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Effects of regional differences in waste composition on the thermal formation of polychlorinated aromatics during incineration

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HIGHLIGHTS

- Concentration of PCDDs, PCDFs, PCBs, and PCNs increased with decreased temperature.
- Abundance of highly chlorinated homologues increased along the post-combustion zone.
- No significant differences in total POPs concentrations between two studied wastes.
- Higher metal and Cl content promoted formation of highly chlorinated aromatics.

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ABSTRACT

Two artificial wastes (A and B) whose contents reflect regional differences in municipal solid waste composition, were used to investigate the thermal formation of polychlorinated dibenzo-*p*-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and naphthalenes (PCNs) during incineration. Flue gas samples were simultaneously collected at three ports in the post-combustion zone corresponding to flue gas temperatures of 400, 300, and 200 °C. The combustion of Waste B, which had a higher chlorine and metal content than Waste A, produced greater levels of highly-chlorinated homologues, as demonstrated by a higher degree of chlorination. The total concentrations of PCDDs, PCDFs, PCBs, and PCNs formed in the combustion of both wastes increased as temperature decreased along the convector. There were no significant differences in total concentrations between Waste A and Waste B combustion at specific temperatures, with exception of PCDFs at 400 °C. Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) modeling, used to evaluate the data for all compound groups, suggest that during flue gas quenching at temperatures of 400 °C low-chlorinated homologues are preferentially formed in the presence of copper, which is known to be a very active catalyst for this process. At 300 and 200 °C, the formation of highly-chlorinated homologues is favored.

1. Introduction

Waste composition varies widely between countries and between different regions of individual countries, and these countries use a wide range of waste management policies such as landfilling, recycling, compost production, and energy recovery (Koneczny et al., 2007). Incineration is a common technique for treating MSW due to the energy recovery and/or waste volume reduction. The formation and emission of Persistent Organic Pollutants (POPs) such as PCDDs and PCDFs during municipal solid waste incineration (MSWI) (Olie et al., 1977; Buser et al., 1978) can cause significant health and environmental problems (UNEP, 2009).

There are two key pathways of PCDD/F formation: *de novo* synthesis from carbonaceous particulates and aromatic hydrocarbons (Stieglitz et al., 1989) and a precursor pathway in which chlorophenols and chlorobenzenes are joined (Altwicker et al., 1993). The main formation reactions during MSWI are believed to occur at the gas/solid interface on particle surfaces at temperatures between 250–450 °C in the post-combustion zone (Vogg and Stieglitz, 1986). PCDD/Fs can be formed directly in the gas phase at higher temperatures (Shaub and Tsang, 1983) but very low concentrations (Aurell et al., 2009; Phan et al., 2012).

Chlorine in the waste plays an important role in PCDD/Fs formation. Chlorine gas (Cl_2), an active chlorinating agent, is formed from HCl via the Deacon reaction (Griffin, 1986), which is favored at 400 °C and which decreases to approximately zero below 300 °C (Gullett et al., 1990). In addition, an alternative chlorination mechanism that involves direct ligand transfer with $CuCl_2$ acting as a direct chloride donor in PCDD/F formation has been proposed (Stieglitz et al., 1991). No significant difference between organic and inorganic chloride effects on PCDD/Fs formation were observed

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(Wikstrom et al., 1996). CuO is believed to act as a catalyst (Vogg and Stieglitz, 1986). Other metals such as Fe and Al exhibit catalytic effects on the formation of POPs. However, copper is the most active catalyst – approximately 25 times more effective than iron (Stieglitz et al., 1991) even when only a very small quantity of copper (0.007% by mass) is available (Hatanaka et al., 2004).

PCBs and PCNs are considered as dioxin-like compounds because of similar structure, physicochemical properties, and probably similar toxicity (Hanberg et al., 1990; Villeneuve et al., 2000). It is believed that PCBs and PCNs are formed via two routes: *de novo* synthesis from carbonaceous particulates and aromatic hydrocarbons (Weber et al., 2001) and a precursor pathway involving smaller chlorinated compounds with similar structures (e.g., chlorophenols and chlorobenzenes) (Lemieux et al., 2001). In addition, the formation of PCBs and PCNs may correlate with PCDFs formation (Imagawa and Lee, 2001; Weber et al., 2001).

Because POPs present a health threat, it is important to study their formation processes during incineration so as to develop strategies and methods to prevent/eliminate their formation *in situ*. Waste composition varies widely and directly affects the formation of PCDDs and PCDFs (Nakao et al., 2006). The differences associated, for example, in plant and boiler design and mode of energy recovery and operation, make it difficult to evaluate the importance of waste composition from different regions on the formation of POPs. To this end, this study investigates the thermal formation of POPs (PCDDs, PCDFs, PCBs, and PCNs) during the incineration of different waste materials. The regional effects were studied using two artificial wastes that simulated typical Swedish MSW and average European MSW. The study's results can be used to estimate the amount of POPs formed from different regions of Europe and to redesign waste management techniques to minimize their formation.

2. Materials and methods

2.1. Combustion experiments and flue gas sampling

Combustion experiments were described elsewhere (Phan et al., 2012) using two artificial wastes: "Waste A", was designed to simulate a typical Swedish MSW, while the second ("Waste B") had a material content and elemental composition that was representative for European MSW (Duncan, 2007) (Table S1). The Fe and Al contents of Waste B were higher than those for Waste A, presumably due to the more extensive discharge of materials containing these metals in Europe as a whole compared to Sweden. The mixed ingredients of each waste were ground into pellets (6 mm i.d. × 10 mm length). The pellets were dried at room temperature and sampled for elemental analysis and characterization (Table S1). Waste composition analyses were performed by ALS Scandinavia (Luleå, Sweden) according to the modified USEPA methods 2008 by inductively coupled plasma-sector mass spectrometry (ICP-SMS). Solutions were prepared from 0.125 g dried sample is melted with 0.375 g $LiBO_2$ and dissolved in HNO_3. A similar type of artificial MSW was successfully used to study the thermal formation of PCDDs and PCDFs that produced homologue profiles and PCDD/F concentrations similar to those typically observed in full scale operations (Wikstrom and Marklund, 1998). The combustion campaign started by combusting Waste A on three consecutive days, followed by two consecutive days combusting Waste B. The day before the Waste B combustion experiments were conducted, Waste B was incinerated and then the reactor was cleaned to remove residues produced from the Waste A combustion experiments.

Samples of flue-gas were isokinetically collected using the cooled-probe method following the EN 1948:1 standard (EN-1948/1, 2006). Phan et al. described the sampling procedure in detail (Phan et al., 2012). Flue-gas samples were collected simultaneously at three fixed locations in the post-combustion zone corresponding to temperatures of 400, 300, and 200 °C (Fig. S1).

2.2. Analytical procedure

All of the steps involved in sample workup and the subsequent analysis of PCDD/Fs, PCBs, and PCNs were described in detail elsewhere (Liljelind et al., 2003; Jansson et al., 2008). PCDD/Fs and PCBs were analyzed using a GC-HRMS (AutoSpec ULTIMA NT 2000D, Waters Corporation, Milford, MA) equipped with a J&W Scientific DB5-MS (60 m × 0.25 mm i.d. and 0.25 µm film thickness) column; and PCNs were analyzed using a J&W Scientific DB5 (60 m × 0.25 mm i.d. and 0.25 µm film thickness) column instead. Peaks were identified using internal standards and the published retention order (Ryan et al., 1991; Abad et al., 1999). All flue-gas volumes were normalized to 11% O_2, 1 atm. and 0 °C. Recoveries of the sampling and internal standards were between 52% and 109%.

2.3. Multivariate data analysis

Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) was used to evaluate the chloroaromatics data and identify correlations with combustion data for all flue gas samples. Prior to OPLS-DA, the PCA was applied to screen data and PCA results were presented in the supporting information (Fig. S2). OPLS-DA model uses a binary matrix Y (waste classification) to decompose the X data (homologues and combustion data) into two variations – predictive (between class variations) and orthogonal (within class variations). All the models were built using the SIMCA-P+13.0 software (Umetrics AB, Umeå, Sweden).

3. Results and discussion

3.1. Waste characterization

Important elements in the flue gases that significantly affected POPs formation were determined (Table 1). Both wastes had identical copper and sulfur contents of approximately 0.015% dw (dry weight) and 0.09% dw, respectively. The dry weight and ash content of Waste A were 91.4% and 11.4%, respectively, while those for Waste B were 91.8% and 16.5%, respectively. Iron and aluminum are both common metals in contemporary household waste. The iron and aluminum contents of Waste A were 4.4% and 2.0%, respectively; for Waste B, these contents were 8.6% and 8.4%, respectively. Carbon accounted for almost 50% by mass of both wastes, but the metallic content of Waste B was greater than that for Waste A, giving the former a higher ash content (16.5% in Waste B compared to 11.4% in Waste A). Chlorine was present in both wastes (0.8% by mass in Waste A and 1.2% by mass in Waste B) and originated primarily from the plastic fraction (PVC), calcium chloride ($CaCl_2{\cdot}6H_2O$) and kitchen residues (mainly NaCl) (Table S1). Despite the 50% higher Cl in Waste B, HCl in flue gas was detected as concentrations of 346 ppm and 371 ppm during combustion of Waste A and B, respectively (Table S2). The transformation of HCl from chlorine in waste depends on source, either organic or inorganic. HCl conversion from inorganic chloride NaCl produced lower yields than organic chloride PVC due to the higher energy of the ionic bond than the molecular bond (Wang et al., 1999). In addition, the small differences of HCl yield in Waste B and A were probably due to the lack of H because the H content was similar in both wastes (Table 1). Since HCl is a key starting material in chlorination processes, high levels of HCl in the flue gas are likely to promote the formation of chlorinated aromatic pollutants. Both wastes had calorific values of 20 MJ kg^{-1} and thus