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Flow analysis of major and trace elements in residues from large-scale sewage sludge incineration

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ABSTRACT

Increase of sewage sludge (SS) has led to the construction of more incineration plants, exacerbating to the production of SS incineration residues. However, few studies have considered the mass balance of elements in large-scale SS incineration plants, affecting the residues treatment and utilization. In this study, flow analysis was conducted for major and trace elements in the SS, the fly ash (sewage sludge ash, SSA) and bottom ash from two large-scale SS incineration plants. The elemental characteristics were compared with those of coal fly ash (CFA), and air pollution control residues from municipal solid waste incineration (MSWIA), as well as related criteria. The results showed that the most abundant major element in SSA was Si, ranging from 120 to 240 g/kg, followed by Al (76–348 g/kg), Ca (26–113 g/kg), Fe (35–80 g/kg), and P (26–104 g/kg), and the trace elements were mainly Zn, Ba, Cu, and Mn. Not all the major elements were derived from SS. Most trace elements in the SS incineration residues accounted for 82.4%–127% of those from SS, indicating that SS was the main source of trace elements. The partitioning of heavy metals in the SS incineration residues showed that electrostatic precipitator ash or cyclone ash with high production rates were the major pollutant sinks. The differences in some major and trace elements could be indicators to differentiate SSA from CFA and MSWIA. Compared with related land criteria, the pollutants in SSA should not be ignored during disposal and utilization.

Introduction

Sewage sludge (SS) is one of the byproducts of wastewater treatment, and the generation of SS increases with the wastewater treatment rate and upgrading of advanced wastewater treatment facilities. The prevalent treatment processes for SS include thickening, conditioning and dewatering, while anaerobic or aerobic digestion, drying, incineration and other thermal treatment technologies are used before landfill disposal, land application, and secondary reuse (Mininni et al., 2015; Panepinto et al., 2016; Yang et al., 2015). In particular, incineration has been adopted increasingly because of its high efficiency waste reduction and harmlessness. Due to the high moisture content of SS, co-incineration with coal or municipal solid waste (MSW) was employed initially, but this process

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was criticized due to the polluting characteristics of the exhaust gas and residues (Barbosa et al., 2009; Cenni et al., 2001). Recently, separate incineration of SS after thermal drying has been implemented widely, thereby generating bottom ash in the boilers, as well as fly ash in the cyclone or electrostatic precipitators (ESP) and air pollution control residues in the bag filter after flue gas cleaning, which are referred to as sewage sludge ash (SSA).

The elemental composition of SSA has been studied for several purposes. A survey investigated the contents of 57 elements in approximately 97% of the SSA produced in Germany annually (Krüger et al., 2014) in order to assess the resource recovery potential. SSA samples were also collected from seven SS incinerators in the UK, to identify whether they could be accepted in landfill according to the EU Hazardous Waste Directive (Donatello et al., 2010). However, most studies were conducted based on SSA samples collected from a few countries in Europe, whereas few have investigated SSA in Asia, where SS treatment is a major issue. As the control of emission from incineration plants is strengthened, the processes and equipment for flue gas treatment are becoming more complicated. Thus, it is necessary to recognize the characteristics of SSA collected from different units.

In order to understand the migration of eight heavy metals during incineration, the residues from different units were analyzed during 33 weeks in a large-scale SS incinerator in Belgium (Van de Velden et al., 2008), where the mass balance results showed that seven heavy metals were concentrated in the ESP ash. However, the major elements and other trace elements were not considered in this study. Other studies of the mass partitioning of elements in large-scale SS incineration are rare.

The fly ash from coal combustion (coal fly ash, CFA) and air pollution control residues from MSW incineration (municipal solid waste incineration ash, MSWIA) have similarities and differences compared with SSA. They share some common elemental characteristics with SSA, but some may vary from the various types of fly ashes. Limited comparisons of those martials have been conducted (Nowak et al., 2013), which is detrimental to their utilization and treatment. The application of CFA occurred much earlier than that of MSWIA and SSA, and thus more studies of its application have led to analogous application of MSWIA. However, recent studies have indicated that more pollutants can be accumulated in MSWIA (Bogush et al., 2015; Shi et al., 2019; Zhang et al., 2008b; Zhou et al., 2015b), and thus pretreatment technologies have been developed to reduce/immobilize the pollutants before disposal or application (Chen et al., 2019; Dontriros et al., 2020; Shi et al., 2019). After incineration, the inorganic pollutants in SS are also transferred into the residues. More comparisons of the SS incineration residues obtained with CFA and MSWIA are needed to explore analogous disposal and application methods. In general, the amount of bottom ash generated in SS incineration plants is low, where it mainly comprises quartz sand, which can be used as a raw construction material, and it is rarely sent to landfill, so the elements present in bottom ash were not compared in the present study. When applied or disposed of onto land, the elements in SSA, especially heavy metals, may affect the quality of the surrounding soil and water systems. Thus, comparisons of SSA and related pollution control criteria can help engineers to select more appropriate utilization and treatment processes.

Therefore, the objectives of this study were: a) to analyze the elemental characteristics of residues from large-scale SS incineration plants; b) to quantify the partitioning of elements during SS incineration by flow analysis; and c) to conduct comparisons with other thermal treatment residues and related criteria for land use in order to understand the potential for contamination with SSA.

1. Materials and methods

1.1. Materials

The samples were collected every 3 months from two large-scale SS incineration plants in East China, which were designated as plants Z and S (with capacities of 250 tons/day and 750 tons/day, respectively, on a moisture content basis of 80%). Thermal drying was applied before circulating fluidized bed incineration. ESP and cyclones were equipped for primary dust removal in plants Z and S, respectively, followed by lime and activated carbon injection as well as bag filtration (BF). Detailed operation processes are explained in Appendix A **S1**. Centrifuge dewatered sludge, thermally dried sludge, bottom ash, ESP ash, cyclone ash, and BF ash were codes as CD, TD, B, ESP, CA and BF, respectively, and the samples were named in the form of "Plant-ash/sludge-month", e.g., S-CA-07 indicates the CA collected from plant S in July 2018. More sampling information are given in Appendix A **S2**.

The moisture contents of the CD sludge, TD sludge, B ash, ESP ash, CA ash, and BF ash were 75%–85%, 6.4%–14.3%, 0.00%–0.09%, 0.00%–1.46%, 15.9%–27.8% and 0.10–1.43%, respectively, and their losses on ignition were 47%–75%, 59%–74%, −0.03%–0.15%, 0.11%–1.56%, 0.16%–0.42%, −0.54%–2.35%. The negative values were due to weight increases caused by carbonation and oxidation during heating.

1.2. Analytical methods

The contents of major elements (except for C, N, and H) in the samples were analyzed with X-ray fluorescence spectrometry (XRF; UniQuant, Thermo, USA). The contents of C, H and N were examined using an elemental analyzer (vario EL III, Elementar, Germany). The trace elements were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES, 720ES, Agilent, USA) and inductively coupled plasma-mass spectrometry (ICP-MS, 7700, Agilent, USA) after digestion with HCl-HNO_3-HF-$HClO_4$ (Zhang et al., 2008b).

1.3. Flow analysis calculation

According to the law of mass conservation, the flow balance of each heavy metal can be described as Eq. (1) (dry basis) (Zhang et al., 2008b):

$$\sum_i M_{\text{input } i} = \sum_j M_{\text{output } j} \quad (1)$$

where $M_{\text{input}\,i}$ and $M_{\text{output}\,j}$ are the dry mass of elements in each input and output subject.

Table 1 – Elemental compositions of the SS and residues samples (%, dry basis).

Samples	C	H	N
Z-CD-03	40.2 ± 0.4	6.14 ± 0.06	6.92 ± 0.17
Z-TD-03	40.5 ± 0.5	6.05 ± 0.10	6.73 ± 0.05
Z-CD-07	33.1 ± 0.3	4.93 ± 0.07	5.61 ± 0.07
Z-TD-07	34.0 ± 0.1	4.84 ± 0.05	5.49 ± 0.03
Z-CD-09	32.4 ± 0.0	4.15 ± 0.31	5.13 ± 0.02
Z-CD-12	33.9 ± 0.1	5.20 ± 0.02	6.06 ± 0.03
Z-TD-12	30.3 ± 0.0	4.78 ± 0.01	5.17 ± 0.05
S-CD-04	25.8 ± 0.5	4.28 ± 0.16	4.31 ± 0.07
S-CD-07	24.7 ± 0.3	4.00 ± 0.00	3.65 ± 0.10
S-CD-10	24.4 ± 0.3	4.40 ± 0.12	3.53 ± 0.03
S-CD-12	25.8 ± 0.3	4.13 ± 0.29	4.36 ± 0.10
Z-ESP-03	0.28 ± 0.05	0.50 ± 0.15	0.06 ± 0.02
Z-ESP-07	0.17 ± 0.03	0.47 ± 0.02	0.01 ± 0.00
Z-ESP-09	0.11 ± 0.00	0.30 ± 0.04	0.01 ± 0.00
Z-ESP-12	0.14 ± 0.02	0.35 ± 0.07	0.21 ± 0.03
Z-BF-03	0.51 ± 0.05	0.52 ± 0.04	0.14 ± 0.01
Z-BF-07	0.23 ± 0.03	0.38 ± 0.02	0.06 ± 0.00
Z-BF-09	0.44 ± 0.01	0.33 ± 0.01	0.04 ± 0.00
Z-BF-12	0.10 ± 0.01	0.36 ± 0.03	0.26 ± 0.01
Z-B-07	0.04 ± 0.01	0.49 ± 0.09	0.00 ± 0.00
Z-B-12	0.07 ± 0.01	0.62 ± 0.11	0.19 ± 0.05
S-CA-07	0.09 ± 0.01	0.35 ± 0.03	0.01 ± 0.00
S-CA-10	0.06 ± 0.01	0.31 ± 0.02	0.00 ± 0.00
S-CA-12	0.06 ± 0.01	0.33 ± 0.01	0.20 ± 0.00
S-A-04	0.16 ± 0.01	0.88 ± 0.06	0.04 ± 0.01
S-BF-07	1.38 ± 0.06	0.44 ± 0.03	0.03 ± 0.01
S-BF-10	0.16 ± 0.01	0.50 ± 0.08	0.02 ± 0.00
S-BF-12	0.16 ± 0.00	0.31 ± 0.10	0.21 ± 0.07
S-B-04	0.38 ± 0.02	0.41 ± 0.08	0.06 ± 0.00
S-B-12	0.10 ± 0.02	0.46 ± 0.05	0.17 ± 0.04

In the incineration of sewage sludge, the source of heavy metals is mainly sludge. Trace amount of heavy metals can be found in reagents used for flue gas pollutants removal. Major sinks for heavy metals include fly ash collected in ESP, cyclones and BF, B ash, and exhaust gas. In this paper, during each sampling process, the amount of incinerated sludge, generation of fly ash and bottom ash and concentrations of heavy metals in each material were used for flow analysis, and the final results were averaged from all sampling results in each plant.

2. Results and discussion

2.1. *Contents of major elements in SS and their incineration residues*

The contents of the major elements in SS and their incineration residues are shown in Table 1 and Fig. 1. The C contents in the CD and TD sludges from plant Z were approximately 3.4%–16.2% higher than those in the samples from plant S. The H and N contents in the sludges from plant Z were also higher than those in the samples from plant S. However, there were larger discrepancies in the samples from plant Z during different seasons, with a difference of up to 10% for C, possibly due to the complex sludge sources processed by plant Z (from four wastewater treatment plants), since small changes in LOI were observed. Almost all wastewater treated in these plants was domestic sewage, which varies slightly among the seasons.

The most abundant element after C/H/N/O in the sludge from plant Z was Si, ranging from 30 to 68 g/kg, which could be attributed to the large amount of sand in the sludge with particle sizes of less than 200 μm. Grit chambers are implemented in many wastewater treatment plants in China, and much sand is carried from the wastewater collection systems (Dai et al., 2014). The Si content of the sludge from plant S was 34–52 g/kg, which was similar to those from plant Z. More Al was found in the sludge from plant S, i.e., up to 60 g/kg (S-CD-10), compared with the sludge from plant Z, i.e., 11–27 g/kg. These contents were all within the ranges of the Al contents reported for sludge samples from EU countries, i.e., 1–60 g/kg (Gawlik, 2012).

In addition to Si and Al, large amounts of Ca, Fe, and P were found in the sludge samples. The Ca and Fe contents were similar in plants Z and S, where they ranged from 10.8 g/kg to 19.1 g/kg. Molysite and unslaked lime are often used as flocculating and dehydrating agents in sewage and sludge treatment processes (Metcalf et al., 2003). The P contents were high in the sludge samples from both plants Z and S, with 12.1–20.5 g/kg. The sludge has good potential for use as a secondary P resource and previous studies have proposed suitable recovery methods (Blocher et al., 2012; Cieslik and Konieczka, 2017; Xu et al., 2015).

In addition, the sulfur (S) contents were around 6.2–12.5 g/kg in the sludge samples from plants Z and S, which may have been present mostly in the form of sulfate and organic matter (Huang et al., 2018). During incineration, the generation of sulfur oxides and sulfates may corrode boilers and heat exchangers via the production of a SO_x-rich atmosphere (Viitala and Taskinen, 2016) or salt deposition (Srikanth et al., 2003). The Cl contents of the sludge samples were too low to be detected by XRF. However, the presence of even a small amount of Cl may exacerbate the corrosion of boilers by sulfur compounds (Nielsen et al., 2000).

Except for S-BF-07, the C, H, and N contents of the residues were lower than 1%, thereby indicating that the organics in the SS were effectively reduced so very little organic matter remained in the residues. The most abundant element in the residues was Si, which ranged in abundance from 120 to 240 g/kg in the ESP ash, CA ash and BF ash, whereas the levels were around 2–4 times higher in S-B-04. The difference in the Si content in S-B-04 might have been due to the addition of a large amount of lime during incineration, as indicated by the higher Ca content in S-B-04 (Fig. 1d). In addition, the utilization of sand as a bed material could have served as another source of Si. High Al, Ca, Fe, and P contents were also found in SSA, with 76–348 g/kg, 26–113 g/kg, 35–80 g/kg, and 26–104 g/kg, respectively. The results were similar with the content from Biswas et al. (2009) and other literature using SSA as secondary P sources. The contents of those elements in BF ash were around 1.2–3.4 times higher than those in the ESP ash and CA ash samples collected in the same season, but the seasonal changes were small in SSA samples collected from the same unit. The Al and P contents of S-BF-07 were twice those found in S-A-04 because of the different flue gas treat-

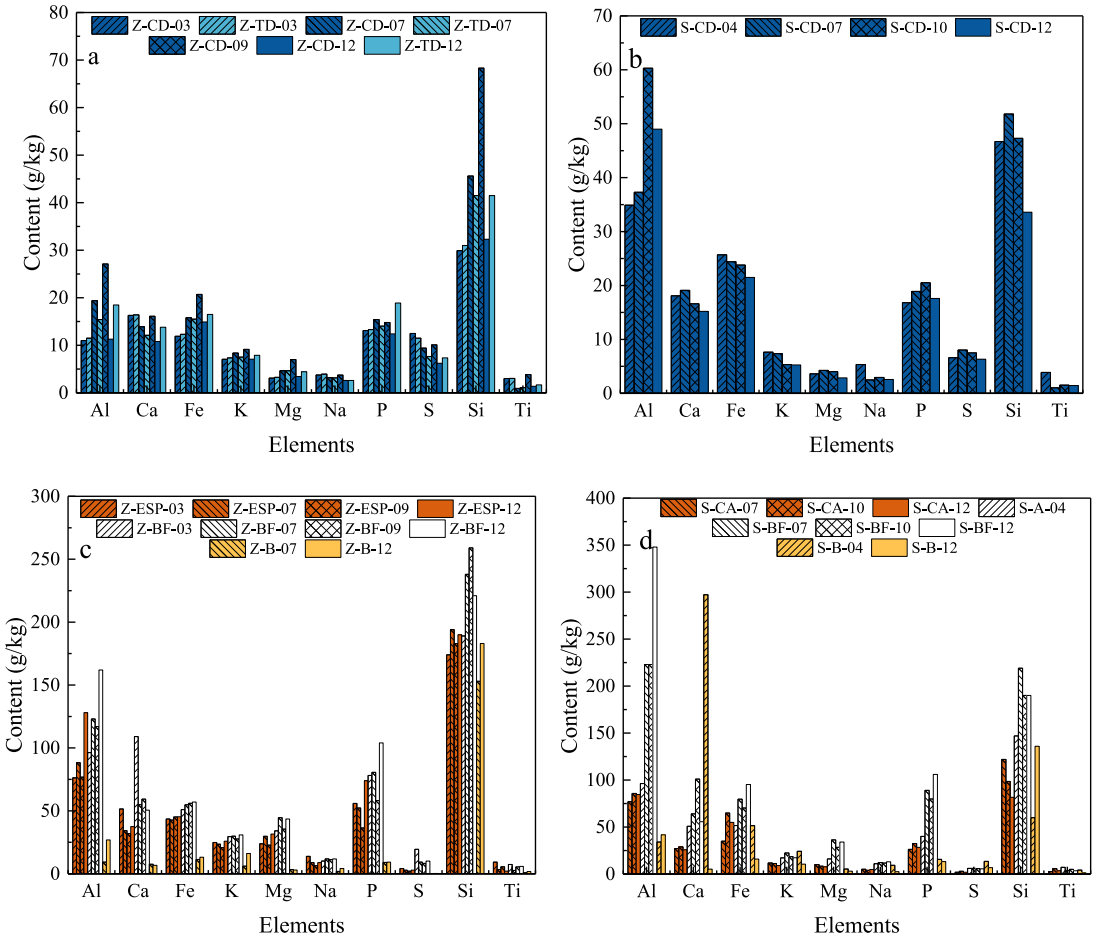

Fig. 1 – Contents of major elements in the SS and residues samples from plants Z (a, c) and S (b, d).

ment processes employed. In April, lime was added to the incinerators to remove sulfur oxides (Cheng et al., 2003) and SSA was collected without cyclone in plant S.

2.2. *Contents of trace elements in SS and their incineration residues*

The trace elements with the highest contents in SS from Z and S plants (Fig. 2) were Ba and Zn, with maximum levels of 850 mg/kg and 1690 mg/kg, respectively. The Zn and Ba contents determined in the present study were higher than those in the sludge samples from 61 wastewater treatment plants surveyed in EU by Gawlik (2012). The Cu, Mn, and Pb contents were lower than the Ba and Zn contents, with 122–463 mg/kg, 177–1094 mg/kg, and 40.5–302 mg/kg, respectively, which were similar to the EU survey results (Gawlik, 2012). There were negligible differences in the trace elements contents between the TD and CD sludge samples from plant Z, thereby indicating that the thermal-drying process had no significant effect on the loss of trace element contents. It also means that calculating total amount of heavy metals input by sludge can use either thermal-dried or centrifuged sludge. However, the trace element contents in SS varied among the seasons, with higher values in March and April compared with the other seasons.

During incineration, most of the organic matter is destroyed, whereas metal elements migrate into the bottom ash or flue gas (Balogh, 1996), and they are then removed. Similar to SS, the trace element with the highest content in the residues was Zn, with 401–5016 mg/kg, followed by Ba, Cu, and Mn, with 145–2700 mg/kg, 77–1859 mg/kg, and 151–2220 mg/kg, respectively. Compared with the CA and BF ash samples from a sludge incineration plant investigated in Hong Kong (Li et al., 2017), the Zn, Cu, Ni, of Pb contents of most the SSA samples examined in the present study were similar, where only a few samples had slightly higher contents of these elements.

The trace elements contents in the B ash from plant Z were much lower than those in the ESP and BF ash samples. Furthermore, the Zn, Ba, Mn, Cu, Pb, Cr, and Sr contents in the BF ash from plant Z were higher than those in the ESP ash, thereby indicating that more trace elements could be enriched in the smaller particles of the BF ash, which has also been shown in terms of the distribution of heavy metals in different particle size fractions of MSWIA (Zhang et al., 2008a; Zhou et al., 2015b). Due to their higher contents in SS, more Ba, Cu, and Zn were detected in the SSA samples collected in March, with approximately 1.5–2 times those found in other samples. In addition, the Ni, Sn, and V contents were high in two samples, with 238 ± 8 mg/kg, 314 ± 14 mg/kg, and 279 ± 13 mg/kg in Z-ESP-03, respectively, and 269 ± 3 mg/kg, 289 ± 49 mg/kg, and 284 ± 5 mg/kg in Z-BF-03.

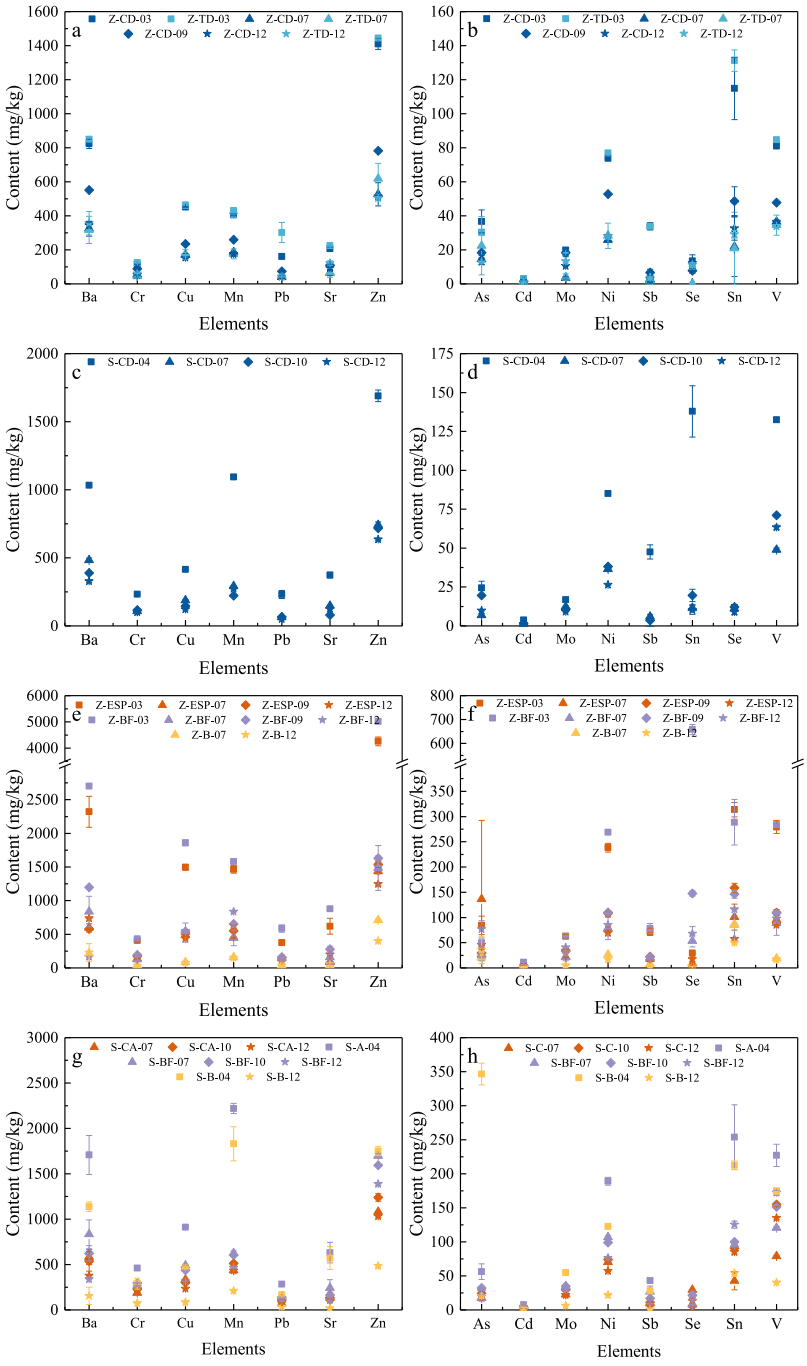

Fig. 2 – Contents of trace elements in SS (a, b, c, d) and residues (e, f, g, h) collected from plants Z and S in different seasons.

The trace elements contents were higher in the BF ash from plant S compared with those of the CA ash and S-B-12. The different flue gas control process used in April 2018 led to differences in the trace elements contents in the S-A-04 and S-B-04 samples compared with those of the samples collected in other seasons. The Mn contents of S-A-04 and S-B-04 were 2220 ± 57 mg/kg and 1830 ± 187 mg/kg, respectively, which were around 3–4 times higher than those in the other samples. The Sn contents of S-A-04 and S-B-04 were also 1–5 times higher than those in the other samples. The As content of S-B-04 was 347 ± 16 mg/kg, which was 7–20 times higher than those of the other samples, possibly due to the addition of lime in the incinerators, which may immobilize much of the As in B ash (Sorum et al., 2003). Se is an important element for pollution control in sanitary landfill sites (MEP, 2008). In the SS samples, the Se contents ranged between 0 and 20 mg/kg, but there were no great variations among different seasons. In the SSA samples, the highest Se content was found in Z-BF-03 with 658 ± 21 mg/kg, which was much higher than those in the other samples. Moreover, all of the BF ash samples from plant Z had higher Se contents than the ESP ash samples.

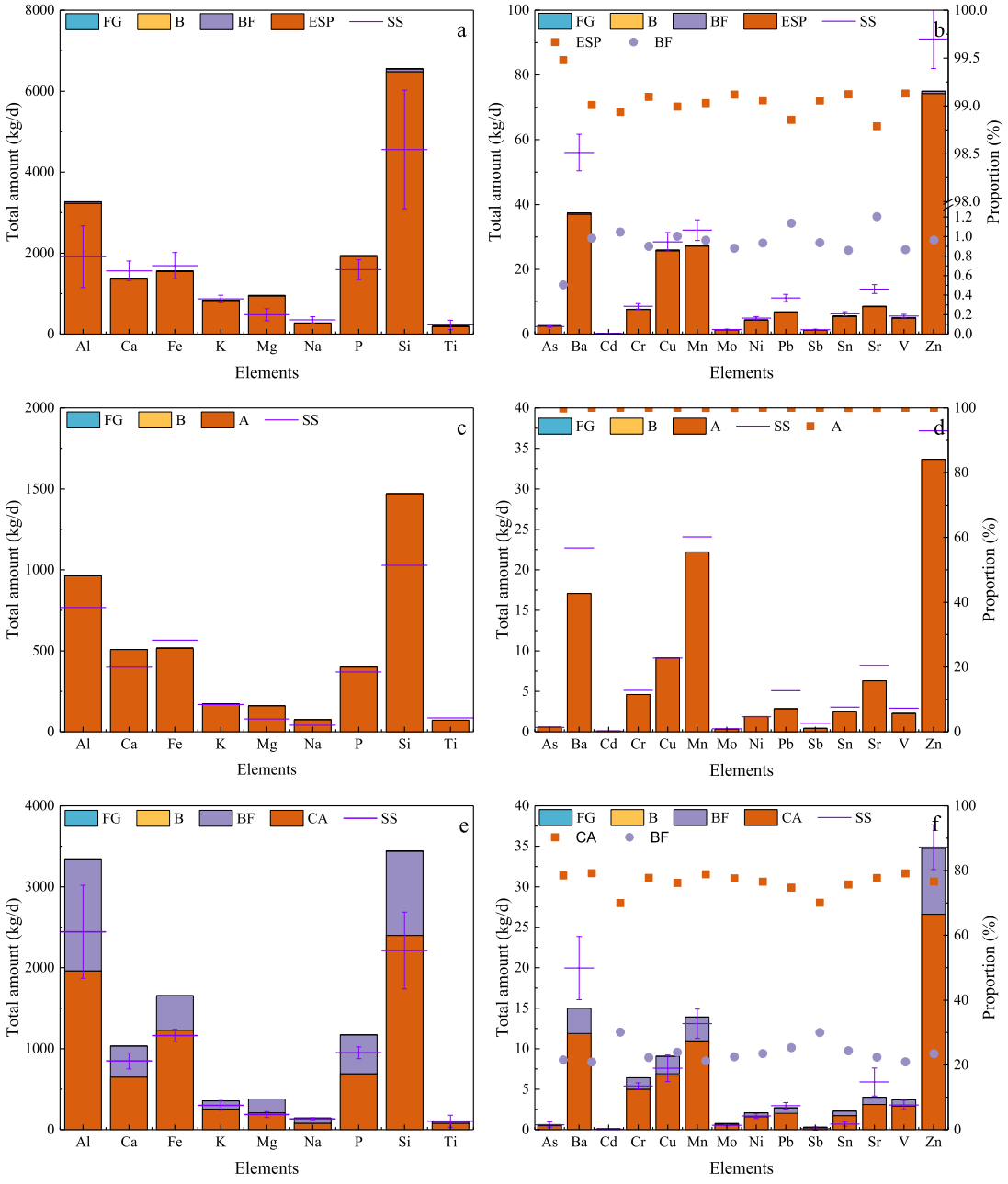

Fig. 3 – Flow analysis and proportion of elements during incineration. Subfigures a and b show the major and trace elements in plant Z, c and d show the major and trace elements in plant S without the separate collection of fly ash in April, and e and f show the major and trace elements in plant S with the separate collection of fly ash in other seasons. Dark orange and purple dots are the proportion of trace elements in each ash, based on the total contents in all residues. SS is sewage sludge, ESP is electrostatic precipitator ash, BF is bag filter ash, B is bottom ash, FG is exhaust gas, A is the mixed ash containing fly ash and air pollution control residues, and CA is cyclone ash. The emissions of elements via flue gas were estimated based on the pollutants' limits in the exhaust gas from the incinerators. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2.3. *Flow analysis of elements during SS incineration*

B ash, SSA, and exhaust gas are generated during the incineration of SS. According to the mass balance principle, metals can migrate into derivative byproducts after a series of physical and chemical reactions. The mass balances determined for the major and trace elements are shown in Fig. 3. The total amounts of major elements in the incineration byproducts (residues and exhaust gas) approximately agreed with those in the SS samples. The total amounts of Al, Mg, P, and Si in the byproducts exceeded those in the SS samples because of several factors. The bed materials comprising sand in both plants, where the major component was Si, were not counted in the calculations. In addition to quartz, other minerals containing

major elements such as Mg and Al could have been present in the bed materials, thereby increasing the amounts of these elements in the residues. Some of the B ash was retained or recycled in the fluidized bed as a bed material, which decreased the amounts of non-volatile elements in the residues. Variations in the contents of the elements in the SS samples could also have influenced the mass balance. The higher amount of Ca in the residues compared with the SS samples from plant S can be attributed to the lime added to the flue gas treatment system.

The trace element contents in the residues and exhaust gas agreed well with those in the SS samples, where they accounted for 82.4%–127%, except the contents of Ba, Pb, Sr, and Sb did not exceed 80% of those in the SS samples. Variations in the generation of residues, the element contents of the SS and residues, the fine particles brought from bed materials, and the B ash retained in the fluidized bed could have influenced the mass balance in the incineration byproducts and the SS samples.

Based on the total amounts of elements in the residues, the partitioning of heavy metals was calculated (Fig. 3). During incineration, more than 90% of the heavy metals accumulated in SSA in a similar manner to the monitoring results obtained in an SS incineration plant in Belgium (Van de Velden et al., 2008). Compared with the incineration of MSW (Belevi and Moench, 2000; Zhang et al., 2008a, b), a higher proportion of heavy metals were found in SSA due to the fluidized bed incineration process where more ash was generated from flue gas than B ash (approximately 2000–3000 times). The BF ash generated in plant Z had high heavy metal contents but low yields (no more than 0.2% of that in the incinerated wet sludge on average), thereby leading to a low proportion of heavy metals partitioning in the residues. In contrast, more BF ash was generated in plant S, which accounted for 1/5th of the generated CA ash, and relatively higher heavy metal contents were found, so more heavy metals partitioned in the BF ash, with around 20.8%–30.1%.

2.4. *Comparison with other thermal treatment residues*

Several similarities and differences can be found between CFA, MSWIA, and SSA compared with the thermal treatment residues obtained from coal combustion and MSW incineration, as shown in Fig. 4. Among the major elements, most of the results determined in previous studies of SSA differed from the values found in CFA and MSWIA. The Al, Ca, Na, and Si contents of SSA ranged between those in CFA and MSWIA, but the Fe and P contents of SSA were higher than those in CFA and MSWIA. Interestingly, the K, Mg, S, and Ti contents partly overlapped, which may suggest that these elements had similar sources. Data regarding the Cl contents of CFA were lacking, but the Cl contents determined for the SSA samples in our study were below the limit of detection and much lower than those in MSWIA, which contains lots of Cl source in the incinerated material (Lu et al., 2019). Thus, analyzing the major elements in residues might be a useful method for identifying the type of fly ash, although more evidence is still required to validate this hypothesis.

One of the most important factors that affect the characteristics of the residues from different incinerations is the materials that undergoes combustion. Thus, the type of coal used (Gollakota et al., 2019), the complex and variable compositions of MSW (Gotze et al., 2016; Zhou et al., 2015a), and the wastewater and sludge sources and treatment processes (Krüger et al., 2014) can influence the elemental compositions of CFA, MSWIA, and SSA. The application of CaO, $Ca(OH)_2$, Na_2CO_3, and other alkaline agents can increase the Ca and Na contents of fly ashes, and fine particles generated from bed materials can also increase the contents of some elements. The characteristics of CFA, MSWIA and SSA are influenced by the specific incinerated material, but also by the type of furnace employed (Zhang et al., 2018), combustion conditions (e.g., temperature and the air: fuel ratio) (Sorum et al., 2003), the addition of reagents in flue gas treatment systems (e.g., types and amounts of chemicals) (Dal et al., 2016), and the generation of fly ash (e.g., yield and collection units) (Li et al., 2017). In the present study, the distributions of most of the major elements were within 25%–75% of the previously reported ranges, and only the Al, Mg, and Si contents varied slightly from the usually reported values. These differences may be explained by the diverse properties of the bed materials used in fluidized bed furnaces. According to the geotechnical properties reported for SSA samples (Li et al., 2017), quartz, montmorillonite and feldspar could have been the sources of Al, Mg, and Si, although the exact minerals present in bed materials are unknown and variable.

The contents of many trace elements did not differ greatly among the three types of fly ash. The Cd, Pb, Sb, and Zn contents were approximately one order higher in MSWIA than SSA, which could be another useful indicator for differentiating residues. The Ba and Mn contents were slightly higher in SSA than MSWIA and CFA, but similar Ba and Mn contents can be observed in different types of fly ash. In the present study, the Ba contents were similar to those in MSWIA and CFA. Another interesting observation was that the Se contents of the SSA samples were higher than the values generally reported in previous studies. Se has both anthropogenic and natural sources and it is important for organic life (Paikaray, 2016), but it can also be bioaccumulated. Thus, the wastewater treatment plants may have received some sewage containing high concentrations of Se, and the Se could have been transferred to the sludge via microorganisms or precipitated during the wastewater treatment process, thereby resulting in a higher Se content in the SSA.

2.5. *Land-related limitations for SS and incineration residues*

The As, Cd, Cr and Ni contents of the SS samples from plants Z and S were lower than the standard limit values for heavy metals in sludge for land-related use (Table 2) (AQSIQ and SAC, 2009; CEC, 1986; MUDEP, 1984). The Cu contents of Z-CD-03, Z-TD-03, and S-CD-04 were 451 ± 3 mg/kg, 463 ± 17 mg/kg, and 414 ± 4 mg/kg, respectively, which are much higher than the limit values for agricultural sludge use in acidic soils and lower than the limit values for other applications. The Pb content of Z-TD-03 was 302 ± 59 mg/kg, which exceeded the lower standard limit, but the Pb contents of the other SS samples were below the limit. High Zn contents were detected in the SS samples from plants Z and S, and they exceeded

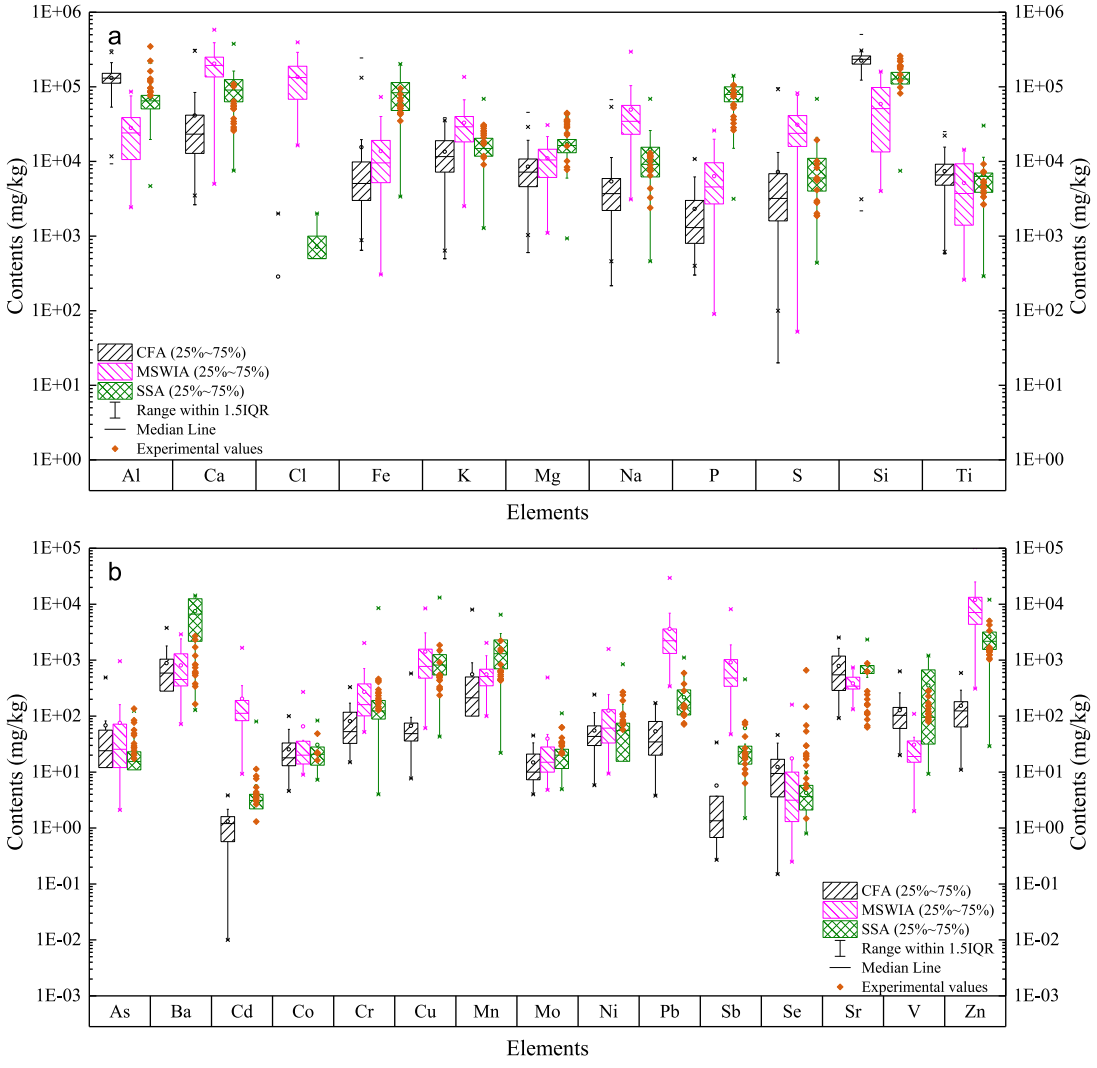

Fig. 4 – Comparison of contents of major elements (a) and trace elements (b) in CFA, MSWIA and SSA. The CFA, MSWIA, and SSA data reported in previous studies (A list of these studies can be found in Supplementary material) are shown in boxes, and the experimental values donated with orange dots are the results obtained in the present study. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2 – Limitations for the application of SS to land (Unit: mg/kg, dry basis).

Standards	As	Cd	Cr	Cu	Hg	Mo	Ni	Pb	Se	Zn	Conditions
GB 4284–84 (MUDEP, 1984)	75	5	600	250	5	—	100	300	—	500	pH<6.5
		20	1000	500	15	—	200	1000	—	1000	pH≥6.5
GB/T 23,486–2009 (AQSIQ and SAC, 2009)	75	5	600	800	5	—	100	300	—	2000	pH<6.5
		20	1000	1500	15	—	200	1000	—	4000	pH≥6.5
40 CFR Part 503 (EPA, 2018)	75	85	—	4300	57	75	420	840	100	7500	Ceiling concentrations
86/278/EEC (CEC, 1986)	—	5	800	800	5	—	200	500	—	2000	—

the limit for Zn in sludge for application to acidic agricultural soils. Moreover, even if the concentrations of toxic substances are below the limit concentrations, the application of SS to agricultural land, forest, or public contact sites is also limited by annual loading rates or cumulative loading rates (AQSIQ and SAC, 2009; EPA, 2018; MUDEP, 1984). The plants grown on amended soil also need to be monitored frequently because they may accumulate metals (Fang et al., 2018).

After incineration, the organic contents of the residues were very low and the loss on ignition was only 0%–2.35%, which is much lower than the nutrient content required for application to land (AQSIQ and SAC, 2009). The possible agri-

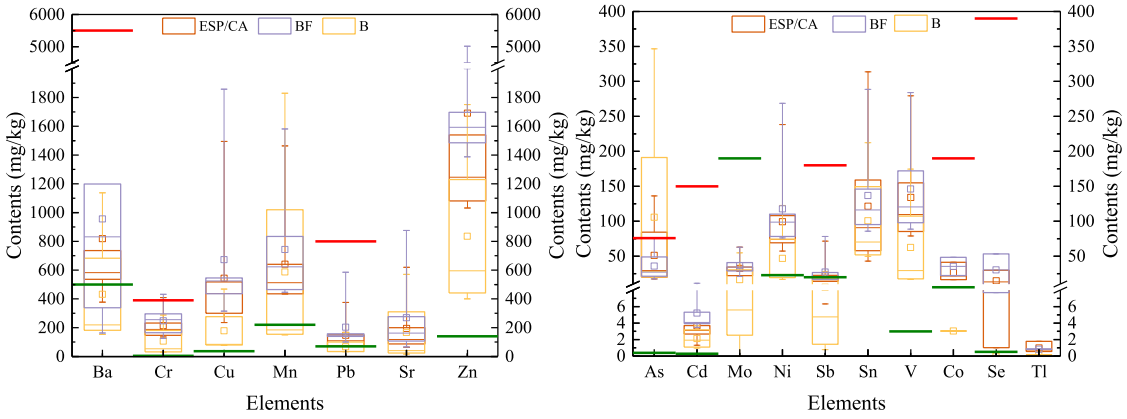

Fig. 5 – Comparisons of trace elements in the SS incineration residues and soil screening limits. The solid lines donate the minimum (green lines) and maximum (red lines) limits found in the relative regulations and standards imposed in China, the USA, Canada, the Netherlands, and Japan. The limit values in Chinese and American standards are the screening values, whereas the intervention values are used in regulations imposed in the Netherlands. The limits for Cr are values for Cr (VI) because it is more toxic in the environment, and the screening values may vary according to the pH and different plants in some standards. The maximum limits of Cu and V are outside the ranges of the axis, and only one limit value was found for Mn and Mo in the standards. No limits were found for Sr, Sn and Tl in the regulations and standards. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

cultural application of SSA is usually assessed based on its potential source for P fertilizer (available P_2O_5 content is 20%–48%, (University of Minnesoda Extension, 2018)) production. The P contents of the SSA samples were 26–104 g/kg, and thus they have high potential as P sources (Franz, 2008; Weigand et al., 2013) for use in agriculture. However, the accumulation of heavy metals in SSA should not be ignored (Vogel et al., 2016). The heavy metal contents of the SSA samples were variable but some exceeded the limitations for the application of SS to land. The highest Zn content was over 4000 mg/kg and the minimum limits for application to acid and base soils in China (MUDEP, 1984) are only 500 and 1000 mg/kg, respectively, and thus the SSA is not suitable for direct application to land.

The Cd, Co, Cr, Cu, Pb, Se, V, and Zn contents of the SSA samples were higher than the minimum screening soil quality standards (CCME, 1999; US EPA, 1996; ME, 2007, 2019; MEE, 2018a, 2018b; VROM, 2009) in different countries (Fig. 5), and thus the application of SSA to land could increase the heavy metal contents of soils. However, the maximum limitations for most elements in soil are much higher, so the application of SSA to land would be allowed in specific areas or situations. The Ba, Mn, and Sb contents of the SSA samples ranged above and below the minimum limits, thereby indicating that they may be potential pollutants in some situations and assessments would be required before application. The As contents of the residues were higher than the maximum soil screening limits, which might lead to severe issues regarding the application of SSA to land. SSA has similar geotechnical properties to soils but more evaluations of trace elements and other characteristics (Shi et al., 2017) on the land application are necessary to avoid potential contamination and other issues.

3. Conclusions

Incineration has been developed for the treatment of various types of waste. However, limited data are available concerning the elemental characteristics and mass balance of SSA obtained from large-scale incineration plants, thereby preventing a comprehensive understanding of the treatment process and possible utilization of the product. Thus, the contents of the major and trace elements in SSA samples were analyzed in this study. The major element in SSA was Si, with contents ranging from 120 g/kg to 240 g/kg, followed by Al, Ca, Fe, P, and S, and the most abundant trace elements were Zn, Ba, Cu, and Mn.

Similar amounts of most of the major elements were found between SS and the residues, but not all of the major elements were derived from SS because the major elements in the bed materials and reagents added to flue gas treatment systems also affected the contents of the major elements in the SSA. However, 82.4%–127% of the trace elements in the residues were derived from SS, thereby indicating that SS was the main source of the trace elements. Analysis of the partitioning of heavy metals in the residues showed that the high amounts of ESP ash or CA produced were the major pollutant sinks. When dealing with SSA, more attention should be paid on the potential pollution of ESP ash or CA, instead of only BF ash.

The Al, Ca, Na, and Si contents of the SSA samples were similar to those of CFA and MSWIA, and the K, Mg, S, and Ti contents overlapped with those of CFA and MSWIA, but higher Fe and P contents were found in SSA. The low Cd, Pb, Sb, and Zn contents, and high Ba, Mn, and Se contents of SSA can be employed as indicators to distinguish SSA from MSWIA and CFA. However, more information is still needed to define these indicators.

When SSA is applied to or disposed of on land, the possibility of pollution should not be ignored. According to various related criteria, SSA can only be applied under a limited range of soil conditions. Thus, careful design, construction, and operation processes are required in order to reduce the release of hazardous elements when SSA is disposed of in landfill sites. In addition, the removal of pollutants is necessary before its utilization as a secondary resource.

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Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2020.09.023.

REFERENCES

AQSIQ, S.A.C., 2009. Disposal of Sludge From Municipal Wastewater Treatment Plant—Quality of Sludge Used in Gardens or Parks.
Balogh, S., 1996. The fate of metals in sewage sludge incinerators. Water Air Soil Pollut. 91 (3–4), 249–254.
Barbosa, R., Lapa, N., Boavida, D., Lopes, H., Gulyurtlu, I., Mendes, B., 2009. Co-combustion of coal and sewage sludge: chemical and ecotoxicological properties of ashes. J. Hazard. Mater. 170 (2–3), 902–909.
Belevi, H., Moench, H., 2000. Factors determining the element behavior in municipal solid waste incinerators. 1. Field studies. Environ. Sci. Technol. 34 (12), 2501–2506.
Biswas, B., Inoue, K., Harada, H., Ohto, K., Kawakita, H., 2009. Leaching of phosphorus from incinerated sewage sludge ash by means of acid extraction followed by adsorption on orange waste gel. J. Environ. Sci. 21 (12), 1753–1760.
Blocher, C., Niewersch, C., Melin, T., 2012. Phosphorus recovery from sewage sludge with a hybrid process of low pressure wet oxidation and nanofiltration. Water Res. 46 (6), 2009–2019.
Bogush, A., Stegemann, J.A., Wood, I., Roy, A., 2015. Element composition and mineralogical characterisation of air pollution control residue from UK energy-from-waste facilities. Waste Manag. 36, 119–129.
CCME, 1999. Canadian Soil Quality Guidelines for the Protection of Environmental and Human Health.
CEC, 1986. Council Directive of 12 June 1986 on the Protection of the Environment, and in Particular of the Soil, When Sewage Sludge is Used in Agriculture.
Cenni, R., Janisch, B., Spliethoff, H., Hein, K.R.G., 2001. Legislative and environmental issues on the use of ash from coal and municipal sewage sludge co-firing as construction material. Waste Manag. 21 (1), 17–31.
Chen, Z., Lu, S., Tang, M., Lin, X., Qiu, Q., He, H., et al., 2019. Mechanochemical stabilization of heavy metals in fly ash with additives. Sci. Total Environ. 694, 133813.
Cheng, J., Zhou, J.H., Liu, J.Z., Zhou, Z.J., Huang, Z.Y., Cao, X.Y., et al., 2003. Sulfur removal at high temperature during coal combustion in furnaces: a review. Prog. Energy Combust. Sci. 29 (5), 381–405.
Cieslik, B., Konieczka, P., 2017. A review of phosphorus recovery methods at various steps of wastewater treatment and sewage sludge management. The concept of "no solid waste generation" and analytical methods. J. Clean. Prod. 142, 1728–1740.
Dai, X., Zhao, Y., Sha, C., Dai, L., Dong, B., 2014. Investigation on the status and causes of sludge sand content of wastewater treatment plants in China. Water Wastewater Eng. S1, 75–79.
Dal, P.A., Antonioni, G., Guglielmi, D., Stramigioli, C., Cozzani, V., 2016. Comparison of alternative flue gas dry treatment technologies in waste-to-energy processes. Waste Manag. 51, 81–90.
Donatello, S., Tyrer, M., Cheeseman, C.R., 2010. EU landfill waste acceptance criteria and EU Hazardous Waste Directive compliance testing of incinerated sewage sludge ash. Waste Manag. 30 (1), 63–71.
Dontriros, S., Likitlersuang, S., Janjaroen, D., 2020. Mechanisms of chloride and sulfate removal from municipal-solid-waste-incineration fly ash (MSWI FA): effect of acid-base solutions. Waste Manag. 101, 44–53.
EPA, 1996. Soil Screening Guidance: User's Guide.
EPA, 2018. Standards for the Use or Disposal of Sewage sludge.
Fang, W., Qi, G., Wei, Y., Kosson, D.S., van der Sloot, H.A., Liu, J., 2018. Leaching characteristic of toxic trace elements in soils amended by sewage sludge compost: a comparison of field and laboratory investigations. Environ. Pollut. 237, 244–252.
Franz, M., 2008. Phosphate fertilizer from sewage sludge ash (SSA). Waste Manag. 28 (10), 1809–1818.
Gawlik, B., 2012. FATE SEES: Results of a Pan-European Snapshot of Randomly Taken Sewage Sludge Sample. European Commission.
Gollakota, A.R.K., Volli, V., Shu, C.M., 2019. Progressive utilisation prospects of coal fly ash: a review. Sci. Total Environ. 672, 951–989.
Gotze, R., Boldrin, A., Scheutz, C., Astrup, T.F., 2016. Physico-chemical characterisation of material fractions in household waste: overview of data in literature. Waste Manag. 49, 3–14.
Huang, Y., Li, H., Jiang, Z., Yang, X., Chen, Q., 2018. Migration and transformation of sulfur in the municipal sewage sludge during disposal in cement kiln. Waste Manag. 77, 537–544.
Krüger, O., Grabner, A., Adam, C., 2014. Complete survey of German sewage sludge ash. Environ. Sci. Technol. 48 (20), 11811–11818.
Li, J.S., Xue, Q., Fang, L., Poon, C.S., 2017. Characteristics and metal leachability of incinerated sewage sludge ash and air pollution control residues from Hong Kong evaluated by different methods. Waste Manag. 64, 161–170.
Lu, P., Huang, Q., Bourtsalas, A., Themelis, N., Chi, Y., Yan, J., 2019. Review on fate of chlorine during thermal processing of solid wastes. J. Environ. Sci. 78, 13–28.
ME, 2007. Ordinance for Enforcement of Soil Contamination Countermeasures Law.
ME, 2019. Agricultural Land Soil Contamination Prevention Law.
MEE, 2018a. Soil Environmental Quality Risk Control Standard for Soil Contamination of Agricultural Land.
MEE, 2018b. Soil Environmental Quality Risk Control Standard for Soil Contamination of Development Land.
MEP, 2008. Standard for Pollution Control on the Landfill Site of Municipal Solid Waste. China Environmental Science Press, Beijing.
Metcalf, Eddy, Burton, F.L., Stensel, H.D., Tchobanoglous, G., 2003. Wastewater Engineering: Treatment and Reuse. McGraw Hill.
Mininni, G., Blanch, A.R., Lucena, F., Berselli, S., 2015. EU policy on sewage sludge utilization and perspectives on new approaches of sludge management. Environ. Sci. Pollut. Res. 22 (10), 7361–7374.

MUDEP, 1984. Control Standards for Pollutants in Sludges From Agricultural Use.
Nielsen, H.P., Frandsen, F.J., Dam-Johansen, K., Baxter, L.L., 2000. The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. Prog. Energy Combust. Sci. 26 (3), 283–298.
Nowak, B., Aschenbrenner, P., Winter, F., 2013. Heavy metal removal from sewage sludge ash and municipal solid waste fly ash – a comparison. Fuel Process. Technol. 105, 195–201.
Paikaray, S., 2016. Origin, mobilization and distribution of selenium in a soil/water/air system: a global perspective with special reference to the Indian scenario. CLEAN Soil Air Water 44 (5), 474–487.
Panepinto, D., Fiore, S., Genon, G., Acri, M., 2016. Thermal valorization of sewer sludge: perspectives for large wastewater treatment plants. J. Clean. Prod. 137, 1323–1329.
Shi, D.Z., Ma, J.Y., Wang, H.L., Wang, P., Hu, C.Y., Zhang, J.L., et al., 2019. Detoxification of PCBs in fly ash from MSW incineration by hydrothermal treatment with composite silicon-aluminum additives and seed induction. Fuel Process. Technol. 195, 106157.
Shi, R., Li, J., Jiang, J., Mehmood, K., Liu, Y., Xu, R., Qian, W., 2017. Characteristics of biomass ashes from different materials and their ameliorative effects on acid soils. J. Environ. Sci. 55, 294–302.
Sorum, L., Frandsen, F.J., Hustad, J.E., 2003. On the fate of heavy metals in municipal solid waste combustion - part I: devolatilisation of heavy metals on the grate. Fuel 82 (18), 2273–2283.
Srikanth, S., Ravikumar, B., Das, S.K., Gopalakrishna, K., Nandakumar, K., Vijayan, P., 2003. Analysis of failures in boiler tubes due to fireside corrosion in a waste heat recovery boiler. Eng. Fail. Anal. 10 (1), 59–66.
University of Minnesoda Extension, 2018. Understanding Phosphorus Fertilizers. Available: https://extension.umn.edu/phosphorus-and-potassium/understanding-phosphorus-fertilizers#available-619562. Accessed September 10, 2020.
Van de Velden, M., Dewil, R., Baeyens, J., Josson, L., Lanssens, P., 2008. The distribution of heavy metals during fluidized bed combustion of sludge (FBSC). J. Hazard. Mater. 151 (1), 96–102.
Viitala, H., Taskinen, P., 2016. Hot corrosion mechanism of steels exposed to heavy metal chlorides and sulphates in SO_2 environment. Oxid. Met. 86 (3–4), 239–262.
Vogel, C., Kruger, O., Herzel, H., Amidani, L., Adam, C., 2016. Chemical state of mercury and selenium in sewage sludge ash based P-fertilizers. J. Hazard. Mater. 313, 179–184.
Vrom, D., 2009. The Circular on Target Values and Intervention Values for Soil Remediation. Ministry of Housing, Spatial Planning and the Environment, the Netherlands.
Weigand, H., Bertau, M., Hubner, W., Bohndick, F., Bruckert, A., 2013. RecoPhos: full-scale fertilizer production from sewage sludge ash. Waste Manag. 33 (3), 540–544.
Xu, Y.F., Hu, H., Liu, J.Y., Luo, J.H., Qian, G.R., Wang, A.J., 2015. pH dependent phosphorus release from waste activated sludge: contributions of phosphorus speciation. Chem. Eng. J. 267, 260–265.
Yang, G., Zhang, G.M., Wang, H.C., 2015. Current state of sludge production, management, treatment and disposal in China. Water Res. 78, 60–73.
Zhang, H., He, P.J., Shao, L.M., 2008a. Fate of heavy metals during municipal solid waste incineration in Shanghai. J. Hazard. Mater. 156 (1–3), 365–373.
Zhang, H., He, P.J., Shao, L.M., 2008b. Flow analysis of heavy metals in MSW incinerators for investigating contamination of hazardous components. Environ. Sci. Technol. 42 (16), 6211–6217.
Zhang, H., Yu, S., Shao, L., He, P., 2018. Influence of air pollution control (APC) systems and furnace type on the characteristics of APC residues from municipal solid waste incinerators. Huanjing Kexue 39, 467–476.
Zhou, H., Meng, A.H., Long, Y.Q., Li, Q.H., Zhang, Y.G., 2015a. An overview of characteristics of municipal solid waste fuel in China: physical, chemical composition and heating value. Renew. Sustain. Energy Rev. 46, 107–122.
Zhou, J., Wu, S., Pan, Y., Zhang, L., Cao, Z., Zhang, X., et al., 2015b. Enrichment of heavy metals in fine particles of municipal solid waste incinerator (MSWI) fly ash and associated health risk. Waste Manag. 43, 239–246.