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Size fractionation of waste-to-energy boiler ash enables separation of a coarse fraction with low dioxin concentrations



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ABSTRACT

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) formed in modern Waste-to-Energy plants are primarily found in the generated ashes and air pollution control residues, which are usually disposed of as hazardous waste. The objective of this study was to explore the occurrence of PCDD/F in different grain size fractions in the boiler ash, i.e. ash originating from the convection pass of the boiler. If a correlation between particle size and dioxin concentrations could be found, size fractionation of the ashes could reduce the total amount of hazardous waste. Boiler ash samples from ten sections of a boiler's convective part were collected over three sampling days, sieved into three different size fractions – <0.09 mm, 0.09–0.355 mm, and >0.355 mm – and analysed for PCDD/F. The coarse fraction (>0.355 mm) in the first sections of the horizontal convection pass appeared to be of low toxicity with respect to dioxin content. While the total mass of the coarse fraction in this boiler was relatively small, sieving could reduce the amount of ash containing toxic PCDD/F by around 0.5 kg per tonne input waste or around 15% of the collected boiler ash from the convection pass. The mid-size fraction in this study covered a wide size range (0.09–0.355 mm) and possibly a low toxicity fraction could be identified by splitting this fraction into more narrow size ranges. The ashes exhibited uniform PCDD/F homologue patterns which suggests a stable and continuous generation of PCDD/F.

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1. Introduction

Incineration is an efficient method to reduce the non-recyclable fractions of municipal solid waste (MSW) and similar waste types in weight and volume while recovering the energy, however some concerns stem from the formation of toxic organohalogen compounds. The most infamous of these are the polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF). They were first identified in MSW incineration residues in the late 1970's (Olie et al., 1977), but since then legislative measures and advanced air pollution control systems have reduced their emissions to air greatly which has transferred most of the PCDD/F from the stack to the solid residues. There are in total 210 PCDD/F congeners which differ with regard to the number and position of the chlorine substituents in the molecule. Their toxicity is expressed relative to the most toxic congener, 2,3,7,8-TCDD, by the toxic equivalency factor, and the combined toxicity of a sample is expressed by the toxic equivalent (TEQ) concentra-

* Corresponding author. E-mail address: eva.weidemann@umu.se (E. Weidemann). tion. Of the 210 PCDD/F congeners, 17 are assigned toxic equivalency factors (Van den Berg et al., 2006).

PCDD/Fs formed during waste incineration are primarily found in ash fractions collected in the air pollution control system (fly ash) and in the energy recovery system (boiler ash). The total ash content of the input waste is typically in the range 15–25%, which distributes into bottom ash (80–90%), boiler ash (2–12‰) and fly ash. (10–20%) (United States Environmental Protection Agency, 2014; Avfall Sverige, 2015). The boiler ash thus corresponds to between 2 kg/t and 12 kg/t of incinerated waste (Hjelmar, 1996), which is in conformance with the studied plant. Fly ash and boiler ash are sometimes mixed and might be considered a hazardous waste, which must be disposed of accordingly (ISWA, 2008).

Detailed literature on characterization of boiler ashes is relatively scarce (Allegrini et al., 2014; De Boom and Degrez, 2015; De Boom et al., 2011) and even fewer have focused on formation of persistent organic pollutants such as PCDD/F in boiler ash. The concentrations from different points along the boiler have been investigated and PCDD/F formation have been found to occur in the temperature range of 370–490 °C (Düwel et al., 1990; Lundin and Marklund, 2008; Mariani et al., 1990). In Allegrini et al.



(2014) a detailed characterization of boiler ash from a Danish Waste-to-Energy plant was presented, with samples collected at 10 different points along the boiler's convective part. These boiler ash samples were analysed for grain size distribution, content of inorganic elements, leaching of metals, and concentrations of PCDD/F, but the relationship between boiler ash particle size and concentrations of PCDD/F were not investigated. This is therefore the objective of the present study in which we explored the possibility of identifying a size fraction of the boiler ash with a lower concentration of toxic dioxins and furans. Determination of a size fraction that could be separated from the boiler ash would reduce the total amount of ash to be handled as hazardous waste, thus reducing the management costs.

Previous studies on size fractionation of MSW incineration ash in relation to PCDD/F concentrations have been performed on bottom ash (Chen et al., 2006), and on the insoluble part of the ash (Moon et al., 2002). No previous studies have targeted boiler ash specifically. To obtain detailed knowledge about the content of PCDD/F in the different grain size fractions of the boiler ash, samples from the ten individual hoppers in the different sections of the boiler were sieved into three different size fractions and analysed for PCDD/F. The objective was to investigate a potential correlation between dioxin concentrations and grain size distribution in the ash samples.

2. Material and methods

2.1. Sampling and analysis of boiler ash

The boiler ash samples were collected from one line at a 27 MW (thermal input) Waste-to-Energy plant that incinerated mixed municipal solid waste from households, local industries, recycling stations, and the commercial/institutional sector. The boiler/ energy recovery system where the boiler ash is generated could be divided in 10 sections (denoted 1–10), with different functions, temperature, and piping configuration. Each of them corresponded to a bottom hopper for ash discharge. A schematic representation of the configuration of the horizontal part of the boiler's convective part is shown in Fig. 1. The flue gas temperature within the boiler dropped from approximately 700 °C (section 1) to 500 °C (section 4), 340 °C (section 7), and 160 °C (section 10). Detailed information about the plant, sample collection, and preparation can be found in Allegrini et al. (2014).

The ash samples were collected during three consecutive days (days 1–3) at the bottom of the individual hoppers (1–10) of the ten horizontal sections. Boiler ash was sampled for approximately 5.5 h during day 1 and day 2, and 3 h during day 3 (Allegrini et al., 2014). One sample was collected each sampling day. All the col-

lected material, between 2.5 kg and 22 kg for each section was mass-reduced by means of a 34 chute riffle-splitter (1 cm chute width) to obtain laboratory samples. Since the material dry weight were above 99%, no drying was done. The results from day 1 – section 10 were excluded from the calculations due to clogging problems in the hopper during sampling. Samples from day 1 and 3 were pooled over all sections before mass reduction and PCDD/F analysis. To further investigate the PCDD/F distribution, the individual samples from each section collected during day 2 were also sieved into three grain size fractions, fine: <0.09 mm, mid-size: 0.09–0.355 mm, and coarse: >0.355 mm. The grain size fractions were chosen to yield three distinct fractions.

The three fractions were then individually analysed for PCDD/F concentrations. As each sample was unique, no PCDD/F analysis replicates were performed. The ashes were extracted by Soxhlet for 48 h in toluene, clean-up was done using multi-silica columns, and analysed using HRGC-MS equipped with a 60 m DB5-ms column (i.d. $0.25 \ \mu$ m) (Liljelind et al., 2003). Laboratory blanks were processed alongside the samples for quality assurance and blank concentrations were found to be below 10 % of sample concentrations.

3. Results and discussions

The mid-size fraction was the largest fraction and constituted 50–60% of the total sample weight, the fine fraction was 35–41%, and the coarse fraction was 5–10%. The mass distribution between the three fractions was calculated by multiplying the daily ash production with the sieving distribution percentages (Fig. 2, left part of the graph). This enabled a mass flow of ash which could be related to the PCDD/F concentrations. As only the toxic equivalent (TEQ) concentrations can be used from a legislative and practical standpoint, this evaluation will focus on the TEQ concentrations of PCDD/F in the three particle size fractions. On weight basis (µg/kg ash), the lowest TEQ concentrations were found in the 0.09-0.355 mm fraction, but when normalized to the daily production of ash (Fig. 2, right part of the graph) the coarse fraction had the lowest loadings. The highest loadings were found in the fine fraction. The actual concentrations of PCDD/F varied between sampling days, which can be expected in full scale MSW incineration due to fuel heterogeneity.

Tetra-chlorinated furans dominated the PCDF profiles, and octachlorinated dioxins dominated the PCDD. This is not uncommon for MSW incineration homologue profiles (i.e., the relative abundance of congeners with different degrees of chlorination) e.g., Lundin and Marklund (2008). Moreover, the profiles displayed a high degree of similarity between sampling days, indicating a stable and continuous generation of PCDD/F (Fig. 3). In MSW



Fig. 1. Schematic representation of the boilers' convective part. Circled numbers represent different sections in the post combustion zone. The dotted line denotes an evaporator screen, the dashed line separates the economizer from the rest of the boiler.

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