



Speciation of Cu, Zn and Cr in Excavated Fine Fraction of Waste at two Landfills

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Mining landfills and open dumpsites is associated with (40-70% by mass) fine fraction of particle sizes less than 20 or 10 mm. Soil and trace elements of considerable concentrations typically dominate the composition of this fraction. In the present paper, a modified three steps sequential extraction procedure was used to fractionate Cu, Zn and Cr in the fine fraction of waste sampled from Högbytorp (Sweden) and Torma (Estonia) landfills. The results showed that the major concentrations of Cu (98.8 and 98.6 wt%) and Cr (98.5% and 98.4 wt %) in fines from Högbytorp and Torma landfills, respectively. These data were found associated to the residual fraction. Noticeable concentrations of Cu and Cr were also found associated within the water-soluble fraction, which could be regarded as a potential risk. The Zn displayed different behavior by distributing in all the sequential extraction fractions in the fine fractions from the two landfills. Specifying the metals content using this method is essential to explore the valorization as well as the potential environmental risks by these fines fractions.

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INTRODUCTION

Landfills and open dumpsites have long been seen as sources for environmental and health hazards due to the generation of greenhouse gases (owing to the degradation of organic wastes) and the leaching of organic and inorganic pollutants to the surrounding water bodies [1]. Despite of that landfills and open dumpsites are still the main disposal fate for our used resources as wastes due to minimum cost [2]. The increase in global population, the consumption of the earth natural resources and the continuous landfilling increased the demand to extract and recycle the dumped wastes as secondary resources [3].

Mining landfills and dumpsites through the landfill mining approach has been associated with (40-70 wt%) fine fraction (FF), the common particle sizes are either <10 or <20 mm [4, 5]. Most of the landfill mining studies defined the FF as a soil-type material or as a residue that could be redisposed again due to the lack of economic feasibility and recycling/reusing options [5-7].

The chemical composition of the FF is dominated by soils from the daily and final cover layers, degraded wastes and minerals [8]. The considerable amount of FF from any reclamation project highlighted the need to store this fraction outdoors [9]. The transfer of pollutants, like trace

elements, within the rain precipitation, irrigation and infiltration water can be significant from this FF compared to other waste fractions due to the small particles sizes [10, 11]. Therefore, it is necessary to identify the possible environmental and health pollutants that can leach out from the FF.

Total trace elements content is often used to address the environmental and health risks despite that the available or mobile concentration is the merely definite hazards [12]. Fractionation methods, like sequential extraction procedure [13], have the ability to identify the mobile besides the resistance concentrations of any trace element. This could help to understand both the potential of leaching to the surrounding recipients as well as the extraction potential of these elements [14, 15]. Assessing the mobility of metals in the fine fraction is also crucial for the management of mining landfills by understanding the fate of reducing the mobility of metals during the excavation process.

Various studies have investigated the environmental and the health impacts of the landfills leachates [16, 17], however, still studies on the fractionation of trace elements in the landfilled FF are missing. Therefore, the goal of the present study is to investigate the fractionation of Cu, Zn and Cr in excavated FF of wastes from two different European landfills the Högbytorp in Sweden [3] and the Torma in Estonia [18] to assess the mobility and

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availability of these trace elements.

MATERIAL AND METHODS

Sites description

Högbytorp landfill is located 40 km northwest of Stockholm (60°32'N, 17°37'E, Sweden). It was established in 1964 and occupies an area of 30 ha. The landfill receives 200-300 trucks of municipal, construction and demolition, commercial, industrial and small parts of household daily wastes. The landfill annually handles around 700 000 tons of wastes. At the site, different waste streams were treated and landfilled ranged from contaminated soil, oily sludge from car washes, organic materials, wood and plastics, metals scrap, ash, medical and hazardous wastes. With more than 4 million tons of wastes the Högbytorp landfill regarded as one of the largest in Sweden and it is Ragn-Sells AB largest waste treatment facility. The excavated area was a temporary heap of wastes (contained municipal, construction and demolition wastes) stored for around 5 years.

Torma landfill is located in Tartu municipality (58°51'N, 26°52'E, Estonia). It was one of the first sanitary landfills constructed according to the European Directive requirements. It was opened in 2001 and occupies an area of 6.2 ha. The landfill is serving more than 100 000 inhabitants in Tartu municipality and receives mostly municipal solid wastes. At the site there are three cells of different ages that are in the stage of closure due to the lack of space. The excavated cell contained wastes (municipal solid waste) of around 5 years old. Detailed information about the two sites can be found in two published characterization studies Jani et al. [3] and Jani et al. [18], respectively.

Sampling

Samples were collected from the fine fraction (< 10 mm) excavated from four test pits at Högbytorp landfill [3] and one test pit at Torma landfill [18]. The maximum excavated depth of each pit was 4 meters from the top of the landfills. These samples were collected from four layers of one meter each using a bucket excavator of 1 m³. These sub-samples were first collected from each hole and layer, sieved to the particle size of (< 10 mm) and then mixed well to make three different samples from each site. These three samples were used during the conducting of the sequential extraction experiments and analyses.

Experiments and Analyses

Total trace elements content

Total trace elements content in the two FF samples was analyzed by a wet digestion method by mixing 1 g from each sample (dried samples at 105 °C and for 24 hours)

with 50 ml of concentrated nitric acid (65% w/v, Merck) and 5 ml of hydrogen peroxide (30% w/v, Merck) for 24 h at room temperature. Then, the mixture was heated on heating block (Biosan) at 160 °C until 50% of the total volume evaporated. The heating continued with the addition of nitric acid until complete mineralization. Then, the solutions were filtered through membrane filters (0.45 µm, Simplepure). Samples were prepared in triplicate including the preparation of blank samples. The total trace elements content in the supernatant was found using ICP-MS at a private laboratory.

Modified sequential extraction procedure

The fractionation of the metals Cu, Zn and Cr was done by modifying the sequential extraction procedure suggested by Tessier et al. [13] and Ure and Davidson [19] as shown in the following steps:

Step 1 (Water-soluble), F1: 3 g from each sample (dried samples) was mixed, in a 100 ml glass beaker, with 50 ml deionized water and heated at 40 °C for 2 h using a mechanical shaker (Tachometer RPM PSU-20, Biosan).

Step 2 (Acid-soluble, bound to carbonate), F2: residues left from the first step were mixed, in a 100 ml glass beaker using mechanical shaker (Tachometer RPM PSU-20, Biosan), with 40 ml of 0.11 M acetic acid (CH₃COOH) for 16 h at room temperature.

Step 3 (Reduced-form, bound to Fe/Mn oxides), F3: residues from step 2 were mixed, in a 100 ml glass beaker, with 40 ml of 0.5 M hydroxyl ammonium chloride (OHNH₂.HCl) using mechanical shaker (Tachometer RPM PSU-20, Biosan) for 16 h at room temperature.

The extract after each of the three steps was filtered by a membrane filter (0.45 µm, Simplepure) into polypropylene tubes and acidified by 0.2 ml nitric acid (0.7 M). Finally, deionized water was added up to 50 ml. The metal content was analyzed using ICP-MS at a private laboratory.

Residue: the metals content in this fraction was determined by calculating the differences between the total trace elements content and the three sequential extraction steps.

Statistical analyses

Statistical analysis was performed using MS Excel software (Microsoft Office 2013) equipped with an extension QI Macros. The analyses and figures were expressed in term of means with standard deviation and standard errors.

RESULTS AND DISCUSSION

Total trace elements content

Table 1 shows the total trace elements content in the excavated FFs from Högbytorp and Torma landfills

compared to the SEPA [20] guidelines values of contaminated soil. The concentrations of Cu and Zn were higher than the SEPA [20] limits of contaminated soil in the two landfills. In addition, the concentrations of Cu and Zn in Högbypörp landfill were higher than that in Torma by 10 and 2 times, respectively. The Cr concentration exceeded the SEPA [20] guidelines values in Torma landfill only. The concentrations of Co, Ni, Cd and Pb were below the SEPA guidelines in the two FFs. Therefore, the focus was given to the fractionation of Cu, Zn and Cr during this study.

The wide variation between the metals concentrations in the FFs from the two landfills could be due to the differences in the sources of the landfilled wastes at Högbypörp (mostly industrial, construction and small part of municipal solid wastes) [3] and Torma (dominated by municipal solid wastes) landfills [18]. In addition, other factors such as the age of landfill, waste management system, climate conditions, the standard of living and culture play important aspects in the type and quantity of wastes deposited at any landfill [21]. Extensive variations in the concentrations of Cr, Cu, Zn and Pb were observed between the samples from the two FFs which could be due to the heterogeneity of the wastes at the two landfills [7].

TABLE 1. Total metal content in the FFs from Högbypörp and Torma landfills compared to the SEPA [20] guidelines values of contaminated soil. Values between brackets represent the standard deviation.

Trace element, mg/kg	Högbypörp landfill	Torma Landfill	SEPA (2009) limits of contaminated soil
Cr	105(54)	261(193)	150
Co	16(4)	7(4)	35
Ni	66(18)	34(18)	120
Cu	3394(1628)	321(181)	200
Zn	2131(716)	1047(572)	500
Cd	2(1)	1(1)	15
Pb	130(39)	141(97)	400

Distribution of metals in the fine fractions

The partitioning of Cu, Zn and Cr in the FFs from Högbypörp and Torma landfills is shown in Figure 1 (a and b). The major parts of Cr (Högbypörp: 98.5 wt %, Torma: 98.4 wt%) and Cu (Högbypörp: 98.8 wt %, Torma: 98.6 wt %) were found associated within the residue fraction in the two fines. The residue fraction mainly consists of mineral compounds. Therefore, these results mean low mobility and bioavailability of Cu and Cr due to the bonding within the crystal structure of the FFs forming minerals and, accordingly, negligible environmental risk potential [22]. Perceptible concentrations of Cu (7.9 mg/kg and 2.7 mg/kg at Högbypörp and Torma landfills, respectively) were found within the water-soluble fraction. In this fraction, metals are easily mobile and available for leaching due to

changes in the redox potential (Flyhammar, 1998). However, the concentrations of Cr bonding to this water-soluble fraction were insignificant with (0.55 mg/kg at Högbypörp) and (0.81 mg/kg at Torma), hence, low leaching potential is appraised from the two FFs [23].

In the acid-soluble fraction metals are bond to carbonates and any reduction in the pH value towards the acidic region leads to the mobility and bioavailability of these metals [13]. Significant concentration of Cu (32.2 mg/kg) in the FF from Högbypörp was found associated with this fraction proposing possible recovery if cost effective methods could be found. In reverse, low concentrations of Cu (1.2 mg/kg) and Cr (2.7 mg/kg) were observed in the FF at Torma landfill, as well as, the concentration of Cr (0.31 mg/kg) in the FF at Högbypörp landfill. The results also showed minor concentrations of Cu and Cr bonded to the reduced-form fraction in the fines from Högbypörp (0.12 mg/kg and 0.73 mg/kg, respectively) and Torma (0.45 mg/kg and 0.72 mg/kg, respectively) indicating low solubility and bioavailability due to the bonding to the Fe/Mn oxides [16].

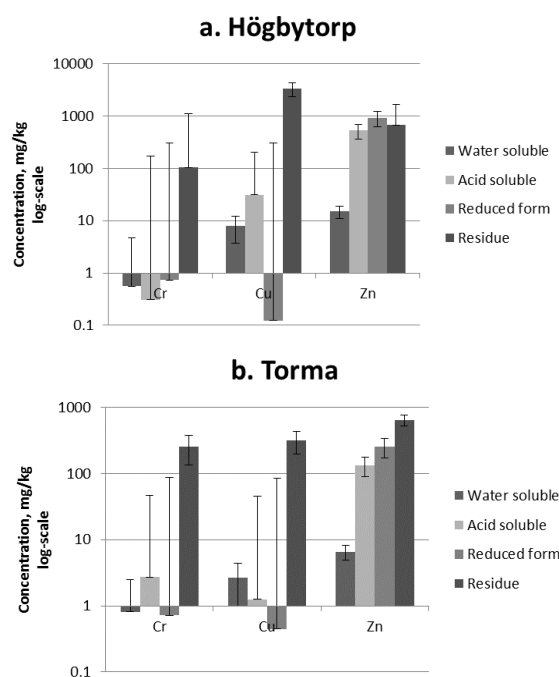


Figure 1. Distribution of Cu, Cr and Zn fractionations in the FFs (< 10 mm) from waste excavated from (a) Högbypörp landfill and (b) Torma landfill in percentage of mass on a logarithmic scale.

The fractionation of Zn displayed different behavior by the significant distribution between the reduced-form (Högbypörp: 43.3 wt %, Torma: 24.6 wt %), acid-soluble (Högbypörp: 24.7 wt %, Torma: 12.8 wt %) and residue (Högbypörp: 31.3 wt %, Torma: 62 wt %) fractions. However, significant concentrations of Zn were also observed connected in the water-soluble fraction with

(14.9 mg/kg) and (6.5 mg/kg) in the FFs from Högbytorp and Torma landfills, respectively. These results showed that Zn could be easily mobilized and become bioavailable among the other studied metals, which may also be considered positively if cost effective extraction method could be found to recover the Zn.

Figure 2 shows the comparison between the distributions of the three metals in the FFs from the two landfills. The same fractionation behaviors of the three metals were observed in the two fines. However, some differences between the two landfills were also observed like the concentrations of Zn that bond to the reduced-form fraction (Högbytorp 922.4 mg/kg, Torma 257 mg/kg) which could be due to the variations in the initial concentrations in the FFs.

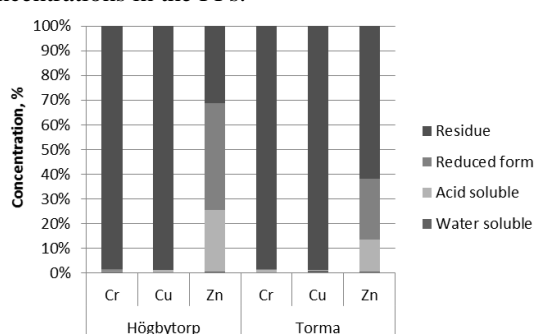


Figure 2. Comparison of the distribution of Cr, Cu and Zn fractionations in the FFs of wastes excavated from Högbytorp and Torma landfills

Assessment of environmental risks potential

The risk assessment code (RAC) is a risk index used to assess the mobility levels of metals in solid wastes [24]. It indicates the percentage of each metal concentration in the mobile fractions (F1 and F2) to the total metal concentration in all fractions and can be calculated as follows:

$$RAC\% = \frac{F1 + F2}{Total\ concentration\ (F1 + F2 + F3 + residue)} * 100 \quad (1)$$

The RAC divided the environmental risks potential into five levels: less than 1% is considered as safe, 1-10% low risk, 11-30% medium risk, 31-50% high risk and more than 50% as very high risk [24].

The RAC results are shown in Figure 3 for each metal in the studied FFs of waste from Högbytorp and Torma landfills. These results revealed that the contribution of Cr and Cu fell in the low risk class (RAC: 1-10%) in the FFs from the two landfills due to the low mobility of these metals. While the Zn results suggested medium risk (RAC: 10-30%) in the FFs from the two landfills due to the distribution of high concentrations of Zn with the water- and acid-soluble fractions. The RAC results were well supported; the findings obtained by the sequential

extraction procedure which is indicated high mobility of Zn in the two FFs.

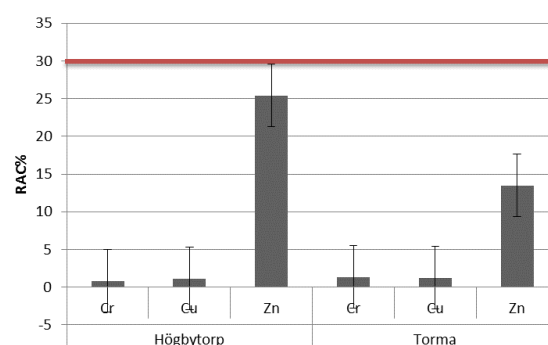


Figure 3. The risk assessment code (RAC) of Cr, Cu and Zn in the FFs of wastes sampled from Högbytorp and Torma landfills with the standard deviation and standard errors.

CONCLUSION

During this work the fractionations of Cu, Cr and Zn in the FFs of wastes sampled from Högbytorp and Torma landfills were studied. Specifying the concentrations of these three metals in each sequential extraction fraction is essential for evaluating: i) the environmental impacts by understanding the mobility, bioavailability and leaching of these metals, ii) the recovery potential of metals, and iii) the valorization of the fine fraction. The results showed that the majority of Cr and Cu were found associated to the residue fraction in the fines from the two landfills, which could be regarded as low mobility and hard for extractability. Noticeable concentrations of Cu were found bonded to the water-soluble (in both landfills) and acid-soluble (Högbytorp landfill) fractions. Metals bond to the water- and acid-soluble fractions are easy to be recovered compared to other fractions if possible extraction technique could be found or developed. At the same time, metals bonded to these two fractions are also regarded as potential hazards. The sequential extraction results revealed that Zn was distributed with significant concentrations in all the sequential extraction fractions, which could be considered as a potential risk (as the RAC results also shown) as well as a possible target for extraction. The fractionation of metals in the FFs of wastes displayed crucial information about the management needs of this fraction during any landfill reclamation projects in terms of environmental protection and valorization potential.

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Persian Abstract

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چکیده

دفع زباله های معدن و دفع زباله ها با (۴۰-۷۰ درصد جرم) کسر خوب ذرات کوچکتر از ۲۰ یا ۱۰ میلیمتر همراه است. عناصر خاکی و رقیق غلظت قابل توجهی به طور معمول در ترکیب این بخش غالب می شوند. در مقاله حاضر، روش استخراج سه مرحله ای اصلاح شده برای تجزیه Cu، Zn و Cr در کسری از ضایعات دفع شده از محل های دفن زباله Högbytorp (سوئد) و تورما (استونی) مورد استفاده قرار گرفت. نتایج نشان داد که غلظت های اصلی Cu (۹۸٫۸ و ۹۸٫۶٪) و Cr (۹۸٫۵٪ و ۹۸٫۴٪) به ترتیب در جایگاه های هگبیتورپ و ترمالا قرار دارند. این داده ها مربوط به کسر باقی مانده است. غلظت قابل توجهی از کروم و کروم نیز در داخل کسر محلول آب وجود دارد که می تواند به عنوان یک خطر بالقوه در نظر گرفته شود. Zn رفتار های مختلفی را با توزیع در تمام بخش های استخراج متوالی در قطعات ضخیم از دو دفن زباله نشان داد. مشخص کردن محتوای فلزات با استفاده از این روش برای کشف ارزش گذاری و نیز خطرات احتمالی زیست محیطی توسط این بخش های جریمه ضروری است.
