Available online at www.sciencedirect.com
ScienceDirect
Journal of Hazardous Materials 156 (2008) 86–94
Journal of Hazardous Materials
www.elsevier.com/locate/jhazmat

Assessment of heavy metal contamination and its mobilization from municipal solid waste open dumping site

Tawach Prechthai, Preeda Parkpian, Chettiyappan Visvanathan *

Environmental Engineering and Management Program, School of Environment, Resources and Development, Asian Institute of Technology, PO Box 4, Klong Luang Pathumthani 12120, Thailand

Received 11 September 2007; received in revised form 29 November 2007; accepted 30 November 2007
Available online 8 December 2007

Abstract

Influence of heavy metals was investigated by conducting various tests on the samples collected from Nonthaburi dumpsite in Thailand. The heavy metal concentration in the solid waste and its mobility potential based on its binding forms was studied. The sequential extraction method was used to determine the binding forms of metals.

From the analysis, Zn was found to be highest concentrated heavy metal compared to Mn, Cu, Cr, Cd, Pb, Ni and Hg in the solid waste. From the sequential extraction, Mn, Zn and Cd mostly found in reducible form, showed its susceptibility to be leached easily. Cu and Cr were found predominantly in oxidizable form and stable under anaerobic condition. Pb and Ni were present in residual form, which is inert. The estimated individual contamination factor (C_f^i), showed Zn with highest affinity to leach. The concentration level of all the heavy metals in the leachate except for Cr was noticed to be below the National effluent standards. Though, indicated to be safe for disposal, its effect in any concentration proved toxic to the plant life from the seed germination toxicity test using synthetic chelate ethylene diamine tetraacetic acid (EDTA).
© 2008 Published by Elsevier B.V.

Keywords: Municipal solid waste; Dumpsite; Heavy metals; Leachate; Sequential extraction; Toxicity

1. Introduction

In Thailand, approximately 65% of Municipal Solid Waste (MSW) is disposed in open dumpsite. Nonthaburi dumpsite is one of the large sites in Thailand. This dumpsite is operating since 1982. Presently, it receives about 750 tonnes/day of MSW from Nonthaburi province and neighboring municipalities. In general, one of the major environmental impacts of solid waste disposed is influence of heavy metals in the waste.

Most of our study compares the condition of landfill with our dumpsite. The rational behind this is to explore the response of heavy metals under controlled condition and uncontrolled condition and relate results that are relevant to our study. The effects of heavy metals were found to vary with the conditions prevailing in the dumpsites and its binding forms. In the case of landfill, in an anaerobic condition, the metals that are bound to carbonate, organic compound and sulfide are more stable and retained in the landfill itself, whereas the metals bound to Fe and Mn oxide are unstable [1]. This is in contrast with the case of an open dumpsite. The open dumpsite being exposed to the atmospheric condition undergoes different effects due to oxygen diffusion. In a high redox condition, the binding of metals to Mn and Fe oxide increases, whereas binding to carbonate, organic compound and sulfide tend to decrease [2]. With more possibility of oxygen diffusion through the upper layer of dumpsite and with sufficient moisture content, the degradation rate and the acid buffer capacity of the dumpsite is highly influenced. Under this condition there is a drop in alkalinity and pH and sulfide oxidation, where heavy metals are easily available and released [3,4]. These heavy metals from the surface layer of dumpsite, creeps into the bottom layer of the dumpsite where anaerobic condition prevails. Under this anaerobic condition, the heavy metals immobilize and retain in the solid waste again. This is confirmed from the observed high concentration of heavy metal at deeper layer of landfill [5,6]. The moisture content and organic carbon are considered as the essential factor influencing the metal stability in landfill. Therefore, determination of moisture content and organic carbon in the waste from dumpsite is necessary. The heavy metals leached from the landfill are usually found in the form of free cation, dissolved organic compound

* Corresponding author. Tel.: +66 2 524 5640; fax: +66 2 524 5640.
E-mail address: visu@ait.ac.th (C. Visvanathan).

0304-3894/$ – see front matter © 2008 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2007.11.119

complex, particulate and colloid [7]. In this viewpoint, to foresee the mobility potential of heavy metals, determination of heavy metals in different forms is necessary. To determine the binding forms of heavy metals, sequential extraction method developed by Tessier and co-workers [8] was followed in this study.

Most of the areas surrounding the dumpsite under study are paddy fields with economic value. The toxicity of heavy metal to rice was also focused in this study because of its sensitivity to the heavy metal toxicity [9–11]. The intensity of toxicity depends on the concentration and various forms that it exists. The metals existing in exchangeable and acid soluble form are considered as mobile fractions that are easily available. The metals in reducible and oxidizable form leach out only under extreme conditions. Those existing in residual form are considered inert and not easily available [5]. Thus, metals in the various forms are assumed to be influencing the bioavailability.

Researches have shown phytoremediation as one of the common methods used for heavy metal polluted soil. Chelating agent EDTA commonly known as a synthetic chelate is used in this method. This synthetic chelate has the ability to increase the bioavailability of heavy metals. However, identifying appropriate dosage limit of EDTA is found to be the controlling factor for the heavy metal bioavailability and toxicity in plant test [12]. Possible formations of EDTA-Heavy metal complexes and its toxicity are the major reasons restricting the use of EDTA. Therefore, a thorough test on its toxicity before use was necessary.

This study was conducted on the samples collected from the Nonthaburi dumpsite. The present study examines basic characteristics of the waste in the dumpsite, then concentration level of heavy metal contaminates and its mobility potential in different forms under various conditions. The concentration of heavy metals was also determined in the runoff leachate and its toxicity potential to the dominant species growing nearby the dumpsite area was investigated.

2. Materials and method

2.1. Description of dumpsite

The dumpsite in this study is 25 years old located at Sai Noi District, Nonthaburi Province, Thailand. The total area of dumpsite is about 108,800 m^2. The height of the dump is about 3 m height above the ground. There is no proper leachate collection system within the dumpsite and accumulated leachate was observed beneath the dumpsite. The runoff leachate is collected through an open pipe system and treated in the stabilization pond situated nearby the site.

2.2. Solid waste sampling and analysis

2.2.1. Solid waste sampling

The representative solid waste samples of the dumpsite were collected from four selected locations (SW1–SW4). The backhole excavator machine was employed to excavate and collect about 150 kg of solid waste at every 1 m depth interval from the surface to 3 m. To prepare the sample for analysis, the representative sample obtained from each depth was homogenized separately and air-dried. The air-dried solid waste was then grinded, screened through a 1.0 mm sieve and subjected to further analysis.

2.2.2. Solid waste analysis for physico-chemical characteristics

The solid waste analyses were performed in duplicates for accuracy. The residual moisture content of solid waste was analyzed by drying at 105 °C, whereas the volatile content was determined by the method of ignition at 550 °C. The pH of sample prepared with 1:10 solid waste and water ratio was measured using meter WWW model pH330i meter. For organic carbon, the concentration of TOC in solid waste was measured according to the method Walkley and Black [13].

The heavy metals in the solid waste were determined according to the standard method indicated in SW-846 published by USEPA [14]. In this method, 1 g of air-dried solid waste was digested with 10 ml of 1:1HNO_3, 5 ml of 65%HNO_3, 3 ml of 30% H_2O_2 and 10 ml of HCl at 95 ± 5 °C, respectively. The concentrations of Mn, Cr, Cd, Pb, Ni, Zn and Cu were measured by using Inductively Couple Plasma-Optical Emission Spectrometer (ICP-OES PerkinElmer Optima 2100DV). For Hg, the waste samples were digested separately by using aqua regia, potassium permanganate and sodium chloride-hydroxylamine sulfate. Finally, the concentration of Hg was measured by using hydride generation system equipped in the ICP-OES.

2.3. Sequential extraction of heavy metal

The binding forms of heavy metals in waste were determined according to the Tessier's sequential extraction method [8]. The sequential extraction procedure of heavy metal is described in Table 1. After each successive extraction, the

Table 1
Sequential extraction of heavy metals

Step	Fraction	Chemical reagents
1	Exchangeable	Add 8 ml of 1.0 N $MgCl_2$ (pH 7) and agitate at 20 °C for 1 h
2	Acid soluble	Add 8 ml of 1.0 M CH_3COONa (pH 5) and agitate at 20 °C for 5 h
3	Reducible	Add 20 ml of 0.04 M $NH_2{\cdot}OH{\cdot}HCl$ in 25%CH_3COOH and agitate at 96 °C for 6 h
4	Oxidizable	Add 5 ml of 30% H_2O_2 (pH 2) and 3 ml of 0.02 M HNO_3 before heat at 85 °C for 2 h Add 5 ml of 3.2 M CH_3COONH_4 in 20% HNO_3 before diluting to 50 ml and agitate for 30 min
5	Residual	1:1HNO_3, 65%HNO_3, 30%H_2O_2 and HCl and 95 ± 5 °C

extraction solution was separated by filtering the supernatant after centrifugation at 3000 rpm for 30 min. The concentration of heavy metals in the solution was then measured by using ICP-OES.

2.4. Leachate sampling and analysis

2.4.1. Leachate sampling

About 1–2 l of samples were collected from two leachate boreholes (BH1, BH2) and from runoff leachate in the period of November 2005 to May 2006 covering both rainy and dry seasons. The collected samples were preserved well and kept at 4 °C until analysis.

2.4.2. Leachate analysis

The leachate analysis was done in triplicates following the standard methods for water and wastewater examination [15]. The pH, Electrical Conductivity (EC) and Total Organic Carbon (TOC) of leachate were measured. TOC was measured using TOC analyzer (SHIMADZU TOC-2000). For heavy metal analysis, 100 ml of leachate sample was digested with 65%HNO_3 initially and then concentration of Mn, Cr, Cd, Cu, Pb, Ni and Zn was determined using ICP-OES. In case of determining Hg concentration, the leachate samples were prepared according to the procedure described in SW-846 [14] and measured by using ICP-OES.

2.5. Heavy metal leaching test

The leaching potential of heavy metals in the solid waste was determined according to the Toxic Characteristic Leaching Procedure (TCLP) test method 1311 [14]. According to this method, the extract solution with a pH of 4.93 ± 0.05 was used for this test. This test was performed in triplicate for accuracy.

The sample was prepared by mixing of solid waste sample and extraction fluid in the ratio of 1:20 (solid:extraction fluid) in a vessel. The sample was then agitated at 30 rpm for 18 h. Finally, the agitated sample was filtered by using Glass Filter Correlation (GFC) filter. The procedure for preparation of samples and measurement of heavy metal concentration in the extracted leachate was done according to the previously used methods for leachate analysis [14,15]. The leaching rate of heavy metals from the solid waste was calculated using Eqs. (1) and (2).

$$\text{Heavy metal leached (mg/kg)} = \frac{C_L \times L}{S_W} \times 1000 \quad (1)$$

$$\text{Heavy metal leaching rate (\%)} = \frac{\text{Heavy metal leached}}{\text{CS}} \times 100 \quad (2)$$

where C_L is the heavy metal concentration in extracted leachate (mg/l); C_S is the heavy metal concentration in solid waste (mg/kg); L is the extracted leachate volume (l); S_W is the quantity of solid waste (g).

Table 2
Seed germination test condition

Test species	*Oryza sativa* L.
Seed pretreatment	10% hypochlorite for 20 min and rinse with deionized water for 10 time
Temperature	25 ± 1 °C
Light	Dark
Container and supporting media	100 mm × 10 mm Petri dish, Whatman filter paper No. 1
Leachate volume	10 ml
Number of seed per dish	15
Number of sample concentration	5
Number of replication	4
Control group	Deionized water
Test duration	96 h
Toxicity end point	Germination rate and root length

2.6. Seed germination toxicity test

2.6.1. Leachate preparation

The analytical grade Na_2EDTA was used in this test. The IC_{50} of EDTA specific to rice seed germination was determined initially. Based on the results obtained for IC_{50}, 0.5 g/l EDTA stock solution was prepared for further analysis. Subsequently, leachate sample was prepared according to the phase I Toxic Characteristic Identification Evaluation (TIE) procedures [16]. The toxicity test was conducted on two samples, one on an untreated runoff and the other on EDTA treated runoff. For the toxicity test on EDTA treated runoff leachate, a varied dosage of 0.2, 0.05, and 0.0125 ml of 0.5 g/l EDTA stock solution was added to the leachate. The deionized water was used for the preparation of control sample and for dilution also. In addition, the toxicity of EDTA used for treating leachate was also conducted at different dosage levels.

2.6.2. Seed germination test

This test was conducted following the standard method [17]. The test was performed on the rice seed (*Oryza sativa* L.) obtained from Department of Agriculture, Bangkok and Table 2 presents the test condition. The Relative Seed Germination rate (RSG) and Relative Root Growth (RRG) were calculated using the Eqs. (3) and (4). Germination Index (GI) was also determined using Eq. (5). In addition, 50% Inhibiting Concentration of leachate (IC_{50}) was determined by using Trimmed Spearman–Karber (TSK) program version 1.5 available from U.S. EPA [18].

$$\text{Relative Seed Germination rate} = \frac{\text{Ss}}{\text{Sc}} \times 100 \quad (3)$$

$$\text{Relative Root Growth} = \frac{\text{Rs}}{\text{Rc}} \times 100 \quad (4)$$

$$\text{Germination Index} = \frac{\text{RSG} \times \text{RRG}}{100} \quad (5)$$

where Ss is the no. of seed germinated in sample; Sc is the no. of seed germinated in control; Rs is the average root length in sample; Rc is the average root length in control.

2.7. QA/QC

Laboratory QA/QC were ensured where every batch of analyses incorporated calibrating standards, a laboratory 'blank' and replicates, a test of both sample homogeneity and laboratory precision at an appropriate frequency. Pre-cleaned and acid-washed glasswares were used. All the reagents and acids used were of analytical grade and were used without further purification. Distilled water was used for the preparation of reagents. Analysis blanks and duplicates were applied regularly. The analytical accuracy was confirmed with duplicates and triplicates throughout the study. The experiments and analyses involving the redox reaction changes were done in duplicate; all other analyses were carried out in triplicate. The accuracy of the sequential extraction procedure was evaluated by comparing the total heavy metal concentrations with the sum of the five individual fractions.

3. Results and discussions

3.1. Solid waste characteristics

3.1.1. Basic characteristics of solid waste

The physical characteristics of solid waste are presented in Table 3. The major identifiable components in the waste were plastics and soil. The composition of waste is presented in Fig. 1. The results for density showed a significant variation at all depths and locations. A higher density was observed at the intermediate depth 1–2 m at all the locations. This is due to the organic content and moisture content at this level. The density at depth 2–3 m was lower than 1–2 m and it is the effect of higher plastic accumulation and leachate beneath the bottom layer. As density, similar trend was noticed for moisture content in the dumpsite. Higher moisture content at depth 2–3 m shows the effect of leachate accumulation beneath. The variations in volatile solid content at each depth and locations show the varying composition of waste with organic content, plastics and moisture content at different depths. This shows the difference in the degree of degradation that has taken place under uncontrolled condition and the influence of waste age on degradation. The composition of waste with more of plastics with its inherent low bulk density indicates the probable influence of water distribution and gas diffusion characteristics of dumpsite that can consequently increase the rate of solid waste degradation [19]. The

Table 3
Physical and chemical characteristics of the solid waste

Location	Depth (m)	Density (kg/m^3)	Moisture (%)	VS (%)	pH	TOC (%)
SW1	0–1	252.0	28.6	52.7	7.3	14.3
	1–2	337.0	43.2	20.0	7.7	17.1
	2–3	270.0	53.0	35.1	7.6	14.0
SW2	0–1	260.0	43.2	24.4	7.2	21.8
	1–2	410.0	48.8	50.8	7.5	17.1
	2–3	370.0	51.7	41.3	7.5	15.1
SW3	0–1	285.0	42.7	30.7	7.3	28.1
	1–2	410.0	59.4	30.9	7.3	15.3
	2–3	302.0	58.5	35.1	7.9	18.3
SW4	0–1	238.0	34.6	52.5	7.3	19.9
	1–2	412.0	50.9	63.4	7.9	8.9
	2–3	225.0	50.9	46.0	7.9	14.9

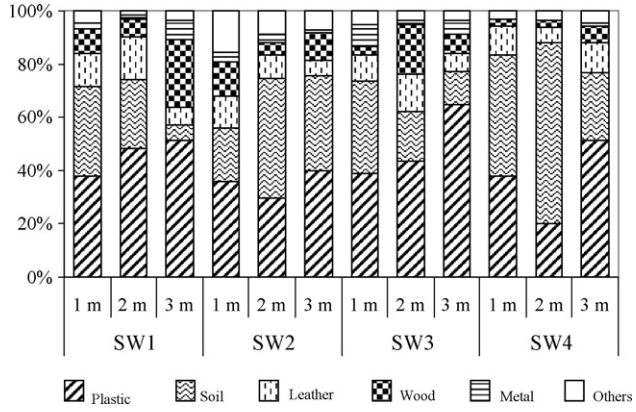

Fig. 1. Composition of solid waste in the dumpsite.

Table 4
Heavy metal concentration in the solid waste

Location	Depth (m)	Heavy metal concentration (mg/kg)							
		Mn	Cr	Cd	Pb	Ni	Zn	Cu	Hg[a]
SW1	0–1	332.7	142.6	38.0	127.0	94.0	556.7	268.6	202.0
	1–2	231.9	57.3	2.0	36.0	52.3	351.0	148.5	319.0
	2–3	161.7	85.2	3.7	13.2	28.7	586.5	274.0	407.0
SW2	0–1	113.4	79.5	0.9	64.0	24.2	290.9	130.2	429.0
	1–2	352.9	91.0	3.0	60.5	47.3	401.3	308.5	264.0
	2–3	289.0	88.0	4.0	36.0	38.0	467.0	313.2	284.0
SW3	0–1	189.5	59.7	4.2	42.3	52.3	275.4	188.0	293.0
	1–2	254.6	58.6	1.2	84.6	51.8	424.0	221.3	428.0
	2–3	190.4	186.2	1.0	35.0	45.0	523.7	178.3	331.0
SW4	0–1	157.0	59.6	3.4	16.3	83.2	563.8	119.0	513.0
	1–2	100.0	76.3	2.7	32.9	38.9	488.0	351.0	301.0
	2–3	209.6	65.8	1.7	13.4	25.7	572.3	544.6	433.0

[a] μg/kg.

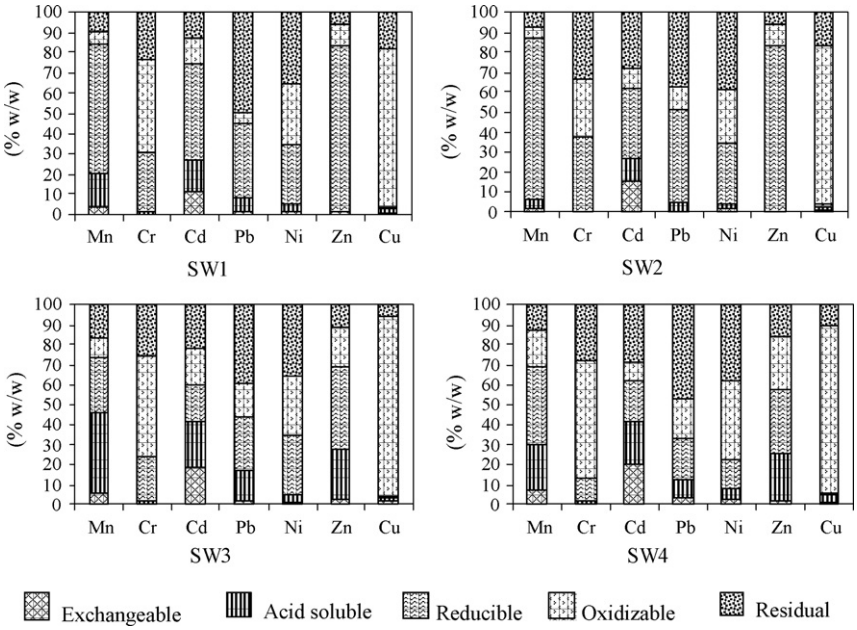

Fig. 2. Heavy metal binding forms in different solid waste collection locations.

observed TOC value 8.9–28.0% (w/w) indicates the existence of biodegradable organic compound in the waste. A lower TOC value was noticed at bottom layer where plastics were dominant reducing the density of the waste in that portion 2–3 m. The basic pH value of solid waste indicates the possibility of waste to neutralize the organic acid that can generate from the anaerobic degradation of organic matter.

3.1.2. Heavy metal concentration

The concentrations of heavy metals in solid waste are presented in Table 4. There was no significant difference of the concentration between the sampling sites and depth interval except for SW1 and SW3. A high concentration of Cd and Pb were noticed at SW1 and high concentration of Cr was found at SW1 and SW3. The source of these observed metals, Cd, Pb and Cr in the site are expected to be plastics, shoes, rubber, electronic waste and non-ferrous metal that were composed in the dumpsite [20]. Based on the average concentration, the heavy metal components in the waste were found in the following order: Zn > Cu > Mn > Cr > Pb > Ni > Cd > Hg. This result shows the contamination level of dumpsite with Zn, Cu and Mn at higher level, whereas the Hg at a lower level into the environment.

3.2. Heavy metal binding forms

The binding forms of heavy metals except Hg, is presented in Fig. 2. Most of the fraction of Mn in solid waste was present as manganese oxide and carbonate bound manganese. The con-

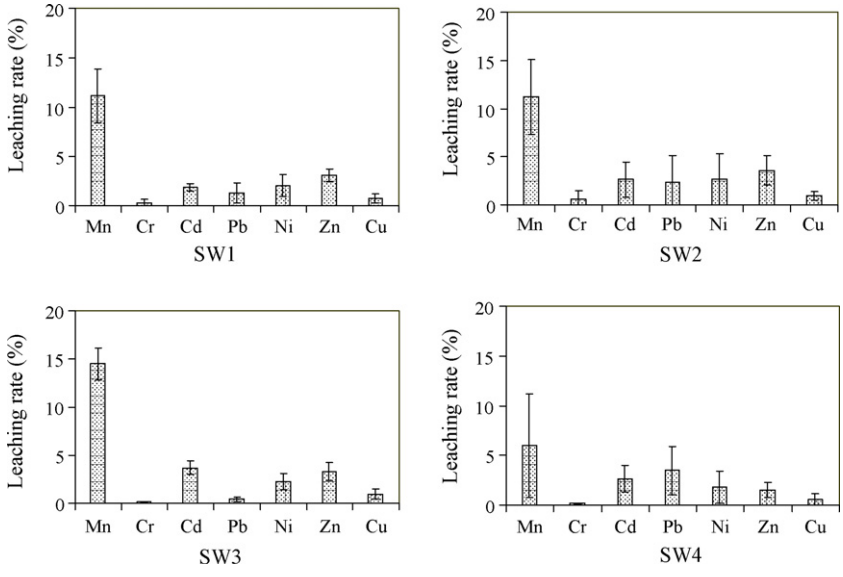

Fig. 3. Heavy metal leaching rate in TCLP leachate.

Table 5
Mobility potential of heavy metals in dumpsite

Step	Condition	Mobility
1	Ion exchange	Cd > Mn > Zn > Cu > Cr > Pb > Ni
2	Acid dissolution	Mn > Cd > Zn > Pb > Ni > Cu > Cr
3	Reduction reaction	Mn > Zn > Pb > Cd > Cr > Ni > Cu
4	Oxidation reaction	Cu > Cr > Ni > Pb > Zn > Cd > Mn
5	Insolubility	Pb > Ni > Cr > Cd > Cu > Mn > Zn

centration of Mn in these forms significantly varied between the collection locations. High reducible portion of Mn was observed at SW2 and SW1. It is observed that under high oxidation–reduction potential, neutral and alkaline environment, manganese oxide tends to be stable [21]. Therefore, the observed high reducible portion of Mn at SW2 and SW1 confirms the oxidizing condition prevailing in the locations. In contrast to this, a relatively low concentration of reducible Mn and acid soluble Mn was noticed at SW3 and SW4 indicating the reducing condition in this location. High fraction of reducible Mn was reported in other dumpsite study [22] (Fig. 3).

Next to Mn, large fractions of Zn and Cd were also found in reducible form. The above results indicate the consequence of ferric hydroxide and manganese oxide to absorb and immobilize Zn and Cd in the dumpsite. In an anaerobic landfill, presence of more fractions of oxidizable form of Zn and residual form of Cd were reported [23]. This difference might be because of inability of dumpsite to maintain a reducing condition. The presence of oxidizable and acid soluble fraction of Zn noticed at SW3 and SW4 shows the prevailing low redox potential at this locations. Among all the metals, Cd was found in highly exchangeable form of about 10–20%.

The influence of organic matter and sulfide to absorb and precipitate Cu and Cr in the dumpsite was noticed. The oxidizable fraction of Cu and Cr was present predominately in the waste and only small fractions were found in exchangeable and acid soluble. The similar trend of oxidizable fraction of Cu was noticed between collection points. This might be due to the high tendency of Cu to be absorbed on organic matter [21]. In the case of Pb and Ni, the largest fraction of these elements was found in residual form. Some of these elements were also present in reducible, oxidizable, acid soluble and exchangeable form.

3.3. Mobility potential of heavy metals

The mobility and immobility and thus toxicity of heavy metals in waste depend largely on their type of binding forms. Table 5 compares the mobility potential of heavy metals in different forms. It was noticed that Cd has highest ability and susceptible to be released from the dumpsite by the simple ion exchanged mechanism. It is seen that the chloride content in the leachate can bind with Cd and enhance its mobility in the solid waste [24]. The presence of acid soluble portion of Mn and Cd indicates its sensitivity to the acidic condition and tendency to leach easily. However, in the case of Cr, it was found relatively insensitive to acid condition. This result is in agreement with other study for high mobility of Mn in the acid environment [25].

Table 6
Contamination factor of heavy metals in the dumpsite

Parameters	Contamination factor (C_f^i)			
	SW1	SW2	SW3	SW4
Mn	9.15	15.37	5.46	7.59
Cr	2.44	2.06	4.62	2.55
Cd	8.96	2.67	3.74	2.01
Pb	0.55	1.55	1.58	1.06
Ni	1.51	1.83	1.52	1.23
Zn	18.56	17.77	7.98	5.26
Cu	4.08	5.61	14.47	7.40
Hg	ND	ND	ND	ND
$\sum C_f^i = C_f$	45.24	46.86	39.36	27.09

Under varied reduction condition, the release of Mn and Zn from the solid waste dumpsite is expected. This is in contrast with Cu and Cr, which precipitates with sulfide, absorbed on the organic mater, and appears to be stable under the anaerobic condition. The moisture content and concentration of organic matter for microbial degradation are found to be important factors influencing the anaerobic condition especially in the deeper layer of dumpsite [6]. With the high oxygen diffusion into the open dumpsite, the precipitated Cu and Cr with sulfide and that are attached with organic matter are expected to be oxidized and remobilized again. On the other hand, with the increased redox potential in dumpsite, possible oxidation of Mn and Fe to Mn oxide and ferric hydroxide are expected that has high ability to absorb and immobilize metals. The presence of high reducible Mn, Zn and Cd therefore, shows its tendency to be immobilized and retained under the oxidizing condition of dumpsite.

The determination of contamination factor of metals is an important aspect that indicates degree of risk of heavy metal to environment in relation with its retention time. A high contamination factor of heavy metal shows low retention time and high risk to the environment. The Individual Contamination Factor (C_f^i) of heavy metals was used to estimate the relative retention time of heavy metals retained in the dumpsite. It is determined by dividing the sum of concentration of each heavy metal in the mobile phase (non-residue phase) by its concentration in the residue phase. The global contamination factor (C_f) is equal to the sum of individual factor (C_f^i) [26,27].

Table 6 shows the estimated contamination factor of each metal in the dumpsite. The calculated factors show highest ability of Zn, Mn and Cu to be released from the dumpsite, whereas Pb and Ni have lowest. The residual concentration of any heavy metal is considered non-mobile fraction and is an important part influencing the mobility nature of the heavy metal. The combined effect of Zn, Mn and Cu in high concentration and with high mobility potential shows the increased possible risk of these metals to the environment. The contamination factor determined for sampling sites indicates the varying mobility condition of all the heavy metals within the dumpsite. The relative mobility of heavy metals in the dumpsite was in the following order: SW2 > SW1 > SW3 > SW4.

Table 7
Heavy metal concentration in the extracted leachate from TCLP test

Parameters	SW1	SW2	SW3	SW4
pH	6.7 ± 0.1	6.3 ± 0.3	6.5 ± 0.1	6.9 ± 0.1
Mn (mg/l)	1.275 ± 0.210	1.250 ± 0.330	1.593 ± 0.140	0.442 ± 0.420
Cr (mg/l)	0.010 ± 0.010	0.026 ± 0.030	0.008 ± 0.004	0.006 ± 0.003
Cd (mg/l)	0.016 ± 0.025	0.003 ± 0.001	0.002 ± 0.001	0.003 ± 0.002
Pb (mg/l)	0.022 ± 0.015	0.048 ± 0.050	0.011 ± 0.001	0.029 ± 0.010
Ni (mg/l)	0.048 ± 0.010	0.040 ± 0.030	0.053 ± 0.015	0.031 ± 0.015
Zn (mg/l)	0.779 ± 0.315	0.650 ± 0.115	0.804 ± 0.335	0.393 ± 0.165
Cu (mg/l)	0.079 ± 0.010	0.117 ± 0.075	0.094 ± 0.015	0.064 ± 0.015
Hg (μg/l)	<0.001	<0.001	<0.001	<0.001

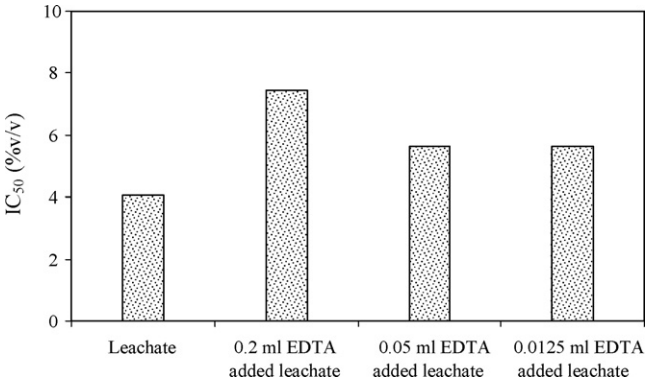

Fig. 4. Toxicity of leachate to the germination index of rice seed.

3.4. Toxic characteristic leaching procedure of heavy metal

The characteristics of leachate determined from the TCLP test are presented in Table 7. The test results showed pH of the leachate ranging from 6.3 to 6.9. Linking this result to the pH value of the solid waste 7.2–7.9, a drop in pH was observed but in the case of extracted leachate, an increase in pH was observed in contrast to the pH of the extraction solution originally was 4.93 ± 0.05. This effect is due to the acid buffer capacity of solid waste to neutralize the pH of extracted leachate. The concentrations of Mn, Zn and Cu analyzed in the TCLP leachate were high. However, all the heavy metal concentration was below the TCLP standard limit. Therefore, the degree of leaching ability and risk of metal contamination in the dumpsite is very low.

Fig. 4 shows leaching rate of heavy metals from the waste. From the TCLP test, Mn, Zn and Cd were observed to have high leaching rate whereas Cr was relatively low. Although Mn concentration in solid waste was lower than Zn and Cu, it was noted that leaching rate of Mn in all the locations was high compared to that of Zn and Cu. In addition, the Cd showed higher leaching rate than Cu and Cr. The average leaching rate of heavy metals was in the following order: Mn > Zn, Cd > Ni > Pb > Cu > Cr. This order was similar to that of the order observed for the acid soluble fraction of metals present in solid waste. This show, under acidic condition, the heavy metals in acid soluble form are much affected and are readily available. Therefore, these results shows the high leaching possibility of Mn, Zn and Cd is highly in acid soluble form and with possible organic acid generation in the dumpsite whereas in the case of Cr, possibility is very low in this condition.

3.5. Characteristics of leachate in the dumpsite

3.5.1. Basic characteristics of leachate

The significant variation of leachate quality among the collection locations is presented in Table 8. The organic and inorganic contents of runoff leachate were much greater than that of the leachate samples collected from the boreholes. The BOD/COD ratio of runoff leachate, in addition, was greater than that of leachate boreholes. Thus, the variations observed in the results show the influence of solid waste age heterogeneity on the degra-

Table 8
Characteristics of leachate from the dumpsite

Parameter	Runoff leachate	Borehole 1	Borehole 2
pH	8.3 ± 0.1	8.8 ± 0.1	8.0 ± 0.4
EC (mS/cm)	30.8 ± 4.5	13.9 ± 0.6	11.6 ± 0.7
TDS (g/l)	20.0 ± 4.5	7.3 ± 1.5	8.3 ± 1.0
Alkalinity (mg/l)	12,000 ± 3500	5500 ± 500	1540 ± 265
BOD (mg/l)	2250 ± 1820	165 ± 185	68 ± 60
COD (mg/l)	8400 ± 950	1600 ± 390	497 ± 110
TOC (mg/l)	3500 ± 400	600 ± 20	185 ± 65
BOD/COD[a]	0.27	0.10	0.13
TP (mg/l)	34.5 ± 16.0	5.6 ± 4.0	1.6 ± 0.6
NO_3^- -N (mg/l)	5.9 ± 5.5	2.4 ± 2.0	0.5 ± 0.6
NH_4^+-N (mg/l)	2200 ± 850	915 ± 130	328 ± 90
TKN (mg/l)	2600 ± 1100	990 ± 120	330 ± 90
Mn (mg/l)	0.490 ± 0.180	0.559 ± 0.700	1.378 ± 1.780
Cr (mg/l)	0.990 ± 0.390	0.211 ± 0.080	0.032 ± 0.010
Cd (mg/l)	0.010 ± 0.001	0.001 ± 0.001	0.001 ± 0.001
Pb (mg/l)	0.100 ± 0.090	0.065 ± 0.080	0.046 ± 0.065
Ni (mg/l)	0.500 ± 0.170	0.143 ± 0.060	0.069 ± 0.030
Zn (mg/l)	1.320 ± 0.610	0.265 ± 0.125	0.200 ± 0.235
Cu (mg/l)	0.630 ± 0.530	0.043 ± 0.006	0.013 ± 0.010
Hg (μg/l)	0.950 ± 0.520	<0.001	0.312 ± 0.110

[a] Ratio of mean value of BOD and COD.

dation rate. The BOD/COD ratio in the results is an indicator of methanogenic phase taking place in the dumpsite. The organic acid generated in the previous acidogenic phase is utilized for methane gas production and carbon dioxide in subsequent methanogenic phase. The result with relative high pH, alkalinity, and ammonia concentration in all the leachate samples analyzed [28] confirms the methanogenic condition of the dumpsite.

3.5.2. Heavy metal concentration in leachate

The heavy metal concentration in the samples, collected from the boreholes and runoff leachate are discussed. The concentration of heavy metals contaminated in the leachate varied significantly between the collection sites. The results are presented in Table 8. The lower concentration of heavy metals in both leachate boreholes shows the influence of solid waste age and the difficulty of organic waste to be degraded at these locations. The observed highest Mn concentration in both boreholes confirms the leaching potential of this metal in the reducing condition of dumpsite. Next to Mn, the concentration of Zn, Cr, Cu and Ni in the runoff leachate was high. This might be due to the binding of these metals with the dissolved organic content generated from degradation of organic matter forming a complex compound.

The concentration of the metals in the runoff leachate was different from the extracted leachate result present in Table 7. The Mn concentration of runoff leachate was much lower than that of Zn, Cu and Cr. This was in contrast with the extracted leachate where Zn, Cu and Cr were in lower concentration than Mn. The lower concentration of Mn in the runoff leachate confirms the methanogenic phase undergone by the dumpsite where Mn precipitates with carbonate and sulfide and retains in the dumpsite itself. Therefore, dissolution of the acid soluble metal in the dumpsite is probably low under this condition of dumpsite. In the case of Cu, Cr and Ni, the affinity towards dissolved organic content generated from the degradation of organic matter confirms the possibility of these metals easily available in the runoff leachate. The TOC of the runoff leachate again proves its leachability. Among all the metals, concentration of Cr in the runoff leachate was found to exceed the national effluent quality standard. This shows the need for the leachate treatment to reduce its toxicity to the environment.

3.6. Seed germination and root elongation toxicity test

Fig. 4 shows the varying toxicity level of leachate with the effect of EDTA added to the leachate. A low toxicity level was observed with 7.4% IC_{50} in the 0.2 ml EDTA dosed leachate. From this test, a decrease in toxicity level was noticed in the EDTA added leachate sample with an increase in dosage level of EDTA. Untreated leachate showed high toxic level with 4.0% IC_{50}.Thus, it indicates the effect of heavy metals in the leachate to inhibit the germination of rice seed. A decreasing toxicity was observed in the EDTA added leachate sample due to the effect of metal–EDTA complex formation. In some cases, the property of EDTA with high molecular weight was found to reduce the bioavailability and toxicity to the plants [29]. Decrease in heavy metal toxicity by adding EDTA, in turn shows an increase in inhibitory toxic effect on rice. The Cu has been proved as highest toxic metal to inhibit the germination of rice seed with the IC_{50} of 0.22 mg/l [10]. Therefore, in addition to the addressed concentration of Cu with high mobility potential in the runoff leachate, potential toxicity of Cu to the environment is also explored. Although toxicity of each metal cannot be explained in this test, however, an attempt to exhibit the influence of heavy metal in the leachate runoff to the plants was made.

4. Conclusions

The leaching potential of heavy metals contaminate in the dumpsite was determined through solid waste characterization, sequential extraction analysis, TCLP test and leachate quality analysis. The concentrations of heavy metals in the waste were in the following order: Zn > Cu > Mn > Cr > Pb > Ni > Cd > Hg. In the case of mobility potential, Zn, Cu and Mn showed relatively high mobility potential compared to other metals. From the TCLP test the leaching potential of carbonate bound Mn, Zn and Cd when the pH level of dumpsite is decreased was proved. On the other hand, the heavy metal concentration in the actual leachate was different from that of the leachate from boreholes and from the results for the mobility potential based on different forms. The leachate quality analysis showed heterogeneity of solid waste age and the methanogenic condition in dumpsite. The possible dissolution of carbonate bound metals is expected to be low from the pH values determined for solid waste and leachate. The presence of optimum moisture content in the waste has influenced the degradation rate generating organic acid. This has enhanced the concentration of heavy metal especially Cu, Cr and Ni in leachate runoff.

Although the concentration of all the metals except for Cr in the runoff leachate was below the effluent standards, potential of these metals to be toxic to the plant species were revealed from the toxicity test. Therefore, the focus on the removal of heavy metals from the leachate in the present condition is necessary.

Acknowledgements

This research is supported by Post-Graduate Education, Training and Research Program in Environmental Science, Technology and Management under Higher Education Development Project of the Commission on Higher Education, Ministry of Education of Thailand and the Swedish International Development Cooperation Agency (SIDA).

References

[1] P. Flyhammar, Estimation of heavy metal transformations in municipal solid waste, Sci. Total Environ. 198 (1997) 123–133.
[2] P. Flyhammar, Use of sequential extraction on anaerobically degraded municipal solid waste, Sci. Total Environ. 212 (1998) 203–215.
[3] S. Bozkurt, L. Moreno, I. Neretnieks, Long-term processes in waste deposits, Sci. Total Environ. 250 (2000) 101–121.
[4] A.M. Måtensson, C. Aulin, O. Wahlberg, S. Ågren, Effect of humic substances on the mobility of toxic metal in a mature landfill, Waste Manage. Res. 17 (1999) 296–304.

[5] P.J. He, Z. Xiao, L.M. Shao, J.Y. Yu, D.J. Lee, In situ distribution and characteristics of heavy metals in full-scale landfill layers, J. Hazard. Mater. B137 (2006) 1385–1394.
[6] M. Östman, O. Wahlberg, S. Ågren, A.M. Måtensson, Metal and organic matter contents in a combined household and industrial landfill, Waste Manage. 26 (2006) 29–40.
[7] J.K. Øygard, E. Gjengedal, O. Røyset, Size charge fractionation of metals in municipal solid waste landfill leachate, Water Res. 41 (2007) 47–54.
[8] F. Rapin, A. Tessier, P.G.C. Campbell, R. Carignan, Potential artifacts in the determination of metal partitioning in sediments by a sequential extraction procedure, Environ. Sci. Technol. 20 (1986) 836–840.
[9] W. Wang, Comparative rice seed toxicity tests using filter paper, Growth Pouch-TM, and seed tray methods, Environ. Monit. Assess. 24 (1993) 257–265.
[10] W. Wang, Rice seed toxicity test for organic and inorganic substances, Environ. Monit. Assess. 29 (1994) 101–107.
[11] N. Ahsan, D.G. Lee, S.H. Lee, et al., Excess copper induced physiological and proteomic changes in germinating rice seeds, Chemosphere 67 (2007) 1182–1193.
[12] S. Cui, Q.X. Zhou, S.H. Wei, W. Zhang, L. Cao, L.P. Ren, Effect of exogeneous chelators on phytoavailability and toxicity of Pb in *Zinnia elegans* Jacq, J. Hazard. Mater. 146 (2007) 341–346.
[13] D.W. Nelson, L.E. Sommers, Total carbon, organic carbon, and organic matter, in: A.L. Page, R.H. Miller, D.R. Keeney (Eds.), Methods of Soil Analysis. Part 2. Chemical and Microbiological Properties, second ed., American Society of Agronomy and Soil Science Society of America, Wisconsin, 1982, pp. 539–579.
[14] US Environmental Protection Agency, SW-846 Test Methods for Evaluating Solid Wastes, August 20, 2006. http://www.epa.gov/sw-846/main.htm.
[15] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, twentieth ed., Washington DC, 1998.
[16] T.J. Norberg-King, D.I. Mount, E.J. Durhan, G.T. Ankley, L.P. Burkhard, Method for Aquatic Toxicity Identification Evaluation: Phase I Toxicity characterization procedures EPA/600/6-9/003, US Environmental Protection Agency, Duluth, MN, 1991.
[17] US Environmental Protection Agency, Ecological Effects Test Guidelines: OPPTS850.4200 Seed Germination/Root Elongation Toxicity Test, EPA 712-C-96-154, 1996.
[18] US Environmental Protection Agency, Trimmed Spearman–Karber (TSK) program version 1.5, January 10, 2007. http://www.epa.gov/nerleerd/stat2.htm.
[19] D.R. Reinhart, T.G. Townsend, Landfill Bioreactor Design and Operation, CRC Press LLC, Boca Raton, FL, 1998.
[20] P. Prudent, M. Domeizel, C. Massiani, Chemical sequential extraction as decision-making tool: application to municipal solid waste and its individual constituents, Sci. Total Environ. 178 (1996) 55–61.
[21] B.J. Alloway, Soil processes and the behavior of heavy metals, in: B.J. Alloway (Ed.), Heavy Metal in Soil, second ed., Blackie Academic & Professional, London, 1995, pp. 11–37.
[22] S. Esakku, A. Selvam, J. Kurian, K. Palanivelu, Assessment of heavy metal species in decomposed municipal solid waste, Chem. Spec. Bioavail. 17 (3) (2005) 95–102.
[23] C. Xiaoli, T. Shimaoka, C. Xianyan, G. Qiang, Z. Youcai, Characteristics and mobility of heavy metals in an MSW landfill: implication in risk assessment and reclamation, J. Hazard. Mater. 144 (2007) 485–491.
[24] P. Kjeldsen, M.A. Barlaz, A.P. Rooker, A. Baun, A. Ledin, T.H. Christensen, Present and long-term composition of MSW landfill leachate: a review, Crit. Rev. Environ. Sci. Technol. 32 (2002) 297–336.
[25] S.A. Watmough, M.C. Eimers, P.J. Dillon, Manganese cycling in central Ontario forest: response to soil acidification, Appl. Geochem. 22 (2007) 1241–1247.
[26] H.M. Fernandes, Heavy metal distribution in sediments and ecological risk assessment: the role of diagenetic processes in reducing metal toxicology in bottom sediments, Environ. Pollut. 97 (1997) 317–325.
[27] A. Borona, I. Aranguiz, A. Elias, Assessment of metal extraction, distribution and contamination in surface soils by a 3-step sequential extraction procedure, Chemosphere 39 (1999) 1911–1922.
[28] H.J. Ehrig, Quality and quantity of sanitary landfill leachate, Waste Manage. Res. (1983) 53–68.
[29] S. Inaba, C. Takenaka, Effects of dissolved organic matter on toxicity and bioavailability of copper for lettuce sprouts, Environ. Inter. 31 (2005) 603–608.