

In situ distributions and characteristics of heavy metals in full-scale landfill layers

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Received 28 February 2005; received in revised form 5 September 2005; accepted 22 March 2006

Available online 28 April 2006

Abstract

The leachate from methanogenic landfill normally contains low concentrations of heavy metals. Little samples had ever been collected from the full-scale landfill piles owing to technical difficulty for well drilling. We drilled two wells in Hangzhou Tianziling landfill, 20 m and 32 m in depth each, and collected solid samples of waste age of 1–4 years from both wells. The total amounts, the sequentially extracted amounts, and the chemical binding forms of heavy metals of the samples collected at different depths were measured. With the correlation between leachate production amount and the yearly rainfall amount, the leached ratio of the heavy metals were estimated only 0.13%, 1.8%, 0.15%, and 0.19% of Cu, Cd, Pb, and Zn, respectively. The heavy metals amounts in the main compositions of MSW, like glass, food waste, paper, coal cinders, were measured using fresh MSW samples. Afterward, the contents of heavy metals initially landfilled were estimated. A positive correlation was noted between the measured and the estimated initial contents of heavy metals, indicating that the low migration of heavy metals in landfill layers. However, among the metals investigated, Zn has shown better mobility inside landfill layers.

Acid volatile sulfide (AVS) and the simultaneously extracted metals (SEM) were measured for all collected samples with optimal reaction conditions identified to yield nearly perfect sulfide recovery as follows: 100 g wet samples, 80 mL min⁻¹ N₂ flow rate, reaction time of 150 min. The SEM/AVS ratios ranged 25–45, indicating that the AVS was insufficient to immobilize the SEM. Sequential extraction using six-fraction scheme revealed that the sum of exchangeable and the avid soluble fractions of heavy metals follow: Zn > Cd > Cu, Ni, Pb > Cr. The insoluble fraction of heavy metals in MSW was high, for instance, over 80% for Cr and Pb high insoluble fractions of heavy metals in the landfilled MSW and the sorption capability of the methanogenic landfill layers should be responsible to the low concentrations of heavy metals found in leachate. © 2006 Elsevier B.V. All rights reserved.

Keywords: Municipal solid waste; Landfill; Heavy metals; Mobilization; Chemical speciation

1. Introduction

The leachate from methanogenic landfill contains low concentrations of heavy metals [1–3]. The evaluation of metal release potential from landfill needs the information of the total deposited refuse amount, its composition, and the historical records of the leachate quality. With limited data, the worse-case simulation could be achieved by analyzing the leachate quality at present time [4].

Bozkurt et al. [5] claimed that the mature refuse contained a high sorption capacity of heavy metals. The sulfide precipi-

tation corresponded to the low heavy metal concentrations in methanogenic leachate [6,7]. For Cr, which could hardly form insoluble sulfide precipitates, Jensen and Christensen [8] proposed that the hydroxide precipitate should be able to bind it firmly in landfill. The ratio of the simultaneously extracted metals (SEM) and acid volatile sulfide (AVS), SEM/AVS, has been used to correlate the bioavailability of heavy metals in sediments [9–13]. At a low SEM/AVS, most heavy metals are claimed to bind in sulfide form and should not be available under anaerobic environment. Martensson et al. [15] noted that the AVS of landfill leachate is far from sufficient to bind most SEM in the landfill. Hydroxide precipitate could form instead at pH above neutral as normally noted for methanogenic leachate [16]. Gounaris et al. [17] and Jensen and Christensen [8] noted that a large fraction of heavy metals was associated with the colloidal

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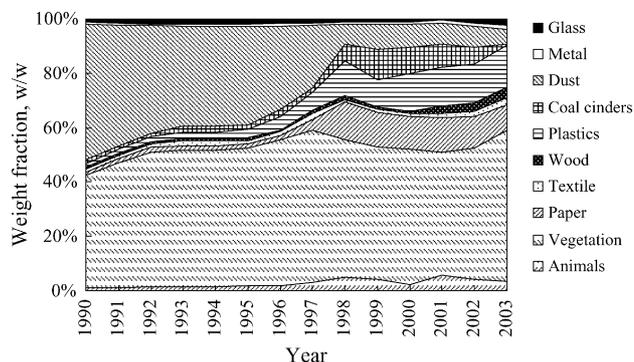


Fig. 1. Main ingredients of MSW of Hangzhou City over 1990–2003.

particles in landfill leachate. Klein and Nissner [18] found that the humic substance dominated colloidal particles in landfill leachate bound the main fraction of heavy metals in leachate. Kjeldsen et al. [19] comprehensively reviewed pertinent literature on leachate characteristics from MSW landfill.

To monitor the landfill leachate alone is hard to interpret why the mass amount of heavy metals could be immobilized in the landfill. However, to sample in situ is difficult in practice since the landfilled refuse contains texture to resist mechanical drilling. Also, the mechanical strength of the landfill body is generally not high enough to stabilize the well's wall. We drilled two wells in a full-scale landfill site, Tianziling landfill in Hangzhou, which is the first sanitary landfill site in PR China, and collected samples at different depths. The contents and the chemical binding forms of heavy metals of the samples collected at different depths were measured and profiled in this work.

2. Materials and methods

2.1. The landfill

The Tianziling landfill has received MSW from Hangzhou City since April 1991. Fig. 1 shows the main compositions of the collected MSW. The food waste presents a major composition which occupies more than 50% (wet basis) since 1992. Since the road dust was landfilled on the other site, its fraction reduced dramatically since year 1996. Coal was widely applied as household fuel over 1998–2002, which has been replaced by town-gas since 2003. The coal cinders presented up to 20% of the MSW around 2000, and had not appeared since 2003. The raw MSW apparently has a significant impact on the spatial changes of compositions in a landfill site.

The cross-section of the landfill site is profiled in Fig. 2, with bottom liners located at 54 m above sea level. The design capacity is 6,000,000 m³ and will be closed at the end of 2005, and the top of the landfill will reach 165 m above sea level. The matured waste was located at bottom layers and the fresh one at top layers. For instance, the MSW of year 1999 was filled over the height of 102.5–110.0 m above sea level, and that of year 2002 over 127.5–135.0 m. Two wells of depth 20 m and 32 m were drilled at the landfill site from the layer located 140 m above sea level, whose locations were also depicted in Fig. 1 for

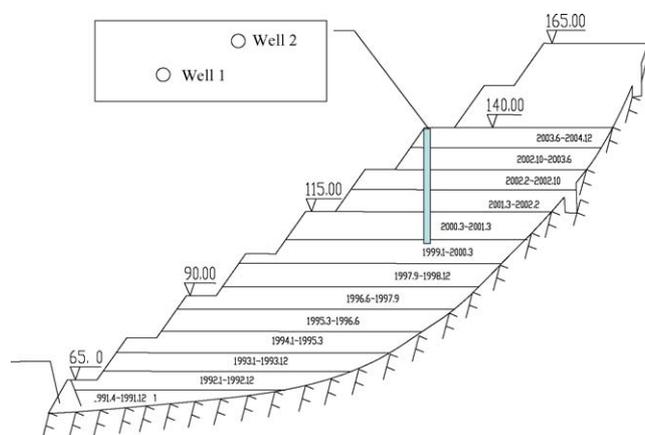


Fig. 2. The landfill site and the sampling wells.

demonstration purpose. The sampled MSW layer had a waste age of 1–4 years old.

2.2. The samples

The samples were collected at depths of 5 m, 10 m, 15 m and 20 m in well 1, and of 5 m, 15 m, 25 m and 32 m in well 2, respectively. The physical characteristics of the MSW at different sites and depths are shown in Table 1. The bulk materials such as glass, plastic, textile, stone had been removed from the collected samples. The remaining part of the collected sample is the sample materials for further examination (the sample (a) in Table 1), occupying 46–84% (wet basis) of the collected samples from the wells. The moisture contents of the wet samples were also listed in the last column of this table. Part of the samples were sealed in polyethylene black bag and kept at 4 °C in a refrigerator for AVS determination [9,10]. The rest of samples were air-dried and shredded into fine grain which was less than 2 mm size for other analysis items [11,12].

2.3. Methods and apparatus

2.3.1. Element analysis

The C, H, S contents in the collected samples (the sample (a) in Table 1) was analyzed using the LECO CHNS-932 elemental analyzer (LECO Corp., USA), and TKN measurement has been conducted for the N content in the collected samples.

2.3.2. Total amounts of heavy metals

The shredded samples were digested with a HCl–HNO₃–HF–HClO₄ [20] mixture according to the procedure described below: (1) Adding 0.2000–0.5000 g sample accurately into a 50 mL-crucible (PTFE). (2) The sample was first digested with 10 mL hydrochloric acid in an open crucible on a heat plate, whose temperature was about 200 °C. Digestion stopped when the hydrochloric acid was left less than 3 mL. (3) Adding nitric acid (5 mL), hydrofluoric acid (5 mL) and perchloric acid (3 mL) in turn. After the crucible was lidded the sample was also heated for 1 h. Then crucible was kept open and shaken occasionally to lose of silicon by its vaporization. The crucible was lidded

Table 1
Physical characteristics of the MSW at different sites and depths

MSW	Depth (m)	pH	Organic matters (% w/w)		Inorganic matters (% w/w)			Bulk material removed (% w/w)				The sample (% w/w) ^a	Moisture content (% w/w)		
			Animal	Plant	Clay	Porcelain	Paper	Plastic/rubber	Textile	Glass	Metals			Wood/bamboo	
Well 1	5	6.88	0.0	0.0	0.0	5.2	0.0	0.0	16.8	5.9	0.0	0.4	1.7	70.0	48.8
	10	7.27	0.0	0.0	0.0	4.4	0.0	0.0	5.2	4.0	0.0	0.5	2.1	83.8	37.7
	15	8.29	0.0	0.0	0.0	2.3	0.0	0.0	27.7	2.8	0.0	0.0	2.9	64.3	65.7
	20	8.60	0.0	0.0	0.0	4.9	0.0	0.0	7.0	4.2	0.5	0.0	5.1	78.3	46.2
Well 2	5	7.85	0.0	0.0	0.0	0.6	0.0	0.0	14.4	7.8	0.0	3.1	0.0	74.1	49.3
	15	8.58	0.0	0.0	0.0	1.7	0.0	0.0	6.1	12.4	0.0	0.7	3.5	75.6	42.8
	25	9.00	0.0	0.0	0.0	6.2	0.0	0.0	26.6	13.9	0.0	5.5	1.8	46.0	58.0
	32	8.62	0.0	0.0	0.0	6.4	0.0	0.0	12.2	0.0	0.1	0.0	0.0	81.3	61.4

^a The samples mentioned here were the sampled refuses with bulk materials such as glass, plastic, textile, stone and pottery removed.

when white fumes appeared. After black organic carbon has disappeared the crucible was open to evaporate white fumes until the sample become dope. (4) The residue was dissolved in nitric acid (1 mL) and then diluted to 50 mL. The solution was then analyzed by atomic absorption spectrometry (AAS), model 3200 (Shanghai Analytical Instrument Overall Factory, China) for Cd, Cu, Pb and Zn, and model AA-6501F (Shimadzu Corporation, Japan) for Cr and Ni.

2.3.3. Sequential extraction procedures

The sequential extraction procedures as follows were adopted to differentiate metals in the sampled waste into different fractions [11,12]:

- (1) Exchangeable fraction: 10 mL of 1 M NH₄Ac (pH 7) were added to 1.00 g shredded dry sample in a 50 mL plastic centrifuge tube. The mixture was continuously agitated (using a mechanical shaker) for 2 h and then centrifuged (3000 rpm for 30 min). The supernatant solution was retained and used for analysis.
- (2) Acid soluble fraction: 10 mL of distilled water were added to the residue from step (1) and centrifuged for 30 min. 10 mL of NaAc and HAc mixture (pH 5) were added to the residue. The mixture was agitated for 5 h and centrifuged. The supernatant solution was used for analysis.
- (3) Easily reducible fraction: 10 mL of distilled water were added to the residue from step (2) and centrifuged for 30 min. Twenty milliliters of 0.1 M NH₂OH·HCl (pH 2) were added to the residue from step (2). The mixture was agitated for 12 h and centrifuged. The supernatant solution was used for analysis.
- (4) Moderately reducible fraction: 20 mL of 0.1 M oxalate buffer (pH 3) were added to the residue from step (3). The mixture was agitated for 24 h and centrifuged. The supernatant solution was used for analysis.
- (5) Oxidizable fraction: 20 mL of 30% H₂O₂ (pH 3) were added to the residue from step (4). The mixture was heated to 90 °C until most of the hydrogen peroxide was evaporated. Following this treatment, 20 mL of 1 M NH₄Ac (pH 7) were added to the residue. The mixture was agitated for 12 h and centrifuged. The supernatant solution was used for analysis.
- (6) Insoluble fraction: the residue from step (5) was dried at 105 °C for 2 h and weighed. Then less than 0.5 g residue was digested following the same procedures in Section 2.3.2.

2.3.4. AVS and SEM measurements

Procedures for the determination of AVS and SEM in Allen and van Griethuysen [13,14] were adopted here. The apparatus for measuring AVS and SEM of the landfill samples were shown in Fig. 3. Firstly nitrogen was deoxygenated by vanadous deoxygenating reagent in the first gas-washing bottle (3), then it was washed again by distilled water in the second gas-washing bottle (4). Hundred grams wet sample was placed in a 1000 mL flask (6) with stirring. Before test, the system was deoxygenated using nitrogen. Then 6 M HCl was added to the sample flask to keep HCl concentration in the mixture to be 1 M [9,13]. Bottles (7) and (8) were H₂S trap containing 0.5 M NaOH. The trapped

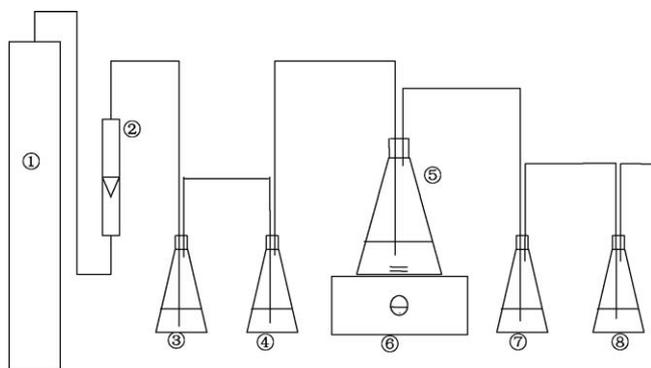


Fig. 3. Apparatus for measuring AVS and SEM in the landfill samples: (1) N_2 cylinder; (2) flow controller; (3) 500 mL gas-washing bottles, containing oxygen scrubbing solution; (4) 500 mL gas-washing bottles, containing deionized water; (5) stirrer; (6) 1000 mL reaction flask (7) and (8) 200 mL trapping bottles, containing 80 mL 0.5 M NaOH solution.

H_2S was analyzed by colorimetric methods, and the solubilized metals (SEM) determined by AAS.

To approach the appropriate testing conditions for AVS/SEM, a standard solution containing 123.7 mg L^{-1} (10 mL) sulfide was used as the testing material. For N_2 flow rates ranging $60\text{--}100 \text{ mL min}^{-1}$, the AVS recovery exceeded 95%, especially, reached 99% at a flow rate of 80 mL min^{-1} (Fig. 4a). We hence fixed the N_2 flow rate used in further analysis at 80 mL min^{-1} . Fig. 4b shows the recovery of H_2S at different sample weight at a N_2 flow rate of 80 mL min^{-1} . Apparently when the sample weight is less than 110 g in the 1000 mL flask, the recovery reaction could be complete in less than 120 min. Therefore, in the subsequent analysis, the reaction conditions were fixed as: 100 g wet samples, 80 mL min^{-1} N_2 flow rate, reaction time of 150 min.

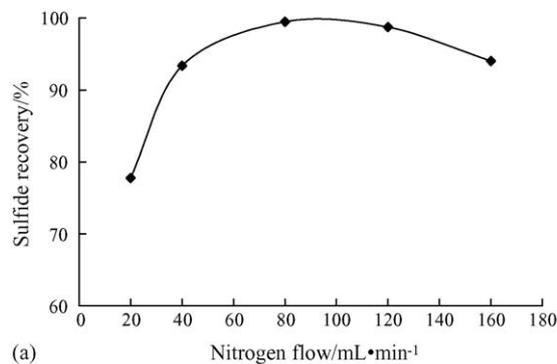
3. Results and discussion

3.1. Element analysis results

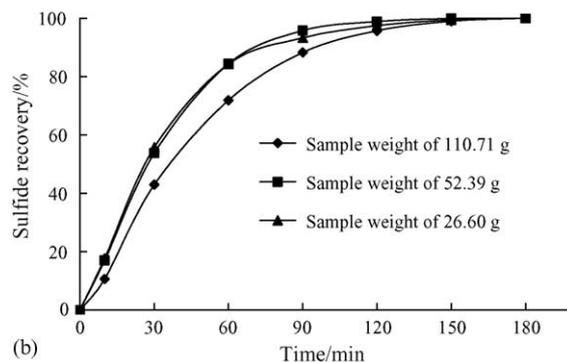
The results for the shredded samples are shown in Table 2. Most nitrogen has been leached out in the landfill, as shown by little nitrogen content in the collected samples, as a result of sufficient hydrolysis occurred in the landfilled MSW. The carbon content ranged 9.1–15.3% (w/w). The sulfur content was about 0.2–0.5% (w/w) in the collected samples.

Table 2
Elemental analysis for collected samples (the sample (a) in Table 1)

MSW	Depth (m)	C (% , w/w)	H (% , w/w)	TKN (% , w/w)	S (% , w/w)
Well 1	5	9.8	1.18	0.7	0.222
	10	15.3	2.09	0.5	0.367
	15	11.2	1.28	0.5	0.268
	20	9.1	1.13	0.3	0.372
Well 2	5	14.8	1.68	0.6	0.252
	10	9.3	1.03	0.3	0.543
	15	10.4	1.27	0.3	0.289
	20	10.2	1.18	0.3	0.216



(a)



(b)

Fig. 4. (a) Effects of nitrogen flow rate on the recovery of H_2S from Na_2S suspension, 180 min. (b) Effects of sample weight and reaction time on the recovery of H_2S from sample.

3.2. The heavy metals in landfill

Table 3 shows the heavy metal contents of collected samples. The contents follow the sequence: $Zn > Pb > Cr > Cu > Ni > Cd$. The heavy metal contents in landfill layers are much higher than those in surface soil samples as the backgrounds. Based on the average heavy metal contents of collected samples in the drilled well and the yearly landfill records, the total amount of Cd, Cu, Pb, and Zn in the landfill could be estimated as 8.7 tonnes, 222 tonnes, 548 tonnes, and 808 tonnes, respectively (calculated from Table 4). Hence, the pollution potentials of the heavy metals from landfill leachate should be extremely high.

Based on the historical records of the precipitation and leachate production in the landfill over the past decade, the leachate production rate could be estimated by the yearly average rainfall rate with the follow equation: (leachate production rate (10,000 tonnes) = $0.0042 \times \text{rainfall (mm a}^{-1})$, with $r^2 = 0.97$).

Table 3
The heavy metal contents of collected samples from landfill at different depths and the estimated contents landfilled with the original MSW based on the historical MSW measured for main ingredients of the MSW

MSW	Depth (m)	Cd ($\mu\text{g g}^{-1}$)		Cu ($\mu\text{g g}^{-1}$)		Cr ($\mu\text{g g}^{-1}$)		Pb ($\mu\text{g g}^{-1}$)		Ni ($\mu\text{g g}^{-1}$)		Zn ($\mu\text{g g}^{-1}$)	
		Sample	Original ^a										
Well 1	5	6.1 ± 0.70	5.2	107 ± 1.1	45.0	456 ± 13.5	74.3	347 ± 0.3	241.7	58.3 ± 5.5	59.6	384 ± 30.1	337.3
	10	5.4 ± 0.89	5.3	133 ± 10.8	44.9	456 ± 51.4	73.5	777 ± 49.4	217.9	54.8 ± 7.4	65.4	626 ± 63.2	305.9
	15	4.9 ± 0.22	5.3	148 ± 10.2	44.5	545 ± 7.6	72.9	237 ± 10.1	212.6	73.5 ± 0.8	65.2	600 ± 145	299.3
	20	4.7 ± 0.35	5.4	133 ± 4.6	45.6	352 ± 35.7	75.0	665.4	219.7	39.6 ± 5.7	68.1	802 ± 47.4	308.1
Well 2	5	4.9 ± 0.69	5.2	178 ± 4.5	45.0	490 ± 79.2	74.3	259 ± 23.7	241.7	76.8 ± 2.4	59.6	447 ± 34.1	337.3
	15	11.3 ± 0.57	5.3	320 ± 1.7	44.5	454 ± 19.3	72.9	206 ± 16.2	212.6	101 ± 3.4	65.2	546 ± 11.2	299.3
	25	6.8 ± 0.43	5.4	146 ± 0.7	45.6	323 ± 4.9	75.0	528 ± 10.5	219.7	82.9 ± 11.5	68.1	519	308.1
	32	7.4 ± 0.86	5.4	165.9	45.7	503 ± 227	74.9	265 ± 9.0	215.6	90.3 ± 5.6	69.4	913 ± 38.9	302.7
Surface soil 1 ^b		0.070 ± 0.059		17.6 ± 12.9		52.9 ± 43.0		23.7 ± 6.8		24.6 ± 11.9		70.6 ± 37.2	
Surface soil 2 ^b		0.065 ± 0.056		21.0 ± 17.5		54.5 ± 31.8		24.0 ± 7.8		27.6 ± 11.9		74.9 ± 33.2	
Intermediate cover materials		28.1 ± 1.1		462.5 ± 18.1		3238.3 ± 549.6		470.1 ± 132.8		135.1 ± 18.7		1040.4 ± 19.1	

Values are based on per gram of dried sample (the sample (a) in Table 1).

^a Estimated, original contents of heavy metals in landfill.

^b The surface soil samples were collected randomly in the same county of the landfill.

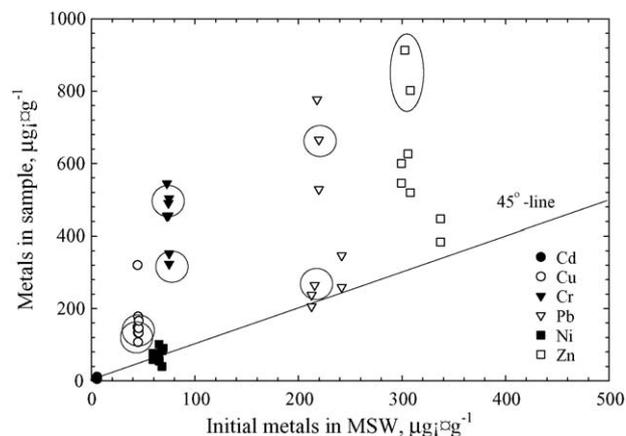


Fig. 5. The measured heavy metal contents and the estimated, initial contents for landfill layers. Circles denote the samples collected at bottom layers of the two wells.

The leachability of the heavy metals could also be estimated according to the historical records of the heavy metal contents in leachate from the landfill.

Over year 1993–2003, the leached amounts of Cu, Cd, Pb, and Zn are 282 kg, 166 kg, 823 kg, and 1560 kg, respectively, representing only 0.13%, 1.8%, 0.15% and 0.19% of the total amount presented (estimated) in the landfill (Table 4). This result consists with the previous works that the heavy metals in landfill leachate are generally low in concentrations [1–3].

To clearly identify the pollution sources, the main compositions of MSW, like glass, food waste, paper, coal cinders, were collected from MSW collection station and their total heavy metal contents were separately measured (Table 5). Based on Fig. 1, the amounts of compositions of landfilled MSW in year 2000 followed: food waste > paper > plastics > coal cinder, dust; while in 2003, food waste > plastics > paper > dust, with negligible coal cinder. Since most food waste and paper were degraded, and since the dust was not physically separable from the samples collected from landfill wells (Table 1), their incorporated heavy metals may be contributing to the measured amounts in Table 3.

3.3. Mobility of heavy metals in landfill

Based on the historical record in Figs. 1 and 2 and the heavy metal measurements in Table 5, the heavy metal contents landfilled with the original MSW over 1999–2003 could be estimated, which were also shown in Table 3 for comparison. The heavy contents in samples collected at different depths are all higher than the estimated, original values. This observation is attributable to the significant reduction in MSW mass after hydrolysis and degradation, and the possible immobilization of the heavy metals in the landfill layers. [21]

Since the refuse would undergo different stages of degradation over various landfill ages, it is not fair to compare the heavy metal contents sampled at different depths. However, at a given sampling point, since the organic degradation level is the same, the herein measured six metals are on the same comparison basis (gram of dried solids). Hence, the data in Table 3 were plotted in Fig. 5 for highlighting the possible correlation between the

Table 4
Precipitation, leachate production, heavy metals concentrations and migration rate of past 11 years from 1993 to 2003

		Year											Sum
		1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	
Landfilled MSW [12] (104 tonnes)		32	38	42	44.7	49	52.4	57.2	61.5	64.5	71.9	76.1	589.3
Precipitation [12,13] (mm)		1751	1399	1449	1482	1435	1538	1824	1198	1567	1744	854	–
Leachate production (10 ⁴ tonnes) ^a		77.4	61.8	64.0	65.5	63.4	68.0	80.6	53.0	69.0	72.1	31.8	706.6
Concentrations (mg L ⁻¹) ^b	Cu	0.025	0.027	0.046	0.038	0.038	0.050	0.057	0.045	0.035	0.038	0.038	–
	Cd	0.012	0.014	0.021	0.022	0.022	0.055	0.034	0.012	0.017	0.022	0.022	–
	Pb	0.166	0.044	0.056	0.112	0.112	0.105	0.210	0.103	0.109	0.112	0.112	–
	Zn	0.119	0.115	0.121	0.245	0.245	0.331	0.261	0.260	0.249	0.245	0.245	–
Leached amount (kg) ^c	Cu	19.4	16.7	29.4	24.9	24.1	34.0	45.9	23.9	24.2	27.4	12.1	282
	Cd	9.3	8.7	13.4	14.4	13.9	37.4	27.4	6.4	11.7	15.9	7.0	166
	Pb	129	27.2	35.8	73.4	71.0	71.4	169.3	54.6	75.2	80.8	35.6	823
	Zn	92.1	71.1	77.4	161	155	225	210	138	172	177	77.9	1560
Migration rates (%) ^d	Cu	0.09	0.08	0.13	0.11	0.11	0.15	0.21	0.11	0.11	0.12	0.05	1.3
	Cd	1.07	0.99	1.55	1.66	1.60	4.30	3.15	0.73	1.35	1.82	0.80	19.0
	Pb	0.23	0.05	0.06	0.13	0.13	0.13	0.31	0.10	0.14	0.15	0.07	1.5
	Zn	0.11	0.09	0.10	0.20	0.19	0.28	0.26	0.17	0.21	0.22	0.10	1.9

^a (Leachate production (10,000 tonnes)) = 0.0042 × (rainfall (mm)).

^b There are no data for 1996, 1997, 2002 and 2003, and the average values of past years are taken.

^c The leached amount (kg) = (heavy metals concentrations in leachate of the year (mg L⁻¹)) × (leachate production (10⁴ tonnes)) × 10.

^d The migration rates of heavy metals (%) = (leached amount (kg)) × 1000 / (total amounts of heavy metals in landfill).

measured heavy metal contents and the estimated, initial contents. If the heavy metals were easily migrated, all heavy metals should be washed out. In Fig. 5, however, a clearly positive correlation is noticeable for all cases. The data circled in Fig. 5 presented the samples collected at the bottom layers of wells. The heavy metals are thereby unlikely to move easily in the landfill. All data located above the 45°-line, mainly attributable to the degradation of organic matter to reduce the solids content.

However, the contents of Cr and Cu in the samples are much higher than in the original waste, which may be attributed to the intermediate cover materials, with extraordinary higher concentration of heavy metals, in the landfill (Table 3), although the mass amount of the intermediate cover materials was less than one tenth of the initially landfilled waste. The data of Zn and Pb deviated significantly from, while those of Ni located close to the 45°-line (Fig. 5). Since the samples collected at the same

Table 5
The heavy metal contents of different ingredients in MSW

Ingredient	Date	Elements and contents (μg g ⁻¹)					
		Cd	Cu	Cr	Pb	Ni	Zn
Paper	9-29-2004	3.4	25.2	35.6	39.3	22.8	73.0
	10-27-2004	6.1	18.3	9.1	39.3	27.7	73.0
Plastics	9-29-2004	3.3	44.9	68.6	119.0	37.0	259.6
	10-27-2004	9.7	45.6	7.2	54.5	224.8	109.6
Glass	9-29-2004	33.9	11.6	426.6	130.0	38.3	378.4
	10-27-2004	6.3	32.8	363.6	84.8	170.2	80.2
Wood	9-29-2004	2.1	24.3	41.0	47.2	28.4	136.3
	10-27-2004	4.4	19.6	36.7	24.7	20.9	40.1
Food waste (vegetation and animals)	9-29-2004	5.7	56.8	88.0	362.5	52.9	499.9
	10-27-2004	5.1	43.7	35.6	56.4	52.9	121.6
Coal cinder	9-29-2004	6.5	78.7	168.1	80.2	49.3	193.4
	10-27-2004	6.3	61.1	28.1	47.5	75.9	255.2
Textile	9-29-2004	0.0	46.1	38.9	192.0	32.9	113.5
	10-27-2004	5.0	50.9	58.3	215.6	148.1	52.8
Dust	9-29-2004	–	–	–	–	–	–
	10-27-2004	6.3	57.4	83.7	47.8	151.7	76.3

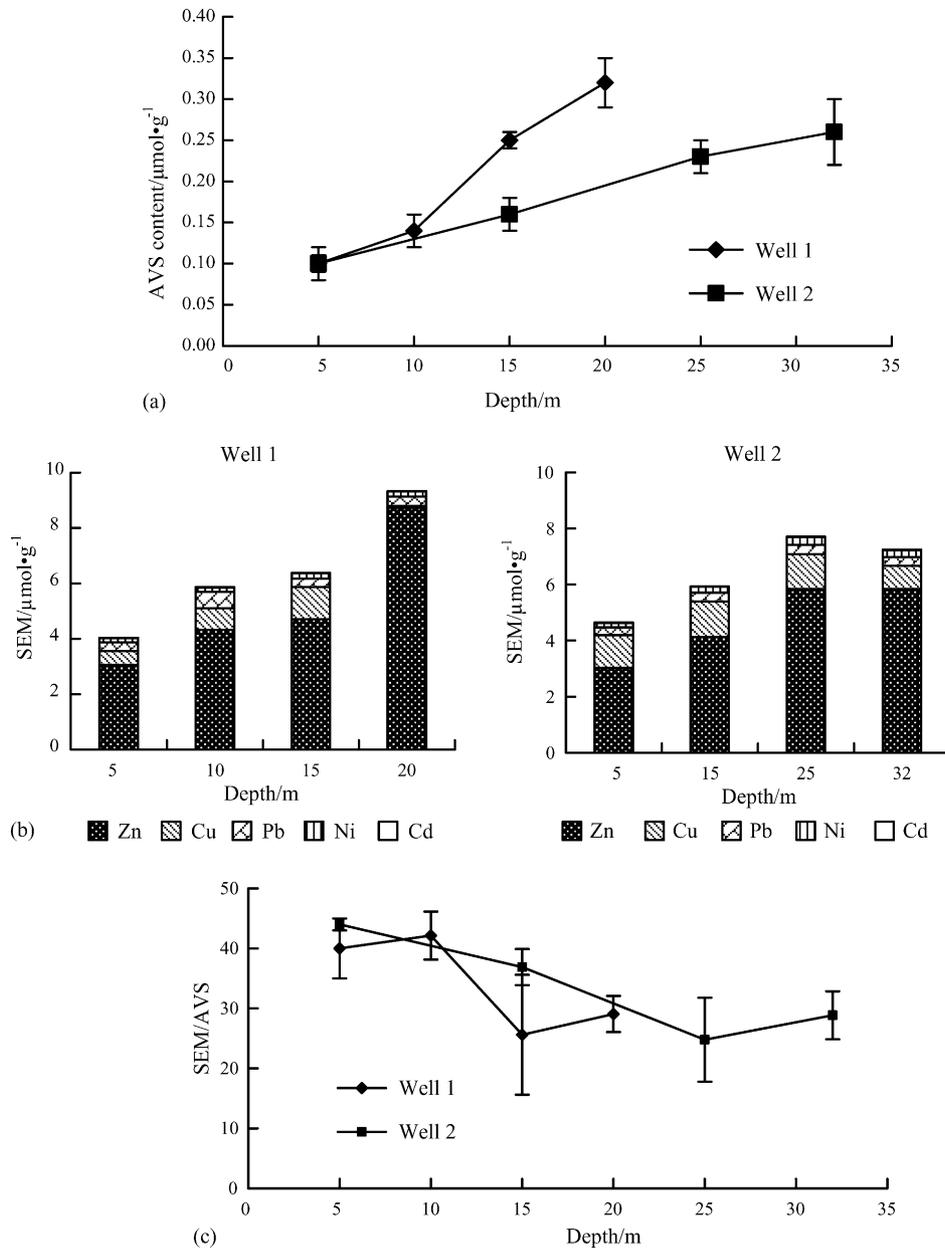


Fig. 6. (a) The AVS contents of the samples collected at different depths. (b) The SEM contents of the samples collected at different depths. (c) The SEM/AVS ratios of the samples collected at different depths.

depth should be having similar waste age, the noted difference (also shown in Table 3) revealed that the more percentage of Ni has been mobilized than Zn and Pb in landfill. However, since the leachate contains a low level of Ni, the heavy metals released in the upper landfill layers may be immobilized again in the bottom layers. Additionally, the Zn concentrations at bottom layers (circled) were high than the initial concentrations, indicating the relatively high mobility of Zn in landfill.

3.4. Measurements of AVS and SEM

The AVS and SEM contents increase with increasing depths (Fig. 6a and b). The AVS ranged $0.10\text{--}0.32\ \mu\text{mol}\ \text{g}^{-1}$ for well 1, and $0.10\text{--}0.26\ \mu\text{mol}\ \text{g}^{-1}$ for well 2. Comparing with

the sulfur contents listed in Table 2 ($2.2\text{--}5.4 \times 10^{-3}\ \text{g}\ \text{g}^{-1}$ or $68.8\text{--}169\ \mu\text{mol}\ \text{g}^{-1}$), only a small fraction of sulfur was present in sulfide form (or the forms soluble in 1 M HCl). The AVS tends to move downward in the landfill. The mobility of sulfide is affected by the local liquid pH, dropping from 6.8 to 7.8 at top layers to 8.6–9.0 at lower layers (Table 1). The sulfide is more readily fixed in environment at elevated pH values.

Hage and Mulder [22] have pointed out that the mobility of the heavy metals in the solid waste should be greatly dependent on pH in the liquid phase. Their results showed that at lower pH more components would be leached out than at neutral or alkaline conditions. As shown in Table 1, the pH of the collected samples raised from 6.8 to 7.8 at top layers to 8.6–9.0 at lower layers of landfill. The heavy metals in an easily mobilizing state

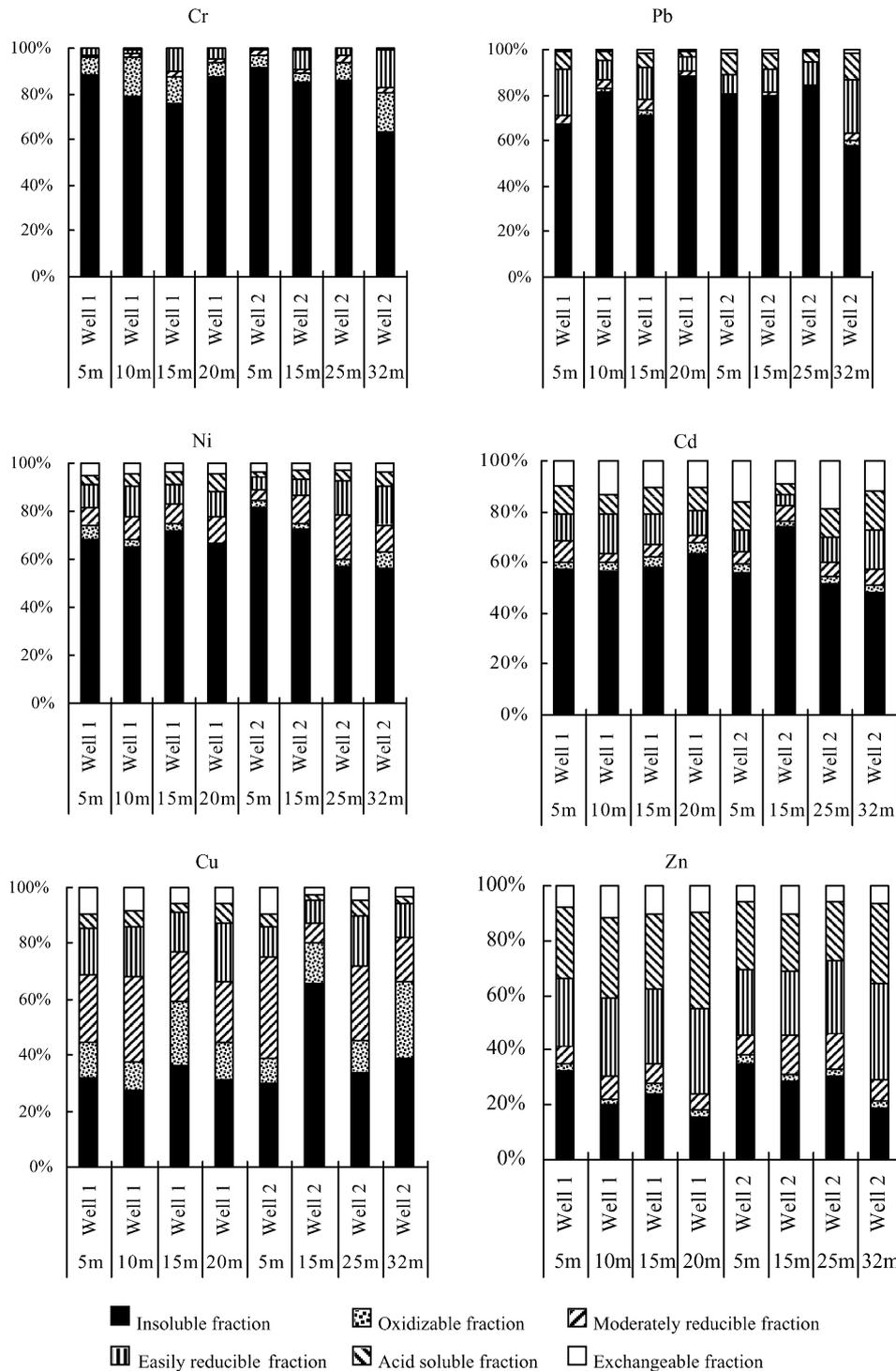


Fig. 7. Metal binding forms in the collected samples from well 1 and from well 2.

in the upper layers may move downward with leachate, and be fixed in the lower layers (Fig. 6b).

As Fig. 6b shows, the SEM mainly comprises of Zn (60–90%) and Cu (up to 30%). Comparing with the total heavy metals in the landfill (Table 3), the content of Zn in SEM ranged 3–8 mol g⁻¹, or 40–80% of the total Zn. The mobility of Zn appears higher than those of the other four metals, corresponding to the observation noted in Table 3. Nonetheless, since the leachate contains a

low level of Zn²⁺, the heavy metals released in the upper landfill layers must be immobilized again in the bottom layers.

The resulting SEM/AVS ratios are much greater than 1, ranging 25–45, and show a decreasing trend with increasing depth (Fig. 6c). The amount of AVS is insufficient to immobilize the SEM, correlating with the results by Martensson et al. [15] that sulfide is not a key binder to heavy metals in landfill. Field monitoring at Tianziling landfill revealed a high concentra-

tion of sulfate in leachate, 90–190 mg L⁻¹ in June, and up to 477 mg L⁻¹ in August 2004. Most sulfur may simply wash out with leachate and insufficient AVS could be provided to bind heavy metals. Other binding forms may be available in landfill to immobilize the heavy metals.

3.5. Metal binding forms

Fig. 7 shows the binding forms of heavy metals of samples collected at different depths in landfill.

The exchangeable fractions of heavy metals follow: Cd > Zn > Cu > Ni > Pb > Cr. This fraction of heavy metals is easily removed by simple ion-exchange mechanisms, and correlated well with the leached amounts of heavy metals estimated in Table 5. The strong complexation of Cd²⁺ and Cl⁻ may result in high mobilization rate of Cd in landfill [19], because of high level of Cl⁻ in landfill leachate.

The acid soluble fractions of heavy metals may be released in acidic environment, account for the possible release during refuse hydrolysis stage. This fraction decreases in the following order: Zn > Cd > Pb > Ni > Cu > Cr. The sum of the exchangeable fraction and the acid soluble fraction present the part of metals which have potential to release during refuse hydrolysis stage, whose magnitudes follow: Zn > Cd > Cu, Ni, Pb > Cr. It is obvious from Table 3 that Zn showed a higher mobility than did the other metals investigated, correlating to the noted, highest content of exchangeable and acid soluble fractions noted herein. However, the leachate contains low levels of Zn, indicating that the leached Zn from the upper layers would be immobilized through certain mechanisms other than bound by sulfide at the bottom layers.

The insoluble fraction of heavy metals is not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature [23]. Most heavy metals in landfill are noted in insoluble fraction. For Cr and Pb, this fraction exceeded 80%, and for Zn and Cu, at least 20% (w/w). The heavy metals in landfilled MSW were mostly in residue fraction, which should be responsible to low concentrations of heavy metals in the leachate.

4. Conclusions

This work profiled how the heavy metals distributed in a full-scale landfill site, Hangzhou Tianziling landfill. Two wells were drilled in the landfill, 20 m and 32 m in depth each, from which solid samples of waste age of 1–4 years were collected. The total amount, the sequentially extracted amounts, and the solid metals binding forms of heavy metals of the samples collected at different depths were measured and profiled. The heavy metal contents of collected samples follow the sequence: Zn > Pb > Cr > Cu > Ni > Cd, while the amounts in the landfill were estimated as 8.7 tonnes, 222 tonnes, 548 tonnes, and 808 tonnes for Cd, Cu, Pb, and Zn, respectively. Based on the noted, linear relationship between leachate production rate and the yearly average rainfall rate, the leached ratio of Cu, Cd, Pb, and Zn with leachate were estimated only 0.13%, 1.8%, 0.15%

and 0.19% of the landfilled amounts over 1993–2003. The heavy metals in landfill were firmly bound and were difficult to release.

The main compositions of MSW, like glass, food waste, paper, coal cinders, were collected from MSW collection station and their heavy metal contents were separately measured. The compositions containing high concentrations of heavy metals include food waste (Cu, Cr, Pb, Zn), plastics (Cd, Cu, Pb, Ni, Zn), coal cinders (Cu, Cr, Zn), glass (Cd, Cr, Ni, Zn), dust (Cu, Cr, Ni), and texture (Cu, Pb, Ni). Based on the landfill ingredient amount and heavy metals contents thus measured, the initially landfilled heavy metals amount could be estimated. Owing to the hydrolysis and degradation of MSW, the measured heavy metal contents in samples collected at different depths were all higher than the estimated, initial values. A positive correlation was noted to exist between the measure and the estimated initial contents of heavy metals, indicating the low mobility of the metals in the landfill interior. Among the metals investigated, Zn has shown better mobility inside landfill layers.

Acid volatile sulfide and the simultaneously extracted metals were measured for all collected samples with optimal reaction conditions identified to yield nearly perfect sulfide recovery as follows: 100 g wet samples, 80 mL min⁻¹ N₂ flow rate, reaction time of 150 min. The AVS and SEM contents increase with increasing depths, with the former ranged 0.10–0.32 μmol g⁻¹ for well 1 and 0.10–0.26 μmol g⁻¹ for well 2, and with the latter, 4.1–9.4 μmol g⁻¹ and 4.3–7.8 μmol g⁻¹, respectively. The SEM/AVS ratios ranged 25–45, indicating that the AVS was insufficient to immobilize the SEM. Most sulfur was leached out with leachate in the form of sulfate ions.

On the other hand, sequential extraction using six-fraction scheme revealed that the sum of exchangeable and the acid soluble fractions of heavy metals follow: Zn > Cd > Cu, Ni, Pb > Cr. This sum presented the fraction of heavy metals that had potential to be released in the refuse hydrolysis stage, corresponding to the noted highest mobility for Zn in the landfill. However, field data showed that the Zn concentration in leachate remained low, indicating that the leached Zn from the upper layers would be immobilized through certain mechanisms other than sulfide at the bottom layers. The insoluble fraction of heavy metals was high, for instance, over 80% for Cr and Pb. The high insoluble fractions of heavy metals of landfilled MSW and the adsorption capability of the methanogenic landfill layers should be responsible to the low concentrations of heavy metals in leachate.

Acknowledgement

Support for this work by the Hi-Tech Research and Development Program (Nos. 2001AA644010, 2003AA644020) of China, is gratefully appreciated. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

References

- [1] P. Flyhammar, Analysis of the cadmium flux in Sweden with special emphasis on landfill leachate, *J. Environ. Qual.* 24 (1995) 612–621.

- [2] H. Belevi, P. Baccini, Water and element fluxes from sanitary landfills, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), *Sanitary Landfilling: Process, Technology and Environment Impact*, Academic Press Ltd., London, 1989.
- [3] C. Aulin, I. Neretnieks, Material balance for an industrial landfill, in: T.H. Christensen, R. Cossu, R. Stegmann (Eds.), *Proceedings of the Sardinia 95, Fifth International Landfill Symposium*, vol. III, CISA Environmental Sanitary Engineering Centre, Cagliari, Italy, 1995, pp. 173–180.
- [4] J.K. Øygaard, A. Mage, E. Gjengedal, Estimation of the mass-balance of selected metals in four sanitary landfills in Western Norway, with emphasis on the heavy metal content of the deposited waste and the leachate, *Water Res.* 38 (2004) 2851–2858.
- [5] S. Bozkurt, L. Moreno, I. Neretsson, Long-term fate of organics in waste deposits and its effect on metal release, *Sci. Total Environ.* 228 (1999) 135–152.
- [6] T.H. Christensen, P. Kjeldsen, H.J. Albrechtsen, et al., Attenuation of landfill leachate pollutants in aquifers, *Crit. Rev. Environ. Sci. Technol.* 24 (1994) 119–202.
- [7] A.S. Erses, T.T. Onay, In situ heavy metal attenuation in landfills under methanogenic conditions, *J. Hazard. Mater.* B99 (2003) 159–175.
- [8] D.L. Jensen, T.H. Christensen, Colloidal and dissolved metals in leachates from four Danish landfills, *Water Res.* 33 (9) (1999) 2139–2147.
- [9] Y.P. Hsieh, C.H. Yang, Diffusion methods for the determination of reduced inorganic sulfur species in sediments, *Limnol. Oceanogr.* 34 (1989) 1126–1130.
- [10] C.E. Pesch, D.J. Hansen, W.S. Boothman, et al., The role of acid-volatile sulphide and interstitial water metal concentrations in determining bioavailability of cadmium and nickel from contaminated sediments to the marine polychaete *neanthes arenaceodentata*, *Environ. Toxicol. Chem.* 14 (1) (1995) 129–141.
- [11] P. Flyhammar, Estimation of heavy metal transformations in municipal solid waste, *Sci. Total Environ.* 198 (1997) 123–133.
- [12] P. Flyhammar, Use of sequential extraction on anaerobically degraded municipal solid waste, *Sci. Total Environ.* 212 (1998) 203–215.
- [13] H.E. Allen, Analysis of acid-volatile sulphide (AVS) and simultaneously extracted metals (SEM) for the estimation of potential toxicity in aquatic sediments, *Environ. Toxicol. Chem.* 12 (1993) 1441–1453.
- [14] C. van Griethuysen, Measuring acid volatile sulphide in floodplain lake sediments: effect of reaction time, sample size and aeration, *Chemosphere* 47 (2002) 395–400.
- [15] A.M. Martensson, C. Aulin, O. Wahlberg, et al., Effect of humic substances on the mobility of toxic metals in a mature landfill, *Waste Manage. Res.* 17 (1999) 296–304.
- [16] D.R. Reinhart, C.J. Grosh, Analysis of Florida MSW landfill leachate quality, Report 97-3, Florida Centre for Solid and Hazardous Management, Gainesville, FL, 1998.
- [17] V. Gounaris, P.R. Anderson, T.M. Holsen, Characteristics and environmental significance of colloids in landfill leachate, *Environ. Sci. Technol.* 27 (1993) 1381–1387.
- [18] T. Klein, R. Nissner, Characterization of heavy-metal-containing seepage water colloids by flow FFF, ultrafiltration, ELISA and AAS, *Mikrochim. Acta* 129 (1–2) (1998) 47–55.
- [19] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, et al., Present and long-term composition of MSW landfill leachate: a review, *Crit. Rev. Environ. Sci. Technol.* 32 (4) (2002) 297–336.
- [20] State Environmental Protection Administration of China, soil quality-determination of total chromium, GB/T 17137-1997.
- [21] P. Jain, H. Kim, T.G. Townsend, Heavy metal content in soil reclaimed from a municipal solid waste landfill, *Waste Manage.* 25 (2005) 25–35.
- [22] J.L.T. Hage, E. Mulder, Preliminary assessment of three new European leaching tests, *Waste Manage.* 24 (2004) 165–172.
- [23] A. Tessier, P.G.C. Campbell, M. Bisson, Sequential extraction procedure for the speciation of particulate trace metals, *Anal. Chem.* 51 (7) (1979) 844–850.