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The effect of a leachate collection ditch on natural attenuation of heavy metal migration from an open dump landfill: An indication from sequential extraction

Krongkaew Mighanetara*[1], Pranitda Peng-ngiw[1] and Rattiyaporn Jaidee[2]

[1]Environmental Science Programme, Faculty of Science and Technology, Thepsatri Rajabhat University, Lopburi 15000, Thailand
[2]Agriculture and Innovation Programme, Faculty of Science and Technology, Thepsatri Rajabhat University, Lopburi 15000, Thailand

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Abstract

Open dump landfills are recognised as potential sources of heavy metal (HM) contamination. Their migration to the wider environment is largely controlled by their speciation; and in this study, results from sequential extraction, pH values and organic matter contents in soils around an open dump landfill and sediments in a leachate collection ditch were investigated in order to study the attenuation processes that lead to a decrease in HM mobility. The results revealed that Cu and Zn leached from the landfill were largely retained by sediments in the collection ditch and mostly bound to organic fraction. A simple mass balance suggested that, in comparison to other sources, HM accumulation in soils that resulted from the landfill was relatively low for Cu and relatively high for Zn. The concentrations observed were within safe limits according to the Thai standard for non-residential soil. This study showed that a leachate collection ditch plays an important role in minimising HM migration. Monitoring and further studies on fate and migration pathways of pollutants from open dump landfills, in particular to those underlain by different geologic settings to our study are needed to develop cost-effective measures to prevent/minimise the effect of landfill leachate and ensure that the environment surrounding landfill sites is safe.

Keywords: Natural attenuation, Migration, Heavy metals, Open dump landfills, Leachate collection ditches

1. Introduction

Solid waste management is one of the most challenging issues for local government authorities in Thailand. According to the Pollution Control Department (PCD), Thailand generated 25.7 million tonnes of solid waste in 2022, of which 5.4 million tonnes, or about 21 percent, was disposed of unsanitarily, mostly into open dump sites [1]. The impact of open dump landfills on air, water, soil and organisms around the disposal sites is well recognised and has been widely studied by numerous researchers, e.g. [2-4]. One of the most significant concerns of open dump landfills is soil and water contamination caused by landfill leachate. For example, a detailed investigation from 54 groundwater samples and 44 surface soil samples that covered a total area of 3,000 km^2 in western Saudi Arabia indicated that some groundwater and soil samples were contaminated by leachates from open dump landfills [3].

The extent of pollutant migration depends on a number of factors such as landfill composition, biogeochemistry of soils and surface/subsurface water underneath the sites as well as pollution prevention measures [5-7]. Depending on waste types, characteristics and ages of landfill sites, their leachates can contain hundreds of different chemicals [8]. Among those, heavy metal (HM) contaminants can be an issue if hazardous household and electronic waste is not segregated from general waste and disposed of in open dump landfills. Once released from solid waste, HMs can migrate via landfill leachate and subsequently contaminate nearby soils and surface/subsurface waters. For example, Alam et al. [9] reported that the concentrations exceeding the permissible limit for Fe, Mn, Cd, and Pb were found in underground wells around a landfill site in Mogla Bazar, Sylhet, Bangladesh, and at some sampling points, soils were polluted with Cd and Pb up to moderate levels.

As the terminology suggests, ‘open dump landfills’ are areas where solid waste of all kinds is dumped uncovered, generally with no structure to prevent the migration of pollutants to their nearby areas. As a result, the government has implemented a policy to ban the use of open dump landfills since the past few years as reflected in the Notification of the Ministry of Interior Re: Solid waste management B.E. 2560 (2017). However, the disposal of solid waste in a sanitary way, either sanitary landfill or incineration, is unaffordable for most local government authorities in Thailand. As a result, open dump landfills are still used by most local authorities as seen from Thailand State of Pollution Report 2022 that 85% of waste disposal sites in Thailand (1,766 out of 2,074) are open dumps [1]. This is not only the case for Thailand but also for other developing countries, where less than 25 percent of waste is sent to regulated landfills [2].

Lopburi Municipality waste disposal site is an open dump site. The landfilling began in 1982, long before the policy on uncontrolled landfills was introduced. Originally, there was no engineering structure to prevent the flow of leachate from the landfill site to its neighboring paddy fields. Later in 2009, due to the complaints from the owners of the paddy fields adjoining the disposal site, the municipality constructed a collection ditch with the width of ca. 2 m and the depth of ca. 1 m around the landfill site. Its primary

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*Corresponding author.
Email address: krongkaew.m@lawasri.tru.ac.th
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function is to prevent direct flows of leachate from the landfill to adjoining lands. However, due to the width and the depth of the ditch is relative small and shallow compared to the landfill size, the collection ditch is often flooded during rainy season.

Besides flood prevention, leachate collection ditches can also be used to minimise the migration of HMs from landfills to their surrounding environment. This is because biochemical processes in the ditches, such as adsorption and precipitation play important roles in regulating mobility of HMs. Attenuation of HMs and other pollutants from landfill sites has been studied by many authors [10-12]. For examples, Christensen et al. [10] carried out a detailed review on attenuation of landfill leachate pollutants in aquifers, which has been followed by hundreds of studies.

Sequential extraction has been widely used to study mobility of HMs in soils and sediments. This is because metals in solid geological media deposit in different phases (e.g. exchangeable, reducible and oxidisable), and at the same time, exist in different mineral species (e.g. carbonates, oxides and silicates). Only the metal fractions that can be readily removed and mobilised from their solid states have potential to migrate from their sources; and sequential extraction allow for the determination of such information [13, 14]. This research applied sequential extraction to investigate HM speciation in soils around the landfill site and sediments in a leachate collection ditch to better understand the attenuation processes of HMs from an open dump landfill to its wider environment.

2. Materials and methods

2.1 Study area

The study area is located in lowlands of Chao Phraya River Basin. It is underlain by alluvial montmorillonite-rich clay of Lop Buri soil series [15]. According to the USDA classification, this soil series belongs to a very-fine, smectitic, isohyperthermic typic haplusterts. Clay contents in top soil (0-30 cm) range from 62% to 68% with sand contents of ≤ 5% [16].

The studied landfill is located on the roadside of Lopburi-Ban Mi Road, approximately 5 km from Lopburi City Centre, Central Thailand (Figure 1). In 2022, the landfill covers an area of 20.6 acres (52 rai), and receives ca. 230 tons per day of unsegregated household, institutional and commercial solid waste [17]. Information from Google Earth Pro [18] showed that the elevations of the studied landfill range from 11-20 m above MSL, whereas the elevations of paddy fields around the landfill site range from 8-10 m above MSL (Figure 1).

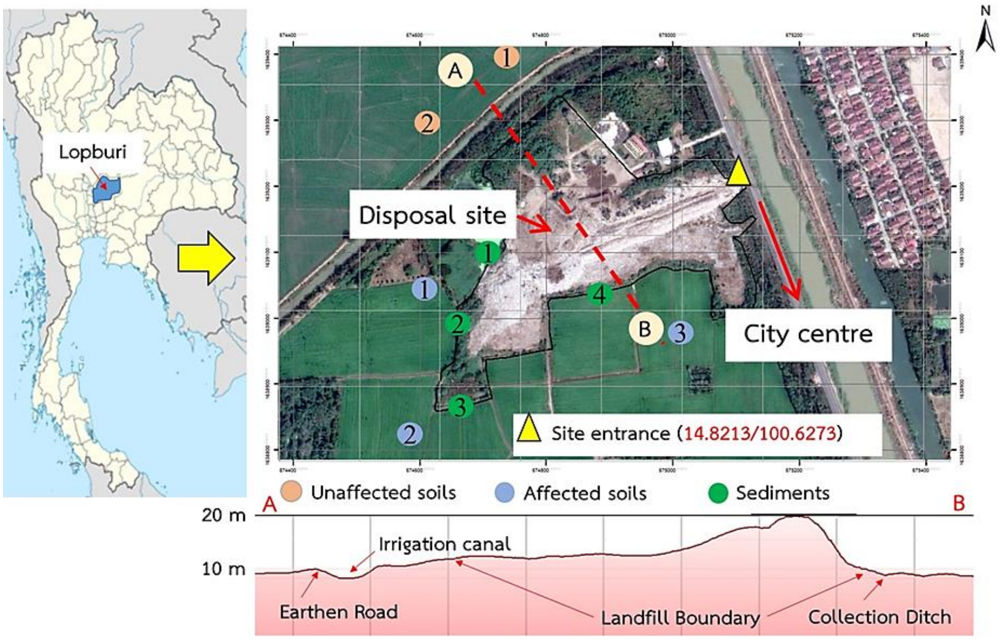


Figure 1 Study area, sampling locations, cross-sectional elevations of the landfill site. Blank line around the landfill site indicates a leachate collection ditch.

2.2 Reagents

All aqueous solutions (standard preparation, acidification, dilution, and digestion) and cleaning processes of laboratory wares were prepared with ultrapure water (18.2 MΩ.cm) (Sartorius arium™) as described by Mighanetara et al. [19].

2.3 Sampling protocol and sample treatment

In order to achieve the aim of the study, stratified random sampling technique was adopted. Based on the leachate migration direction, the study area was stratified into three groups, namely an unaffected zone, an affected zone, and a leachate collection ditch. For each group, strata were further divided into sub-zones of ca. 120x120 m; and numbers were assigned for each sub-zone. Sampling points of each strata were then chosen from sub-zones using a simple random sampling approach. Once sub-zones were selected, a sampling location within each selected sub-zone was determined by tossing a coin on a 30x30 cm board; and an acquired location on a 30x30 cm board was then related to the location in a 120 x 120m sub-zone. Locating of predefined sampling points in the field was determined using Google Map. Unaffected samples were taken from paddy fields north of the landfill site. This area is separated from the studied landfill by an irrigation canal and an earthen road; and has never been affected by landfill leachate. Therefore, the samples from this area were seen as a controlled group. The paddy fields south and south-west to the landfill site often receive landfill leachate during rainy season, therefore representing an affected group. All samples were collected during 11-15 November 2019.

In general, the number of samples is calculate from Equation 1 as follow:

$$n = \frac{t^2 s^2}{E^2} \quad (1)$$

in which n = number of samples, s = standard deviation, and E = acceptable error.

In order to determine the sample size according to the above equation requires prior knowledge of the standard deviation of soil analysis in the area, and guidelines on acceptable error (E), which were unavailable at the sampling time. Therefore, a minimum of three samples per sample group were collected to allow statistical analysis. In total, 14 samples from three sample groups were collected including four samples from unaffected soil, six samples from affected soil and four sediment samples from the leachate collection ditch. It was assumed that variability of unaffected soil was lower than other groups, therefore fewer samples were taken from this group. Due to a relatively small sample size for each sample group, validation of the sample size will be discussed later in the result section. The locations of sampling points is presented in Figure 1.

For soil samples (both unaffected and affected samples), at each sampling point, two samples namely surface and subsurface were taken. They were taken from 30x30 cm pits at a 0-15 cm depth (surface samples) and 30-45 cm depth (subsurface samples). For each sample, approximately 500 g of soil were achieved by the quartering method, and stored in 7x10 inch Kraft paper bags. For sediments, approximately same quantity of soil samples were taken using a plastic dipper, and stored in 750 mL polypropylene plastic boxes.

After returning to the laboratory, the samples were dried in a hot air oven at 40°C until no further decrease in weight was detected. The samples were then disaggregated and passed through a 2 mm sieve. These fractions of sample were used for analysis of soil pH and organic matter. For metal analysis, the $\leq$ 2 mm fractions were further sampled by the quartering method until ca. 20 g of the samples were obtained. These 20 g of samples were then ground with pestle and mortar until at least 18 g (90%) were passed through 180 µm sieve and stored in plastic zip bags for further analysis.

2.4 Soil pH and organic content

Soil pH was analysed on a 1:1 soil to water (w/v) solution using a pH meter (Mettler Toledo). A soil mixture was subjected to 5 min shanking (rigorously) and another 10 min for settling. A reading was then taken on the supernatant after properly calibrated against pH 4 and pH 7 buffer solutions. Soil organic matter content was determined by the Walkley-Black method. Duplicate analysis was carried out for each sample and for both pH and organic matter analysis.

2.5 Sequential extraction

In this study, the five-step sequential extraction scheme proposed by Tessier et al. [20] was adopted with a modification of reagents used in Step 5. Due to safety concerns, this research substituted HF with aqua regia (a 3:1 mixture of concentrated HCl: HNO_3) for the extraction of residual fraction in the last step.

Duplicate samples of 1 g (< 180 µm) were extracted in 50 ml polypropylene centrifuge tubes using reagents and extraction conditions tabulated in Table 1. At the end of each step, the extract was centrifuged at 3000 rpm for 30 min. The supernatant was then carefully transferred into a polyethylene bottle and stored at 4°C prior to analysis. The residue was centrifuged with 8 ml of 18.2 MΩ.cm water for 30 min. The washing was discarded, while the washed residue was used for the next stage.

Pseudo-total metal was also carried out to determine the recovery of the sequential extraction method. One gram of the samples were digested on a digestion unit (DigiBlock, Lab Tech) using the same reagents and conditions in Step 5.

Table 1 Reagents and conditions used in sequential extraction.

Step	Fraction	Reagent	Extraction condition
1	Exchangeable	8 mL of 1 M $MgCl_2$, pH 7.0	1 h, room temperature, continuous agitation
2	Bound to carbonates	8 mL of 1 M NaOAc, pH 5.0	5 h, room temperature, continuous agitation
3	Bound to Fe/Mn oxides	20 mL of 0.04 M $NH_2OH{\cdot}HCl$ in 25% HOAC (v/v)	6 h at 96°C in water bath, occasional agitation
4	Bound to organic matters	3 mL of 0.02 M HNO_3 + 5 ml of 30% H_2O_2 (pH 2 with HNO_3)	2 h at 85°C in water bath, occasional agitation
		3 mL of 30% H_2O_2 (pH 2 with HNO_3)	3 h at 85°C in water bath, intermittent agitation
		after cooling, 5 mL of 3.2 M NH_4OAC in 20% HNO_3 (v/v)	Diluted to 20 ml, 30 min continuously agitation
5	Residual	8 mL of 1:3 HCl:HNO3	2 h at 120°C, refluxed, filtered (Whatman no. 42), diluted to 25 ml

Determination of HM concentrations was carried out on a flame atomic absorption spectrophotometer (Shimadzu, AA-6200). The wavelengths used for Cu, Pb and Zn were 324.7, 217.0 and 213.9 nm respectively; and their 1% absorption concentrations were 0.04, 0.1 and 0.011 mg L^{-1} respectively. The linear ranges were prepared at 10-80% of their 1% absorption concentrations. Standard calibration curves were prepared from 1,000 mg L^{-1} standard solutions for AAS (Spectrosol, Ajax Finechem) and diluted accordingly to their linear ranges.

3. Results and discussion

3.1 Validation of sample sizes

In order to validate the sample sizes collected, the acceptable error (E) in Equation 1 was calculated by substituting the number of samples collected (n) and the standard deviation from Cu and Pb analysis results. Only Cu and Pb were calculated for their E values for the comparison with their regulated values. The results are shown in Table 2.

Table 2 The acceptable errors (E) obtained in this study. The t value for n = 4 (df=3) is 3.182, and n= 6 (df=5) is 2.571.

Sample Group	**n**	**Cu (mg kg^{-1})**		**Pb (mg kg^{-1})**	
		Results (min-max)	**E**	**Results (min-max)**	**E**
Unaffected soil	4	36.7±5.1(33.8-41.9)	8.1	15.7±4.1 (13.9-28.2)	6.5
Affected soil	6	42.8±6.8 (31.8-42.7)	7.1	18.7±2.2 (15.2-20.9)	2.3
Sediments	4	55.1±9.9 (41.0-68.5)	15.8	27.0±3.7 (22.7-31.5)	5.9

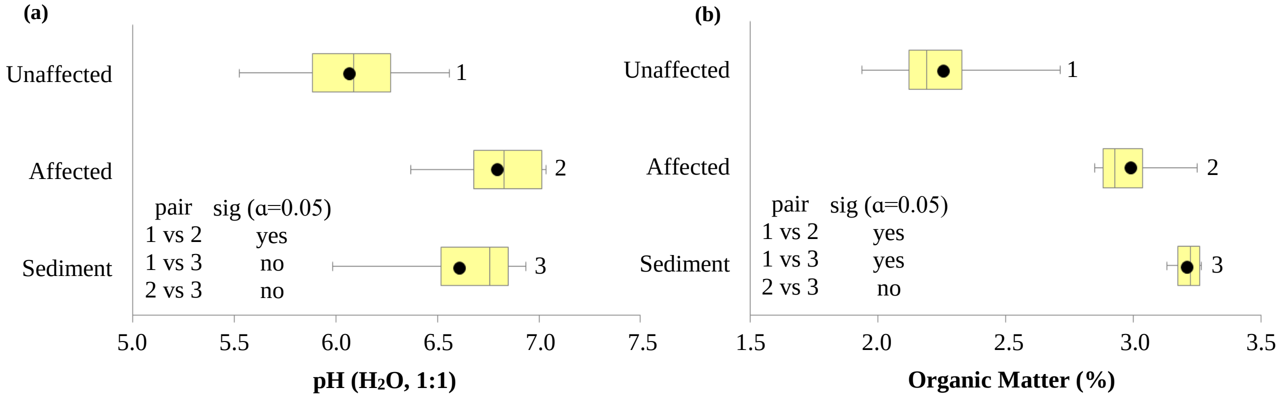
From the table, the accepted errors of all sample groups ranged from 7.1-15.8 mg kg^{-1} for Cu and 2.3-5.9 mg kg^{-1} for Pb. The values obtained were much lower than the regulated values of Thailand's Soil Quality Standard (35,040 mg Cu kg^{-1} and 800 mg Pb kg^{-1} for non-residential soil) [21]. Therefore, the number of samples collected in this study was considered adequate for the study's objective. It should also be noted that soils in the study area are of the same soil series, and their colours as well as textures were relative similar visually. Furthermore, the statistical analysis results yielded some useful in formation that points out the role of leachate collection ditches on preventing heavy metal migration from open dump landfills, as will be seen in later sections.

3.2 Soil pH

The results of pH values in unaffected, affected and sediment samples are given in Figure 2a. As it can be seen, the pH values of studied samples varied both within and between groups, ranging from 5.52 to 6.79. According to the Land Development Department [22], the values found can be classified as moderately acid (5.6-6.0) to neutral (6.6-7.3). It is also clear from the figure that unaffected soils were more acidic (5.5-6.6 with an average of 6.1±0.4) compared to affected soils (6.4-7.0 with an average of 6.8±0.3) and sediments (6.0-6.9 with an average of 6.6±0.4).

In comparison to the pH ranges for acidogenesis in young landfills (4.5-7.5 with an average of 6.1) and methanogenesis in old landfills (7.5-9 with an average of 8.0) as reported by Christensen et al. [10], the pH values observed in sediments from a leachate collection ditch were relatively acidic, even though the studied landfill has been in operation for over 40 years. This may suggest that, in open dump landfills that are still in operation, several decomposition stages may take place at the same time at different locations; and the resulting leachate was later mixed upon arriving at collection ditches. Further changes of pH may also take place in collection ditches as a result of biogeochemical processes in the ditches.

Statistical analysis (ANOVA followed by Tukey-Kramer at $\alpha = 0.05$) confirmed the graphical presumption that the pH values of unaffected soils were indeed significantly lower than that of the affected one. However, no significant difference in pH values between that in sediments and unaffected soils; and between that in sediments and affected samples (Figure 2a). The reason for more acidic pH in unaffected soils is not clear but may be explained by natural variation, particularly considering that the sample size of unaffected soils was relatively small. Soil acidification may also cause by excessive application of nitrogen fertilizer, which reported by several authors e.g. [23, 24]. The neutral pH values observed in affected soils were within a pH range reported for Lop Buri soil series (pH values of 6.5-8.0) [16].



pair	sig (α=0.05)
1 vs 2	yes
1 vs 3	no
2 vs 3	no

pair	sig (α=0.05)
1 vs 2	yes
1 vs 3	yes
2 vs 3	no

Figure 2 The boxplots and the mean values (black dots) of soil pH (a) and soil organic matter (b) in unaffected soils (n=4), affected soils (n=6) and sediments (n=4). Each value was the average from duplicate analysis.

3.3 Soil organic matter

Figure 2b shows that the lowest organic matter was observed in an unaffected group (1.77-2.71%), followed by that in affected one (2.73-3.33%) and that in sediments (3.01-3.33%) respectively. Statistical test confirmed graphical presumption that organic matter in the unaffected group was significantly lower than the others; while the organic matter in affected soils and sediments were not different statistically. It is likely that higher contents of soil organic matter in affected soils were resulted from landfill leachate. This is because both unaffected and affected soils are from the same soil series, and have the same land use (paddy fields relying on chemical fertilisers). Therefore, except for landfill leachate, the sources of organic contents for both areas were similar, i.e. rice stubbles and rice straws. As a result, it is reasonable to rationalise that elevated soil organic matter in affected soils were caused by the landfill leachate, which usually contains large amount of organic matter [10].

3.4 Heavy metal speciation

For clarity, the term metal speciation used in this study refers to the fractions in which HMs are bound to solid matrices at the operationally defined conditions described Table 1. It is important to note that aqua regia used for extracting residual and total concentrations is not able to totally dissolve most soils; however, because it is safer, it has been used for replacing HF in many soil analysis laboratories [25]. Furthermore, this study focused on the non-residual fractions (F1-F4) that can be mobilised under normal environment conditions, at which are sufficiently achieved by aqua regia extraction. Therefore, aqua regia is considered adequate for this study, and the summation of metals in F1-F4 fractions are considered as mobile metals.

The limits of detection (LOD), pseudo-total concentrations, distribution of Cu and Zn speciation and recoveries for Cu and Zn are presented in Figure 3. The variations of Cu and Zn obtained from both the pseudo-total and sequential extractions were relatively high, particularly in sediment samples. These were likely to be part of spatial variations (different sampling locations and depths) and relatively poor repeatability of sequential extraction. Spatial variation is not uncommon in soil investigation. This is because soil is a complex, heterogeneous and dynamic substance, and is known for its high variability in physical and chemical properties at macro and micro scales [26]. As for sequential extraction, although it has been widely used to study HM speciation in soils and sediments e.g. [27, 28], readsorption has been identified e.g. [29, 30]. The fact that sequential extraction is a series of wet extractions, an increase in numbers of the extraction steps can lead to an accumulation of errors from each step, particularly at the end of each step. It is possible that small amounts of samples are lost during transferring of a supernatant liquid and residue washing at the end of each step, which contributed to variation observed.

In this study, the pseudo-total metals were analysed to determine the recoveries of HMs obtained by sequential extraction method. The average percentage recoveries, calculated from the sum of all fractions (F1-F5) to their pseudo-total concentrations, were determine to justify the reliability of the sequential extraction procedure. In general, the average percentage recoveries (Figure 3) ranged from 80-115%, indicating good agreement with their pseudo-total concentrations, and therefore the extraction procedures were reliable.

The pseudo-total concentrations can also be used to determine the effect of landfill leachate on HM accumulation in soils around the landfill site. The results showed that the pseudo-total metals in sediments (55.1±9.9 mg Cu kg^{-1}, 27.0±3.7 Pb kg^{-1}, 50.5±11.8 mg Zn kg^{-1}) were significantly higher than ($p<0.05$) that in affected (42.8±6.5 mg Cu kg^{-1}, 18.7±2.2 mg Pb kg^{-1}, 26.6±5.9 mg Zn kg^{-1}) and unaffected soils (36.7±5.1 mg Cu kg^{-1}, 15.7±4.1 mg Pb kg^{-1}, 22.0±6.0 mg Zn kg^{-1}). The latter two, however, were not different statistically, indicating that accumulation caused by landfill leachate was small. The concentrations found were within safe limits according to the Thai standard for non-residential soil (35,040 mg Cu kg $^{-1}$, 800 mg Pb kg^{-1}, and no limit value for Zn) [21]. However, it should be noted that the Cu pseudo-total contents observed in some affected samples were higher than the investigation value for Thai soil suggested by Zarcinas et al. [31], who proposed the investigation value of 44 mg Cu kg^{-1}, 55 mg Pb kg^{-1}, and 70 mg Zn kg^{-1} for Thai soils.

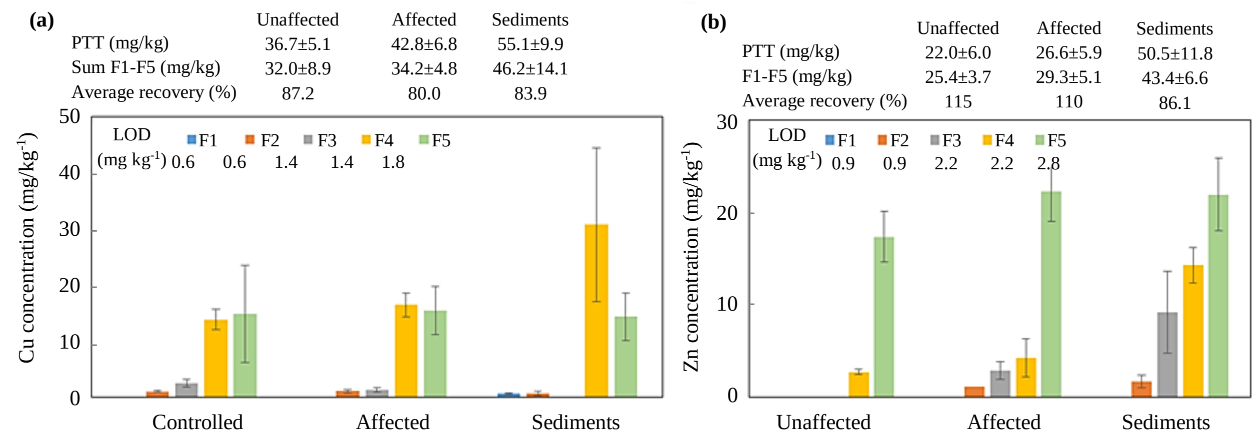


Figure 3 The speciation distribution of Cu (a) and Zn (b) in unaffected (n=4), affected (n=6) and sediment (n=4) samples. Each value was the average from duplicate analysis. psT indicates pseudo-total concentrations. The LOD in mg kg^{-1} were calculated from analysis LOD (0.05 mg Cu L^{-1} and 0.09 mg Zn L^{-1}), weight of sample used (1 g), and final volume adjusted (8 mL for F1 and F2; 20 mL for F3 and F4; and 25 mL for F5).

3.4.1 Copper

From Figure 3a, it can be seen that exchangeable Cu (F1) in soil samples, both in unaffected and affected groups, were less than LOD (0.4 mg kg^{-1}); and the values in sediments were also low (0.56±0.09 mg kg^{-1}). The carbonate bound Cu (F2) were found in all sample groups, but the concentrations were relatively low, ca. 1-3% to all fractions (the sum of F1-F5). For distribution of Cu associated with Fe/Mn oxides (F3), the highest contents were observed in unaffected soils (7.5±2.2 % to all fractions, followed by affected soils (3.8±1.1 % to all fraction); while F3 fraction in all sediment samples were below LOD. Large amounts of Cu were found in organic bound (F4) and residual (F5) fractions. In soil samples, both unaffected and affected, Cu in F4 and F5 fractions were found at relatively similar contents (ca. 13-16 mg kg^{-1} for both F4 and F5); while in sediment samples, the Cu in F4 fraction (30.7±13.8 mg kg^{-1}) was about two times higher than that in F5 fraction (14.4±4.3 mg kg^{-1}). The F5 fraction in all sample groups were relatively similar in term of the amount found (14.8±8.7 mg kg^{-1}, 15.4±4.3 mg kg^{-1} and 14.3±4.2 mg kg^{-1} in unaffected, affected and sediment samples respectively). Discussion on large amounts of Cu in F4 fraction, especially that in sediments, and the distribution of F5 fraction will be discussed in the following sections.

3.4.2 Zinc

Figure 3b shows that for unaffected soils, Zn in F1-F3 fractions were lower than LOD; and their F4 fraction was also low compared to the other two groups. As for affected and sediment samples, speciation distribution followed the order of F5>F4>F3>F2. For all sample groups, most of Zn were found in F5 fraction. This finding was in good agreement with the results reported by [32, 33], who reported that residual fraction is the most abundance form of Zn in soils.

Similar to Cu results, residual Zn (F5) was also distributed equally in all sample groups. This finding confirmed the fact that all sample groups were from the same parent materials or of the same origin i.e. Lopburi soil series. The concentrations observed (14.9±0.6 mg Cu kg^{-1} and 21.2±1.6 mg Zn kg^{-1}) represent the metals bound to mineral lattices and are considered immobile under normal environments and can be mobilised only from long-term biogeochemical processes.

The average mobility, defined as percentages of metals in mobile fractions (F1-F4) to all fractions of Cu in unaffected, affected and sediment samples were 53.7 %, 54.8 %, and 69.1 % respectively; while the results for Zn were 12.5 %, 27.2 %, and 53.5% respectively. This findings suggested that Cu was relatively more mobile than Zn. The result found was in good agreement to that obtained by [34, 35], who reported that mobility of Cu is higher than Zn. However, there are also studies that reported higher mobility of Zn than Cu, e.g. [36, 37]. The latter reviewed the mobility and bioavailability of trace metals in tropical soils and reported that Cu is often found to be less mobile than Zn.

3.4.3 Lead

For Pb, only a few readings from sequential extraction were above LOD (0.48 mg L^{-1}). The LOD obtained may seem relatively high, however, it is not uncommon for Pb. This owes to the fact that the 1% absorbance concentration (the instrument detection limit as suggested by the manufacturer) for Pb (0.1 mg L^{-1}) is relatively high compared to Cu (0.04 mg L^{-1}) and Zn (0.01 mg L^{-1}). In general, the analysis LOD for flame AAS is somewhat in between the1-10 % absorbance concentration (or the instrumental detection limit and the bottom standard). In this study, the analysis LOD for Pb was 0.48 mg L^{-1}, or ca. 5% absorbance concentration. Based on the samples used (1 g) and the volume extracted, the LOD in mg kg^{-1} for F1 and F2 (8 mL) was 3.8, for F3 and F4 (20 mL) was 9.6, and for F5 (25 mL) was 12.0. Due to this reason, there were not enough results to draw a firm conclusion for Pb. It should also be noted that pseudo-total concentrations of Pb observed in this study were also low, i.e. 15.7±4.1 mg kg^{-1}, 18.7±2.2 mg kg^{-1}, 27.0±3.7 mg kg^{-1} in unaffected, affected and sediment samples respectively, all values found were lower than the investigation value for Thai soils (55 mg kg^{-1}) proposed by [31].

3.4.4 Effect of pH and soil organic matter on metal mobility

Soil pH is the most important parameter influencing metal-solution and soil-surface chemistry [38]. In general, at low pH, metal mobility increases due to dissolution processes. On the other hand, at high pH, metal retention increases due to adsorption/precipitation processes. This can be explained by the point of zero charge (PZC), which is the pH at which the net surface charge is zero. When the pH values are lower than the PZC value, the adsorbent surface (e.g. clay minerals, organic matter function groups) has a net positive charge (e.g. Equation 2), therefore attracting anions (expelling cations or HMs are dissolved). Conversely, at pH values higher than the PZC value, the adsorbent surface has a net negative charge (e.g. Equation 3), consequently attracting cations (HMs become adsorbed or form insoluble metal hydroxides). Different minerals have different PZC values, for example, PZC values for quartz and goethite are 2-3 and 7.3-7.8 respectively [39].

For acidic pH; $\mathrm{Si\text{-}OH + H^+ \dashrightarrow Si\text{-}OH_2^+}$ (2)

For alkaline pH; $\mathrm{Si\text{-}OH + OH^- \dashrightarrow Si\text{-}O^- + H_2O}$ (3)

In this study, pH showed negative relationships with F2 and F3 fractions, however, its effects were not significant (Table 3). This may be due to their concentrations in F2 and F3 were low and a number of extracts were below LOD, resulting in small sample sizes and therefore decreasing statistical power. It could also be that most of the pH values observed were circumneutral (6-7, Figure 2); and at these pH ranges, the effect of pH on metal retention were not pronounced and their relationship was not linear.

In contrast to pH values, soil organic contents showed significant relationships with the pseudo-total, the sum of F1-F5, the mobile fractions (sum of F1-F4) and the F4 fraction. These relationships, except for the relationship with the F4 fraction, were likely be a result of a cumulative effect of F4 fraction, for F4 itself was part of pseudo-total metals, sum of F1-F5 fractions and mobile metals. Although, F4 fraction of Cu (43.0-66.4% to all fractions) were higher than that of Zn (13.7-30.3% to all fractions), as seen in Figure 3, the relationships between F4 fraction and organic matter of Cu was not as strong as that of Zn (Table 3). This may be explained by the fact that Cu in F4 fraction in unaffected and affected soils were relatively similar (13.8±1.8 and 16.4±2.1 mg kg^{-1} respectively, Figure 3), while their soil organic contents were different significantly (2.3±0.3 and 3.0±0.2% respectively, Figure 2).

Table 3 Pearson’s correlation matrix for pseudo-total, fractions and soil properties (pH and organic contents); psT = pseudo-total; n = number of samples; ** and * indicate significance at 5 and 10 percent confidence levels respectively.

Metal Fraction	pH	OM
Cu_{psT} (n=14)	0.44	0.53**
$Cu_{F1\text{-}F5}$ (n=14)	0.41	0.68**
$Cu_{F1\text{-}F4}$ (n=14)	0.18	0.59**
Cu_{F5} (n=14)	0.25	0.07
Cu_{F4} (n=13)	0.44	0.52*
Cu_{F3} (n=8)	-0.52	-0.49
Cu_{F2} (n=14)	-0.34	-0.36
Zn_{psT} (n=14)	0.23	0.66**
$Zn_{F1\text{-}F5}$ (n=13)	0.27	0.64**
$Zn_{F1\text{-}F4}$ (n=12)	0.19	0.61**
Zn_{F5} (n=14)	0.04	0.18
Zn_{F4} (n=10)	0.26	0.64
Zn_{F3} (n=6)	-0.25	0.68
Zn_{F2} (n=7)	-0.27	0.52

Soil organic matter plays an important role in regulating HM mobility in soil due to its ability to bind metals. The predominant active components in metal binding by organic matter are negatively-charged functional groups of carboxyl and acidic hydroxyl groups in humic and fulvic acids [40]. These functional groups show a gradual increase in negative charge with increasing pH due to the dissociation of protons. As a result, soil organic matter in known to have high ability to retain cations including HMs as seen in its high cation exchange capacity (CEC). According to Saha [41], CEC of organic matter (200-400 meq/100 g) is higher than kaolinite clay (3-15 meq/100 g) and montmorillonite clay (80-100 meq/100 g). It should also be noted that depending on its phases (soluble or insoluble), organic matter can either mobilise or immobilise metals. In general, only small proportions of humic and fulvic acids are dissolved in solution. However, presence of soluble organic matter has significant implications on migration of HMs, particularly for those strongly bind to humic and fulvic acids, e.g. Cu [40] or in conditions known to have high dissolve organic matter. Landfill leachate usually contains large quantities of dissolved organic matter, which forms water soluble complexes with metals, subsequently leading to an increase in metal mobility and enhancing their migration/redistribution to wider environments [42].

3.4.5 Natural attenuation enhanced by a leachate collection ditch

Natural attenuation plays an important role in reducing distribution, migration, and bioavailability of HMs in soil. According to Yong and Mulligan [43], natural attenuation is described as natural processes, such as dilution, surface partitioning with soil solids and transformation of contaminants that lead to a decrease in concentrations or toxicities of contaminants. The following discussion on natural attenuation was focused only on the mobile metals. This is because HMs found in landfill leachate as a result of decomposition/dissolution of solid waste are mobile. Furthermore, the study results suggested that there was no indication of spatial redistribution of residual fraction among the studied samples as discussed in section 3.4.2. Therefore, taking residual fraction into account contradicts the existing conditions in this study, subsequently underestimate the efficiency to retain HMs resulted by the collection ditch.

The following estimation of natural attenuation is based on the assumptions that: 1) Cu and Zn concentrations in all sample groups before landfill contamination took place were similar both in quantities and speciation distribution; 2) other than the studied landfill, sources of HMs in unaffected and affected paddy fields were identical. The first assumption is based on the fact that soils underlying the study area is Lopburi soil series, which is confirmed by similar concentrations of residual fraction as discussed in section 3.4.2. The second assumption is justified by their similar land use and environmental conditions.

Based on the above assumption, it can be inferred that the mobile metals in unaffected soil were seen as the metals derived from other sources than the studied landfill. The mobile metals observed in affected soils were resulted from both landfill leachate and other sources. Therefore the difference between them represented the accumulation of HMs caused by landfill leachate. The collection ditch directly received the leachate from the landfill, thus all mobile metals accumulated in the sediments were likely to cause solely by landfill leachate, and therefore representing HMs resulted from the studied landfill. Based on a simple mass balance, the quantification of HM sources is illustrated in Figure 4. The figure shows that most mobile metals from the studied landfill were found in the sediments (95.4% for Cu and 81.9% for Zn); and only a few of them were observed in the affected samples (4.6% for Cu, and 18.1% for Zn). This was likely to be a result of their affinity to organic matter as evidenced in high percentages of F4 to all mobile fractions. The findings showed that the percentages of F4 to all mobile fractions were 80.1- 96.1% for Cu, which were much higher compared to 51.4-56.7% for Zn. This finding was in good agreement with several other studies, which reported that Cu has higher affinity to soil organic matter than Zn [44, 45]. The latter reported that Cu forms more stable organo-mineral compounds, and its stability constants (at pH 7.0) with humic acids was 12.3 compared to 10.3 for Zn. Not only to organic matter, but higher affinity to goethite, Fe-oxides, soils and mineral soils for Cu than Zn was also reported by McLean and Bledsoe [42]. This may explain generally higher mobility for Zn than Cu as discussed in section 3.4.2.

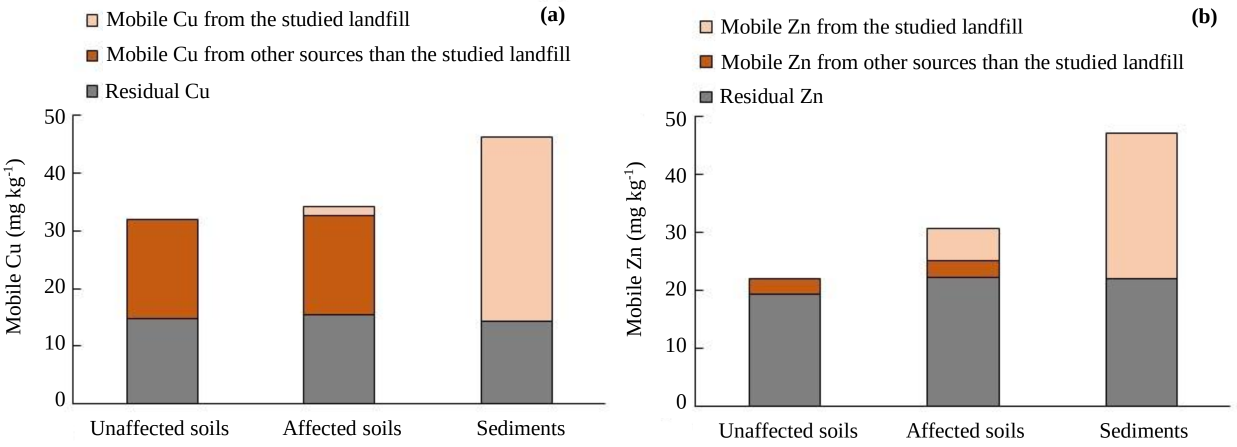


Figure 4 Simple mass balance of Cu (a) and Zn (b) sources in unaffected, affected and sediment samples.

It is important to note that the above estimation is over simplified for it lacks of contaminant loading originating from the landfill site (metal concentrations in landfill leachate). Nevertheless, it does point out that a leachate collection ditch play an important role in retaining HMs from an open dump landfill. It should also be noted that the Cu in affected soils that caused by landfill leachate were relatively low compared to that from other sources, which are likely to derived from agrochemicals, while Zn in affected soil that caused by landfill leachate was relatively high compared to that from other sources. It was likely that dispersion/ dilution also plays an important role in natural attenuation of HMs. Additionally, metals in paddy fields are also taken and translocated by rice plant.

4. Conclusions and recommendations

Soils from paddy fields around an open dump landfill, and bottom sediments from a leachate collection ditch were sampled and analysed for their pH values, organic matter contents, pseudo-total metals, and metal speciation using Tessier sequential extraction scheme in order to study HM mobility and natural attenuation processes in soils and sediments. The results showed that most Cu was found associated with organic fraction, while Zn was largely found in a residual form. The mobile concentrations in sediments were much higher than that in soils, indicating an important role of a collection ditch in minimising HM migration from the landfill site. The results also suggested that, in comparison to accumulation caused by other sources, e.g. agrochemicals, accumulation of HMs in affected soils caused by landfill leachate were relatively low for Cu and relatively high for Zn. Apart from surface partitioning with organic matter, other biogeochemical processes such as dispersion/ dilution and translocation by rice plant may also contribute to natural attenuation processes, which did not cover by this study due to the constraints inevitably linked to research projects. Quantifying the latter two components can provide better conceptual models for HM migration from landfills. Notwithstanding these limitations, results from sequential extraction and a simple mass balance yielded some useful information for decision making on solid waste management. For the reason that most local authorities in Thailand cannot afford sanitary landfills, the government should encourage and support the use of simple and cost-effective measures such as leachate collection ditches to prevent the migration of contaminants to the wider environment. The efficiency of the ditches can be improved by plantation buffer zones and an embankment on the outer side of the ditches. Through this study, it is also recognised that future investigation on pollutant migration from open dump landfills that underlain by different soil types/geologic settings are needed in order to better understand pollution migration and develop effective prevention strategies.

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