Insights into metals in individual fine particles from municipal solid waste using synchrotron radiation-based micro-analytical techniques

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ABSTRACT

Excessive inter-contamination with heavy metals hampers the application of biological treatment products derived from mixed or mechanically-sorted municipal solid waste (MSW). In this study, we investigated fine particles of <2 mm, which are small fractions in MSW but constitute a significant component of the total heavy metal content, using bulk detection techniques. A total of 17 individual fine particles were evaluated using synchrotron radiation-based micro-X-ray fluorescence and micro-X-ray diffraction. We also discussed the association, speciation and source apportionment of heavy metals. Metals were found to exist in a diffuse distribution with heterogeneous intensities and intense hot-spots of <10 μm within the fine particles. Zn–Cu, Pb–Fe and Fe–Mn–Cr had significant correlations in terms of spatial distribution. The overlapped enrichment, spatial association, and the mineral phases of metals revealed the potential sources of fine particles from size-reduced waste fractions (such as scraps of organic wastes or ceramics) or from the importation of other particles. The diverse sources of heavy metal pollutants within the fine particles suggested that separate collection and treatment of the biodegradable waste fraction (such as food waste) is a preferable means of facilitating the beneficial utilization of the stabilized products.

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Introduction

The application of biologically stabilized products from mixed-collection or mechanically-sorted municipal solid waste (MSW) is frequently limited by the presence of excessive heavy metals (Amlinger et al., 2004; Farrell and Jones, 2009). This is inevitable for a mixed waste feedstock, even if subsequent separation and treatment procedures are applied, due to inter-contamination between various waste streams (Smith, 2009). It was reported that the small fraction of fine particles notably contributed to heavy metal pollution in MSW (Prudent et al., 1996; Veeken and Hamelers, 2002; Zhang et al., 2008). For example, Prudent et al. (1996) found that the contents of Cu, Pb and Zn in the fine particles from MSW were 2–20 times higher than those in other waste fractions. Veeken and Hamelers (2002) noted that the biowaste fraction of <0.05 mm was mainly comprised of organo-minerals and possessed significantly high concentrations of Cu, Pb and Zn. Zhang et al. (2008) reported that 37%–57% of heavy metals in the organic fraction of MSW, including

Cd, Cr, Cu, Hg, Ni, Pb and Zn, were concentrated in fine particles, which accounted for only 28% (*m/m*) of the total waste content.

During the collection, transfer, transportation, processing and treatment of MSW, the fine particles tend to adhere to or be entrapped in wet/adhesive surfaces of some MSW fractions. Leachate, released during MSW processing due to compression and hydrolysis of putrescible waste with high water content, can also promote mobility of fine particles. As a result, the distribution of heavy metals in different MSW fractions may change. It was observed that heavy metals tended to concentrate on the surface and in "hot-spots" of the organic fraction of MSW (Wu et al., 2013). Zhang et al. (2008) suggested that the high concentrations of heavy metals in the organic fraction from mixed MSW were mainly a result of interfusion of fine particles with high heavy metal loads. This implies that when the metal contents of MSW fractions from a mixed waste feedstock in collection, transportation, treatment and disposal facilities were used to calculate the contribution of each fraction to the heavy metal pollution in MSW, the waste fractions, such as food waste or paper, may be overestimated. In such cases the contribution of other sources to metal contamination would be underestimated. Considering the significant role of fine particles in terms of occurrence and mobility of heavy metals in MSW, the pollution characterization and source identification for these particles are of vital importance for policy makers, so as to improve pollution control by optimizing MSW separation or collection measures. This will facilitate the development of methods aimed at producing "cleaner" products during waste management.

The fine particles referred to above may originate from natural background sources (such as dust-falls, rocks or surface soils) or from anthropogenic activities (such as road dust, metal scraps, residues or household waste) (Amlinger et al., 2004; García et al., 2005; Veeken and Hamelers, 2002). The visual identification of such sources is challenging, due to the small size of the particles under investigation. Previous studies on heavy metals within fine particles were mainly based on the total amounts of metals in bulk samples. The chemical forms and sources of heavy metal pollutants from many fine particles are still unavailable. Synchrotron radiation-based (SR-based) microprobe techniques, which represent a combination of a high-energy light source and precise microscopy, can be used to determine elemental composition, spatial distribution, and speciation down to micro-scales while avoiding chemical destruction (Thieme et al., 2007). Such methods have been successfully applied to the analysis of trace metal pollutants in dusts, soils etc. from complex sources (Jacobson et al., 2007; Langner et al., 2013; Walker et al., 2011). In this study, fine particles in MSW were evaluated by means of SR-based micro-X-ray fluorescence (μ-XRF) and micro-X-ray diffraction (μ-XRD) with regard to association and speciation of heavy metals. Based on these results, the potential sources of heavy metal pollutants were proposed.

1. Materials and methods

1.1. Sample collection and preparation

The MSW sample was collected in April 2013, from the pit of a MSW incineration plant (mass burn) in Shanghai, with a capacity for treating 1500–2000 tons of mixed MSW on a daily basis, from residential, institutional, and commercial sources, as well as from urban green lands and street-sweeping collection.

About 50 kg of MSW was collected from randomly selected regions within the pit. By means of coning and quartering, a sub-sample (about 10 kg) of the collected waste was used for the wet-sieving process. A stainless steel sieve (with mesh size of 10 mm and diameter of 1 m) was used to physically separate the adhered fine particles from the waste. Distilled water was circularly sprayed over the sample at a liquid-to-solid ratio of 0.85 L/kg by wet weight. The particles and water passing through the 10 mm sieve were then successively filtered through a 2 mm sieve and a 0.45 μm membrane, producing a <2 mm MSW fraction and the eluate. The <2 mm fraction (defined as the fine particles used in this study) was then freeze-dried and later used for further analysis.

1.2. Bulk analysis of the fractionated particles

Prior to analysis, the fine particles were ground for 120 sec by an oscillating mill (MM 400, Retsch, Germany). The grinding jars and balls were made of tungsten carbide without heavy metal contamination. The contents of C, H, N, and S were measured by an elemental analyzer (Vario EL III, Elementar, Hanau, Germany). The ash content and volatile matter were measured by heating in a muffle furnace at 550°C for 3 hr. The major elemental composition of the particles was determined by means of an X-ray fluorescence spectrometer (XRF, SRS3400, Bruker, Germany). The total concentrations of heavy metals in the bulk samples and the eluate were determined using an inductively coupled plasma optical emission spectrometer (ICP-OES, 720ES, Agilent Technologies, USA) after digestion with aqua regia. All analytical procedures were conducted in triplicate.

1.3. SR-based microprobe investigation of individual particles

Individual particles under SR-based microprobe investigation were measured directly after wet-sieving and freeze drying,

Table 1 – Properties of the <2 mm particles and eluate.[a]							
	<2 mm particles					Eluate	
Items	Contents (%)	Major elements	Contents (%)	Trace elements	Concentration (mg/kg)	Trace elements	Concentration (mg/L)
Ash	57.8	Si	15.80	Pb	205 ± 37	Pb	0.18
Volatile matter	42.2	Ca	4.83	Cu	515 ± 188	Cu	0.12
C	22.38	Al	3.01	Zn	721 ± 210	Zn	6.18
H	3.36	Fe	2.96	Cd	1.84 ± 0.60	Cd	0.09
N	1.48	K	1.10	Mn	318 ± 84	Mn	0.15
S	0.10	Mg	0.87	Ni	42.1 ± 11.4	Ni	0.41
		Na	0.56	Cr	172 ± 38	Cr	0.29
		Ti	0.36	Hg	4.23 ± 0.30	Hg	0.01

[a] The result was on a dry basis.