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# Source Analysis of Heavy Metals and Arsenic in Organic Fractions of Municipal Solid Waste in a Mega-City (Shanghai)

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Heavy metals and arsenic contamination in municipal solid waste (MSW) and its treatment products has garnered increasing attention. This study investigated the heavy metals and arsenic flows in organic fractions of MSW (OFMSW) in Shanghai, China, through a one-year monitoring program. The OFMSW separated directly from the source (sourceseparated, pure organic waste), obtained from the treatment facilities were sampled and compared with pure foodstuffs. The heavy metals and arsenic contents in the source-separated OFMSW resembled those in foodstuffs, whereas the OFMSW from the treatment facilities was significantly contaminated with heavy metals and arsenic and failed to meet the government standards for land use. Using flow analysis, >80% of heavy metals and arsenic were from extrinsic inorganic waste with high ash content that was combined with OFMSW during MSW collection, transfer, transportation, and storage stages. Based on source analysis of heavy metals and arsenic, suggestions for reducing heavy metals and arsenic contents in the current MSW management system in Shanghai are presented.

### Introduction

Municipal solid waste (MSW) can be reused to enrich soil following composting or digestion (1), or as fuel in incinerators for energy recovery. Heavy metals and arsenic contents are of great concern to MSW management (2, 3). The organic fraction of biological origin in MSW collected separately at the source (source-separated), or mechanically/manually separated at centralized treatment facilities (centrally separated) is widely adopted to recover valuable materials, improve MSW disposability, and alleviate pollution risk that collected MSW poses to the environment. Organic compost from centrally separated MSW frequently fails to meet the heavy metals and arsenic standards set by different governments (4, 5).

Richard and Woodbury (6) examined the impact of various separation strategies for organic fractions of MSW (OFMSW), including source separation prior to collection, wet or dry

collection schemes, and manual or mechanical central separation, on heavy metals concentrations in MSW compost. Richard and Woodbury determined that source separation of compostable materials generated the lowest levels of contaminants among all procedures examined. Epstein et al. (7) identified a significant difference in Cd, Pb, Cu, and Zn contents between mixed MSW compost and source-separated organic waste compost.

Veeken and Hamelers (8) demonstrated that heavy metals in biowaste were associated with organic particles sized 0.05–1 mm and organo-mineral particles sized <0.05 mm. Hseu (9) determined that Zn and Pb were bound to compost particles sized <1 mm. Veeken and Hamelers (5) claimed that the excess heavy metals in biowaste-compost might be from natural backgrounds (soil organic matter, soil minerals, plant materials, food products). Amlinger et al. (10) hypothesized that food waste was primarily contaminated by adhering soil particles (e.g., for root crops) or atmospheric deposition during processing. García et al. (11) also proposed without experimental proof that high heavy metal levels in household refuse were attributable to its inorganic fractions generated by substances such as cans, sand, metals, and particles.

Heavy metals and arsenic in the OFMSW determine the potential use of MSW-derived compost as fertilizer and influence pollution control efficiencies in subsequent incineration or landfilling. Most empirical studies investigated contaminant levels in compost yielded from MSW (12) or in byproducts from MSW incinerators (13, 14). Few studies investigated "contaminants flows" in OFMSW collection and treatment systems, applicable to small towns or mega-cities (with > 10 million residents), which could assist policy makers in eliminating the major contaminant sources and effectively modifying MSW collection/treatment practices.

This study presents a network analysis that considers contaminant flows in the OFMSW generated by a typical mega-city which has integrated treatment facilities (incinerators, composting plant, and landfills). This proposed analysis can be easily modified or simplified to accommodate specific MSW management system and waste fractionation methods. The MSW management system in Shanghai, China, was monitored for one year and used as an illustrative example for the network analysis proposed in the next section.

#### **Materials and Methods**

#### Setup of Contaminant Flow in a MSW Management System.

In mega-cities, an integrated management system is typically adopted to deal with MSW from diverse sources (residential, institutional, commercial, and industrial, as well as that from street sweeping and maintaining urban green land) using various treatment and disposal facilities (composting, anaerobic digestion, incineration, and landfilling). Transfer stations are typically utilized as intermediate handling stations that facilitate MSW transfer. For mixed-waste collection systems, central mechanical or manual sorting for recyclable waste and noncombustibles is generally applied prior to composting or anaerobic digestion. The mechanical separation system for organic waste can be bypassed when a source separation system is adopted by households and restaurants. MSW can be categorized as different types, such as organic and inorganic fractions for biological treatment, combustible and incombustible fractions for incineration, or phases (vapor, liquid, solid) for disposal.

The proposed network for contaminant flows in a MSW management system, including collection, handling, treatment and disposal, is presented in detail in the Supporting Information. The network for MSW management comprises

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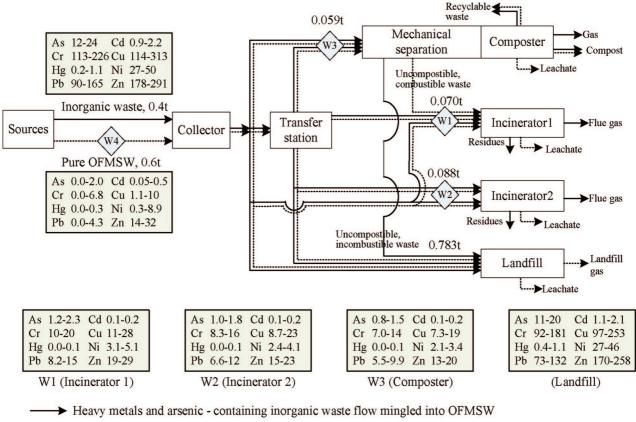


FIGURE 1. Schematic diagram and mass balance of the heavy metals and arsenic flows (g-heavy metals and arsenic/t-OFMSW by dry weight) in OFMSW in Shanghai. W1, W2, and W3 are samples from the incinerator 1 and 2, and the composting plant. W4 denotes the pure organic waste sample.

a number of nodes that represent sources generating MSW, and handling, treatment, and disposal facilities. Nodes are interconnected, through which contaminants migrate. When heavy metals and arsenic are the target contaminants (Figure 1), the mass of heavy metals and arsenic input to treatment and disposal node i from node i - 1 is equal to that from the source node which is finally transported to node i:

$$\overline{C}_{i_{\rm in}}^{\rm x} \times \sum w_{i_{\rm in}} = \overline{C}_{{\rm org} \cdot i_{\rm source}}^{\rm x} \times \sum w_{{\rm org} \cdot i_{\rm source}} + \overline{C}_{{\rm inorg} \cdot i_{\rm source}}^{\rm x} \times \sum w_{{\rm inorg} \cdot i_{\rm source}}$$
(1)

$$\sum w_{i_{\rm in}} = \sum w_{{\rm org} \cdot i_{\rm source}} + \sum w_{{\rm inorg} \cdot i_{\rm source}}$$
 (2)

where  $\overline{C}_{i_{\rm in}}^{\it x}=$  the average concentration of heavy metal  $\it x$  or arsenic in all waste flows input to node  $\it i; \, \overline{C}_{{\rm org}.i_{\rm source}}^{\it x}$  and  $\overline{C_{\text{inorg-}i_{\text{course}}}^x}$  = the average concentrations of heavy metal x or arsenic in organic and inorganic waste from the source, which is finally transported to node *i*;  $\sum w_{i_{in}} =$  the total quantity of waste input to node i;  $\sum w_{\text{org-}i_{\text{source}}}$  and  $\sum w_{\text{inorg-}i_{\text{source}}}$  = the total quantities of organic and inorganic waste from the source, and is finally transported to node i.

In this work, heavy metals and arsenic in pure organic waste (source-separated OFMSW) and the organic fraction separated from mixed MSW (centrally separated OFMSW) are denoted as  $\overline{C}_{\text{org-}i_{\text{source}}}^{\text{x}}$  and  $\overline{C}_{i_{\text{in}}}^{\text{x}}$ , respectively. Based on eqs 1 and 2, the heavy metals and arsenic flows from organic waste origin  $(\overline{C}_{\text{org-}i_{\text{source}}}^{\text{x}} \times \Sigma w_{\text{org-}i_{\text{source}}})$ , and from other origins  $(\overline{C}_{\text{inorg-}i_{\text{source}}}^{\text{x}} \times \Sigma w_{\text{inorg-}i_{\text{source}}})$ , can be estimated to clarify the contamination flow of the OFMSW during MSW management processes.

Sample Collection. The MSW samples in Shanghai were collected monthly from two incinerators with capacities of 1200 t/d and 1500 t/d, and one composting plant (1000 t/d) with a two-stage composting process during October 2004 to September 2005. These treatment facilities accept MSW from households, commercial and industrial sources, institutions, and that generated from sweeping streets and maintaining urban green lands.

For each sample, 100-150 kg of mixed MSW was collected from randomly selected locations in MSW pits in the incinerators or in precomposting piles at the composting plant prior to treatment. Plastics, paper, wood, textiles, metals, construction and demolition (C&D) debris, and glass were separated from the collected waste and weighed. The resulting residual waste was collected and treated as OFMSW<sub>end</sub>, namely, W1 and W2 (from the two incinerators), and W3 (prior to two-stage composting) (Figure 1). The three series of 12 samples were similar in terms of source (about 70% of the MSW were from residential areas, and 30% were from commercial, institutional and industrial areas), processing  $(collector \rightarrow transfer station \rightarrow MSW pit, or collector \rightarrow MSW$ pit) and sample preparation process, except that they were from different districts in Shanghai.

Eight pure organic waste samples, each 25-30 kg, acquired directly from the source (OFMSW<sub>source</sub>, W4 in Figure 1) were collected from three restaurants (kitchen waste and food products were collected separately), one food market, and one rubbish can in a residential area. The contents of heavy metals and arsenic in the OFMSW<sub>source</sub>  $(\overline{C}_{org-i_{source}}^{x})$  and  $OFMSW_{end}$   $(\overline{C}_{i_n}^x)$  were evaluated. Road sweeping dust samples were collected from six streets of 4–8 lane thoroughfares in downtown Shanghai.

Washing and Fractionation. The W2 sample was divided into two samples. One sample was washed with distilled water at a liquid-to-solid ratio of 2.5 L/kg by wet weight to remove adhered mineral-like particles. The other sample was physically divided into fractions of different particle sizes (>20 mm, 10–20 mm, and 5–10 mm, 2–5 mm, 0.5–2 mm, and <0.5 mm) using a wet-sieving process. The mixture of the waste and water passed through the 0.5 mm sieve was filtered through a 0.45  $\mu m$  membrane, producing the <0.5 mm fraction and the eluate. Mass composition, heavy metals, and arsenic contents in the fractions and eluate were then analyzed.

**Analysis.** Moisture content in samples was measured by drying and weighing. The dried samples were ground into < 0.15 mm prior to analysis. The ash content in samples was determined by heating at 550 °C for 3 h in a muffle furnace. The As and Hg contents in the waste samples were measured using an atomic fluorescence spectrometer (XGY1012) (Institute of Geophysical and Geochemical Exploration, Chinese Academy of Sciences, China) following acid digestion by HCl/ HNO<sub>3</sub>/HF/HClO<sub>4</sub> and aqua regia/H<sub>2</sub>O<sub>2</sub> respectively. The Cd, Cr, Cu, Ni, Pb, and Zn contents were determined using an atomic absorption spectrophotometer (AA320N) (Shanghai Analytical Instrument Overall Factory, China) following HCl/ HNO<sub>3</sub>/HF/HClO<sub>4</sub> digestion. The metals concentrations in the eluate sample were analyzed after digestion by concentrated HNO<sub>3</sub>. Each sample was analyzed in triplicate. The X-ray diffraction (XRD) (D/max 2550, Rigaku, Japan) and X-ray fluorescence (XRF) (S4 EXPLORER, Bruker-AXS, Germany) analyses were performed for the washed particles and road dust.

**Statistical Analysis.** Descriptive statistics and correlation analysis using Pearson's correlation coefficients were applied to analyze the analytical data using SPSS 13.0 for Windows (15). One-way ANOVA analysis was performed to elucidate the correlations among mean values of moisture, ash, heavy metals and arsenic contents in the wastes from different treatment facilities.

# **Results and Discussion**

Heavy Metals and Arsenic Contents in the OFMSW from Shanghai. The W4 samples had high moisture content (63–93% w/w on wet basis) and low ash (4.1–22% w/w) on dry basis) content (Figure 2a–b). The corresponding heavy metals and arsenic contents, except for that of Zn, were <25 mg/kg (all of the ash, heavy metals and arsenic contents are on dry basis herein) (Figure 2c–j).

The OFMSW<sub>end</sub> accounted for 58  $\pm$  9% (mean value  $\pm$  standard deviation) and 52  $\pm$  9% of wet and dry MSW samples, respectively. Figure 2 shows the moisture, ash, heavy metals and arsenic contents of the OFMSW<sub>end</sub> from the incinerators (W1 and W2) and composter (W3). The OFMSW<sub>end</sub> from the treatment facilities had high water content—60  $\pm$  8%, 59  $\pm$  13%, and 69  $\pm$  8% for W1, W2 and W3, respectively (Figure 2a). The ash contents of the W1 (39  $\pm$  11%) and W2 (46  $\pm$  11%) samples were similar and higher than that of W3 (24  $\pm$  4%) (Figure 2b).

High levels of heavy metals and arsenic were identified in the OFMSW<sub>end</sub> (Figure 2c–j). With a large range in data, due to the heterogeneous nature in compositions of the collected MSW, the main contaminants in the OFMSW<sub>end</sub> were Zn, Cr, Cu, and Pb, followed by Ni, As, Cd, and Hg. The mean contents of As, Cd, Cr, Cu, Hg, and Pb in the OFMSW<sub>end</sub> were statistically the same (the level of significance large than 0.05) among samples from different treatment facilities (The statistical proof using one-way ANOVA analysis was shown in the Supporting Information). The heavy metals contents in the OFMSW<sub>end</sub> were similar to (As, Hg, and Ni), relatively lower (Cd, Cu, Pb, and Zn), or much higher (Cr) than those in MSW reported in literatures (16), (17): As, 8–23

mg/kg; Cd, 5–12 mg/kg; Cr, 21–105 mg/kg; Cu, 335–1021 mg/kg; Hg, 0–1.5 mg/kg; Ni, 14–51 mg/kg; Pb, 229–503 mg/kg; Zn, 759–1430 mg/kg.

Table 1 lists the 95% confidence intervals for mean contents of heavy metals and arsenic in the OFMSW $_{end}$  (W1, W2, and W3) and OFMSW $_{source}$  (W4), based on descriptive statistics. The heavy metals and arsenic contents in OFMSW $_{source}$  were significantly lower than those in OFMSW $_{end}$ . Based on the proposed flow system (Figure 1), the high ash content in the OFMSW $_{end}$  (Figure 2) demonstrated the mingling of large quantities of inorganic substances into the organic fraction during waste collection, handling, transportation and/or storage.

Table 2 presents Pearson's correlation coefficients for heavy metals and arsenic and ash in the OFMSW from source and treatment facilities. The contents of Cd, Cr, Cu, Hg, Ni, Pb, and Zn were positively correlated at 95% or higher confidence levels, with the exception of Cr—Cu and Cr—Hg pairs, which likely suggests that most of these metals have a common origin. Since As was very weakly correlated with Cd, Cr, Cu, Hg, and Pb (0.052–0.285), it may be derived from a different source. All metal—ash pairs were significantly and positively correlated at 95% or higher confidence levels, suggesting the important effect of inorganic substances on the abundance of heavy metals in the OFMSW.

Contaminant Flow Analysis of Heavy Metals and Arsenic in the OFMSW of Shanghai. To conduct mass balance calculations using eqs 1 and 2, the contaminant flows  $(\overline{C}_{i_-}^{x} \times \sum w_{i_-})$  in the studied treatment facilities are required, and are taken as the heavy metals and arsenic contents corresponding to 95% confidence intervals (Table 1). Additionally, in 1 ton of OFMSW ( $\Sigma w_{i_n}=1$ ), 13.7–25.8 g of As, 1.37–2.65 g of Cd, 118–231 g of Cr, 124–323 g of Cu, 0.49–1.40 g of Hg, 34.9-58.1 g of Ni, 93.6-168 g of Pb, and 217-330 g of Zn were introduced into the facilities. In Shanghai, the OFMSW treatment ratios for the composter, incinerators 1 and 2, and the landfill (Figure 1) were 5.9, 7.0, 8.8, and 78.3% w/w, respectively. Therefore, the heavy metals and arsenic flows to each facility could be derived as  $\overline{C}_{i_n}^x \times w_{i_n}$ , assuming that  $C_{i_n}^{\kappa}$  of the OFMSW from these facilities was the same and equal to  $\overline{C}_{i_n}^x$ . Most heavy metals and arsenic in Shanghai's OFMSW were sent to the landfill. Compared with Riber et al. (17) and Øygard et al. (16), more Cr, less Cu, Pb, and Zn were discharged into the landfill in Shanghai, which could be also deduced from the heavy metals contents in bottom ash which is frequently disposed of in MSW landfills. In the study of Øygard et al. (18), the contents of Cr, Cu, Pb, and Zn in MSW incineration bottom ash were 100–130, 1500-2700, 1300-2400, and 4200-6600 mg/kg respectively, while in Shanghai, the corresponding values in bottom ash, 192–655, 233–820, 234–938, and 1210–2780 mg/kg were found

The distilled water-washed waste (to remove indiscernible particles) is regarded as "the organic waste from the source"; hence, the total quantity of inorganic waste ( $\Sigma w_{\text{inorg-}i_{\text{source}}}$ ) can be estimated. In the current practices in Shanghai, dry weight content of organic waste is approximately 60% of total waste (dry basis, i.e.,  $\Sigma w_{\text{org-}i_{\text{source}}}=0.6$ ). The

$$\overline{C}_{\text{org-}i_{\text{source}}}^{x} \times \sum w_{\text{org-}i_{\text{source}}}$$

values are estimated at 95% confidence intervals for heavy metals and arsenic contents in pure organic waste (Table 1). The organic waste carried 0.00–2.05 g of As, 0.05–0.51 g of Cd, 0.00–6.78 g of Cr, 1.06–10.4 g of Cu, 0.00–0.32 g of Hg, 0.34–8.94 g of Ni, 0.00–4.31 g of Pb, and 14.3–32.5 g of Zn in 1 ton of OFMSW (Figure 1).

Given the estimated  $\overline{C}_{\text{org-}i_{\text{ourg-}i_{\text{sourge}}}}^{\text{x}} \times \sum w_{\text{org-}i_{\text{sourge}}}$  and ash contents in the organic waste (OFMSW<sub>source</sub>), the heavy metals

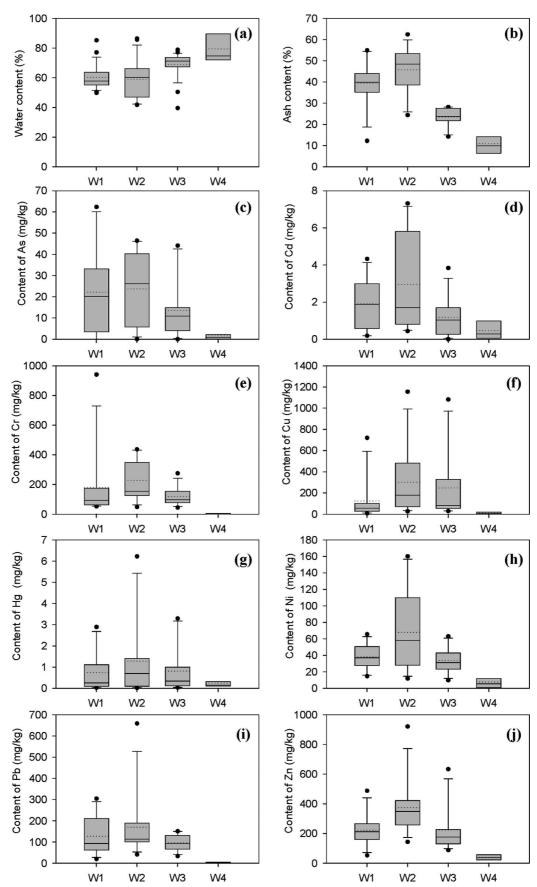


FIGURE 2. Characteristics of the OFMSW from the source and different treatment facilities. Median, 10th, 25th, 75th, 90th percentiles were plotted as horizontal solid lines of the boxes. The dashed line indicated the mean content value. Each outlier was shown as the dot. W1, W2, and W3 are samples from the incinerator 1 and 2, and the composting plant. W4 denotes the pure organic waste sample.

and arsenic flows and ash contents in inorganic waste can be estimated using eqs 3 and 4:

$$\overline{C}_{\text{inorg-}i_{\text{source}}}^{\text{x}} \times \sum w_{\text{inorg-}i_{\text{source}}} = \overline{C}_{i_{\text{in}}}^{\text{x}} \times \sum w_{i_{\text{in}}} - \overline{C}_{\text{org-}i_{\text{source}}}^{\text{x}} \times \sum w_{\text{org-}i_{\text{source}}}$$
(3)
$$\operatorname{Ash}_{\text{inorg-}i_{\text{source}}} = \frac{\operatorname{Ash}_{i_{\text{in}}} \times \sum w_{i_{\text{in}}} - \operatorname{Ash}_{\operatorname{org-}i_{\text{source}}} \times \sum w_{\operatorname{org-}i_{\text{source}}}}{\sum w_{\operatorname{inorg-}i_{\text{source}}}}$$
(4)

where  ${\rm Ash}_{i_{\rm in}}$ ,  ${\rm Ash}_{{\rm org}\text{-}i_{\rm source}}^{}$  and  ${\rm Ash}_{{\rm inorg}\text{-}i_{\rm source}}^{}$  = the ash content of the waste input to node i, of the organic and inorganic waste from the source.

The inorganic waste was primarily composed of inorganic substances with high levels of heavy metals and arsenic as well as ash contents (63.2-85.2%). The input of heavy metals and arsenic was noted at all waste generation nodes (Figure 1). Consequently, the significant increase of heavy metals and arsenic in the OFMSW<sub>end</sub> compared with those in pure organic waste OFMSW<sub>source</sub> was attributable to the intermingling of inorganic waste during collection and handling. More than 80% of heavy metals and arsenic were from sources other than pure organic waste (Figure 1), accounting for 40% of the OFMSW<sub>end</sub>, or 20% of total MSW by weight.

Heavy Metals and Arsenic in the Foodstuffs and OFMSW. The summary Table 1 compared the heavy metals and arsenic contents in pure foodstuffs and those in the OFMSW from Shanghai with those in literature (3, 10, 19–24). The full data of various foodstuffs, organic wastes from the literature were listed in Supporting Information Table S2. All raw foodstuffs had very low levels of heavy metals and arsenic. The heavy metals and arsenic in the OFMSW<sub>source</sub> (W4), including vegetable, kitchen and restaurant waste, were comparable in quantities (As, Cd, Cu, and Hg) or slightly higher (Cr, Ni, Pb, and Zn) than those in foodstuffs. However, levels of all heavy metals and arsenic in the OFMSW<sub>end</sub> from treatment facilities (W1-W3) were significantly higher than those in foodstuffs or pure organic waste. Hence, the heavy metals and arsenic contamination in the OFMSW<sub>end</sub> was principally from external sources. Additionally, the heavy metals and arsenic contents in the OFMSW<sub>source</sub> and OFMSW<sub>end</sub> resembled those in source-separated and centrally separated OFMSW in literature (Table 1) respectively.

Source of Heavy Metms and Arsenic in the OFMSW<sub>end</sub>. Two groups of heavy metals were identified (Table 3). The first group, Cd, Cu, Hg, Pb, and Zn, were at similar levels in the OFMSW<sub>end</sub> with particle sizes >2 mm, and reached relatively higher levels at particle sizes <0.5 mm. The levels of second group, Cr and Ni, peaked at particle sizes 0.5-2 mm. Arsenic was not detected in this OFMSW<sub>end</sub> sample for fractionation experiment; therefore, it was not included in Table 3.

Table 3 summarizes the contribution of the OFMSW<sub>end</sub> with different particle size ranges to the total heavy metals contents in the waste. Most centrally separated OFMSW was vegetable and fruit waste in particle sizes > 20 mm, accounting for 42% of total dry OFMSW. However, the corresponding range of heavy metals contents was 19.9-35.1% of those in

TABLE 1. Heavy Metals and Arsenic Contents in Foodstuffs and OFMSW

item		As	Cd	Cr	Cu	Hg	Ni	Pb	Zn
	heavy	metals a	nd arsenic	in the OF	MSW in this	study (mg/k	g)		
OFMSW <sub>source</sub>	range		ND-1.0	0.2 - 24	ND-23	0.02-0.97	ND-26	0.3-14	19–62
Oliviovvsource	mean <sup>a</sup>	ND-2.0		ND-6.8	1.1–10	0.00-0.32	0.3–8.9	ND-4.3	14–32
OFMSW <sub>end</sub>	range	ND-62	ND-7.3	44-940	8–1150	ND-6.2	10–160	20-660	53-920
OFIVISAVend	mean <sup>a</sup>	14-26	1.4-2.6	118–231	124–323	0.49-1.4	35–58	94–168	217-330
heavy i	netals aı	nd arseni	ic in foodst	uffs and C	FMSW from	n the literatur	es (mg/kg	<b>J</b> )	
foodstuff (19)		ND-1.5	ND-1.3	0.08-1.9	0.14-40	0.0005-0.96	0.04-1.8	ND-3.3	0.12-26
food waste ( <i>3, 10</i> )		0.91	0.06 - 1.4	1.6–18	10–25	0.029-0.60	1.6-30	0.42 - 20	6–112
yard trimmings ( <i>10</i> )			0.07-0.65	3–25	11–69	0.05-0.18	3–17	6–30	46-100
source-separated organics compost (20, 21)			0.8–1.0	29–30	43–50	0.2	7.0	76–180	230–235
centrally separated organics compost (22)			2.5	70	270			700	800
centrally separated OFMSW ( <i>3, 19, 22</i> )		0.5–18	0.11–6	11–90	7–260	0.01-0.54	6–107	11–317	76–2020
limit values of heavy metals and arsenic in MSW or sludge for agricultural use (mg/kg)									
China-MSW (23)		30	3	300		5		100	
EU-sludge (24)			20-40		1000-1750	16–25	300-400	750–1200	2500-4000
<sup>a</sup> 95% confidence interval	for mear	ıs.							

TABLE 2. Pearson Correlation Matrix for Heavy Metal, Arsenic, and Ash Contents of the OFMSW from Source and Treatment Facilities (n = 44)

As	Cd	Cr	Cu	Hg	Ni	Pb	Zn	Ash
1	0.285 1	0.271 0.336 <sup>a</sup> 1	0.200 0.394 <sup>b</sup> 0.199 1	0.052 0.377 <sup>a</sup> 0.089 0.519 <sup>b</sup>	0.479 <sup>b</sup> 0.377 <sup>a</sup> 0.600 <sup>b</sup> 0.418 <sup>b</sup> 0.427 <sup>b</sup>	0.208 0.490 <sup>b</sup> 0.508 <sup>b</sup> 0.522 <sup>b</sup> 0.556 <sup>b</sup> 0.635 <sup>b</sup>	0.371 <sup>a</sup> 0.582 <sup>b</sup> 0.402 <sup>b</sup> 0.822 <sup>b</sup> 0.478 <sup>b</sup> 0.666 <sup>b</sup> 0.694 <sup>b</sup> 1	$0.556^{b}$ $0.526^{b}$ $0.500^{b}$ $0.352^{a}$ $0.396^{b}$ $0.664^{b}$ $0.579^{b}$ $0.622^{b}$
	<b>As</b> 1		1 0.285 0.271	1 0.285 0.271 0.200 1 0.336 <sup>a</sup> 0.394 <sup>b</sup>	1 0.285 0.271 0.200 0.052 1 0.336 <sup>a</sup> 0.394 <sup>b</sup> 0.377 <sup>a</sup> 1 0.199 0.089	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

<sup>&</sup>lt;sup>e</sup> Correlation is significant at the 0.05 level (2-tailed). <sup>b</sup> Correlation is significant at the 0.01 level (2-tailed).

TABLE $3.$ Heavy Metals in the OFMSW $_{ m end}$ with Different Size Ranges	: OFMSW <sub>end</sub> with Dif	erent S	ize Ranı		and in Some Possible Sources					
items		mass	ash <sup>a</sup>	PO	č	Cu	Hg	ž	Pb	Zn
				OFM	OFMSW <sub>end</sub> with different size ranges	ent size ranges				
> 20 mm	content (mg/kg)		33.8	5.33	77.9	146	1.94	45.3	147	339
	proportion (%)	42.0		35.1	29.0	19.9	24.4	26.3	32.3	26.3
10–20 mm	content (mg/kg)		52.6	4.78	143	177	2.07	88.4	154	330
	proportion (%)	19.7		14.8	25.1	11.4	12.2	20.4	15.8	12.0
5–10 mm	content (mg/kg)		55.4	4.55	106	272	1.83	75.8	115	372
	proportion (%)	7.1		5.0	6.7	6.2	3.9	6.5	4.2	4.8
2–5 mm	content (mg/kg)		8.89	4.64	59.7	269	1.88	33.7	114	378
	proportion (%)	3.3		2.4	1.7	2.9	1.8	1.5	1.9	2.3
0.5–2 mm	content (mg/kg)		72.0	8.09	200	458	5.75	167	249	006
	proportion (%)	9.4		11.9	16.7	14.0	16.2	21.8	12.3	15.7
<0.5 mm	content (mg/kg)		63.1	10.6	126	752	7.43	91.1	343	1130
	proportion (%)	18.6		26.3	50.6	43.3	40.2	22.9	33.4	34.6
Eluate	content (mg/L)			0.20	0.17	4.87	0.03	0.29	60.0	15.6
	proportion (%)			4.5	0.2	2.3	1.3	9.0	0.1	4.3
					possible sources <sup>b</sup> (19)	es <sup>b</sup> (19)				
dust fall in urban area ofXi'an citv (mg/kg)					28–853 (167)	20–1070 (95)	0.11-5.2 (0.64)		29–3060 (230)	80–2110 (421)
duet fall in Guandona										
province (mg/kg)				1–52		8–79			43–314	155–794
road dust in Shanghai citv (mg/kg)				0-0.4 (0.1)	90–140 (120)	147–697 (390)		44-56 (50)	148–1460 (421)	390–770 (516)
background level of soil in Shanghai city (mg/kg)				0.13	64.6	23.5	0.22	31.2	21.3	76.8
urban surface soil in Hangzhou city (mg/kg)				0.7–2.4 (1.2)		14–150 (46)			20–493 (84)	47–1250 (202)
metals from the mixed MSW <sup>c</sup> (mg/kg)				0–5.2 (2.7)	0–299 (162)	0-664 (234)	0-0.9 (0.3)	0–208 (102)	0–108 (46)	0-417 (207)
glass from the mixed MSW <sup>c</sup> (mg/kg)				0-7.5 (5.3)	0–421 (163)	0-66 (30)	0-0.4 (0.2)	0–33 (22)	0–568 (181)	0–288 (124)
C&D waste from the MSW°(mg/kg)				0-4.6 (2.4)	17–321 (121)	3–49 (28)	0-0.9 (0.4)	0-69 (34)	33–371 (182)	80–1430 (561)

<sup>a</sup> The unit of ash content is %. <sup>b</sup> The values in the bracket were the means of the tested samples. <sup>c</sup> The components were separated from the 36 MSW samples from the three treatment plants; the data range from 10 to 90 percentile value.

TABLE 4. Chemical Composition of the <2 mm OFMSW $_{\rm end}$  and of the Road Dust by XRF Analysis

	OFMSW <sub>end</sub> (%)			road dust (%)							
composition	<0.5 mm	0.5–2 mm	Tongji Road	Siping Road	Lancun Road	Rushan Road	Weihai Raid	Quyang Road			
Na <sub>2</sub> O	2.14	1.35	0.93	0.73	0.50	0.61	0.32	0.46			
MgO	2.24	2.04	1.38	1.23	0.87	1.05	0.79	0.75			
$Al_2O_3$	6.12	7.29	9.39	7.57	5.38	6.57	4.06	4.29			
SiO <sub>2</sub>	24.64	21.64	45.43	37.29	26.14	27.86	17.85	20.25			
$P_2O_5$	1.57	1.71	0.20	0.20	0.19	0.27	0.22	0.28			
SO <sub>3</sub>	2.58	2.33	0.94	1.13	0.92	1.01	0.96	1.02			
CI	3.19	1.56	0.00	0.13	0.20	0.34	0.24	0.35			
K <sub>2</sub> O	3.27	2.21	1.90	1.74	1.54	1.81	1.14	1.53			
CaO	21.28	15.96	10.57	15.96	8.88	7.88	12.96	9.63			
TiO <sub>2</sub>	0.65	0.47	0.68	0.70	0.51	0.53	0.43	0.42			
$MnO_2$	0.19	0.14	0.15	0.16	0.11	0.12	0.11	0.12			
$Fe_2O_3$	6.56	4.90	6.30	8.03	5.47	5.81	4.33	4.79			

waste. The organic content in the OFMSW $_{\rm end}$  decreased as particle size decreased. Although particles <2 mm had high inorganic content and accounted for only 28% of the waste, their contribution to the total amounts of Cd, Cr, Cu, Hg, Ni, Pb, and Zn were 38.2, 37.3, 57.3, 56.4, 44.7, 45.6, and 50.3%, respectively. The amounts of heavy metals in the eluate were relatively low, accounting for <4.5% of the total heavy metals. Hence, the heavy metals in the OFMSW $_{\rm end}$  were generally adhered to or entrapped in organic waste particles sized <2 mm

Table 3 also lists the heavy metals contents from possible extrinsic sources, i.e., dust, surface soils, road dust, and metal, glass, and C&D waste fractions in the collected MSW. The surface soil or background values of soils have markedly lower heavy metals contents than those in the OFMSW $_{\rm end}$  particles sized <2 mm. According to the Shanghai Environmental Protection Bureau (25), the average dust fall in the Shanghai area (6340.5 km²) in 2005 was roughly 0.29 t/km²·d. If 20% w/w of this fallen dust was mixed with MSW (16700 t/d in 2004), it would contribute to approximately 4.3% of the heavy metals in the OFMSW $_{\rm end}$ . Therefore, dust may only be one source among many that contribute to significant quantities of heavy metals in the OFMSW.

The major fractions of the OFMSW $_{\rm end}$  of particles sized <2 mm exhibit similar chemical composition as road dust, mainly Si, Ca, Al, Fe, Cl, K, Na, Ma, S, and P (Table 4). However, their mineralogy (Supporting Information Figure S2) differed significantly. The particles from the OFMSW $_{\rm end}$  were more complex in shape and composed of diverse minerals, including aluminum and calcium silicate, quartz, chloride, carbonate, and vitreous substances.

The levels of Cr, Cu, and Ni in metal fractions, Cr and Pb in glass fractions, and Cr, Pb, and Zn in the C&D waste were comparable to those in the OFMSW $_{\rm end}$  of particles sized  $^{<2}$  mm (Table 3). However, the heavy metals and arsenic contents in the OFMSW $_{\rm end}$  and in the three inorganic MSW fractions, metal, glass, and C&D waste, were not correlated as all the absolute Pearson correlation coefficients were less than 0.26 (Supporting Information Table S3). The Cd and Hg contents in these three MSW fractions were obviously lower than those in the OFMSW $_{\rm end}$  of particles sized  $^{<2}$  mm. Hence, sources other than these three MSW fractions contaminate the OFMSW.

Hazardous household components and dust-like or glass-like substances were likely the major sources of heavy metals and arsenic in the OFMSW. One suspected source is hazardous household waste, such as fluorescent lamps that are illegally dumped at collection stations in Shanghai. Further study is needed for confirmation.

**Implications to OFMSW Management.** Central separation of MSW is a common practice to recover recyclable waste

and increase compost quality. Table 3 clearly demonstrates that the effect of central separation of OFMSW on heavy metals reduction was negligible. The contamination level of OFMSW $_{\rm end}$  markedly exceeded the allowable limits for agricultural use of MSW in China, 30 mg/kg for As, 3 mg/kg for Cd, 300 mg/kg for Cr, 5 mg/kg for Hg, and 100 mg/kg for Pb (23), but lower than the standards for sludge in the EU regulations (Table 1) (24).

As OFMSW is the most valuable component used as input material for composting and anaerobic digestion, separate collection, transportation, and composting of kitchen waste and food products directly from households, food markets, and restaurants, should reduce heavy metals and arsenic contents and yield a product that meets the government standards (Table 1) for agricultural use or other land applications. Another measure is to decrease interpollution of organic and inorganic waste during collection, transportation, handling, and treatment, or decreasing the contact probability between them. For incineration, components in addition to food waste, such as paper, textiles, and wood, are necessary to generate sufficient heat; it is not advisable to separately collect OFMSW in practice. Conversely, measures to prevent the blending of inorganic materials, such as diversion of C&D materials, source separation of hazardous components is encouraged for pollution control of OFMSW blended with MSW during collection and disposal. For cities lacking well-established source separation systems, which is common in China and in many other countries, physicochemical fractionation of fine particles with high levels of heavy metals and arsenic from the mixed product is the best option, and could reduce 50% of heavy metals and arsenic by about 40% in mass loss in dry weight, or by 25% in wet weight.

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# Supporting Information Available

Setup of contaminant flow in a MSW management system in detail; difference of the heavy metals and arsenic contents among the OFMSW<sub>end</sub> samples; schematic diagram of contaminant flows in MSW management system; XRD spectrum of the washed particles from the OFMSW<sub>end</sub> and street (Siping, Lancun, Tongji, Weihai, Quyang Road) sweepings; one-way ANOVA analytical results for the waste from different facilities; heavy metals and arsenic contents in foodstuffs and OFMSW; Pearson correlation coefficients of heavy metals and arsenic in the OFMSW<sub>end</sub> and in the inorganic MSW compositions. This material is available free of charge via the Internet at http://pubs.acs.org.

#### **Literature Cited**

- Soumaré, M.; Demeyer, A.; Tack, F. M. G.; Verloo, M. G. Chemical characteristics of Malian and Belgian solid waste composts. *Bioresour. Technol.* 2002, 81, 97–101.
- (2) Jung, C. H.; Matsuto, T.; Tanaka, N. Flow analysis of metals in a municipal solid waste management system. *Waste Manage*. 2006, 26, 1337–1348.
- (3) Zennaro, M.; Cristofori, F.; Formigoni, D.; Frignani, F.; Pavoni, B. Heavy metal contamination in compost. A possible solution. Ann. Chim. -Rome 2005, 95, 247–256.
- (4) Ciba, J.; Zolotajkin, M.; Kluczka, J.; Loska, K.; Cebula, J. Comparison of methods for leaching heavy metals from composts. Waste Manage 2003, 23, 897–905.
- (5) Veeken, A.; Hamelers, B. Sources of Cd, Cu, Pb, and Zn in biowaste. Sci. Total Environ. 2002, 300, 87–98.
- (6) Richard, T. L.; Woodbury, P. B. The impact of separation on heavy metal contaminants in municipal solid waste composts. *Biomass Bioenerg.* **1992**, *3*, 195–211.
- (7) Epstein, E.; Chaney, R. L.; Henry, C.; Logan, T. J. Trace elements in municipal solid waste compost. *Biomass Bioenerg.* 1992, 3, 227–238.
- (8) Veeken, A.; Hamelers, B. Assessment of heavy metal removal technologies for biowaste by physico-chemical fractionation. *Environ. Technol.* **2003**, *24*, 329–337.
- Hseu, Z.-Y. Evaluating heavy metal contents in nine composts using four digestion methods. *Bioresour. Technol.* 2004, 95, 53– 59.
- (10) Amlinger, F.; Pollak, M.; Favoino, E. Heavy metals and organic compounds from wastes used as organic fertilizers (Final Report); ENV.A.2./ETU/2001/0024, 2004; Available at http:// ec.europa.eu/environment/waste/compost/pdf/hm\_finalreport. pdf.
- (11) García, A. J.; Esteban, M. B.; Márquez, M. C.; Ramos, P. Biodegradable municipal solid waste: characterization and potential use as animal feedstuffs. Waste Manage. 2005, 25, 780–787.
- (12) Déportes, I.; Benoit-Guyod, J.-L.; Zmirou, D. Hazard to man and the environment posed by the use of urban waste compost: a review. Sci. Total Environ. 1995, 172, 197–222.

- (13) Chandler, A. J.; Eighmy, T. T.; Hartléen, J.; Hjelmar, O.; Kosson, D. S.; Sawell, S. E.; van der Sloot, H. A.; Vehlow, J. Municipal Solid Waste Incinerator Residues; Elsevier: Amsterdam, 1997.
- (14) Morf, L. S.; Brunner, P. H. The MSW incinerator as a monitoring tool for waste management. *Environ. Sci. Technol.* 1998, 32, 1825–1831.
- (15) SPSS Inc. SPSS 13.0 for Windows®; 2004; Available at http://www.spss.com/.
- (16) Øygard, J. K.; Måge, A.; Gjengedal, E. Estimation of the massbalance of selected metals in four sanitary landfills in Western Norway, with emphasis on the heavy metal content of the deposited waste and the leachate. Water Res. 2004, 38, 2851– 2858.
- (17) Riber, C.; Fredriksen, G. S.; Christensen, T. H. Heavy metal content of combustible municipal solid waste in Denmark. Waste Manage. Res. 2005, 23, 126–132.
- (18) Øygard, J. K.; Gjengedal, E.; Måge, A. Mass-balance estimation of heavy metals and arsenic and selected anions at a landfill receiving MSWI bottom ash and mixed construction wastes. J. Hazard. Mater. 2005, A123, 70–75.
- (19) Zhang, H. Source and fate of heavy metals in municipal solid waste incineration residues. Ph.D. thesis; Tongji University: Shanghai, 2006 (in Chinese).
- (20) O'Leary, P. R.; Walsh, P. W. Decision Maker'S Guide to Solid Waste Management, EPA 530-R-95-023; U.S. Environmental Protection Agency: Washington, DC, 1995.
- (21) US Environmental Protection Agency. Composting Yard Trimmings and Municipal Solid Waste, EPA 530-R-94–003; U.S. Environmental Protection Agency: Washington, DC,1994.
- (22) Manios, T. The composting potential of different organic solid wastes: experience from the island of Crete. *Environ. Int.* 2004, 29, 1079–1089
- (23) Control Standards for Urban Wastes for Agricultural Use, GB 8172–87; State Environmental Protection Administration of China: Beijing, 1987.
- (24) Council Directive of 12 June 1986 on the Protection of the Environment, And in Particular of the Soil, When Sewage Sludge Is Used in Agriculture, 86/278/EEC; European Union, 1986.
- (25) Shanghai Environmental Protection Bureau. 2006 Shanghai Environmental Bulletin; 2006; Available at http://www. envir.gov.cn/law/bulletin/b2006/c\_h003.htm.

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