



## Chemical state of mercury and selenium in sewage sludge ash based P-fertilizers



Christian Vogel<sup>a,\*</sup>, Oliver Krüger<sup>a</sup>, Hannes Herzel<sup>a</sup>, Lucia Amidani<sup>b</sup>, Christian Adam<sup>a</sup>

<sup>a</sup> Division 4.4 Thermochemical Residues Treatment and Resource Recovery, Bundesanstalt für Materialforschung und –prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany

<sup>b</sup> ESRF–The European Synchrotron, 71 Avenue des Martyrs, 38000 Grenoble, France

### HIGHLIGHTS

- Mercury bonded to carbon/organic material was detected in some sewage sludge ashes.
- After thermochemical treatment some mercury remains stabilized in the SSA matrix.
- Analysis of the chemical state of mercury and selenium in highly diluted samples.

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### ABSTRACT

Phosphorus-fertilizers from secondary resources such as sewage sludge ash (SSA) will become more important in the future as they could substitute conventional fertilizers based on the nonrenewable resource phosphate rock. Thermochemical approaches were developed which remove heavy metals from SSA prior to its fertilizer application on farmlands. We analyzed the chemical state of mercury and selenium in SSA before and after thermochemical treatment under different conditions for P-fertilizer production by X-ray absorption near edge structure (XANES) spectroscopy. In some incineration plants the mercury loaded carbon adsorber from off-gas cleaning was collected together with the SSA for waste disposal. SSAs from those plants contained mercury mainly bound to carbon/organic material. The other SSAs contained inorganic mercury compounds which are most probably stabilized in the SSA matrix and were thus not evaporated during incineration. During thermochemical treatment, carbon-bound mercury was removed quantitatively. In contrast, a certain immobile fraction of inorganic mercury compounds remained in thermochemically treated SSA, which were not clearly identified. HgSe might be one of the inorganic compounds, which is supported by results of Se K-edge XANES spectroscopy. Furthermore, the chemical state of selenium in the SSAs was very sensitive to the conditions of the thermochemical treatment.

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### 1. Introduction

Phosphorus (P) is of fundamental importance to all living organisms, including humans who depend on phosphorus for healthy and productive lives, and as an essential nutrient for crop production. Thus, there is no substitute for phosphorus in nature. P-fertilizers are currently sourced predominantly from phosphate rock. More than 80% of the mined phosphorus is used to manufacture fertilizers. Due to the fluctuation of the phosphate rock price in the last years [1] and in order to save the limited resources new options for

the production of phosphate fertilizers from secondary resources are required. Furthermore, phosphate rock is contaminated with heavy metals like U, Th, and Cd [2–4] that are put onto farmlands via mineral fertilizers and might pose health hazards. P from secondary sources can help to diminish these problems.

One important secondary resource is sewage sludge (SS). For landfilling or phosphorus recycling SS is often mono-incinerated to destroy organic pollutants. However, the resulting sewage sludge ash (SSA) is often polluted with toxic heavy metals and contains phosphorus with a low plant-availability [5,6]. The limit value for mercury in the German fertilizer ordinance is 1 mg/kg [7]. Previous analyses of German SSAs showed mercury mass fractions of 0.1–3.6 mg/kg [5]. During mono-incineration of SS most of the mercury is separated as metallic mercury in the off-gas cleaning before

\* Corresponding author.

E-mail address: [cv.vogel@yahoo.de](mailto:cv.vogel@yahoo.de) (C. Vogel).

or after the electric precipitator [8,9]. Furthermore, in some incineration plants the carbon adsorber of the off-gas cleaning after the electric precipitator is collected together with the SSA, explaining higher mercury mass fractions in those SSAs.

In the last years several wet chemical or thermochemical processes were developed to separate toxic heavy metals from SSA and to increase the plant-availability of the contained phosphorus [10]. We developed two different thermochemical processes. Previously, we worked on a thermochemical method using chlorine-donors [11,12] under oxidizing conditions at approx. 1000 °C to separate toxic heavy metals and to increase the plant-availability of the phosphorus in the fertilizer. A second process was developed to further increase the plant availability. Therefore, SSA is thermochemically treated with Na<sub>2</sub>CO<sub>3</sub> or Na<sub>2</sub>SO<sub>4</sub> at 850–1000 °C under reducing conditions [13].

Table 1 shows the mercury mass fractions of the different SSAs and thermochemically treated SSAs that were used for this investigation. SSA 1 has a relatively high mercury mass fraction of 2.6 mg/kg. This SSA was thermochemically treated with chlorine donors under oxidizing conditions at 1000 °C (SSA 1-O) and with Na<sub>2</sub>SO<sub>4</sub> under reducing conditions [14] at 950 °C (SSA 1-R), respectively. With both processes only part of the mercury mass fraction was separated from the SSA. Herzel et al. [15] showed results of an industrial demonstration trial for SSA treatment at 950 °C under reducing conditions, where also only approx. 65% of mercury was separated (whereby the limit of the German fertilizer ordinance was met). Those results were not expected as mercury compounds are generally very volatile already at lower temperatures [16].

To determine the remaining high temperature stable mercury compounds in the SSAs we analyzed the chemical state of mercury in SSAs and SSA based P-fertilizers by X-ray absorption near edge structure (XANES) spectroscopy. Previously, Hg L<sub>3</sub>-edge XANES spectroscopy was already used for other environmental analyses of mercury compounds [17–22]. Because of very low mass fractions of mercury in the SSA based P-fertilizers (0.6–3.8 mg/kg) and only little features of the normal-resolution Hg L<sub>3</sub>-edge XANES spectrum [22] the experiments were performed at the high-brilliance and high-resolution X-ray spectroscopy beamline ID26 at ESRF [23].

Since selenium is a likely element to bind mercury at high temperature, Se K-edge XANES spectra were collected of these samples, additionally. Se K-edge XANES spectroscopy was also previously used for environmental investigations [17,19–21,24].

## 2. Materials and methods

### 2.1. SSAs and preparation of SSA based P-fertilizers

The used SSAs 1–3 were from industrial fluidized bed incinerators in Germany and the Netherlands which originated from waste water treatment plants primarily using Fe-salts for phosphate precipitation. SSA 4 stemmed from an industrial fluidized bed incinerator in Germany which originated from enhanced biological P removal (EBPR) and complementary precipitation with Al-salts. Furthermore, from this mono-incineration plant also the carbon adsorber of the off-gas cleaning after the electric precipitator was analyzed (SSA 4-A), which is disposed separately from SSA 4. The mass fractions of the main and trace elements in the SSA based samples are listed in Table 1. SSA 4-A contains 153.6 ± 1.8 mg/kg Hg and 5.6 ± 0.6 mg/kg Se. The thermochemical treatment of SSA1 with MgCl<sub>2</sub> (SSA 1-O) was carried out using a quartz glass reactor in a gas tight lab-scale rotary furnace (Carbolite HTR 11/150, Ubstadt-Weiher, Germany). 400 g solid matter (mixture of SSA with magnesium chloride (MgCl<sub>2</sub>·6H<sub>2</sub>O; cryst., Merck, Darmstadt, Germany)) was heated to 1000 °C with a rate of 20 K/min. This temperature was held for 30 min. The quartz glass reactor was

continuously moved during thermal treatment (alternating rotation of 315° in both directions) and flushed with an air flow rate of 3 L/min. The thermochemical treatment of SSA1 with Na<sub>2</sub>SO<sub>4</sub> under reducing conditions (SSA 1-R) was done in a muffle furnace (Nabertherm LH 15/14, Lillenthal, Germany). Therefore, 10.0 g of SSA was mixed with 4.0 g Na<sub>2</sub>SO<sub>4</sub> (AppliChem, Darmstadt, Germany) and 1.0 g lignite. The mixture was thermally treated in a corundum crucible at 950 °C for 30 min.

### 2.2. Analysis of the elemental composition of SSAs and SSA based P-fertilizers

The mass fractions of main elements and trace elements of the SSA samples were analyzed by ICP-OES (Thermo iCAP 7000, Dreieich, Germany) and ICP-MS (Thermo iCAP Q, Dreieich, Germany) after microwave-assisted total digestion (HNO<sub>3</sub>/HClO<sub>4</sub>/HF; mikro-PrepA, MLS GmbH, Leutkirch, Germany; heating with 1200 W; 20 min isotherm segment at 240 °C). All digestions and ICP measurements were carried out in triplicates. More details on the analytical procedure can be found in our previous article [5].

### 2.3. Reference compounds

For XANES spectroscopy the following mercury and selenium reference compounds were used: Hg<sub>2</sub>Cl<sub>2</sub>, HgCl<sub>2</sub>, HgS (red), HgSO<sub>4</sub>, Na<sub>2</sub>SeO<sub>3</sub> (all Sigma-Aldrich, Weinheim, Germany), CH<sub>3</sub>HgI, Na<sub>2</sub>SeO<sub>4</sub> (both Alfa Aesar, Karlsruhe, Germany) and HgSe (ABCR, Karlsruhe, Germany). Because residual Hg is resistant to the incineration process, the set of the references chosen to interpret the spectra is mainly composed of inorganic compounds stable at high temperature. Because Huggins et al. [25,26] mentioned that iodine-activated carbon is often used as adsorber and sorption of mercury depends on the dopant element used to activate the carbon, we added to the set of references CH<sub>3</sub>HgI as organic mercury reference.

### 2.4. XANES spectroscopy

XANES spectroscopy measurements were carried out at ID26 beamline at the electron storage ring ESRF (Grenoble, France). The incident beam energy was monochromatized with a Si<111> double crystal monochromator. An emission spectrometer with five crystal analyzers (5 × Si <555>, R = 1 m for Hg L<sub>α1</sub> detection; 5 × Si <664>, R = 1 m for Se K<sub>α1</sub>) was used to Bragg select a small portion of the characteristic fluorescence line around the maximum intensity (bandwidth around 1.7 eV). This detection method results in better resolved spectral features (high energy resolution fluorescence detected X-ray absorption spectroscopy) and optimal suppression of background. The scans were acquired at 40 K, to reduce radiation damage in the sample. The XANES scan range was 12260–12360 eV at the Hg L<sub>3</sub>-edge and 12640–12700 eV at the Se K-edge, respectively.

All spectra were background subtracted and normalized to an edge jump of Δmd = 1. Afterwards Hg L<sub>3</sub>-edge XANES and Se K-edge XANES spectra of SSAs were fitted with linear combinations of Hg and Se reference compounds, respectively, with the software Demeter Athena [27].

### 2.5. Thermogravimetry

Thermogravimetry (TG) experiments were carried out on Netzsch STA 449 F3 Jupiter (Selb, Germany). Samples of 10–20 mg were heated at a rate of 10 K/min from 30 °C to 1000 °C. The gas flow of air was 50 mL/min.

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