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Research Paper

Speciation of copper and zinc compounds relevant for the hazard property (HP) 14 classification of municipal solid waste incineration bottom and fly ashes

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ABSTRACT

The analysis of the presence and content of substances that are toxic to aquatic life in waste is essential for classification of waste with regard to hazard property (HP) 14 'ecotoxic'. For the determination of HP14 classified copper (Cu) and zinc (Zn) compounds in various municipal solid waste incineration bottom ashes (IBA) and one fly ash (FA) from Germany we applied X-ray absorption near-edge structure (XANES) spectroscopy in combination with linear combination fitting. The analysis showed that approx. 50–70% of Cu in the IBA are Cu(I) compounds and elemental Cu(0), but these compounds were not equally distributed in the different IBA. In contrast, the majority (approx. 50–70%) of Zn in all IBA is elemental zinc, which originates from brass or other alloys and galvanized metals with a large content of zinc in the waste. The FA contain higher mass fraction on Zn and other toxic elements, but similar Cu and Zn species. Additional performed selective extraction at a pH of 4 with an organic acid of some IBA showed that the ecotoxic Zn fraction is mainly elemental zinc and zinc oxide. In contrast, for the ecotoxic Cu fraction within the IBA no specific compound could be identified. Furthermore, the XANES analysis showed that the HP14 properties of especially Cu in IBA is overestimated with current best-practice guidelines for sample processing for the current substance-related approach with the 0.1% cut-off rule for each substance. However, it should be considered whether it would not be better from an environmental point of view to take the ecotoxicologically leachable copper and zinc as a reference value.

1. Introduction

In Germany around 100 solid waste incineration plants are currently in operation which generate approx. six million tons of municipal solid waste incineration bottom ash (IBA) annually (ITAD, 2021). Moreover, approx. 640,000 tons of fly ash (FA) occurs annually. Because the composition of IBA is similar to mineral raw materials it can be used as secondary building material (Simon and Kalbe, 2023; Singh et al., 2023) e.g. as subbase material in road construction (Di Gianfilippo et al., 2018). There are two mirror entries in the European Waste Catalogue for bottom ash and slag from waste incineration: 19 01 11* and 19 01 12. Entry 19 01 11* describes a waste material containing hazardous substances. It was shown that only the hazardous property HP14 (ecotoxic) is of relevance for the classification (Nordsieck et al., 2018). However, the classification of wastes regarding hazardous property (HP) 14 (ecotoxicity) is essential for the use of IBA and FA in proper waste management (Stiernström et al., 2016). There are several hazardous statement codes (HSC) for HP14 classification – H400 (aquatic acute 1); H410, H411, H412, H413 (aquatic chronic 1–4) and H420 'ozone depleting'. In practice, no substances classified as H420 occur in IBA. Various constituents of IBA comprising heavy metal ions are labelled with HSC H410 (e.g. CuO, ZnO, all Pb compounds), the most stringent HSC for HP14. An example for a substance with HSC H411 is $ZnCO_3$. The HP14 classification is performed with a calculation method. The most decisive calculation rule is displayed in equation (1).

$$HP14 = 100 \times \Sigma\ c(H410) + 10 \times \Sigma\ c(H411) + \Sigma\ c(H412) \geq 25\% \quad (1)$$

The concentrations must be calculated with the molecular weight of each substance (see table S1) rather than concentration of the respective heavy metal only (except for As, Cd, Pb and Sb, according to 'Note 1'in

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CLP), so called 'Note 1′ substances. As can be seen, the highest contribution to HP14 arises from H410 substances. Therefore, substances being classified with H410 must be considered for IBA and FA in detail (Nordsieck et al., 2018). The limit value for HP14 is 25 %, but with a cut-off value of 0.1 % of each H410 substance (1 % for H411, H412 and H413 substances). The classification rule are explained in detail elsewhere (Hennebert, 2019). Therefore, only heavy metals with concentrations above approx. 500 mg/kg need to be considered for the HP14 classification (in the case of Pb: 1000 mg/kg). According to previous data on the elemental composition of IBAs (Vogel et al., 2024) elements considered for HP14 are "only" Cu and Zn, due to the cut-off value of 0.1 %.

There have been attempts for the HP14 assessment using ecotoxicology tests (Bandarra et al., 2023; Bandarra et al., 2022; Beggio et al., 2021). Aquatic bioassays are predominantly used, and the acute toxicity is addressed. But compulsory guidelines for sample processing are still lacking. One problem is that the pH values in the eluates from the IBAs are often outside the biological tolerance range (>8.5) (Ferrari et al., 1999; Lapa et al., 2002).

Appropriate tests should quantify water-soluble (surely H410), slightly soluble (potentially H410) and insoluble substances (surely not H410) of IBA relevant elements such as copper (Cu) and zinc (Zn) (Tang and Steenari, 2016), which can probably estimate their critical hazardous property. Because this is mostly not possible in detail a worst-case scenario is assumed, where the highest ecotoxicity of the containing Cu and Zn compounds is assumed. However, therefore the ecotoxicity of IBA is often overestimated. To determine the water and slightly soluble Cu and Zn compounds which are surely and potentially H410 a selective extraction with organic acids at a pH of 4 is in the testing phase (Nordsieck et al., 2018; Simon and Scholz, 2024). However, this approach requires elaborately sample processing which is not easy for all Cu and Zn compounds.

Therefore, we applied Cu and Zn K-edge X-ray absorption near-edge structure (XANES) spectroscopy to analyze the chemical species of Cu and Zn in various IBA and one FA from Germany to estimate their potential hazard. XANES spectroscopy was already previously applied for Cu (De Matteis et al., 2024; Hsiao et al., 2002; Lassesson et al., 2014; Lassesson and Steenari, 2013; Rissler et al., 2020) and Zn (De Matteis et al., 2024; Rissler et al., 2020; Takaoka et al., 2005) in IBAs and FAs from waste incineration. Moreover, we additionally applied linear combination (LC) fitting (Calvin and Furst, 2013) to the recorded XANES spectra to calculate the concentrations of Cu and Zn compounds in the analyzed IBAs and FA and finally assess their HP14 properties.

2. Materials and methods

2.1. Sampling

Four IBA (BA1, BA2, BA3, BA4) and one FA (FA1) from various thermal waste treatment plants in Germany were analyzed in this study. BA1 and BA3 were sampled at municipal waste incineration (MSWI) plants in northern Germany with grate technology and wet ash extraction systems. BA2 was sampled at a MSWI plant in southern Germany also equipped with a wet ash extraction system. However, the water supply of the extraction system was stopped and dry bottom ash, i.e. IBA with no contact to water, was sampled. A similar procedure was applied in the study of (Quicker and Stockschläder, 2018) at the MSWI MHKW Mainz (Germany). BA4 was sampled at an industrial incineration plant treating substitute fuel. FA1 stemmed from a waste incinerator where a multicyclone is placed between the boiler and spray dryer so that no flue gas cleaning products are contained in this fly ash. The mass fractions (in mg per kg dry weight) of Cu and Zn in the samples were analyzed by ICP-OES (Thermo iCAP 7000, Dreieich, Germany) after microwave-assisted aqua regia digestion (HNO_3/HCl; mikroPrepA, MLS GmbH, Leutkirch, Germany). All digestions and ICP-OES measurements were carried out in triplicates.

2.2. Selective extraction of copper and zinc

To access the water and slightly soluble H410 pool of Cu and Zn compounds in the IBAs and FA1 extraction with organic acids at a pH of 4 is a promising approach (Nordsieck et al., 2018; Simon and Scholz, 2024). Based on this the selective extraction of Cu and Zn from the IBAs and FA1 was carried out with 0.1 M maleic acid and 0.1 M sodium acetate. Therefore, 40 ml of extraction solution was added to 1 g of the sample in a centrifuge tube. After addition, the sample was briefly shaken, and afterwards the pH was adjusted to 3.8–4.0 using HNO_3 and NaOH. The mixture was then shaken at 150 rpm for 24 h, during which the pH was adjusted to 4.0 after 1/2/4/6 h if necessary, typically by lowering it with additional HNO_3. After 24 h, the liquid was separated from the solid. To achieve this, the sample containers were centrifuged for 5 min at 6000 rpm, and then the liquid phase was decanted. The solid residue was washed twice with 4 ml of MilliQ water each, centrifuged, and decanted again. The resultant solution of approximately 48 ml was topped up to 50 ml and preserved for cation analysis using ICP-OES (Thermo iCAP 7000, Dreieich, Germany) and ICP-MS (Thermo iCAP Q, Dreieich, Germany), respectively. The selective extraction process was carried out in triplicate for all samples. For XANES spectroscopy, the solid residues of BA2 and BA3 only were dried for 24 h at 80 °C (samples are referred hereafter as BA2_SE and BA3_SE).

2.3. Copper and zinc K-edge XANES spectroscopy

The Cu and Zn K-edge XANES spectroscopic measurements were carried out at KMC-2 beamline at the electron storage ring BESSY II, Helmholtz-Zentrum, Berlin, Germany (Többens and Zander, 2016). The incident beam was monochromatized with a Si $< 111 >$ double crystal monochromator. The scans were performed at room temperature. The Cu and Zn K-edge XANES spectra were collected in the range of 8830 – 9230 eV and 9515–9900 eV, respectively, in transmission mode for the reference compounds and fluorescence mode for the IBA and FA samples.

Based on literature and presumption the following Cu reference compounds (Cu foil, Cu_2O, CuO (both Acros Organics), CuS (ABCR, Karlsruhe, Germany), CuCl (Alfa Aesar, Karlsruhe, Germany), Cu_2S, $CuCl_2$ (both Thermo Scientific, Kandel, Germany), $CuCO_3$ (Carl Roth, Karlsruhe, Germany), $CuSiO_3$ (precipitated from $CuSO_4{\cdot}5H_2O$ (Honeywell Fluka, Germany) and $Na_2SiO_3{\cdot}5H_2O$ (J.T. Baker, Deventer, the Netherlands) solutions (Gmelin-Institut, 1961)), $CuFe_2O_4$ (Sigma-Aldrich, St. Louis, USA), Cu containing malachite (Berliner Mineralien Zentrum, Berlin, Germany), Cu containing whitlockite) and Zn reference compounds (Zn foil, ZnO (Merck, Darmstadt, Germany), $ZnCl_2$, $ZnCO_3$, $ZnSO_4{\cdot}7H_2O$ (all three Sigma-Aldrich, Weinheim, Germany), $ZnFe_2O_4$, ZnS, $Zn_3(PO_4)_2{\cdot}xH_2O$ (all three Thermo Scientific, Kandel, Germany), Zn $(NO_3)_2$ (Carl Roth, Karlsruhe, Germany) and Zn containing whitlockite) were used for the experiments.

The Cu- and Zn-containing whitlockite were prepared as following: Stoichiometric mixtures of $NH_4H_2PO_4$, $CaCO_3$, CuO and ZnO (all p.a. grade) were thoroughly mixed for synthesis of $Ca_{19}Zn_2(PO_4)_{14}$ and $Ca_{19}Cu_2(PO_4)_{14}$, respectively. They were heated at 900 °C for 1 h, grinded in a vibrating tungsten-carbide cup mill (Pulverisette, Siebtechnik, Germany) and afterwards sintered at 1000 °C with interruption of regrinding after 4, 24 and 48 h followed by XRD analysis of the final product.

All spectra were background subtracted and normalized to an edge jump of $\Delta\mu d = 1$ using the Athena software from the Demeter 0.9.26 package (Ravel and Newville, 2005). Additionally, the Cu and Zn K-edge XANES spectra were analyzed with linear combination (LC) fitting using LCF-Linest (https://vminteq.com/lcf-linest/; (Gustafsson et al., 2020)). Here, the spectral fitting range was set from -20 to $+150$ eV of the respective edge. The maximum number of compounds in the final LC fit was limited to four and the sum of the compounds was forced to add up to 100 %. From all possible LC fits the best five combinations with the best R^2-value were chosen. Examples for the LC fitting of the Cu and Zn XANES spectra are plotted in Figs. S1 and S2.

Furthermore, a difference spectrum of BA2 and BA3 before and after selective extraction was calculated by subtraction of the unnormalized spectra. For the LC fits of the difference spectra the same settings were used as before, but only the HP14 relevant substances of Cu (Cu, Cu_2O, CuO, CuCl, $CuCl_2$, $CuCO_3$, Cu containing malachite, Cu containing whitlockite) and Zn (Zn, ZnO, $ZnCl_2$, $ZnCO_3$, $ZnSO_4 \cdot 7H_2O$, $Zn_3(PO_4)_2$, $Zn(NO_3)_2$ and Zn containing whitlockite).

3. Results and discussion

3.1. Copper K-edge XANES spectroscopy of IBA

Fig. 1 shows the Cu K-edge XANES spectra of various pure Cu compounds (top) and the investigated IBAs and FA (bottom). The analyzed copper compounds show a clear edge shift between Cu(I) and Cu(II) compounds (see for comparison the oxides, sulfides and chlorides). Moreover, the copper sulfides (Cu_2S and CuS) show a completely different structure than the other copper compounds. In general, the spectra of the pure Cu compounds are in agreement to previous measurements (Lassesson and Steenari, 2013; Rissler et al., 2020).

The analyzed IBAs and FA show an absorption edge energy and white line (most intense absorption) which cannot be assumed visible to any specific Cu compound. Therefore, the IBA and FA samples contain most probably a mixture of various Cu compounds. Therefore, we applied additionally LC fitting (see Table S2). For each IBA and FA the best five LC fits are displayed. The best LC fits of BA1 show approx. 50 % of Cu(II) compounds and approx. 50 % of Cu(I) compounds and elemental Cu(0). This agrees with previous work (De Matteis et al., 2024; Rissler et al., 2020) that Cu can be observed in all three oxidation states (0, +I, +II) in IBAs. A similar distribution to BA1 could be also found in BA3. In contrast, BA2 shows up to approx. 90 % of Cu(I) compounds. This is also visible on the little shoulder in the edge of the XANES spectrum (see Fig. 1). In comparison to previous work of Rissler et al., 2020 the content of Cu(I) compounds in IBA from Sweden is strongly increased. Normally, CuO is converted to Cu_2O at temperatures from 800 °C under nitrogen and oxygen atmosphere (Gmelin-Institut, 1958). Therefore, there might be partly a higher temperature on this waste incineration facility. Moreover, BA2 was extracted without any contact to water which might affect the formed Cu species (Inkaew et al., 2016; Yang et al., 2016). Also, for BA4 a higher percentage of Cu(I) compounds was found, but here in contrast Cu_2S was found as major Cu compound. Additional wet chemical treatment with acid and H_2S development proved that the investigated IBA contain sulfides. Surprisingly, FA1 do not show difference in the XANES spectrum compared to the IBAs. Their Cu distribution is also very similar to BA1 and BA3 with approx. 50 % of Cu(I) compounds.

3.2. Zinc K-edge XANES spectroscopy of IBA

Fig. 2 shows the Zn K-edge XANES spectra of various pure Zn compounds (top) and the investigated IBAs and FA (bottom). All pure Zn compounds, except Zn and ZnS show a relative strong white line. In addition, all compounds have their own characteristic features in the post edge/white line region. The reference spectra agree also with

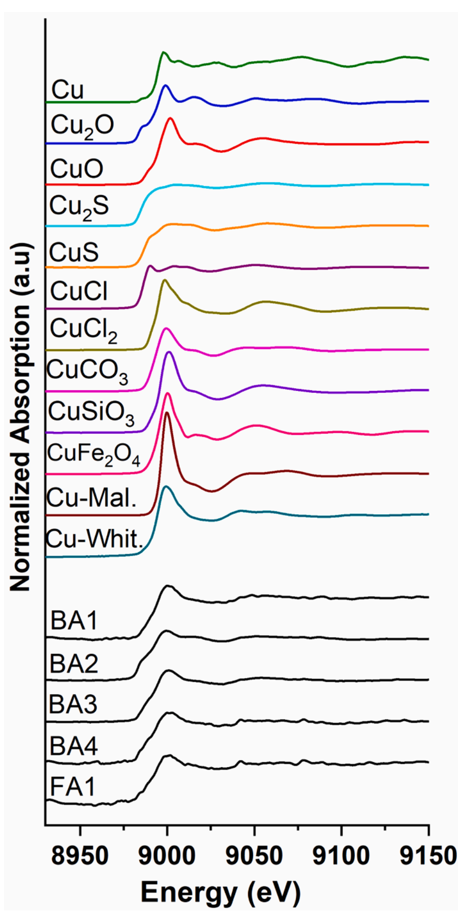

Fig. 1. Copper K-edge XANES spectra of various copper compounds and BA1-BA4 and FA1; Cu-Mal. = copper containing malachite; Cu –Whit. = copper containing whitlockite.

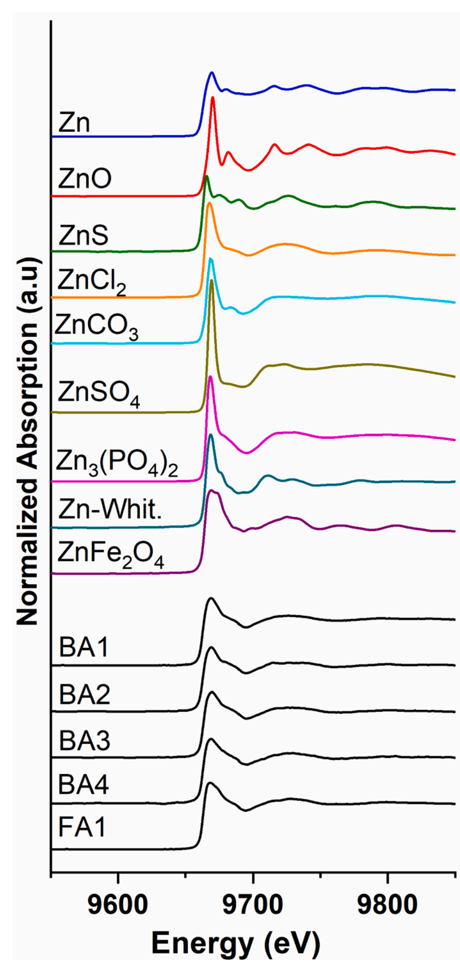

Fig. 2. Zinc K-edge XANES spectra of various zinc compounds and BA1-BA4 and FA1; Zn –Whit. = zinc containing whitlockite.

previously published papers (De Matteis et al., 2024; Rissler et al., 2020; Takaoka et al., 2005).

Similar to the Cu XANES analysis, also for zinc all analyzed IBAs and FA1 show relative similar spectra features. Because these features cannot be assumed to any specific Zn compound also LC fitting was applied (Table S3). The LC fits showed that the majority (approx. 50–70 %) of all IBAs is elemental zinc. This is mainly in form of brass or other alloys or galvanized metals (Rissler et al., 2020) which were not be separated during the metal recovery after incineration (Šyc et al., 2020). Moreover, the LC fits determined minor fractions of ZnS, $ZnFe_2O_4$ and Zn-whitlockite in the BAs. In contrast, Rissler et al., 2020 determined much lower elemental zinc fractions for the IBAs from Sweden. Moreover, De Matteis et al., 2024 analyzed a IBA from Italy with micro-XANES. Their LC fits did not include elemental zinc and show very different combination of zinc compounds for various Zn particles in the analyzed IBA. Moreover, FA1 show, similar to Cu, also very similar LC fits in comparison to the investigated IBAs.

3.3. Selective extraction and HP14 assessment

In addition to the XANES measurements we also performed a selective extraction with organic acids at pH 4 for Cu and Zn from the investigated IBAs. Tables 1 and 2 show the amount of extractable Cu and Zn in relation to the respective total amount and as calculated value for HP14 (see equation (1). For the worst-case scenario calculation of the HP14 values, the compounds $CuCO_3$ and ZnO were used because they have the largest stochiometric factor in the molar mass conversion. Due to the 0.1 % cut-off value for each compound and the factor of 100 for H410 substances no HP14 results between 0–10 % are possible, e.g. the value of 597.3 mg Cu/kg multiplied with the stochiometric factor for $CuCO_3$ (1.94) gives 0.1158 % and multiplied with 100 (see equation (1) results in a HP14 value of 12 %.

For assessment of HP14 the contribution of all substances has to be summarized, in this case the contribution of $CuCO_3$ and ZnO are assumed as worst-case substances. The sums are 14 ± 0 % for BA1 and 26 ± 1 % for BA2-4 (see HP-14 SE in Table 1 and 2). Moreover, the FA has a much higher HP14 value of 46 ± 4 %. We additionally calculated the HP14 value using the LCF data and the total copper and zinc content (see Tables 1 and 2).

For BA1 both HP14 assessment methods show a result of 0 % for copper. However, for BA2 and BA3 only some of the best five LC fits results in a value of 0 % HP14, the other show results up to 25 ± 1 % (BA2) and 12 ± 1 % (BA3) for copper. For BA4 the value from the extraction is 15 ± 1 % in contrast to 0 % for the LCF approach. Furthermore, FA1 show for both methods a HP14 of 0 %. Thus, it is likely that the selective extraction of Cu from IBA overestimates the HP14 value.

In opposite, the HP14 data from the selective Zn extraction are very similar to them of the LC fitting approach (with a little bit higher values for the LCF for BA3 and BA4). In contrast to Cu, for Zn FA1 shows a high HP14 value of 32 ± 2 % to 45 ± 2 % which is close to 46 ± 4 % for the selective extraction. Thus, it suggests that the selective extraction with maleic acid and sodium acetate at pH 4 capture the right pool of Zn compounds in both IBA and FA.

Table 1
Total and selective extractable (SE) copper in BA1 to BA4 and their HP14 values calculated from selective extraction (SE-Cu) and copper K-edge XANES spectroscopy (LCF-Cu).

	Total Cu (mg/kg)	SE Cu (mg/kg)	HP14 SE-Cu	HP14 LCF-Cu
BA1	1196.5 ± 80.1	430.8 ± 23.8	0 %	0 %
BA2	2080.4 ± 135.3	597.3 ± 77.1	12 ± 1 %	0 % – 25 ± 1 %
BA3	2883.7 ± 99.8	559.6 ± 61.4	11 ± 1 %	0 % – 12 ± 1 %
BA4	1430.1 ± 41.6	746.5 ± 63.7	15 ± 1 %	0 %
FA1	1704.6 ± 211.7	353.0 ± 102.3	0 %	0 %

Table 2
Total and selective extractable (SE) zinc in BA1 to BA4 their HP14 values calculated from selective extraction (SE-Zn) and zinc K-edge XANES spectroscopy (LCF-Zn). For a specified standard deviation of ± 0 for HP14, the value is between 0.0–0.4.

	Total Zn (mg/kg)	SE Zn (mg/kg)	HP14 SE-Zn	HP14 LCF-Zn
BA1	3172.5 ± 0.4	1113.0 ± 38.4	14 ± 0 %	15 ± 1 % – 17 ± 1 %
BA2	2138.4 ± 171.4	1132.6 ± 102.0	14 ± 1 %	13 ± 1 %
BA3	3114.0 ± 186.4	1231.0 ± 107.0	15 ± 1 %	18 ± 1 % – 22 ± 1 %
BA4	2244.9 ± 55.3	886.6 ± 43.7	11 ± 1 %	11 ± 1 % – 15 ± 1 %
FA1	7271.1 ± 68.0	3677.3 ± 319.9	46 ± 4 %	32 ± 2 % – 45 ± 2 %

Moreover, we analyzed also BA2 and BA3 after selective extraction by Cu and Zn K-edge XANES spectroscopy. Fig. 3 shows the Cu- and Zn-XANES spectra before and after selective extraction of BA2 and BA3. Additionally, a difference spectrum of the XANES spectra before and after selective extraction was calculated by subtraction of the unnormalized spectra (marked in yellow and violet).

The difference spectra stand for the dissolved Cu and Zn fraction, respectively, during the selective extraction at pH 4. Some of the difference spectra show already visible contrasts. Therefore, we applied also LC fitting for these spectra (Tables S4 and S5). The LC fits for Zn confirm the visible assumption that the extracted fraction is almost exclusively elemental zinc and ZnO. For Cu the LC fit of both spectra show some differences. For the extracted fraction only approx. 10 % of BA2 and approx. 25 % of BA3 is elemental copper. BA2 contain further large amounts of CuCl and $CuCl_2$. In opposite to BA3 where the larges fraction is $CuCO_3$ with smaller amounts of CuCl, Cu_2O and CuO. Furthermore, the LCFs of BA2_SE and BA3_SE show a large fraction of Cu_2S (see Table S4). This confirms that the slightly soluble Cu compounds are dissolved out and the insoluble Cu compounds such as Cu_2S remain in the IBA during selective extraction. The same can be observed for zinc (Table S5). Here, BA2_SE and BA3_SE contain large amounts of insoluble ZnS and $ZnFe_2O_4$.

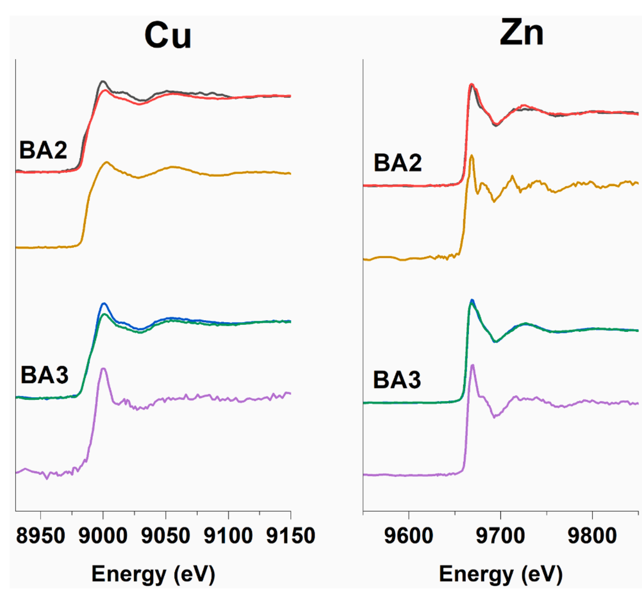

Fig. 3. Copper (left) and zinc (right) K-edge XANES spectra of BA2 (black) and BA3 (blue) before and after selective extraction (red: BA2_SE; green: BA3_SE); The yellow (BA2) and violet (BA3) spectrum is the difference spectrum of the unnormalized XANES spectra before and after selective extraction.

3.4. XANES spectroscopy versus ecotoxic/HP14 classification

The ecotoxic Zn fraction of the four IBAs is mainly elemental zinc and ZnO. Tiberg et al., 2021 identified Zn_2SiO_4 in their studied IBA samples. This compound was not included in the present study. However, it is unclear whether the formation of Zn_2SiO_4 is possible at the temperature of solid waste incineration. At 800° C the conversion of ZnO and SiO_2 to the orthosilicate is 2.2 % only (Gmelin-Institut, 1956). In contrast, for the ecotoxic Cu fraction of the IBAs no specific compound could be identified. For each IBA different Cu compounds were determined. Moreover, the XANES data show that especially for Cu the HP14 value is overestimated by selective extraction with the current substance-related approach with the 0.1 % cut-off rule for each substance. If the content of several substances is just below the cut-off, then the HP14 value is 0 %, but the total value of the ecotoxicological substances together is well above 0.1 %. However, for Cu and Zn, the release of the respective metal ions are the ecotoxicological hazard and not their counter ions. Further, according to the ECHA registration dossiers copper is an essential nutrient for all living organisms but in the HP14 assessment Cu compounds are treated more stringent than more toxic Pb compounds. Whereas the Cu concentrations have to be multiplied with the respective stochiometric factor, for Pb compounds the concentration limit apply to the element only (so called 'Note 1′ in CLP). The reason for that is not known.

4. Conclusion

The Cu and Zn K-edge XANES spectroscopic investigations show on the one hand, that the majority (approx. 50–70 %) of Zn in all IBA and FA1 is elemental zinc. This is mainly in form of brass or other alloys and galvanized metals with a large content of zinc. On the other hand, for Cu all IBA and FA show different compounds. Approx. 50–70 % of Cu in the BAs are Cu(I) compounds and elemental Cu(0). However, the Cu(I) + Cu (0) to Cu(II) ratio is different for the various thermal waste incineration systems. Moreover, LC fitting of the XANES data and additional selective extraction were able to determine the proportion of ecotoxic substances with the HSC H410. Furthermore, FA1 contains no H410 compounds based on Cu, but in addition to a large amount of Zn-based H410 substances it also contains larger amounts of Pb and Cd (compared to the IBAs). Therefore, FA1 greatly exceeds the HP14 limit of 25 %.

Overall, the XANES approach in combination with LC fitting comes very close to the actual Cu and Zn compounds in the samples (visible on the very good R^2-factor). However, a few compounds have similar features in the XANES spectra (e.g. $ZnSO_4$ and $Zn_3(PO_4)_2$), which makes it impossible to be 100 % accurate. Therefore, we have indicated the best 5 fits to give the best possible overview. Moreover, XANES spectroscopy requires irradiation by a synchrotron light source, which in practical application cannot be realized in a commercial analytical laboratory.

CRediT authorship contribution statement

Philipp Scholz: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Christian Vogel:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Conceptualization. **Götz Schuck:** Writing – review & editing, Methodology, Investigation. **Franz-Georg Simon:** Writing – original draft, Supervision, Investigation, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2024.09.001.

References

Bandarra, B.S., Silva, S., Pereira, J.L., Martins, R.C., Quina, M.J., 2022. A Study on the Classification of a Mirror Entry in the European List of Waste: Incineration Bottom Ash from Municipal Solid Waste. Sustainability 14. https://doi.org/10.3390/su141610352.

Bandarra, B.S., Mesquita, C., Passos, H., Martins, R.C., Coelho, P.A.L.F., Pereira, J.L., Quina, M.J., 2023. An integrated characterisation of incineration bottom ashes towards sustainable application: Physicochemical, ecotoxicological, and mechanical properties. J. Haz. Mat. 455, 131649 https://doi.org/10.1016/j.jhazmat.2023.131649.

Beggio, G., Bonato, T., Giardina, S., Grenni, P., Mariani, L., Maggi, L., Hennebert, P., Loro, F., Alberto, P., 2021. Challenges and perspectives of direct test methods for assessing waste Hazardous Properties (HP). Detritus 15. https://doi.org/10.31025/2611-4135/2021.14090.

Calvin, S., Furst, K.E., 2013. XAFS for everyone. Crc Press Inc.

De Matteis, C., Pollastri, S., Mantovani, L., Tribaudino, M., 2024. Potentially toxic elements speciation in bottom ashes from a municipal solid waste incinerator: A combined SEM-EDS, μ-XRF and μ-XANES study. Environ. Adv. 15, 100453 https://doi.org/10.1016/j.envadv.2023.100453.

Di Gianfilippo, M., Hyks, J., Verginelli, I., Costa, G., Hjelmar, O., Lombardi, F., 2018. Leaching behaviour of incineration bottom ash in a reuse scenario: 12years-field data vs. lab test results. Waste Manage. 73, 367–380. https://doi.org/10.1016/j.wasman.2017.08.013.

Ferrari, B., Radetski, C.M., Veber, A.-M., Ferard, J.-F., 1999. Ecotoxicological assessment of solid wastes: A combined liquid- and solid-phase testing approach using a battery of bioassays and biomarkers. Environ. Toxicol. Chem. 18, 1195–1202. https://doi.org/10.1002/etc.5620180618.

Gmelin-Institut, 1956. Zink und Silicium, das System ZnO-SiO2, Gmelins Handbuch der anorganischen Chemie, Zink (Ergänzungsband). Verlag Chemie, Weinheim, pp. 989–993.

Gmelin-Institut, 1958. Kupfer(I)-Oxid, Gmelins Handbuch der anorganischen Chemie, Kupfer (Teil B, Lieferung 1). Verlag Chemie, Weinheim, pp. 35–37.

Gmelin-Institut, 1961. Kupfer(II)-silicate, Gmelins Handbuch der anorganischen Chemie, Kupfer (Teil B, Lieferung 2). Verlag Chemie, Weinheim, pp. 899–901.

Gustafsson, J.P., Braun, S., Tuyishime, J.R.M., Adediran, G.A., Warrinnier, R., Hesterberg, D., 2020. A Probabilistic Approach to Phosphorus Speciation of Soils Using P K-edge XANES Spectroscopy with Linear Combination Fitting, Soil Systems.

Hennebert, P., 2019. Hazard classification of waste: Review of available practical methods and tools. Detritus 7, 13–28. https://doi.org/10.31025/2611-4135/2019.13846.

Hsiao, M.C., Wang, H.P., Wei, Y.L., Chang, J.-E., Jou, C.J., 2002. Speciation of copper in the incineration fly ash of a municipal solid waste. J. Hazard. Mater. 91, 301–307. https://doi.org/10.1016/S0304-3894(02)00015-8.

Inkaew, K., Saffarzadeh, A., Shimaoka, T., 2016. Modeling the formation of the quench product in municipal solid waste incineration (MSWI) bottom ash. Waste Manage. 52, 159–168. https://doi.org/10.1016/j.wasman.2016.03.019.

ITAD, 2021. Jahresbericht 2021 (Annual report 2021). ITAD – Interessengemeinschaft der Thermischen Abfallbehandlungsanlagen in Deutschland e.V, Düsseldorf.

Lapa, N., Barbosa, R., Morais, J., Mendes, B., Méhu, J., Santos Oliveira, J.F., 2002. Ecotoxicological assessment of leachates from MSWI bottom ashes. Waste Manag. 22, 583–593. https://doi.org/10.1016/S0956-053X(02)00009-0.

Lassesson, H., Steenari, B.-M., 2013. Speciation of Copper in Ash from a Fluidized-Bed Boiler Fired with Municipal Solid Waste. Energy Fuel 27, 3891–3897. https://doi.org/10.1021/ef400386j.

Lassesson, H., Fedje, K.K., Steenari, B.-M., 2014. Leaching for recovery of copper from municipal solid waste incineration fly ash: Influence of ash properties and metal speciation. Waste Manag. Res. 32, 755–762. https://doi.org/10.1177/0734242X14542147.

Nordsieck, H., Wambach, K., Rommel, W., 2018. Hazardous Property HP14 of MSWI Bottom Ash. In: Thiel, S., Thomé-Kozmiensky, E., Winter, F., Juchelková, D. (Eds.), Waste Management, Volume 8. TK-Verlag, Nietwerder, pp. 287–300.

Quicker, P., Stockschläder, J., 2018. Möglichkeiten einer ressourcenschonenden Kreislaufwirtschaft durch weitergehende Gewinnung von Rohstoffen aus festen Verbrennungsrückständen aus der Behandlung von Siedlungsabfällen. Dessau-Roßlau, Umweltbundesamt, p. 124.

Ravel, B., Newville, M., 2005. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. J. Synchrotron Radiat. 12, 537–541. https://doi.org/10.1107/S0909049505012719.

Rissler, J., Klementiev, K., Dahl, J., Steenari, B.-M., Edo, M., 2020. Identification and Quantification of Chemical Forms of Cu and Zn in MSWI Ashes Using XANES. Energy Fuel 34, 14505–14514. https://doi.org/10.1021/acs.energyfuels.0c02226.

Simon, F.-G., Kalbe, U., 2023. Case Study on Secondary Building Materials for a Greener Economy. Appl. Sci. 13, 6010. https://doi.org/10.3390/app13106010.

Simon, F.-G., Scholz, P., 2024. Sequential extraction of incineration bottom ash: Conclusions regarding ecotoxicity. Appl. Sci. 14, 5541. https://doi.org/10.3390/app14135541.

Singh, P., Boora, A., Kumar Gupta, A., 2023. A Review on Utilizing Municipal Solid Waste Incineration (MSWIA) in Construction Activates. IOP Conference Series: Earth and Environmental Science 1110, 012042. https://doi.org/10.1088/1755-1315/1110/1/012042.

Stiernström, S., Wik, O., Bendz, D., 2016. Evaluation of frameworks for ecotoxicological hazard classification of waste. Waste Manag. 58, 14–24. https://doi.org/10.1016/j.wasman.2016.08.030.

Šyc, M., Simon, F.G., Hykš, J., Braga, R., Biganzoli, L., Costa, G., Funari, V., Grosso, M., 2020. Metal recovery from incineration bottom ash: State-of-the-art and recent developments. J. Hazard. Mater. 393, 122433 https://doi.org/10.1016/j.jhazmat.2020.122433.

Takaoka, M., Yamamoto, T., Tanaka, T., Takeda, N., Oshita, K., Uruga, T., 2005. Direct Speciation of Lead, Zinc and Antimony in Fly Ash from Waste Treatment Facilities by XAFS spectroscopy. Phys. Scr. 943 https://doi.org/10.1238/physica.topical.115a00943.

Tang, J., Steenari, B.-M., 2016. Leaching optimization of municipal solid waste incineration ash for resource recovery: A case study of Cu, Zn, Pb and Cd. Waste Manag. 48, 315–322. https://doi.org/10.1016/j.wasman.2015.10.003.

Tiberg, C., Sjöstedt, C., Karlfeldt Fedje, K., 2021. Speciation of Cu and Zn in bottom ash from solid waste incineration studied by XAS, XRD, and geochemical modelling. Waste Manag. 119, 389–398. https://doi.org/10.1016/j.wasman.2020.10.023.

Többens, D., Zander, S., 2016. KMC-2: An X-Ray Beamline with Dedicated Diffraction and XAS Endstations at BESSY II. Journal of Large-Scale Research Facilities 2, A49. https://doi.org/10.17815/jlsrf-2-65.

Vogel, C., Scholz, P., Kalbe, U., Caliebe, W., Tayal, A., Vasala, S.J., Simon, F.-G., 2024. Speciation of antimony and vanadium in municipal solid waste incineration ashes analyzed by XANES spectroscopy. J. Mater. Cycles Waste 26, 2152–2158. https://doi.org/10.1007/s10163-024-01954-2.

Yang, S., Saffarzadeh, A., Shimaoka, T., Kawano, T., Kakuta, Y., 2016. The impact of thermal treatment and cooling methods on municipal solid waste incineration bottom ash with an emphasis on Cl. Environ. Technol. 37, 2564–2571. https://doi.org/10.1080/09593330.2016.1155651.