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# Trace element partitioning in ashes from boilers firing pure wood or mixtures of solid waste with respect to fuel composition, chlorine content and temperature



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#### ABSTRACT

Trace element partitioning in solid waste (household waste, industrial waste, waste wood chips and waste mixtures) incineration residues was investigated. Samples of fly ash and bottom ash were collected from six incineration facilities across Sweden including two grate fired and four fluidized bed incinerators, to have a variation in the input fuel composition (from pure biofuel to mixture of waste) and different temperature boiler conditions. As trace element concentrations in the input waste at the same facilities have already been analyzed, the present study focuses on the concentration of trace elements in the waste fuel, their distribution in the incineration residues with respect to chlorine content of waste and combustion temperature.

Results indicate that Zn, Cu and Pb are dominating trace elements in the waste fuel. Highly volatile elements mercury and cadmium are mainly found in fly ash in all cases; 2/3 of lead also end up in fly ash while Zn, As and Sb show a large variation in distribution with most of them residing in the fly ash. Lithophilic elements such as copper and chromium are mainly found in bottom ash from grate fired facilities while partition mostly into fly ash from fluidized bed incinerators, especially for plants fuelled by waste wood or ordinary wood chips. There is no specific correlation between input concentration of an element in the waste fuel and fraction partitioned to fly ash. Temperature and chlorine content have significant effects on partitioning characteristics by increasing the formation and vaporization of highly volatile metal chlorides. Zinc and cadmium concentrations in fly ash increase with the incineration temperature.

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#### 1. Introduction

Incineration processes for solid waste has the unique benefit of about 90% volume and 60–75% mass reduction, energy recovery and nearly complete destruction of organic material giving an answer to the many problems of sustainable waste management and increased disposal cost (De Boom and Degrez, 2012; Chimenos and Segarra, 1999; Hjelmar, 1996). Bottom ash, fly ash and air pollution control (APC) residues are by-products of waste incineration. Fly ash and APC residues are often considered together to have a unique output from incineration plants. Both these residues are often considered hazardous waste due to the content of toxic trace elements such as Cd and Pb with increased levels of chlorides and soluble salts also observed that can pose a serious threat to human health and the environment (Pan et al.,

2013; Okkenhaug et al., 2013; Chang et al., 2000). Therefore possible understanding of the formation of these residues and distribution of trace elements in them are imperative for their further use and to select appropriate waste management strategies to make inroads towards a sustainable future.

In Sweden, total ash production including all types of ashes has increased by 20% (1.2–1.5 million tons) dry substance, from 2006 to 2010 (Lövström, 2010) which shows an increase in the use of incineration technology for solid waste management. A study by Swedish Waste Management (2011) has found that, in 2010, total production of bottom ash, fly ash, mixed ash and flue gas purification products were 0.6, 0.4, 0.06 and 0.02 million tons respectively. 60% of total produced bottom ash is being utilized as construction material at landfills while 8% in road construction and surfacing applications (SEPA, 1996b) whereas the rest of the bottom ash has found uses in soil improvement, capping of mine waste, forest fertilization and some unspecified uses. Fly ash and other mixed ashes are detoxified and are either landfilled or sent for treatment to other enterprises (Swedish Waste Management, 2011).

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During incineration, generally highly volatile mercury and cadmium are found completely in flue gas or fly ash and elements with medium volatility like lead and zinc are distributed equally among both residues or more to fly ash while others having low vapor pressure and high boiling point like copper and iron mainly stays in the bottom ash (Arena and Gregorio, 2013; Shi et al., 2004; Wang et al., 1999). Recent research (Zhang et al., 2008, 2012; Chang et al., 2009; Astrup et al., 2011) have suggested that the fate of trace elements might be a function of several factors such as incineration temperature, complex waste composition, feed chlorine content, oxygen concentration, flue gas treatment process, physico-chemical properties of trace elements, their compounds and reaction affinity of trace elements with non-metals like chlorine. Since incineration of unsorted MSW (containing PVC and food waste), industrial waste and other type of waste can significantly enhance the formation of volatile element chlorides, promoting the emission of harmful trace elements. So in order to minimize such risks and to make the better use of residues it is essential to attain deep understanding about factors affecting the transfer characteristics of trace elements during incineration. A study similar to our work by Rendek et al. (2007) was conducted to investigate the influence of waste fuel and incineration technology on bottom ash properties. It was reported that addition of industrial and demolishing waste increase sulfur content while plastic waste added significant amount of chlorine. Both these components are water soluble and also affect the fate of trace elements, so part of these wastes in total amount must be addressed to predict the partitioning and leaching behavior of trace elements.

Volatility of trace elements and presence of chlorine in the waste are responsible factors for the formation of metallic chlorides. In unsorted MSW (Municipal Solid Waste), plastic (PVC) and food (NaCl) waste can add significant amounts of organic and inorganic chlorine, respectively, which will affect the distribution of trace elements (Shi et al., 2004). In another study by Pedersen et al. (2009), different types of waste fractions were fired during normal operation to examine their effect on trace element partitioning during waste incineration and it was reported that the firing of chlorine rich waste (PVC, salt) and shoes increased volatilization of lead and an increased recovery was observed in fly ash and aerosol fractions. Also, organically bound chlorine was vaporized as HCl(g) whereas inorganically bound chlorine was recovered in bottom ash as alkali metal chlorides thus making chlorine a critical element not only for partitioning but also for corrosion and deposition problems. Forest waste (bark, sawdust, stem chips, logging residues) contains comparatively lower concentrations of chlorine (0.01-0.03 wt.%) (Alakangas, VTT, 2005). Use of waste wood and virgin wood as fuel is also an increasing trend in Sweden and waste wood often contains high contents of Zn, Pb, As, Cu and S compared to virgin wood (Krook et al., 2006). Apart from chlorine, zinc also evaporates from the combustion chamber and forms deposits especially in grate fired conditions (Amande et al., 2006). In previous studies, thermodynamic calculations have shown that the presence of chlorine compounds like HCl and a reducing atmosphere usually increase the rate of volatilization especially for Pb, Cu, Cd and Zn, therefore increasing enrichment of these elements in fly ash (Zhang et al., 2008; Wang et al., 1999). Influence of chlorine on trace element partitioning has also been reported to be temperature dependent (Chiang et al., 1997). The effect of moisture and chlorine on element partitioning in a laboratory tubular furnace was investigated by Li et al. (2010) and it was observed that chlorine has higher impact on the volatilization rate of elements at 800 °C than at 600 °C especially for Pb, Cu, Ni, Cr and Cd whereas Hg is volatile even at low temperatures. Temperature has a pronounced impact on vapor pressure of trace elements and hence on partitioning, it usually increases with temperature. It has been reported that during waste incineration Hg is most likely to vaporize, followed by Cd, Pb, and Zn, while Cr and Ni are least likely to evaporate (Jianxin et al., 2007). Impact of temperature on trace element partitioning has been subject to some studies (Abanades et al., 2002; Zhang and Kasai, 2004; Asthana et al., 2010).

Various incineration facilities can have different trace elements partitioning behavior in the final residues. Jung et al. (2004) reported high concentration of some elements (Cu, Cr, Al) in fly ash for fluidized bed boiler compared to grate furnaces. Temperature, turbulence and residence time are crucial factors affecting the distribution of trace elements. Grate furnaces are the most commonly employed incinerators for MSW combustion where fuel is fed onto a moving grate with supply of excess air and there is a minimal need for pre-sorting and fine size reduction (Blasiak et al., 2006). In Europe, about 90% of the installations are using different types of grates for MSW treatment (European Commission, 2006). Normally residence time for the waste on the grate is not more than 60 min and for the flue gases it is about  $\ge 2$  s to have enough time for trace elements distribution between phases to reach equilibrium (European Commission, 2006). Typical reaction conditions for oxidative combustion process are a temperature in the range of 800–1450 °C under pressure of 1 bar (European Commission, 2006). In bubbling or circulating fluidized bed (BFB or CFB) boilers, a bed of inert material like quartz sand is used to distribute the heat evenly to water tubes in order to maintain low temperature to minimize the overall NO<sub>x</sub> production as nitrogen supply will be reduced (Bontoux, 1999). The difference in temperatures and oxygen concentrations in both sorts of combustion systems will definitely affect the fate of trace elements.

The present study focuses on the discussion of trace element partitioning in different ashes resulting from the combustion of various waste fuels including household, industrial, forest chips, waste wood and mixture of different wastes, being treated in Swedish waste incineration facilities. Waste materials contain varying contents of chlorine and trace elements. The influence of combustion temperature on the rate of volatilization of trace elements is discussed here with the guidance of literature and previous research. Six incineration facilities across Sweden including two grate fired, three circulating fluidized bed boilers (CFB) and one bubbling fluidized boiler (BFB) have been considered to have a broad overview of trace elements behavior in various boiler types and variable incineration conditions like temperature. This study will help to further explore the impact of various factors affecting the fate of trace elements during incineration such as type of waste fuel, input chlorine content and incineration technology.

#### 2. Materials and methods

#### 2.1. Sampling and characterization of waste fuels

Waste fuels sampling for analysis is complicated process due to the uncertainty of being able to ensure a representative sample from a relatively heterogeneous mixture. Heterogeneity is the single largest cause of sampling error. A sample, with a mass of only a few grams, to be used for the chemical analysis, is intended faithfully to represent the composition of the materials in a bulk waste body. A sample can be used if sampling has been correctly performed and in a representative manner, but with the reservation that it represents only one particular body of waste and its unique composition at the time of taking the sample. According to theory of sampling by Gy (1976) it is always a compromise between cost and accuracy during sampling. To minimize cost and effort it is to keep in mind that all parts of bulk sample must be accessible and should have an equal chance of inclusion in the sample and hence final sample must be representative of whole population. However

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