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# A Study on Sugar Mill Pressmud Compost for Some Heavy Metal Content and their Bio-availability

Bhupander Kumar<sup>1\*</sup>, Sanjay Kumar<sup>1</sup>, Dev Prakash<sup>1</sup>, S. K. Singh<sup>1</sup>, Meenu Mishra<sup>1</sup>, P. K. Jain<sup>1</sup>, R. B. Lal<sup>2</sup>, C. S. Sharma<sup>1</sup> and D. P. Mukherjee<sup>3</sup>

<sup>1</sup>Central Pollution Control Board, East Arjun Nagar, Delhi, India <sup>2</sup>HSM Division, Ministry of Environment & Forest, Lodhi Road, Delhi, India <sup>3</sup>Central Pollution Control Board, Rajdanga Main Road, Kolkata, India

# ABSTRACT

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In this study, the content of heavy metals (zinc, manganese, iron and aluminum) has been analysed, and their bioavailability was assessed using extraction method. The total heavy metal concentration was in order as: Fe>Al>Mn>Zn and the average concentration was 115 µg g<sup>-1</sup>, 288 µg g<sup>-1</sup>, 6169 µg g<sup>-1</sup> and 2233 µg g<sup>-1</sup> dry weight for Zn, Mn, Fe and Al, respectively. Watersoluble percentages of heavy metals are quite low (<0.01 – 0.79%), but the presence of chelating agents in the samples increase the bio-availability of heavy metals (22-89%). The most bioavailable heavy metals were Zn, Mn and Fe as their potential availability is high with 90%, 78% and 48%, respectively. The concentration of the heavy metals does not exceed the recommended reference values. Further, it is suggests that pressmud compost does not shows heavy metal pollution, besides a good source of soil elements and organic matter to the agricultural land.

Keywords: heavy metal, pressmud compost, Bioavailability.

# **INTRODUCTION**

Contamination of soils with heavy metals is of environmental concern because the accumulated metals may adversely affect soil ecology, agricultural production, product quality, animal and human health as well as groundwater quality [1]. Indeed, unlike organic contaminants, most heavy metals do not undergo microbial or chemical degradation and therefore total concentrations and ecotoxicological effects persist for very long periods after their introduction to the soil. The addition of an amendment to the soil increases the proportion of total metal burden within the intransigent solid phase, either by increased metal precipitation or sorption, thereby reducing the soluble and exchangeable metal fractions. That is, the contaminant metals are rather transformed into forms less biologically available. Reported waste materials trialled as

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amendment agents include fly ash, blast furnace slag, steel slag, red mud, bark/sawdust, animal manures, composted wastes and pressmud compost [2-4].

Increasing regulation of the burning of crop residues and processing by-products has stimulated interest in the utilization of composted agricultural processing by-products as soil amendments and horticultural growing media [5-7]. Composting is an effective method for changing organic solid waste into fertilizer that is rich of nutrients. Many types of waste, such as straw, leaves, sludge, manure, faeces and so on, are suitable for composting. Because compost is biologically more compatible than chemical fertilizers for soils and plants, composting has become a preferred choice for treating organic solid waste. Physical improvements in soils amended with composts through added organic matter appears to be the greatest potential benefit as a partial fertilizer substitute for N, P and K.

However, the wide distribution of heavy metals in soil, water and atmosphere, make the raw materials for compost possible sources of heavy metal pollution [8-11]. Their existing formations can be changed by materials such as lime, which are added to compost materials [12]. After their introduction into the soil, the mobility or bioavailability of heavy metals in compost can be altered by many factors arising simultaneously from soil, plants or rain [13-15].

In India, Sugar industry with 571 sugar mills is the major agro-industry in the country and produced 24.5 million tons of sugar during 2010-11[16]. About 500 tons of industrial wastes (liquid and solid) are discharged daily from sugar factory during crushing season as Pressmud, boiler ash and distillery waste water [17]. Pressmud is a solid waste by-product of sugar-mill and about 3% produced from total quantity of cane crushed. Pressmud is a rich source of organic carbon, NPK and other micronutrients [18]. Several studies have been conducted on Pressmud for its suitability to use in agriculture and for energy production [19-25]. The purpose of this study was to investigate the sugar mill Pressmud waste for bioavailability of some heavy metals.

# MATERIALS AND METHODS

## Sampling

Compost samples collected from a sugar mill in north Bihar, India. Samples in duplicate collected from different compost pits and after removing the sticks and pebbles, samples mixed thoroughly and an aliquot was taken into a pre-cleaned plastic bags. The collected samples were labelled and then transferred to the laboratory for further chemical processing.

## Treatment of samples

**Total metals:** Wet samples in triplicates were processed as per USEPA method 3050 [26]. Briefly, five grams of sample was placed in a 50 ml screw-capped centrifuge tube, and 30 ml of digestion acid and  $H_2O_2$  was added and digested at  $90^{\circ}C$  for 30 min. The samples were centrifuged, and the supernatant was filtered through Whatman No 42 filter paper and analyzed for metal contents by Flame Atomic Absorption Spectrometry (FAAS). Moisture contents were calculated to report the results on dry weight basis.

*Bio-available metals:* The single extraction method was adopted after MAFF [27]. 5 g sample was extracted with 50 ml of deionised distilled water and 0.05M EDTA (pH 7.0), respectively in

a shaker for one hour at  $25^{\circ}$ C and centrifuged. The supernatants were carefully transferred to plastic bottles and analyzed by FAAS.

*Organic Carbon*: The estimation of organic carbon was made after Walkley and Black [28]. One g dry sample was digested with potassium dichromate solution and sulphuric acid for 30 min at room temperature. Digested mixture was diluted to 200 with distilled water and phosphoric acid with ammonium fluoride was added, then after addition of diphenylamine solution as indicator titrated with ferrous ammonium sulphate solution. Organic carbon was calculated and reported on percent basis.

## Instrumental analysis

Concentrations of Zn, Mn, Fe and Al were measured by Flame Atomic Absorption Spectrometry (FAAS, Thermo UK) using individual hollow cathode lamps and by applying background corrections whenever required with deuterium lamp. The method of standard additions was used to compensate for matrix effects.

Heavy Metals	Reference value	Massurad value*	Pecovery (%)	CV(+%)
Tieavy wietais	Reference value	Weasured value	Recovery (70)	$CV(\pm 70)$
Zinc	289	312	108	8
Manganese	582	644	111	11
Iron	16500	13771	96	4
Aluminum	11,400	10,851	95	5
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Table 1: Concentration (µg g<sup>-1</sup>) of measured heavy metals in certified standard reference material (SW-8022)

*Note:* \* *denote average of three replicate* 

#### Analytical quality control

Performance of the instrument was checked by analyzing the standard reference material solutions (Merck NJ, USA) concurrently to check the precision of the instrument. After appropriate dilutions of stock standard solutions a five level calibration curve was prepared. Samples were analyzed in triplicate. The values obtained from the sample then corrected for final digestion volume and sample weight taken. The results were reported on dry weight basis. The detection limits for Zn, Mn, Fe and Al was 0.01, 0.05, 0.06 and 0.30 mg  $1^{-1}$ , respectively. Duplicate method blanks were also processes and analyzed alongside the samples to check any loss or cross contamination. A certified reference material (SW 8022) was processes along with samples to determine the accuracy of the method and the results were comparable to the acceptable limits (Table 1). In this study, Fe and Al were less than the certified values (- 4% to - 5%) while, Zn and Mn were above than the certified values (+8% to +11%).

## **RESULTS AND DISCUSSION**

## Total metal concentration

The concentrations of total metals in compost samples are presented in Table 2. The order of abundance of metals was observed as: Fe > Al > Mn > Zn, which follows a natural progressive concentration of heavy metals [30].

Metals	Range		$M_{con} \mid SE^1$	$C V^2$
	Min	Max	WICall±SL	Cv
Zinc	103	131	115±2.83	7.42
Manganese	273	306	288±4.21	4.39
Iron	5807	6467	6169±84.62	4.11
Aluminum	1683	3159	2233±172.60	23.19
OC	13.20	14.60	$13.92 \pm 0.14$	3.04
<sup>1</sup> standard error= SD/ $\sqrt{n}$ , <sup>2</sup> CV= Coefficient of variation				

Table 2: Range and mean of heavy metals (µg.g<sup>-1</sup>) and organic carbon (%)

The average concentration of zinc, manganese, iron and aluminum was;  $115\pm2.83 \ \mu g \ g^{-1}$ ,  $288\pm4.21 \ \mu g \ g^{-1}$ ,  $6169\pm84.62 \ \mu g \ g^{-1}$  and  $2233\pm172.60 \ \mu g \ g^{-1}$ , respectively. The observed concentration ranges between103-131  $\ \mu g \ g^{-1}$ ,  $273-306 \ \mu g \ g^{-1}$ ,  $5807-6467 \ \mu g \ g^{-1}$  and  $1683-3159 \ \mu g \ g^{-1}$  for Zn, Mn, Fe and Al, respectively. The observed concentrations of the metals were compared with earth's background values [30-31] and found to be lower than background levels, except zinc (Table 3).

Table 3: Comparative analysis of results with earth's metal concentration ( $\mu g g^{-1}$ )

Motol	Earth's Metal	Present	
Ivicial	Cont. Crust [30]	Shale value [31]	Study
Manganese	950	850	288
Iron	50000	47200	6169
Zinc	70	95	115
Aluminum	81300	80000	2233

As pollution point of view, the disposal of these composts may induced the levels of heavy metals in soils of landfill or dumpsites, on the other hand, would be useful as nutrient to the agricultural soils. An evaluation of total metal levels in the soils may be useful as an index of contaminations, but it provides little or no indication of their bioavailability, mobility and reactivity. As such, extraction of metals may help to assess the bioavailability and possibility of mobilization of metals in the compost.

Table 4: Range and mean of heavy metal concentrations (µg.g<sup>-1</sup>) extracted from samples by water and EDTA

Metals -	Water -extractable		EDTA -extractable	
	range	mean±SE	range	mean±SE
Zinc	0.17-0.86	$0.44\pm0.08$	88-112	$102\pm2.77$
Manganese	0.41-4.47	$2.22\pm0.48$	211-225	221±1.48
Iron	4.63-6.73	5.50±0.24	2617-3146	2962±60.32
Aluminum	BDL		367-607	473±31.76

#### **Bio-available fraction of heavy metals**

Water and EDTA extractable metals and their percentage of their 'total' are presented in Table 4 and Table 5. Water extractable phase contains most mobile and bio-available metals [32], whereas EDTA is capable of extracting metals in non silicate bound phase, where silicate bound metals are considered as residual metals. The percentage of water extractable fraction of metals were very less and it was 0.39 (range, 0.16-0.79), 0.79 (range, 0.14-1.64) and 0.09 (range, 0.08-0.11) percent for Zn, Mn and Fe, respectively, whereas, Al was not extractable by water. EDTA

extracts much higher percentage of metals compared to water. The average percentage of EDTA extracting efficiency for Zn, Mn, Fe, and Al was 89.17, 77.25, 48.08 and 22.60, respectively.

The other reports also shows that water is less capable in extraction of metals, but the presence of chelating agents (such as soluble organic species) increase the metals extractability and make them bioavailable to the biota and into the food chain [32-33]. Results of present study show that most mobile, readily bioavailable water-soluble percentages of metals are quite low (< 2%) while addition of chelating chemicals (i.e. EDTA) may induced extractable fraction of the metals (22 - 89%), which may be available to the biota.

### **Residual fraction:**

The residual fraction is concerned with the most stable and least bioavailable of all the chemical fractions of the soils, since it is believed that metals are occluded within the crystal lattice of silicates [34].

Metals	Water -extractable		EDTA -extractable	
	range	mean±SE	range	mean±SE
Zinc	0.16-0.79	$0.39\pm0.07$	82.57-96.90	89.17±1.58
Manganese	0.14-1.64	$0.79\pm0.18$	69.79-81.79	$77.25 \pm 1.52$
Iron	0.08-0.11	$0.09\pm0.01$	43.23-52.74	$48.08 \pm 1.15$
Aluminum	-	-	14.38-34.85	$22.60 \pm 2.83$

 Table 5: Range, mean of heavy metals (percent of their 'total') extracted from samples by water and EDTA

The residual fraction of the soil is a major carrier of metals in most aquatic environmental systems. The percent of this fraction can be taken as a guide to the degree of non-availability of metals to biota. The metals of the residual fraction are usually considered to be fragments of the primary mineral phase. All other fractions can be of secondary mineral phases as they involve materials formed through physical and chemical processes of weathering of primary minerals. This fraction is not available to biological or diagenetic processes except over long time scales [35-36]. The smaller the percentages of the metal present in this fraction, the greater the pollution of the area. In all the samples analyzed in the sugar mill composts, Al (77%), Fe (52%) and Mn (22%) were the predominant metals of this fraction (Figure 1). Zinc in this fraction was relatively small (10%). The relatively small amount of Zn and Mn in this fraction indicates their high mobility and therefore high environmental contamination risk.



Figure 1: The available and non-available concentrations of heavy metals in compost samples from sugar mill Note: Available= sum of water and chelating agent extracting metal fractions. Non-available= fraction of total metals-available fraction.

#### Inter-Metal Relationship

Inter-heavy metal correlations in the compost samples were investigated and the results were presented in Table 6. The Pearson's moment correlation coefficient was used to measure the strength of the association between heavy metal concentrations and organic carbon and presented in correlation matrices [29]. The *p*-values of less than 0.1 and 0.05 were considered to indicate statistical significance. The correlations between the different metals may result from the similar accumulation behaviour of the metals in the composts and their interactions. Noted significant correlations among metals may reflect a common source of occurrence and indicative of similar biogeochemical pathways for subsequent geo-accumulation in the compost.

Table 6: Pearson's moment correlation coefficients between heavy metals and organic carbon in compost samples.

	Mn	Fe	Al	OC
Zn	-0.397	$0.541^{a,b}$	-0.482	-0.005
Mn	1.000	0.030	0.931 <sup>a,b</sup>	-0.312
Fe		1.000	0.312 <sup>a</sup>	$0.450^{a, b}$
Al			1.000	0.493 <sup>a, b</sup>

Note: significant correlations at p < 0.1 are mark as <sup>a</sup>, and at p < 0.05 are mark as <sup>b</sup>

In the present study, manganese is strongly correlated with zinc and aluminum. Organic carbon showed high correlation with iron and aluminum. No other significant correlation was observed between studied heavy metals.

#### CONCLUSION

The results showed that the concentration of analysed heavy metals were lower than recommended values. Single extractions study shows that trace elements were not readily available as indicated by the water extraction experiment, but the presence of chelating agents in sediments can render the metals more bioavailable. Therefore, it is suggested that during composting of pressmud, some chelating agent should be applied for leaching of metals considering safe use in agriculture.

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