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## Base-metals and organic content in stream sediments in the vicinity of a landfill

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### Abstract

Landfill facilities are essential to modern societies as repositories for municipal solid wastes (MSW). However, irrespective of the regulations necessary to their construction there is always a certain risk of environmental impact. For this reason monitoring should be essential to their operation. In the present work, the environmental impact of such a landfill is studied, whose operation has been running for only 3 a. The approach used was to sample a series of stream sediments along two contaminated run-off water paths. These sediments were chemically analysed, and their mineralogy was also studied. Their most important feature is the existence of some contamination in Cu, Zn, and Pb above background levels in the first 200 m in the direction of water flow, whose concentration gradually decreases until background levels are reached. Although some artificial alloys and sulphides (sphalerite) were shown to be present, they could not account for the analysed concentrations, and cannot explain the negative gradient concentration by themselves. Sequential metal extraction methods together with solid phase extraction for the isolation of organic content, showed that metals adsorbed on the sediments are mostly associated with organic compounds. Although monocarboxylic organic acids were among the most important organic compounds present both in the contaminated waters and sediments, there is no clear correlation between these and base metal concentrations in the sediments. A stronger correlation exists if the total concentration of organic compounds is considered, which suggests that base metals can be easily partitioned into the sediments by the rapid adsorption onto their surfaces by organic compounds near the pollution source. The organic content identified decreases down stream as do base metal concentrations. This can be explained by the formation of complexes with organic acids as is extensively reported in natural and laboratory systems. The overall results point to the limited capacity for pollutant retention in this system, and suggest that in case of serious failure the contaminated plumes are likely to disperse rapidly into the environment.

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### 1. Introduction

Safe storage and recycling of domestic and municipal wastes is a key issue in environmental engineering as a consequence of the increasing amounts of waste produced by modern societies. The construction of waste disposal sites according to specific regulations becomes

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a central focus of interest in order to minimise their environmental impact (Stengele and Plötze, 2000). The study of fracture density and connectivity in regions of waste disposal facilities are fundamental to the understanding of potential risks resulting from liner failure, such that models to predict the development and migration of contaminated water plumes may be constructed. On the other hand, monitoring by means of geochemical and geophysical surveys within critical zones is of major importance in order to anticipate and remediate potential problems caused by leakage. Accordingly some studies have tried to build up a series of criteria for waste disposal site location (Dorn and Tantiwanit, 2001). The characterisation of the impacts on the quality of surface and ground waters has been a matter of concern for a long time (Albaiges et al., 1986; Harmsen, 1983; Kehew and Passero, 1990). In some of these studies, it has been properly acknowledged that organic acids are major landfill leachate constituents (Harmsen, 1983; Pohland and Kim, 2000), which in turn may have some influence on metal uptake by mineral surfaces (Schroth and Sposito, 1998). In the present paper, a case study is investigated in order to evaluate the impact on the surrounding environment of a 3 a old waste disposal facility located over a muscovite-biotite granite. In the vicinity of the facility it has been verified that during rainy periods, run-off waters that interact to various degrees with waste being prepared for storage or recycling, flow out to the neighbourhood. Such waters have been chemically modified (they become chemically similar to diluted municipal solid waste leachate). Special attention is given to their base metal contents and how these are partitioned into the stream sediments since these are the most important inorganic pollutants present in the analysed sediments. An assessment of the organic compound content in surface waters and sediments has also been investigated because they are potential complexing agents for the inorganic pollutants, therefore determining a complex interaction in the partitioning of these metals between the surface waters and the stream sediments.

## 2. Materials and methods

Samples of stream sediments were collected in the vicinity of an operating waste disposal facility in Northern Portugal after two main run-off water paths were identified (Fig. 1). These samples were prepared in the laboratory to obtain information about their bulk chemistry, mineralogy, metal speciation, and organic evaluation. Several surface and ground waters have also been seasonally sampled and analysed (Figueiras et al., *in press*), so that a full picture of the most important variables was obtained. All reagents used in the experimental techniques described below were reagent grade

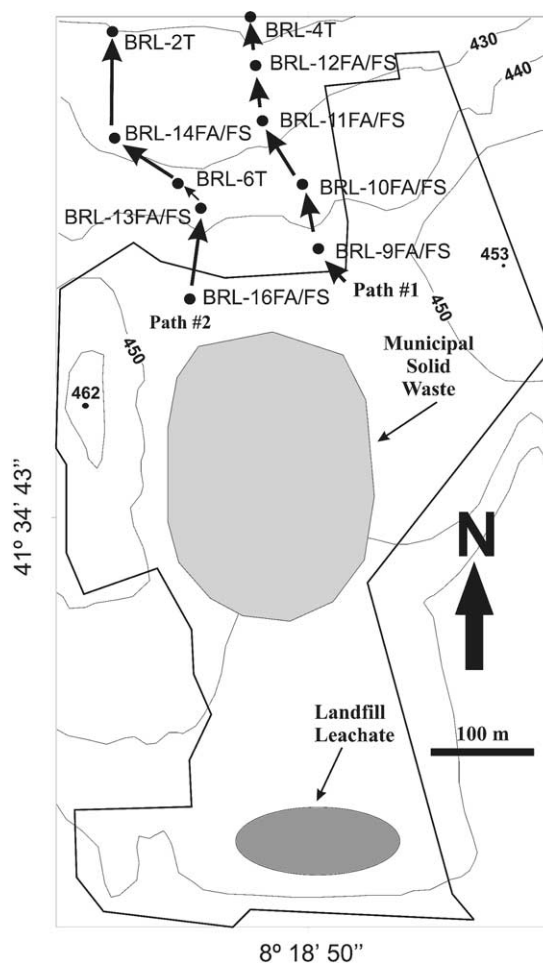


Fig. 1. Stream sediment sample locations along the two run-off water paths (identified as path Nos. 1 and 2) resulting from raining periods. Waters flow in the direction of the arrows. The boundary of the waste disposal facility is outlined with the indication of the Municipal Solid Waste disposal and Landfill Leachate collecting pools. Some contour lines are also shown.

or HPLC-grade for gas chromatography–mass spectrometry (GC–MSD) analysis. Standard in-house solutions of Cu, Zn and Pb, and international mineral standards (total digestion) were used to calibrate the quality of the obtained results by Atomic Absorption Spectrophotometry (AAS). Standard solutions of hexanoic, heptanoic, octanoic, nonanoic and decanoic acids (Sigma-Aldrich; >97% purity) for GC–MSD analysis, were prepared by weighing 1 g of each in 100 ml of *n*-hexane. For calibration purposes, several dilutions in hexane (20–1000 ppm) of the previous solutions were made.

### 2.1. Sampling

For this study, stream sediments in the neighbourhood of the waste disposal site were collected along the

stream paths. In most cases, only the top layers (a few mm thick for sites where a 2–5 cm thick layer has accumulated) were sampled since these layers correspond to the volume of sediment, which is kept in direct contact with the contaminated waters for longer time periods. The sediment samples were taken along two run-off water paths labelled as Nos. 1 and 2 (Fig. 1).

## 2.2. Sample preparation and bulk chemical analysis

The stream sediment samples were collected dry in the field and some of them were sieved in the laboratory in order to obtain 2 size fractions in the range 63–90  $\mu\text{m}$  (referenced as FS), and < 63  $\mu\text{m}$  (referenced as FA). The size fraction above 90  $\mu\text{m}$ , which corresponds grossly to <10% in weight of the total sample was rejected. The remaining samples (referenced as T) were ground to powder with an agate mortar. All samples were analysed, including both size fractions. Chemical analyses were carried out in Activation Laboratories (Canada) by Instrumental Neutron Activation Analysis (INAA) and Inductively Coupled Plasma (ICP), using a 4-acid (HF, HClO<sub>4</sub>, HNO<sub>3</sub> and HCl) digestion technique.

## 2.3. X-ray powder diffraction

X-ray powder diffraction was performed on several samples in a Phillips PW1710 Diffractometer, using Cu-K $\alpha$  radiation, a curved graphite crystal monochromator and a PW1820 Bragg-Brentano goniometer. Samples were ground to powder with an agate mortar when necessary. A separation of the finer particles (<1  $\mu\text{m}$ ) was required for both sample series FA and FS. A suspension of particles with the desired dimension was obtained which was filtered under vacuum using 0.4  $\mu\text{m}$  Millipore® filters. The filtrate was mounted in a glass and dried to analyse in the diffractometer.

## 2.4. Optical and electronic microscopy

Selected samples were observed using both an Optical Microscope (OM) and a Scanning Electron Microscope (SEM) in order to define the mineralogy. SEM observations used a FE-SEM Jeol 6300 F, operating with a current of  $6 \times 10^{-11}$  A, and an accelerating voltage of 20 kV (unless otherwise stated), and a SEM Jeol JSM-840A, operating with a current of  $6 \times 10^{-9}$  A, and the same voltage. Both microscopes have EDX Spectrometers of Oxford Instruments and an image analysis program. Elemental EDX maps were collected in the JSM-840A model using counting times of 10 ns per pixel. Selected samples for microscopic observations were prepared by dispersing the sediment grains in epoxy cylinders which were then fixed in unpolished glass plates, cut and polished to mm height discs. Observations in the OM were done in reflected light.

Observation and analysis in the SEM used both the polished sections and the sample powders mounted directly on the sample holder with an adhesive tape.

## 2.5. Sequential metal extraction

In order to elucidate the speciation of the metals between different phases and different binding modes, sequential extraction techniques were used. The procedure used follows the sequence proposed by Tessier et al. (1979), and further improved by Hirner (1992; 1996) and is generally outlined in Table 1. Because X-ray diffraction and microscopy studies failed to reveal the presence of carbonates and (hydr)oxide phases it was assumed they were absent or in concentrations too low to account for their sequential extraction, which greatly simplified the procedure. Details of the procedure are outlined in Tessier et al. (1979), and the modifications as presented in Table 1 are provided by Hirner (1996). In step 3, small amounts of the oxidising solutions, in excess of the proposed volumes were added until no significant reaction was seen to occur, therefore ensuring the sediment was properly oxidised. For metal speciation, the sampled solutions were analysed by AAS using a Philips Pye Unicam SP9 spectrophotometer.

Three sets of the same sample references were prepared. All sets of samples followed the full sequence of steps in sequential extraction, but one of the sample sets was also used for the analysis of organic content between steps 2 and 3 by GC-MSD, after which it followed the sequential extraction procedure until the end. Blank samples of all solutions were analysed and all concentrations of Cu, Zn and Pb in standard samples were reproduced within analytical error.

## 2.6. Organic analysis

Two sets of the same sample references were used for the identification of the main organic content, one of which comes from step 2 of the previous procedure. The organic compounds from the samples studied were isolated by solid phase extraction (SPE) procedures followed by capillary gas chromatography-mass spectrometry (GC-MSD) analysis (Nogueira et al., 2001).

The sediment samples were manually homogenised and to each accurate dry weighed sample (1 g), 50 ml of HCl (5%) was added. The mixture was ultrasonically treated (Branson 3510) for 15 min, and then centrifuged (Hermule Z 300) at 4000 rpm for 15 min in order to recover the supernatant.

In the SPE assays, each cartridge (Envi-18; 3 ml, 500 mg, octadecyl, 17% C, endcapped; Supelco) attached to a vacuum manifold (Visiprep 12-port model; Supelco), was pre-conditioned with 2 ml of ethyl acetate and allowed to dry for 10 min under vacuum. For conditioning, 2 ml of

Table 1  
Sequential extraction steps and general procedure

Step	Description	Reagents	Obs.	Reference
1	Non-specific adsorbed	NH <sub>3</sub> NO <sub>3</sub> (1 M)	Continuous agitation (1 h); ambient temp.	Hirner (1996)
2	Specific adsorbed	NH <sub>4</sub> OAc (1 M)	Continuous agitation (1 h); ambient temp.	Hirner (1996)
3	Bound to organic matter	HNO <sub>3</sub> (0.02 M); H <sub>2</sub> O <sub>2</sub> (30%; pH 2 with HNO <sub>3</sub> ) NH <sub>4</sub> OAc (3.2 M in 20% v/v HNO <sub>3</sub> )	Some agitation (2 h + 3 h at 85° ± 2)  Continuous agitation (1 h); ambient temp.	Tessier et al. (1979)
4	Residue	HClO <sub>4</sub> ; HF; HCl (12 N)		Tessier et al. (1979)

methanol and 2 ml of HCl (5%) were used without allowing the tubes to dry and then the tubes were loaded with the whole volume of the supernatant solutions, which were then left to dry for 1 h. Subsequently, the elution step was made with 3 times 0.5 ml portions of ethyl acetate into a glass vial (2 ml; Alltech). After gently evaporating under purified N<sub>2</sub>, 0.2 ml of *n*-hexane was added to the residue and the vial was closed with a seal (aluminium seals with TFE/Butyl septa) using a hand crimper. After agitation in Vortex (1 min; Velp Z×3), the vials were placed into the autosampler tray prior to analysis by GC-MSD.

During the SPE assays, 3 blanks using 50 ml of HCl (5%) instead of the supernatant aqueous sample solutions were performed as above, in order to control the contamination levels, as well as possible interferences in the present methodology. The analysis of the leachate solution (3 ml), were also made according to the remaining procedures as previously described, after a clean-up step using 0.45 µm filters (nylon; Sigma-Aldrich).

The GC-MSD analysis were performed with an Agilent 6890 Series gas chromatograph having an Agilent 7683 automatic liquid sampler, connected to an Agilent 5973 Network mass selective detector.<sup>2</sup> A programmed temperature vaporization injector (PTV), having a deactivated liner and cooling with liquid nitrogen was used, operating in the solvent vent mode at constant pressure (150 ml/min; 0 psi; 0.30 min). The inlet temperature was programmed at 40 °C (0.35 min) then a rate of 600 °C/min to 320 °C and 2 µl of each organic sample was injected (100 µl/min) using a Hamilton syringe (50 µl). High purity He as a carrier gas having a 17.30 psi of inlet pressure and a fused silica capillary column, 30 m × 0.25 mm id. × 0.25 µm (HP-5MS; 5% diphenyl, 95% dimethylpolysiloxane) was used. The oven temperature was programmed at 70 °C (2 min) and then a rate of 25 °C/min to 150 °C, followed by 3 °C/min to 200 °C and 8 °C/min to 280 °C (10 min). The quadrupole, source and transfer line temperatures were maintained at 150, 230 and 280 °C, respectively. Electron ionisation mass spectra in the full-SCAN mode were recorded at 70 eV electron energy in the range 35–

550 Da. A turbo molecular pump was used (10<sup>−5</sup> Torr) and a solvent delay of 3 min was programmed. All data were recorded using a MSD ChemStation [G1701CA; Rev C.00.01]. The compounds were identified by comparison with the Wiley's library spectral data bank [G1035B; Rev D.02.00], as well as, by comparison of their retention with pure standards. For quantification purposes, calibration plots using the external standard method were made, using standard solutions of each organic acid identified and the abundance of the correspondent extracted ion at *m/z* 60. All analytical data were performed in duplicate.

### 3. Results and discussion

Chemical bulk compositions of the stream sediment samples are given in Table 2 and average chemical compositions of some minor elements for altered/non altered granite, taken as background reference values, are given in Table 3. These background values are also based on several analyses of soil profiles, sediments, surface and ground waters occurring in uncontaminated areas (Figueiras et al., *in press*). Base metal concentrations in uncontaminated surface and ground waters are in the order of 1 mg/l or lower, while for contaminated waters they rise to levels of several tens of mg/l (locally to a hundred mg/l), with the exception of Pb which remains always below 10 mg/l. The measured pH of the contaminated waters rises to the range 6–6.5, in contrast to unaffected ground and surface waters which have a pH range of 4.2–4.6 and 5.1–5.5 respectively (Figueiras et al., *in press*). It is mainly the base metals (Cu, Zn and Pb) which denote some degree of contamination in the stream sediment samples, with a down-stream negative concentration gradient (Fig. 2). Dispersion of base metals from source reached 200 m along both streams, after which concentrations fall to the granite background level. It may be noted that waters running along path No. 1 start having a patch of diffuse circulation beyond the last sampling location. Some other elements were found only slightly above the background for the area, and these include Ni, V, Ba, P<sub>2</sub>O<sub>5</sub> and Y. As noted below, only the first 3 of these elements have

<sup>2</sup> Agilent Technologies, Little Falls, DE, USA.

Table 2

Bulk chemical analysis results for the stream sediments for major and most important minor elements. Analytical error is 1–3% for major elements, and 4–8% for minor elements

SAMPLE <sup>a</sup>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI <sup>b</sup>	Ba	As	Y	Cu	Zn	Pb	Ni	V
BRL-2T	73.56	12.43	2.16	0.040	0.59	0.37	1.22	4.48	0.514	0.16	4.94	617	7	11	6	61	39	3	26
BRL-4T	56.81	17.16	3.20	0.057	0.89	0.66	1.74	4.62	0.522	0.25	12.97	610	10	16	33	118	41	7	42
BRL-6T	76.39	11.18	1.91	0.031	0.50	0.41	1.28	4.45	0.345	0.18	3.84	603	6	9	25	75	30	3	19
BRL-9 FA	60.41	19.16	4.08	0.071	1.05	2.07	2.37	4.73	0.943	0.55	3.82	789	15	54	1016	852	117	34	52
BRL-10 FA	35.81	23.86	6.62	0.076	1.50	1.02	0.52	2.88	0.758	0.56	25.12	484	58	36	478	785	125	22	79
BRL-11 FA	46.84	20.39	4.73	0.073	1.20	1.19	1.75	4.32	0.729	0.45	16.86	644	18	33	258	455	86	21	59
BRL-12 FA	48.29	21.00	4.84	0.082	1.16	1.27	1.76	4.08	0.798	0.52	16.36	625	19	39	262	449	83	23	65
BRL-13 FA	44.58	21.99	4.52	0.056	1.15	0.74	1.43	3.94	0.678	0.30	19.25	513	21	27	55	162	45	9	50
BRL-14 FA	42.57	24.51	3.62	0.041	0.89	0.44	1.24	3.23	0.470	0.33	21.66	365	31	29	42	126	46	4	34
BRL-16 FA	44.71	23.87	4.68	0.055	1.15	0.82	1.40	3.97	0.687	0.38	18.54	531	23	33	100	199	49	10	56
BRL-9 FS	63.35	16.16	3.30	0.048	0.95	1.67	2.21	4.98	0.642	0.36	4.88	740	11	23	591	485	66	21	36
BRL-10 FS	34.87	23.58	6.66	0.076	1.54	1.04	0.57	2.81	0.761	0.58	26.65	440	61	36	427	692	121	21	75
BRL-11 FS	53.86	18.56	4.19	0.065	1.13	1.03	2.01	4.91	0.660	0.32	12.02	617	13	20	163	313	57	14	47
BRL-12 FS	54.00	18.55	4.22	0.084	1.08	1.25	1.99	4.51	0.929	0.43	12.65	620	16	29	206	324	63	16	52
BRL-13 FS	43.84	21.59	5.69	0.075	1.74	0.70	1.40	4.26	0.811	0.26	18.55	523	17	22	56	195	39	12	71
BRL-14 FS	42.53	25.07	4.08	0.041	1.00	0.42	1.21	3.48	0.496	0.34	21.39	331	32	27	33	106	38	5	39
BRL-16 FS	43.38	23.09	5.29	0.066	1.57	0.76	1.33	4.04	0.760	0.31	18.17	542	20	26	90	198	46	11	65

<sup>a</sup> Major oxides and LOI in %, minor elements in ppm.

<sup>b</sup> LOI—Loss On Ignition.

Table 3

Average granite concentrations of some minor elements as obtained for fresh and altered samples

Elements	Fresh/altered granite (ppm)
As	2/5
Br	2/4
Cr	26/8
V	40/22
Cu	5/8
Ni	8/<7
Pb	29/38
Zn	89/68

some significance for the system under study. What is also worth noting is the lack of a clear partitioning of these elements between the different size fractions. Only samples BRL-9FA and FS clearly showed a partitioning of this kind. As well, samples BRL-9 showed the lowest values of LOI (Table 2). In these sediments the reported values of LOI are an indication of the amount of phyllosilicate minerals present, therefore samples BRL-9FA and FS had comparatively lower amounts of these minerals, a fact that was also indicated by their higher SiO<sub>2</sub> and lower Al<sub>2</sub>O<sub>3</sub> contents. Their LOI values lay between the values for the fresh and altered granite samples, and are 3–5 times lower than the reported values for the sediment samples (with the exception of some samples with the T reference, representing the coarser and finer fractions mixed together).

In the previous section it was noted that it was necessary to separate fine particles (<1 µm) from both

size fraction samples. Because it was important to keep the sampled sediments chemically undisturbed, the samples were only mechanically sieved which proved to be ineffective. Therefore, both size fractions showed the presence of clay minerals as revealed by X-ray diffraction, and later confirmed by observation with the SEM (Fig. 3) as expected. This observation is important because clay minerals are major adsorbent mineral substrates, and if their content actually differed in each of the size fractions they could account for a differential concentration of the metals too. Therefore, the verification that metal concentrations were not very different does not mean that the hypothesis that metals adsorb predominantly onto clay mineral surfaces is not a valid one for this case. Another possible hypothesis is the presence of organic matter in both size fractions, as it may act as a competitive agent for the adsorption of metals. In this case, the results from samples BRL-9FA and FS seem to be important, since they were the most contaminated in metals and have the lower phyllosilicate content. Being the only samples showing a clear partitioning that can be attributed to an effect of total available surface area as a function of average mineral dimensions. As a matter of fact, specific geometric surface areas for spherical particles may be as great as 1.5 times higher per gram of material for the finer fraction. This suggests that the available surface area for metal adsorption is independent of the mineral type. This effect is less pronounced for the remaining samples because of their much greater content of phyllosilicate minerals, and consequently of clay minerals, distributed among each size fraction. Therefore, the difference in

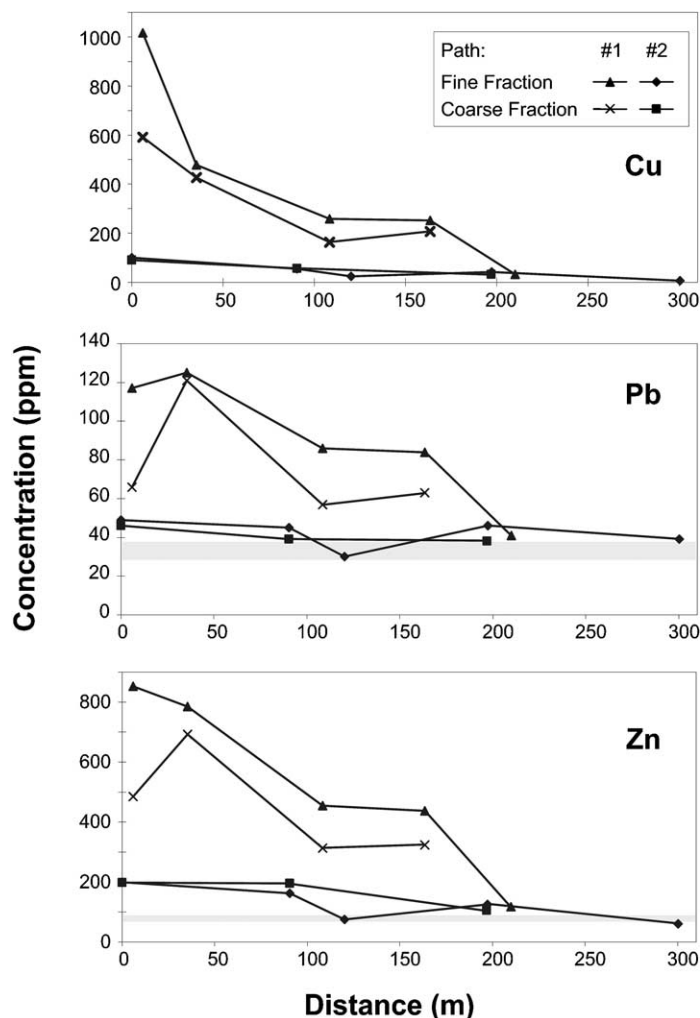


Fig. 2. Base metal concentration in each sampled location as analysed in the fine and coarser fractions, along each run-off water path.

total specific surface area among each size fraction becomes less effective in such partitioning. This would mean that metals should bind preferentially to organic compounds either adsorbed or forming coatings on the available mineral surfaces.

### 3.1. Mineralogy

The mineral suite in these samples comprises the main minerals present in the parent granite, which are ubiquitous: quartz, alkali feldspar, biotite, and muscovite. X-ray diffraction of the finer fractions ( $< 1 \mu\text{m}$ ) revealed (besides the micas mentioned above) kaolinite, illite, chlorite, and an illite-smectite interstratified (restricted to a few samples). Ilmenite, monazite, sphalerite, and barite, identified by SEM, appear as minor mineral phases. These minerals were more concentrated up-stream, which explains the higher concentrations in

phosphate and Y (monazite), and Ba (barite). Apart from these mineral phases, some grains of finely divided artificial alloys were also found, namely of Fe/Cr/Ni, Cu/Zn, and Fe pellets. Most of these higher density phases are observable in reflected light microscopy, and their abundance increases in the up-stream sediments. Their total modal composition does not exceed 1% in the most abundant samples. Optical characterisation and extensive analytical work in the SEM showed that monazite, ilmenite, and the several Fe-rich artificial phases are by far the most represented in the sediments. The Cu and Zn phases (including alloys) together with other high reflectance phases have a modal composition clearly below 0.1% in the most concentrated samples, and remain undetected in the less concentrated ones. No traces of Fe (hydr)oxides or carbonates were detected in these samples by microscopy techniques or X-ray diffraction. It may be noted however that in some samples,



a few X-ray diffraction peaks were best explained if one considers the existence of gibbsite.

### 3.2. Metal speciation

It is widely known that clay minerals are important media for chemical adsorption, as they account for about 30% of the cation exchange capacity in soils (Appelo and Postma, 1993). The remaining cation exchange capacity is mainly accounted for by the organic matter, which has a significant role in surface reactions. In either case, it is expected that a certain percentage of the total chemical concentration in base metals is adsorbed onto the mineral surfaces, either directly or chelated with organic ligands. Therefore, several X-ray maps were obtained for different elements in the SEM in order to investigate their distribution on the surface of minerals. For this investigation both powders and polished sections were used, and it was found that the signal was either low or nonexistent for both Cu and Zn. However, in sample BRL-9FA it was possible to identify a peak in the Cu position during the scanning of several images. This peak in the Cu position was weak indicating that it may have been close to the detection limit of this element. Even when a signal from Cu was detected, the X-ray image was noisy which prompted scanning the sample using the background X-ray frequencies in the vicinity of the Cu peak in order to make sure the maps are not simply an artefact of grain geometry (Fig. 4). The resulting EDX spectrum is also shown in the figure, where peak heights are proportional to the number of counts registered during the time of image acquisition. The spectrum clearly shows the build up of a peak in the Cu position, and the X-ray image for this element, albeit noisy, is different from the image from the background. The X-ray map highlights some mineral shapes, suggesting that the source of the signal comes from the mineral surfaces. It may be noted that in the example of Fig. 4 and in some other cases where the Cu signal was detected, the minerals whose surfaces may have bound Cu are not necessarily phyllosilicates, or clay mineral aggregates as seen in all samples (Fig. 3). On the other hand, polished sections corresponding to the same samples did not show an X-ray signal from Cu. A possible explanation is readily available assuming a surface adsorption of Cu, since in the polished sections the external surfaces of the mineral grains are not exposed. In such conditions, the resulting signal could not be identified even in the case of considerable surface Cu adsorption. For Zn the results were always negative, as well as for Pb (its concentration is rather low in all samples). Detection of Zn was restricted to some phases containing S (sphalerite) or Cu (artificial alloys). Recent results using a  $\mu$ -PIXE on the polished thin sections have confirmed the previous statements (Gonçalves et al., 2002). Given the much

better signal to noise ratio and deeper beam penetration in the epoxy, a clear Cu and Zn signal was observed on most of the deeply lying mineral surfaces.

In order to complement the results obtained with the SEM, selective sequential extraction techniques were used in some samples. Fine fraction samples were predominantly chosen with special emphasis on the set of the most contaminated ones along path No. 1 (Fig. 1). Samples BRL-16FA and FS were those used from path No. 2.

There is some controversy in the literature regarding the efficiency of these techniques (Hirner, 1996; Kheboian and Bauer, 1987) and although there is a proposal for a standard sequential extraction method (Quevauviller et al., 1994), this is also not free from criticisms (Hirner, 1996). Some of the shortcomings include the specificity of the extractant to each of the phases, variation of solution pH, and prevention of chemical species able to be released from a given phase to re-adsorb onto other phases (Bermond, 2001; Kheboian and Bauer, 1987). Any attempt to make such a technique quantitative is, therefore, severely compromised considering the effect these factors may have on the final results, even more so if there is no uniform method used (Quevauviller et al., 1994). However, Tessier's original method is still widely used in the current literature, with or without modifications (Bruder-Hubscher et al., 2002; Hodson et al., 2001; Li and Thornton, 2001; Li et al., 2001).

The sequential extraction steps included (Table 1) non-specific and specific adsorption of metals (as defined in Schindler, 1990), metals bound to organic matter, and residual phases. Results of the sequential extraction steps is provided in Fig. 5, and it can be noted that a significant percentage of base metals was actually adsorbed to the mineral surfaces, some as surface complexes but most of them with organic compounds. The results from both sets of samples are mostly consistent, but Zn shows some variability in samples BRL-10FA, 16FA, and 16FS. Because Zn is the most important element forming some of the identified alloys and occurs as a sulphide, a small heterogeneous distribution of particles can easily appear as a disparate result at the end of the sequence. Table 4 shows the total concentration of each metal as the sum of all concentrations obtained in each step, with the corresponding error. A comparison with the bulk chemical composition of the sediments (Table 2) shows that nearly all concentrations are reproduced within analytical error, with some tendency for overestimation in the lower concentration range. Organic matter accounts for about 50–80% of Cu adsorption, but its role becomes highly variable for Zn, ranging from 20 to 70%, and for Pb it is reduced to 20–50%. Consequently, the residue has variable concentration fractions depending on the metal considered, namely circa 20–50% of the Cu, 30–80% of the Zn, and 50–80% of the Pb. It may be

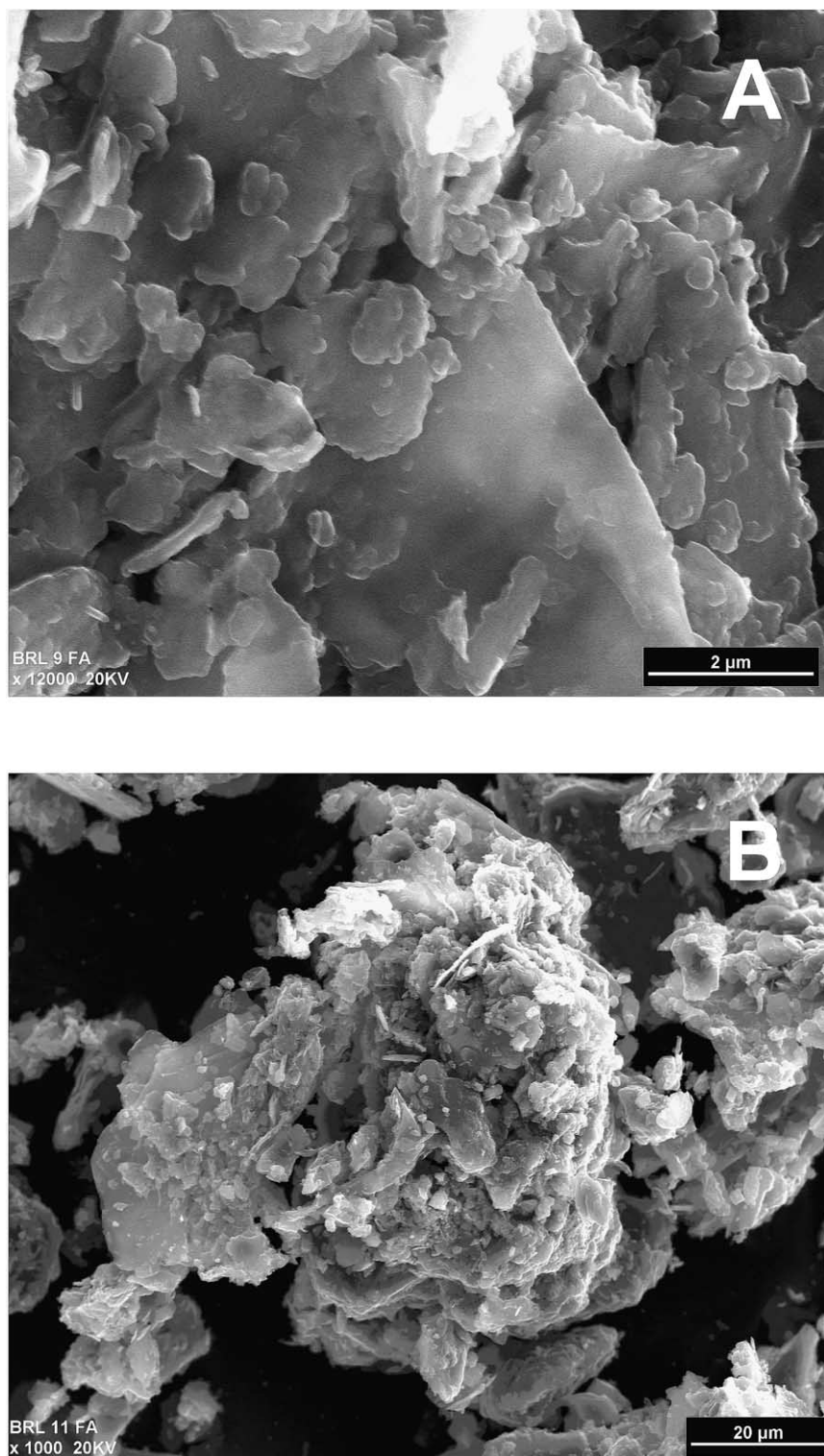


Fig. 3. Scanning electron microscope images of sediment samples: (A) sample BRL-9FA showing an aggregation of small particles where a transparent film appears in the centre of the image (a possible organic film?). Magnification: 12,000 $\times$ ; 20 kV; (B) sample BRL-11FA showing the aspect of the particle aggregates that are common either in the finer or coarser fractions. Magnification: 2000 $\times$ ; 20 kV.



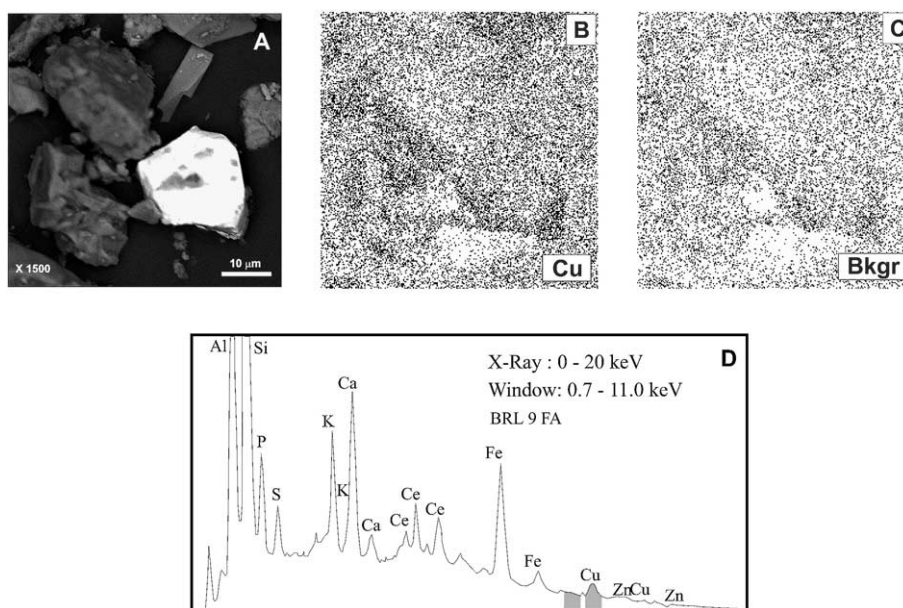


Fig. 4. Backscattered electron image of a portion of sample BRL-9FA (A) with the corresponding X-ray maps for Cu (B), and background (Bkg) (C). The full EDX spectrum (D) is presented showing a peak in the Cu position; shaded areas represent the energy window used for the scan of (B) and (C). Phosphorous and Ce are due to the bright mineral on the image (Monazite), and S is due to the adhesive tape used in the sample holder. The remaining minerals are feldspars and quartz. Copper signal is stronger from some surfaces of the minerals at the centre of the image, and in the minerals on the upper left.

noted that sulphides dissolve during the oxidation of organic matter by  $\text{H}_2\text{O}_2$  at  $\text{pH}=2$ , which will interfere with the amount of each metal effectively bound to the organic matter. However, the previously reported mineralogical investigation seems to indicate that such an effect is likely to be minor. Preliminary results also indicate that either Cu or Zn may concentrate along some Fe-sulphide rims or forming distinct co-precipitated phases over sulphide surfaces (Gonçalves et al., 2002). The estimated modal percentage limit for the Cu/Zn phases could only account for about 40% of the reported concentrations in Cu and 50–60% in Zn (depending on the amount of sphalerite considered) for the most concentrated samples, but this result is not certain and is likely to be an overestimation since it considers the upper limiting conditions. This means that no more than 20% of Cu and 20–30% of Zn concentration in solid phases can be attributed to their dissolution during the oxidation of organic matter. A similar evaluation for Pb is not possible due to lack of information. Metals extracted during total digestion are likely to correspond mainly to the artificial alloys. Carbonates have also remained undetected, but it is known that they can occur as precipitates from waste stabilisation (Manning, 2001). The chemistry of the waters interacting with the analysed sediments indicates that they are clearly undersaturated in several carbonate phases, including calcite and smithsonite. In any case, it may be concluded that all these base metal bearing

phases cannot account for the whole observed negative downstream gradient, because the total amount of metals they include is much lower than the concentration difference observed along the streams. Also interesting is the minor importance of non-specific and specific adsorption of metals onto the mineral surfaces. However, these remarks can only be qualitative, as there is no way to control the precise amount of metals re-adsorbed onto the sample after each sequential extraction step. Nevertheless, the importance of organic compounds in the fixation of the metals in the sediments is clearly shown. The critical study by Kheboian and Bauer (1987) on Tessier's method using synthetic sediments showed that Cu is unlikely to be released earlier in the extraction sequence in the presence of organic matter (they used humic acids as a proxy). On the contrary, Pb could easily be equally released in all steps of the extraction, a behaviour that was not shown in the present work. The suggested absence of carbonates and (hydr)oxide phases in the studied samples also contributed to less error and variation in the results. These results also support the previously discussed SEM observations with respect to Cu adsorption.

### 3.3. Organic evaluation

The same set of sediment samples used from the sequential extraction was analysed by SPE/GC-MSD in order to identify the main organic compounds. In a first

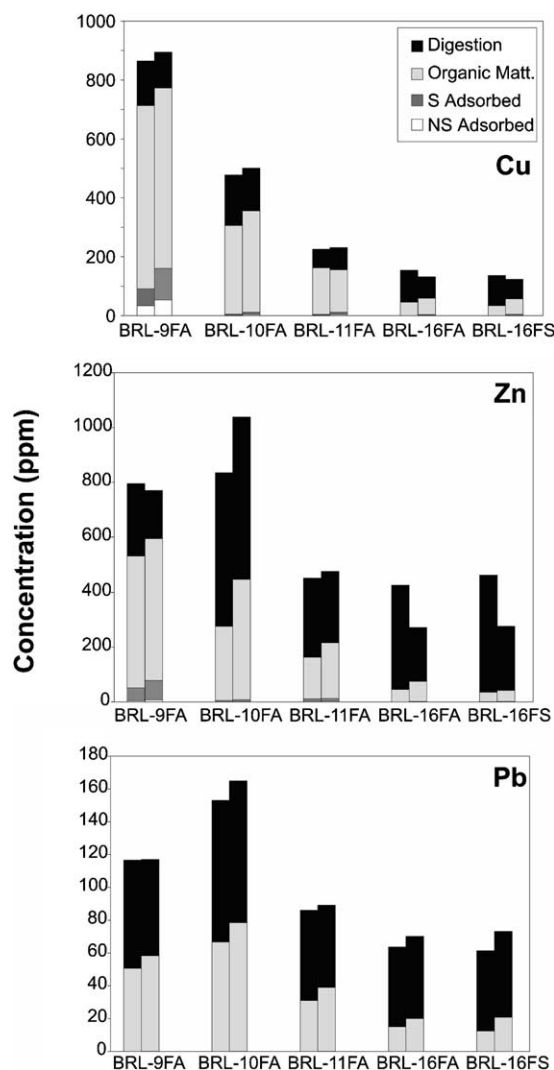


Fig. 5. Sequential extraction results for two sets of samples showing the concentrations of Cu, Zn, and Pb extracted in each step, according to non-specific adsorption, specific adsorption, bound to organic matter, and residual. The results are fairly reproducible with the exception for Zn (see text). Total concentrations and uncertainty are given in Table 4.

Table 4

Total metal concentration in sediments resulting from the sum of the concentrations obtained in each sequential extraction step with the respective uncertainty (concentrations in ppm)

	Cu		Zn		Pb	
	Set 1	Set 2	Set 1	Set 2	Set 1	Set 2
BRL-9FA	865 ± 163	895 ± 168	796 ± 176	770 ± 117	117 ± 27	117 ± 26
BRL-10FA	477 ± 85	501 ± 90	834 ± 121	1038 ± 151	153 ± 27	165 ± 29
BRL-11FA	224 ± 94	231 ± 97	452 ± 85	477 ± 63	86 ± 24	89 ± 24
BRL-16FA	154 ± 32	132 ± 27	426 ± 54	272 ± 35	64 ± 21	70 ± 23
BRL-16FS	137 ± 32	126 ± 29	461 ± 70	276 ± 42	61 ± 21	73 ± 26

approach, the focus was on the content of carboxylic acids as these are known to be the major constituents of landfill leachates (Harmsen, 1983; Manning, 2001; Pohland and Kim, 2000). A comparison between sediment and leachate samples provided some useful information on the likely interactions of the contaminated waters with the sediments.

The total ionic current chromatogram of the leachate sample (Fig. 6A) clearly shows that 5 low molecular weight aliphatic carboxylic acids are among the most important organic compounds. Characteristic features of the presence of carboxylic acids in the leachate sample, could be observed through the profile of the corresponding mass spectra patterns, showing the typical decomposition of the alkyl moiety producing the  $C_nH_{2n+1}$  and  $C_nH_{2n-1}$  ion series, a small molecular ion and the presence of an abundant ion at  $m/z$  60 (base peak). This ion is characteristic of the McLafferty rearrangement for aliphatic carboxylic acids having 3 or more C atoms in the chain moiety (McLafferty, 1980). In order to screen the evidence of all carboxylic acids in the total ionic current chromatogram from the leachate sample, the extraction of all ions at  $m/z$  60 was performed (Fig. 6B). By automatic library search, it could be clearly seen that the main carboxylic acids are hexanoic, heptanoic, octanoic, nonanoic and decanoic acids, which also confirmed the use of the pure standards. Substantial amounts of these organic acids were present in the leachate at 1.2, 6.6, 10.4, 1.0 and 0.3 g/l, respectively (Table 5).

These results, the leachate inorganic chemical composition, and pH ( $\approx 6.5$ –7), are indicative of the acidic stage of the landfill (Pohland and Kim, 2000), although most studies quote a pH in the range of 4–5 for this stage.

In the total ionic current chromatograms from the sediment samples (BRL-9FA, BRL-10FA, BRL-11FA and BRL-16FS), the corresponding peaks of the same carboxylic acids could also be observed (Fig. 7), but in lower amounts, ranging from 0.5 to 1.0  $\mu\text{g/g}$  (Table 5). Heptanoic and octanoic acids dominate the acid content of the leachate, but in the sediments, differences in the individual acid concentrations are almost negligible,

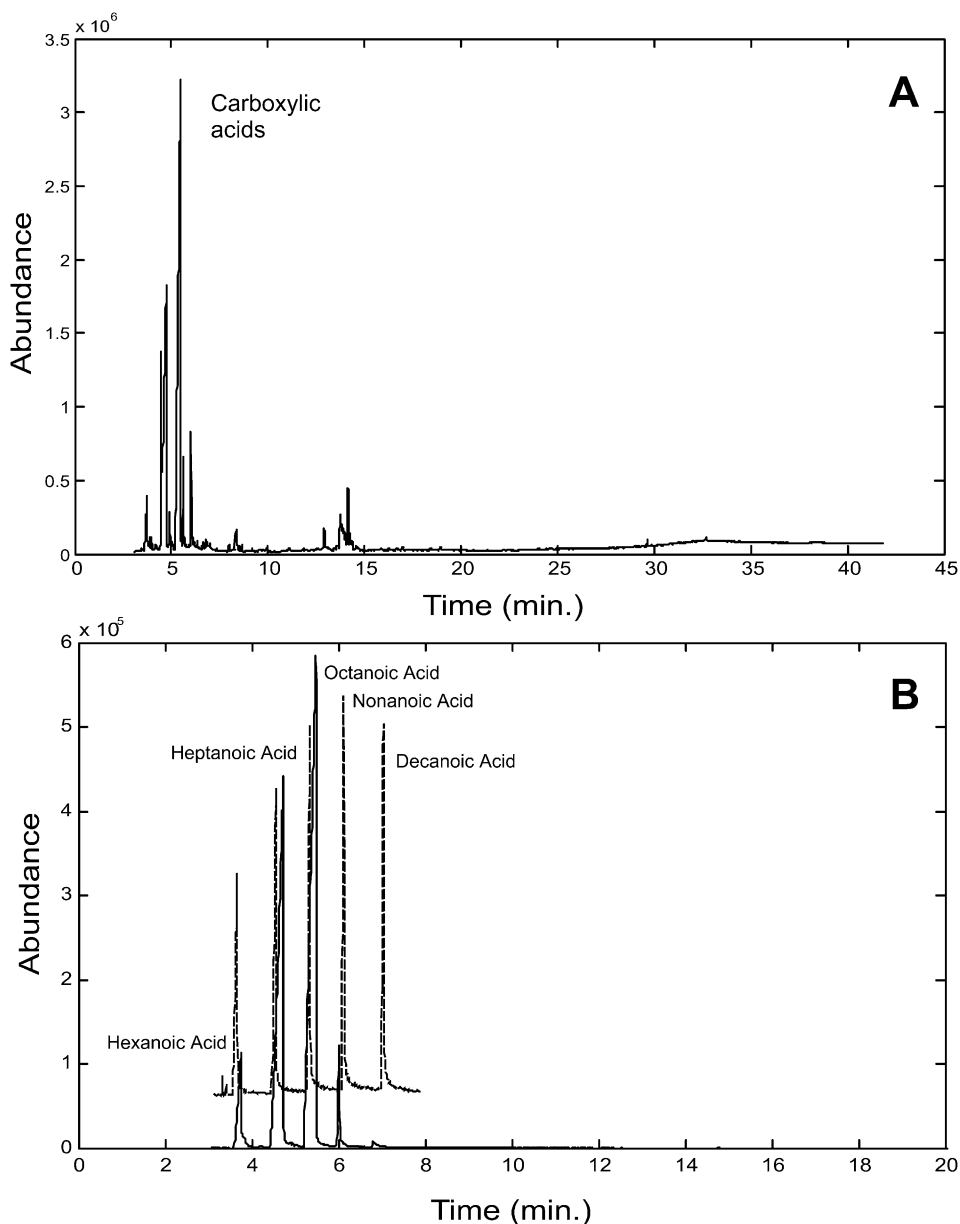


Fig. 6. Total ionic current chromatogram of the leachate water sample indicating the main organic acids analysed by SPE/GC–MSD (A). The correspondent chromatogram of the extracted ion at  $m/z$  60, showing the sequence of  $C_6$ – $C_{10}$  monocarboxylic acids identified (B); A standard solution (0.1 g/l) of the identified acids is also shown in dashed line (shifted  $6 \times 10^4$  units upward for clarity).

showing that an equilibrium could be established between the stream leachate and sediment sites.

Considering the total ionic current chromatogram of sample BRL-9FA, it shows a greater content of organic compounds than BRL-11FA sample (Fig. 7). The fractional organic content in relation to the leachate (taking the ratio of total areas for each sample to total areas for the leachate) is 0.283 (BRL-9FA), 0.084 (BRL-10FA), and 0.108 (BRL-11FA). Both BRL-16FA

and FS samples show generally lower organic content (fractional content of 0.066 and 0.071, respectively). Some test analyses indicate that the same may be true of the BRL-13FA sample as well, showing that this is a characteristic of the samples collected along path No. 2. Besides carboxylic acids, it was possible to identify other organic compounds either in the leachate or in the sediments, e.g. xylene, cresol and trimethyl benzene, that are also reported in other municipal solid waste (MSW)

Table 5

Average content of monocarboxylic acids in leachate and sediments analysed by SPE/GC-MSD. Analytical error is <20% for sediment samples and <4% for leachate samples

Acids	Hexanoic	Heptanoic	Octanoic	Nonanoic	Decanoic
Leachate (g/l)					
ABRL-7	1.204	6.627	10.380	1.014	0.264
Sediments (µg/g)					
BRL-9FA	0.926	0.740	0.774	0.773	0.536
BRL-10FA	0.748	0.712	0.756	0.838	0.517
BRL-11FA	0.817	0.776	0.880	1.063	—
BRL-16FS	0.716	0.697	0.727	0.784	—

leachates (e.g., El-Fadel et al., 2002; Soliman et al., 1998).

Taking into consideration the set of samples that followed the first two steps of sequential extraction previously to SPE isolation of organic compounds, it is worth noting that these samples lost 20–80% of the organic acids in the first steps of sequential extraction. When these samples underwent the remaining steps of sequential extraction it was also verified that a significant percentage of the metals were also lost during the acid leaching of the samples to separate the organic compounds by SPE. These losses are highly irregular, depending on each element, but varied in the range of 30–80%. The acid leaching of the samples did not extract all organic matter in the sediments (especially high molecular weight compounds, such as fulvic and humic acids). In step 3 of sequential extraction, these samples reacted vigorously with H<sub>2</sub>O<sub>2</sub> in very much the same way as the untreated samples. These observations have some implications for the interpretation of sequential extraction results. They seem to imply (although by no means prove) that organic acids may have only a very limited importance as metal adsorbents, a remark previously made by Schroth and Sposito (1998). However, some questions may be put forward, such as what is the real fraction of metals extracted in steps 1 and 2 that may have formed complexes with the organic acids; and what fraction of metals extracted along with organic compounds during SPE are complexed with them. The pH of a 5% (v/v) HCl solution is below 1, and metals as well as sulphides are known to be very soluble under these conditions, which certainly explains the high losses observed during the subsequent sequential extraction steps.

The combined studies with sequential extraction demonstrated that not only a significant amount of the base metals are adsorbed onto the surfaces but also that the majority of the adsorbed metals are associated with organic matter. This association may be via formation of ternary surface complexes (Fein, 2002; Schindler, 1990; Schroth and Sposito, 1998), or bonding to organic films of more complex organic compounds. Modelling results indicate that at the pH of interest in this study,

Cu may be easily bound mainly to fulvic acids and less so to humic acids as representatives of organic matter, while for Zn such binding is much weaker (Tipping et al., 2002). The SPE/GC-MSD results show that monocarboxylic acids are the most important organic compounds found in the leachate, which was taken as an indication of the acid stage of the landfill. However, measured pH lying in the range 6.5–7 may also be an indication that the landfill is evolving into the methanogenic stage, where the leachate pH rises to around 8. In this stage, more complex organic acids such as fulvic and humic acids may develop, and metals may reduce their mobility because of the formation of sparingly soluble precipitates (Pohland and Kim, 2000). However, knowing that most of these acids are important complexing agents of metal ions, especially the formation of acetate complexes (Pittman and Lewan, 1994; Fein, 2002), it is very likely that organic acids are fundamental in metal partitioning between waste waters and sediments. The results do not show a correlation between monocarboxylic acids and base metals in the sediments, but the remaining organic compounds in the leachate may be important for metal uptake by sediments. Water chemistry near the source and taken 200 m away from it in path No. 1 (near the location of BRL-12FA/FS samples) was very similar, both in metal and organic content. The suggested mechanism to explain the base metal pattern in the sediment samples is to consider a rapid adsorption of several organic compounds present in the waste waters onto the mineral surfaces near the source which then act as metal scavengers. These probably compete for the metals with the organic acids. However, since the latter clearly dominate water chemistry, metals can be kept and transported in solution resulting in the rapidly decreasing concentration in metals of the sediments down stream, and unchanged water chemistry. Along path No. 2 the metal concentrations are almost an order of magnitude lower and BRL-16FA/FS samples also show the lowest organic content as detected by GC-MSD, although they are located very close to the source in a flat region. This situation implies longer residence times for wastewater and lower turbulence regimes, which would favour water-sediment exchange.

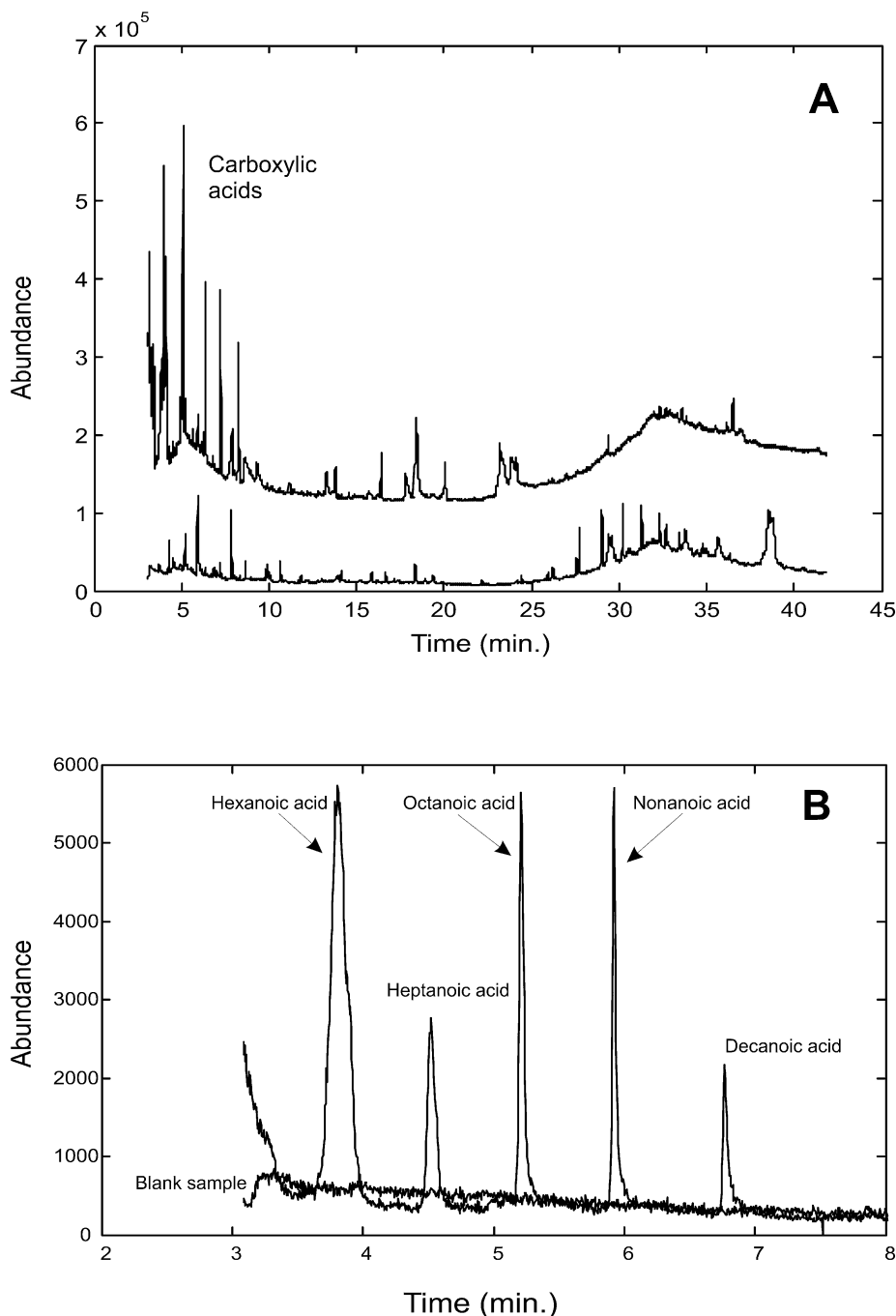


Fig. 7. Total ionic current chromatograms of BRL-9FA (top; shifted  $10^5$  units in the  $y$  direction for clarity) and BRL-11FA (bottom) samples by SPE/GC-MSD (A). The corresponding chromatogram of the extracted ion at  $m/z$  60 for BRL-9FA sample and a blank is also displayed, showing no signal for those acids (B).

#### 4. Conclusion

In the present work it has been verified that certain base metals are partitioned from waste run-off waters to the top layers of stream sediments. Bulk chemical analyses show

that base metal concentrations decrease rapidly downstream, which may imply the limited interaction that these waters have with the sediments, especially when the flux is high enough which is the most frequent case. Given that the coarser size fraction of the stream sediments



contains a substantial quantity of clay minerals, as demonstrated by X-ray diffraction and SEM, the possibility cannot be ruled out that all mineral surfaces serve as a base for metal fixation, either by adsorption or via organically bound compounds. Although some base metal bearing phases were identified in the sediments, these could not represent more than 40–60% of total metal concentration as a limiting condition, depending on the metal considered. The SEM was shown to be a useful resource to identify contaminated sediments through their surface analyses provided metal concentration is high enough. According to the data obtained for Cu, SEM becomes sensitive whenever bulk Cu composition exceeds at least 500 ppm; for the remaining metals, the highest bulk concentrations observed must be taken to be lower than the detection limit of the technique.

The sequential extraction method was able to show the relevance of metal adsorption onto mineral surfaces, and the major importance of the organic matter on metal fixation in spite of the underlying uncertainty of these extraction techniques. Existence of a down-stream gradient concentration in metals, and the lower concentration of organic compounds in the samples of path No. 2, suggests that the organic compounds from the waste water act as important adsorbent media for metal uptake and partitioning onto the sediments. Although organic acids are shown to be major leachate constituents, their role in metal fixation appears to be negligible. However, as recognised important metal ligands they may be responsible for metal transport in solution, competing with the most insoluble organic compounds likely to be fixed within the sediments. As to the substrate, evidence points to an equal importance of all mineral surfaces, and in this system the likely importance of clay minerals seems diminished.

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