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Abstract: As the demand for critical and valuable metals increases due to industrial developments, especially in electronics and high-technology industries, the search for novel and sustainable sources grows in significance. Incinerated municipal solid waste (MSW) is a potential source of valuable metals, since a lot of waste from electrical and electronic equipment (WEEE) is not recycled properly and are is managed together with the refuse fraction of MSW, which is often landfilled or incinerated. Bottom Ash (BA) is the main by-product of incinerated MSW, which has been characterized to assess the potential recovery of valuable metals. The determination of the total amount of valuable metals (Ag, Al, Au, Be, Co, Cu, Ga, Ge, In, Ir, Li, Ni, Pd, Pt, Sb, Ta, and W) in seasonal samples of weather bottom ash (WBA) was performed by a total acid digestion followed by a chemical analysis. Besides, a sequential extraction procedure (SEP) is conducted to define their partition. The characterisation has shown that the content of valuable metals in the incineration WBA, which was highest in the 0 - 2 mm fraction was much lower than in concentrated ores commonly used as primary sources. Moreover, the SEP showed little potential for the valorisation of most of the metals, as they are embedded in or bound to a silicic matrix or sintered metal oxides, and so their extraction requires strong-acid digestion or a highly oxidizing environment. This work contributes to the use of residual sources as secondary resources and to the correct management of the end-of-life electrical and electronic equipment.

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We thank the Editor for his valued comments.

1. Kindly avoid having one heading after another heading without any text in between as shown in Section 3.

Done.

2. Kindly proof read the document for grammatical errors. An example is in the first line of the abstract

An English advisor from the University of Barcelona has reviewed the manuscript.

3. Kindly highlight in the abstract, introduction and conclusion how the work proposed contributes towards the promotion or adoption of cleaner production or the improvement in environmental impact.

Done

Sincerely,

JM Chimenos

**Characterisation and partition of valuable metals from WEEE in
weathered municipal solid waste incineration bottom ash, with a view
to recovering.**

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Highlights

WEEE are not recycled properly and are managed with the refuse fraction of MSW

MSWI bottom ash is a potential source of valuable metals coming from WEEE

MSWI bottom ash has been characterized to evaluate the recovery of valuable metals

Valuable metals are mainly in fine fractions with lower contents than mineral sources

Valuable metals are embedded in Si-matrix and require severe condition for extraction

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3 **Characterisation and partition of valuable metals from WEEE in**
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6 **weathered municipal solid waste incineration bottom ash, with a view to**
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8 **recovering.**
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Abstract

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3 As the demand for critical and valuable metals increases due to industrial developments,
4 especially in electronics and high-technology industries, the search for novel and sustainable
5 sources grows in significance. Incinerated municipal solid waste (MSW) is a potential source
6 of valuable metals, since a lot of waste from electrical and electronic equipment (WEEE) is
7 not recycled properly and are is managed together with the refuse fraction of MSW, which is
8 often landfilled or incinerated. Bottom Ash (BA) is the main by-product of incinerated MSW,
9 which has been characterized to assess the potential recovery of valuable metals. The
10 determination of the total amount of valuable metals (Ag, Al, Au, Be, Co, Cu, Ga, Ge, In, Ir,
11 Li, Ni, Pd, Pt, Sb, Ta, and W) in seasonal samples of weather bottom ash (WBA) was
12 performed by a total acid digestion followed by a chemical analysis. Besides, a sequential
13 extraction procedure (SEP) is conducted to define their partition. The characterisation has
14 shown that the content of valuable metals in the incineration WBA, which was highest in the
15 0 - 2 mm fraction was much lower than in concentrated ores commonly used as primary
16 sources. Moreover, the SEP showed little potential for the valorisation of most of the metals,
17 as they are embedded in or bound to a silicic matrix or sintered metal oxides, and so their
18 extraction requires strong-acid digestion or a highly oxidizing environment. This work
19 contributes to the use of residual sources as secondary resources and to the correct
20 management of the end-of-life electrical and electronic equipment.
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47 *Keywords:* municipal solid waste incineration, weathered bottom ash, valuable metals,
48 sequential extraction, total acid digestion, metal recovery.
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1. Introduction

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3 Incineration has become the preferred treatment of municipal solid waste (MSW) in Europe,
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5 as the most feasible alternative to landfilling, since it allows both waste volume and weight to
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7 be reduced (Bontempi et al., 2010; Puma et al., 2013). Bottom ash (BA) is the most
8
9 significant by-product from MSW incineration: as it accounts for 85–95% of the solid product
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11 resulting from combustion and it is considered a slag and granular material (Izquierdo et al.,
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13 2002), which is catalogued as a non-hazardous material (del Valle-Zermeño et al., 2017a).
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15 However, BA is heterogeneous material whose composition and chemical characterization is
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17 a function of particle size (Chimenos et al., 2003). Overall, BA is mainly composed of silicon,
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19 calcium, iron, aluminium, and sodium; and it can be revalorized as a secondary building
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21 material after being stabilized through a weathering process (del Valle-Zermeño et al., 2017b,
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23 2014, 2013). Nevertheless, it also contains a considerable amount of heavy metals and
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25 therefore in some countries it is disposed of in landfills (Wielgosinski et al., 2014).
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33 Currently, waste from electrical and electronic equipment (WEEE) is one of the fastest
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35 growing categories of waste streams in the EU, with a growth rate of 3%-5% per year; much
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37 higher than the rate for MSW (Eurostat, 2018). However, not all of the electrical and
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39 electronic equipment used goes through the official WEEE treatment system. While most
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41 large household appliances are collected separately and managed appropriately, a high
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43 percentage of smaller household appliances, telecommunications equipment, lighting
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45 apparatus, and electrical and electronic tools still find their way into the refuse
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47 (undifferentiated household) fraction of MSW, which is often incinerated or disposed of in
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49 landfills.
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55 Modern WEEE may contain more than 60 different elements; many of them are valuable,
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57 some are hazardous and others are both (Kaya, 2016; Schluep et al., 2009; Zhang and Xu,
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2016). It is mainly composed of metals (~60% weight), followed by plastics (~15% weight),
and both CRTs and LCD screens (12% weight). For instance, in the specific case of mobile
phones (of which metals represent some 23% of the weight), there can be 40 elemental
metals: basic metals, such as Cu, Fe or Sn; special metals, such as Co, Li, Be, Ir or Sb;
precious metals, such as Ag, Au or Pd; and also rare earth elements (REEs). In this regard,
although WEEE only accounts for a small percentage of MSW, the variety and proportion of
valuable metals in it is far higher than in other refuse waste fractions (Li and Xu, 2015). Most
of the metals come from non-renewable resources; with some already having seen more than
60% of total reserves in the earth's crust mined. According to the European Commission,
some of these metals present a higher risk of future shortage, this is due to their supply being
highly dependent on imports from only a few countries which are sometimes politically or
economically unstable, and due to their considerable importance for specific economic sectors
(Commission of the European Communities, 2008). Moreover, compared with the production
of primary metals, recycling metal resources from WEEE has significant advantages, such as
producing less secondary waste and lower energy consumption. Additional studies are
therefore needed on the fate of metals throughout the entire WEEE recycling and treatment
system, including the treatment of residues containing WEEE.

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During the incineration of MSW, the metals contained in WEEE are concentrated into one of
the forms of waste generated by the combustion process: BA or fly ash. Considering the
diversity and complexity of the physical and chemical phenomena involved in the
transformation, the behaviour of metals depends on their tendency to react and to change their
aggregate state (Zhang et al., 2012). For instance, Hg and Cd are two volatile metals that can
be considered negligible in BA; meanwhile metals such as Fe, Cu, Cr, Co, Ni and other
volatile metals such as Pb and Zn mostly remain in BA (Belevi and Moench, 2000; Jung et

1 al., 2004; Yao et al., 2010; Zhang et al., 2008, 2012). Similarly, metals with higher densities,
2 such as Cu, Au, Ag, and Sn, undergo no significant damage or oxidation.
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5 Although ferrous and non-ferrous metals are frequently removed from BA by means of
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Although ferrous and non-ferrous metals are frequently removed from BA by means of
electromagnets and Eddy current separators, respectively, the processes are mostly effective
in the size fraction containing particles larger than 5–8 mm (Biganzoli et al., 2014; del Valle-
Zermeño et al., 2017b). For instance, Al recovery has long been used because it is easy to
reuse and the process allows up to 95% of the energy required for primary production to be
saved (Hu et al., 2011; Zhou et al., 2006). However, 90% of total Al (metal and Al
compounds) is found in the fraction smaller than 1 mm and it is regarded to come mainly
from light packaging and Al foils (Biganzoli et al., 2013). Just as for Al, it is expected that
some valuable metals also remain in BA, and that many of these come from incinerated
WEEE (del Valle-Zermeño et al., 2017b). Nevertheless, given the highly heterogeneous
distribution of the materials in BA (Loginova et al., 2019), the contents of one specific metal
may differ as a function of particle size. Therefore, depending on their nature and
composition, the metals contained in certain size fractions potentially has recycling value.

Spain acquires and disposes of a large amount of electrical and electronic equipment (EEE)
every year. In 2016, a total of 626 kT of new electrical and electronic goods were placed on
the market (according to the Spanish Ministry of Agriculture, Fisheries, Food and the
Environment), while only 313 kT (3.8 kg per inhabitant) of WEEE was recovered or reused in
the same period (Eurostat, 2018). So, it can be assumed that around 50% of WEEE went into
the refuse fraction of MSW. Meanwhile, MSW incineration has increased in Spain in recent
years, and there are currently 10 waste-to-energy (WtE) plants. Four of these WtE plants are
located in Catalonia (north-east Spain), an autonomous region where more than 17% of MSW
collected was incinerated in 2016 and 134 kT of BA was produced (AEVERSU, 2018). Reuse
of BA as a secondary raw material is regulated by the Standards of the Catalanian authorities.

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However, for its proper reutilization, after removing ferrous and non-ferrous metals, BA must be stabilized through a weathering process (of some 2-3 months) in order to obtain weathered bottom ash (WBA).

In accordance with this situation, the main objective of this research is to assess the possibility of recovering valuable metals contained in WBA generated from MSW incineration, depending on the fractions of different particle sizes and based on their content and chemical nature. Along with the commonly studied Al, Ni and Cu, other valuable metals usually present in WEEE are also determined. In addition to total contents using total acid digestion, a four-step sequential extraction procedure for each particle-size fraction is also performed, in order to determine the partitioning of valuable metals and their availability to an extraction process. Finally, an important objective of this research is to define whether it is possible to recover the valuable metals contained in WBA from WEEE, or whether different management options would better facilitate their recovery.

2. Materials and methods

For the present research, WBA was collected from a WtE plant located in Tarragona (NE Spain). The incineration plant feed stream mainly consisted of household rubbish, with a small input from commercial sources. Approximately 32 kT of fresh BA is produced in the incineration plant and further treated in a conditioned/revalorization process for the recovery of ferrous and non-ferrous metals, and to remove lightweight materials. After being conditioned, the BA is stock-piled in the open for at least three months to ensure immobilization of heavy metals by weathering. In order to determine possible seasonal changes in the composition of the MSW, three sampling campaigns were carried out, during the months of February, July, and October. For each sampling period, around 40 kg of WBA was taken from various stockpiles, homogenized and stored in a 30 L plastic container.

1 The particle size distribution (PSD) of each seasonal sample (Fig. 1a) was determined using a
2 procedure employed in previous research (del Valle-Zermeño et al., 2017b). This consisted of
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4 sieving the WBA (dried overnight at 105 °C) with openings of 2, 4, 8 and 16 mm (EN 933-2).
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6 As can be seen in Fig. 1a, PSD analysis showed similar profiles for all seasons and the small
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8 differences could be explained by the consumption of different seasonal materials.
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12 After sieving, in order to facilitate chemical characterization, each fraction (Entire, >16, 8-16,
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14 4-8, 2-4 and 0-2 mm) was initially crushed in a jaw crusher and subsequently milled in a
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16 vibratory disc mill, using a hardened steel grinding set. Milling continued until the whole
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18 sample passed through an 80 µm mesh and produced a fine homogeneous powder. Likewise,
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20 for each size fraction, metal particles larger than 500 µm, plastically deformed by impacts
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22 during crushing and milling, were removed manually and quantified using a magnet and a
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24 magnifying glass, and kept separately for further chemical analysis (Fig. 1b). The metal
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26 content increased in the finer fractions (< 8 mm) where the metal removal (electromagnetic
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28 and Eddy currents) devices were not operative (del Valle-Zermeño et al., 2017b).
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35 The chemical composition of the major elements in the non-metallic fraction of each WBA
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37 size fraction was determined by X-ray fluorescence spectroscopy (XRF) using an S2 Ranger
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39 spectrometer (Bruker/AXS GmbH, Germany). For each size fraction, the contents of major
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41 elements were similar regardless of the season. Table 1 shows the average content of major
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43 elements according to WBA particle size. As reported elsewhere (del Valle-Zermeño et al.,
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45 2013), Si, Ca, and Al were the most abundant constituents, which mainly come from soda-
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47 lime glass and other natural or synthetic ceramic materials. Accordingly, the content of Si is
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49 greater in the size fractions where soda-lime glass is also more common; while the Ca and Al
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51 contents are higher when the ceramics content is also high (del Valle-Zermeño et al., 2017b).
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1 The mineral and crystalline phases in the WBA (see Table 3) were identified by powder X-ray
2 diffraction analysis (XRD) using an Expert diffractometer (Panalytical, Netherlands). It
3
4 should be emphasized that while some mineralogical phases usually considered in the
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6 literature were identified (Chimenos et al., 1999; Gonzalez et al., 2017; Xia et al., 2017), the
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8 initial sample presented an amorphous phase because of its glass content, which is the main
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10 component of the WBA (del Valle-Zermeño et al., 2017b), and therefore could not be
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12 identified by XRD. However, this packaging glass (primary glass) is one of the precursors of
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14 secondary glass, which is newly formed during the combustion process at high temperatures.
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20 **2.1. Total acid digestion**

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23 Total acid digestion of all the sub-samples studied (metal and non-metal fractions) was
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25 carried out to quantify the total contents of valuable metals contained in WBA, as a function
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27 of particle size. Around 0.5 g of dry powdered ash was accurately digested at 90 °C in Teflon[®]
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29 closed-reactors using a sequence of mineral acids (HNO₃/HF, HClO₄/HNO₃/H₂O₂). The
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31 resulting leachates were diluted to 100 mL with 2% HNO₃ and stored in polyethylene tubes at
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33 4 °C until analysis using inductively coupled plasma mass spectrometry (ICP-MS).
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38 From all the valuable metals contained in WEEE, after prior semi-quantitative analysis, the
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40 list of determined metals (Ag, Al, Au, Be, Co, Cu, Ga, Ge, In, Ir, Li, Ni, Pd, Pt, Sb, Ta, and
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42 W) differs from those critical metals established by the European Community for reasons.
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44 Firstly, some critical metals, such as the REEs, are in extremely low concentrations in WBA
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46 (Allegrini et al., 2014; Morf et al., 2013), and their concentrations in the leachates would be
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48 below the ICP-MS limit of detection. Secondly, there are some valuable metals (e.g., Al, Cu
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50 and Ni) which are not considered critical but their abundance in the sample makes their
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52 recovery economically feasible (Gonzalez et al., 2017; Morf et al., 2013). Finally, there are
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1 also other valuable metals, such as Ag and Au, whose high prices make their recovery
2 feasible, although their contents are not very high.
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5 **2.2. Sequential Extraction**

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8 An SEP was performed to determine the partition of valuable metals contained in WBA. The
9 principle of the sequential extraction was a solid sample treatment in several consecutive
10 steps with different solutions, increasing the chemical attack intensity. Each step leads to a
11 solution (separated by centrifugation) and also a residual solid, which is then subjected to the
12 next extraction solution. A modified BCR sequential extraction procedure defined by Rauret
13 et al. (1999) was applied to all the WBA sub-samples. All the reagents were of analytical
14 grade and the extracting solutions were prepared immediately before performing the leaching.
15 The leachates obtained were analysed using ICP-MS and the metals quantified were the same
16 as those analysed in the total acid digestion (Section 2.1.). Due to the similarities between the
17 three seasonal WBA samples, the SEP was only conducted on the July sample: it may be
18 assumed that the main results and conclusions can be extrapolated to the other two samples.
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36 In accordance with the proposed SEP, five operational fractions were established:
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39 *Exchangeable fraction* (Step 1): 1 g of the sample was extracted by shaking for 16 h
40 (overnight) at room temperature with 40 mL of ultrapure water.
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44 *Carbonate fraction* (Step 2): the residue from the previous step (Residue 1) was extracted
45 with 40 mL of acetic acid 0.1 M (pH \approx 2.9), by shaking for 16 h (overnight).
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50 *Hydroxide fraction* (Step 3): the residue from the previous step (Residue 2) was extracted
51 with 40 mL of a solution of hydroxylamine hydrochloride 0.5 M acidified with 2.5% HNO₃
52 2.0 M (pH \approx 1.3), by shaking for 16 h (overnight).
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Organic matter fraction (Step 4): the residue from the previous step (Residue 3) was extracted with 10 mL of 30% hydrogen peroxide adjusted to pH=2-3 with HNO₃, by shaking for 1 h at room temperature, while covered with a watch glass to avoid excessive evaporation. Then, the uncovered solution was shaken at 85 ± 2 °C in a water bath for an hour. Then, a further 10 mL of hydrogen peroxide (30%, pH=2-3 with HNO₃) was added and the covered sample was heated to 85 ± 2 °C in a water bath and maintained in it for a total of an hour. Finally, the liquid volume was reduced to 1 mL by heating; 50 mL of ammonium acetate 1 M was added; and the sample was extracted for 16 h (overnight) by shaking.

Residual fraction (Step 5): the residue of the previous step (Residue 4) was digested following the procedure carried out in the total acid digestion (Section 2.1).

3. Results and Discussion

In this section, the results of the total acid digestion and the SEP will be discussed. The former involves acid digestion with HNO₃ of each sieved fraction of WBA to elucidate its chemical composition. The latter allows us to determine the fractionation and mobility of valuable metals analysed in each extraction environment, which is related to the metal chemical speciation.

3.1. Total Acid Digestion

Table 2 shows the results of the total acid digestion for all the seasonal WBA samples studied. A comparison has been established between the results of each WBA fraction. As can be observed, for each particle-size fraction, the content of the metals analysed is highly similar for the three seasonal samples (February, July, and October). However, in cases the metal content in a specific fraction is unexpectedly high, (e.g., Co in the 8 - 4 mm size fraction of WBA samples collected in July, Table 2). This can be explained by the heterogeneous nature of the samples, especially in the metal fraction of each particle size, even though all the

1 samples were carefully quartered. Moreover, the heterogeneity of these metal fractions can
2 also explain the unusually large error bars in a few cases (see Figs. 2 and 3). However, for
3 most of the valuable metals analysed, taking into account the PSD and the ratio of each size
4 fraction (Fig. 1a), the sum of the contents of each fraction is very similar to the metal content
5 determined for the entire sample. That is, the samples are representative and properly
6 quartered.
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15 It should be noted that the highest metal contents in WBA corresponded to Al (around 75
16 $\text{g}\cdot\text{kg}^{-1}$); while Cu and Ni also have considerable concentrations (around 2 $\text{g}\cdot\text{kg}^{-1}$ and 0.1 $\text{g}\cdot\text{kg}^{-1}$,
17 respectively). Although these contents might appear to indicate abundance, they are far
18 below the typical levels concentration in ores commonly used as primary resources (Allegrini
19 et al., 2014). Only Cu, in some size fractions, is just two or three times less concentrated than
20 the content of primary ores. The highest content of all, with an occasional exception, was
21 found in the finer fractions (< 8 mm), where non-ferrous metal recovery devices (i.e., Eddy
22 current separators) cannot be use (del Valle-Zermeño et al., 2017b) or are not efficient
23 enough. While Cu and Ni are mainly present as base metals or as alloying elements (e.g.
24 wrought Al alloys or austenitic stainless steels), Al is also present in a large range of natural
25 and synthetic ceramics like clays, soda-lime glass, tiles and aluminosilicate-based ceramics.
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43 According to total content, a second group of metals ranged from 10 to 100 $\text{mg}\cdot\text{kg}^{-1}$,
44 including Sb, Li, Co, and Ga; although these contents are again much lower than those found
45 in the concentrated minerals used as primary resources for beneficiation (Allegrini et al.,
46 2014). The amount of Li determined might come mainly from rechargeable and non-
47 rechargeable batteries; although to a lesser extent it is also used in some ceramics and glass.
48 Sb is used as an alloying element (mainly Pb alloys), but also in electric and electronic
49 industries for cable sheathing to make semiconductor devices or in TV screens, as well as
50 being a flame retardant for many polymeric materials. Co is found in Li-ion batteries, as well
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1 as in some non-ferrous alloys to make powerful magnets; meanwhile Ga is used mainly in the
2 electronics industry in semiconductor devices.
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5 Ag, Be, Pd, and W were found in contents ranging between 1 and 10 mg·kg⁻¹. Ag, Pd, and Be
6 are all widely used in EEE; they can be found in cable and high-definition televisions,
7 electrical contacts, connectors, and screens in cell phones and computers, for example. While
8 W mainly comes from incandescent light bulbs, W-alloyed steel is used for tools, and even
9 from the balls of ballpoint pens (Morf et al., 2013).
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12 The lowest concentrations of metals were found for Au, In, and Ta; whereas Ir, Pt, and Ge
13 were analysed, but most of the size fractions or replicates analysed presented values below the
14 ICP-MS limit of detection (Ir < 0.025 mg·kg⁻¹; Pt < 0.25 mg·kg⁻¹; Ge < 0.25 mg·kg⁻¹). In is
15 used in semiconductors and in flat-screen TVs and computer screens; Au is present in most
16 connectors in EEE; and Ta is found in semiconductors and crystals for infrared instruments.
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19 Although the concentrations of the metals studied are relatively low, if considering
20 valorisation, and lower than concentrated ores used as primary resources, it must be
21 considered that the production of WBA in this conditioning plant is about 2,400 tonnes per
22 month. This leads to approximately 86 kg per year of Ag and 29 kg per year of Au, as
23 examples. Moreover, taking into account the PSD and the greater content of metals in the fine
24 fractions, it is possible to increase recovery performance for some valuable metals by treating
25 only the finer fractions (e.g. < 8 mm, which represents around 70% of total WBA).
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28 **3.2. Sequential Extraction Procedure**

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30 The potential extraction depends on different factors including: pH, the mineralogical phases
31 present, the amount of organic matter, salt concentrations, complexation agents, and the
32 presence of Fe/Mn/Al oxides or hydroxides (Hursthouse, 2001).
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Table 3 shows the major mineral phases for the WBA sample collected in July, as well as the crystallographic phases contained in the residues generated in each sequential extraction step. It should be noted again that the diffraction patterns obtained for each residue show an important presence of amorphous phases, most probably due to the large content of vitreous phases. The packaging (primary) glass which is present in large quantities in the MSW acts as one of the precursors of secondary glass, which is formed at high temperatures during the combustion process and could embed other materials and mineral phases. XRD analysis of the SEP Residues 1 - 4 corroborates the solving of some mineralogical phases from one step to the next. Most of the mineralogical phases were dissolved after carrying out Step 3 (oxidizing environment), with the notable exception of quartz and these phases of the silicic matrix, which were still present in Residue 4. It is worth noting the presence of ammonium chloride in Residue 3, as its origin is the extraction reagent used in Step 3 (hydroxylamine hydrochloride), which remains in the residue after the extraction procedure. In contrast, other crystalline phases, such as anhydrite and hydrocalumite, which are present in the initial WBA sample, disappear after carrying out the first step (aqueous environment).

The chemical characterization of each of the residual fractions obtained in the SEP, determined by XRF (Table 4), corroborates the solving of some mineralogical phases during the different extraction steps. As can be seen, the SiO_2 and Fe_2O_3 contents of the Residues increase as the extractive steps progress; while the contents of Al_2O_3 and CaO decrease. This variation in the content of silica, alumina, hematite or lime can be better appreciated by considering the $\text{SiO}_2/\text{Al}_2\text{O}_3$, SiO_2/CaO , $\text{Fe}_2\text{O}_3/\text{CaO}$ or $\text{Al}_2\text{O}_3/\text{CaO}$ ratios. All of these increase significantly, due to the greater dissolution of the mineralogical phases containing calcium and, to a lesser extent, aluminium; while the particles with a siliceous matrix or iron (hydr)oxides remain unchanged and are concentrated in the final solid phase of the extractive process (Residue 4). At this point, it must be taken into account that the presence of iron

1 should not only be attributed to crystalline phases, but also to the presence of amorphous Fe-
2 (hydr)oxides, as determined in BA (Dijkstra et al., 2006). Highlight again the high chloride
3 content of Residue 3, from the hydroxylamine hydrochloride used as the reagent in Step 3,
4 which remains in the residue after the extraction.
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10 The concentrations ($\text{mg}\cdot\text{kg}^{-1}$) of valuable metals extracted in each step of the SEP are plotted
11 in Figs. 2 and 3. A comparison between the total amount of each metal extracted during the
12 SEP and the value obtained for the total acid digestion is also shown with the aim of
13 evaluating the effectiveness of the SEP compared to the total acid digestion. Theoretically,
14 total digestion metal concentrations should be equal to the sum of the individual SEP fractions
15 for each metal.
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25 It is noticeable from Figs. 2 and 3 that, with some possible exceptions, the correlation
26 between extractability using the total digestion approach and the sum of the individual
27 fractions of metals from the SEP is not excellent. This is more evident in some particle-size
28 fractions of some of the metals analysed. The main reasons for this may have to do with the
29 heterogeneity and aggregation state of the metal fractions analysed for each particle size;
30 although other authors discuss other reasons, including the re-adsorption and re-distribution of
31 metals among phases during the extraction process, and incomplete dissolution of the target
32 phase during extraction (Gómez-Ariza et al., 1999). In addition, new solid phases may be
33 precipitated from the leachate, the reagents may not be sufficiently selective for the target
34 phase, and the extraction may be inefficient and hence incomplete (Bacon and Davidson,
35 2008).
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52 However, for almost all the valuable metals analysed, it should be highlighted that the relation
53 between the fractions established in the SEP (partition) was quite similar for all the size
54 fractions. That is, although the content of a metal is different for each size fraction, its
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1 distribution between the five operational fractions of the SEP did not depend on the WBA
2 particle size. In this regard, it was found that Au, Be, Li, Ni, Sb, Ta, and W were mainly
3 contained in Residue 4 and were released in Step 5, requiring strong-acid digestion to extract
4 them. That is, these valuable metals would be mostly bound to or embedded in silicate
5 minerals (e.g. a glass matrix) or metal oxides sintered at high temperatures (e.g. iron oxides),
6 which prevent the reagents from gaining access to the metals.
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9 For Ag, Al, Ga, In, and Pd, the content extracted in Steps 4 and 5 were quite similar. Thus, it
10 is to be expected that these metals would be both embedded in a silicic structure (e.g. a glass
11 matrix) and bound to oxidizable matter. Ga was also extracted in Step 1 (water environment);
12 therefore it is partly adsorbed on the surface of solid particles and is easily released.
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14 Meanwhile, Cu was mainly in its oxidized chemical form, as it was extracted in quantity in
15 Step 3; and Co was mainly released during Step 2, which means that it might be bound to
16 carbonates and released in the acid environment.
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32 **4. Conclusions**

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34 Although a high percentage of WEEE goes to the refuse fraction of MSW, which is
35 increasingly managed in WtE plants, it has been determined the content of valuable metals in
36 WBA, which is much lower than the concentration of these metals in the concentrated ores
37 commonly used as primary sources. Most critical metals, such as REEs, are found in very low
38 concentrations, even below the limits of detection the analysis techniques used. Accordingly,
39 only some valuable metals (Ag, Al, Au, Be, Co, Cu, Ga, Ge, In, Ir, Li, Ni, Pd, Pt, Sb, Ta, and
40 W), due to their higher contents, high market price or industrial interest, have been estimated
41 to evaluate the feasibility of recovering them from WBA generated during the incineration of
42 MSW.
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1 The content of these valuable metals increases as the particle size decreases, with the highest
2 in the 0 - 2 mm fraction, although this is still well below the content of naturally occurring
3 concentrated ores. According to bibliographic data, of all the valuable metals studied, only the
4 concentration of copper was within a factor of two or three of the contents of concentrated
5 minerals. However, the difference in content between the different size fractions is not large
6 enough to make separation by particle sizes alone a feasible option for concentrating the
7 valuable metals enough for their recovery to be economically viable.
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10 The sequential extraction performed shows that most of the metals analysed are mainly
11 extracted from the Residue 4, where strong-acid digestion is required to extract them.
12 Accordingly, most of these valuable metals can be assumed to be embedded in secondary
13 glass formed during the combustion process, linked to a silicic matrix, or to form part of the
14 structure of other metal oxides, such as iron oxides sintered at elevated temperatures. This
15 makes recovery even more difficult, given that more severe conditions are required.
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18 To extend and complete this study, similar research should be performed on the non-ferrous
19 fraction of BA, recovered in the conditioning plant by Eddy current devices. This would
20 determine if these valuable metals are more concentrated in this fraction and their extraction
21 easier.
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24 Despite the low concentrations of valuable metals and the difficulty in their extraction from
25 BA, it must be noted that due to a large amounts of BA generated each year, considerable
26 amounts of valuable metals are not recovered and end up in landfills or as secondary building
27 materials. Therefore, the recovery of these valuable metals should be based on a more
28 effective policy of WEEE management, i.e. separate collection and proper management,
29 rather than difficult and expensive extraction processes of the MSWI weathered bottom ash.
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1 Proper management of WEEE prior to incineration of RSU will contribute to more
2 sustainable uses of resources.
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7
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Table 1. Average of major component of seasonal WBA samples according to particle size, analysed by means XRF. Values reported in % (wt/wt) with relative standard deviation.

Component	Particle Size Fraction (mm)					
	Entire	> 16	16 - 8	8 - 4	4 - 2	2 - 0
SiO₂	42.01 ± 6.14	51.08 ± 4.82	54.00 ± 7.77	53.74 ± 4.44	43.73 ± 3.58	25.32 ± 3.14
CaO	26.55 ± 7.57	14.84 ± 7.16	15.26 ± 2.60	16.84 ± 2.21	20.99 ± 5.39	25.94 ± 4.05
Al₂O₃	8.07 ± 2.57	8.93 ± 3.54	5.43 ± 0.62	5.48 ± 0.20	8.23 ± 2.15	9.64 ± 2.81
Na₂O	4.62 ± 1.19	3.44 ± 0.96	6.24 ± 1.94	6.46 ± 1.81	4.75 ± 1.77	2.36 ± 1.17
Fe₂O₃	4.80 ± 0.20	2.67 ± 0.75	4.94 ± 1.09	3.72 ± 0.13	4.75 ± 1.10	5.09 ± 1.69
MgO	3.37 ± 0.28	1.97 ± 0.72	2.01 ± 0.06	1.58 ± 0.23	2.85 ± 0.29	2.75 ± 0.16
SO₃	2.51 ± 0.21	1.91 ± 0.33	0.52 ± 0.04	0.89 ± 0.09	1.51 ± 0.08	2.97 ± 0.76
K₂O	1.86 ± 0.13	1.96 ± 0.27	1.40 ± 0.38	1.25 ± 0.08	1.56 ± 0.37	1.32 ± 0.37
P₂O₅	1.56 ± 0.45	0.36 ± 0.05	0.43 ± 0.08	0.89 ± 0.19	1.60 ± 0.28	2.02 ± 0.1
TiO₂	0.81 ± 0.31	0.58 ± 0.13	0.37 ± 0.15	0.49 ± 0.13	0.69 ± 0.23	0.93 ± 0.21
MnO	0.08 ± 0.02	0.04 ± 0.01	0.07 ± 0.01	0.06 ± 0.02	0.09 ± 0.02	0.11 ± 0.03

Table 2. Total acid digestion data for of WBA seasonal samples. Values reported in mg·kg⁻¹ with standard deviation.

WBA collected on February														
(mm)	Ag	Al	Au	Be	Co	Cu	Ga	In	Li	Ni	Pd	Sb	Ta	W
> 16	1.32±0.78	56682±752	0.325±0.181	5.25±0.21	11.5±0.0	81.1±1.2	15.4±0.0	0.030±0.007	34.8±0.2	26.5±0.5	1.51±0.02	18.5±0.3	0.590±0.344	4.38±0.10
16 – 8	1.38±0.02	58789±4804	0.330±0.154	1.61±0.27	8.81±0.25	2837±222	8.07±0.35	0.055±0.025	29.2±0.4	62.2±6.7	0.595±0.022	46.6±1.6	0.610±0.402	1.56±0.09
8 – 4	2.83±0.33	62562±3164	0.325±0.202	1.04±0.48	9.81±0.65	1359±55	7.84±0.37	0.050±0.032	33.7±1.0	38.1±6.0	0.927±0.118	64.9±4.2	0.660±0.350	1.69±0.86
4 – 2	3.50±0.61	89414±4989	0.320±0.180	0.730±0.193	15.6±2.0	4092±512	11.8±0.2	0.055±0.030	39.6±1.4	71.5±9.1	0.985±0.076	41.2±2.8	0.535±0.434	2.23±0.52
2 - 0	3.45±0.35	58301±559	0.803±0.319	1.20±0.21	32.7±0.9	2074±59	10.9±0.1	0.065±0.023	26.9±0.6	109±11	0.917±0.062	45.6±4.3	0.750±0.283	4.58±0.23
Entire	2.44±1.44	64038±3465	0.420±0.231	1.02±0.23	12.4±0.7	2498±86	10.8±0.3	0.055±0.019	32.6±0.4	88.0±4.6	0.991±0.053	26.1±1.3	0.590±0.361	1.73±0.14
WBA collected on July														
(mm)	Ag	Al	Au	Be	Co	Cu	Ga	In	Li	Ni	Pd	Sb	Ta	W
> 16	2.64±0.39	49340±363	1.00±0.22	1.24±0.28	21.5±0.6	446±11	13.7±0.1	0.083±0.008	36.6±0.7	38.2±1.5	0.992±0.021	50.3±1.0	0.705±0.361	2.60±0.17
16 – 8	3.88±1.52	69717±216	1.25±0.45	1.50±0.42	9.04±0.67	612±219	11.3±0.5	0.053±0.014	36.4±3.6	26.9±4.6	0.904±0.073	20.0±0.8	0.935±0.442	2.31±0.38
8 – 4	2.74±0.66	67798±3272	0.925±0.434	2.02±0.33	252±52	1721±57	7.93±0.30	0.055±0.010	59.9±3.1	109±10	0.811±0.043	41.6±1.4	0.745±0.381	2.65±0.24
4 – 2	2.30±0.25	42470±7732	0.775±0.242	1.05±0.21	18.0±5.4	2323±79	12.6±2.9	0.054±0.020	42.5±0.7	145±51	1.21±0.06	57.8±1.8	0.820±0.674	4.01±1.19
2 - 0	4.18±0.26	54165±2791	0.770±0.152	0.835±0.103	36.1±3.1	2996±304	10.8±0.4	0.096±0.021	38.0±1.6	159±16	1.03±0.06	73.1±2.3	0.990±0.630	5.45±0.29
Entire	5.90±0.35	76605±12242	1.44±0.19	0.565±0.170	65.5±6.1	2122±530	10.9±0.1	0.268±0.123	30.2±0.7	140±36	1.06±0.10	47.7±4.3	0.720±0.431	3.78±0.43
WBA collected on October														
(mm)	Ag	Al	Au	Be	Co	Cu	Ga	In	Li	Ni	Pd	Sb	Ta	W
> 16	1.34±0.10	51474±288	1.24±0.05	1.39±0.12	33.5±1.5	381±9	12.5±0.4	0.070±0.009	29.1±0.5	61.4±3.7	0.834±0.067	11.0±0.9	1.27±0.09	3.51±0.74
16 – 8	2.09±0.18	43626±311	0.490±0.087	1.28±0.18	10.3±0.3	364±26	8.82±0.24	0.052±0.006	144±1	35.3±2.5	0.679±0.012	108±1	0.85±0.09	2.31±0.04
8 – 4	2.28±0.21	36747±3081	0.440±0.021	1.31±0.05	12.4±0.6	840±18	6.90±0.29	0.030±0.001	35.1±0.3	48.9±10.7	0.802±0.031	38.8±0.7	0.72±0.07	3.09±0.12
4 – 2	16.6±9.9	57746±8072	1.07±0.12	1.55±0.27	17.4±3.6	2410±262	10.6±1.2	0.100±0.012	35.7±0.4	125±22	0.796±0.072	62.3±9.5	1.63±0.07	4.19±0.53
2 - 0	5.68±1.96	59494±301	1.40±0.09	1.25±0.02	38.6±2.2	2708±141	9.00±1.11	0.160±0.017	26.8±5.0	133±9	0.730±0.098	52.7±46.5	5.60±4.90	5.08±3.74
Entire	3.30±1.00	56389±1801	1.44±0.13	1.84±0.17	22.3±4.5	2008±40	9.85±0.52	0.060±0.004	31.5±1.6	298±16	0.808±0.130	40.5±3.0	1.49±0.11	14.90±0.7

Table 3. Major crystallographic phases identified by XRD from the initial (Entire) WBA sample collected on July and from the Residue fractions generated in each step of the SEP.

Initial phases in WBA	Residue 1	Residue 2	Residue 3	Residue 4
Calcium Silicate Hydroxide	✓	✓	✓	✓*
Quartz	✓	✓	✓	✓
Gehlenite	✓	✓	x***	x
Hydroxylapatite	✓	✓	✓	x
Hydrocalumine	x	x	x	x
Calcium Aluminum Chloride Hydroxide Hydrate	x	x	x	x
Calcite	✓	✓*	x***	x
Anhydrite	x	x	x	x
Sodium Calcium Aluminum Silicate	✓	✓	✓	✓*
Potassium-Feldspar	✓	✓	x***	x
Orthoferrosilite	✓	✓	✓	✓
Hematite	✓	✓	✓	✓
Calcium Silicate	✓	✓	x***	x
Ammonium Chloride	---	---	✓**	x

✓ identified by XRD

x not identified by XRD

* decreasing of peaks intensity

** coming from the extraction reagent used

*** dissolved completely because of the pH of the reagent, not for its reducing properties

Table 4. Chemical characterization determined by XRF from the Residue fractions generated in each step of the SEP. Values reported in % (wt/wt).

	Residue 1	Residue 2	Residue 3	Residue 4
SiO₂	34,00	46,15	44,35	54,95
CaO	37,55	23,50	14,95	9,44
Fe₂O₃	6,23	7,64	8,26	11,95
Al₂O₃	4,60	6,97	4,76	5,69
MgO	2,29	2,40	1,61	1,32
SO₃	2,00	0,45	0,38	0,17
P₂O₅	1,97	2,71	2,87	1,64
K₂O	1,70	1,83	1,99	2,28
TiO₂	1,62	1,92	2,39	3,16
Cl	0,45	0,31	12,90	2,27
SiO₂/Al₂O₃	7,40	6,63	9,32	9,67
SiO₂/CaO	0,91	1,96	2,97	5,82
Al₂O₃/CaO	0,12	0,30	0,32	0,60
Fe₂O₃/CaO	0,17	0,32	0,55	1,27

Figure Caption

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3 Fig. 1. (a) Particle size distribution (PSD) of the seasonal weather bottom ash (WBA)
4 samples; (b) Average of metal content in each fraction of the seasonal WBA samples. Particle
5 size fractions reported in mm.
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10 Fig 2. Partition and total content of valuable metals (In, Au, Pd, Ta, Be, Ag and W) extracted
11 from WBA sample collected on July, in accordance with each step of the sequential extraction
12 and total digestion procedures. Particle size fractions reported in mm.
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18 Fig 3. Partition and total content of valuable metals (Ga, Li, Sb, Co, Ni, Cu and Al) extracted
19 from WBA sample collected on July, in accordance with each step of the sequential extraction
20 and total digestion procedures. Particle size fractions reported in mm.
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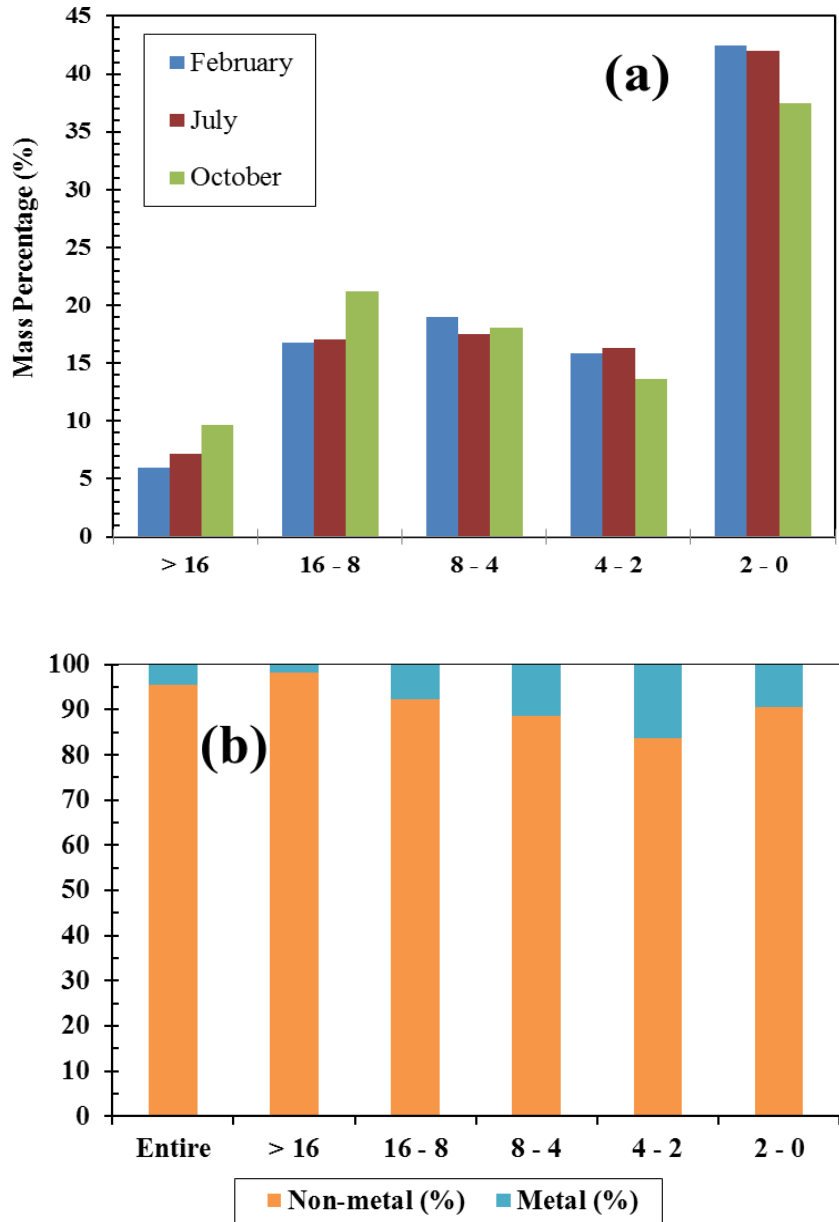


Fig. 1

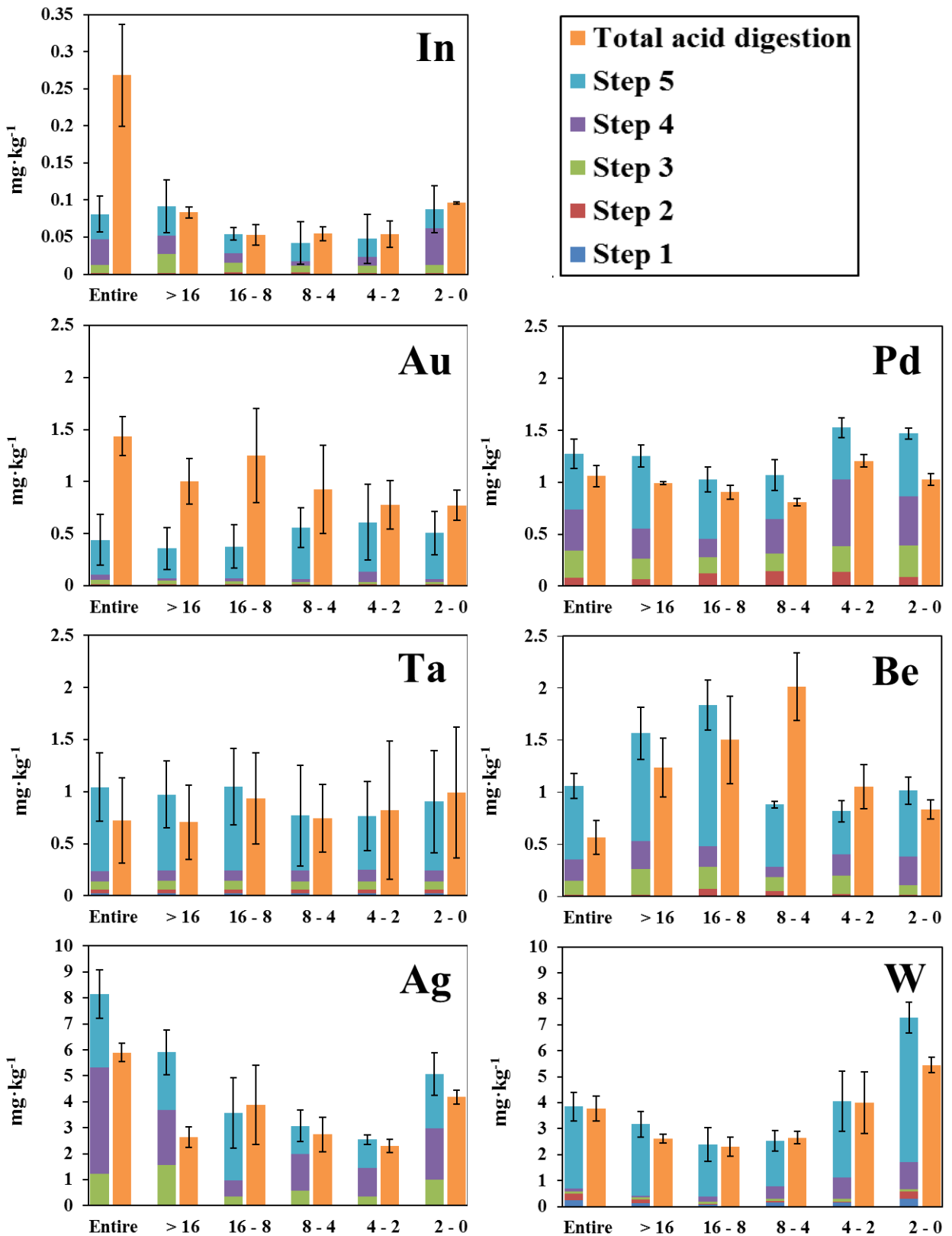


Fig 2.

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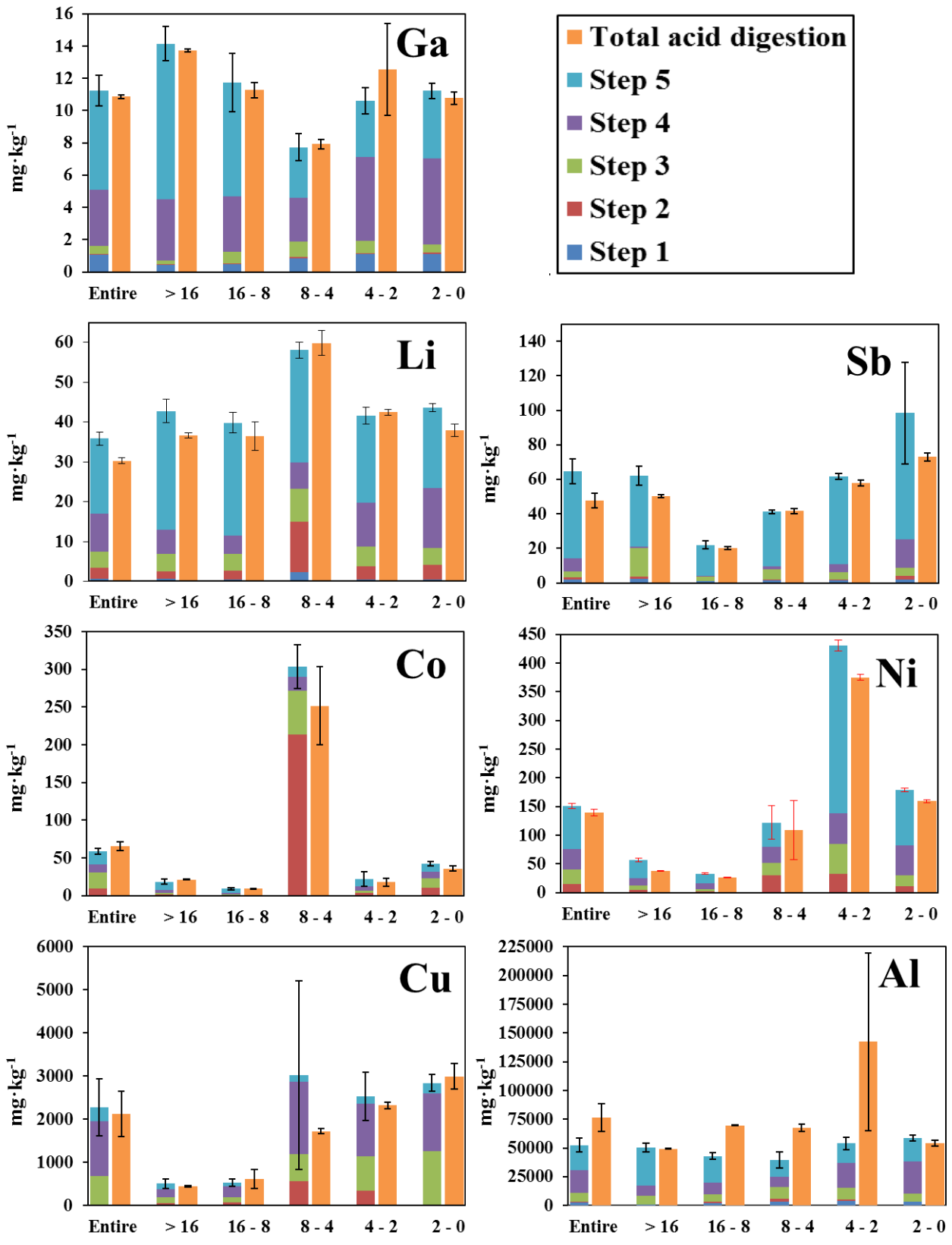


Fig. 3