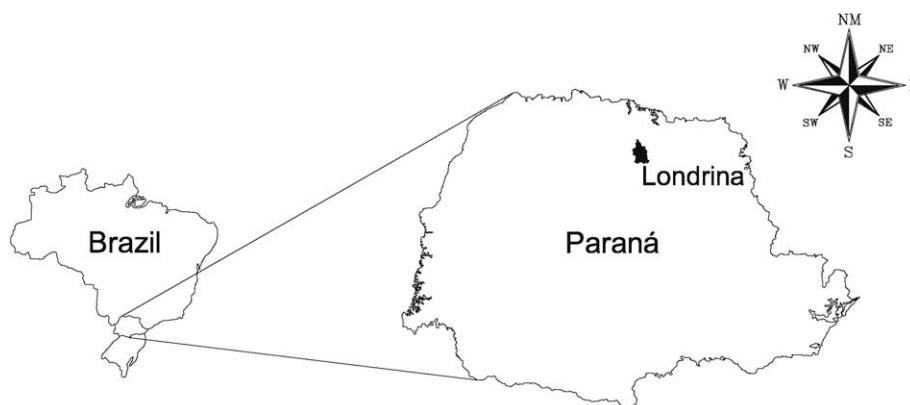


Fig. 1. Location of Londrina in the state of Paraná, Brazil.

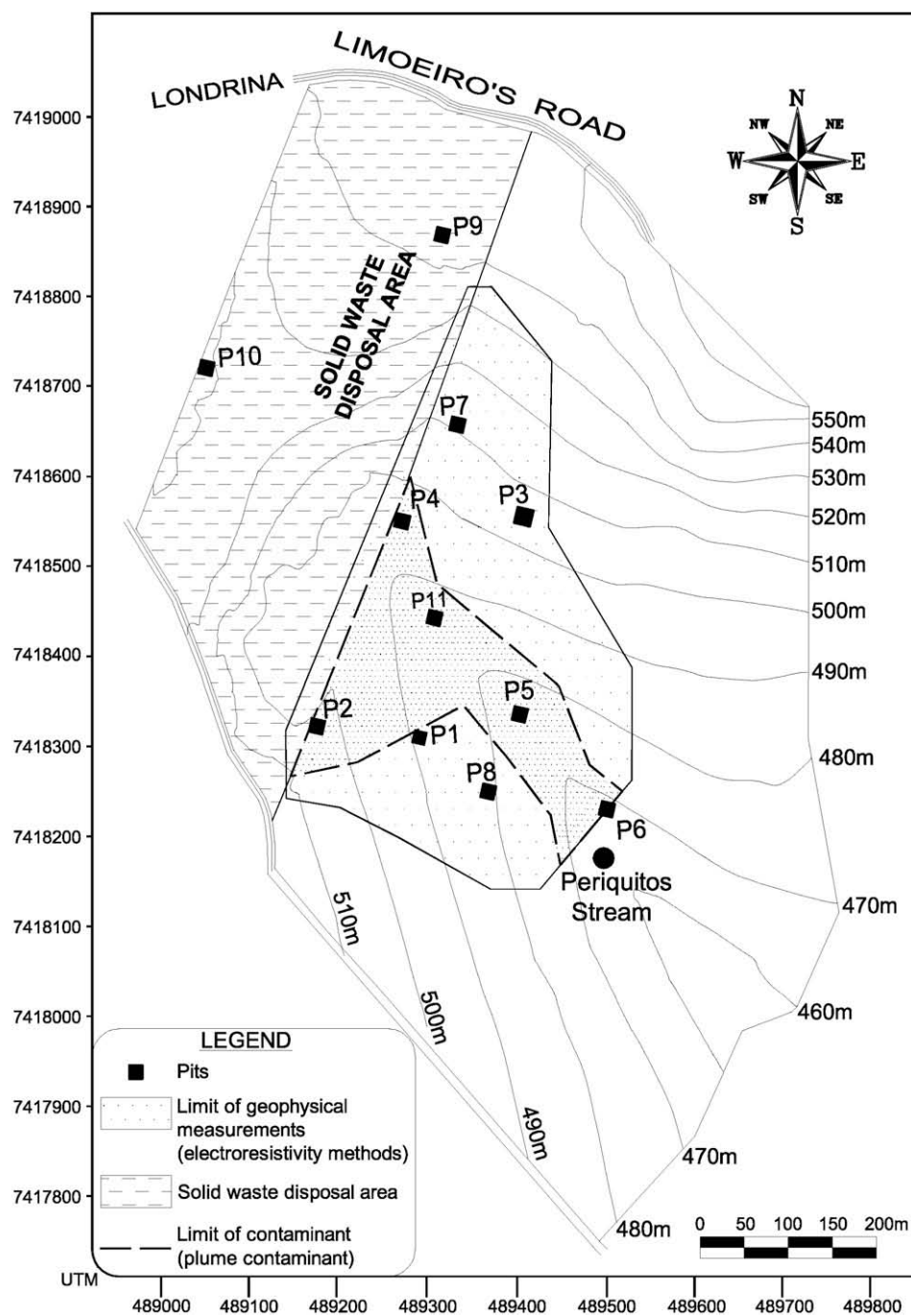


Fig. 2. The limit of the area contaminated and topographic map of the MSW disposal area of Londrina.

2.3.2. Chemical characterization

The representative samples were air dried over 5 days, disaggregated and passed through a # 10 sieve (2 mm aperture). Analyses of exchangeable cations (Ca^{2+} , Mg^{2+} , K^+ , Al^{3+} and H^+), organic C content, and pH in H_2O and KCl were performed by the soil laboratory at the Agronomic Institute of Paraná (IAPAR, Londrina), following the Soil Analysis Methods Manual from EMBRAPA (1997). Briefly, pH was determined in water and 1 M KCl (soil:solution 1:10); Ca, Mg and Al were extracted with 1 M KCl, Ca and Mg being measured by the titrimetric method with EDTA, Al being determined by titration with NaOH; the potential acidity ($\text{H}^+ + \text{Al}^{3+}$) was determined by the SMP method at pH 7 (Shoemaker et al., 1961), using a solution of triethanolamine, *p*-nitrophenol, K_2CrO_4 , $\text{Ca}(\text{CH}_3\text{COO})_2$ and CaCl_2 ; K was extracted with Mehlich-1/1 (solu-

tion: 0.05 M HCl + 0.0125 M H_2SO_4); the C content was determined by the Walkley Black method. The organic matter content was estimated from organic C by using a multiplier of 1.72. ΔpH was defined as the difference between the values of pH in KCl and in water, and the cation exchange capacity (CEC) by the sum of exchangeable Ca^{2+} , Mg^{2+} , K^+ and ($\text{H}^+ + \text{Al}^{3+}$).

2.3.3. Major element analyses

These analyses were performed at the SGSGeosol Laboratory in Belo Horizonte (Minas Gerais, Brazil). The major oxides were determined by X-ray fluorescence and the loss on ignition (LOI) by calcination at 1000 °C. Two-gram samples were dried at 110 °C, mixed with 2 g of lithium tetraborate, and fused in a Lavoisier mufla (Quimis) at 1000 °C. The LOI was determined at the

Table 1
Pedologic classification, location and encoding of the samples.

Profiles – coordinates (UTM) elevation (m)	Sampling depths (m)	Encoding	Classification	
			Horizon	Pedology
P3 E-W 489409 N-S 7418560 513 m	0.5	P3-0.5	A	Latosol
	2.0	P3-2		
	4.0	P3-4	B	
	6.0	P3-6		
	7.0	P3-7		
P4 E-W 489271 N-S 7418552 495 m	0.5	P4-0.5	A	Latosol
	2.0	P4-2		
	4.0	P4-4	B	
	7.0	P4-7		
	P11 E-W 489311 N-S 7418433 486 m	0.5		
2.0		P11-2		
3.0		P11-3	B	
5.0		P11-5		
7.0		P11-7		

same time. After that, the melted glass was broken up and boric acid added. The mixture was poured into 20 mL tungsten carbide vessels and pressed at 250 kN, using a Herzog press (I model HTP40) and a Spex vessel mill (Shatterbox). The tablets were analyzed in a Philips X-ray fluorescence spectrometer PW 1480 model.

2.4. Mineralogical analyses

X-ray diffraction (XRD) was carried out at UR251-PESSAC (INRA, Versailles, France) on P3 and P11 soils, on the whole air dried samples reduced to powder, and on oriented deposits of their clay fractions. These fractions were prepared from suspensions containing 0.1 g of soil, two drops of sodium pyrophosphate solution and about 50 mL of water. After ultrasonic dispersion, shaking and then settling for 4 h, 2 mL of the supernatant was pipetted, spread on a glass slide and left to dry at room atmosphere.

The instrument used was a Siemens D5000, equipped with a Co tube. The traces were recorded with a 0.02° 2θ step every 15 s, from 3° to 80° 2θ for the whole samples and with a 0.02° step every 5 s from 2° to 35° 2θ for the clay deposits.

2.5. Sequential extraction and metal analyses

Chemical extractions and elemental analyses were performed at UR251-PESSAC. A sequential extraction, using chemical reagents with increasing strength, is often used to characterize the different forms of metals in soils. The BCR scheme (Community Bureau of Reference; Rauret et al., 1999; Sahuquillo et al., 1999) was adapted by using its first two steps, in order to evaluate the most mobile forms, and a total digestion procedure for the initial samples and some residues from the BCR extractions, in order to control the quality of analyses (see below). The fractions corresponding to the partial extractions were labeled E1 and E2, respectively, and also referred to as the labile and easily reducible fractions, in relation to the reagents used, dilute acetic acid (HOAc) and acidified hydroxylamine ($\text{NH}_2\text{OH}\cdot\text{HCl}$).

Large soil samples were sieved again to <2 mm, their water content determined on aliquots, and other aliquots were prepared for the extractions in duplicate. 0.8 g of soil was accurately weighed in a polycarbonate centrifuge tube and 32 mL (1:40) of 0.11 M HOAc was added. All tubes were shaken for 16 h at room temperature. The supernatants were separated by centrifugation (Beckman Avanti J-25i) at 5000 rpm for 20 min, transferred to polyethylene bottles, acidified with 1% (v:v) analytical grade concentrated HNO_3 69%, and kept at 4°C until analysis.

After this first step, the solid was rinsed by adding approximately 10 mL Milli-Q water and centrifuged again under the same

conditions. The supernatant obtained was discarded and the solid kept at 4°C overnight before the second step: 32 mL of 0.1 M $\text{NH}_2\text{OH}\cdot\text{HCl}$, pH 2 adjusted with HCl, was added and the same procedure, with 16 h shaking, led to the second extract.

2.5.1. Total digestion

Duplicate 0.5 g samples were accurately weighed and transferred to 120 mL Teflon tubes with 1 mL of Milli-Q water. Then, 9 mL HNO_3 (69%) and 3 mL of HF (37%) were added and the mixture was left to react for 15 min. The tubes were sealed and heated in a micro-wave oven (CEM MARS XPress, 2455 MHz, 1600 W). The temperature was progressively increased up to 183°C and maintained at that point for 15 min. The contents of each tube were collected with Milli-Q water into a Teflon crucible in order to evaporate the remaining HF on a sand bath. The residue was dissolved with 0.5 mL HNO_3 and transferred to 50 mL volumetric vessel. The final solutions were transferred to polyethylene bottles and kept at 4°C until analysis.

2.5.2. Metal analyses and quality control

Iron, Mn, Co, Cu, Pb and Zn were analyzed in the solutions obtained from the sequential extractions and from total digestion by Flame Atomic Absorption Spectrophotometry (FAAS), using a VARIAN SpectrAA220. These elements were chosen due to their significant presence in the MSW leachates and, on another hand, to the particular role of soil Fe and Mn oxides in the retention of other metals. To assess the quality of analyses ($\pm 10\%$ recovery on accuracy), the following controls were included in each series: blanks using allotted reagents and vessels, a sample with measured additions of elements from standard solutions (to check matrix effects), a certified reference material (CAN-LKDS-1) for the total digestion series. For sequential extractions, a series was submitted, after the second step, to total digestion and the sum of extracted elements was compared to the result of total digestion on initial samples.

2.6. Soil water extracts and soluble elements

The analysis of water-soluble metals was performed according to NBR 10006/2004. A soil solution was obtained from contact between 50 g of air-dry soil and 200 mL deionized water (1:4). The suspension was shaken for 5 min and left for 7 days at room temperature. The samples were filtered through $0.45\ \mu\text{m}$ membranes and kept at 4°C until analyses, which were completed with a multi element inductively coupled plasma optical emission spectrometer (ICP/OES, View-Pro Varian). The pH and the electrical conductivity of the solutions after filtering were also measured.

2.7. Micro-morphology analyses

2.7.1. Optical microscope

Morphological observations of thin sections of the undisturbed samples were performed with a Zeiss Axiophot optic microscope, under natural light, in the Histology laboratory at the State University of Londrina.

2.7.2. Transmission electron microscope (TEM)

Clay fractions of the samples were prepared in the same way as for X-ray diffraction, but adjusted dilutions were applied to the pipetted volumes. Then the solution was ultrasonically dispersed again for 15 min before a drop was deposited onto C-coated grids and left to dry for 24 h, at room temperature. The microscope used was a Philips 420 STEM operated at 120 V and equipped with a Megaview II CCD camera.

3. Results

3.1. Physical and textural analyses

The physical parameters obtained from the geotechnical characterization carried out on P3, P4 and P11 profiles are presented in Table 2. The natural (γ), dry (γ_d) and solid (γ_s) specific weights, the water content (w), void ratio (e), and porosity (n) are very similar between the three profiles and vary little with depth, the major noticeable differences being lower void ratios at the surface of P3 and in a deep layer (P11-5) of P11. The water table was not detected in the three profiles. The solid specific weight is high in all horizons, close to 30 kN m^{-3} , which reflects the high Fe_2O_3 contents (see below), whereas the natural specific weight is low, corresponding to high void indexes, particularly around 2–4 m depth. The texture of the soil, based on the particle size analyses after dispersion with Na hexametaphosphate, is silty clay, except for the deepest layers of P3 and P11 which are clay silt. On another hand, without dispersing agent, all soil samples would be classified as sandy silt, except for P11-0.5 and P11-2 which appeared as clay silt.

3.2. Chemical characteristics of soil

The results of pH, exchangeable cations, CEC and organic matter contents are presented in Table 3. The pHs are generally acidic, with the lowest values found in the deep layers of P3, down to 4.1 for the pH in KCl at 6–7 m in this profile. The pH values are higher in P4 and P11, reaching slightly alkaline values for the pH in water of P11 samples between 3 and 7 m deep. The ΔpH are negative, between -0.2 and -1.4 , except in the P11-2 sample where it is zero and for P3-4 and P4-7 with positive values. A negative ΔpH , apart from the case of exchangeable Al as in P3-6 and P3-7, implies that soil samples have variable charges protonated at the pH in water. These charges are probably in Fe oxides since the zero points of charge (ZPC) of kaolinite and magnetite for example, are about 4.6 and 6.5, respectively (Meurer, 2004). The layers P3-4 and P4-7 which have positive ΔpH are also characterized by the lowest CEC (Table 3), that might indicate the neutralization of variable charges by specific counteractions between kaolinite and oxides.

The CEC values at 0.5 m are relatively high and decrease with depth, except for P3 where they increase again between 4 and

Table 2
Physical characteristics of the samples.

Samples	Depth (m)	γ^a (kN m^{-3})	γ_d^b (kN m^{-3})	γ_s^c (kN m^{-3})	w (%)	e	n (%)	PSD (%) ^d using a dispersing agent (%)				PSD (%) no dispersing agent (%)				Ratio Silt/clay
								Clay	Silt	Fine sand	M. sand	Clay	Silt	F. sand	M. sand	
P3-0.5	0.5	16.2	11.5	29.7	40.5	1.6	61.2	75	16	8	1	11	67	21	1	0.2
P3-2	2.0	14.3	10.1	31.4	41.8	2.1	67.9	55	26	18	1	0	60	39	1	0.5
P3-4	4.0	15.0	10.6	33.8	41.0	2.2	68.5	55	20	24	1	0	70	28	2	0.4
P3-6	6.0	15.4	10.9	30.0	40.7	1.7	63.6	45	39	15	1	0	77	22	1	0.7
P3-7	7.0	15.2	10.6	30.1	43.8	1.8	64.8	28	50	21	1	0	72	27	1	1.8
P4-0.5	0.5	15.4	11.3	32.6	36.5	1.9	65.4	60	27	12	1	2	60	37	1	0.5
P4-2	2.0	14.2	10.2	29.6	39.4	1.9	65.6	74	17	8	1	1	83	15	1	0.2
P4-4	4.0	14.9	11.0	30.6	35.6	1.8	64.1	71	14	14	1	2	72	27	1	0.2
P4-7	7.0	14.9	10.8	30.4	37.5	1.8	64.4	56	28	15	1	0	66	33	1	0.5
P11-0.5	0.5	16.2	12.0	33.3	35.2	1.8	64.0	52	35	12	1	34	36	28	2	0.7
P11-2	2.0	14.9	10.5	30.8	41.5	1.9	65.8	71	19	14	1	16	76	7	1	0.3
P11-3	3.0	14.6	10.5	31.1	39.5	2.0	66.3	64	26	9	1	5	77	17	1	0.4
P11-5	5.0	17.0	12.1	31.2	40.0	1.6	61.1	52	35	12	1	10	72	17	1	0.7
P11-7	7.0	ns	ns	31.5	35.5	ns		45	36	17	1	3	67	28	2	0.8

ns = No sample; w , water content; e , void ratio; n porosity.

^a Natural specific weight.

^b Dry specific weight.

^c Solid specific weight.

^d Particle size distribution with Na hexametaphosphate; upper limits are 2, 60, 200 and 600 μm for clay, silt, fine sand and medium sand fractions, respectively.

Table 3
Chemical characteristics of the samples.

Sample	pH		ΔpH	CEC ^a ($\text{cmol}_c \text{ dm}^{-3}$)	Ca^{2+} ($\text{cmol}_c \text{ dm}^{-3}$)	Mg^{2+} ($\text{cmol}_c \text{ dm}^{-3}$)	Al^{3+} ($\text{cmol}_c \text{ dm}^{-3}$)	$\text{H}^+ + \text{Al}^{3+}$ ($\text{cmol}_c \text{ dm}^{-3}$)	K^+ ($\text{cmol}_c \text{ dm}^{-3}$)	OM ^b (g kg^{-1})
	H_2O	KCl								
P3-0.5	6.2	5.6	-0.6	11.0	5.9	1.9	<LD	3.2	0.1	8.5
P3-2	6.3	5.9	-0.4	9.0	4.2	1.7	<LD	2.7	0.4	3.6
P3-4	5.6	5.7	0.1	7.9	3.0	1.9	<LD	2.9	0.1	1.7
P3-6	4.9	4.1	-0.8	15.5	0.6	0.7	3.0	14.1	0.2	1.6
P3-7	5.0	4.1	-0.9	16.5	0.3	0.2	3.1	15.2	1.0	1.4
P4-0.5	6.9	5.9	-1.0	13.0	6.9	2.1	<LD	2.9	1.0	21.1
P4-2	6.9	6.1	-0.8	10.0	4.9	0.9	<LD	2.5	1.7	5.4
P4-4	6.5	6.0	-0.5	8.5	4.1	1.6	<LD	2.7	0.1	2.1
P4-7	5.5	5.8	0.3	7.8	2.7	2.3	<LD	2.7	0.1	1.4
P11-0.5	6.5	6.2	-0.3	21.1	8.2	3.9	<LD	2.9	6.1	28.9
P11-2	5.6	5.6	0.0	17.2	5.0	2.8	<LD	4.0	5.4	7.5
P11-3	7.4	7.0	-0.4	14.5	4.3	2.2	<LD	2.4	5.6	8.2
P11-5	7.1	6.7	-0.4	13.7	4.3	2.1	<LD	2.4	4.9	7.5
P11-7	7.7	6.8	-0.9	10.3	1.9	1.2	<LD	2.2	5.1	3.2

^a Cation exchange capacity, equal to exchangeable $\text{Ca} + \text{Mg} + \text{K} + \text{H} + \text{Al}$; LD limit of detection.

^b Organic matter (1.72 times the organic carbon content, see Section 2).

Table 4Total chemical analyses of the samples^a.

Sample	Al ₂ O ₃ (%)	CaO (%)	Fe ₂ O ₃ (%)	K ₂ O (%)	MgO (%)	MnO (%)	Na ₂ O (%)	P ₂ O ₅ (%)	SiO ₂ (%)	TiO ₂ (%)	IL ^b (%)
P3-0.5	27.9	0.22	23.4	0.08	0.15	0.22	<0.1	0.17	34.6	3	10.45
P3-2	26.2	0.15	26.8	0.08	0.26	0.24	<0.1	0.15	31.3	4.1	9.85
P3-4	25.3	0.11	29.4	0.07	0.25	0.22	<0.1	0.15	32.6	3.7	7.36
P3-6	26	0.03	25.2	0.08	0.34	0.16	<0.1	0.15	34.3	3.5	10.13
P3-7	25.9	0.02	23.7	0.24	0.43	0.2	<0.1	0.2	34.7	3	10.59
P4-0.5	22.9	0.36	28.5	0.13	0.23	0.45	<0.1	0.24	30.2	5.1	10.97
P4-2	26.4	0.16	25.4	0.14	0.29	0.27	<0.1	0.2	32.8	3.9	9.47
P4-4	26.8	0.11	26.2	0.07	0.23	0.22	<0.1	0.18	32.3	4.2	9.63
P4-7	27.1	0.09	26.7	0.06	0.26	0.14	<0.1	0.16	32.3	4.3	8.98
P11-0.5	20	0.25	31.4	0.39	0.37	0.53	<0.1	0.28	29.5	6.5	9.98
P11-2	25.7	0.16	25.7	0.36	0.19	0.44	<0.1	0.2	32.4	4.4	9.87
P11-3	25.1	0.19	26.2	0.39	0.29	0.33	<0.1	0.21	33.4	4.3	9.72
P11-5	24.6	0.13	26.3	0.36	0.22	0.19	<0.1	0.23	33.2	4.7	9.76
P11-7	24.7	0.12	26.7	0.34	0.2	0.24	<0.1	0.28	32.3	4.8	10.63
Rock	13.7	9	15.4	1	3.8	0.24	2.5	0.31	51.8	2.2	0.97

^a Elemental analysis by X-ray fluorescence.^b IL: ignition loss at 1000 °C.

7 m. The largest CEC is found at 0.5 m in the P11 profile. With respect to exchangeable cations, the most acid samples P3-6 and P3-7 consistently contain exchangeable Al and more exchangeable H⁺ than any other sample, these cations being mainly responsible for the CEC increase at the bottom of this profile. Considering the other exchangeable cations and referring to the unaffected P3 profile, one can notice the relative abundance of K, Ca and Mg in the whole of profile P11 and in some layers of P4.

The largest contents of organic matter are found at 0.5 m, which is due to the biological activity in the superficial layers. But relatively high contents of organic matter are also observed in P4-2, compared to deeper layers, and in the whole of profile P11 compared to P3 and P4.

3.3. Total chemical analyses by X-ray fluorescence

X-ray fluorescence was carried out on the soil samples and on a sample of the bedrock. Table 4 presents the results, normalized with respect to the sum of oxide contents plus the ignition loss. The contents of Fe₂O₃ and TiO₂ increase as SiO₂ decreases in the profiles, whereas the Al₂O₃ content generally shows the same trend as SiO₂, demonstrating the advanced degree of weathering in these soil profiles.

3.4. Mineralogical analyses by X-ray diffraction

All XRD diagrams of the samples of P3 and P11 profiles show that kaolinite is the dominant clay mineral. Iron oxides are also identified in the form of hematite, magnetite and goethite, and Al as gibbsite (Al(OH)₃) in some clay fractions. Quartz was identified, although only with small intensity peaks, showing the low content of this mineral in the studied clay samples.

XRD was also carried out on oriented clay samples saturated with ethylene glycol, or heated, in order to detect the presence of expandable phyllosilicates. Such minerals were not detected, confirming the high degree of weathering of the studied profiles.

3.5. Metal fractionation and mobility in the profiles

The results of sequential extractions and total digestions are given below for Fe, Mn, Cu, Zn, and Co. To outline the reproducibility between duplicates, their means and standard deviations are given in graphs showing the different fractions of each element versus depth in each profile (Figs. 3–7, left side). These figures also give the percentages of extracted metals E1 and E2 with respect to their total contents (right sides).

3.5.1. Assessment of the quality of analyses

FAAS analyses were first validated on the recovery between 91% and 109% of 26 standard additions in solution samples for all studied elements, except for Fe in hydroxylamine extracts where recoveries lay between 89% and 130%. All reported results correspond to concentrations above the quantification limits (QL), and all blanks were below QL except once with Zn and once for Fe. The certified total content values for the sample CAN-LKDS-1 were recovered between 91% (Zn) and 103% (Co). The sums of the metal fractions plus the residual contents were equal to 101 ± 13% (mean, standard deviation, *n* = 40) of the total contents determined on initial sample aliquots.

The reproducibility of results obtained for the total contents was quite satisfactory, with variations generally much lower than 10%, except for Mn with two samples, one for Fe and one for Co (Figs. 3, 4 and 7). Heterogeneity of surface samples and the occurrence of mangano-ferric concretions in deeper layers may explain these few cases. The variations for the metal fractions were frequently high, particularly for Zn and Co in fraction E2 (Figs. 6 and 7). This can be related to difficulties when using the same sample in two successive moderate extractions (Egreja Filho, 2000; Lã et al., 2003; Lee and Kao, 2004). Nevertheless, the reproducibility of the data presented in Figs. 3–7 allows for the comparisons detailed below.

3.5.2. Iron

The high and rather constant Fe contents are typical of lateritic soils originated from basalt, with no accumulation in any particular horizon (Fig. 3). The extractions of Fe by acetic acid or hydroxylamine are very low (less than about 0.1% or 1% of the total, respectively). The highest values for E2 fractions are found in the surface layers (0.5 m), but in P11, this fraction remains at the same level, about 1 g kg⁻¹, through the whole profile (Fig. 3).

3.5.3. Manganese

The total Mn contents are higher in P11, down to 7 m, and in P4-0.5, by comparison with P3 (Fig. 4). The fraction E2 shows the same trends, since total and reducible Mn vary together. This fraction is always important, falling between about 20% and 70% of total Mn except in P4-7. In contrast, the labile fraction E1 is very low in the P3 and P4 profiles, but represents 7–33% of total Mn in P11, the maximum lying in P11-0.5.

3.5.4. Copper

The total Cu contents are roughly constant throughout the three profiles, between 330 and 375 mg kg⁻¹ (Fig. 5). The mobile

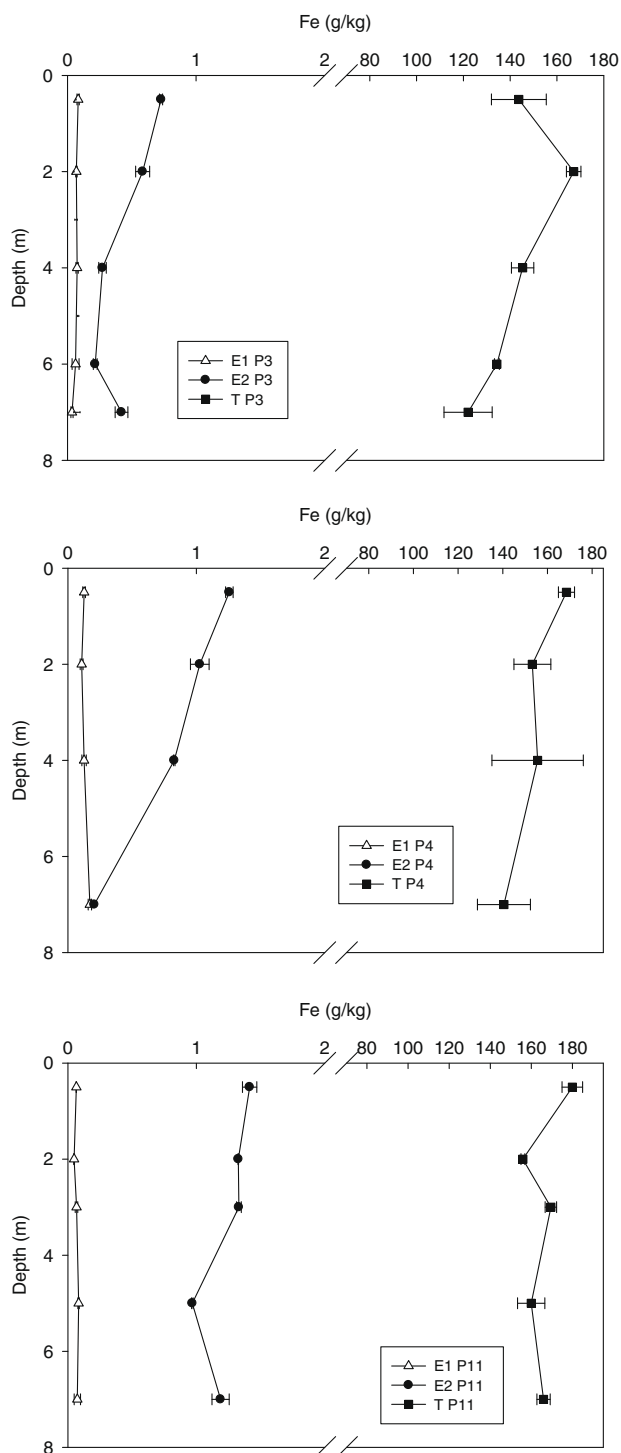


Fig. 3. Behaviour of Fe down the studied profiles (different scales for total and mobile fractions; bars represent standard deviations).

fractions vary more, between 1.4 and 12% of total Cu. The E1 fraction at 0.5 and 2 m is larger in P11 than in P3, but the largest values are found in P3 at 6–7 m. The E2 fraction is relatively high in surface layers of P4 and P11, and indeed throughout the P11 profile (Fig. 5).

3.5.5. Zinc

The total contents of Zn vary a little more than those of Cu throughout the profiles and P11 shows values above 158 mg kg^{-1} ,

systematically higher than in P3 or P4 (Fig. 6). The mobile fractions are low, between 0.4 and 10 mg kg^{-1} for E1 and between 0.2 and 10 mg kg^{-1} for E2. In P11 only, these fractions appear parallel to the total content, and they are generally higher than in the other profiles. They are also relatively higher in surface layers (0.5 m). Then, as for Cu, the mobile fractions increase again in the deep layers of P3 (6–7 m).

3.5.6. Cobalt

The analyses of Co generally show the decreasing order $\text{TD} > \text{E2} \gg \text{E1}$ and for the profiles $\text{P11} > \text{P4} \cong \text{P3}$ (Fig. 7). Cobalt showed the largest fraction in E2 when compared to the other analyzed elements. The fraction E1 represents less than 1% of the total content of Co in P3 and P4, but about 15% in P11. Figs. 4 and 7 strongly suggest that the behaviour of Co is similar to that of Mn in all the profiles and fractions.

3.6. Characterization of soil water extracts

The results for pH, electrical conductivity, major and trace elements of soil water extracts obtained in the laboratory are presented in Table 5. The concentrations of Cu, Zn, Co, Al and Fe generally fall under the quantification limit of the analytical technique used, except for Al in the surface horizons and for Cu and Co in several samples of P11 and the deep samples of P3. For all other measurements, the main trend is that small values are observed with P3 and large values occur with P11 and the surface layers of P4. Above all, the electrical conductivity in P11, although decreasing down the profile, remains very high when compared to the other profiles, which is also the case with K and Na concentrations. One noticeable result concerns pH, generally higher in P11 and P4 compared to P3, except for P11-0.5 where it is particularly low (pH 4.9).

3.7. Micro-morphology analyses

Based on observations by optical and transmission electron microscopy, the morphologies of the structures and of the particles of the soil down the profiles were described, with the particular aim of identifying transformations induced by MSW leachates.

3.7.1. Optical microscopy

The observations on the optical microscope were made from a thin section of soil using natural light. Fig. 8 shows a typical image of the A horizon from P3 at 0.5 m depth. A clayey matrix with continuous dense and dark red areas in relation to the more yellowish red fissured areas can be seen. The denser and redder clayey areas are round and surrounded by clearer matrix, which probably has a lower Fe content.

The structure in general, is organized in angular polyhedron microaggregates, separated by larger and smaller natural fissures, respectively, called non-conformed and conformed. The larger fissures were produced by the passage of water and they make up the percolation path. The porosity becomes variable between the macro to micro porous aggregates.

Fig. 9 shows an image of P11 at 0.5 m depth. One of the different features observed is dark color impregnation on the borders of the pores that was not identified in the P3 plates. This impregnation suggests the accumulation of a leached substance, due to the dynamics of the profile. The presence of the impregnation of the voids was observed in all of the ultra thin sections of P4 and P11 samples.

3.7.2. Transmission electronic microscopy

The observations by TEM were made for the samples from the P3 and P11 profiles and they allowed the visualization of the morphologies of the mineral particles. Fig. 10 shows images of the P3

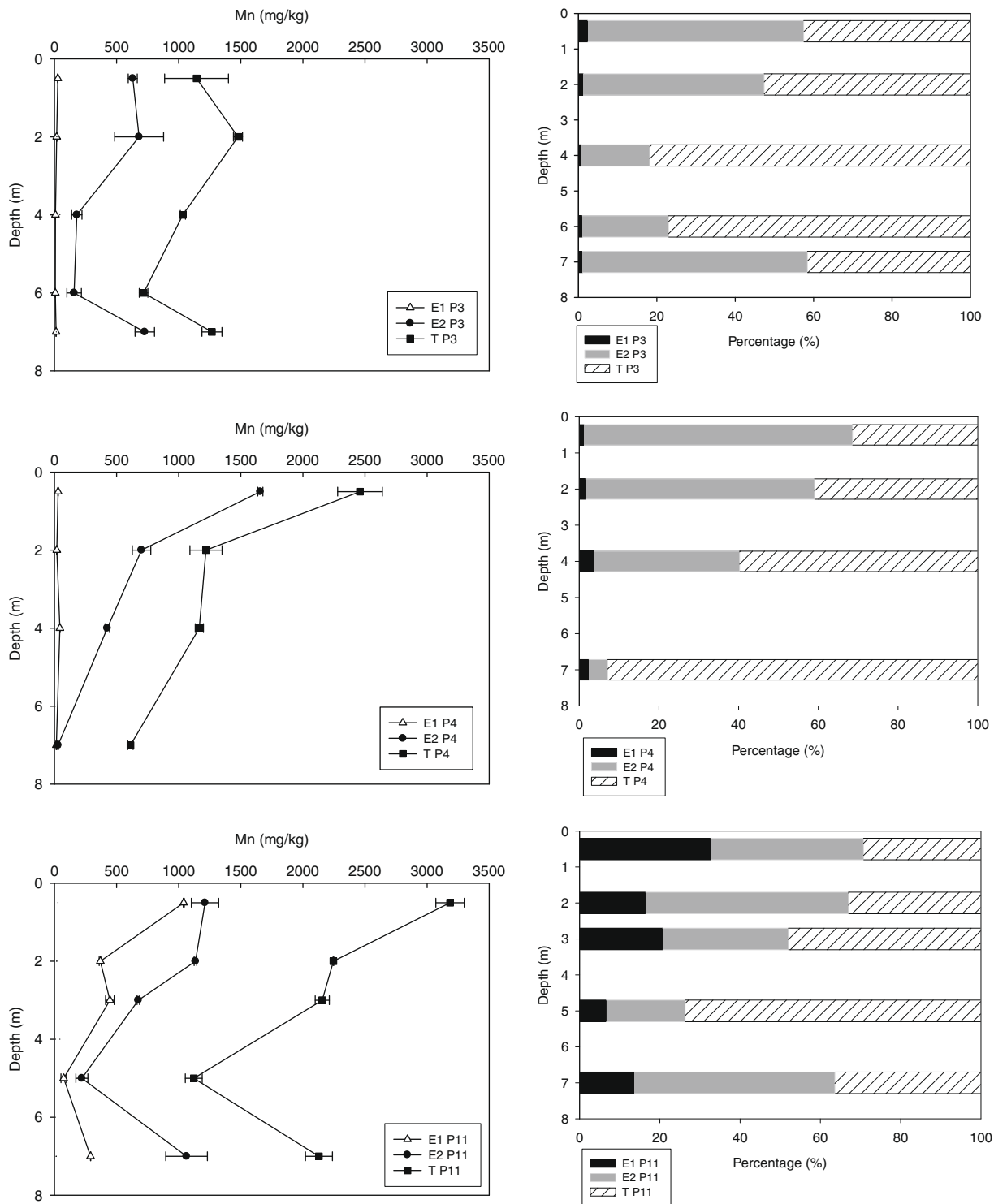


Fig. 4. Behaviour of Mn down the studied profiles (bars represent standard deviations) and percentages of mobile E1 and E2 fractions.

samples at 0.5 m depth where different sized hexagonal particles and the kaolinite clay mineral are observed in abundance in the two images. The presence of Fe oxides, possibly dark colored and rounded hematite and magnetite, and also halloysite, in baton format can be noticed. The presence of quartz is recognized as triangular and dark minerals which are larger than the others. Some aggregates with several clay associated particles can be seen.

The images obtained of the P11 samples at 0.5 and 5 m depths (Fig. 11) show the same mineralogy, as well as the same morphology and the presence of kaolinite clay, quartz and Fe oxides. But

characteristic images of organic matter that have undefined and translucent form also appear. Organic matter was ubiquitous in the sample 5 m depth, always occurring surrounding minerals.

4. Discussion

4.1. Physical, chemical and mineralogical characteristics of soil

The texture of the soil determined by particle size analyses varies from silty clay, after dispersion with sodium hexametaphosphate,

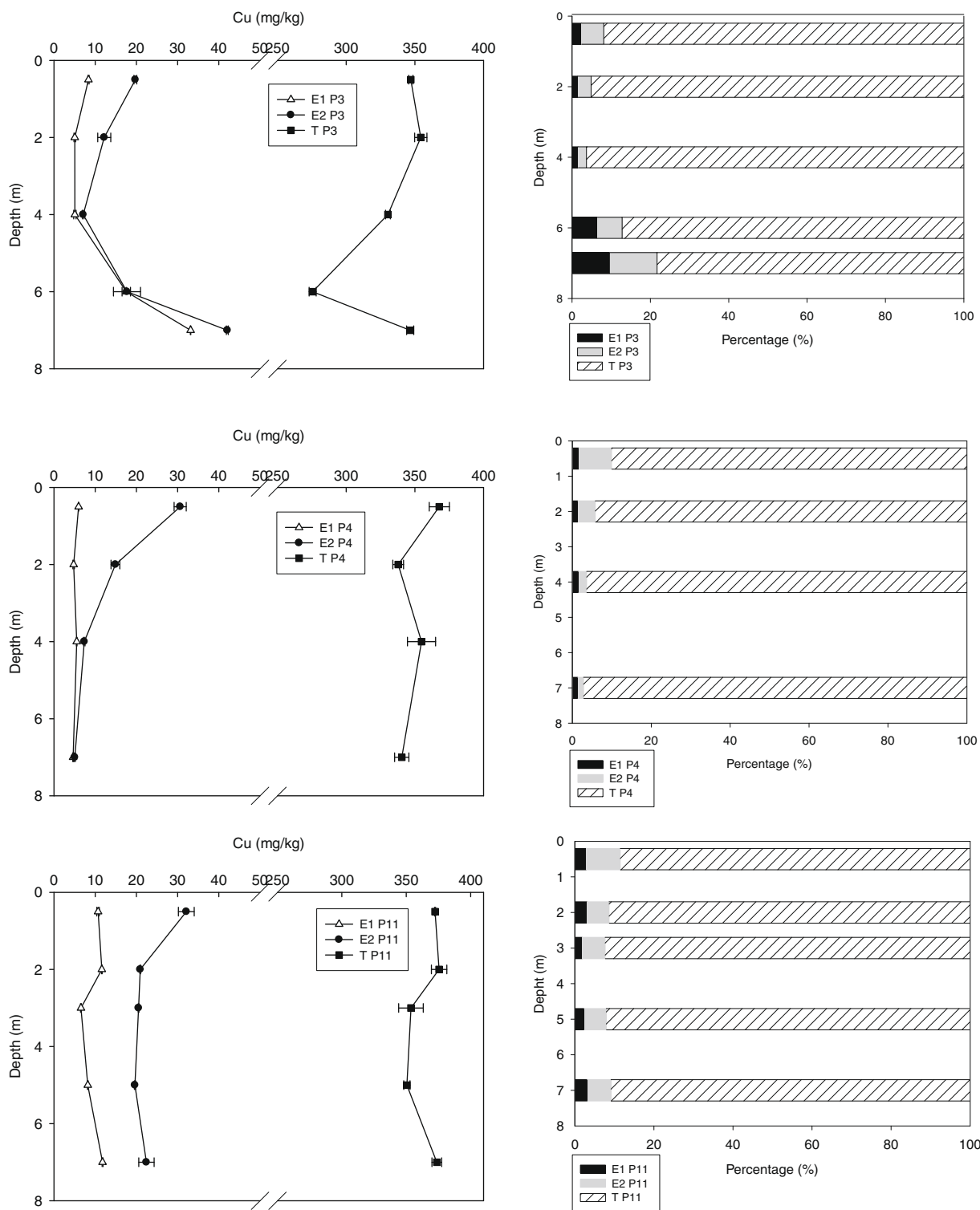


Fig. 5. Behaviour of Cu down the studied profiles (bars represent standard deviations) and percentages of mobile E1 and E2 fractions.

to sandy silt, without dispersing agent. Such variation in the textural classification reveals the aggregation of clay-oxide particles (Cambier and Picot, 1988), which is also responsible for the high porosity, providing good permeability. This behaviour is typical of soil exposed to tropical weathering, rich in Fe oxides and with a high Al content, as described by Delvigne (1960), Chauvel (1977) and Melfi and Pedro (1978a,b) amongst others. The predominance of kaolinite, gibbsite and ferric oxides, as seen from XRD and TEM confirm this

relationship. Apart from the surface ones, the studied samples belong to the thick B horizon of this highly weathered soil. However the silt/clay ratio indicates that the deepest sampled layers of the profiles P3 and P11 approach the C horizon, since values >0.7 are specific characteristics of the C horizon (EMBRAPA, 1999). With regard to the possible impact of the MSW, the unexpected similarity between particle size analyses with and without hexametaphosphate for the P11-0.5 sample could be due to changing interactions be-

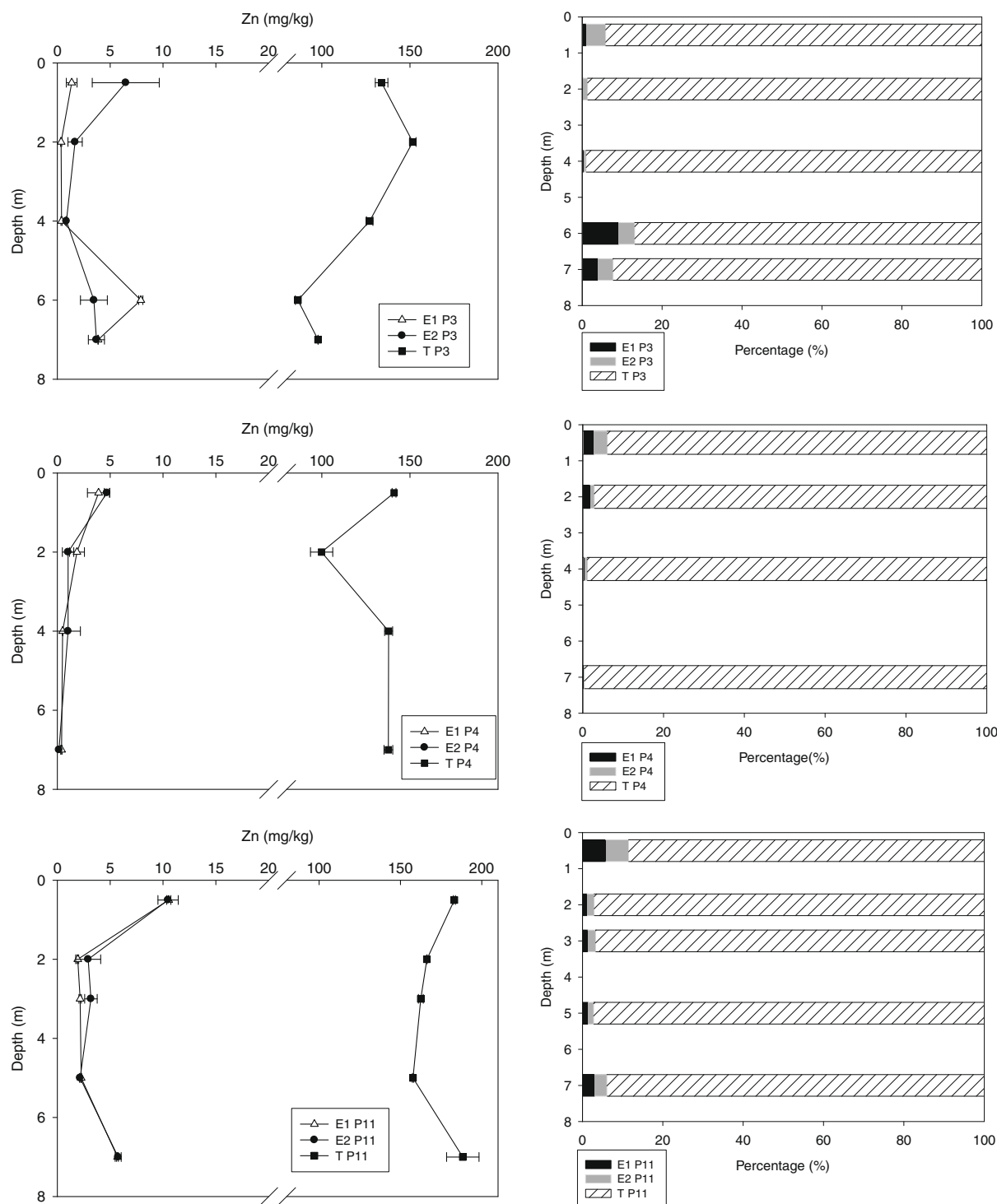


Fig. 6. Behaviour of Zn down the studied profiles (bars represent standard deviations) and percentages of mobile E1 and E2 fractions.

tween constituents in relation to the composition of leachates (see Section 4.2).

Latosols usually have A and B horizons which are acid and poor in base cations, these being replaced by exchangeable Al and protons. In this work, only a few of the studied samples are markedly acid. It is noteworthy that the whole area was or is being cultivated, so that pH and other chemical characteristics may be affected by tillage and fertilizers. But the differentiation of pH in the deep horizons between the profile P3 where it is lower than 5, and the profile P11 where it is around 7, can be attributed to waste

landfill leachates which appear to have reached the bottom of the latter. Indeed, the organic matter content, apart from the usual decrease below the surface horizons, has enhanced values in the whole P11 profile, and in the upper layers of P4.

There is a positive and significant correlation between organic matter and the CEC in these profiles. This is not the case for P3, where another contribution to the CEC makes it increase in the deepest layers, because of the way CEC is calculated, i.e., by the sum of exchangeable cations including the potential acidity determined at pH 7. This CEC measured in all samples from <0.5 m

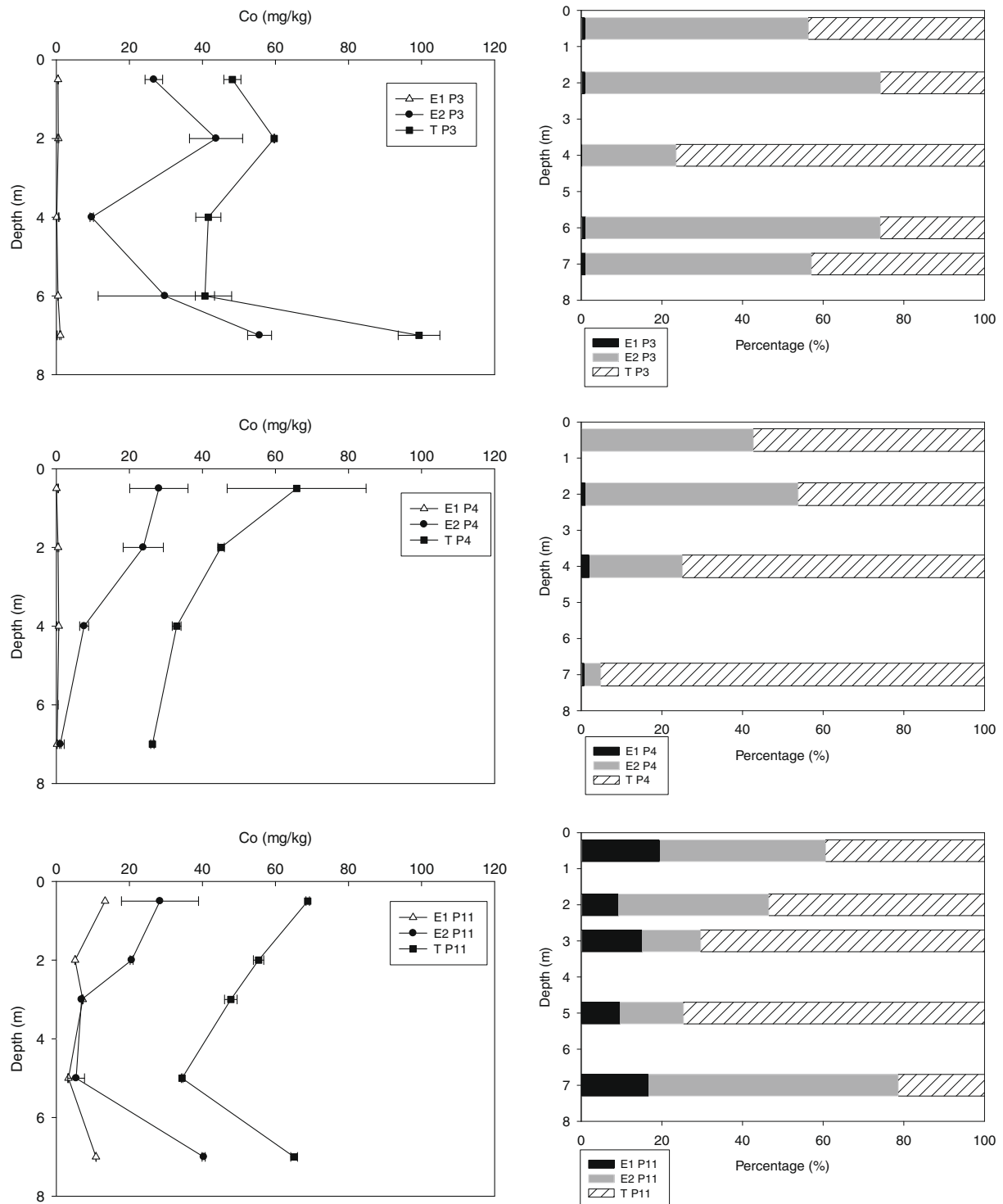


Fig. 7. Behaviour of Co down the studied profiles (bars represent standard deviations) and percentages of mobile E1 and E2 fractions.

depth, as is common for Brazilian latosols, is $<17 \text{ cmol}_c \text{ kg}^{-1}$, the threshold value used to classify the B horizon of latosols by EMB-RAPA (1999). The ΔpH values are most often negative, and the ZPC are lower than the pH. According to Uehara (1979), these conditions lead to the appearance of negative surface variable charges. These charges can be attributed to oxide surfaces, kaolinite edges, and to organic substances particularly in P11 samples as suggested above. The exchangeable cations also indicate the impact of waste leachates, with the importance of K^+ in P11, and to a lesser extent in P4-0.5 and P4-2.

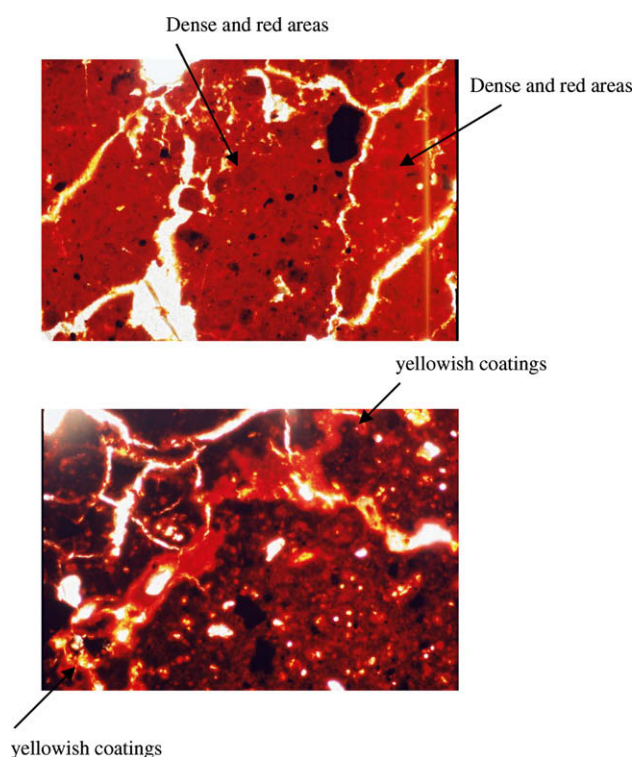
4.2. Soil water extracts

The data obtained from soil water extracts confirm several trends in the chemistry of soil samples, and reinforced the description of waste leachate impacts. The electrical conductivity in P11 decreases with depth, as in P4, but with very high values in P11 compared to the other profiles. The same trends are observed in the concentrations of K and Na, and to a lesser extent with Ca, Mg and Mn. Similar differences between profiles were noticed for exchangeable K and Ca (Table 3). By contrast, a major difference

Table 5

pH, electrical conductivity, major and trace element concentrations of the soil water extracts.

Sample	pH	Elec. cond. ($\mu\text{S cm}^{-1}$)	K (mg L^{-1})	Mg (mg L^{-1})	Mn (mg L^{-1})	Na (mg L^{-1})	Ca (mg L^{-1})	Al (mg L^{-1})	Fe (mg L^{-1})	Cu (mg L^{-1})	Zn (mg L^{-1})	Co (mg L^{-1})
P3-0.5	7.4	56.3	<0.50	2.9	0.4	0.3	15.5	0.31	0.11	<0.01	<0.01	<0.01
P3-2	5.9	114.0	5.3	4.4	1.1	0.3	17.8	<0.05	<0.05	<0.01	<0.01	<0.01
P3-4	5.8	126.0	0.7	3.3	0.3	0.3	4.6	<0.05	<0.05	<0.01	<0.01	<0.01
P3-6	5.3	35.8	1.3	2.0	0.3	0.6	2.8	<0.05	<0.05	0.02	<0.01	<0.01
P3-7	5.2	39.3	10.4	1.9	0.2	0.3	2.3	<0.05	<0.05	0.02	<0.01	0.01
P4-0.5	7.7	177.0	17.2	9.1	1.0	4.3	20.8	0.22	<0.05	0.01	<0.01	<0.01
P4-2	7.4	160.0	24.6	2.8	0.2	10.8	11.4	<0.05	<0.05	<0.01	<0.01	<0.01
P4-4	6.8	97.9	<0.50	3.4	0.8	4.9	10.1	<0.05	<0.05	<0.01	<0.01	<0.01
P4-7	5.2	124.0	0.5	4.3	0.2	11.2	7.5	<0.05	<0.05	<0.01	<0.01	<0.01
P11-0.5	4.9	2440.0	313.0	51.0	26.4	158.0	124.0	0.25	<0.05	0.02	<0.01	0.03
P11-2	7.6	1292.0	220.0	11.1	0.8	100.0	30.0	<0.05	<0.05	<0.01	<0.01	0.01
P11-3	7.7	1212.0	202.0	6.0	0.2	106.0	19.3	<0.05	<0.05	0.01	<0.01	0.02
P11-5	7.5	1041.0	164.0	2.3	0.0	88.4	9.7	<0.05	<0.05	<0.01	<0.01	<0.01
P11-7	7.7	884.0	143.0	1.3	0.0	62.6	4.0	<0.05	<0.05	0.03	<0.01	0.02

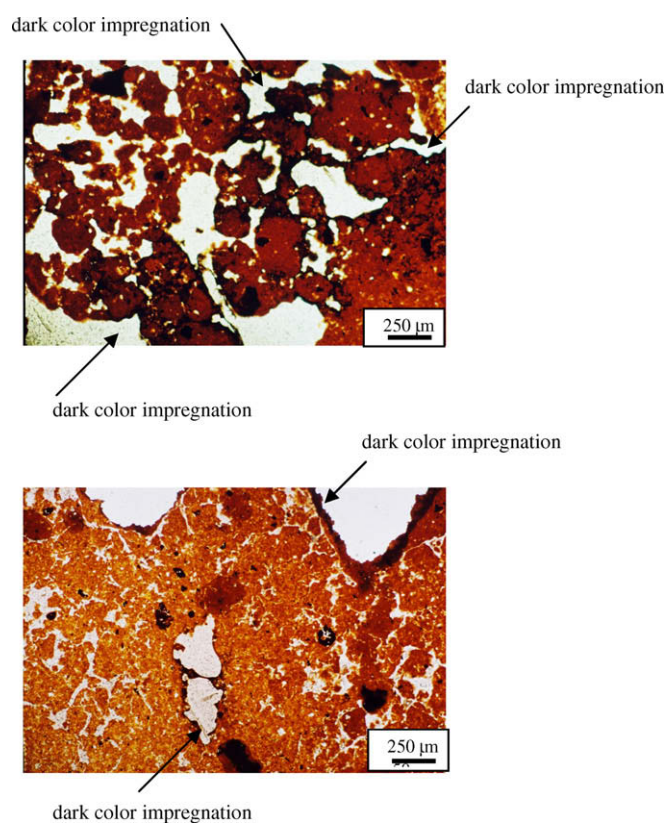
**Fig. 8.** Images of the ultra thin section of soil of P3 at 0.5 m depth.

of soil chemical data lies in the low pH value of the water extract obtained from the P11-0.5 sample (about 4.9). This may be due to the decomposition of organic matter by acetogenic bacteria (Chernicharo, 1997). This may have also increased the concentration of metals, particularly Mn, in this solution.

According to Prado (2003), high K and Na concentrations and a soil pH above its ZPC, can induce the dispersion of clay and may explain the similar clay content found in P11-0.5, with or without chemical dispersant (Table 2).

4.3. Fractionation of metal

The high contents of Fe and some other metals are typical of latosols of Paraná, originating from basic rocks under a tropical climate (Souza et al., 1996; MINEROPAR, 2005; Melfi et al., 1979). The casual impacts of MSW on their total contents seem low or insignificant. Thus the following discussion considers first the variations of metal fractions between the three profiles.

**Fig. 9.** Images of the ultra thin section of soil of P11 at 0.5 m depth.

4.3.1. Mobility of Fe and Mn

The low Fe content of E1 and E2 fractions are consistent with the dominant crystalline forms of ferric oxides in the latosol profiles of the investigated area (Melfi et al., 1979; Matos et al., 2001 Ghidin et al., 2006). However a significant increase of Fe was found in the E2 fraction of P11 in comparison to P3, which could be attributed to waste leachates carrying reduced or organic complexed forms of Fe. Manganese was extracted in step E2 in much greater proportion than Fe, consistent with the reduction of Mn oxides by hydroxylamine and the specificity of this dissolution with respect to ferric oxides (Chao, 1972; Shuman, 1985; Hernández-Moreno et al., 2007). The differences of Mn behaviour between the studied profiles, particularly between P3 and P11, are found in all fractions. It can then be concluded that the impact

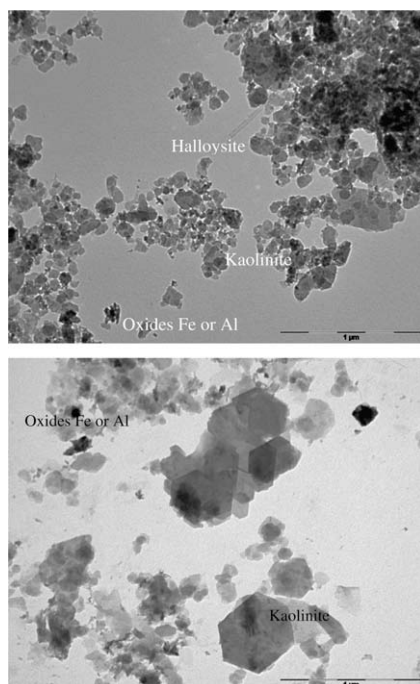


Fig. 10. TEM images of P3 samples at 0.5 m depth.

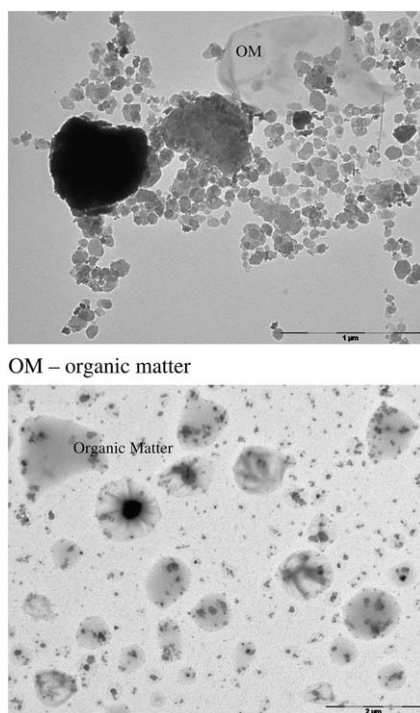


Fig. 11. TEM images of P11 samples at 0.5 and 5 m depths.

of waste leachates is limited to the reducible fraction of Fe but is reflected in the labile, reducible and total contents of Mn.

4.3.2. Cobalt

Cobalt was found to have similar behaviour to Mn in the three soil pits, suggesting a strong association between both elements. Several other researchers have already underlined this association, according to Alloway (1995). However the very noticeable differ-

ence between profiles is shown for the E1 fraction, having very low Co in P3 or P4 but being in the range 9–19% of total Co in P11, evincing a major impact of waste leachates on metal mobility.

4.3.3. Copper

According to Bradl (2004), depending on the pedoclimatic conditions, the mobility of Cu is low because it has a marked affinity with soil components following in decreasing order: Mn oxide > organic matter > Fe oxide > clay minerals. Matos et al. (2001) concluded from metal extraction experiments carried out on Brazilian latosols, that the strong association between organic matter and Cu leads to its retention in surface A horizons. Egreja Filho (2000) using a similar approach underlined the role of oxides and organic matter in Cu retention by lateritic horizons. The present results show high and rather constant Cu contents in all horizons, with more than 90% extracted only by total digestion. Thus this element is mainly linked to mineral structures. On the other hand, moderate increases in the E2 fraction of P11 and at the surface of P4 can be ascribed to contamination from the MSW deposit, this fraction being associated to parallel organic matter inputs. In contrast, the high values of the E1 and E2 fractions in P3 at 6–7 m are probably due mainly to the naturally acid pH. Mouta et al. (2008) underlined the sharp variation of Cu retention on variable charge subsoil material with pH in the 4.0–5.0 range.

4.3.4. Zinc

Zinc with its +2 valency and its atomic size, can substitute for Fe^{+2} and Mg^{+2} in different rock minerals, mainly in the silicate and oxide groups. It can also replace a few% of Fe^{3+} in goethite. When deriving from anthropogenic sources, Zn is known to be a relatively mobile and bioavailable metal in the soil, having a significant exchangeable or labile fraction as here in the E1 fraction, and a comparable reducible fraction. These fractions are commonly attributed to adsorbed Zn on permanent and above all variable charge surface sites of Fe, Mn or Al oxides. Zinc can also be fixed by organic matter although less specifically than Cu. Thus the present data provide evidence for the predominance of natural Zn in the soil, with a minor component of mobile fractions E1 and E2 in surface horizons, and a small increase of labile Zn in the P11 profile and in P4-0.5. These latter differences between profiles, as similar differences for Cu, show a limited impact of the MSW leachates.

4.4. Micro-morphology

With regard to the soil structure and the morphology of the constituents, some important features were observed in surface horizons (Fig. 8) such as the continuous clayey matrix with denser dark red color areas, where the microaggregation begins and incipient yellowish red zones, that can be more sensitive areas with lower Fe content. For the P11-0.5 undisturbed sample (Fig. 9), the presence of dark colored material was also observed, impregnating the borders of the voids and coating features. The dark colored material does not seem to be mineral; on the other hand it seems to be from the accumulation of the leaching. The coatings are clay composition features, yellowish in color and occurring around the pores. They are particularly affected, in contrast to the clayey matrix of the original P3 soil, and they were identified in the profiles that are located in the contaminating plume flow, showing the effect of leachate in the soil.

The morphology of the soil clay fraction, observed in TEM (Figs. 10 and 11), confirms the presence of minerals common in latosol profiles with a high degree of weathering: kaolinite, Fe oxides and quartz. The phyllosilicate occurs in different stages of weathering, from the well crystallized kaolinite in a hexagonal format to poorly crystallized rounded forms.

The abundant presence of organic matter was verified in the TEM images taken from the P11 samples at 0.5 and 5 m depth (Fig. 11). The presence of isolated organic matter was identified in the P3 samples in only one image at 0.5 m depth. These observations confirm the presence of organic contamination, in the P11 profile, and its absence in the reference P3 profile.

5. Conclusions

The soil samples investigated belong to dark red thick clayey A and B horizons of residual latosols, located well above the water table and the bedrock, although the deepest layers of two profiles reached more silty and less weathered material. The P3 profile is located mid-slope out of direct streaming from the MSW deposit, whereas the P4 and P11 profiles are on a dip slope, with greater contamination as defined by geophysical resistivity methods. The high electrical conductivity and concentration of some cations in soil water extracts of samples taken from P4 and, in particular, P11 result from contact between MSW leachates and the soil, which also increased the soil pH values, the organic matter content, the CEC and exchangeable base cations.

The most acid soil pHs were obtained from the deepest layers of the unaffected pit P3. These conditions induce relatively high fractions of mobile metals at the bottom of this profile. But similarly high mobile fractions of Co, Mn and Zn were observed at the bottom of P11, despite the neutral or slightly alkaline pH which should favor the adsorption of these metals on variable charge oxide and clay surfaces. When considering surface horizons where pHs are more alike, higher E1 fractions of Co, Mn and Zn in P11, and higher E2 fractions of Cu, Mn and Zn were found in P11 and P4 compared to P3. Thus the systematic higher concentrations of mobile metals in the P4 and P11 profiles, indicated by the sequential extractions, clearly shows the influence of MSW leachates from both surficial and subsurface flows.

The leachates streaming into the soils from the RSU landfill of Londrina did not affect their physical characteristics (soil and solid specific weights, void ratio, mineralogy, particle morphology) except for a limited dispersion effect on clay microaggregation in the surface horizon of P11. However, such dispersion has apparently not hampered impregnations of this profile down to deeper layers, affecting their color, inducing a smell of decomposing organic matter and the migration of contaminants. More detailed studies should focus on the interactions between MSW organic compound transformations and the mobility of Fe and potentially harmful metals in impacted horizons.

Acknowledgements

The first author gratefully acknowledges the support of the CAPES/Brasil during doctoral training at the Research Unit PESSAC of INRA Versailles. All persons in this laboratory are thanked for their help and warm support. We also thank Professor N. Lepp and an anonymous reviewer for their constructive criticisms and comments of an earlier version of this manuscript.

References

Alloway, B.J., 1995. Heavy Metals in Soils, second ed. Blackie Academic & Professional, London.

Alloway, B.J., Ayres, D.C., 1997. Chemical Principles of Environmental Pollution, second ed. Blackie Academic & Professional, London.

Baba, A., Kavdr, Y., Deniz, O., 2004. The impact of an open waste disposal site on soil and groundwater pollution. *Int. J. Environ. Pollut.* 22, 676–687.

Banat, K.M., Howari, F.M., Al-Hamad, A.A., 2005. Heavy metals in urban soils of central Jordan: Should we worry about their environment risk? *Environ. Res.* 97, 258–273.

Barazani, O., Sathiyamoorthy, P., Manandhar, U., Vulkan, R., Golan-Goldhirsh, A., 2004. Heavy metal accumulation by *Nicotiana glauca* Graham in a solid waste disposal site. *Chemosphere* 54, 867–872.

Bradl, H.B., 2004. Adsorption of heavy metal ions on soils and soil constituents. *J. Colloid Interface Sci.* 1, 277, 1–18.

Cambier, P., Picot, C., 1988. Nature des liaisons kaolinite-oxyde de fer au sein des microagregats d'un sol ferrallitique. *Sci. du Sol* 26, 223–238.

Chao, T.T., 1972. Selective dissolution of manganese oxides from soils and sediments with acidified hydroxylamine hydrochloride. *Soil Sci. Soc. Am. Proc.* 36, 764–768.

Chauvel, A., 1977. Recherches sur les transformations des sols ferrallitiques dans la zone tropicale à saisons contrastées. Evolution et réorganisation des sols rouges en Moyenne Casamance. Travaux et Documents. ORSTOM, Paris.

Chen, T.B., Zheng, Y.M., Lei, M., Huang, Z.C., Wu, H.T., Chen, H., Fan, K.K., Ye, K., Wu, X., Tian, Q.Z., 2005. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. *Chemosphere* 60, 542–551.

Chernicharo, C.A.L., 1997. Princípios do tratamento biológico de águas residuárias: reatores anaeróbios. DESA/UFMG, Belo Horizonte.

Delvigne, I., 1960. L'altération des basaltes du Kivu méridional (Congo Belge). Université de Louvain, Louvain, Belgique.

Egreja Filho, F.B., 2000. Extração sequencial de metais pesados em solos altamente intemperizados: utilização de componentes-modelo e planeamentos com misturas ternárias na otimização do método. Thesis Dr. Univ. Federal de Viçosa, Viçosa.

Empresa Brasileira de Pesquisa Agropecuária – EMBRAPA, 1999. Manual brasileiro de classificação de solos. Embrapa Produção de Informação, Brasília.

EMBRAPA, 1997. Manual de métodos de análise de solo. Serviço Nacional de Levantamento e Conservação de Solos, Rio de Janeiro.

Fernandes, F., Silva, S.M.C.P., Andreoli, C.V., Celligoi, A., Rocha, G.C., 1995. Análise do impacto causado no meio físico pelo vazadouro de resíduos sólidos de Londrina e medidas mitigadoras propostas. *Semina: Ciências Exatas/Tecnológicas* 4 (16), 574–580.

Ghidin, A.A., Melo, V.F., Lima, V.C., Costa Lima, J.M.J., 2006. Topossequências de latossolos originados de rochas basálticas no Paraná. I: mineralogia da fração argila. *Revista Brasileira de Ciência do Solo* 30, 293–306.

Gonçalves, M.A., Nogueira, J.M.F., Figueiras, J., Putnis, C.V., Almeida, C., 2004. Base-metals and organic content in stream sediments in the vicinity of a landfill. *Appl. Geochem.* 19, 137–151.

Heitzmann, F.J., 1999. Alterações na composição do solo nas proximidades de depósitos de resíduos domésticos na Bacia do Rio Piracicaba, São Paulo, Brasil. Associação Brasileira de Geologia de Engenharia. Síntese de Tese, 9, São Paulo.

Hernández-Moreno, J.M., Rodríguez-González, J.L., Espino-Mesa, M., 2007. Evaluation of the BCR sequential extraction for trace elements in European reference volcanic soils. *Eur. J. Soil Sci.* 58, 419–430.

Jucá, J.F.T., Monteiro, V.E.D., Oliveira, F.J.S., Maciel, F.J., 1999. Avaliação ambiental do aterro de resíduos sólidos da Muribeca. In: Proc. 4th Congresso Brasileiro de Geotecnia Ambiental/REGEO'99. 419–446, São José dos Campos, Brasil.

Lã, O.R., Barra, C.M., Sobrinho, N.M.B.A., Mazur, N., Veloso, A.C.X., 2003. Avaliação dos métodos de extração sequencial de Tessier, Keller e Miller na determinação de ferro nativo em três tipos de solos: orgânico, brunizem e latossolo. *Química Nova* 3 (26), 323–330.

Lee, C.S., Kao, M.M., 2004. Effects of extracting reagents and metal speciation on the removal of heavy metal contaminated soils by chemical extraction. *J. Environ. Sci. Health, A* 39 (5), 1233–1249.

Matos, A.T., Fontes, M.P.F., Costa, L.M., Martinez, M.A., 2001. Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils. *Environ. Pollut.* 111, 429–435.

Melfi, A.J., Pedro, G., 1978a. Estudo geoquímico dos solos e formações superficiais do Brasil. Parte 1. Caracterização e repartição dos principais tipos de evolução pedogeométrica. *Revista Brasileira de Geologia* 7, 272–286.

Melfi, A.J., Pedro, G., 1978b. Estudo geoquímico dos solos e formações superficiais do Brasil. Parte 2. Considerações sobre os mecanismos envolvidos na alteração superficial e sua repartição no Brasil. *Revista Brasileira de Geologia* 8, 11–12.

Melfi, A.J., Pedro, G., Volkoff, B., 1979. Natureza e distribuição dos compostos ferríferos nos solos do Brasil. *Revista Brasileira de Ciência do Solo* 3, 47–54.

Meurer, E.J., 2004. Fundamentos de química do solo, second ed. Gênesis, Porto Alegre, Brasil.

Minerais do Estado do Paraná S.A (MINEROPAR), 2005. Geoquímica de solo – horizonte B: relatório final de projeto, vol. 2. Curitiba, Brasil.

Mouta, E.R., Soares, M.R., Casagrande, J.C., 2008. Copper adsorption as a function of solution parameters of variable charge soils. *J. Brazilian Chem. Soc.* 19, 996–1009.

Mwiganga, M., Kansiime, F., 2005. The impact of Mpererwe landfill in Kampala–Uganda on the surrounding environment. *Phys. Chem. Earth* 87, 98–108.

NBR 6508, 1984. Determinação da Massa Específica dos Grãos. ABNT (Associação Brasileira de Normas Técnicas). Rio de Janeiro.

NBR 6504, 1984. Determinação do teor de umidade do solo. ABNT (Associação Brasileira de Normas Técnicas). Rio de Janeiro.

NBR 7181, 1984. Análise Granulométrica. ABNT (Associação Brasileira de Normas Técnicas). Rio de Janeiro.

NBR 10838, 1988. Determinação da massa específica aparente de amostras indeformadas, com emprego da balança hidrostática. ABNT (Associação Brasileira de Normas Técnicas). Rio de Janeiro.

NBR 10006, 2004. Procedimentos para obtenção de Extrato Solubilizado de Resíduos sólidos. ABNT (Associação Brasileira de Normas Técnicas). Rio de Janeiro. Site:

- <<http://www.scribd.com/doc/7323924/NBR-10006-2004-Procedimento-Para-Obtenção-de-Extrato-Solubilizado-de-Resíduos-Sólidos>>.
- Piantone, P., Bodénan, F., Chatelet-Snidaro, L., 2004. Mineralogical study of secondary mineral phases from weathered MSWI bottom ash: implications for the modeling and trapping of heavy metals. *Appl. Geochem.* 19, 1891–1904.
- Prado, R.M., 2003. A calagem e as propriedades físicas de solos tropicais: revisão de literatura. *Revista Biociência* 3 (9), 7–16.
- Rauret, G., Lopez-Sanchez, J.F., Sahuquillo, A., Rubio, R., Davidson, C., Ure, A., Quevauviller, P., 1999. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J. Environ. Monitor.* 1, 57–61.
- Roy, S., Bhattacharyya, P., Ghosh, A.K., 2004. Influence of toxic metals on activity of acid and alkaline phosphatase enzymes in metal-contaminated landfill soils. *Aust. J. Soil Res.* 42, 339–344.
- Sahuquillo, A., López-Sanchez, J.F., Rubio, R., Rauret, G., Thomas, R.P., Davidson, C.M., Ure, A.M., 1999. Use of a certified material for extractable trace metals to assess sources of uncertainty in the BCR three-stage sequential extraction procedure. *Anal. Chim. Acta* 382, 317–327.
- Segura-Muñoz, S.I., Takayanagui, A.M.M., Trevilato, T.M.B., Santos, C.B., Hering, S.E., 2004. Trace metal distribution in surface soil in the area of a municipal solid waste landfill and a medical waste incinerator. *Environ. Contam. Toxicol.* 72, 157–164.
- Shoemaker, H.E., Mclean, E.O., Pratt, P.F., 1961. Buffer methods for determining lime requirement of soils with appreciable amounts of extractable aluminium. *Soil Sci. Soc. Am. Proc.* 25, 274–277.
- Shukurov, N., Pen-Mouratov, S., Steinberger, Y., 2005. The impact of the Almalyk Industrial Complex on soil chemical and biological properties. *Environ. Pollut.* 136, 331–340.
- Shuman, L.M., 1985. Fractionation method for soil microelements. *Soil Sci.* 140, 11–22.
- Sígolo, B.J., 1998. Aplicação da geoquímica de superfície na análise da mobilidade e concentração de metais pesados em ambiente tropical. Thesis (Livre Docência) – Departamento de Geologia Geral do Instituto de Geociências – Universidade de São Paulo, São Paulo, Brasil.
- Souza, M.L.P., Andreoli, C.V., Amarai, M.B., Domaszak, S.C., 1996. Levantamento preliminar dos teores de metais pesados em alguns solos do Paraná. *Sanare* 5 (5), 68–75.
- Sposito, G., 1989. *The Chemistry of Soils*. Oxford University Press, New-York.
- Teixeira, R.S., Belincanta, A., Lopes, F.F., Gutierrez N.H., Branco, C.J.M.C., 2004. Avaliação do colapso do solo da camada superficial da cidade de Londrina/PR. *Proc. 5th Simpósio Brasileiro de Solos Não Saturados*, São Carlos, Brasil, 495–499.
- Teixeira, R.S., Lopes, D.D., Silva, S.M.C.P., Fernandes, F., Celligoi, A., Dall'Antonia, L.H., Furlan F., 2006. Investigação preliminar da área de disposição de resíduos sólidos do Município de Londrina/PR. *Proc. 13rd Congresso Brasileiro de Mecânica dos Solos e Engenharia Geotécnica*, Curitiba, Brasil, 3, 1389–1394.
- Uehara, G., 1979. Mineralo-chemical properties of oxisols. In: *Proceedings of 2nd International Soil Classification Workshop, Part I*, Malaysia, 45–60.
- Vargas, M., 1978. *Introdução à Mecânica dos Solos*, 1st ed. Mc Graw-Hill do Brasil, São Paulo, Brasil.
- Yong, R.N., Mohamed, A.M.O., Warkentin, B.P., 1996. *Principles of Contaminant Transport in Soils*, second ed. Elsevier, Amsterdam.