The relationship between fly ash chemistry and the thermal formation of polychlorinated pollutants during waste incineration

Phan Dương Ngọc Châu

Department of Chemistry
Umeå University

Doctoral thesis
Akademisk avhandling

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Fakultetsopponent: Professor Bogdan Dlugogorski,
Faculty of Engineering and Built Environment, The University of Newcastle, Australia
Umeå 2013
To my parents and my family,

To my beloved wife and children,
Title
The relationship between fly ash chemistry and the thermal formation of polychlorinated pollutants during waste incineration

Abstract
The thermal formation of polychlorinated dibenzo-p-dioxins (PCDDs), dibenzofurans (PCDFs), biphenyls (PCBs), and naphthalenes (PCNs) is a major problem in waste incineration. Ideally, rather than relying on air cleaning systems and treatment techniques, their formation should be minimized or, if possible eliminated. The work presented in this thesis was conducted to obtain a deeper understanding of the thermal formation of PCDDs, PCDFs, PCBs, and PCNs during incineration using a 5 kW laboratory scale incinerator and two artificial wastes that were designed to reflect regional differences in waste composition.

The first part of the thesis focuses on the validation of a recently-developed flue-gas sampling probe with enhanced cooling capabilities. Artifact formation of PCDDs and PCDFs can occur during the sampling of hot flue gases if the cooling is insufficient. The new probe was successfully used to collect samples at 700 °C without biasing the measured POP levels. The thermal formation of PCDDs, PCDFs, PCBs, and PCNs in the post-combustion zone of the incinerator was then studied by collecting flue gas samples at 400 °C, 300 °C, and 200 °C during the incineration of the two artificial wastes. Highly chlorinated POPs were formed in larger quantities when burning the waste with the higher content of metals and chlorine, which suggests that high metal levels in the waste favor the chlorination of less chlorinated POPs or otherwise facilitate the formation of highly chlorinated polyaromatics, possibly via the condensation of highly chlorinated phenols. The concentrations of these pollutants and the abundance of highly chlorinated homologues increased as the flue gas cooled. Fly ash particles play an important role in thermal POP formation by providing essential elements (carbon, chlorine, etc.) and catalytic sites. The chemical and mineralogical properties of fly ash samples were studied by X-ray diffraction (XRD), Fourier Transform Infrared (FTIR), Scanning Electron Microscopy/Energy Dispersive X-ray (SEM/EDX), and X-ray photoelectron spectroscopy (XPS) to determine their impact on thermal POP formation. Orthogonal Partial Least Squares (OPLS) modeling was used to identify correlations between the observed POP distributions and the physicochemical data. This investigation provided new insights into the impact of fly ash chemistry on thermal POP formation.

In addition, the POP isomer distribution patterns generated during waste combustion were examined. These patterns are used to “fingerprint” mechanisms of POP formation. It was found that wastes containing large quantities of metals and chlorine favored the formation of highly chlorinated homologues including the very toxic 2,3,7,8-congeners. The data suggest that reducing fly ash emissions might increase the SO2 content of the flue gas and thereby suppress the Deacon process and the formation of harmful highly chlorinated aromatic species.

Keywords: Incinerations, dioxins, PCDD/Fs, PCBs, PCNs, flue gas, fly ash, sampling, particle characterization, XPS, XRD, SEM/EDX, formation, chlorination, PCA, OPLS, OPLS-DA

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List of papers

The thesis is based on the papers listed below, which are referred to in the text by the indicated Roman numerals.

I. **Accurate sampling of PCDD/F in high temperature flue-gas using cooled sampling probes**
   
   *Duong Ngoc Chau Phan, Eva Weidemann, Lisa Lundin, Stellan Marklund, Stina Jansson*
   
   Chemosphere, 2012, 88, 832-836

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

   *Duong Ngoc Chau Phan, Stina Jansson, Stellan Marklund*
   
   Chemosphere, 2013, in press

III. **Physicochemical properties of fly ash particles formed during municipal solid waste combustion**

   *Duong Ngoc Chau Phan, Stina Jansson, Jean-Francois Boily*
   
   Submitted to Energy & Fuels

IV. **A link between fly ash particle chemistry and the thermal formation of PCDDs, PCDFs, PCBs, and PCNs during waste incineration**

   *Duong Ngoc Chau Phan, Stina Jansson, Stellan Marklund, Jean-Francois Boily*
   
   Manuscript in preparation

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**Author contribution:**

Paper I: The author contributed significantly to the planning and conduct of the experiments and made additional contributions to the quantification and evaluation of the data and the writing of the manuscript.

Paper II: The author was heavily involved in the planning and conduct of the experiments and the interpretation of their results, and made a major contribution to the writing of the manuscript.

Paper III: The author was heavily involved the planning and conduct of the experiments and the interpretation of their results, and made a major contribution to the writing of the manuscript.
Paper IV: The authors contributed to the planning of the experiments, was responsible for the quantification and evaluation of the data, and wrote the manuscript.

Publications by the author that are not included in this thesis:

I. Contamination of surface, ground, and drinking water from pharmaceutical production
   Jerker Fick, Hanna Söderström, Richard H. Lindberg, D N Chau Phan, Mats Tysklind, D. G. Joakim Larsson
   Environmental Toxicology and Chemistry, 2009, 28 (12), 2522-2527

II. Minimizing artifact formation of PCDD/F during high temperature flue gas sampling using cooled probes
    Duong Ngoc Chau Phan, Eva Weidemann, Lisa Lundin, Stina Jansson, Stellan Marklund
    Conference proceeding at 31st International Symposium on Halogenated Persistent Organic Pollutants – Dioxin 2011, Brussels Belgium

III. Characterizing the formation of polychlorinated aromatics during waste incineration
     Duong Ngoc Chau Phan, Stina Jansson, Stellan Marklund
     Conference proceeding at 32nd International Symposium on Halogenated Persistent Organic Pollutants – Dioxin 2012, Cairns, Australia
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>APCDs</td>
<td>Air pollution control devices</td>
</tr>
<tr>
<td>d.w.</td>
<td>Dry weight</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-ray</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infrared</td>
</tr>
<tr>
<td>GC/HRMS</td>
<td>Gas chromatography high resolution mass spectrometry</td>
</tr>
<tr>
<td>IS</td>
<td>Internal standard</td>
</tr>
<tr>
<td>I-TEQ</td>
<td>International Toxic Equivalents</td>
</tr>
<tr>
<td>IUPAC</td>
<td>International Union of Pure and Applied Chemistry</td>
</tr>
<tr>
<td>MSWI</td>
<td>Municipal solid waste Incineration</td>
</tr>
<tr>
<td>OPLS-DA</td>
<td>Orthogonal Partial Least Squares Discrimination Analysis</td>
</tr>
<tr>
<td>OPLS</td>
<td>Orthogonal Partial Least Squares</td>
</tr>
<tr>
<td>PCDDs</td>
<td>Polychlorinated dibenzo-p-dioxins</td>
</tr>
<tr>
<td>PCDFs</td>
<td>Polychlorinated dibenzofurans</td>
</tr>
<tr>
<td>PCBs</td>
<td>Polychlorinated biphenyls</td>
</tr>
<tr>
<td>PCNs</td>
<td>Polychlorinated naphthalenes</td>
</tr>
<tr>
<td>PCDD/F</td>
<td>Polychlorinated dibenzo-p-dioxins/furans</td>
</tr>
<tr>
<td>PCA</td>
<td>Principal Component Analysis</td>
</tr>
<tr>
<td>PLS</td>
<td>Partial Least Squares</td>
</tr>
<tr>
<td>POPs</td>
<td>Persistent Organic Pollutants</td>
</tr>
<tr>
<td>PVC</td>
<td>Polyvinyl chloride</td>
</tr>
<tr>
<td>PUF</td>
<td>Polyurethane foam</td>
</tr>
<tr>
<td>RS</td>
<td>Recovery standard</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>S/N</td>
<td>Signal to noise</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Definitions

Isomer – A compound with the same molecular formula (and thus number of chlorines) as another but different substitution patterns

Homologue – A group of compounds with the same molecular formula and number of chlorine substituents but different substitution patterns

Profile – the distribution of concentrations or relative abundance of homologue groups within a sample.

Pattern – the distribution of concentration or relative abundance of individual isomers within a homologue group.

Homologue fraction – the sum of the concentrations of all isomers belonging to a particular homologue group expressed as a fraction of the summed concentrations of all isomers of interest: $\Sigma C_{\text{homologue}} / \Sigma C_{\text{total}}$

Isomer fraction – the concentrations of an individual isomer expressed as a fraction of the summed concentrations of every isomer within the same homologue group: $\Sigma C_{\text{isomer}} / \Sigma C_{\text{homologue}}$

Degree of chlorination – a measure of the average number of chlorine atoms across all isomers of a given class of POPs: $\Sigma((\text{Homologue sum}/\Sigma(\text{Homologue sum})) \times \text{No. of Cl})$
1. Introduction

Municipal solid waste (MSW) is commonly known as the trash or garbage that is discarded by households. The amount of MSW produced by individual households and across populated areas is increasing. It was recently estimated that on average, citizens of the European countries (EU27) produce 503 kg of municipal waste per year [1], an increase from 474 kg/person in 1995 [2]. Swedes generated more than 500 kg MSW per capita in 2008, corresponding to an increase of more than 100 kg/capita from the 1995 value [2, 3]. The composition of this waste varies widely between countries, and between different regions of individual countries. This reflects the adoption of diverse waste management policies within different regions, including landfilling, recycling, compost production and energy recovery [4]. Across the EU27 countries, 37 % of all MSW is landfilled, 23 % is incinerated, 25 % is recycled, and 15 % is composted [1]. Incineration is an increasingly popular option for treating household waste due to the need to reduce the volume/mass of waste to handle and the desire to recover energy, especially in the Nordic countries. Denmark and Sweden make the most extensive use of incineration in the EU, burning 54 % and 51 % of their total MSW output, respectively [1]. The uptake of incineration in these countries has increased over the last few years: in 2006, Sweden incinerated only 46 % of its total MSW production [5].

The formation and emission of contaminants such as heavy metals, greenhouse gases, and Persistent Organic Pollutants (POPs) such as polychlorinated dibenzo-p-dioxins (PCDDs), furans (PCDFs), biphenyls (PCBs), and naphthalenes (PCNs) into the environment is perhaps the biggest problem associated with municipal solid waste incineration (MSWI). PCDDs, PCDFs, PCBs and PCNs are unwanted by-products that are formed during the combustion of the waste and by subsequent thermal processes, and have been listed in the Stockholm Convention [6] due to their toxicity, bioaccumulation, and persistence. The latter trait means they are readily transported over long distances and so can cause worldwide problems. Over the last few decades, a number of attempts have been made to develop efficient air purification techniques in order to trap these pollutants and others. Air pollution control devices (APCD) featuring particle separators (e.g. electrostatic precipitators or cyclones), gas removal systems (e.g. wet scrubbers), and activated carbon adsorption are widely utilized in the end-of-pipe equipment that is fitted to most modern incinerators. However, these devices do not prevent the formation of
contaminants, which remain associated with the ashes or the adsorbents and must subsequently be landfilled or treated to make them less harmful. The most common form of treatment is thermal treatment, which is both costly and time consuming. Therefore, instead of relying on expensive end-of-pipe cleaning systems, it would be preferable to eliminate or minimize the formation of these chlorinated pollutants in the first place. To achieve this, it will be necessary to have a detailed understanding of their mechanisms of formation, which will facilitate the development of efficient and inexpensive treatment techniques.

The fly ash generated during MSWI can cause significant adverse health effects due to its high content of PCDD/Fs, heavy metals, alkali chlorides, and soluble salts [7, 8]. In addition, fly ash particle surfaces provide numerous reactive sites that can facilitate PCDD/Fs formation during MSWI at temperatures as low as 250-450 °C in the post-combustion zone [9-14]. Fly ash particles from MSWI plants contain a variety of chemical species that may promote/enhance the thermal formation of polychlorinated aromatics, i.e. PCDDs, PCDFs, PCBs, and PCNs. Although fly ash chemistry has been studied extensively in a variety of contexts, little is known about the fly ash formed in MSWI plants and the relationship between its properties and the thermal formation of polychlorinated aromatics at temperatures of 250-450 °C.

2. Aim of the thesis

The main objective of the work presented in this thesis was to investigate the thermal formation of polychlorinated aromatics during MSWI, with particular emphasis on PCDDs, PCDFs, PCBs, and PCNs. An improved understanding of these processes will enable the development of new strategies and methods for preventing or minimizing the in situ formation of such compounds. Fly ash particles play an important role in the formation of these pollutants by providing sources of essential elements (carbon, chlorine, etc.) and active catalytic sites. The catalytic capacity of fly ash depends on the concentration of metals within the ash, the identity of the metal-containing species present, its mineralogical properties, and the relative abundance of accessible elements at the particles’ surfaces. The relationships between fly ash chemistry and the thermal formation of
polychlorinated aromatics were therefore also studied. The results obtained in these investigations were presented in the following papers, which provided new insights into the thermal formation of PCDDs, PCDFs, PCBs, and PCNs during incineration and the relationship between these processes and fly ash chemistry:

**Paper I** – This paper describes an investigation into the accuracy of PCDD/F sampling in hot flue gases using two cooled sampling probes: the original sampling probe described in EN 1948/1 and a modified probe containing a salt/ice mixture to facilitate cooling, were evaluated. It was found that the modified probe can be used to perform flue gas sampling at high temperatures (up to 700 °C) without biasing the measured PCDD and PCDF concentrations.

**Paper II** – This paper describes studies on the effects of regional differences in waste composition on the thermal formation of PCDDs, PCDFs, PCBs, and PCNs using two synthetic wastes: “waste A”, designed to simulate typical household MSW produced in Sweden; and “waste B”, which was designed to resemble the average European MSW.

**Paper III** – This paper describes investigations into the chemistry of fly ash and its effects on the thermal formation of PCDDs, PCDFs, PCBs, and PCNs. Physicochemical properties including morphology, speciation and oxidation state, and the mineralogical and elemental composition of the particles’ surface and subsurface were studied using diverse spectroscopic techniques.

**Paper IV** – This paper describes an attempt to provide new insights into the link between fly ash chemistry and the thermal formation of PCDDs, PCDFs, PCBs and PCNs by using multivariate data analysis. Details on the isomer distributions for individual congeners of these pollutants are also discussed.

### 3. Background

#### 3.1 Incineration

Incineration is a complex process that involves the exothermic oxidation of the combustible fractions contained in waste materials. Typical products of incineration are ash, flue gas, and heat, which may be used to generate steam for district heating or electricity generation. The quantity and composition of the incineration products depends on the properties of the waste material. During incineration, many processes such as gasification, pyrolysis, and combustion occur either simultaneously or continuously. It can therefore be challenging to ensure
that the incinerator operates in a way that provides acceptable burning efficiencies at all times. The composition of the flue gas reflects the burning efficiency of the incineration process. Poor or incomplete incineration occurs when the oxygen supply to the incinerator is inadequate, and is usually indicated by rising levels of carbon monoxide (CO) in the flue gas.

To achieve efficient burning, incineration processes should follow the “three T” rules: (i) the Temperature should be high enough to ensure that all incineration reactions go to completion; (ii) the Time (residence time) should be sufficient to allow the reactions to occur; (iii) the Turbulence of the air and combustible gases should be sufficient to enable adequate mixing of oxygen with the combustibles such that oxidation can take place. Ideally, all incineration systems would achieve the complete combustion of their fuels. However, this goal is often impossible or impractical to achieve. Therefore, trace quantities of incomplete combustion products will almost always be present in the flue gas, particularly when burning MSW.

3.2 Dioxins and related compounds

The general term “dioxins” is used interchangeably to refer to polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs), which are usually detected together as complex mixtures in environmental samples. These compounds constructed of two benzene rings that are interconnected by either two oxygen bridges (PCDDs) or one oxygen bridge and a single C-C bond (PCDFs), resulting in planar molecular structures (Figure 1). Chlorine substitution can occur at carbon atoms numbered 1 – 9 in the structures shown in Figure 1, resulting in a total of 75 and 135 individual PCDD and PCDF congeners, respectively (Table 1). Polychlorinated naphthalenes (PCNs) are an emerging group of persistent organic pollutants with significant toxicities [15]. PCNs consist of two fused benzene rings that share two carbon atoms (Figure 1). Any and all of the hydrogen atoms of naphthalene can potentially be replaced with chlorine atoms, giving a total of 75 different PCN congeners (Table 1). Polychlorinated biphenyls (PCBs) are another group of chlorinated aromatic compounds that are formed by the coupling of two phenyl radicals. There are 10 positions at which chlorine substitution could occur on the biphenyl skeleton, resulting in more than 200 potential chlorinated congeners (Figure 1, Table 1). At room temperature and atmospheric pressure,
these compounds exist as crystalline solids with low vapor pressures and low water solubility [16].

PCNs and PCBs were once produced commercially for use in various industrial applications due to their chemical and thermal stability. Notably, they were offered as heat transfer fluids for heat exchangers and dielectrics (insulating fluids) in electrical equipment [17-19]. Under trade names such as Aroclor, Clophen, and Kanechlor, more than 1.5 tons of PCBs are estimated to have been produced in the late 1920s [20]. Around one third of this supply is believed to have been used over the years and released into the environment [21, 22]. While these compounds have not been produced commercially for a very long time, they are still present in the environment. Unlike PCNs and PCBs, PCDDs and PCDFs have not been intentionally produced for any known purpose with the exception of very limited laboratory scale synthesis for use in research.

![Structures and chlorine substitution positions of PCDDs, PCDFs, PCNs, and PCBs.](image-url)

Figure 1. Structures and chlorine substitution positions of PCDDs, PCDFs, PCNs, and PCBs.
Table 1. Homologues and congeners of PCDDs, PCDFs, PCBs, and PCNs

<table>
<thead>
<tr>
<th>Cl Substituents</th>
<th>Prefix</th>
<th>PCDD</th>
<th>PCDF</th>
<th>PCN</th>
<th>PCB</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Mono</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>2</td>
<td>Di</td>
<td>10</td>
<td>16</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>Tri</td>
<td>14</td>
<td>28</td>
<td>14</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>Tetra</td>
<td>22</td>
<td>38</td>
<td>22</td>
<td>42</td>
</tr>
<tr>
<td>5</td>
<td>Penta</td>
<td>14</td>
<td>28</td>
<td>14</td>
<td>46</td>
</tr>
<tr>
<td>6</td>
<td>Hexa</td>
<td>10</td>
<td>16</td>
<td>10</td>
<td>42</td>
</tr>
<tr>
<td>7</td>
<td>Hepta</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>24</td>
</tr>
<tr>
<td>8</td>
<td>Octa</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>Nona</td>
<td></td>
<td></td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>Deca</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

Total 75 135 75 209

3.3 Sources and toxicity

Dioxins and related compounds were rapidly identified as the causative agents of a number of environmental and human health problems [23-25]. They have been studied extensively due to their toxicity, bioaccumulation, high stability, and persistence in nature. They enter the environment in a variety of ways involving both natural phenomena and anthropogenic activities. Numerous studies have concluded that incineration/combustion is currently the main source of dioxin emissions and those of related compounds. In the European Dioxin Air Emission Inventory Project, Quaß et al. reported that iron ore sintering is the second important emission source after municipal waste incineration[26], followed by various other combustion processes (e.g. cement kilns, wood burning...), industrial processes (paper and pulp milling, chemical production) and reservoirs (a category that includes accidental releases and miscellaneous sources)[27].

In the environment, dioxins and related species tend to penetrate fatty tissues and accumulate in food chains, ultimately ending up in humans. These compounds are known to be highly toxic to animals and humans. Various studies have been conducted on laboratory animals at very low exposure levels, revealing a wide range of detrimental effects on health including teratogenicity (i.e. the growth of malformed fetuses), liver damage, decreased rates of reproduction and growth,
cancer promotion, and behavioral changes [28, 29]. Inside the cells of living organisms, dioxins bind very efficiently to a particular receptor protein in the cytoplasm known as the aryl hydrocarbon (Ah) receptor, due to their planar structures. This causes the activated receptor to enter the cell nucleus, triggering the transcription of various genes including a sequence. In addition, dioxins can bind to and damage DNA [22]. The most toxic known dioxin congener is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2378-TCDD) [30]. PCBs and PCNs have been classified as new environmental contaminants and are regarded as dioxin-like compounds because of their similar structures, physicochemical properties, and probably similar toxicity [15, 31, 22, 32].

In environmental samples, dioxins and related compounds are usually found as mixtures of many congeners with varying concentrations. The concept of Toxic Equivalency Factors (TEFs) was introduced to facilitate toxicity comparisons between different samples/mixtures. Standardized TEFs were first introduced in 1998 and then re-evaluated in 2005. The basic idea is that the toxicity of each dioxin congener is determined in the laboratory and then quantified in relation to that of 2,3,7,8-TCDD (Table 2) [33, 34]. Thus, 2,3,7,8-TCDD is assigned a TEF value of 1, and less toxic congeners are given TEF values of between 0 and 1. The closer a compound’s TEF is to 1, the more toxic it is. Analogous I-TEF values for PCBs were introduced in the early 1990s. The toxic equivalency (TEQ value) for a given compound in a particular sample is determined as the product of its concentration in the sample and its I-TEF value (TEQ = I-TEF x C sample). PCB congeners are generally less potent than PCDDs but they are often much more abundant [35, 36], so their relative contribution to the overall TEQ value of a given sample can be considerable [37]. PCN congeners are also planar aromatic compounds that resemble 2,3,7,8-TCDD and can bind to the aryl hydrocarbon receptor [18]. Although I-TEF values have not yet been determined for most PCNs, some PCN congeners have been suggested to be active enzyme inducers, as have some planar PCBs [38, 15, 32]. Regulations on dioxin emissions from MSWI facilities are generally based on TEQ values, with many countries adopting a maximum tolerable level of 0.1 ng TEQ/m³ [39, 40].
Table 2. Toxic equivalence factors for various PCDDs, PCDFs, and PCBs [34]

<table>
<thead>
<tr>
<th>Compounds</th>
<th>WHO-TEF</th>
<th>Compounds</th>
<th>WHO-TEF</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,3,7,8-TCDD</td>
<td>1.0</td>
<td>3,4,4’,5-TeCB</td>
<td>0.0003</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>1.0</td>
<td>3,3’,4,4’-TeCB</td>
<td>0.0001</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>0.1</td>
<td>3,3’,4,4’5-PeCB</td>
<td>0.1</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.1</td>
<td>3,3’,4,4’,5,5’-HxCB</td>
<td>0.03</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.1</td>
<td>2,3,3’,4,4’-PeCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>0.01</td>
<td>2,3,4,4’,5’-PeCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.0003</td>
<td>2,3’,4,4’5-PeCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>2,3,7,8-TCDF</td>
<td>0.1</td>
<td>2’,3,4,4’,5-PeCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>2,3,4,7,8-PeCDF</td>
<td>0.3</td>
<td>2,3,3’,4,4’,5-HxCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDF</td>
<td>0.03</td>
<td>2,3,3’,4,4’,5’-HxCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.1</td>
<td>2,3’,4,4’,5,5’-HxCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.1</td>
<td>2,3’,4,4’,5,5’-HpCB</td>
<td>0.00003</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HxCDF</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDD</td>
<td>0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OCDF</td>
<td>0.0003</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.4 Thermal formation of dioxins and related compounds

The presence of dioxins and related compounds in MWSI effluents was first reported in the late 1970s [41-43]. These chemicals might be present in the combusted materials and survive the incineration processes; alternatively, they can be formed during combustion. The emissions of chlorinated aromatics are determined by their rates of degradation and formation [44]. However, these compounds are rapidly destroyed at the temperatures found in the combustion zones of typical incinerators (800 – 1200 °C) [45, 46]. Their levels increase gradually within the post-combustion zone, indicating that their formation occurs primarily in this area [47]. Incineration has been studied extensively in both laboratory scale systems and full-scale facilities in order to better understand the processes responsible for the thermal formation of dioxins and related species. However, the mechanisms involved have not yet been fully elucidated due to their great complexity [48].
These compounds are believed to form via two primary mechanisms: (i) \textit{de novo} synthesis from carbonaceous particulates, chlorine and aromatic hydrocarbons \cite{49-51}; and (ii) synthesis from chlorinated precursors with related structures, such as chlorophenols and chlorobenzenes \cite{52-55}. Although PCDD/Fs can form directly in the gas phase (homogeneous formation) at high temperatures (500 – 800 °C) \cite{56}, these processes typically have low yields and therefore cannot account for the levels seen at MSWI sites or in laboratory experiments \cite{10, 57}. The bulk of the PCDD/F formation during MSWI is believed to occur at the gas/solid interface on particle surfaces at temperatures of 250-450 °C in the post-combustion zone\cite{10, 12-14}.

A number of experimental studies have focused on resolving the mechanisms of \textit{de novo} PCDD/F formation by heating real or synthetic fly ashes at temperatures of 250 – 450 °C in the presence of metal catalysts \cite{13, 58}. Huang and Buekens suggested that there are two key steps in PCDD/F formation: (i) the catalytic addition of elements (e.g. chlorine, oxygen) to the carbon on fly ash particle surfaces, and (ii) the subsequent release of chlorinated precursors, which go on to form PCDD/Fs \cite{49}. The formation of chlorinated aromatic PCDD/F precursors via surface-mediated pathways has been studied using a number of chlorinated phenols and benzene compounds \cite{59-61}. Dioxin formation may occur via tautomerization reactions between two surface-bound chlorophenols or one surface-bound and one gaseous compound. Heterogeneous precursor pathways of PCDDs formation from pentachlorophenol were 72 – 99000 times higher efficient than PCDDs are formed by activated charcoal, air, inorganic chloride, or Cu(II) catalysts\cite{62}. Fly ash particles play an important role in both the homogeneous and heterogeneous pathways as sources of active sites. The chlorination of non- or lightly-chlorinated aromatics can also take place on the particle surfaces via two possible pathways. The first involves surface-bound metal salts such as copper (II) chloride and oxide\cite{63, 64}, and the well-known Deacon reaction\cite{65}:

$$4\text{HCl} + \text{O}_2 \leftrightarrow 2\text{Cl}_2 + \text{H}_2\text{O} \quad (1)$$

The alternative pathway involves direct chlorination whereby a Cl atom from a metal chloride is directly transferred to an aromatic molecule adsorbed on the fly ash surface\cite{66}.

The literature contains little information on the thermal formation of PCBs and PCNs during waste incineration, and the mechanisms involved have not been
studied as extensively as the related processes that form PCDD/Fs. PCBs and PCNs are regarded as dioxin-like compounds because of their similar structure, physicochemical properties, and probably similar toxicity [15, 32]. As with PCDD/Fs, it is believed that PCBs and PCNs are formed via two different routes: de novo synthesis from carbonaceous particulates and aromatic hydrocarbons [67]; and a precursor pathway involving smaller chlorinated compounds with related structures (e.g. chlorophenols and chlorobenzenes) [68-70]. In addition, it has been proposed that the formation of PCBs and PCNs correlates with that of PCDFs [71, 67]. The further chlorination of lightly-chlorinated compounds is believed to be important in PCN formation[31].

The basic elements that provide the building blocks for dioxins and related compounds (carbon, oxygen, hydrogen, and chlorine) are ubiquitous in combusted materials. Other key factors that can affect their formation include the presence of catalysts and sulfur, as well as the combustion conditions. These factors are discussed more extensively in the following sections:

3.4.1 Chlorine

The main chlorine-containing materials in municipal solid waste are usually the plastic PVC and inorganic chloride salts. During incineration, the degradation of these species leads to the release of chlorine in the form of hydrogen chloride [72]. Before it can contribute to the formation of dioxins and furans, the chlorine in hydrogen chloride must be converted into the more reactive chlorine gas via the Deacon reaction (R1), which is reversible but exothermic ($\Delta H^o = -28,4$ kJ/mol HCl) [73, 74].

Polyvinyl chloride (PVC), HCl, Cl$_2$, inorganic metal chlorides, the Cl radical and ash-bound chlorine have all been identified as important sources of chlorine in emitted dioxins, and the PVC content of incinerated plastic has been shown to be directly proportional to the amount of chlorine in the flue gases of MSW incinerators [75-77]. However, in a simulated combustion setup, ash-bound chlorine was found to be the most important chlorine source in dioxin formation rather than gaseous chlorine [78]. The addition of HCl to the flue gas did not significantly increase dioxin yields or the abundance of more highly chlorinated dioxins due to the limited chlorinating ability of HCl, even though it is the most abundant chlorine-containing species in the flue gas. In contrast, the addition of gaseous chlorine into the incineration system strongly promoted dioxin formation
and especially that of the more highly chlorinated congeners, as indicated by a pronounced increase in the observed degree of chlorination. Moreover, dioxin formation was found to increase linearly with the amount of added Cl₂ [79]. Ryan et al. [80] concluded that the addition of copper (II) chloride increases dioxin formation by 5 times as much as the addition of an equimolar quantity of iron (II) chloride, although it should be noted that the concentration of iron in municipal waste is typically 10-100 times higher than that of copper. Both organic and inorganic chlorine sources can contribute chlorine for dioxin formation, and no significant difference was observed between the effect of adding additional organic chlorine (PVC) on dioxin formation and that of adding an inorganic chlorine source (e.g. NaCl, HCl, CaCl₂·6H₂O etc.) [81-84]. The combustion of artificial wastes containing PVC in the absence of HCl produced very similar dioxin emissions to those generated using wastes containing a mixture of organic and inorganic chlorine and PVC-free waste in the presence of HCl, provided that the total chlorine content of the waste was below 1%. The rate of dioxin formation was found to increase when the chlorine content of the waste exceeded this threshold [84].

3.4.2 Catalysts

Fly ash/soot particles are important in the formation of dioxins and related compounds both as carbon sources and as catalysts that promote key reactions. The presence of metallic species on the surface of particles is crucial for the occurrence of the metal-mediated reactions that are essential for dioxin formation. Insignificant levels of dioxins were detected during combustion experiments in which no catalysts were present [85, 86].

The Deacon reaction is believed to be catalyzed by CuO [14]. Other metals such as iron and aluminum have also been reported to catalyze the formation of chlorinated aromatic pollutants. However, copper is the most potent known catalyst of this process, being approximately 25 times more effective than iron [58]. Even very small quantities of copper (0.007% by mass) in waste materials to be incinerated can significantly catalyze PCDD/F formation [87]. Copper is also known as a catalyst for the Ullmann coupling reaction which may contribute to PCDD/F formation [88]. The identity of the copper species present in the fly ash is known to affect the thermal formation of chlorinated aromatics. The content of copper chloride hydroxide (CuCl₂·Cu(OH)₃) and cuprous chloride (CuCl) in fly ash has been shown to correlate with dioxin formation; notably, there is a linear
correlation between the content of the chloride hydroxide and dioxin emissions [89]. While copper chloride (CuCl₂) is known to be the most efficient catalyst of dioxin formation and chlorination [90], it has not been detected in real fly ash samples.

3.4.3 Moisture

In general, the presence of water vapor in the combustion system should change the position of equilibrium for the Deacon reaction (R1) and reduce the levels of gas phase chlorine. However, experimental results showed that the presence of water vapor in the flue gas increased the overall yields of PCDDs [91]. This finding was consistent with the results of Ross et al., who studied the effects of having water present in the flue gas [92]. High moisture levels (15 %) were found to enhance the catalytic effects of fly ash and were therefore predicted to increase dioxin yields.

Other studies have indicated that the presence of moisture reduces dioxin formation and shifts the dioxin distribution to favor less chlorinated congeners [93]. Notably, water-induced shifts in the PCDF homologue profile of flue gas samples in favor of less chlorinated species has been observed [94]. However, a more recent study found that the presence of water had negligible effects on the formation of such compounds [95]. Overall, the precise effects of moisture on dioxin formation remain unclear.

3.4.4 Incineration conditions

The carbon monoxide (CO) concentration in the flue gas is routinely used as an indicator of the combustion conditions in the incinerator: low CO levels imply good combustion while high CO levels indicate poor combustion. There is a clear correlation between the abundance of PCDD/Fs and the CO content of the flue gas, indicating that combustion quality has a profound effect on the formation of polychlorinated aromatics [96]. The concept of combustion efficiency (CE) was introduced to facilitate quantitative analyses of combustion conditions (Eq1 and Eq2). It is affected by the use of fuel additives, fuel processing techniques, the oxygen level in the incinerator, the combustion temperature and the residence time [97]. High incineration efficiencies are required to ensure the degradation of dioxins during combustion or to avoid their formation in the first place.
The combustion temperature and residence time are key parameters in the formation of dioxins. The combustion temperature depends on a range of factors including the fuel's heating value, the way it is processed, and which additives (if any) are used. The residence time depends on the supply of air to the incinerator and the vacuum pressure. The temperature profile within the post-combustion zone of the incinerator is commonly measured when monitoring dioxin emissions. Dioxin concentrations fall rapidly as the temperature of the secondary combustion zone increases, whereas high temperatures in the primary combustion zone tend to increase dioxin concentrations [75]. It has also been demonstrated that changing the composition of the air in the secondary combustion zone can significantly reduce the temperature and promote dioxin formation [95].

Transient combustion involves combustion under non-steady-state conditions. This is known to increase the likelihood of incomplete combustion leading to enhanced dioxin and furan formation [98, 99]. In addition to increasing dioxin levels, transient combustion also changes the dioxin homologue profiles and isomer distribution patterns. The increased PCDD/F emissions caused by transient combustion can persist for some time after normal combustion conditions have been re-established [100, 101] due to so-called “memory effects”. Weber et al. identified two types of memory effects: “adsorptive memory effects” that are due to pollutants that form under transient conditions but subsequently adsorb onto surfaces within the post-combustion zone and are gradually released over the time; and de novo memory effects” caused by the deposition of carbon-containing particles following their de novo synthesis [96]. The elevated PCDD/F levels caused by memory effects can bias dioxin measurements and must be accounted for when establishing strategies for controlling dioxin emissions.

3.4.5 Sulfur

Sulfur is an important inhibitor of dioxin formation. The addition of SO₂ suppresses the formation of dioxins and furans in both simulated municipal waste combustion and the co-combustion of municipal waste with coal [102]. The addition of elemental sulfur to either fly ash or waste being incinerated significantly reduces dioxin emissions during incineration processes [103]. This inhibition is believed to
arise from the homogeneous reaction of SO$_2$ with chlorine in the gas phase, which converts it into species that do not favor dioxin formation (SO$_3$ and HCl, R$_3$) [65]. In addition, Gullett et al. proposed that sulfur poisons CuO by converting it into CuSO$_4$, a less effective catalyst of the Deacon reaction (R$_3$, R$_4$ and R$_5$) [104]:

$$\text{SO}_2 + \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{SO}_3 + 2\text{HCl} \quad (\text{R}_2)$$

$$\text{CuO} + \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CuSO}_4 \quad (\text{R}_3)$$

It was found that while CuSO$_4$ is a capable catalyst for the Deacon reaction, its optimum temperature is 500 °C compared to 400 °C for CuO [104]. However, the chlorine-depleting effect of sulfur (R$_2$) is believed to be primarily responsible for the reduced PCDD/F yields because the conversion of HCl to Cl$_2$ mediated by a CuO catalyst was not affected by the addition of SO$_2$ to the gas flow, either before or after it had passed through the catalyst bed [105]. The replacement of CuO with CuSO$_4$ had a negative effect on the catalysis of biaryl-forming reactions using chlorophenols as substrates [104]. In addition, metal chlorides on the surface of the fly ash particles were converted to the corresponding sulfates, thereby reducing the number of surface active sites at which chlorination/oxidation can occur [106].

$$2\text{CuO} + \text{Cl}_2 \leftrightarrow 2\text{CuOCl} \quad (\text{R}_4)$$

$$2\text{CuOCl} + \frac{1}{2}\text{O}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightarrow 2\text{CuSO}_4 + 2\text{HCl} \quad (\text{R}_5)$$

Two other mechanisms have been proposed to explain the negative effects of SO$_2$ on dioxin formation: the sulfonation of phenolic precursors (which would prevent their chlorination and impede biaryl-forming reactions) and the formation of sulfur analogs of dioxins (thiophenes) [88]. Other sulfur compounds have also been identified as effective inhibitors of dioxin formation, including ammonium sulfate and ammonium thiosulfate [107].

### 3.5 Destruction and removal techniques

There are two main pathways by which dioxins are degraded during incineration processes: destruction/decomposition to form smaller molecules, and dechlorination/hydrogenation to form less chlorinated congeners. Reactions of both types generally require the presence of a catalyst. Copper and other metallic
compounds in ash are important in both the catalysis of dioxin formation and in promoting their subsequent degradation [108]. Collina et al. studied the dechlorination and destruction of PCDD/Fs by spiking of OCDD and OCDF onto pre-treated fly ash samples at temperatures of 200 °C - 350 °C with reaction times of 15 to 240 min in dry and moist air flows [109]. Their results showed that decomposition and dechlorination occurred independently and that the rates of the two processes depended on the properties of the different polychlorinated aromatics. Thus, while the physical adsorption of OCDF onto the fly ash particles resulted in decomposition, the chemical adsorption of OCDF resulted in its dechlorination [109]. The most important parameters in determining the rate of degradation were the reaction time and temperature, but at relatively low temperatures, the temperature had a greater influence than the reaction time. Longer reaction times and higher temperatures both increased the degradation efficiency [8, 110].

POP degradation could potentially cause the formation of new POPs, so it is essential to carefully consider the impact of new POPs on human health and the environment [111, 90]. Due to their high toxicity, it is essential to remove dioxin from incinerator wastes or otherwise minimize their emissions. Most current efforts towards this objective are focused on improving the efficiency of combustion to minimize the formation of pollutants, introducing additives to inhibit POP formation, and the development of end-of-pipe equipment to remove pollutants before they are released into the environment. The catalytic destruction of POPs in situ represents an alternative approach to minimizing the emissions of these compounds from incinerators. Catalysts based on noble metals such as platinum and palladium are effective at promoting the decomposition of dioxins and furans but they are very costly, so it would be desirable to develop more inexpensive alternatives [112, 113].

3.6 Multivariate data analysis

When attempting to obtain an overview of the correlations between multiple variables, the easiest approach is to focus on one variable at a time; analyzing all of the variables simultaneously can be very challenging. However, the latter approach is essential in order to identify interactions between variables. The studies presented herein used two chemometric tools for multivariate data analysis to uncover the relationships between the variables of interest: Principal component
analysis (PCA) and Orthogonal Projections to Latent Structures (OPLS). PCA is a core technique in multivariate data analysis [114]. It is used to identify patterns in data sets and highlight their similarities and dissimilarities. When considering multi-variable datasets, each variable can be regarded as a single dimension in a vector space. While this vector space can be visualized easily enough as long as there are no more than three dimensions, the visualization and identification of patterns in high dimensional vector spaces is extremely challenging. PCA addresses this issue by identifying a small number of principal components that explain the maximum possible amount of variation in the original dataset and effectively reduce its dimensionality without much loss of information. The data can then be projected onto this lower dimensional space, facilitating its interpretation.

OPLS was firstly proposed by Trygg and Wold in 2002 as an improvement of ordinary PLS. It aims to identify correlations between two blocks of variables, X and Y [115]. The OPLS model separates the systematic variation in the X matrix into two parts: the $Y_{\text{predictive}}$ part, which is linearly related to the Y matrix; and the $Y_{\text{orthogonal}}$ part, which is unrelated to the Y matrix. The greatest advantage of this technique is that it enables the analysis of the variation in X that is not related to variation in Y. In addition, the correlation between the systematic variations in X and specific responses in Y can be investigated.

4. Materials and Methods

4.1 Combustion experiments

A 5 kW laboratory-scale fluidized-bed reactor that has been described in detail elsewhere [98, 116] was used for all experiments (Figure 2). The reactor was designed to simulate the behavior of a full scale MSWI plant and consists of a primary combustion zone, a secondary combustion zone, a post-combustion zone, and an air-cleaning device that incorporates a cyclone, filter box, wet scrubber, and activated carbon filter. The reactor is equipped with electrical heaters (H1 – H7) that allow the operator to efficiently control its internal temperature. The temperatures within the reactor are continuously monitored using type-K thermocouples (T1 – T12). This setup makes it possible to study the thermal formation of dioxins and related compounds in both the combustion and post-combustion zones. In addition, the design gives the user precise control over the combustion conditions, making it possible to conduct studies that would be
impossible in a full-scale facility while minimizing memory effects and being much cheaper to operate than a full-scale incinerator.

The waste is introduced to the incinerator via a fuel feeder that is regulated by a stepped motor. The whole system is controlled semi-automatically by a computer using the Labview 7.1 software package (National Instruments Corporation, Austin, TX).

![Figure 2. Schematic of the 5 kW laboratory scale fluidized bed incinerator used in the studies reported in papers I – IV.](image)

Each combustion experiment was preceded by 2 hours of propane combustion that was immediately followed by four hours of waste combustion to allow the system to reach equilibrium. Sampling was only initiated once stable waste combustion had been established [10]. Levels of the combustion gases (CO₂, H₂O, CO, HCl, SO₂, NH₃, NO₂, NO, N₂O and CH₄,) were determined by FT-IR (ABB Bomem 9100 Gas Analyzer) every 30 seconds, and the oxygen levels in the flue gas were measured every second using a zirconium dioxide cell (ScanTronic OC 2010). Before each experimental run, the FT-IR instrument was zero-calibrated using nitrogen gas. The average fuel-feeding rate during the experiments was 0.57 ± 0.02 kg/h. The wastes were combusted in the primary chamber at 800 °C, and the resulting flue gases were re-combusted in the secondary chamber at 850 °C. The primary and secondary airflows were set at 80 and 30 L/min, respectively. To minimize memory effects, the post-combustion zone of the reactor was thoroughly cleaned between experiments by applying negative pressures and fluxes of pressurized air. The freeboard was swept and the bed sand material was replaced prior to each experiment.
4.2 Artificial wastes

Combustion experiments were performed using two artificial waste mixtures. The first (“Waste A”) was designed to be representative of typical Swedish MSW [98], while the second (“Waste B”) had a material content and elemental composition that was very similar to average European household waste (Table 3). The composition of Waste B was based on the results presented in a report produced by the European Environmental Agency [117]. The Fe and Al contents of Waste B were higher than those for waste A, presumably because materials containing these metals are used more widely in Europe as a whole than they are in Sweden [118]. The ingredients of each waste were mixed mechanically and ground into pellets with a mean diameter of 6 mm and lengths of approximately 10 mm. The pellets were dried at room temperature and sampled for elemental analysis and characterization. Full details on the composition of each waste are presented in Table 7. All waste composition analyses were performed by ALS Scandinavia (Luleå, Sweden) and Belab (Norrköping, Sweden).
Table 3. Compositions of the wastes used in this work.

<table>
<thead>
<tr>
<th>Material</th>
<th>Waste A (%)</th>
<th>Waste B (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper</td>
<td>36</td>
<td>31</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>10.5</td>
<td>9.5</td>
</tr>
<tr>
<td>PVC</td>
<td>0.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Peat</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Sawdust</td>
<td>10.5</td>
<td>12.4</td>
</tr>
<tr>
<td>Wheat starch</td>
<td>15.5</td>
<td>15</td>
</tr>
<tr>
<td>Gelatin</td>
<td>7.5</td>
<td>8</td>
</tr>
<tr>
<td>Oil</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Sand</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>Silica gel</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Kaolin</td>
<td>1.7</td>
<td>1.7</td>
</tr>
<tr>
<td>Cu(CH₃COO)₂</td>
<td>0.04</td>
<td>0.04</td>
</tr>
<tr>
<td>Fe</td>
<td>1.2</td>
<td>2.5</td>
</tr>
<tr>
<td>Al</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>CaCl₂.6H₂O</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.5</td>
<td></td>
</tr>
</tbody>
</table>

Only waste A was used in the combustion experiments presented in paper I. The experimental campaign that generated the data used in Papers II-IV ran over six days: first, waste A was burned on three consecutive days. To remove the residues generated by the combustion of waste A, waste B was then burned on a pre-burn day after which the reactor was cleaned and then waste B was burned on two consecutive days.

4.3 Flue gas sampling: low vs high temperature

The flue-gas samples were collected according to the EN 1948:1 standard method [119] (Paper I – IV). The flue-gases were extracted from the duct and drawn
through the sampling train using a vacuum pump. The sampling train consisted of two impinger flasks containing water and ethylene glycol, respectively, and two PUF plugs layered with a glass-fiber aerosol filter. Any PCDD/Fs that desorbed from the first PUF plug and glass filter were captured on the second.

The probe referred to as the ‘original probe’ consisted of two concentric stainless steel pipes that form a jacket surrounding a probe liner made of borosilicate glass with an inner diameter (i.d.) of 8 mm and an outer diameter (o.d.) of 10 mm. The probe liner was fixed in place inside the two pipes using rubber-sealed metal bolts to create a watertight seal (Figure 3a) and the pipes were fitted with connectors to enable cooling water to be passed through the space between them. A quartz nozzle was mounted in the flue-gas duct and connected to one end of the probe liner, while the opposite end of the probe liner was connected to the sampling equipment. When monitoring emissions at industrial sites, flue gas sampling is usually performed at temperatures below the range at which PCDDs and PCDFs are formed (i.e. below 250 – 450 °C). Conversely, for research purposes, flue gas sampling is typically performed at high temperatures (≥ 450 °C), which means that the samples must be rapidly cooled prior to analysis in order to prevent the formation of PCDDs and PCDFs inside the sampling probe. In order to obtain accurate measurements of PCCD and PCDF levels in the flue gas, the sampling probe must therefore be cooled very efficiently.

A modified cooling probe known as the ‘sub-zero probe’ was developed and has been described in detail elsewhere [120]. It was 0.6 m in length and had an external compartment containing a salt/ice (1/4 w/w) mixture that could achieve a temperature of around -15 °C (Figure 3b). To maintain this temperature, the salt/ice mixture was continuously replenished during sampling. The sub-zero
probe used a custom-made titanium one-piece nozzle/probe liner rather than a glass liner of the sort used in the original probe.

For **Paper I**, flue gas samples were collected at two sampling locations (corresponding to flue gas temperatures of 700 °C and 400 °C) in the post-combustion zone using the same probe configurations as were employed during the temperature measurements. Replicate samples were collected on different days to determine the repeatability of the results and the variation of the sampling efficiency and to obtain a measure of the day-to-day variation in PCDD/F levels.

At 700 °C, two different configurations of the original probe were used: horizontal, which reflects the typical setup used for sampling in full-scale MSWI plants; and vertical, which was more suitable for this laboratory-scale setup (Figure 4). In the vertical configuration, the probe liner was connected to the quartz nozzle in the flue-gas duct via a glass elbow, and a second glass elbow was used to attach the liner to the sampling equipment. This configuration allowed the sampling equipment to be placed below the sampling port. It was expected that the horizontal configuration would yield a more laminar flow inside the probe due to the turbulence associated with vortexes caused by elbows.
Figure 4. The two different setups used at 700 °C. A) shows the original vertical probe configuration and B) shows the original horizontal probe configuration. Adapted from [57]

The internal temperature of the cooling probes was measured at 5 cm intervals using a type-K thermocouple. Measurements were collected during a single experimental day and were acquired in triplicate for each measuring point. In all cases, the thermocouple was directed to the center of the gas stream using a metal spider in order to avoid measurement bias arising from proximity to the probe’s
walls. Temperature measurements were performed at two locations in the post-combustion zone. The first location corresponded to a flue gas temperature of 700 °C; measurements at this temperature were conducted using the sub-zero probe in the horizontal configuration and the original probe mounted in both the horizontal and vertical configurations. The second location corresponded to a flue gas temperature of 400 °C using the sub-zero probe and the original probe mounted vertically.

For Papers II – IV, flue-gas samples were collected simultaneously at three fixed locations in the post-combustion zone, corresponding to temperatures of 400, 300 and 200 °C. Flue-gas sampling was performed on five successive combustion days (3 for Waste A and 2 for Waste B) with identical combustion conditions and temperatures on each occasion.

4.4 Fly ash particles sampling

Fly ash samples were collected from the post-combustion zone of the fluidized bed incinerator at a location corresponding to a temperature of 300 °C (Figure 2) once stable combustion had been achieved (Paper III – IV). Fly ash sampling was performed isokinetically for 1 hour. Particles were collected using a glass fiber filter (type A/E 142 mm, fine porosity, fast flow rate, particle retention ≥ 1.0 µm, PALL Corporation, Michigan USA). To prevent water condensation and particle coagulation, the sampling filter temperature was maintained at 250 °C using an external heater throughout the sampling procedure.

4.5 Analysis of dioxins and related compounds

All steps involved in the analysis of dioxins and related compounds in flue gas samples have been described in detail elsewhere [31, 121]. The water and ethylene glycol from the impingers were combined, treated with internal standards, acidified, and filtered using a pre-filter followed by a 0.45 µm membrane filter. The solution was then filtered again to collect organic substances using a solid phase extraction disk (ENVI-18 DSK SPE disk, 47 mm, SUPELCO-Sigma Aldrich). The filters from the filtration steps were then combined and subjected to Soxhlet extraction for 24 h using 200 ml of toluene. The solvent was then removed under reduced pressure and replaced with cyclohexane. For cleanup, each extract was loaded on to a multilayer silica column consisting of a plug of sodium sulfate on top
of layers of acidic, neutral, and basic silica. The columns were eluted with 40 ml n-
hexane and the eluent was immediately loaded onto an alumina column. The
alumina column was eluted with 40 ml n-hexane, which was discarded, and then
with 40 ml of a 1:1 (v/v) dichloromethane/cyclohexane mixture. Tetradecane (40 µl)
was added to the eluent as a keeper and the resulting solution was concentrated
under reduced pressure using a TurboVap instrument (Zymark Corp.). A glass
column containing a mixture (1:11.7 w:w) of AX21 carbon (Anderson Development
company) and Celite 545 (Fluka) was then prepared to fractionate the resulting
material. The concentrated solution was loaded on the carbon:celite column and
eluted with 40 ml dichloromethane:n-hexane (1:1 v/v) to yield a PCB-containing
eluate. The carbon:celite column was then inverted and eluted with 40 ml of
toluene to yield an eluate containing the PCDDs, PCDFs, and PCNs from the flue
gas sample. Tetradecane (40 µl) was then added to each fraction, and the resulting
solutions were cleaned up again using the same series of elutions as reported above
on small multilayer silica columns. Finally, the re-clean-up eluates were evaporated
and recovery standards were added.

The samples were analyzed for PCDDs, PCDFs, and PCBs by GC-HRMS using an
AutoSpec ULTIMA NT 2000D high-resolution mass spectrometer (Waters
Corporation, Milford, MA) equipped with a J&W Scientific DB5-MS column (60 m
x 0.25 mm i.d. and 0.25-µm film thickness). PCN analysis was performed using the
same GC-HRMS system equipped with a J&W Scientific DB5 column (60 m x 0.25
mm i.d. and 0.25-µm film thickness). The mass spectrometer was operated in
electron impact ionization/selected ion monitoring mode and the analytes were
quantified using the isotope dilution technique. Peaks were identified using
internal standards and the retention order published in the literature [122-125]. All
sampling volumes were normalized to 11 % O₂, 1 atm., and 0 °C.

4.6 QA/QC

All laboratory work was performed according to validated methods. The
isotopically labeled species ³⁷Cl₄ 2,3,7,8-TeCDD, ¹³C₁₂ 1,2,3,4,6,7-HxCDD and ¹³C₁₂
2,2’,3,3’,5,5’,6-HpCB (PCB 178) were used as sampling standards and pre-spiked
into the water flask of the sampling train to test the sampling efficiency. All
samples including blanks were spiked with selected ¹³C₁₂-labeled PCDD, PCDF, and
PCB internal standards. Recoveries of the sampling and internal standards were
satisfactory in all cases and well within the recommended ranges (58 – 109 %).
The PUFs were Soxhlet extracted for 24 h in toluene and 24 h in acetone prior to use, and dried under a stream of $N_2$ gas. The analyte concentrations measured for all laboratory blanks were below 10% of those observed in the experimental samples for all analytes other than MoCDD and DiCDD in the Paper I experiments. In these cases, it was necessary to correct the concentrations measured for the samples to reflect the relatively high blank concentrations.

### 4.7 Particle characterization

Elemental analysis of the fly ash was performed by inductively coupled plasma-sector field mass spectrometry (ICP-SFMS) using a modified version of US EPA method 200.8. Solutions were prepared from ash samples that had been fused with 0.4 g LiBO$_2$ and subsequently dissolved in diluted nitric acid.

The crystalline mineral content of the fly ash was characterized by X-ray diffraction (XRD). All XRD measurements were conducted using a Bruker d8 Advance instrument working in $\theta$-$\theta$ mode with an optical configuration consisting of a primary Göebel mirror, a Cu-K$_\alpha$ radiation source (1.5418 Å) and a Vântec-1 detector. The PDF-2 databank [126] was used in conjunction with software supplied by Bruker to make initial qualitative identifications. The data were further analyzed using the Rietveld technique and data from ICSD [127] to obtain semi-quantitative information on the presence of crystalline phases.

FTIR spectra were collected on a Vertex 80/V spectrometer (Bruker) equipped with a DLaTGS detector. Measurements were acquired in vacuo using fly ash powders pressed onto the diamond cell of an attenuated total reflectance (Golden Gate, single bounce) accessory. All spectra were collected in the 600-4500 cm$^{-1}$ range at a resolution of 4.0 cm$^{-1}$ and a forward/reverse scanning rate of 10 Hz. Each spectrum was constructed from an average of 100 scans. The Blackman-Harris 3-term apodization function was used to correct the phase resolution.

The size and morphology of the particles were characterized by scanning electron microscopy (SEM) using a Cambridge 360ixp microscope equipped with a LaB$_6$ electron emitter (Leica Cambridge Ltd, Cambridge, UK). The equipment was operated at 10 kV with a 100 pA probe current, and a 0° tilt angle. Three images with an approximate size of 1000 µm$^2$ each were chosen at random from each sample and re-acquired at magnifications of 1000×, 5000×, and 15000×. In
addition, the chemical composition of the topmost layer (with a thickness of ~ 2 µm thick) of the fly ash particles was determined qualitatively and quantitatively using energy-dispersive X-ray (EDX) analysis. Uncoated samples were used in these analyses in an effort to obtain unbiased chemical composition data. It should be noted that this necessarily entailed some degradation of image quality.

Elemental analyses of the topmost ~ 2 nm layer of the fly ash particle surfaces were performed by X-ray photoelectron spectroscopy (XPS). Spectra were recorded with a Kratos Axis Ultra electron spectrometer using a monochromated AlKα source operating at 150 W. The survey scans were performed using a pass energy of 160 eV with a step size of 1 eV. For separate photoelectron lines, a pass energy of 10 eV was used with a step size of 0.1 eV. To compensate for the charging of the surface, charge-neutralizing equipment was used. The binding energy (BE) scale was referenced to the C 1s peak at 285.0 eV, which originates from adventitious carbon. The presence of specific elements on the particles’ surfaces was confirmed by matching the experimentally determined binding energies to the corresponding values recorded in the NIST XPS database [128].

4.8 Multivariate data analysis

Principal Component Analysis (PCA) and Orthogonal Projections to Latent Structures Discriminant Analysis (OPLS-DA) were used to evaluate the data on the chloroaromatic profiles of the samples and to identify correlations between these results and the combustion data for the flue gas samples (Paper II). In Paper IV, Orthogonal Projections to Latent Structures (OPLS) regression was used to evaluate the correlations between the flue gas results and the particle characterization data. These techniques have been used successfully in several related studies with varied scopes [129-132], and are provide an objective overview of the correlations between various experimental observations. Before the OPLS and OPLS-DA models were constructed, the data were screened using PCA. The main purpose of PCA modeling is to obtain an overview of the patterns in the datasets of interest. In paper II, the X dataset consisted of objects (flue gas samples) and measured variables (homologue abundance data for PCDDs, PCDFs, PCBs, PCNs). In paper IV, the X dataset consisted of objects (fly ash samples) and measured variables (particle characterization data generated by XPS, EDX, and XRD). The number of principal components in each case was calculated using a cross validation approach. Cross validation generates R2 and Q2 values that
indicate the PCA model’s goodness of fit and predictive ability, respectively. In general, high R2 values (close to 1) are indicative of a good model while high Q2 values (> 0.5) reflect good predictivity. The output of the PCA models was visualized using score and loading plots.

The OPLS-DA model uses a binary matrix Y (waste classification) to decompose the X data (homologue profiles and combustion data) into two types of variation: predictive variation and orthogonal components. These reflect between- and within-class variation, respectively.

5. Results and Discussion

5.1 Combustion conditions

Table 4. Composition of emitted gases in the flue gas during the combustion experiments

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Paper I</th>
<th>Paper II - IV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Waste A</td>
<td>Waste A</td>
</tr>
<tr>
<td>H2O (%)</td>
<td>Average</td>
<td>Average</td>
</tr>
<tr>
<td>6</td>
<td>5%</td>
<td>6</td>
</tr>
<tr>
<td>CO2 (%)</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>O2 (%)</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>4</td>
<td>7</td>
</tr>
<tr>
<td>NO (ppm)</td>
<td>310</td>
<td>331</td>
</tr>
<tr>
<td>HCl (ppm)</td>
<td>381</td>
<td>346</td>
</tr>
<tr>
<td>SO2 (ppm)</td>
<td>11</td>
<td>17</td>
</tr>
<tr>
<td>NO2 (ppm)</td>
<td>10</td>
<td>n.d.</td>
</tr>
<tr>
<td>N2O (ppm)</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>NH3 (ppm)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>CH4 (ppm)</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
</tbody>
</table>

|            | Waste B | Average | RSD b |
|------------|---------|---------|
| H2O (%)    | 5       | 1%      |
| CO2 (%)    | 6       | 1%      |
| O2 (%)     | 14      | 1%      |
| CO (ppm)   | 7       | 42%     |
| NO (ppm)   | 2       | 59%     |
| HCl (ppm)  | 2       | 3%      |
| SO2 (ppm)  | 4       | 17%     |
| NO2 (ppm)  | n.d.    | 5%      |
| N2O (ppm)  | n.d.    | 15%     |
| NH3 (ppm)  | n.d.    | 13%     |
| CH4 (ppm)  | n.d.    | n.d.    |

- Calculated from 7 combustion experiments.
- RSD = Relative standard deviation.
- n.d. = not detected, limit of detection 1 ppm.
- Calculated from 2 combustion experiments.

In general, the combustion conditions were very stable in all of the experiments. Low CO levels were achieved consistently (<4 ppm in Paper I; and <7 ppm in Paper II – IV), indicating high combustion efficiencies (Table 1). Based on the average CO (4 x 10⁻⁶ %) and CO2 (7 %) levels in the flue gas, the combustion efficiency was determined to be 99.99 % ([CO2]/([CO2]+[CO])). There was
relatively little variation in the inorganic gas content of the combustion gases between experiments, as indicated by the low (<25 %) relative standard deviations (RSD) for these species (Table 1). The RSD for CO (39 % in Paper I, and 42 – 59 % in Paper II – IV) was comparatively high because it is very sensitive to fuel-feeding irregularities and because the CO concentration was typically close to the detection limit of 1 ppm.

5.2 The temperature profile of the post-combustion zone

The temperature profile of the post-combustion zone, where the bulk of the POP formation occurs, was recorded once the combustion process had stabilized (Figure 5). Fängmark et al. used an earlier version of this combustion reactor to study the influence of the post-combustion zone quenching profile on PCDD/F yields and found that the levels of these species peaked at 340 °C with a flue gas residence time of 2.9 seconds[133]. Different post-combustion zone temperature profiles and residence times yielded different total yields and also affected the homologue and congener distribution[10]. However, in the previous work, quenching profiles were only determined at specific sampling points. In contrast, in this study the quenching profile of the entire post-combustion zone was recorded to clarify the impact of temperature quenching on the measured yields of PCDDs, PCDFs, PCBs, and PCNs. The temperature at the outlet of the secondary combustion zone was 835 °C. In the first part of the post-combustion zone, the flue gas temperature rapidly decreased to approximately 700 °C within the first 0.4 m and then to 450 °C by the end of the first 3.8 m of the post-combustion zone. The temperature immediately in front of the air-cleaning device was approximately 200 °C (Figure 5). There was little variation in the measured temperatures for each measurement point (< ±9 °C), indicating that the temperature distribution within the post-combustion zone was stable. PCDD/F formation is most favored at temperatures of 250 - 450 °C [12-14], which were observed in a zone approximately 7 m long, corresponding to a calculated residence time of around 6 seconds. The concentrations of PCDD/Fs entering the post combustion zone (at 700 °C) were low, with some homologues being below the limits of detection. This confirms that these species are primarily formed in the post-combustion zone, where the temperatures are lower [10, 57]. The longer the flue gas is allowed to remain within the 250 - 450 °C temperature window where PCDD/F formation is favored, the
greater the final concentrations of these pollutants [134]. Rapid quenching of the flue gas can thus be used to terminate the formation of chlorinated organic pollutants [97]. Quenching rates ranging from 400 – 300 °C over the first 2.8 meters of the post-combustion zone and 300 – 200 °C over the following 6.0 meters of the post-combustion zone were observed in this study. These differences might influence the mechanisms by which PCDDs and PCDFs are formed in the post-combustion zone. As mentioned previously, the production of active Cl₂ gas via the Deacon reaction is most favored at around 400 °C and the rate of this process decreases to approximately zero below 300 °C [64]. Ryu et al. (2003) concluded that chlorination processes during post-combustion are highly efficient at temperatures of 300 - 200 °C [135]. It may be that chlorination reactions occur in parallel with chlorine production at temperatures between 400 and 300 °C, while only chlorination occurs at 300 – 200 °C.

Figure 5. Quenching profile for the reactor’s post-combustion zone.

5.3 Validation of high temperature flue gas sampling results (paper I)

The internal measurements generated using the sub-zero probe and the original probe in its two configurations (vertical and horizontal) revealed that flue gas samples collected at an initial temperature of 700 °C were cooled to below 200 °C within the first 5, 20 and 35 cm of the cooling zones, respectively (Figure 6a). The difference in quenching behavior between the vertical and horizontal configurations was probably due to differences in the extent of uncontrolled cooling.
of the flue gases before entering the cooling zone of the probe (Figure 4). Another possibility is that the temperature measurements were influenced by the layering of the flue gas due to laminar flows generated by the relatively low flow rates inside the cooling probes and the straight route in the horizontal configuration. This might also explain why the temperature measurement curve was not as smooth for the horizontal configuration as for the other two setups (Figure 6a). At 400 °C (Figure 6b), the flue gases were cooled to below 200 °C before they even entered the cooling zone of the sub-zero probe. Conversely, with the original probe, this level of cooling was only achieved around 25 cm along the probe’s length.

5.3.1 The importance of rapid quenching of hot flue gas samples (>650 °C)

The total PCDD concentrations measured at 700 °C varied greatly depending on the type of probe used, from < 1 ng/m³ to 510 ng/m³ (Table 5). The lowest PCDD concentrations were found in the samples collected using the sub-zero probe. The greatest variation (12 - 510 ng/m³) in total PCDD concentrations was observed between samples collected using the original probe in its horizontal configuration. Both the highest overall PCDF concentrations and the greatest degree of variation in the measured PCDF concentrations (17-260 ng/m³) were achieved using the original probe in the horizontal configuration, whereas the lowest total PCDF concentrations (4.1-9.7 ng/m³) were measured using the sub-zero probe. Some PCDD/F homologues were undetectable in flue gas samples collected at 640 °C using the sub-zero probe in subsequent experiments using the same reactor and a similar model waste [10](Table 5)
The considerable variation in measured PCDD/F concentrations observed using the different probe configurations probably reflects inadequacies in sample cooling and artifacts originating from the formation of PCDD/Fs inside the probe in some cases. These results clearly show that the original probe is not suitable for flue gas sampling at high temperatures: it is not capable of adequately cooling the sampled gas and so reactions continue inside the sampling equipment rather than being instantly terminated. Artifact formation renders the sample useless because its PCDD/F content will be much greater than that in the flue gas stream. The more rapid cooling achieved using the ice/salt mixture of the sub-zero probe eliminates this problem. The temperature data shown in Figure 6a clearly show how critical the first few centimeters of the cooling zone are in rapidly quenching the flue gases.

Table 5. Concentrations of PCDD/Fs (ng/m³) in flue-gas samples collected at 700 °C using the sub-zero probe and the original probe in its vertical and horizontal configurations

<table>
<thead>
<tr>
<th>Run order</th>
<th>Horizontal</th>
<th>Vertical</th>
<th>Sub-zero</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>6</th>
<th>7</th>
<th>9</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>Ref Aurell et al. 2009[10]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoCDF</td>
<td>35</td>
<td>120</td>
<td>4.3</td>
<td>n/a</td>
<td>n/a</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>DiCDF</td>
<td>13</td>
<td>72</td>
<td>3.1</td>
<td>6.9</td>
<td>21</td>
<td>0.88</td>
<td>2.9</td>
</tr>
<tr>
<td>TriCDF</td>
<td>12</td>
<td>32</td>
<td>1.0-3.4</td>
<td>5.5</td>
<td>16</td>
<td>0.72-2.4</td>
<td>0.36</td>
</tr>
<tr>
<td>TeCDF</td>
<td>12</td>
<td>11</td>
<td>1.1</td>
<td>2.5</td>
<td>8.7</td>
<td>0.38</td>
<td>0.09-0.3</td>
</tr>
<tr>
<td>PeCDF</td>
<td>9.9</td>
<td>8.3</td>
<td>1.3</td>
<td>2.3</td>
<td>7.3</td>
<td>&lt;0.27</td>
<td>0.05-0.20</td>
</tr>
<tr>
<td>HxCDF</td>
<td>6.5</td>
<td>5.4</td>
<td>1.6</td>
<td>2.2</td>
<td>6.2</td>
<td>&lt;0.25</td>
<td>&lt;0.09</td>
</tr>
<tr>
<td>HpCDF</td>
<td>1.7</td>
<td>1.6</td>
<td>1.1</td>
<td>1.4</td>
<td>3.1</td>
<td>&lt;0.18</td>
<td>0.06-0.2</td>
</tr>
<tr>
<td>OCDF</td>
<td>0.43</td>
<td>0.72</td>
<td>0.70</td>
<td>0.73</td>
<td>1.3</td>
<td>&lt;0.07</td>
<td>0.2</td>
</tr>
<tr>
<td><strong>Sum PCDF</strong></td>
<td><strong>90</strong></td>
<td><strong>250</strong></td>
<td><strong>17e</strong></td>
<td><strong>22f</strong></td>
<td><strong>64f</strong></td>
<td><strong>9.7f</strong></td>
<td><strong>5.0f</strong></td>
</tr>
<tr>
<td>MoCDD</td>
<td>1.5</td>
<td>23</td>
<td>0.2b</td>
<td>n/a</td>
<td>n/a</td>
<td>&lt;0.14</td>
<td>0.03</td>
</tr>
<tr>
<td>DiCDD</td>
<td>1.8</td>
<td>24</td>
<td>0.5b</td>
<td>0.40</td>
<td>1.0</td>
<td>&lt;0.27</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>TriCDD</td>
<td>8.2</td>
<td>62</td>
<td>0.67-2.2</td>
<td>0.94</td>
<td>3.5</td>
<td>&lt;0.48</td>
<td>0.02-0.05</td>
</tr>
<tr>
<td>TeCDD</td>
<td>19</td>
<td>72</td>
<td>1.2</td>
<td>0.25</td>
<td>0.54</td>
<td>0.16</td>
<td>0.02-0.08</td>
</tr>
<tr>
<td>PeCDD</td>
<td>54</td>
<td>120</td>
<td>1.8</td>
<td>2.5</td>
<td>6.2</td>
<td>0.14-0.48</td>
<td>&lt;0.04</td>
</tr>
<tr>
<td>HxCDD</td>
<td>100</td>
<td>140</td>
<td>3.7</td>
<td>4.1</td>
<td>6.8</td>
<td>0.14-0.48</td>
<td>&lt;0.1</td>
</tr>
<tr>
<td>HpCDD</td>
<td>52</td>
<td>58</td>
<td>1.8</td>
<td>1.1</td>
<td>3.3</td>
<td>0.15-0.18</td>
<td>n/a</td>
</tr>
<tr>
<td>OCDD</td>
<td>7.5</td>
<td>7.3</td>
<td>0.80</td>
<td>0.85</td>
<td>1.7</td>
<td>&lt;0.07</td>
<td>n/a</td>
</tr>
<tr>
<td><strong>Sum PCDD</strong></td>
<td><strong>240</strong></td>
<td><strong>510</strong></td>
<td><strong>12e</strong></td>
<td><strong>9.3f</strong></td>
<td><strong>23f</strong></td>
<td><strong>2.6f</strong></td>
<td><strong>0.34f</strong></td>
</tr>
</tbody>
</table>
Values below limit of quantification (LOQ) but above limit of detection (LOD). LOD and LOQ values were calculated for each individual sample. Intervals indicate LOD-LOQ.  Measured value was below LOD, so the LOD is shown. Omitted due to analytical error. Sum calculated using LOD or LOQ values, respectively.

A comparison of the measurements obtained using the horizontal and vertical configurations of the original probe at 700 °C (Figure 6a), indicates that the horizontal configuration quenches the flue gases more rapidly than the vertical configuration. On the other hand, the between-run variation in PCDD/F concentrations was higher for the horizontal configuration (Table 5); as discussed above, this may have been due to the poor cooling of the flue gas in this case. An alternative explanation for this observation is that measurements acquired using the horizontal configuration may be highly affected by laminar flow, which could vary significantly between runs. Thus, when using the horizontal configuration, the temperature measurements may not accurately reflect the temperature along the probe, and the large between-run variation in concentrations may be due to variations in cooling capacity that are not apparent from the recorded initial temperatures of the flue gas samples.

5.3.2 No artifact formation occurs at 400 °C

The results obtained for flue gas samples collected at 400 °C using the sub-zero probe were in good agreement with those obtained using the original probe and with lower variation between runs. No In particular, there were significant differences between the PCDDs and PCDFs concentrations measured using the two probes. The measured PCDD and PCDF concentrations ranged from 7.7 - 15 ng/m³ and 220 - 360 ng/m³, respectively (Table 6). As before, the sub-zero probe cooled the flue gas to less than 200 °C much more quickly than the original probe (Figure 6b). At 400 °C, the cooling capacity of the original probe appeared to be sufficient to avoid artifact PCDD/F formation in the sampling equipment and achieve representative sampling.
Table 6. Concentrations of PCDD/Fs (ng/m³) in flue-gas samples at 400 °C measured using the sub-zero probe or the original probe in the vertical configuration.

<table>
<thead>
<tr>
<th>Run order</th>
<th>Sub-zero</th>
<th>Vertical</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>8</td>
<td>10</td>
</tr>
<tr>
<td>MoCDF</td>
<td>93</td>
<td>140</td>
</tr>
<tr>
<td>DiCDF</td>
<td>66</td>
<td>84</td>
</tr>
<tr>
<td>TriCDF</td>
<td>38</td>
<td>46</td>
</tr>
<tr>
<td>TeCDF</td>
<td>11</td>
<td>12</td>
</tr>
<tr>
<td>PeCDF</td>
<td>5.7</td>
<td>6.0</td>
</tr>
<tr>
<td>HxCDF</td>
<td>2.9</td>
<td>3.2</td>
</tr>
<tr>
<td>HpCDF</td>
<td>1.1</td>
<td>1.3</td>
</tr>
<tr>
<td>OCDF</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td><strong>Sum PCDF</strong></td>
<td><strong>220</strong></td>
<td><strong>290</strong></td>
</tr>
<tr>
<td>MoCDD(^a)</td>
<td>1.6</td>
<td>1.6</td>
</tr>
<tr>
<td>DiCDD(^b)</td>
<td>1.7</td>
<td>2.0</td>
</tr>
<tr>
<td>TriCDD</td>
<td>0.71-2.4(^a)</td>
<td>2.4</td>
</tr>
<tr>
<td>TeCDD</td>
<td>0.91</td>
<td>1.0</td>
</tr>
<tr>
<td>PeCDD</td>
<td>0.29-1.0(^a)</td>
<td>0.29-1.0(^a)</td>
</tr>
<tr>
<td>HxCDD</td>
<td>0.44</td>
<td>0.46</td>
</tr>
<tr>
<td>HpCDD</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>OCDD</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td><strong>Sum PCDD</strong></td>
<td><strong>8.5(^c)</strong></td>
<td><strong>8.1(^c)</strong></td>
</tr>
</tbody>
</table>

\(^a\) Values below limit of quantification (LOQ) but above limit of detection (LOD). LOD and LOQ values were calculated for each individual sample. Interval denotes LOD-LOQ. \(^c\) Sum was calculated using LOQ values for homologues whose measured concentrations were below the LOQ.

5.4 **The influence of waste composition (paper II)**

The levels of various elements that affect POP formation were determined, as shown in Table 7. When this work was conducted, no data on the sulfur contents of typical Swedish and European wastes were available. The dry weight (d.w.) 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, while those for Waste B were 8.6 % and 8.4 %, respectively. Carbon accounted for almost 50 % by mass of both wastes, but the inorganic 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 A, 1.2 % by mass in B) and originates primarily from the plastic fraction (PVC) and kitchen residues. The combustion of Wastes A and B produced flue gas HCl concentrations of 346 ppm (± 5%) and 371 ppm (± 3%), respectively. Because it 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 if they can be converted into potent chlorinating agents. Both wastes had calorific values of 20 MJ/kg and thus have energy outputs comparable to those for fuel materials such as biomass and wood. This value seems to be relatively independent of the precise composition of the waste [136].

Previous combustion experiments using a similar artificial MSW yielded homologue profiles and PCDD/F concentrations that were comparable to those typically observed in full scale waste incinerators[137].

Table 7. Elemental compositions of the artificial wastes and the corresponding fly ashes generated during the combustion experiments.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Fuel</th>
<th>Fly ash</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Waste A</td>
<td>Waste B</td>
</tr>
<tr>
<td>Al (% dw)</td>
<td>2.0</td>
<td>8.4</td>
</tr>
<tr>
<td>Fe (% dw)</td>
<td>4.4</td>
<td>8.6</td>
</tr>
<tr>
<td>Ca (% dw)</td>
<td>0.87</td>
<td>0.88</td>
</tr>
<tr>
<td>Na (% dw)</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Mg (% dw)</td>
<td>0.068</td>
<td>0.066</td>
</tr>
<tr>
<td>K (% dw)</td>
<td>0.32</td>
<td>0.19</td>
</tr>
<tr>
<td>Si (% dw)</td>
<td>6.6</td>
<td>7.3</td>
</tr>
<tr>
<td>P (% dw)</td>
<td>0.12</td>
<td>0.12</td>
</tr>
<tr>
<td>Cl (% dw)</td>
<td>0.8</td>
<td>1.2</td>
</tr>
<tr>
<td>O (% dw)</td>
<td>29</td>
<td>26</td>
</tr>
<tr>
<td>C (% dw)</td>
<td>49</td>
<td>47</td>
</tr>
<tr>
<td>Cu (% dw)</td>
<td>0.015</td>
<td>0.015</td>
</tr>
<tr>
<td>S (% dw)</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td>Moisture 105°C (%)</td>
<td>8.6</td>
<td>8.2</td>
</tr>
<tr>
<td>Ash 550°C (% dw)</td>
<td>11.4</td>
<td>16.5</td>
</tr>
</tbody>
</table>
5.4.1 Thermal POP formation in the post-combustion zone

The total PCDD, PCDF, PCB, and PCN concentrations in the flue gas increased as the temperature decreased within the post-combustion zone (Table 8).

**PCDDs:** There were no significant differences between Wastes A and B in terms of the total concentration of PCDDs formed during combustion at each sampling location. At 400 °C, PCDDs were observed at levels of 6.0 – 9.3 ng/m³ for Waste A combustion, while the combustion of Waste B generated levels of 7.0 – 7.5 ng/m³. At 300 °C, the PCDD concentrations for Waste A combustion were 9.2 – 27 ng/m³ while those for B were 20 – 25 ng/m³. At the lowest investigated temperature, 200 °C, the PCDD levels for the combustion of Wastes A and B ranged from 21 – 69 ng/m³ and 33 – 40 ng/m³, respectively. For both wastes, PCDD levels were found to increase as the flue gas flowed through the post-combustion zone. When burning Waste A, PCDD concentrations increased substantially as the flue gas was cooled from 400 ºC to 200 ºC (or equivalently, as its residence time in the post-combustion zone increased) for samples collected on the same combustion day. Aurell et al. used the same laboratory fluidized bed reactor as was used in this work and observed insignificant changes in the PCDD concentrations at three sampling ports located within the post combustion zone[10]. However, the waste used in this work contained twice as much copper as that studied by Aurell et al., which may account for the apparent discrepancy given this metal’s known ability to catalyze PCDD formation. The total PCDD concentrations in replicate samples decreased with run order. Similar decreases have previously been observed and attributed to the consumption of carbon-based structures and/or metals and metal oxides over time [10, 138]. Aurell et al. mentioned that even though the post-combustion zone was cleaned by applying vacuum and fluxes of compressed air after each combustion experiment, a thin layer of fine residual particulate matter remained on the convector wall [10]. Increases in the total PCDD concentration were also observed for the combustion of Waste B as the temperature of the flue gas decreased along the post-combustion zone. In this case, the average PCDD concentration increased from 7.3 ± 0.3 ng/m³ at 400 °C to 22.5 ± 2.5 ng/m³ at 300 °C and 36.5 ± 3.5 ng/m³ at 200 °C. The concentrations measured in duplicate flue
gas samples collected simultaneously during Waste B combustion were very consistent with one-another. To facilitate analysis of differences in the homologue profiles for the different wastes and flue gas temperatures, the concentrations of individual PCDDs were expressed as fractions of the total concentration of all homologous PCDD species, as shown in Figure 7.

Table 8. Total concentrations of PCDDs, PCDFs, PCBs, and PCNs in flue gas samples collected at 400 °C, 300 °C, and 200 °C during the combustion of Waste A and Waste B.

<table>
<thead>
<tr>
<th>ng/m³</th>
<th>Waste A</th>
<th>Waste B</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400 °C</td>
<td>300 °C</td>
</tr>
<tr>
<td>Run order</td>
<td>1st</td>
<td>2nd</td>
</tr>
<tr>
<td>Σ PCDD</td>
<td>9.3</td>
<td>8.7</td>
</tr>
<tr>
<td># Cl</td>
<td>2.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Σ PCDF</td>
<td>187</td>
<td>188</td>
</tr>
<tr>
<td># Cl</td>
<td>2.2</td>
<td>2.3</td>
</tr>
<tr>
<td>Σ PCB</td>
<td>13</td>
<td>14</td>
</tr>
<tr>
<td># Cl</td>
<td>4.5</td>
<td>4.3</td>
</tr>
<tr>
<td>Σ PCN</td>
<td>198</td>
<td>117</td>
</tr>
<tr>
<td># Cl</td>
<td>2.9</td>
<td>3.0</td>
</tr>
</tbody>
</table>

n.a. not available due to analytical errors; # Cl: degree of chlorination, calculated as Σ((Homologue sum/Σ(Homologue sum)) x No. of Cl)
Figure 7. Homologue fraction data for PCDDs, PCDFs, PCBs, and PCNs in flue gas samples collected simultaneously at 400 ºC, 300 ºC, and 200 ºC during the combustion of wastes A and B. Error bars correspond to ±1 SD.

When expressed in terms of homologue fractions, the levels of individual PCDDs were highly consistent from run to run. At 400 ºC, the PCDD profiles in samples collected during the combustion of both wastes were dominated by Mo-TriCDD, with MoCDD being the most abundant PCDD homologue. Further downstream, when the flue gas had cooled to 300 ºC, the PCDD profiles for Waste A combustion were still dominated by Mo-TriCDD, but the tetra- through octo-chlorodibenzo-p-dioxin homologues were becoming increasingly abundant. In contrast, the PCDD profiles for Waste B combustion at the same temperature were dominated by Pe-
HpCDD. At 200 °C, the PCDD profiles for both wastes were mainly dominated by Pe-HpCDD. Interestingly, the relative abundance of highly chlorinated homologues such as Te-OCDD increased with distance along the post-combustion zone for both wastes. This strongly suggests that either chlorination somehow occurred progressively as the flue gas cooled or that there is some specific process that forms more highly-chlorinated homologues directly at lower temperatures, for instance by the condensation of highly-chlorinated phenols. The degree of chlorination for the PCDDs generated by the combustion of each waste was calculated using the expression Σ((Homologue sum/Σ(Homologue sum)) x No. of Cl). For Waste A, the degree of chlorination was 3.0 ± 0.2 at 400 °C and 5.0 ± 0.4 at 200 °C, while the corresponding values for waste B were 3.7 ± 0.1 and 5.4 ± 0.1, respectively.

**PCDFs:** For Waste A combustion, the total PCDF concentration increased as the flue gas temperature fell from 400 °C to 200 °C (Table 8). PCDF concentrations were also observed to decrease with the run order. At 400 °C, PCDF concentrations of 138 – 188 ng/m³ were observed for Waste A combustion whereas those for Waste B were somewhat lower, at 87 - 88 ng/m³. Interestingly, although Waste A produced higher PCDF levels at 400 °C, the degree of chlorination was greater for Waste B combustion. At 300 °C and 200 °C there were no significant differences in the flue gas PCDF concentrations for the two wastes. The total PCDF concentration for waste B combustion exhibited the same trend as was observed for PCDD concentrations, increasing from 87.6 ± 0.6 ng/m³ at 400 °C to 174 ± 21 ng/m³ at 300 °C and 264 ± 32 ng/m³ at 200 °C.

The PCDF profiles for the two wastes were similar at all temperatures, with Mo-TriCDFs being dominant and MoCDF being the most abundant homologue (Figure 7). For both wastes, the relative abundance of the highly chlorinated Te-OCDF homologues (particularly HpCDF and OCDF) increased on moving downstream within the post-combustion zone while that of the less-chlorinated Mo-TriCDF homologues decreased. This trend was very pronounced for Waste B, as demonstrated by the increase in the degree of chlorination from 3.3 ± 0.1 at 400 °C to 4.0 ± 0.1 at 200 °C. Interestingly, Waste B displayed a higher degree of chlorination than Waste A at each sampling temperature, indicating that Waste B combustion favored the formation of Te-OCDF homologues, or that some species in the flue gas promoted the degradation or transformation of less-chlorinated homologues, thereby increasing the relative abundance of their more highly chlorinated counterparts. The formation of highly chlorinated PCDF homologues
could be due to either the chlorination of less-chlorinated homologues or other formation pathways (e.g. the condensation of precursors). The maximum rates of PCDF and PCDD formation occur at temperatures of 500 – 400 °C and 400 – 300 °C, respectively [94], while chlorination reactions are most efficient at temperatures of 300 – 200 °C [135]. Therefore, the shift towards more highly chlorinated homologues in flue gas samples collected on moving downstream within the post combustion zone may be due to the increased rate of chlorination reactions at lower temperatures. The higher degree of chlorination observed for PCDDs relative to PCDFs suggests that the mechanisms of PCDD chlorination differ from those for PCDFs or that chlorination is more important in PCDD formation than for PCDFs. Ryu et al. [139] studied PCDD/F formation in municipal waste incinerators and found that PCDFs were more prone to chlorination. However, this conclusion was based on data obtained in experiments examining the effects of co-combusting coal with municipal waste and may therefore not be directly applicable [140].

**PCBs:** No significant difference was observed between the two wastes in terms of flue gas PCB concentrations (Table 8). The total measured PCB concentrations were of the same order of magnitude as those for PCDDs and increased as the flue gas temperature decreased from 400 – 200 °C. At 400 °C, PCBs were detected at levels of 12 – 14 ng/m³ for the combustion of Waste A and 10 ng/m³ for Waste B. At a flue gas temperature of 300 °C, PCBs were detected at 21 – 39 ng/m³ and 21 – 28 ng/m³ for Wastes A and B, respectively, and the corresponding levels at 200 °C were 28 – 85 ng/m³ and 34 – 47 ng/m³. To compare PCB formation to that of the more intensively-studied PCDDs and PCDFs, the ratios of the total PCB concentration to the total PCDD and total PCDF concentrations were computed. The PCB/PCDD ratio was approximately 1 and did not change significantly for either waste as the flue gas temperature fell and the residence time in the post-combustion zone increased. This indicates that the temperature and residence time have similar effects on the net formation of compounds from these two groups. This result could also be taken to mean that PCBs and PCDDs are formed by similar pathways or that they are formed via different routes that are affected in similar ways by waste composition, combustion conditions and the temperature profile of the post-combustion zone. For Waste A combustion, the PCB/PCDF ratio was approximately 0.07 at 400 °C, increasing to 0.10 at 300 °C and 200°C. A similar result was obtained for Waste B combustion, with the PCB/PCDF ratio being 0.11 at
400 °C and 0.15 at 300 and 200 °C. This indicates that PCB and PCDF formation respond differently to conditions in the post-combustion zone. It has previously been reported that PCBs (especially non-ortho and mono-ortho PCBs) behave similarly to PCDDs and PCDFs during both primary and secondary combustion [141]. However, the main route of PCB formation is believed to involve the dimerization of chlorobenzenes, which may be less important in PCDD/F formation [142].

The PCB homologue profiles differed slightly at the three temperatures examined (Figure 7). At 400 °C, OCB, NCB, DeCB were not quantified because they were below the limit of quantification (here defined as the concentration that would give a S/N ratio of 10; LOQ = 5 pg). However, at lower temperatures (300 °C and 200 °C), these homologues were clearly quantifiable and their relative abundance increased as the temperature fell. At 400 °C, the PCB profiles for both wastes were dominated by Tri-HpCBs, with TeCB and PeCB being the most abundant congeners. As the flue gas cooled to 300 °C, the relative abundance of Tri-TeCBs decreased slightly and those of Hp-NCBs increased. This was reflected in an increased degree of chlorination (from 4.4 ± 0.1 to 4.9 ± 0.3 in waste A and from 5.0 to 5.7 ± 0.1 in Waste B). The PCB profile of the flue gas did not change greatly between 300 °C and 200 °C for either waste. The degree of PCB chlorination for Waste B was higher at every investigated temperature than that for Waste A, which suggests that one of its constituents or combustion products promotes the formation of highly chlorinated species such as the Hp-NCBs.

PCNs: The two wastes did not differ significantly in terms of the total PCN concentrations of their flue gases (Table 8). The total PCN concentration increased as the flue gas temperature decreased from 400 °C to 200 °C in both combusted wastes: at 400 °C, PCNs were detected at levels of 119 – 198 ng/m³ and 78 – 135 ng/m³ for Wastes A and B, respectively, whereas at 200 °C the corresponding flue gas PCN levels were 274 – 635 ng/m³ and 273 – 455 ng/m³, respectively. Jansson et al. have previously reported similar results, showing an increase in PCN concentrations along the post-combustion zone [31].

Although the PCN concentrations decreased from run to run, the PCN homologue profiles remained consistent between runs (Figure 7). At 400 °C, the flue gas PCN profile for Waste A combustion was dominated by Di-TeCNs, while OCN could not be detected (i.e. was present below its limit of detection of 10 pg). This is consistent with the findings of Jansson et al. [31] and Oh et al.[143]. When the flue gas
temperature decreased to 300 ºC, the abundance of Hx-OCN homologues increased slightly. However, there were no significant changes in the PCN profile between 300 ºC and 200 ºC. The PCN profiles for waste B combustion at the studied temperature intervals were dominated by Tri-TeCNs; there was no significant change in the PCN profile along the post-combustion zone. This is demonstrated by the unchanging degree of chlorination values at all temperatures. Compared to Waste A, the PCN profile for Waste B combustion exhibited lower DiCN levels and higher levels of the TeCN and PeCN homologues at each sampling temperature, suggesting that some species present in Waste B or produced by its combustion promotes the formation of highly chlorinated homologues. The relationship between the formation of PCNs and PCDFs has been studied by Imagawa and Lee, who found that these two compound classes are formed via very similar pathways [71]. To obtain new insights into this relationship, the PCN/PCDF ratio (based on the summed concentrations of all compounds in each group) was calculated for Wastes A and B. In both cases, the PCN/PCDF ratio was approximately 1, indicating that the rate of PCN formation was rather similar that for the PCDFs, independent of the waste’s composition. The PCN/PCDD ratio was also calculated but proved to be highly variable and it was not possible to identify any relationship between the levels of these two groups. The differing behaviors of these two groups may indicate that PCDDs and PCNs react via different pathways under the same post-combustion conditions. Further studies on the fate of PCNs during waste incineration will be required to clarify this issue.

5.4.2 Effects of increasing the waste’s metal and chlorine contents

An OPLS-DA model was used to evaluate the relationships between POP formation, waste classification, and combustion parameters. The waste composition data was not included in the model due to the use of a binary Y matrix that was designed to discriminate between the results for wastes A and B. The model yielded one predictive and two orthogonal (1+2) components and had a predictive ability of $Q^2_Y = 95.9\%$. These components explained $R^2_X = 79.8\%$ of the total variance in the data, and $R^2_{pX} = 36\%$ of the variance related to the differences between two wastes. The OPLS-DA model was evaluated using a bi-plot (a co-plot of the scores and loadings, Figure 8A) which illustrates the similarities and dissimilarities between
the observations (flue gas samples). This allowed us to interpret the observations in terms of the variables (i.e. the combustion data and the homologue profiles). The predictive component clearly separates samples collected during combustion of wastes A and B; in addition, samples collected at different temperatures are also clearly separated. For both wastes, the samples at 400 °C are widely separated from those collected at 300°C and 200 °C, but the latter two sets of results cluster together. This indicates that the dominant routes of PCDD, PCDF, PCB, and PCN formation at 400 °C are different to those that dominate at lower temperatures. The HCl content of the flue gas correlated strongly with the abundance of highly-chlorinated homologues (OCDF, HxCN...etc.), suggesting that HCl favors the formation of these species, possibly by promoting chlorination reactions. There was no correlation between POP formation and the levels of CO, CO₂, NO, or H₂O. This was probably because the efficiency of combustion was quite high in all cases. Other inorganic flue gases such as NO₂ and SO₂ did not contribute significantly to the model.

The VIP plot (Figure 8B) summarizes the importance of the variables in the homologue distribution and combustion data sets that contribute significantly to the model and to the differentiation between the two waste types and/or the results obtained at different temperatures. The VIP plot highlights a number of homologues that make particularly significant contributions to the differentiation in homologue profiles, including the Pe-OCDFs, Hx-OCNs, TriCBs, and TriCDDs.

Figure 8. (A): An OPLS-DA biplot illustrating the relationships between the formation of polychlorinated aromatics in the flue gas and the abundance of different combustion gases. (B): A VIP plot showing the relative importance of the different variables that contribute to the model.
The OPLS-DA model highlights the most important difference between the two wastes in terms of thermal POP formation: the combustion of waste A produced more aromatics with a low degree of chlorination than waste B; while the combustion of waste B promoted the formation of highly chlorinated homologues to a greater degree than waste A. This suggests that the higher levels of Al, Fe, and Cl in waste B promote the chlorination reactions that form highly chlorinated homologues. The OPLS-DA model also confirmed that residence time and temperature are the combustion variables with the greatest impact on the formation of highly chlorinated homologues. This is consistent with previous reports that chlorination is particularly efficient at temperatures of 300 – 200 °C [135]. The formation of highly chlorinated homologues in this work may have been primarily driven by chlorination. The POP formation data and the results of the multivariate analyses suggest that the formation of chlorinated organic pollutants in the post-combustion zone is initiated by the catalytic synthesis of lightly-chlorinated homologues promoted by copper in the combusted waste. The temperature and residence time then directly affect the further chlorination of these species to produce more highly chlorinated homologues; these processes are also facilitated by the presence of other metals such as Al and Fe. Our results are consistent with a previously proposed mechanism that was put forward to explain the formation of chlorinated naphthalenes [31]. Experimental injections of dibenzo-p-dioxin into the post-combustion zone of the incinerator also caused an increase in overall PCDD concentrations[144]. It was hypothesized that this was due to an initial rupture of the bridging C-O bonds of the dioxin to form phenolic species that were rapidly chlorinated and then underwent re-condensation[144]. When the biphenyl backbone was introduced into the post-combustion zone in a similar way, there was no significant change in the PCB homologue profile [145]. This may indicate that its residence time in the post-combustion zone was too short for chlorination to occur given the abundance of catalytically active species and chlorinating agents in the flue gas under the studied conditions.

5.5 **Fly ash chemistry (paper III)**

Various physicochemical properties of fly ash samples were determined, including their mineralogical composition, particle morphology, sub-surface composition, and top-surface composition.
5.5.1 Particle formation (XRD spectroscopy)

Mineralogical analyses of the fly ashes formed during the combustion of wastes A and B (Table 9) revealed that they had several properties in common but also differed in various ways that could be related to the compositions of the original wastes and the fly ashes themselves (Table 7).

Table 9. Semi-quantitative XRD data for the fly ash samples

<table>
<thead>
<tr>
<th>Mineral name</th>
<th>Formula</th>
<th>waste A</th>
<th>waste B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>Fe$_2$O$_3$</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>Aluminium</td>
<td>Al</td>
<td>***</td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>CaSO$_4$</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
<td>*</td>
<td>***</td>
</tr>
<tr>
<td>Quartz</td>
<td>SiO$_2$</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>Gehlenite</td>
<td>Ca$_2$Al$_2$Si$_2$O$_7$</td>
<td>**</td>
<td>**</td>
</tr>
<tr>
<td>Akermanite</td>
<td>Ca$_2$Mg(Si$_2$O$_7$)</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>Diopside</td>
<td>CaMgSi$_2$O$_6$</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>Na-tecto-Al-silicate</td>
<td>NaAlSiO$_4$</td>
<td>***</td>
<td></td>
</tr>
</tbody>
</table>

Compounds are provided as major (***)), abundant (**) and minor (*).

The XRD results revealed that the ashes contained mixtures of crystalline phases. Hematite ($\alpha$-Fe$_2$O$_3$) was one of the dominant phases in both fly ashes, and the sole Fe-bearing mineral. It is likely to have formed from iron in the fuel and/or the reactor wall. The Al-bearing minerals in the ash were more diverse. While gehlenite (Ca$_2$Al$_2$Si$_2$O$_7$) was the only Al-bearing phase present in both fly ashes, a Na-tecto-Al-silicate (NaAlSiO$_4$) and elemental Al were also important in the ashes of waste B. The greater diversity of Al-containing minerals in the waste B ashes probably reflects the greater Al content of the parent waste. The presence of elemental Al in fly ash samples is probably due to the deposition of particle layers over and around Al that is situated in fly ash pores during combustion. Quartz (SiO$_2$) is more abundant in the fly ashes of waste A but is still present in those from waste B. It is likely to have originated from the fluidized bed material and/or been formed during combustion. The calcium-bearing minerals sorosilicate gehlenite (Ca$_2$Al$_2$Si$_2$O$_7$) and akermanite (Ca$_2$Mg(Si$_2$O$_7$)) were present in both fly ashes.
Anhydrite (CaSO₄) was present in both wastes, and was the sole sulfate-bearing crystallographic phase detected by XRD. The waste B ashes were comparatively rich in sodium-bearing minerals such as aluminosilicates and halite (NaCl), which is consistent with the compositional analysis (Table 7). Finally, although Cu is expected to be a key catalyst in the production of chlorinated aromatic pollutants, none of the observed XRD diffraction peaks could be linked to any of its known crystallographic phases.

FTIR spectroscopic analyses of the fly ashes demonstrated that they were rich in dehydroxylated and dehydrated phases due to the low intensities of the O-H stretching and bending regions of the spectra. Indeed, some of the peaks that were observed in this region may have been due to the adsorption of atmospheric water vapor during particle storage rather than being present in the original ashes (Figure S2 in Paper III). There is a broad set of bands in the 1350-1600 cm⁻¹ region that originate from sorbed atmospherically-derived carbonate species and possibly polychlorinated aromatics. However, given the low intensities of the C-H stretching region, the contributions of the latter are unlikely to contribute significantly to the ashes’ FTIR spectra. Of all the phases that were detected by XRD, the ones that produced the strongest signatures in the FTIR spectra were the silicate-bearing minerals due to their strong Si-O stretching vibration bands at ~1000 cm⁻¹. In addition, sulfate species could be identified due to the presence of peaks on the higher energy side of the strong ~1000 cm⁻¹ band, and particularly because of a shoulder at ~1100 cm⁻¹, which is a typical absorption maximum for the S-O stretching modes of sulfate species.

5.5.2 Surface and sub-surface composition (XPS and EDX)

SEM images of the fly ashes revealed irregularly shaped particles with diameters ranging from 1 to 100 µm (Figure 9). Attempts at determining the particles’ specific surface areas by analyzing their N₂ (g) adsorption/desorption isotherms yielded values in the range of 2.56 – 5.72 m²/g, which is consistent with the size distributions determined by SEM. Imaging at a magnification of 10⁵ x (see the 1-µm scale bar in Figure 9) revealed irregularly shaped and/or agglomerated particles, with no clear morphological differences between ashes formed during repeat runs or from different wastes. The particles’ shapes are presumably due to mineral smelting or mineral-gas reactions, which would have been responsible for the formation of new or newly-coated particles during the cooling period.
EDX analyses provided insights into the elemental composition of the topmost 2 µm layer of the particles' surfaces (Figure 10). The surface composition data generally correlate with the bulk compositions determined by solution-phase analyses of acid-dissolved ashes (Table 7). The predominant elements include silicon, aluminum, iron, calcium, and sodium (Table 9), which were distributed over most of the particles as can be seen in the distribution maps of Figure 10. Less abundant elements included chlorine, potassium, magnesium, sulfur, phosphorous, and titanium, many of which were not major elements in any of the dominant phases identified by XRD. The sodium levels in the waste B fly ash (8.0 – 9.4 %) were twice as high as those for the waste A ash (3.8 – 5.7 %), which is consistent with the higher levels of halite (NaCl) in fly ash B and the other composition data (Table 7). In addition, figure 10 clearly shows that fly ash B contains zones composed entirely of NaCl, some of which are associated with Fe; such zones are much less common in A. Similarly, the abundance of aluminum in fly ash B was 24.9 – 29.3 % but in A it was only 16.5 – 18.3 %. This confirmed the predominance of Al-bearing minerals in fly ash B. Calcium and silicon were more abundant in fly ash A, in keeping with its relatively high content of anhydrite (CaSO₄) and quartz (SiO₂) as determined by XRD. These findings also imply that fly ash A has a greater content of S than ash B, as can be seen in the EDX results (Figure 10).

Finally, EDX detected trace levels of Cu in all fly ash samples. While there were appreciable differences between the measured Cu contents of the two ashes (0.25 – 1.88 % in ash A and 0.25 – 0.93 % in ash B), it is impossible to say how meaningful these are due to the uncertainties of the measurements: the peaks in the two cases were of similar sizes and overlapped extensively with the spectral background. However, these results clearly demonstrate the presence of trace quantities of Cu, which is believed to catalyze the production of chlorinated aromatics. The quantities of Cu found on the fly ash surfaces are comparable to those detected in the fly ashes from full-scale MSWI facilities [146, 147] as determined in by atomic absorption spectroscopy.
Figure 9. SEM images of fly ash particles formed from wastes A and B. Scale: 10 µm and 1 µm.

Figure 10. EDX spectra of waste A (top, left) and B (top, right) fly ash particles, and distribution maps showing the elemental composition of fly ashes A (bottom, left) and B (bottom, right).

The XPS results (Figure 11; Table 10) showed that the elemental composition of the surface layers of the fly ash particles were dominated by O, Si, and C, and also...
contained appreciable levels of Fe, Al, and Mg (Table 10). The catalytic effects of iron and aluminum on PCDD and PCDF formation have been documented extensively in the literature; iron is known to be the second most potent catalyst of dioxin formation [148, 58]. It is important to note that the rather high iron contents of the ashes could contribute significantly to their overall catalytic capacity. Interestingly, no Cu could be detected with this highly sensitive technique even though trace amounts were found buried in the top 2 µm of the ashes by EDX. The fly ash surface therefore appears to be depleted of this catalytic element during the combustion reactions. Moreover, this depletion may be a significant limiting factor in the production of polychlorinated aromatics.

Narrow scans of the O 1s region revealed oxide (529.7 eV), hydroxide (530.8 eV), and water (532.0 eV) peaks in the waste A spectrum, with a combined atomic concentration of 72.5 to 78.2 %. Conversely, the spectrum of the waste B fly ash contained only the oxide peak, which accounted for 76.2 % of the surface atomic composition. This difference is explained by the higher levels of sodium and aluminum in waste B, which would promote the formation of metal oxides, and therefore of fly ash (Table 7) in waste A. These compositional differences are also directly reflected in the fly ashes’ contents of both sodium (1.8 – 2.0 % in fly ash A and 2.8 – 2.9 % in fly ash B) and aluminum (4.2 – 5.6 % in fly ash A and 6.7 – 7.0 % in fly ash B). However, the wastes and their ashes had much more similar levels of iron: the Fe content of waste B (2.5 %) was around twice that of waste A (1.2 %), but the ashes had very comparable Fe levels (1.8 – 3.2 % in A and 2.8 – 2.9 % in B). This could be due to the fact that Fe tends to remain in the bottom ash rather than fly ash [149].
Figure 11. Representative XPS spectrum of a waste A fly ash sample referenced to the 285.0 eV peak of the C 1s region.

The presence of Cl in the fly ashes was confirmed by the observation of peaks at 199.0 and 270.0 eV. A narrow scan of the Cl 2p region demonstrated that inorganic chloride from halite was the sole chlorine-containing species present on the ash surface. No peaks corresponding to polychlorinated aromatic species were detected. In contrast, the C 1s region contained peaks corresponding to both organic and inorganic species. A narrow scan spectrum of this region revealed C-H (285.0 eV), C-O (286.5 eV), COOH (288.7 eV), and CO$_3^{2-}$ (289.7 eV) peaks, reflecting the presence of both combustion-derived organic compounds and carbonate species of atmospheric origin [128].
Table 10. Elemental composition of fly ash surface and sub-surface

<table>
<thead>
<tr>
<th>Element</th>
<th>waste A (atomic %)</th>
<th>waste B (atomic %)</th>
<th>Element</th>
<th>waste A (atomic %)</th>
<th>waste B (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>1.8 - 2.0</td>
<td>2.8 - 2.9</td>
<td>Na</td>
<td>3.8 - 5.7</td>
<td>8.0 - 9.4</td>
</tr>
<tr>
<td>Fe</td>
<td>1.8 - 3.2</td>
<td>2.8 - 2.9</td>
<td>Fe</td>
<td>8.3 - 11.3</td>
<td>8.9 - 12.3</td>
</tr>
<tr>
<td>Ca</td>
<td>4.4 - 5.1</td>
<td>4.7 - 4.8</td>
<td>Ca</td>
<td>20.4 - 21.2</td>
<td>15.1 - 17.1</td>
</tr>
<tr>
<td>K</td>
<td>0.6 - 0.8</td>
<td>1.0 - 1.1</td>
<td>K</td>
<td>2.0 - 2.3</td>
<td>1.7 - 1.8</td>
</tr>
<tr>
<td>Cl</td>
<td>0.3 - 0.4</td>
<td>1.2 - 1.4</td>
<td>Cl</td>
<td>1.0 - 1.5</td>
<td>3.1 - 5.4</td>
</tr>
<tr>
<td>S</td>
<td>1.5 - 2.1</td>
<td>1.0 - 1.1</td>
<td>S</td>
<td>0.7 - 0.9</td>
<td>0.5 - 0.6</td>
</tr>
<tr>
<td>Si</td>
<td>10.1 - 11.8</td>
<td>8.5 - 9.0</td>
<td>Si</td>
<td>38.9 - 40.7</td>
<td>25.3 - 30.2</td>
</tr>
<tr>
<td>Al</td>
<td>4.2 - 5.6</td>
<td>6.7 - 7.0</td>
<td>Al</td>
<td>16.5 - 18.3</td>
<td>24.9 - 29.3</td>
</tr>
<tr>
<td>Mg</td>
<td>2.2 - 2.9</td>
<td>3.3 - 3.5</td>
<td>Mg</td>
<td>1.3 - 2.0</td>
<td>1.5 - 1.6</td>
</tr>
<tr>
<td>F</td>
<td>0.6 - 0.9</td>
<td>0.5 - 1.1</td>
<td>Ti</td>
<td>0.2 - 0.4</td>
<td>0.4 - 0.5</td>
</tr>
<tr>
<td>O</td>
<td>60.3 - 60.8</td>
<td>55.7 - 59.0</td>
<td>P</td>
<td>0.7 - 1.4</td>
<td>0.5 - 0.7</td>
</tr>
<tr>
<td>C</td>
<td>7.6 - 9.1</td>
<td>6.6 - 11.2</td>
<td>Cu</td>
<td>0.25 - 1.88</td>
<td>0.25 - 0.93</td>
</tr>
</tbody>
</table>

Note*: concentrations below 0.5 % should be considered unreliable as the presence is very low in the sample and some of their peak-data is hidden in the spectrum background.

5.6 The relationships between isomer distributions and particle chemistry (Paper IV)

5.6.1 Dioxin isomer patterns (PCDDs, PCDFs, and PCNs)

The isomeric distribution of the POPs produced during incineration serves as a fingerprint that can be used to determine the dominant mechanisms of formation for polychlorinated aromatics in the process of interest. The different classes of POPs are believed to form via different pathways. To increase the amount of information that can be gleaned from homologue distribution data and to better understand the factors that govern the distribution of homologues within a given compound class and isomers of a given homologue, isomer distribution patterns were studied separately for each group of PCDD, PCDF, and PCN homologues. Unfortunately, due to a lack of data, no such analysis could be performed for PCBs.

PCNs: The PCN isomer distributions for the two wastes are shown in Figure 12. While the total PCN yields and homologue distributions did differ appreciably...
between the two wastes, the isomer distributions for individual homologues were much less variable [150]. The predominant DiCN compounds in the flue gas at 300 °C were the co-eluting 14-/16- and 15-/27- isomers followed by 13-, 12-, and 17-/26-DiCN. The formation of 14-/16-/17-/26-DiCN has been experimentally confirmed to occur via the oxidation of chlorophenols followed by tautomerization and CO elimination [69]. The main TriCN isomers were found to be 1,2,7- and 1,2,3-TriCN, followed by a unique pattern of other congeners. In case of TeCN isomer distribution, the dominant isomers were the co-eluting 1,2,5,7-/1,2,4,6-/1,2,4,7-TeCNs and the 1,2,3,4-/1,2,3,7-/1,2,6,7-TeCNs. The most abundant PeCN isomers were the co-eluting 1,2,3,5,7-/1,2,4,6,7-PeCNs followed by 1,2,3,5,6- and 1,2,3,6,7-PeCN. The HxCN isomer distributions for the two wastes were also very similar: the most abundant HxCN isomers in both cases were 1,2,3,4,6,7-/1,2,3,5,6,7-(co-eluted), 1,2,3,4,5,7-, and 1,2,3,5,7,8-HxCN. The dominant HpCN isomer for both wastes was 1,2,3,4,5,6,7-HpCN, which accounted for 85% of the total HpCN content.

Homologue data in previous paper showed the predominance of low chlorinated PCNs [31]. This suggests that the thermal formation of highly chlorinated PCN homologues in the flue gas is probably disfavored relative to less chlorinated PCNs. This could be due to either the predominance of less chlorinated PCN precursor compounds (i.e. phenols and benzenes) [151]; alternatively, it may be because highly chlorinated phenols are not efficient substrates for condensation reactions, as was demonstrated in a gas-phase study of PCDF formation [152]. However, highly chlorinated PCNs can be formed via surface-mediated chlorination reactions in the flue gas [139]. Recent experiments revealed that PCNs undergo highly selective chlorination at the 1 and 4 positions [153], which suggests that the thermal formation of PCN during MSWI is not primarily due to chlorination reactions. However, the conditions in a MSWI plant are more complex than those used in the experimental copper chloride-catalyzed system. The formation of PCNs can occur via two different pathways: one involving the condensation of chlorophenols via intermediates produced by the ortho-ortho coupling of phenoxy radicals [154, 69], and another involving the breakdown of carbon matrices formed from species such as PAHs [50]. The observation of additional peaks corresponding to PCN isomers may be due to intramolecular chlorine migration reactions via processes such as the 1,5-sigmatropic shifts that occur in cyclopentadiene rings. Notably, the barriers to chlorine migration in such systems are comparable to those
for hydrogen [155, 156]. It is also possible that the observed chlorine substitution patterns are due to the α-oriented dechlorination of higher PCNs [71].

Overall, the mechanisms responsible for the thermal formation of PCNs during MSWI remain unclear and more information on the isomer patterns associated with different mechanisms of PCN formation is required. The combustion of waste B produced more ash than waste A. Moreover, the waste B ash had a higher Cl content, which may favor the formation of highly chlorinated POPs. Jansson et al. suggested that the chlorination of PCNs may be somewhat favored at the lateral 2,3,6,7-positions in the same way that PCDDs and PCDFs are preferentially chlorinated at the 2,3,7,8-positions [31]. The work of Ryu et al. demonstrated that PCNs are preferentially chlorinated at the 1,4,6,8-positions [153]. However, our isomer distribution data for Di-OCN compounds suggest that the chlorination of MoCNs occurs preferentially at the 2,4,5,7-positions, suggesting that 1-MoCN is the predominant monochlorinated PCN isomer that further chlorination of MoCNs occurs via electrophilic ortho-/para- substitution. It should be noted that no data on the isomer distributions for non- and mono-chlorinated naphthalenes were collected in this work; there is therefore a need for further studies to address this deficiency.
Figure 12. Isomer distribution patterns for PCDFs, PCNs, and PCDDs. Error bars represent ±1 standard deviation (results for waste A are based on triplicate experiments; those for waste B are based on duplicate experiments)

**PCDFs:** The most abundant MoCDF isomers generated by the combustion of wastes A and B were the 2- and 3-congeners, which is consistent with the results of a stability study in which it was found that furan chlorination is disfavored at carbon atoms adjacent to the oxygen bridge [157]. The most abundant DiCDFs were
the co-eluting 2,3-/2,6-3,6-/4,6-DiCDF isomers, followed by 27-DiCDF. The formation of these compounds was attributed to chlorophenol condensation reactions [68]. The TriCDF distribution was dominated by two peaks representing three co-eluting compounds each: 2,3,4-/2,3,6-/2,4,6-TriCDF and 1,4,9-/2,6,7-/3,4,7-TriCDF. The 2,3,4- and 3,4,7-TriCDF isomers both derive from condensation reactions of 2,3-dichlorophenol [68]. The most abundant TeCDFs were the co-eluting 2,3,6,8-/1,2,3,8-/1,2,3,4-/1,6,7,8-/1,4,6,9-TeCDF isomers. The PeCDF distribution was relatively uniform; the most abundant isomers were 1,2,4,6,8-/1,3,4,6,8-, 1,2,4,6,7-/1,3,4,6,7-, 1,2,4,7,8-/1,3,4,7,8-, 1,2,3,4,6-/1,2,4,6,9-/2,3,4,6,8-, 1,2,3,6,7-/1,2,6,7,8-, 1,2,3,6,9-/2,3,4,6,7-, and 1,2,4,8,9-/2,3,4,7,8-PeCDF. The major HxCDF isomers were 1,3,4,6,7,8-/1,2,4,6,7,8-, 1,2,3,6,7,8-, and 1,2,3,6,8,9-/2,3,4,6,7,8-HxCDF. The main HpCDF congener was 1,2,3,4,6,7,8-HpCDF, which accounted for 65% of the total HpCDF mass.

The mechanisms of PCDF formation were found to correlate closely with those of PCN formation and are believed to be driven by chlorination and/or dechlorination [61, 139]. The isomer distributions observed in this work are consistent with both the chlorination and dechlorination mechanisms, particularly the PeCDF and HxCDF patterns [158]. The high levels of the 1,2,4,6,7,8- and 2,3,4,7,8-PeCDF isomers are in good agreement with the chlorination model, while the high levels of 2,3,4,6,7-, 2,3,4,6,8-, and 1,2,4,8,9-PeCDFs can be explained by the dechlorination model [158]. Similarly, the high levels of 1,2,3,6,7,8-HxCDF can be attributed to the chlorination mechanism, while the abundance of 1,3,4,6,7,8- and 2,3,4,6,7,8-HxCDF supports the dechlorination mechanism. Finally, the HpCDF isomer distribution is most consistent with the dechlorination pattern.

**PCDDs:** The PCDD isomer distribution patterns (for Te-HpCDDs) generated during the combustion of waste A and B are shown in Figure 12. The isomer pattern indicates that PCDD formation is mainly driven by both chlorophenol condensation reactions and the chlorination of lightly chlorinated products. No data on the distributions of Mo-TriCDDs were available, so these compounds were not considered. The TeCDD pattern was dominated by 1,3,6,8-, 1,2,4,6-/1,2,4,7-/1,2,4,8-, and 1,2,3,7-/1,2,3,8-TeCDD, followed by 1,3,7,8- and 1,3,7,9-TeCDD. The 1,3,6,8- and 1,3,7,9-TeCDD isomers are known to be formed by the condensation of 2,4,6-trichlorophenol [55]. Moreover, the chlorination and dechlorination models
predict that the most abundant TeCDD isomers should be 1,3,7,8-/1,2,4,6-/1,2,4,7-/1,2,4,8-, and 1,2,3,7-/1,2,3,8-TeCDD [158, 135].

The most abundant PeCDD isomers were the co-eluting 12468-/12479-PeCDDs, followed by 1,2,3,6,8- and 1,2,3,7,9-PeCDD. These isomers are the major products formed during the condensation of 2,4,6-trichlorophenol and 2,3,4,6-tetrachlorophenol [61]. The HxCDD pattern was dominated by the co-eluting 1,2,3,6,7,9-/1,2,3,6,8,9- isomers, followed by the 1,2,3,4,6,8-, and 1,2,4,6,7,9-/1,2,4,6,8,9-HxCDD congeners. Ryu and Muholland found that the 1,2,3,6,7,9-/1,2,3,6,8,9- and 1,2,4,6,7,9-/1,2,4,6,8,9- isomers were largely generated from condensation reactions involving two molecules of 2,3,4,6-tetrachlorophenol while the 1,2,3,4,6,8- isomer was produced via tautomerization-condensation reactions between 2,4,6-trichlorophenol and pentachlorophenol [61]. The high observed levels of these isomers were also in good agreement with the pattern expected for a dechlorination-driven process [158]. However, a chlorination-based process would be expected to produce large quantities of 1,2,3,4,6,7-/1,2,3,7,8,9-HxCDD, and a large peak corresponding to these isomers was indeed detected in this work. The HpCDD isomer distribution was relatively even, although 1,2,3,4,6,7,8-HpCDD was slightly more abundant than the 1,2,3,4,6,7,9 isomer in the combustion products of waste B.

5.6.2 Correlations with fly ash particle chemistry

Most of the mechanisms that have been put forward to explain the formation of polychlorinated aromatic species during combustion are heavily reliant on surface-mediated pathways [9]. Given their abundance and particle sizes, fly ash surfaces (and especially those that support reactive forms of Cu) are suspected to be the most important catalysts for such reactions.

OPLS modeling was used to explore the potential links between the formation of polychlorinated aromatic species and fly ash composition. This multivariate statistical method was used to compare the XPS, XRD, and EDX data (X variables) to the homologue distribution results for different aromatic compounds (Y variables). PCA-X and PCA-Y models were created individually for the X and Y variables to provide a summary of the variation within each dataset. The results generated using the PCA-Y block model are discussed extensively in the supporting information of a previous publication [150]. The PCA-X model (no outliers were detected) yielded three significant principal components that together explained 95
% of the variation in the data, and had a predictive ability of 60%. A biplot constructed using the first two principal components, which together explained 84% of the variation in the data set, revealed a clear delineation between the mineralogical and compositional attributes of fly ashes A and B (Figure S2 in Paper IV). The strong agreement between the results generated using different techniques (XPS, EDX, XRD) demonstrates that the samples used in all of the experiments were reasonably homogeneous.

Figure 13. Loading plot for the OPLS model showing the relationship between the X variables (chemical composition of the fly ash as determined by XPS and EDX, and mineralogical data determined by XRD) and the Y variables (organic pollutant homologue distributions).

The OPLS model yielded one predictive component describing the joint X/Y variation and two orthogonal components describing variation in the X block that was not correlated to the Y block. The loading scatter plot (Figure 13) shows the relationship between the X-variables and the Y-variables based on the first predictive component and the first Y-orthogonal component. There is a clear separation between the lightly chlorinated homologues and the more highly chlorinated ones, and this separation correlates with differences in the particle characterization results. The plot clearly reveals a strong relationship between the abundance of chlorine and aluminum-containing species (Al, NaAlSiO₄) and that of
highly chlorinated homologues (Pe-OCDF, Hx-HpCDD, Hx-HpCB, and OCN) on the other, since all of these species were located on the left-hand side of the loading plot (Figure 13). Notably, these minerals are substantially more abundant in waste B than waste A, and are associated with S-poor flue gases. The right hand side of the biplot is populated by the less chlorinated homologues (Mo-DiCDF, Di-TriCDD, Tri-TeCB, and DiCN). The levels of these homologues correlate more strongly with the presence of S, Ca, CaSO₄, Si, and SiO₂, all of which are abundant in waste A, and are associated with S-rich flue gases. Finally, in keeping with the expectation that Cu is the most active catalyst in both wastes, it is located in the middle of the loading plot. This results from its equal loadings in both of the original wastes (155 ppm in waste A and 154 ppm in waste B) and the corresponding fly ashes (0.25 – 1.88 % in ash A and 0.25 – 0.93 % in ash B).

The loading plot of the OPLS model thus revealed a clear correlation between the composition of waste B and the abundance of highly chlorinated species among its combustion products. Similarly, the high levels of less chlorinated aromatics among the combustion products of waste A could be linked to its chemical and mineralogical composition. The analysis also demonstrated the existence of a strong correlation between the abundance of less chlorinated species and the presence of sulfur-bearing minerals, even though both original wastes contained similar quantities of sulfur (Table 7). Because the flue gases produced from wastes A and B contained similar levels of HCl, O₂, and H₂O, the Deacon reaction (R1) should proceed at similar rates in both cases. However, this reaction is inhibited by sulfur [65]:

\[ \text{Cl}_2 + \text{H}_2\text{O} + \text{SO}_2 \leftrightarrow 2\text{HCl} + \text{SO}_3 \] (R7)

Consequently, the higher S content of the flue gases formed during waste A combustion should favor the formation of less chlorinated polyaromatic compounds. This difference between the flue gas compositions of wastes A and B thus has a profound impact on the polyaromatic profiles of the MWSI emissions. Interestingly, the levels of S in the flue gas appear to correlate with the wastes’ ash contents (Table 7). Chemical analyses suggest that while carbon accounts for represents almost 50 wt% of the ashes of both wastes, the inorganic content (Fe, Al, Na, etc.) of waste B is 1.45 times greater than that of Waste A (16.5 % in Waste B compared to 11.4 % in Waste A). *It therefore seems that the inorganic content of
Waste B results in the formation of more ash during MWSI, and that this ash traps sulfur, reducing the S content of the flue gas. This proposal is consistent with the observations of Chang et al. [159], who reported a positive correlation between the levels of highly chlorinated PCDD and PCDF homologues and the metal contents of fly ash.

The OPLS models (Figure 14) for the individual POP groups (i.e. PCDFs, PCNs and PCDDs) revealed that the formation of larger quantities of ash during the combustion of waste B also favored the thermal formation of highly toxic 2,3,7,8-tetrachloro PCDDs and PCDFs. It is therefore important to minimize the formation of ash and fly ash during combustion in order to prevent the thermal formation of highly chlorinated homologues and toxic congeners.
Figure 14. OPLS models for the PCDF, PCN, and PCDD distributions.
6. Conclusion and future perspectives

The work presented in this thesis has produced a number of key results. First, a reliable method for sampling flue gases at temperatures above 450 °C has been developed and validated. This is important because conventional sampling tools have inadequate cooling for hot gas samples, resulting in extensive PCDD and PCDF formation inside the sampling apparatus. Consequently, they overestimate POP levels in flue gases. It should be noted that while the standard EN-1948 probe yields unreliable results for PCDD and PCDF levels in hot flue gases, it does not suffer from such problems when used at the much lower temperatures at which sampling is performed in MSWI facilities. However, a probe with a more powerful cooling system is required when sampling hotter gases, and the sub-zero probe described in this work is entirely suitable for this purpose.

Secondly, the thermal formation of POPs at various points within the post-combustion zone has been investigated in detail. The PCDD/F concentrations were quite low in the first part of the post-combustion zone, where the flue gases are very hot (700 °C). In fact, the levels of some homologues in this region were below the limit of detection, confirming that their formation occurs only at lower temperatures. The effects of varying the composition of the waste on the thermal formation of polychlorinated aromatics were investigated using two artificial wastes, one representing typical Swedish MSW and one representing the Europe-wide average MSW composition. The combustion of waste B, which had a higher chlorine and metal content than waste A, yielded significantly higher levels of highly-chlorinated homologues. By analyzing POP formation using OPLS-DA modeling, it was found that less-chlorinated homologues are formed preferentially at temperatures of 400 °C. Further downstream, at temperatures of 300 and 200 °C, the formation of more highly-chlorinated homologues becomes favored. This may occur via the chlorination of less chlorinated homologues using chlorine produced by the Deacon process or via special formation pathways such as the Al- or Fe-mediated condensation of chlorinated phenols.

Thirdly, the physicochemical properties of MSWI fly ash particles generated during the combustion of different synthetic wastes were investigated to determine their impact on thermal POP formation. FT-IR, XRD, SEM/EDX, and XPS analyses revealed that the chemistry and reactivity of fly ash particles are largely determined by the composition of the waste fuel. Waste B contained higher levels of Al and thus
produced fly ash that was relatively rich in Al-bearing minerals and elemental Al. No such difference between the fly ashes of the two wastes was observed for Fe even though the Fe content of waste B was twice that of waste A. The most active catalyst for the formation of polychlorinated aromatics, copper, could not be detected in the uppermost 2-nm layer of the fly ash particles by XPS. However, copper was detected in the 2-µm surface layers of the fly ash particles by EDX. The Cl in the ashes was invariably associated with Na (in the form of halite, NaCl), which is consistent with XPS data confirming the presence of inorganic chloride was the sole species present on the ash surfaces.

The fly ash characterization results were used to study the connection between the properties of the fly ash and thermal POP formation during waste incineration. There was a clear separation between the highly chlorinated organic pollutants and their less chlorinated counterparts that was related to the contents and mineralogical properties of the fly ashes and the S content of the flue gas. The combustion of waste B produced large quantities of ash and flue gases with relatively low levels of S, along with large quantities of highly chlorinated polyaromatic compounds (i.e. tetra- through octa-chlorinated species). Conversely, waste A produced less ash, had flue gases with a relatively high S content, and primarily formed less-chlorinated polyaromatic species. These results suggest that minimizing the amount of ash formed during MSWI may increase the S content of the flue gas and thereby suppress the Deacon process that enables the formation of highly chlorinated POPs. OPLS models for individual groups of PCDFs, and PCDDs also showed that the production of large quantities of ash during the incineration of waste B favored the thermal formation of highly toxic 2,3,7,8-tetrachlorinated PCDD and PCDF congeners. It will therefore be important to minimize the formation of ash and fly ash during waste combustion in order to minimize emissions of these harmful compounds. This could be achieved efficiently by reducing the metal content of the waste prior to combustion, for instance by implementing a simple waste sorting and separation policy.

Finally, based on the results discussed above, some potentially fruitful areas of research for future investigation can be identified. First, it should be noted that results presented in this work were obtained by studying a 5 kW lab-scale incinerator. To expand on and verify these findings, it would be desirable to perform similar experiments on a full-scale incineration system. In addition, the use of more powerful analytical methods (particularly, the use of improved GC/MS
instruments that can more effectively separate the various POP congeners) will enable a more comprehensive analysis of the PCDD, PCDF, PCB and PCN distributions formed during waste combustion, which will make it possible to better understand the mechanisms of POP formation. Moreover, in an ideal case, each POP isomer of interest would have its own unique quantification standard rather than having to use one standard for several target analytes as is the case at present.

The results presented in this thesis confirm that the concentrations of PCDDs and PCDFs in the material that enters the post-combustion zone are low. However, they could not be quantified exactly in many cases, so a second experimental campaign using longer sampling times may be warranted. In addition, it would be desirable to perform lab-scale experiments involving the injection of chlorobenzene compounds into the post-combustion zone while burning wastes with various metal and chlorine contents in order to study how the presence of aromatic precursors with different chlorination patterns affects the formation of POPs. The physicochemical properties of fly ash and their effects on thermal POP formation have been studied in detail. However, ash particles were only sampled at a single temperature, so it would be desirable to conduct further investigations with different sampling temperatures and to examine ashes formed under a broader range of combustion conditions.
7. Acknowledgement

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