Bull Environ Contam Toxicol (2008) 80:274–279
DOI 10.1007/s00128-008-9361-5

Temporal Variation of Trace Elements in Waters Polluted by Municipal Solid Waste Landfill Leachate

Vojtěch Ettler · Martin Mihaljevič · Marek Matura · Markéta Skalová · Ondřej Šebek · Petr Bezdička

Received: 10 July 2007 / Accepted: 11 January 2008 / Published online: 22 February 2008

Abstract Landfill leachate-polluted stream waters were monitored in three sampling campaigns (November 2001 to June 2006), with emphasis on trace elements. The data were evaluated by means of statistics and speciation modelling. Two statistically different groups of trace elements were distinguished: (1) Ba, Sr, Al, Fe, Mn, Cr, Co, Ni, V, As, Se, Sb, U, Li, Rb and Cs decrease during the rain event due to dilution; (2) Pb, Zn, Cu and Cd increase during the rain event due to the dissolution of hydrous ferric oxides and calcite, on whose surfaces these elements are bound, mainly in the stream sediments downgradient to the landfill.

Keywords Trace elements · Landfill leachate · Temporal variation · Speciation

The migration of landfill leachates into surface or groundwater is considered to be a serious environmental problem at both uncontrolled and engineered municipal landfill sites (Mor et al. 2006; Durmusoglu and Yilmaz 2006). Landfill leachates might contain toxic elements in considerable concentrations (Mostbauer 2003; Pinel-Raffaitin et al. 2006). In recent years, a large number of works have focused on metals in landfill leachates, in particular on their speciation (e.g., Baun and Christensen 2004) and improvement of their sampling/analytical protocols (Pinel-Raffaitin et al. 2006). In addition to metals, other trace elements can also be present in landfill leachates and leachate-polluted waters, although in relatively low concentrations (μg to mg L^{-1}).

The purpose of this article is to evaluate the temporal variation of the chemical composition of leachate-polluted stream waters at one old uncontrolled municipal landfill site in the Czech Republic with emphasis on the trace elements. The long-term periodic changes (five years) as well as changes during rain events were evaluated. This is the first study focused, not only on metals, but also on other trace elements in the leachate-polluted waters. The relationship between the trace element concentrations and other chemical and physico-chemical parameters was investigated through a combination of analytical and statistical approaches combined with speciation-solubility modelling.

Materials and Methods

The leachate-polluted water samples were collected in the vicinity of the 20-year old, now inactive municipal landfill located at Dolní Chabry, 5 km N of Prague, Czech Republic (N 50°9′, E 14°27′). The landfill was constructed without any lining preventing leaking of the leachate and served as the principal municipal waste disposal dump between 1984 and 1993 (for details see Ettler et al. 2006a). Water samples (n = 55) were taken from tubes draining

V. Ettler (✉) · M. Mihaljevič · M. Matura · M. Skalová
Institute of Geochemistry, Mineralogy and Mineral Resources,
Charles University, Albertov 6, 128 43 Praha 2, Czech Republic
e-mail: ettler@natur.cuni.cz

M. Skalová
Ministry of Environment of the Czech Republic, Vršovická 65,
110 00 Praha 10, Czech Republic

O. Šebek
Laboratories of Geological Institutes, Charles University,
Albertov 6, 128 43 Praha 2, Czech Republic

P. Bezdička
Institute of Inorganic Chemistry, Academy of Science of the
Czech Republic, 250 68 Rez u Prahy, Czech Republic

the landfill leachate and conducting it directly to the small stream during three sampling campaigns: November 2001–December 2002 (n = 5), September 2003–January 2004 (n = 30) and January–June 2006 (n = 20).

The values of the pH, Eh, specific conductivity and temperature were recorded in the field using the Schott Handylab multimeters. The samples were stored in clean 500-mL HDPE bottles (Azlon®, UK) for inorganic analysis and in clean 100-mL borosilicate glass bottles (Schott Duran®, Germany) for organic carbon analysis and were immediately treated in the laboratory. All the samples were filtered through a 0.45-µm Millipore® membrane filter prior the analysis for dissolved organic carbon (DOC) and total inorganic carbon (IC) (Skalar Formacs^{HT} TOC analyzer). The solution for inorganic analysis was filtered through a 0.1-µm Millipore® membrane filter. The first aliquot of this sample was used to determine the alkalinity (microtitration to pH 4.5 using Schott TitroLine Easy automatic titrator with 0.05 M HCl) and the major anions (Agilent HP^{3D}CE capillary electrophoresis system or Dionex ICS-2000 ion chromatography). The second aliquot was acidified by HNO_3 or HCl and analyzed for major anions (Varian SpectrAA 200 HT flame atomic absorption spectrophotometer) and trace elements (VG Elemental PQ3 inductively-coupled plasma mass spectrometer). The following elements and compounds were determined (without the charge for the sake of simplicity): Na, K, Ca, Mg, Fe, Mn, Si, Al, Ba, Sr, Cl, SO_4, NO_3, NH_4, I, Br, HCO_3, DOC, Pb, Zn, Cu, Cd, Cr, Co, Ni, V, As, Se, Sb, U, Li, Rb, Cs. Following standard materials were used for quality control of instrumental analyses: internal laboratory standards for AAS determinations, Analytika CRM CZ9102 (MIX 022-IC) for HPLC determinations and NIST standard reference materials 1640 (Trace Elements in Natural Water) and 1643d (Trace Elements in Water) for trace element measurements by ICP-MS. The accuracy of all the determinations was generally <10% of the relative standard deviation (RSD).

The data were treated using the NCSS statistical software (Hintze 2001). The correlations between the individual elements were expressed by the Pearson correlation coefficients. For the purposes of multivariate analysis, each of the 55 water samples was considered to be a vector with 38 variables (element concentrations, physico-chemical parameters and precipitation values). Thus, a data matrix with dimensions of 55 × 38 formed the basis for the correlation matrix. Values below the detection limits (DL) were set to the value of DL.

Speciation-solubility modelling was carried out using the PHREEQC-2 software (Parkhurst and Appelo 1999). The Minteq.v4.dat thermodynamic database (derived from MINTEQA2 code, version 4, released by U.S. EPA in 1999) was used for all the calculations. This database does not contain species of Cs and Rb, but the thermodynamic data from llnl.dat (developed by Lawrence Livermore National Laboratory) indicate that these elements will be present in all the studied samples as free ionic species. Due to the lack of thermodynamic data, the PHREEQC-2 code is not capable of calculating the extent of binding of trace elements to dissolved organic matter (DOM), which was observed at numerous landfill sites (e.g., Baun and Christensen 2004). For this reason, the WHAM 6 speciation code equipped with Model VI (Tipping 1998) was used for this purpose. The DOC was entered into the code as fulvic acid, being predominantly present in landfill leachate (Christensen et al. 1998). The “best average” default parameters were used for the WHAM calculations.

Results and Discussion

Trace elements found in the leachate-polluted waters are significantly more concentrated than in the groundwater and rain water penetrating the landfill body. A simple comparison of the chemical composition of groundwater sampled upgradient from the landfill with stream waters downgradient to the landfill (and studied in this investigation) yields enrichment factors with values varying from units to 80 (Matura 2003). Whereas metals and metalloids can be released from the metallic (batteries, electronics), plastic and textile compounds of municipal solid waste (MSW) (Nakamura et al. 1996; Mor et al. 2006), alkali metals and alkali-earth elements such as Li, Rb, Cs, Ba and Sr tend to originate rather from admixtures of salts. Al, Fe and Mn may result from alteration of building materials that were also deposited in the studied landfill (Matura 2003; Mor et al. 2006). The variation in the chemical composition of the leachate-polluted waters expressed in ranges and means is given in Table 1.

The conductivities and the concentrations of basic cations and anions are generally higher in the dry season and decrease by simple dilution during precipitation events. This is also the case of some trace elements such as Ba, Sr, Fe, Mn, Co, Ni, V, As, Se, U, Li, Rb and Cs as is also shown by significant correlation of these elements with the conductivity and contents of major compounds (such as HCO_3) (Table 2). In addition, negative correlations with cumulative precipitation can be observed for the majority of these trace elements (Table 2). Dilution by rainfall has also been observed at other landfill sites (Durmusoglu and Yilmaz 2006; Johnson et al. 1999; Pinel-Raffaitin et al. 2006). No significant correlations with major compounds (and conductivities) can be observed for Pb, Zn, Cu, Cr and Sb (Table 2). Copper and Cd even exhibit a positive correlation with the cumulative precipitation values (Table 2).

Taking into account the data presented in Table 1, the behaviour of some trace elements seems to be

Table 1 Ranges and mean values of the basic chemical properties of leachate-polluted surface waters

Parameter	Units	DL[b]	All dataset (n = 55)		Dry season (n = 33)[a]		Wet season (n = 22)[a]	
			Range	Mean	Range	Mean	Range	Mean
pH	Std. units	–	6.1–8.3	7.8	7.3–8.3	7.8	6.1–8.3	7.7
Eh	mV	–	80–237	185	110–237	189	80–234	179
Conductivity	μS cm^{-1}	–	203–6170	4473	2510–6170	5046	203–6160	3613
Na	mg L^{-1}	0.004	11–1573	231	81–465	229	11–1573	234
K	mg L^{-1}	0.012	10–855	307	61–727	326	10–855	279
Ca	mg L^{-1}	0.004	24–410	226	99–410	253	24–322	186
Mg	mg L^{-1}	0.002	2–245	78	37–245	93	2–101	56
Si	mg L^{-1}	0.5	1.1–13	8.6	6.0–11	9.9	1.1–13	6.7
DOC[c]	mg L^{-1}	0.1	6.6–188	59	35–90	61	6.6–188	55
HCO_3	mg L^{-1}	1	56–2074	1108	680–1657	1253	56–2074	889
Cl	mg L^{-1}	1	40–1286	768	305–1285	845	40–1286	653
SO_4	mg L^{-1}	1	5.3–284	146	82–280	164	5.3–284	119
NO_3[d]	mg L^{-1}	1	4.8–50	23	8.3–49	27	4.8–50	20
NH_4[d]	mg L^{-1}	–	8.8–28	15	11–16	14	8.8–28	16
I	mg L^{-1}	0.005	0.04–16	3.7	1.0–12	4.4	0.04–16	2.7
Br	mg L^{-1}	0.01	0.13–10	5.8	2.3–10	6.8	0.13–9.2	4.3
Ba	μg L^{-1}	0.01	18–394	148	92–213	161	18–394	127
Sr	μg L^{-1}	0.02	36–3132	1535	589–3132	1751	36–3080	1212
Al	μg L^{-1}	0.7	1.2–452	40	1.2–237	27	4.2–452	62
Fe_{tot}	μg L^{-1}	12	18–447	229	18–447	267	24–396	172
Fe^{2+}[e]	μg L^{-1}	–	0.14–188	24	0.14–110	24	0.33–188	24
Fe^{3+}[e]	μg L^{-1}	–	0.44–424	205	17–424	243	0.44–378	148
Mn	μg L^{-1}	0.01	4.0–610	365	4.0–610	379	51–590	345
Pb	μg L^{-1}	0.03	<0.03–26	2.8	0.07–26	3.2	<0.03–13	2.1
Zn	μg L^{-1}	0.6	3.9–66	19	3.9–66	17	4.9–46	21.71
Cu	μg L^{-1}	0.1	<0.1–12	5.7	<0.1–9.8	4.2	0.78–12	7.4
Cd	μg L^{-1}	0.003	<0.003–1.5	0.12	<0.003–0.11	0.04	<0.003–1.5	0.18
Cr	μg L^{-1}	0.05	1.3–323	16	4.1–41	10	1.3–323	24
Co	μg L^{-1}	0.01	0.43–14	6.6	2.6–8.3	7.0	0.43–14	5.9
Ni	μg L^{-1}	0.1	3.8–651	67	20–76	58	3.8–651	80
V	μg L^{-1}	0.05	3.3–100	13	5.3–36	11	3.3–100	15
As	μg L^{-1}	0.6	3.7–53	19	7.3–32	21	3.7–53	16
Se	μg L^{-1}	0.5	<0.1–42	19	3.0–40	23	<0.1–42	14
Sb	μg L^{-1}	0.1	0.24–1.5	0.67	0.29–1.2	0.58	0.24–1.5	0.81
U	μg L^{-1}	0.3	<0.3–13	2.4	1.2–4.5	2.4	<0.3–13	2.3
Li	μg L^{-1}	0.05	0.73–225	76	24–149	84	0.73–225	66
Rb	μg L^{-1}	0.1	2.0–187	95	37–187	114	2.0–184	67
Cs	μg L^{-1}	0.2	<0.1–2.7	1.3	0.58–2.1	1.4	<0.1–2.7	1.0

[a] Dry season corresponds to cumulative precipitation of (5 days prior to sampling) <5 mm, wet season >5 mm of cumulative precipitation; [b] DL-Detection limit; [c] DOC-Dissolved organic carbon; [d] Nitrogen species calculated by PHREEQC; [e] Fe species calculated by PHREEQC according to pH-Eh values

contradictory within these two statistically distinct groups: Pb yields slightly higher mean values in the dry season than in the wet season; in contrast, Cr, Ni and V exhibit higher mean values in the wet season. These findings may be related either to numerous observations with very low concentrations close to the detection limit (Pb) or to single statistically outlying values (Cr, Ni and V with 323, 651 and 100 μg L^{-1}, respectively) (Table 1).

The inorganic speciation calculation using PHREEQC-2 permitted estimation of the speciation of elements and the

Table 2 Correlation matrix for trace elements and other selected parameters

	Cond[a]	Al	Ba	Sr	Pb	Zn	Cu	Cd	Cr	Co	Ni	V	As	Se	Sb	U	Li	Rb	Cs	HCO_3
Al	0.095																			
Ba	0.843**	−0.169																		
Sr	0.865**	−0.131	0.968***																	
Pb	0.040	−0.118	0.168	0.028																
Zn	0.042	0.248	−0.028	−0.049	−0.513															
Cu	−0.169	0.154	−0.416	−0.461	−0.215	0.717*														
Cd	−0.190	0.364	−0.575	−0.431	−0.445	0.212	0.565													
Cr	0.618	−0.354	0.551	0.527	−0.030	0.039	0.180	0.075												
Co	0.872**	−0.044	0.960***	0.988***	0.036	0.054	−0.367	−0.381	0.515											
Ni	0.853**	−0.092	0.979***	0.988***	0.106	−0.011	−0.439	−0.492	0.469	0.989***										
V	0.849**	0.333	0.721*	0.796**	0.087	−0.028	−0.220	0.031	0.454	0.842**	0.798**									
As	0.872***	−0.132	0.978***	0.996***	0.102	−0.045	−0.434	−0.452	0.532	0.991***	0.994***	0.805**								
Se	0.875***	−0.137	0.950***	0.994***	0.051	−0.076	−0.449	−0.386	0.525	0.982***	0.982***	0.818**	0.992***							
Sb	−0.193	−0.456	0.109	−0.096	0.691*	−0.016	0.184	−0.484	0.148	−0.076	−0.018	−0.281	−0.029	−0.109						
U	0.732*	−0.184	0.934***	0.945***	0.015	−0.169	−0.652*	−0.606	0.389	0.903***	0.935***	0.636*	0.929***	0.918***	−0.099					
Li	0.777**	−0.274	0.862***	0.916***	0.186	−0.336	−0.523	−0.309	0.585	0.885***	0.891***	0.788**	0.917***	0.937***	−0.052	0.848**				
Rb	0.831**	−0.193	0.969***	0.964***	0.240	−0.196	−0.550	−0.587	0.448	0.940***	0.975***	0.736*	0.973***	0.962***	0.042	0.942***	0.917***			
Cs	0.826**	−0.184	0.951***	0.944***	0.299	−0.238	−0.556	−0.588	0.423	0.919***	0.960***	0.738*	0.957***	0.948***	0.061	0.917***	0.915***	0.996***		
HCO_3	0.799**	−0.210	0.979**	0.959***	0.274	−0.175	−0.539	−0.627	0.450	0.938***	0.974***	0.709*	0.971***	0.951***	0.122	0.939***	0.899***	0.994***	0.988***	
prec[b]	−0.388	0.524	−0.688*	−0.651*	−0.282	0.457	0.776**	0.844**	−0.116	−0.554	−0.653*	−0.177	−0.644*	−0.637*	−0.177	−0.794**	−0.641*	−0.771**	−0.773**	−0.774**

Notes: * $p < 0.05$, ** $p < 0.01$, *** $p < 0.001$; [a] conductivity; [b] cumulative precipitation (5 days prior to sampling) oversaturation of the solutions with respect to the solid phases. Whereas numerous trace elements are present in free ionic forms (Sr^{2+}, Ba^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Li^{+}, Rb^{+}, Cs^{+}), some metals are predominantly present as carbonate complexes ($ZnCO_3^0$, $NiCO_3^0$, $NiHCO_3^+$, $PbCO_3^0$, $PbHCO_3^+$, $UO_2(CO_3)_3^{4-}$). For Zn and Ni, free ionic species may also be present, but generally constitute <10% of the total speciation. Al, trivalent Fe and Cr predominantly form hydroxocomplexes. Metalloids are generally present as anionic species ($H_2VO_4^-$, SeO_3^{2-}, $HSeO_3^-$, SbO_3^-, $HAsO_4^{2-}$) and cadmium exhibits a high tendency to form complexes with Cl^-, mainly $CdCl^+$. The present calculations do not indicate any significant change in speciation during precipitation events (except slightly lower percentages of carbonate species for Zn and Ni at the expense of free ionic species).

The results of the speciation calculations with the organic matter using WHAM 6 indicated that alkalis and alkali-earths are practically not bound to organic matter (only up to 7% for Ca speciation). In contrast, the fractions bound to organic matter were significantly higher for heavy metals (e.g., up to 99% Cu and Pb, up to 55% Cd and 25% Zn of the total speciation). During the wet sampling periods, the relative abundances of organic matter-bound metals increase slightly. A similar phenomenon was observed by Ettler et al. (2006a), who calculated the metal speciation in landfill waters by MINTEQA2, and explained this fact by a dramatic decrease in the alkalinity during precipitation events, followed by a decrease in the metal fraction bound to carbonate complexes. The PHREEQC-2 calculations showed that waters were generally oversaturated with respect to calcite ($CaCO_3$) and undersaturated with respect to other carbonate species. Hydrous ferric oxides (HFOs) also yield positive saturation indices (SI) (Table 3).

The controlling mechanisms governing trace element release from a landfill body can be depicted from the most detailed sampling during precipitation events. The changes in leachate-polluted water composition during a December 2003 rain event are reported in Fig. 1. Within 24 h after the beginning of the precipitation, the conductivity decreases to half of the initial value (Fig. 1). This is a common phenomenon, where a decrease in the conductivity is a response to a decrease in the concentrations of the major components, such as Na, K, Ca, HCO_3 and Cl through dilution by rainwater (Johnson et al. 1999). Similar behaviour can also be observed for metals such as Fe, Al, Ba, Sr, Ni, Cr, Co, U, Li, Rb, Cs and metalloids such as Sb, As, Se and V (only representative trace elements shown in Fig. 1). The changes in the concentrations of Zn, Cu and Cd (Pb was below DL for this sampling) with an increasing trend during a precipitation event cannot be explained by a simple hydrological mechanism. This phenomenon probably results from more complex geochemical/mineralogical reactions, which may include desorption or dissolution of solid phases in the landfill or in the bottom sediment in the stream downgradient to the landfill (similar mechanisms were observed by Johnson et al. 1999).

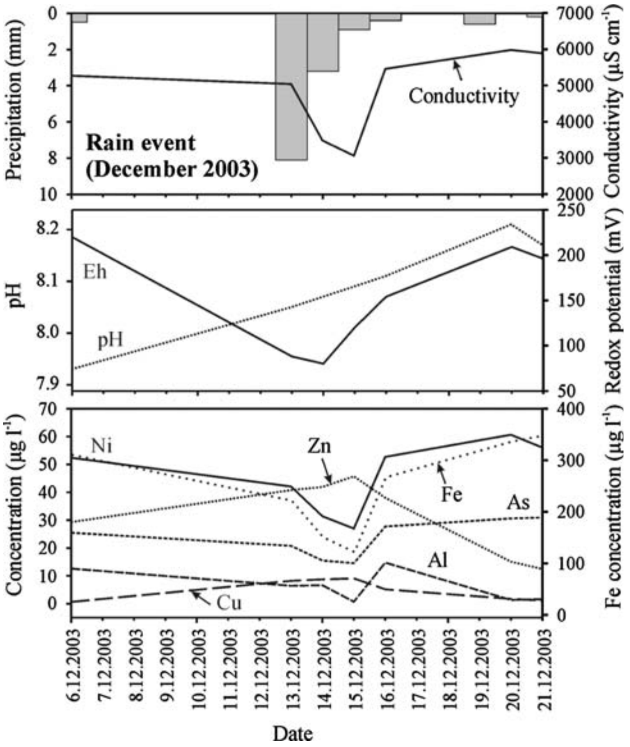

Fig. 1 Patterns of precipitation, physico-chemical parameters and selected trace elements during a December 2003 rain event

Previous works on the studied landfill site showed that the solid speciation of metals is dominated by binding to the surfaces of HFOs and newly formed calcite. Furthermore, HFO and calcite were detected in stream sediments downgradient to the landfill by voltammetry of microparticles (VMP), X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) (Ettler et al. 2006a, Ettler et al. 2006b). Table 3 reports the results of calculation of the saturation indices (SI) of these phases in landfill

Table 3 Saturation indices (SI) of selected solubility-controlling phases

Phase		Dry season (n = 33)		Wet season (n = 22)	
		Range	Mean	Range	Mean
Calcite	$CaCO_3$	0.67–2.08	1.51	−2.60–1.96	0.97
Ferrihydrite	$Fe(OH)_3$	2.19–3.99	3.38	−0.74–3.94	2.91
Goethite	FeOOH	4.89–6.69	6.08	1.96–6.64	5.62

Note: when SI = 0, the solution is saturated with respect to the solid phase, SI < 0 corresponds to undersaturation and SI > 0 to oversaturation of the solution with respect to the solid phase waters using PHREEQC-2. During the rain events, a significant drop in SI was observed for both HFOs and calcite, indicating that these phases could dissolve and release some of trace elements bound to their surfaces.

A decrease in Eh is not accompanied by an appropriate increase in pH (7.93–8.21) and can be observed immediately after the first precipitation in the precipitation event (Fig. 1). Furthermore, the Eh decrease precedes the decrease in conductivity caused by dilution. Consequently, this phenomenon can be related to the release of more reducing leachate discharged from the landfill body in rain water (Fig. 1) and may be responsible for the dissolution of HFOs in stream sediments. This reaction is then accompanied by subsequent release of some trace elements in the water (e.g., Cu, Zn). The eventual increase in the Fe concentration related to the HFO dissolution cannot be discerned in the Fe pattern, probably being only a minor fraction of the total Fe released from the landfill and mostly affected by the dilution effect (Fig. 1).

In landfill environments, the mobility of metals, metalloids and other trace elements is controlled by (i) simple hydrological mechanisms such as dilution (Johnson et al. 1999; Pinel-Raffaitin et al. 2006) often combined with (ii) complex geochemical reactions (Mostbauer 2003). As landfills are generally calcite-buffered systems, the principal geochemical reactions will include (de)sorption of trace elements from/on calcite surfaces (Ettler et al. 2006b) or binding to HFOs (Mostbauer 2003; Ettler et al. 2006a). The present study shows how detailed sampling of landfill effluents, especially before, during and after significant precipitation events may lead to responses in the mechanisms controlling the mobility of inorganic contaminants in the environments surrounding the landfill.

Acknowledgments This study was financed through projects of the Grant Agency of the Academy of Sciences of the Czech Republic (KJB3111402) and the Ministry of Education, Youth and Sports of the Czech Republic (MSM 0021620855).

References

Baun DL, Christensen TH (2004) Speciation of heavy metals in landfill leachate: a review. Waste Manage Res 22:3–23

Christensen JB, Jensen DL, Filip Z, Gron C, Christensen TH (1998) Characterization of the dissolved organic carbon in landfill polluted groundwater. Water Res 32:125–135

Durmusoglu E, Yilmaz C (2006) Evaluation and temporal variation of raw and pre-treated leachate quality from an active solid waste landfill. Water Air Soil Pollut 171:359–382

Ettler V, Matura M, Mihaljevič M, Bezdička P (2006a) Metal speciation and attenuation in stream waters and sediments contaminated by landfill leachate. Environ Geol 49:610–619

Ettler V, Zelená O, Mihaljevič M, Šebek O, Strnad L, Coufal P, Bezdička P (2006b) Removal of trace elements from landfill leachate by calcite precipitation. J Geochem Explor 88:28–31

Hintze J (2001) NCSS and PASS. Number Cruncher Statistical System, Kaysville, Utah

Johnson CA, Kaeppeli M, Brandenberger S, Ulrich A, Baumann W (1999) Hydrological and geochemical factors affecting leachate composition in municipal solid waste incinerator bottom ash. Part II. The geochemistry of leachate from Landfill Lostorf, Switzerland. J Contam Hydrol 40:239–259

Matura M (2003) Heavy metal attenuation processes in leachates from a MSW landfill. M.Sc. Thesis, Charles University of Prague, Czech Republic (in Czech)

Mor S, Ravindra K, Dahiya RP, Chandra A (2006) Leachate characterization and assessment of groundwater pollution near municipal solid waste landfill site. Environ Monit Assess 118:435–456

Mostbauer P (2003) Criteria selection for landfills: do we need a limitation on inorganic total content? Waste Manage 23:547–554

Nakamura K, Kinoshita S, Takatsuki H (1996) The origin and behavior of lead, cadmium and antimony in MSW incinerator. Waste Manage 16:509–517

Parkhurst DL, Appelo CAJ (1999) User's guide to PHREEQC (version 2)—a computer program for speciation, batch-reaction, one-dimensional transport and inverse geochemical calculations. US Geological Survey report 99–4259, Denver, Colorado

Pinel-Raffaitin P, Ponthieu M, Le Hecho I, Amoroux D, Mazeas L, Donard OFX, Potin-Gautier M (2006) Evaluation of analytical strategies for the determination of metal concentrations to assess landfill leachate contamination. J Environ Monit 8:1069–1077

Tipping E (1998) Humic ion-binding Model VI: an improved description of the interactions of protons and metal ions with humic substances. Aquat Geochem 4:3–48