

Assessment of heavy metals in RDF for thermochemical conversion

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Abstract. Thermal treatment applications towards production of energy from raw and pre-treated municipal solid waste (MSW) are continuously growing context in contemporary waste-to-energy technology. The quality of MSW needs an improved analysis to enhance her choice of energy exploitation and environmental assessment of fly and bottom ashes associated with thermochemical conversions. The MSW were collected from municipal solid waste disposal facilities (MSWDF) in Cape Town to investigate heavy metals distributions in MSW. The MSW were pre-treated to improve the quality of MSW. The 7700 Series quadrupole ICP-MS solution method was used to determine concentrations and distributions of some heavy metals from MSWDF in Cape Town. This study further predicted distributions of heavy metals in fly and bottom ashes by a model. The results showed that accumulation of high concentrations of heavy metals in bottom ash residue could be a good remedy for heavy metals control. The heavy metals (especially Pb, Zn and Hg) emissions could be technically monitored and controlled from escaping to urban air-sheds atmosphere and prevent from their consequential secondary environmental and health implication.

1 Introduction

The contemporary solid waste management systems include waste collections and segregating followed by one or more of the following options: recovery of secondary materials by recycling of solid wastes, biological treatment of organic waste, production of marketable composts, and thermal treatments by various forms thermochemical conversions to recover energy in the form of heat and electricity and landfilling [1-8]. The application of the solid waste management systems in developing and under-developed countries are not fully employed to tackle the challenges of municipal solid wastes (MSW). The rate of production of MSW in developing countries demands paramount attention to tackle ever growing challenge of untreated amount of MSW in most developing and under-developed nations [9-11]. This is because the impacts are becoming serious in terms of lingering environmental challenges on (air, land, surface and subsurface water flow) as well as short and long-time health implications [1, 10, 12-14]. The classification of solid waste in some African countries are not conclusive because more than 48 million tonnes of solid wastes are still left unclassified. The order of 10 % of all solid wastes generated in South Africa was recycled in 2011. Landfilling of MSW releases GHGs and volatile organic compounds along with leachable toxic heavy metals to the surrounding environment [15-17]. The enormous emission of GHGs from some existing and closed landfilling site in South Africa is calling for thorough and serious solution [18, 19]. Okonkwo and Mothiba [20] found a high concentration of lead in the Madanzhe and Mvudi Rivers in Thohoyandou, South Africa, which was attributed to the effluent from a nearby sewage treatment plant and a waste dumping site.

These heavy metals contaminants pose severe health implication when released and find the way into the ecosystem. Similar experiences were observed by the following authors suggesting actions that might lead to the uncontrolled release of heavy metals into ecosystem through disposal of untreated incineration ashes and MSW [17, 19, 21-27]. Mangizvo [28] identified in a study of the Muccheke MSW dumpsite in Masvingo, Zimbabwe, that soil within a 50 m radius had been contaminated by trace metals of lead, iron, copper, zinc, and phosphorus. These heavy metals migration and temporal distribution concentrations of heavy metals contaminants [29-31] deserve further study to reduce the infiltration into the ecosystem. Moreover, incineration of MSW to generate energy is one of the traditional methods of dealing with combustible waste efficiently because it reduces the volume and mass of MSW. Although heavy metals are inert and give off no energy when they are incinerated, the high temperatures of a MSW furnace cause metals to partially volatilize, resulting in release of toxic poisonous fumes and fly ash [29-32]. In addition, it has drawbacks as well particularly hazardous emissions (NO_x, SO_x, HCl and harmful organic compounds) [14, 33-35] and harmful process residues [36]. Incineration of MSW generates fly and bottom ashes which release leachable toxic heavy metals, dioxin, furans and volatile organic compounds [24, 25, 29, 37]. The thermal treatments may be very promising remedy for control dangerous emission of furan, dioxin and other harmful emissions but choice of the thermochemical conversion is very important. The results data of heavy metals concentrations in pre-treated MSW were presented and discussed also determination of spatial distribution of heavy metals in bottom ash residues was obtained via model used by the studies of Belevi and Moench [38] and Yao, Li, Kong, Wu, He and Shen [23]. The focus of this study was to quantify the distribution of

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these heavy metals (Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Mo, Ni, Pb, and Zn) present in various MSWDF in Cape Town.

2 Methodology

2.1 ICP-MS solutions method

The MSW samples were collected from solid waste disposal facilities (SWDF) around the settlements in Cape Town. They are Kraaifontein, Athlone, Woodstock, Tygerdal, Belhar, Killarney, Wynberg, Macassar, Delft, Welengen, Ladies Mile, Retreat and Coastal Park (KF, ARTS, WS, TG, BL, KL, WY, MC, DF, WG, LM, RT, and CP). The MSW were pre-treated, shredded again, milled and sieved at a specific mesh (2 - 5 mm) this was to ensure that MSW was properly homogenized. The pre-treated MSW samples (0.25 - 0.40g) were first digested with USEPA standard procedure for digestion was used. The procedures normally use acid and heat to break organo-metallic bonds and free ions for analysis. The ICP-MS solution method was used to determine heavy metals (Al, Fe, Zn, Cu, Cr, Mn, Co and Hg) concentration in MSW. The 7700 Series quadrupole ICP-MS from Agilent Technologies provides an unmatched combination of high performance and simplicity of operation, redefining the benchmark for ICP-MS.

3 Results and discussion

The heavy metals concentrations in pre-treated MSW measurement were considered in order to evaluate modelled environmental implications during and after thermochemical conversion. This was necessary to prepare for mitigation procedures to corrosion and emissions that maybe exposed to environment after disposal residues containing heavy metals (except Hg and Cd) within the thermochemical conversion process, its residues and disposals. In this study, the main composition of MSW was categorized to combustible and non-combustible substances. Heavy metals found in MSW have fundamental implications on production of fly and bottom ash and their disposals. They might be responsible for fouling effects, corrosion and pollutant emissions during thermochemical reactions [39].

3.1 Heavy metals and environment

The heavy metals are found naturally in the environment and are released from a range of anthropogenic activities such as combustion processes. Though some studies had been conducted, there is need to know more on heavy metals distributions in pre-treated MSW relating to thermochemical conversions [1, 8, 31, 36, 40-44].

Environmental impacts of heavy metals behaviour during thermochemical conversion were also discussed.

Nonetheless, there is dearth of studies on availability and spatial distribution of heavy metals in Cape Town MSW.

3.2 Quantification of heavy metals in pre-treated MSW

The overall concentrations of the heavy metals in pre-treated MSW obtained from the MSWDF in Cape Town were summarily presented in table 1 and figure 1. Al and Fe concentrations data from MSW were the highest for obvious reason and similar to the range usually obtained in most soil samples. Both concentrations showed a wide range of high concentration which was very significant for MSW. These concentrations may not be seriously affect thermochemical implication but contribution to base line earth natural concentrations which might be point of concern (figure 1). The Cd concentration was noticed to have had widest range of concentration but there was odd relations with one facility have extremely high concentration of Cd compared to others. The average concentrations of heavy metals were pre-treated MSW samples were in the following order of concentrations; Al > Fe > Cr > Zn > Mn > Ba > Ni > Cu > Pb > Co > V > As > Mo > Sb > Cd > Se > Hg unlike the study of Haiying, Youcai and Jingyu [24] which reported this order of heavy metals from MSW incineration Plant showed that content of heavy metals follows the sequence of Zn > Pb > Cu > Cr > As > Ni > Cd. Highest concentrations of heavy metals were observed in Al, Fe, Zn and Cr were 13508.10 mg/Kg (CP), 10230.40 mg/Kg (KF), 316.14 mg/Kg (TG), and 312.60 mg/Kg (KF) respectively. These heavy metal quantifications were shown in table 1 while other remaining quantifications of heavy metals were also presented in figures 1 - 6 respectively. Relatively high standard deviation was observed among all the heavy metals content of pre-treated MSW except for Sb while Al and Fe (figure 2) were unusually high compare to other heavy metals as earlier observed for apparent reason. This might be due to heterogeneous distribution of the heavy metals in all the sampling locations.

The heavy metal concentrations from pre-treated MSW were compared with that of soils. The concentrations of heavy metals obtained were quite below the recommended for residential, industrial and commercial locations in china [23]. The results indicated that the average values of all the heavy metals from all the pre-treated MSW were within the standard limits [45]. However, useful application through possible recovery of these heavy metals may be considered depending on the concentration of heavy metals in MSW among other factors.

Table 1. Concentrations distribution of heavy metals in pre-treated MSW in Cape Town

Heavy Metals	Concentrations Range (mg/Kg)	Mean Concentrations (mg/Kg)	Standard Deviation
Fe	788.01 - 10230.40	4978.294	2731.064
Al	593.44 - 13508.10	5220.651	3403.408
Zn	67.76 - 316.10	156.154	62.249
Cr	66.44 - 312.60	171.694	69.576
Mn	57.96 - 199.10	109.169	38.603
Ni	27.03 - 122.50	72.727	27.406
Cu	15.81 - 134.40	50.563	33.588
Co	6.12 - 100.00	26.743	21.764
As	2.23 - 103.50	12.616	25.490
Sb	0.18 - 3.00	1.390	0.799
Cd	0.13 - 96.30	7.720	24.779
Hg	0.04 - 105.30	7.173	27.151
Pb	9.41 - 97.50	35.256	26.811

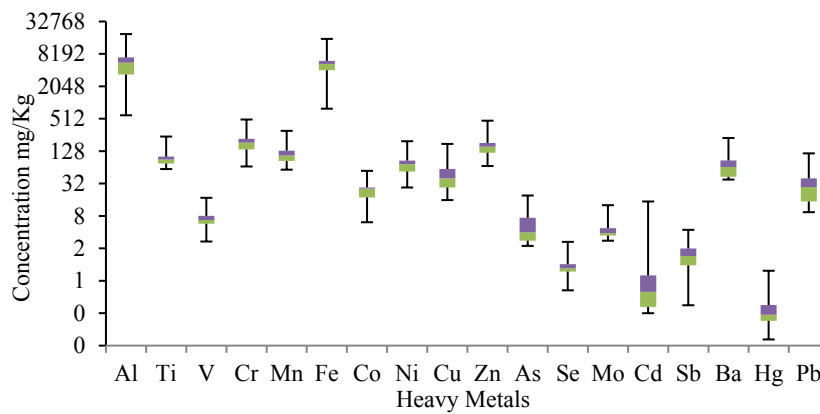


Figure. 1. Log plot distributions of heavy metals concentrations in pre-treated MSW from SWDF in Cape Town

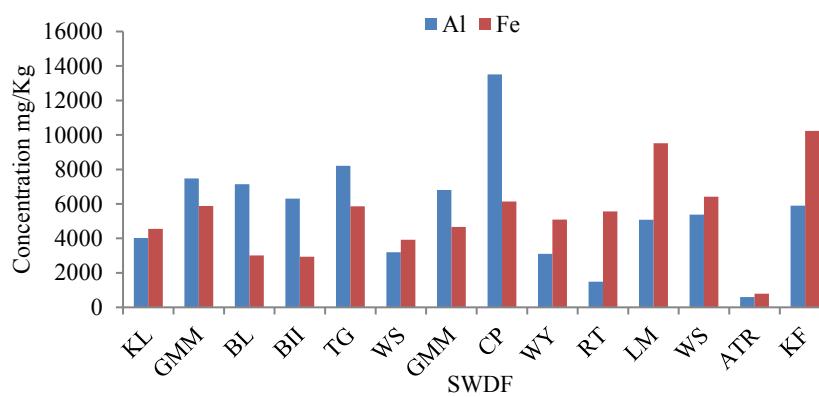


Figure. 2. Al and Fe concentrations in pre-treated MSW from SWDF in Cape Town.

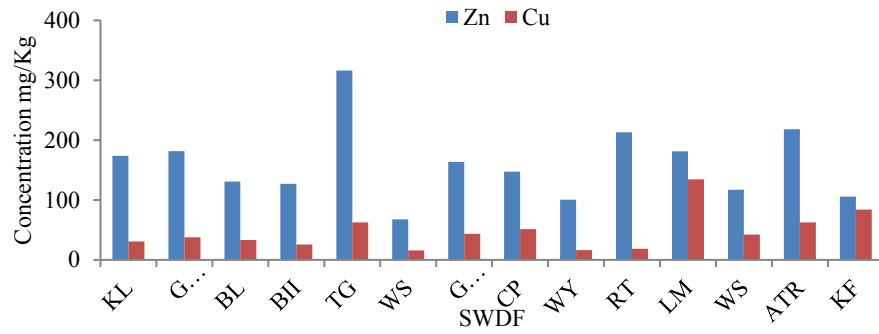


Figure 3. Zn and Cu concentrations in pre-treated MSW from SWDF in Cape Town.

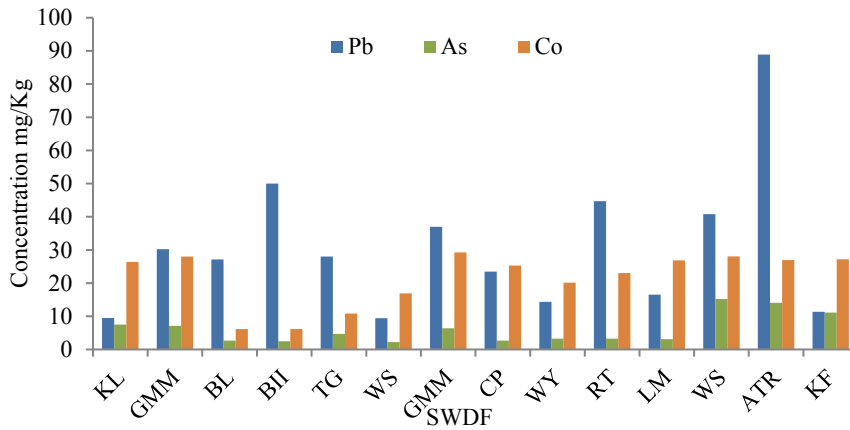


Figure 4. Pb, As and Co concentrations in pre-treated MSW from SWDF in Cape Town.

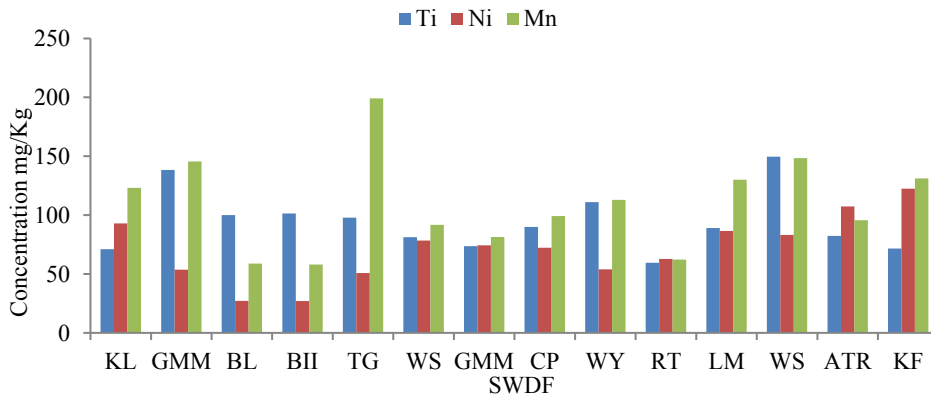


Figure 5. Ti, Ni, and Mn, concentrations in pre-treated MSW from SWDF in Cape Town.

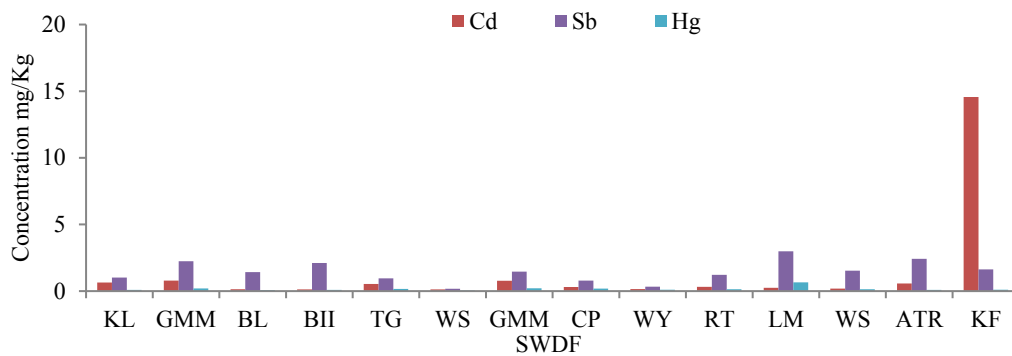


Figure 6. Cd, Sb, and Hg concentrations in pre-treated MSW from SWDF in Cape Town.

3.3 Quantification of heavy metals in bottom ash

Apart from likely catalytic contribution of some compounds of heavy metals (Alkali metals, Al, Ti) available in pre-treated MSW, most heavy metals will be concentrated in both fly and bottom ashes. Studies had reported larger fractions of heavy metals fractions concentrated in bottom ashes and most of these heavy metals may be recovered [23, 26, 38, 41, 46-49]. Generally bottom ashes contain SiO₂, CaO, Al₂O₃, Fe₂O₃, Na₂O, K₂O and MgO [46-48]. The study of Yao, Li, Kong, Wu, He and Shen [23] on distribution of heavy metals between fly and bottom ashes using transfer coefficient and they concluded that the average range of transfer coefficient for Cu, Cr, Mn, Ni, Cd, Co, As, Mo, Pb, and Zn range between 0.533 and 0.947 for As and Mn respectively. Also the study of Belevi and Moench [38] investigated group of eighteen heavy metals and non-metals show a range of 0.120 - 0.989 for heavy metals and for non-metals. However the transfer coefficient of Hg for both studies are significantly low or negligible (almost not detected). This showed Hg had been completely transferred to fly ashes. The following studies [23, 26, 46-52] used incineration towards waste-to-energy technology with untreated MSW. Most of the studies recommended pre-treatment in the form of source re-classification of MSW [53] to enhance the quality of bottom ash residue for effective heavy metals recovery.

Yao, Li, Kong, Wu, He and Shen [23] reported some studies on heavy metals concentration distribution in MSW thermochemical conversion plant were mostly concentrated into the bottom ash residues during the incineration process. The reports indicated heavy metals like As, Fe, Cu, Cr, Pb, Co, Ni and Zn were highly concentrated mainly in the bottom ash residues with up to an average of 80%. However, special attention was paid to these metals Cd, As, Cu, Cr, Pb and Zn because of proven high toxicity to the environment. This relation below was used to quantify possible heavy metals that will

Table 2. Calculated heavy metals concentrations in bottom ashe residue

Heavy Metals	HMCBAIJ Min (mg/Kg)	HMCBAIJ Max (mg/Kg)
Al	1890.106	43023.29
Cr	218.5813	1028.547
Fe	2727.698	35412.6
Co	18.85146	307.9555
Ni	90.82455	411.6455
Cu	53.11093	451.5965
Zn	101.9803	475.789
As	5.922989	275.2099
Mo	8.370719	301.7468
Cd	0.043768	33.70738
Hg	0.002848	7.372194
Pb	14.48866	150.0975

be transferred to bottom ash residue during and after thermochemical conversions [23, 38].

$$K_{ij} = \frac{C_{BAij} * R_j}{C_{wij} * (1 - y_j)} \tag{1}$$

Where K_{ij} was the transfer coefficient of the heavy metal i from the input MSW to the bottom ash of location j . C_{BAij} was the content of the heavy metal i in the bottom ash of city location j (mg/kg dry weight). C_{wij} was the content of heavy metal i in the input MSW of location j (mg/kg dry weight). R_j was the bottom ash mass production ratio of the incinerator in location j , which was about 0.2 - 0.3. y_j was the water ratio of the input MSW of the incinerator in location j . The results data obtained for quantification of heavy metals in bottom ash residue through that model equation related above were presented in table 2. Using coefficient of transferred from the studies of Belevi and Moench [38] and Yao, Li, Kong, Wu, He and Shen [23] the quantity of heavy metals obtained had substantial decreased and transferred to bottom ash (tables 2 - 3). Litophilic characteristic made some heavy metals (Al, Cr, Cu, and Fe) to remain in bottom ash. All the heavy metals have significant presence in bottom ash except Sb and Hg. This is similar to previous studies mentioned early in the discussion. The result data presented in table 2 is substantially lower than that of Yao, Li, Kong, Wu, He and Shen [23] and [31], Jung, Matsuto, Tanaka and Okada [54] for set of heavy metals except for Co, Mo and Ni while the study of Hu *et la.* [55] presented lower value for Cu and Cd, Pb and Zn were higher. The distribution of heavy metals during thermochemical conversion have significant variance depending on the choice of reactions mechanisms [30, 32, 43, 44]. Heterogeneity of the raw MSW was expected to be main factor for this wide difference in concentrations. The heterogeneous characteristics were reflected with high concentration of some heavy metals such as Cr, Cu, Mn and Zn.

Table 3. Heavy metals concentrations in bottom ash from literature [54]

Heavy Metals	HMCBAIJ Min (mg/Kg)	HMCBAIJ Max (mg/Kg)
Al	10600 - 43420	147000 - 68060
Cr	6.6 - 60	2260 - 256
Fe	500 - 22000	200000 - 86800
Cu	77 - 414	13200 - 3720
Zn	500 - 1280	33000 - 4800
As	0 - 0.1	93 - 3.5
Cd	0.04 - 0.8	91 - 14
Sb	5 - 37	306 - 192
Hg	0.001	5.5
Pb	8 - 140	10900 - 1320

High transfer coefficients indicate the heavy metals are mainly transferred to the bottom ash. Though Hg has potential environmental health risk but the amount is expected to be below required standard for emissions. Also, some bottom ashes heavy metals (Cd, Cu, Pb, and Zn) are regarded as relatively unstable, thus it will be very crucial to conduct further studies for recovery and reuse of the heavy metals to avoid contamination of immediate ecosystem and bio-toxicity.

4 Conclusions

The accumulation of high concentrations of heavy metals in bottom ash residue from thermochemical conversion could be a good remedy for heavy metals control. The heavy metals (Pb, Zn and Hg) emissions were

technically monitored and controlled from escaping to urban air-sheds atmosphere and prevent from their consequential secondary environmental and health implication. The thermochemical technology hence offers heavy metals emission mitigation to uncontrolled emission from open-air incinerations and the likes. This study pre-treated all the samples of MSW used for its heavy metals quantification before and after thermochemical conversion and it was shown in the concentrations of the heavy metals found in all the samples falling behind all those obtained in incinerator without sorting or pre-treatment of MSW. However, before disposal or reuse of bottom ash residue, the residue will require further evaluation study for potential environmental impacts. This will be helpful for crucial considerations for policy and decision maker on heavy metals mobility in MSW thermochemical conversion technology from cradle-to-grave in Cape Town.

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