Effect of sample pretreatment on speciation of copper and zinc in MSW

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ABSTRACT

Copper and zinc were determined in MSW samples collected from *Tianziling* landfill site in *Hangzhou*, *Zhejiang*, east China by modified BCR sequential extractions. Three pretreatment methods, including fresh, air drying, and oven drying, were studied. It showed that the main cause of fraction transfer after drying could be ascribed to the variation of sample status, including the evaporation of ammonia nitrogen and volatile fatty acid (VFA), the shift of sample pH, and the oxidation of sulfur, when contacted with atmospheric oxygen or exposed in high temperature during drying processes. Effect of sample pretreatment methods on speciation of copper and zinc in MSW concluded that oven drying should not be used because the changes are more numerous and generally of greater amplitude, air drying was a 'neutral' treatment relatively, while fresh sample might be the best choice if possible. To validate the effect and determine the source of pretreatment methods clearly, certified reference materials of MSW should be confirmed in the future research.

1. Introduction

Sequential extractions, where sample is treated with a series of extractants selected on the basis of their ability to release analytes bound to different components of the matrix [1], are widely used for exploration purposes and to study element speciation in materials such as soils [2–5] and sediments [6–8]. Recently, sequential extractions have also been applied for the fractionation of heavy metals in municipal solid waste (MSW) due to its sufficient information for assessing the environmental behavior of heavy metals [9–19]. However, since their creation, sequential extraction methods have been extensively criticized, mainly for the lack of selectivity of reagents, readsorption and redistribution of heavy metals solubilised during extraction, and sample pre-treatment [20,21]. At present, the only laboratory routine available to determine metal binding forms is sequential extraction. Logically, speciation analysis is of major importance in environmental research as it provides crucial evidence on the mineral phases and chemical form of target metals present in the waste matrix. Therefore, the results given by sequential extraction experiments are more representative of cer-

tain, operationally defined groups of metal forms and associations rather than the true species in the sediments. As a consequence, sequential extraction procedures, using extraction fluids of increasing strengths, still have been used to characterize the physical and chemical properties of the matrix though the results from them are often suffered criticism and suspicion. Tessier and Campbell [22], whose procedure presented is the most commonly used since 1979 [23], denounced the fact that these criticisms were based on experiments carried out with artificial phases, which do not have the same characteristics as natural circumstance.

Strictly speaking, small operational variations can lead to non-comparability during sequential extractions [24]. Whatever the methods used for sample pretreatment of the solid materials can alter the results of the speciation [25,26]. It is thus important to study its effect on the fractionation of heavy metals in different materials. Various approaches of sample pretreatment for metal speciation in soils and sediments have recently been reviewed by Rubio and Ure [25], while none in MSW. Bordas and Bourg [27] conducted that none of the sample pretreatment completely preserved the distribution of Cu, Pb, Zn and Cd in the various geochemical fractions, particularly when the heavy metal content was low. Indeed, prior to sampling, materials were in relation (in equilibrium or steady state) with the surrounding environment. When materials are sampled and stored, redox potential, temperature, pH, and pressure will be changed and this relationship can be broken [28]. Possibly, the physicochemical composition of sample will be

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modified and material can therefore be restructured, which modified the speciation of metals greatly. Authors [27,28] agree that the ideal is to work with fresh material, but this is not always possible. Conservation of samples is sometimes necessary, using either wet storage (cooling) or dry storage (air drying or oven drying). Wet storage at 4 °C was established could preserve the integrity of materials if they are not stored for more than 2 weeks [29,30]. Air drying at temperature below 40 °C without mentioning the possible consequences, was recommended as French standard procedure [27]. However, oven drying was not recommended because their effects are marked [29].

MSW is an extremely heterogeneous material independent of its geometry, particle size or chemical composition [9]. The high organic matter content and the heterogeneity of MSW differentiate with soil or sediment greatly. The drying of organic matter tends to decrease the concentrations of readily extractable elements [31]. Drying of materials prior to extract with selective reagents may affect the extractability of elements [32]. The distribution of metals varies according to the drying method [33]. Moreover, differentiating with soil or sediment greatly, there're no certified MSW materials existed till now [34]. Therefore, the sample pretreatment of MSW should be of more concern in speciation of heavy metals.

In the present work, two sample pretreatment methods (air drying and oven drying) and reference pretreatment (fresh) were applied to a variety of MSW samples from landfill site with different degradation degree. Copper and zinc, the two elements with highest level among all heavy metals in MSW [35], were performed for speciation with modified BCR sequential extraction procedure. It aims to evaluate the effect of sample pretreatment on the speciation of heavy metals in MSW, study the possible modifications of different pretreatment, and present an appropriate pretreatment method best adapted to the needs of the study for MSW.

2. Experimental

2.1. Sampling

The MSW samples in the experiment were all collected from *Tianziling* MSW landfill site in *Hangzhou, Zhejiang* province, east China. The *Tianziling* MSW landfill site, whose design capacity is 6,000,000 m^3, was carried out business since April 1991. Its bottom liners located at 54 m above sea level and the top of the landfill will reach 165 m above sea level. The matured refuse was located at bottom deposit layers and the fresh one at top deposit layers. Sample A was 0 year aged refuse, which was fresh MSW and sampled from a temporary dumping tank at the top layer of *Tianziling* landfill site. The other four MSW samples were sampled from four different deposit layers with different depth of the landfill in a sampling well drilled in landfill with the depth of 3, 13, 25, and 40 m below top layer, respectively. The four sampling layers were with the deposit age of 0.5(B), 1(C), 3(D) and 7(E) year, respectively.

2.2. Apparatus

Sequential extraction of heavy metals in MSW was performed in 100 ml centrifuge tubes. Samples were grinded by jam crasher (Retsch, German). For each element, calibration solutions were prepared with standard solution (1000 ± 2 µg ml^{-1}) purchased from Merck (Darmstadt, Germany). Extraction solutions were prepared with deionized water obtained from a Milli-Q system, 18.2 MΩ cm^{-1} resistivity (Millipore, France). Heavy metals were determined by atomic absorption spectrophotometer (Shimadzu, Japan).

2.3. Reagents

Extractants were prepared according to the following procedure. All dissolutions and dilutions were performed with 18.2 MΩ cm Milli-Q water.

Solution A (acetic acid, 0.11 mol l^{-1}): 25 ± 0.2 ml of redistilled glacial acetic acid was added, in a fume cupboard, to about 0.5 l of water in a 1 l polyethylene bottle and made up to exactly 1 l with further water. 250 ml of this solution (0.43 mol l^{-1} acetic acid) was diluted to 1 l to obtain an acetic acid concentration of 0.11 mol l^{-1}.

Solution B (hydroxylamine hydrochloride, 0.5 mol l^{-1}, pH 1.5): 34.75 g of hydroxylamine hydrochloride was dissolved in 900 ml of water. The solution was acidified with concentrated nitric acid to pH 1.5 and made up to 1 l. This solution was prepared on the same day as the extraction was carried out.

Solution C (hydrogen peroxide, 8.8 mol l^{-1}): hydrogen peroxide was used as supplied by the manufacturer, i.e. acid-stabilised to pH 2.0–3.0.

Solution D (ammonium acetate 1.0 mol l^{-1}): 77.08 g of ammonium acetate was dissolved in 900 ml of water. The solution was acidified to pH 2.0 with concentrated nitric acid and made up to 1 l.

2.4. Pretreatment

MSW samples were immediately placed in an airtight plastic bag after being sampled. Larger inert objects (including stones, pieces of brick, concrete and cinders) were removed before analysis. A part of them (~200 g for each sample) were used to determine the pH, biodegradable matter, moisture content, ash content, and sulfur content. The moisture of samples was determined by drying them at 105 °C in a ventilated drying box until a constant weight was achieved. The ash content was determined by burning the dried sample in an oven at 550 °C for 2 h. The pH was measured in 1:5 (w/w) suspensions using a pH-meter (Delta 320). The biodegradable matter of the MSW was analyzed using the potassium dichromate method [36]. The sulfur content was determined by methylene blue spectrophotometry.

The rest samples (~2000 g for each sample) were divided into three parts after homogenization:

- the first part was not dried but treated immediately after sampling as the reference sample,
- the second was air dried at 25 °C for 2 weeks,
- the third was oven dried at 105 °C for 24 h.

Before sequential extraction, the fresh samples were shredded as small as possible manually (approximately 1 mm) because it is hard to screen them with respect to their moisture. Then, they were divided into four equivalent parts time and again to homogenize thoroughly and reduce the represent sample volume and weight and finally the most represent sample was gotten. Then the fresh sample was conducted with sequential extraction and aqua regia digestion, respectively. In order to keep the liquid-to-solid ratio in sequential extraction, the extractant added was revised according to the moisture of fresh samples.

Hard material and soft material in samples (air dried and oven dried) were crashed by BB51 (Retsch, German) and SM2000 (Retsch, German), respectively. In order to unify the final size of sample, both the out-put fineness of SM2000 and BB51 were set as 1 mm. In other words, samples were all crashed into 1 mm or less in our pretreatment. Therefore, there were no samples above 1 mm sieve left. Finally, the crashed hard material and soft material of a sample were filled into a PE flask and mixed by vortex to get a homogeneous sample. Sequentially, sample was then moved out from flask and placed on a clean watertight board with a shape of taper. A clean crisscross

Table 1
Schemes of modified BCR sequential extraction procedure.

Extraction step	Reagents	Fraction
1	0.11 mol l^{-1} CH$_3$COOH	Acid soluble
2	0.5 mol l^{-1} NH$_2$OH·HCl at pH 1.5	Reducible
3	8.8 mol l^{-1} H$_2$O$_2$ followed by 1.0 mol l^{-1} CH$_3$COONH$_4$ at pH 2	Oxidable
Residual	Aqua regia	Residual

board was cut from the top of the taper sample, and the sample was separated into four parts. The two diagonal parts was mixed again and quartered as the above process time and again till the sample was about 5 g. Finally, the homogenized sub-samples were removed for sequential extractions (1 g) and aqua regia digestion (1 g), respectively.

2.5. Speciation procedures

2.5.1. Sequential extractions

Sequential extractions were performed using the modified BCR protocol recommended in studies (Table 1) [5,37]. Extractions were performed using the reagents given in Section 2.3. Sequential extractions procedures were described below in detail.

Step 1: A total of 40 ml of solution A (acetic acid) was added to 1 g fresh/air dried/oven dried MSW sample in a 100 ml centrifuge tube and shaken for 16 h at room temperature (overnight). No delay occurred between the addition of the extractant and the shaking beginning. Finally, the extractant was separated from the solid residue by centrifugation (5000 × g) and decantation of the supernatant liquid into a high density polyethylene container. The container was stoppered and the extract was stored at 4 °C. In order to keep the sample similar with the original sample in next extraction procedure as possible, the residue was washed by adding 20 ml of water, shaking for 15 min and finally centrifuging the resulting suspension (5000 × g). The supernatant was decanted and discarded, taking care not to discard the solid residue. This washing process was conducted three times for each sample. The residue obtained upon centrifugation was broken manually using a vibrating rod prior to the next step.

Step 2: 40 ml of solution B (hydroxylammonium chloride) was added to the residue from Step 1 in the centrifuge tube, and the extraction was performed as described above, especially for residual washing.

Step 3: 10 ml of solution C was added carefully, in small aliquots to avoid losses due to violent reaction, to the residue from Step 2 in the centrifuge tube. The tube was covered with a watch glass and the contents digested at room temperature for 1 h with occasional manual shaking. The digestion was continued heating the covered flask for 1 h at 85 °C in a water bath, then the cover was removed and the volume reduced to a few ml. A further aliquot (10 ml) of solution C was added. The tube was heated again (85 °C for 1 h) then the watch glass was removed and the volume reduced to a few ml. 50 ml of solution D was added to the cool residue, which was extracted as described above. The solid residue was retained for aqua regia digestion.

Blank extractions, i.e. without MSW sample, were carried through the complete procedure for each set of analysis and using the same reagents. In addition, for correction to dry mass, a separate, 5 g air dried refuse of each MSW was dried in oven at 105 °C until constant mass was achieved (i.e. successive weightings differed by less than 1 mg). To provide data against which the results of sequential extractions could be compared, each sample was handled in triplicate.

2.5.2. Aqua regia digestion

Pseudototal metal content was determined by digestion with aqua regia. One gram of the sample was weighed into the PTFE vessel, 0.5–1.0 ml of water was added to obtain slurry, and then 7.0 ml of 12.0 mol l^{-1} HCl followed by 2.3 ml of 15.8 mol l^{-1} HNO$_3$, drop by drop, to reduce foaming, was added. The PTFE vessel was allowed to stand for 16 h (overnight) at room temperature for slow oxidation of the organic matter of the MSW. The temperature of the reaction mixture was slowly raised, until reflux conditions were reached and maintained for 2 h. After cooling the PTFE vessel to room temperature the digests were filtered into 100 ml volumetric flasks and diluted to the mark with distilled water. Each sample was handled in triplicate.

The residues after Step 3 were also performed as the same aqua regia digestion above.

3. Results and discussion

3.1. Properties of MSW samples

Samples used in experiment were all collected from the *Tianziling* MSW landfill site in *Hangzhou, Zhejiang*, east China. The main characteristics of them were given in Table 2. The five samples, with the deposit age of 0, 0.5, 1, 3 and 7 years, respectively, represented different biodegradation state of different depth and different cell of *Tianziling* MSW landfill site. As Table 2 shown, the biodegradable matters of the five samples, which decreased from 30.7% (A) to 3.99% (E) during the deposition process, were significantly different. It directly confirmed that the samples collected from different depth of landfill site had different degree of biodegradation. However, unlike the attenuation of biodegradable matter, the heavy metal contents in MSW experienced a rising period during decomposition. In the 7 year's decomposition (from A to E), the 1 year aged refuse (C) had the highest level of heavy metals among all samples. The copper and zinc contents in MSW increased from 100 ± 5.03 µg g^{-1} dry weight (DW^{-1}) and 136 ± 10.2 µg g^{-1} DW^{-1} to 205 ± 28.3 µg g^{-1} DW^{-1} and 493 ± 32.6 µg g^{-1} DW^{-1} during 1 year's decomposition (from A to C) and then decreased to 79.9 ± 6.98 µg g^{-1} DW^{-1} and 376 ± 19.4 µg g^{-1} DW^{-1} in the next 6 year's decomposition (from C to E), respectively. That's might be ascribed to the biodegradation of landfill refuse. From 0 to 1 year (A to C), the landfill experienced a process of fast degradation called acidification stage, where the degradable organic matter (biodegradable matter) abated from 30.7% to 15.5%. After 1 year, the landfill turned into a process of slow degradation called stabilization stage and the abating of organic matter kept at a mild rate, which was from 15.5% to 3.99% in the next years (C to E). Though heavy metals in MSW were dissolved by leachate during decomposition simultaneously, they would experience process of adsorbed again during the leaching in MSW landfill. In our previous studies [34,38,39], the characteristics of MSW with different landfill ages vary very much, especially parameters relevant with heavy metals retention such as CEC and humus. Therefore, it suggested that the retention of heavy metals caused by the degradation was strengthened. That's to say, the heavy metal which had dissolved by leachate was then bound with solid matter again while organic matter in MSW kept decomposing all along. Therefore, heavy metal contents in MSW were increased relatively but not decreased. In other words, the rate of heavy metal released by leachate from MSW landfill was lower than the rate of organic matter degradation and then their level (percentage) was increased relatively. This phenomenon was more obvious in the acidification stage than in stabilization stage. However, the total amount of heavy metals in MSW reduced because they were taken away by leachate after all.

Table 2
Characteristics of MSW samples studied.

Sample	MSW sources	Moisture content (%)[a]	Loss on ignition (%)[b]	Biodegradable matter (%)	Content of copper[c] ($\mu g\,g^{-1}$ dry weight)	Content of zinc[c] ($\mu g\,g^{-1}$ DW^{-1})
A	0-year aged refuse	45.7 ± 0.1	33.8 ± 0.2	30.7 ± 2.1*	100 ± 5*	136 ± 10*
B	0.5-year aged refuse	69.5 ± 0.2	43.6 ± 0.2	23.4 ± 1.1*	102 ± 19*	235 ± 24*
C	1-year aged refuse	43.7 ± 0.3	20.9 ± 0.1	15.5 ± 1.1*	205 ± 28*	493 ± 33*
D	3-year aged refuse	46.6 ± 0.3	24.1 ± 0.2	8.18 ± 0.94*	130 ± 13*	447 ± 29*
E	7-year aged refuse	45.2 ± 0.1	17.7 ± 0.2	3.99 ± 0.42*	79.9 ± 7.0*	376 ± 19*

[a] Obtained by drying to constant mass at 105 °C.
[b] Obtained by combustion at 550 °C.
[c] The heavy metal contents were the fraction of aqua regia soluble.
* Means are significantly different at $p < 0.05$ based on LSD comparisons.

3.2. Comparison of pretreatment methods

In the present work, recoveries of copper and zinc in different samples with different pretreatment methods were exceedingly variable (Tables 3 and 4). Amounts of copper and zinc released from all refuses by the sequential extractions differed obviously with pseudototal digestion. Since no suitable certified reference materials were available to validate either the extraction or the aqua regia digestion of MSW, it was hard to determine the source of the variability. Moreover, because total contents of heavy metals extracted differed between three pretreatment methods, comparisons were aided by computing relative fraction-specific percentages. Figs. 1 and 2 indicated that differences exist among three pretreatment methods for a given fraction of copper and zinc for different MSW samples.

3.2.1. Acid soluble fraction (F1)

Acid soluble fraction is the amount of heavy metal that would be released into the environment if conditions became more acidic. It is the fraction with the most dangerous for the environment [40]. Therefore, in order to evaluate their environmental behavior pertinently, it is important to quantify this fraction of heavy metals correctly. As Table 3 and Fig. 1 shown, the acid soluble fraction of copper by reference pretreatment (fresh) of samples A–E were 8.85%, 7.35%, 7.34%, 7.13% and 4.13%, respectively. Obviously, the acid fraction of copper was low and had a trend of decreasing during the decomposition process. Comparing with reference pretreatment, the acid soluble fraction of copper almost all were modified after air drying or oven drying in all samples except sample E (4.13%,

4.41% and 4.33% by three pretreatment, respectively). For example, there were a loss of 2.69% of copper (from 7.35% to 4.66%) for sample B and an increase of 3.11% of copper (from 7.13% to 10.2%) for sample D by oven drying. Considering the low content of acid soluble fraction of copper in MSW samples, this modification was seriously. As for air drying, there's also some modification but lower than that in oven drying. For instance, a loss of 1.32% of copper (from 7.35% to 6.03%) for sample B and an increase of 2.02% of copper (from 7.13% to 9.15%) for sample D by air drying could be observed. Comparing with copper, the acid fraction of zinc was modified more greatly by the drying methods. As Table 4 and Fig. 2 shown, all samples were modified by different drying methods. Took samples B and D for instance still, the loss of zinc in sample B were 5.40% (from 27.6% to 22.2%) and 8.41% (from 27.6% to 19.1%) by air drying and oven drying, respectively. However, there were also an increase of 6.20% (from 23.9% to 30.1%) and 9.38% (from 23.9% to 33.3%) in sample D caused by the two drying methods, respectively. The modification caused by air drying or oven drying were more obviously in the younger MSW samples (A–C) than the elder ones (D and E). Generally, the modification caused by drying methods was more serious for copper than zinc because the acid fraction of zinc was much higher than copper. Therefore, information of environmental behavior of MSW samples studied here with different deposition age got from drying methods seemed greatly differed with reference pretreatment. Therefore, the results of sequential extractions got from drying samples masked the real behavior when such results used for behavior evaluation.

Probably, when samples were treated, the decrease or increase in acid soluble fraction was largely associated with the change in the
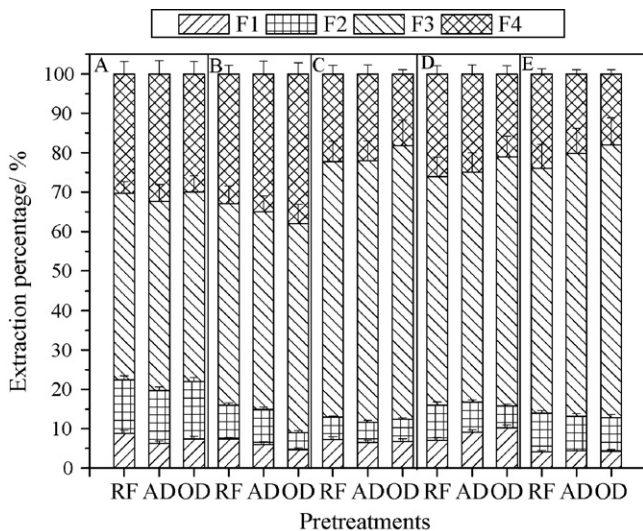

Fig. 1. Drying influence on copper fractions of different MSW samples (RF, reference; AD, air drying; OD, oven drying).
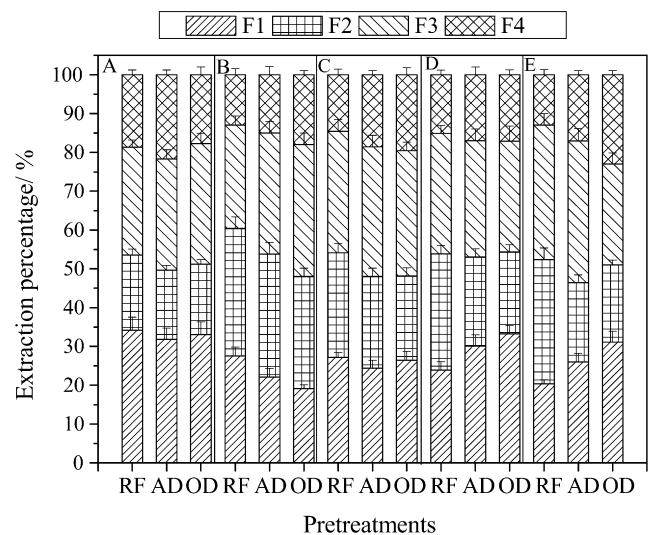

Fig. 2. Drying influence on zinc fractions of different MSW samples (RF, reference; AD, air drying; OD, oven drying).

Table 3
The comparison of the sum of the four fraction of copper by modified BCR sequential extraction in different samples with different drying methods ($\mu g\,g^{-1}\,DW^{-1}$).

Sample	Drying methods	F1	F2	F3	F4	Sum	Pseudototal	Recovery
A	RF	8.83 ± 0.86	13.6 ± 1.5	47.0 ± 1.5	30.2 ± 2.0	99.7		99
	AD	6.26 ± 0.55	13.2 ± 1.9	47.1 ± 1.7	31.8 ± 2.3	98.4	100	98
	OD	7.16 ± 0.65	14.0 ± 1.3	46.1 ± 3.4*	28.9 ± 2.7*	96.2		96
B	RF	7.89 ± 0.67*	9.29 ± 0.92*	54.7 ± 3.2*	35.4 ± 3.2*	107		104
	AD	6.95 ± 0.58*	10.2 ± 1.1*	57.7 ± 3.3*	40.3 ± 5.1*	115	103	112
	OD	5.39 ± 0.45*	5.11 ± 0.36*	61.2 ± 5.8*	43.9 ± 4.5*	116		112
C	RF	14.3 ± 1.9*	11.0 ± 1.2	126 ± 7*	43.3 ± 1.0*	195		95
	AD	14.4 ± 2.8*	11.4 ± 1.0	147 ± 13*	48.7 ± 3.0*	221	204	108
	OD	15.4 ± 1.3*	12.7 ± 1.2*	158 ± 15*	41.3 ± 3.8*	227		111
D	RF	9.28 ± 0.78*	11.6 ± 0.8	75.3 ± 7.1*	33.9 ± 2.3*	130		100
	AD	13.9 ± 1.1*	11.5 ± 1.1	88.4 ± 9.2*	37.9 ± 2.2*	152	130	117
	OD	14.6 ± 1.8*	7.85 ± 0.69*	89.8 ± 7.8*	30.0 ± 1.0*	142		110
E	RF	3.89 ± 0.23*	9.21 ± 0.74*	58.5 ± 5.8	22.6 ± 1.6*	94.3		118
	AD	3.84 ± 0.52	7.62 ± 0.73	58.1 ± 1.7	17.5 ± 1.8*	87.1	79.9	109
	OD	3.90 ± 0.43	7.68 ± 0.88*	62.2 ± 8.2*	16.2 ± 1.1*	90.0		113

RF, reference; AD, air drying; OD, oven drying.
Recovery = (F1 + F2 + F3 + F4)/pseudototal × 100.
 * Means are significantly different at $p < 0.05$ based on LSD comparisons.

Table 4
The comparison of the sum of the four fraction of zinc by modified BCR sequential extraction in different samples with different drying methods ($\mu g\,g^{-1}\,DW^{-1}$).

Sample	Drying methods	F1	F2	F3	F4	Sum	Pseudototal	Recovery
A	RF	53.1 ± 4.5*	30.1 ± 1.8*	43.0 ± 3.5*	29.1 ± 1.2	155		114
	AD	45.4 ± 5.1	25.6 ± 1.6*	40.8 ± 4.3	31.1 ± 2.5	143	136	105
	OD	42.2 ± 3.7	23.2 ± 1.6*	39.7 ± 5.0	22.7 ± 2.0*	128		94
B	RF	64.0 ± 7.8*	76.3 ± 8.4*	61.7 ± 5.1*	30.2 ± 2.1*	232		99
	AD	64.1 ± 5.9	91.5 ± 8.1*	90.2 ± 8.6*	43.4 ± 3.5*	289	235	123
	OD	57.9 ± 7.1	87.3 ± 8.8*	102 ± 14*	54.4 ± 3.2*	302		129
C	RF	130 ± 12	128 ± 12*	149 ± 14*	69.3 ± 3.6*	476		97
	AD	142 ± 14*	138 ± 13*	194 ± 20*	108 ± 9*	581	493	118
	OD	126 ± 15	103 ± 11*	154 ± 18*	93.1 ± 8.2*	475		96
D	RF	126 ± 13*	158 ± 13*	163 ± 13*	79.5 ± 6.5	526		118
	AD	151 ± 13	115 ± 10*	150 ± 17*	85.0 ± 8.0*	500	447	112
	OD	152 ± 11	96.0 ± 8.4*	130 ± 14*	78.1 ± 9.1	456		102
E	RF	74.6 ± 8.7*	118 ± 10*	127 ± 14*	47.7 ± 4.2*	367		98
	AD	105 ± 10.90*	82.9 ± 7.45	148 ± 17*	69.4 ± 5.7*	406	376	108
	OD	125 ± 12*	79.9 ± 5.22	104 ± 10*	92.3 ± 10.9*	401		107

RF, reference; AD, air drying; OD, oven drying. Recovery = (F1 + F2 + F3 + F4)/pseudototal × 100.
 * Means are significantly different at $p < 0.05$ based on LSD comparisons.

Table 5
Variation of pH after each extraction procedure.

Sample	Drying methods	After F1	After F2	After F3
A	RF	4.12 ± 0.19	1.96 ± 0.17	1.21 ± 0.03
	AD	4.27 ± 0.41	2.13 ± 0.11	1.34 ± 0.04*
	OD	4.06 ± 0.15	2.24 ± 0.09*	1.18 ± 0.01
B	RF	4.21 ± 0.23	1.72 ± 0.13	1.12 ± 0.07
	AD	4.63 ± 0.28*	3.09 ± 1.58	1.28 ± 0.04*
	OD	4.47 ± 0.04	2.18 ± 0.13	1.11 ± 0.03
C	RF	4.66 ± 0.03	2.40 ± 1.00	1.20 ± 0.03
	AD	4.52 ± 0.21	2.92 ± 0.30	1.58 ± 0.01*
	OD	4.44 ± 0.01	2.78 ± 0.00	1.30 ± 0.04*
D	RF	4.14 ± 0.08	1.83 ± 0.07*	1.16 ± 0.04*
	AD	4.11 ± 0.07	2.42 ± 0.46*	1.42 ± 0.03*
	OD	4.37 ± 0.01*	3.62 ± 0.18*	1.23 ± 0.03*
E	RF	4.59 ± 0.20	2.32 ± 0.30	1.18 ± 0.03*
	AD	4.35 ± 0.09	2.75 ± 0.88	1.41 ± 0.06*
	OD	4.46 ± 0.04	2.35 ± 0.03	1.30 ± 0.01*

RF, reference; AD, air drying; OD, oven drying. pH after each extraction means that the pH were determined when the extraction was finished immediately.
 * Means are significantly different at $p < 0.05$ based on LSD comparisons.

chemistry of Fe and Mn by exposure to air [41]. As Table 5 shown, pH decreased during the first extraction with 0.11 M acetic acid from 7.0 to 4.06–4.63 (after F1 in Table 5) for all pretreatment and for the reference. That's because the pH not was being regulated during extraction with the procedure of modified BCR [5,37]. This could cause an attack of fractions 2 and 3 which are large fractions. Therefore, acid soluble fraction was overestimated in our samples. This overestimation would mask a limited modification of the acid soluble fraction. However, we could also not ignore the variation of volatile fatty acid (VFA) of MSW samples when drying. As Table 6 shown, the VFA concentrations of MSW samples decreased sharply after drying. This decrease caused heavy metals bound with VFA radical were also extracted by the 0.11 mol l^{-1} acetic acid in Step 1 and led this fraction overestimated.

3.2.2. Reducible fraction (F2)

Reducible fraction was also modified but less than the first fraction (acid soluble fraction). Unlike the first fraction, the elder MSW samples (D and E) accounted for a larger modification than the younger ones (A–C). With air drying, copper decreased slightly. Like Fig. 1 shown, the largest modification caused by different drying methods were observed in sample D where the decreases of 1.34% (from 8.92% to 7.58%) by air drying and 3.40% (from 8.92% to 5.52%)
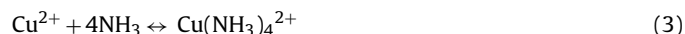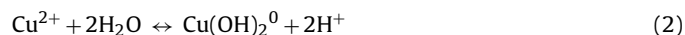
Table 6
Variation of characteristics of MSW samples after different drying methods (μg g^{-1} dry weight, excluding pH).

Sample	pH			Volatile fatty acid (VFA)			Ammonia nitrogen (NH$_4^+$–N)			Sulfur (S^{2-})		
	RF	AD	OD	RF	AD	OD	RF	AD	OD	RF	AD	OD
A	6.82	6.94	7.64	28.3	35.7	1.41	28.1	2.16	0.08	16.7	4.09	3.98
B	8.71	8.42	8.22	35. 9	37.6	2.75	55.0	5.46	1.56	13.4	2.11	2.01
C	8.06	8.28	7.89	31.0	34.6	0.86	277	21.2	8.90	10.3	1.06	0.79
D	7.88	7.72	7.72	15. 8	17.8	0.16	33.7	5.05	0.87	3.87	0.98	0.66
E	8.06	7.92	7.69	22.0	23.6	0.61	4.38	2.45	0.67	1.09	0.35	0.26

RF, reference; AD, air drying; OD, oven drying.

by oven drying were determined, respectively. As for zinc, greater decrease than copper could be observed by the two different drying methods where decreases of 9.6% (from 32.0% to 20.4%) and 12.1% (from 32.0% to 19.9%) were determined in sample E, respectively.

Thomson [42] suggested that heavy metals might be converted into more insoluble forms when sample treated with air drying or oven drying with different temperature. That's might fit with our results partly. However, the variation of reductive condition of sample during extraction might also be an important factor. As Table 6 shown, pH value and ammonia nitrogen content of MSW samples varied greatly in different pretreatment. Like Eqs. (1)–(3) shown, these balances might be suffered breaking and the reducible fraction such as hydroxide then reduced correspondingly. Moreover, as Table 5 shown, the pH values of solution after extraction of this fraction (after F2 in Table 5) were also varied greatly. The reducible fraction of copper and zinc would be released due to more reductive condition [40]. Therefore, modifications of this fraction were observed. However, it is hard to depict the process of modification clearly because it cannot quantify the relation between metals and sample characteristics such as pH and ammonia nitrogen exactly.

$$Cu^{2+} + H_2O \leftrightarrow CuOH^+ + H^+ \tag{1}$$

$$Cu^{2+} + 2H_2O \leftrightarrow Cu(OH)_2{}^0 + 2H^+ \tag{2}$$

$$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4{}^{2+} \tag{3}$$

3.2.3. Oxidable fraction (F3)

As Tables 3 and 4 and Figs. 1 and 2 shown, oxidable fraction of copper and zinc both increased in different drying methods except for zinc in samples D and E by oven drying. This modification of the speciation might be ascribed to the change in the chemistry of sulfur. Air drying and oven drying promoted sulfur oxidation. Therefore, heavy metals bound to sulfur were modified, which could be concluded from the variation of sulfur in Table 6. As Eq. (4) shown, the decrease of sulfur caused by oxidation led more copper bounded to sulfur release easily by the extractant of oxidable fraction.

$$Cu^{2+} + S^{2-} \rightarrow CuS \tag{4}$$

Regardless of the drying methods, the modification effect was more significant for copper than for zinc. The reason of that might be ascribed to their difference on the geochemical nature of them. Zinc has stronger regulation power than copper. Therefore, its speciation can keep steady relatively once the environment changed, which could be confirmed by the variation of pH values of solution after extraction of this fraction (after F3 in Table 5). The steady pH value of solution after oven drying weakened the modification effect on zinc.

3.2.4. Residual fraction (F4)

The residual fraction of metals is bound with the strongest association to the crystalline structures of the minerals. Generally, copper seemed more stable than zinc in MSW because it bound to the crystalline structures of the minerals easier. It is always not easy to separate them from material extracted, and MSW is not

especial either. Consequently, residual fraction of metals in MSW was little affected (Tables 3 and 4 and Figs. 1 and 2). The only modification in different drying methods could be attributed to the increase or decrease in the former three fractions because the sum of the four fractions was constant for a given MSW sample. In a word, the variation of MSW environment with different pretreatment methods had little influence on residual fraction of heavy metals.

4. Conclusions

Pretreatment with air drying or oven drying can modify the speciation of copper and zinc in MSW sample with different extent. The results of drying samples might mislead the evaluation of environment behavior. The modification caused by fraction transfer could ascribed to the variation of sample state, for instance the evaporation of ammonia nitrogen and VFA, the shift of sample pH, and the oxidation of sulfur, when contacted with atmospheric oxygen or exposed in high temperature during drying processes. Effect of sample pretreatment methods on speciation of copper and zinc in MSW concluded that none of the studied pretreatments appeared to be suitable for keeping the original metal-fractionation distribution. Oven drying should not be used because the changes are more numerous and generally of greater amplitude. Air drying was a 'neutral' treatment relatively. However, fresh sample might be the best choice if possible. To validate the effect and determine the source of pretreatment methods clearly, certified reference materials of MSW should be confirmed in the future research.

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