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PÄIVI RUOKOJÄRVI

Effect of Chemical Inhibitors on Polychlorinated Dibenzo-*p*-dioxin and Dibenzofuran Formation in Waste Incineration

Doctoral dissertation

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Series editor:

Professor Lauri Kärenlampi, Ph.D.
Department of Ecology and Environmental Science

Professor Jari Kaipio, Ph.D.
Department of Applied Physics

Author´s address:

National Public Health Institute
Laboratory of Chemistry
P.O.Box 95
FIN-70701 KUOPIO
FINLAND
Tel. +358 17 201 349
Fax +358 17 201 265
E-mail: Paivi.Ruokojarvi@ktl.fi

Supervisors:

Professor Juhani Ruuskanen, Ph.D.
Department of Environmental Sciences
University of Kuopio

Professor Terttu Vartiainen, Ph.D.
National Public Health Institute and
Department of Environmental Sciences
University of Kuopio

Dr Helena Manninen, Ph.D.
TEKES, National Technology Agency, Helsinki

Reviewers:

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Professor Juha Knuutinen, Ph.D.
Department of Chemistry
University of Jyväskylä

Opponent:

Professor (emeritus) Jaakko Paasivirta, Ph.D.
Department of Chemistry
University of Jyväskylä

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ABSTRACT

Prevention of the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/F) with chemical inhibitors was studied in a pilot scale incinerator. Inhibitors were used to block the PCDD/F formation, and the effect of different supply points, feeding temperatures and process parameters were studied to gain an understanding of which factors can influence the PCDD/F formation and inhibition mechanisms during waste incineration. The role of chlorophenols as PCDD/F precursors was investigated in particular.

Both light heating oil and refuse derived fuel were used as test fuels. Gaseous inhibitors (sulfur dioxide, ammonia, dimethylamine and methyl mercaptan) were sprayed at different concentrations into the flue gases after the furnace. In addition urea was dissolved in water and injected at different concentrations into the flue gases after the furnace. Residence time of the flue gas between the furnace and the PCDD/F and chlorophenol sampling point was varied in the tests. In another set of urea tests, three concentrations of urea-water solutions were mixed with the RDF fuel prior to incineration. PCDD/F and chlorophenol concentrations as well as other flue gas parameters (e.g. temperature, O_2, CO, CO_2 and NO) were analysed from the cooling flue gases. PLS-analysis was then used to study the relationships between flue gas components, PCDD/Fs and chlorophenols.
Gaseous and liquid inhibitors both reduced notably the PCDD/F flue gas concentrations in the pilot scale incinerator. PCDD/F reductions with gaseous inhibitors varied from 50 to 78 %, with dimethyl amine being the most effective tested inhibitor. Urea reduced the PCDD/F concentrations by up to 90 %. PCDD/F reductions became greater with increased inhibitor concentrations and with increased residence time of the flue gas between the furnace and the PCDD/F sampling point. The inhibitors decreased clearly more the PCDD/F concentrations in the particle phase than in the gas phase. The urea inhibitor did not alter the particle size distribution of PCDD/Fs when the amount of inhibitor was adequate.

With PLS analysis it was possible to predict the PCDD/F concentrations in the flue gases from the flue gas chlorophenol concentrations, which corroborates the fact that chlorophenols are some of the principal PCDD/F precursors in waste incineration.

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Kuopio, April 2002

Päivi Ruokojärvi

ABBREVIATIONS

APD	air protection device
EDTA	ethylene diamine tetraacetic acid
ESP	electrostatic precipitator
FBC	fluidized-bed combustor
IARC	International Agency for Research on Cancer
K_{OW}	octanol-water partition coefficient
K_{PW}	particle-water partition coefficient
LFO	light fuel oil
MWI	municipal waste incineration
MSWI	municipal solid waste incineration
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PCDD/F	polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans
PCB	polychlorinated biphenyl
PIC	product of incomplete combustion
PLS	partial least squares or projection to latent structures
PVC	polyvinylchloride
TEQ	toxic equivalent quantity
RDF	refuse-derived fuel

ORIGINAL PUBLICATIONS

This thesis is based on the following publications referred to in the text by Roman numerals.

I Ruokojärvi P, Halonen I, Tuppurainen K, Tarhanen J, Ruuskanen J (1998): Effect of gaseous inhibitors on PCDD/F formation. Environmental Science & Technology 32, 3099-3103.

II Ruokojärvi P, Aatamila M, Tuppurainen K, Ruuskanen J (2001): Effect of urea on fly ash PCDD/F concentrations in different particle sizes. Chemosphere 43, 757-762.

III Ruokojärvi P, Asikainen A, Ruuskanen J, Tuppurainen K, Mueller C, Kilpinen P, Yli-Keturi N (2001): Urea as a PCDD/F inhibitor in municipal waste incineration. Journal of the Air & Waste Management Association 51, 422-431.

IV Ruokojärvi P, Tuppurainen K, Mueller C, Kilpinen P, Ruuskanen J (2001): PCDD/F reduction in incinerator flue gas by adding urea to RDF feedstock. Chemosphere 43, 199-205.

V Tuppurainen K, Ruokojärvi P, Asikainen A, Aatamila M, Ruuskanen J (2000): Chlorophenols as precursors of PCDD/Fs in incineration processes: Correlations, PLS modeling, and reaction mechanisms. Environmental Science & Technology 34, 4958-4962.

CONTENTS

1 INTRODUCTION

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) represent a class of tricyclic, almost planar aromatic compounds with 1 or 2 oxygen atoms and 1 to 8 chlorine atoms attached to the molecular backbone (Figure 1). Alltogether 210 possible PCDD/F congeners exist, with the congeners containing chlorine substituents in positions 2, 3, 7 and 8 being of special concern due to their extreme toxicity. In 1997 2,3,7,8-TeCDD, the most toxic congener of PCDD/Fs, was classified by the International Agency for Research on Cancer as carcinogenic to humans (IARC 1997).

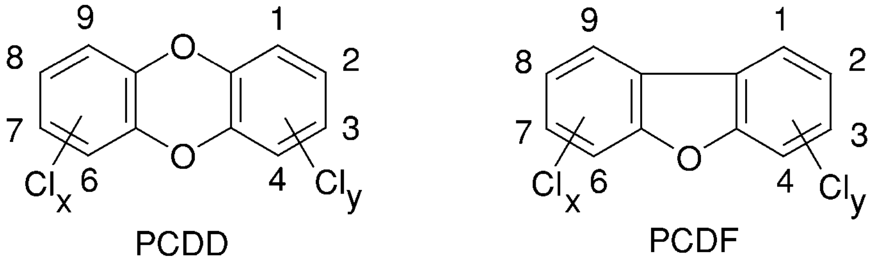

Figure 1. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs)

PCDD/Fs are unwanted byproducts formed in combustion processes and many chemical industrial processes and have never been produced intentionally (except for scientific purposes). After formation, once they are released into the atmosphere, they can be transported far from their original source. Due to their stability and lipophilicity, they accumulate in fatty tissues and in carbon-rich matrices such as soils and sediments. This is the reason why they have presently spread ubiquitously into almost all environmental compartments, including animals and humans.

The majority of PCDD/F emissions have been estimated to originate from combustion processes. Municipal solid waste incineration has been considered to be one of the major sources of polychlorinated dibenzo-*p*-dioxin and furan emissions, a fact that has sparked intensive debates among populations living adjacent to functioning or planned waste incineration facilities. However, with the proper processing, the problem of PCDD/F emissions from combustion can nowadays be controlled to a major extent.

Attempts to reduce PCDD/F emissions into the atmosphere have led to the use of different PCDD/F end of pipe -abatement technologies. As a consequence, the pollutants are removed from flue gases but the total PCDD/F amount entering the environment does not necessarily decrease in the process. As a result the PCDD/F containing waste - usually in the form of some kind of ashes recovered with a variety of air protection equipment- has to be handled further to avoid an additional burden on the environment.

In the present study, the prevention of PCDD/F formation has been studied with a pilot scale incinerator. Different chemical inhibitors were used to block the formation. The effects of different supply points, temperatures and process parameters were studied to better understand the factors influencing the PCDD/F formation and inhibition mechanisms during waste incineration. Special emphasis was put on the role of PCDD/F precursors in this process. The ultimate purpose was to find an easy to use, non-toxic and inexpensive inhibitor that in the future could be applied in full-scale plants.

2 REVIEW OF THE LITERATURE

2.1 Sources and fate of PCDD/Fs

A great many different combustion processes have been demonstrated to produce PCDD/Fs. Municipal solid waste incineration (MSWI) has been the major primary source of the PCDD/Fs emitted into atmosphere during the last decades (Brzuzy and Hites 1996, UNEP Chemicals 1999) (Table 1), but since closure of some old incineration facilities and the development of new air protection technologies in MSWI, also other sources have arisen as important sources.

Table 1. Global emissions for major PCDD/F sources to atmosphere (according to Brzuzy and Hites 1996)

Sources	Emissions (kg/yr)
Municipal waste incineration	1130
Biomass combustion	350
Ferrous metal production	350
Cement kilns (burning hazardous waste)	680
Cement kilns (no hazardous waste)	320
Secondary copper smelting	78
Medical waste incineration	84
Unleaded fuel combustion	1
Leaded fuel combustion	11
Total	**3000**

The European emission inventory (Quass et al. 2000) designated the same proportion for MSWI (30 % of the total emissions) as the study of Brzuzy and Hites (1996), with sinter plants and residential wood combustion being the next important sources.

Overall, the decreased PCDD/F concentrations emitted into the environment have led to decreasing ambient air concentrations during the last decades (Fiedler 1996). This has been a consequence of awareness of the problem of PCDD/F formation and activities designed to avoid emissions into the environment e.g. with better combustion conditions, advanced flue gas cleaning technologies and better burn-out of ashes and slags. The decreased emissions have subsequently led to a decrease in PCDD/F concentrations in biological matrices in the environment as well as in humans (Alcock and Jones 1996, Kiviranta et al. 1999, Liem and Zorge, 1995, Wittsiepe et al. 2000). However, since they are such highly persistant, bioaccumulative (log K_{ow} values 6.5- 9.3 (Paasivirta et al. 1999)) and lipophilic compounds (Shiu et al. 1988) they still can be found almost in all biological matrices on a global scale.

PCDD/Fs from primary sources are transmitted to other matrices, so called secondary sources (sludge, compost, soil etc.). PCDD/Fs tend to stay absorbed to organic carbon present in soil or particles (log K_{PW} 6.2-11.0 (Govers and Krop 1998)). However, re-entrainment from these sources is also possible for example in the case of lipophilic solvents, erosion or dredging but re-entrainment is not thought to play an important role as a global PCDD/F source (UNEP Chemicals 1999).

2.2 Formation mechanisms of PCDDs/PCDFs during incineration

Three main pathways have been proposed to explain the formation of PCDD/Fs during incineration (Shaub and Tsang, 1983, Vogg and Stieglitz 1986, Karasek and Dickson 1987)

- pyrosynthesis: formation in the gas phase at high temperatures
- *de novo* mechanism: formation from macromolecular carbon and chlorine at low temperatures
- formation from precursors

Previously it was thought that PCDD/Fs present already in the waste could survive the incineration process and pass into flue gases. However, it was later demonstrated that these compounds are destroyed at the temperatures present in combustion chambers (Vogg and Stieglitz 1986) and therefore they cannot be the sources of the high concentrations present in the flue gases.

The relative importance of these formation mechanisms has been a subject of debate, and is still controversial but the following order is considered to be most likely:

pyrosynthesis< *de novo*-mechanism< formation from precursors

The latter two mechanisms have been considered to be significant, and Altwicker and Milligan (1993), Dickson et al. (1992) and Lujik et al. (1994) have proved that formation from pentachlorophenol is 100 to 10 000 times faster than *de novo*-synthesis from macromolecular carbon. This indicates that the precursor reaction mechanism may dominate in the real incineration, although opposite claims have also been presented on the basis of results from kinetic modeling (Huang and Buekens 2001).

2.2.1 Pyrosynthesis

The key step in pyrosynthesis (i.e. homogenous gas phase formation) involves the dimerization of a phenol molecule and a phenoxy radical to PCDD. This gas phase formation of PCDDs during incineration has been calculated to be unlikely to occur at high temperatures (Shaub and Tsang 1983). Recently, however, attention has been drawn to the fact that model predictions from this mechanism have been several orders of magnitude lower than the actual measured dioxin formation (Sidhu et al. 1995). Huang and Buekens (1999) suggested after re-evaluation of the Shaub and Tsang model that the reason for the gap between the calculated and the measured formation is probably unknown reactions of PCDD formation in the model. The potential contribution of gas-phase reactions to PCDD formation might thus have been underestimated so far.

2.2.2 *De novo* mechanism

It has been shown that four basic elements are needed in PCDD/F formation: a carbon source (organic starting material), a chlorine source, the presence of oxygen and a metal catalyst.

The use of the term *de novo* synthesis has been somewhat indefinite. The term is often considered to refer to the combination of dissimilar starting materials such as elemental carbon and sources of oxygen, chlorine and hydrogen (Milligan and Altwicker 1993). Iino et al. (1999a) suggest a more accurate definition would be breakdown reactions of the carbon matrix.

Heterogenous formation of PCDD/Fs can be detected as a consequence of thermal treatment of fly ash itself, since all the elements needed for PCDD/F formation are present there. *De novo* synthesis occurs at low temperatures (250 – 450 °C) in the post combustion zone of the incinerator (Vogg and Stieglitz 1986, Vogg et al. 1987, Hagenmaier et al. 1987a). Recent evaluation of the literature data (Shin et al. 1999) reveals that maximum temperature of the PCDD/F formation is probably around 350 –400 °C, instead of the previously designated 300 °C.

Oxidation of carbon in the fly ash may serve as the first step towards the formation of PCDD/Fs (Vogg et al. 1987). Of course, the formation of PCDD/Fs and other organochloro compounds represent only minor byproducts, and most of the carbon (65-75 %) is oxidised to carbon dioxide (Schwarz and Stieglitz 1992). Fly ash matrix is a complex structure, and it has been found that the carbon morphology of the fly ash can have a marked influence on the *de novo* synthesis (Stieglitz et al. 1989, Jay and Stieglitz 1991). Huang and Buekens (1995) concluded that degenerated graphitic structures (activated carbon, charcoal, carbon black and soot) are oxidised to PCDD/Fs, whereas amorphous carbon and graphite sheets do not serve as a major source for the formation of chlorinated aromatic compounds. Once the *de novo* formation has started, the condensation reactions may take place either via precursors or from structurally distant reagents. Addink et al. (1995), Iino et al. (1999a, 1999b) and Weber et al. (2001) have proved that also anthraquinones, polyaromatic hydrocarbons and even aliphatic and monocyclic aromatic hydrocarbons are potential carbon sources for the formation of PCDD/Fs.

Both inorganic and organic chlorine are capable of serving as a chlorine source during incineration (Halonen et al. 1994), although certain differences between chlorine sources exist: e.g. some researchers have showed that NaCl is a relatively poor chlorine source (Addink and Altwicker 2001). The presence of catalysts is also essential for the formation of PCDD/Fs as they reduce the activation energies of condensation reactions thus making the PCDD/F formation possible. Copper was identified as the strongest catalyst (Vogg et al. 1987) and also other metal chlorides have been tested in this respect (Hinton and Lane 1991, 1992). $FeCl_3$ has also been found to catalyze PCDD/F formation (Stieglitz et al. 1990, Halonen et al. 1997). Copper (II) has catalyzed not only the *de novo* synthesis from carbon, but also from the aromatic ring condensation (Ullmann reactions) and the aromatic chlorination reactions. Also other metal oxides (Ni, Fe and Zn) have been proven to catalyze the PCDD/F formation from chlorophenol precursors (Gullett et al. 1992a).

Metal catalysts may be essential in the Deacon reaction, which is described by Hisham and Benson (1995) as:

(1) $CuCl_2 (s) \leftrightarrow CuCl (s) + ½ Cl_2 (g)$

(2) $2 CuCl (s) + ½ O_2 (g) \leftrightarrow CuO (s) + CuCl_2 (s)$

(3) $CuO (s) + 2 HCl (g) \leftrightarrow CuCl_2 (s) + H_2O (g)$

The net reaction for the Deacon reaction is

(4) $2 HCl + ½ O_2 \leftrightarrow H_2O + Cl_2$

Also other copper species promote this (4) reaction (Gullett et al. 1992a). Both Cl_2 and HCl in reaction (4) can indeed act as chlorinating agents for PCDD/Fs, but Cl_2 has been considered as a more efficient agent in this respect (Bruce et al. 1991).

An important factor affecting the PCDD/F formation is the amount of water present during formation of PCDD/Fs. It has been stated by several researchers that an increase in the amount of water in the system where fly ash is heated at around 300 °C leads to more PCDD/Fs being formed, and additionally, a shift towards a lower chlorinated congener pattern can be detected (Vogg et al. 1987, Ross et al. 1990, Stieglitz et al. 1990). However, Addink et al. (1995) did not observe any increase of PCDD/F formation in the presence of water and in several incineration tests in laboratory scale incinerators or real scale incineration of biosludges, the effect of water has been negligible (Fängmark et al. 1991, 1993, Halonen et al. 1993). Jay et al. (1991) reported a decrease in the amount of PCDD/Fs formed from charcoal and additives at 300 °C in the presence of water and similar results were obtained by Cains et al. (1997), who also noticed a shift towards lower chlorinated dibenzofurans when water was present.

The role of water in PCDD/F formation is probably based on several mechanisms: Water could act as an additional source of hydrogen or it could also be a source of hydroxyl radicals (Addink and Olie 1995a), which play an important role in the formation of PCDD/Fs as described later. Water may also favor the possible formation of HCl instead of Cl_2 in the Deacon reaction (4); then less free chlorine would be available for PCDD/F formation and thus an increase of water during incineration would inhibit PCDD/F formation (Addink and Olie 1995a). Water could also compete with possible precursors for adsorption to the fly ash surface (Addink and Olie 1995a). Water spray injection may act as an absorber of PCDD/Fs, and additionally cool the flue gases to temperatures which do not favor PCDD/F formation (Akimoto and Nito 1994). The ultimate affect of the water seems to depend on the PCDD/F formation conditions, for example it may depend on the starting materials for PCDD/F formation. In this kind of multivariate problem, even laboratory scale tests give contradictory results of the actual effect of water in PCDD/F formation.

Another important factor affecting the PCDD/F formation in flue gases is the particle size distribution of flue gas. The smallest particles (< 2.2 μm) have been shown to contribute most to the formation of chlorinated aromatics in flue gases (Fängmark et al. 1994, 1995). This is due to fact that smallest particles constitute most of the surface area, and heavy metals that can catalyze PCDD/F formation are enriched in the smallest particles (Fernandez et al. 1992). The fly ash build up of small particles during cooling of the flue gases should thus be avoided, if possible, to minimize PCDD/F formation in flue gases.

2.2.3. Formation of PCDD/F precursors (PICs)

As the carbon matrix begins to fragment, the *de novo* formation inevitably seems to form aromatic chlorinated structures (Froese and Hutzinger 1996a) which can further undergo copper-catalyzed coupling reactions into biphenyl structures (Ullmann I reaction) (Lippert et al. 1991) and finally into PCDDs/PCDFs. The formation of bisaryl ether compounds from halobenzenes and phenols (Ullmann II type reactions) is another important route as well when formation of halogenated biphenyls and PCDD/Fs is considered.

Since long reaction times (1-2 hours) are required for *de novo* synthesis, Froese and Hutzinger (1996a) state that there must also be a faster reaction route to these aromatic chlorinated structures. Formation products of incomplete combustion (PIC compounds) proceed by various radical mechanisms (the major reactants being •H, •OH, •O, •O_2H) and are greatest at approximately 750 °C. (Ballschmiter et al. 1988). The diversity of PICs varies along with the amount of oxygen in the combustion. High variability of possible PICs from the combustion reactions can be described with examples of the compounds produced from the combustion of 1,2-dichlorobenzene: chlorinated benzenes, chlorinated phenols, chlorinated biphenylenes, aromatic compounds and chlorinated polyaromatic compounds (Young and Voorhees 1991).

These fast heterogenous reactions are probably critical as they form the aromatic rings, which can further be converted into PCDD/Fs. Chlorobenzenes and chlorophenols were found to be formed from acetylene, HCl and metal catalysts at a temperature of 500°C (Froese and Hutzinger 1996a). Even aliphatic precursors have been found to form aromatic and chlorinated aromatic structures (Addink et al. 1995, Froese and Hutzinger 1996a,b, Lenoir et al. 2001).

Some aromatic compounds have arisen as the most important immediate PCDD/F precursors: chlorobenzenes, polychlorinated biphenyls, polychlorinated diphenyl ethers and chlorophenols:

The formation of **chlorobenzenes** may proceed via a radical based mechanism or by combination of chlorine and chlorophenyl radicals (Tuppurainen et al. 1998). Lenoir et al. (2001) suggest that a metallacyclization mechanism can produce hexachlorobenzene from acetylene.

Biphenyl structures from Ullman reaction may be chlorinated to form **polychlorinated biphenyls**. Also, as two chlorophenyl radicals combine, PCBs are formed and can be further oxidised to PCDFs (Ballschmiter et al. 1988).

Diphenyl ethers from Ullmann II reaction oxidise into hydroxylated diphenyl ethers and eventually produce PCDDs or PCDFs (Lippert et al. 1991). Polychlorinated diphenyl ethers may be formed from chlorophenols and chlorobenzenes (Ballschmiter and Swerev 1987) followed by a ring closure to PCDD/Fs.

Formation of **chlorophenols** from PICs probably occurs through aryl compounds, aromatic rings or substituted aromatics (e.g. chlorobenzenes) (Ballschmiter and Swerev 1987, Ballschmiter et al. 1988).

2.2.4 PCDD/F formation from chlorophenol precursors

The decisive role of chlorophenols as PCDD/F precursor has been well established in the literature. Chlorophenol conversion to PCDDs and PCDFs has been thoroughly demonstrated (Dickson et al. 1989a, Born et al. 1993, Rappe et al. 1996, Weber and Hagenmaier 1999, Hell et al. 2001). The most abundant PCDD congeners have been shown to be condensation products of the thermodynamically most stable chlorophenols (2,4,6-TCP, 2,3,4,6-TeCP and PCP). These condensation reactions are postulated to occur via Smiles rearrangement, with a dioxaspiro-type compound (Figure 2) as an intermediate (Born et al. 1993).

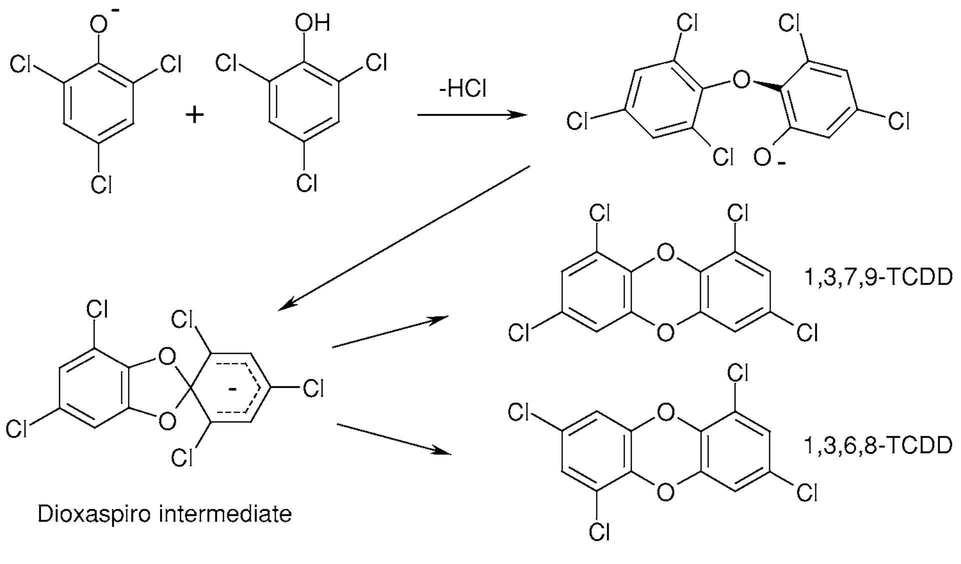

Figure 2. Dioxaspiro pathway for the formation of PCDDs (According to Tuppurainen et al. 1998)

The formation of the stable tricyclic ring structure has been rationalized with the coupling of neutral resonance-stabilized chlorophenoxy-radicals (in the gas phase) (Wiater et al. 2000) or chlorinated phenolate anions (in fly ash mediated surface reactions) followed by oxidative ring closing (Tuppurainen et al. 1996). Weber and Hagenmaier (1999) postulated that after two phenoxy radicals dimerize, polychlorinated dihydroxybiphenyls can be produced as intermediates of PCDFs. PCDDs are formed in the gas phase via *ortho*-phenoxyphenols, with both the chlorine atom and the hydrogen atoms capable of substitution. Recent *ab initio* calculations support this mechanism (Okamoto and Tomonari 1999).

2.2.5 Connective theory for formation of PCDD/Fs

When the *de novo* formation has started, the condensation reactions seem to take place either via precursors or from structurally distant reagents. Lujik et al. (1994) proposed that PCDD formation from the macromolecular carbon proceeds via a chlorophenol intermediate, indicating that the *de novo* synthesis and precursor mechanisms are closely related. This proposition has also gained support from other researchers (Froese and Hutzinger 1996a, Tuppurainen et al. 1998). This reasonable theory combines the most important mechanisms considered for formation PCDD/Fs (i.e. *de novo*- and precursor theories), and also takes into account the previously discussed formation from aliphatic precursors (Figure 3).

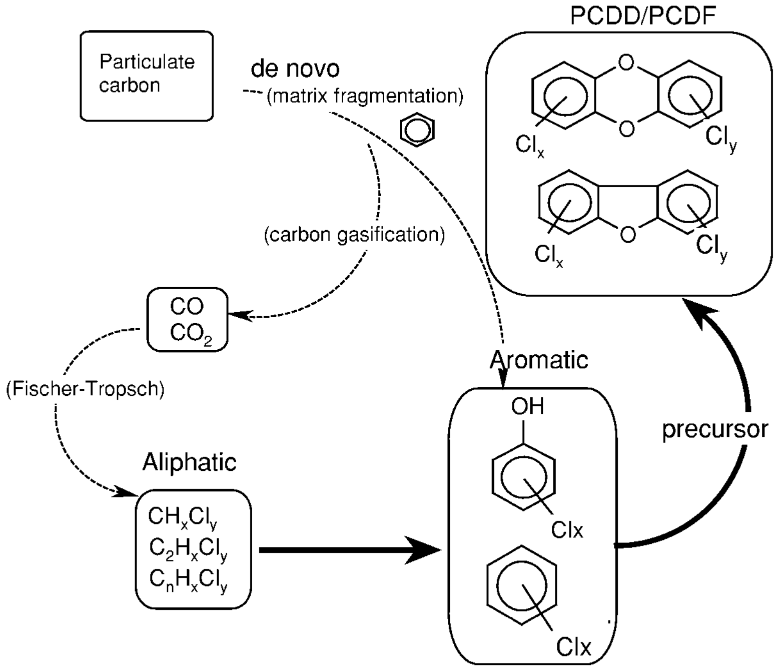

Figure 3. Potential PCDD/F formation routes described in the on literature (According to Froese and Hutzinger 1996a)

2.3 Abatement technologies for PCDDs/PCDFs in municipal waste incineration

Emission control techniques for PCDDs/PCDFs have been studied mainly with the emphasis on removal of PCDD/Fs from flue gases with end-of-pipe techniques (Buekens and Huang 1998). Other possible emission control techniques include control of waste composition, improvement of combustion conditions and prevention of PCDD/F formation in the postcombustion zone.

2.3.1 Techniques for removal of PCDD/Fs from flue gases

Around 1990, several European countries issued a stringent emission limit of 0.1 ng-TEQ/Nm^3 PCDD/F for municipal solid waste incinerators. The technologies to achieve this limit have been under active development. A number of devices have been tested as end-of-pipe techniques: electrostatic precipitators (ESP), bag filters, scrubbers, adsorbents and combinations of these devices. The most promising techniques have been found to be a combination of scrubber, bag filter and activated carbon injection.

Fabric filters and electrostatic precipitators have been used to reduce the amounts of PCDD/Fs in flue gases (Musdalslien et al. 1991, Hunsinger et al. 1997, Sam-Cwan et al. 2001) up to 95 %, but in several studies they have also been observed to increase the PCDD/F emissions (Yamamoto et al. 1989, Takeshita et al. 1992, Sam-Cwan et al. 2001). Wet gas scrubbing (Wevers et al. 1992), and combinations of wet scrubber and fabric filter (Marklund et al. 1992), dry scrubber and fabric filter (Hahn et al. 1992) and spray absorber and ESP (Düwel et al. 1991) have been used to decrease PCDD/Fs. On the other hand, wet gas scrubbers have also been shown to increase the PCDD/F concentrations (Vogg et al. 1994, Sam-Cwan et al. 2001). Also catalytic decomposition of PCDD/Fs has been recently used successfully to eliminate PCDD/Fs from flue gases. However, the combination of a scrubber and a bag filter together with activated carbon injection has turned out to be the most effective technique for PCDD/F emission control.

Three possible ways of supplying active carbon into the process exist: the entrained-flow, moving-bed and fixed-bed process. In the entrained-flow, activated carbon is injected before the bag filter, and after it reaches the filter it builds up a PCDD/F adsorbing carbon layer on the filter. At certain time intervals, the layer is then cleaned off the bag filter together with other particulate material. With this technique, PCDD/F reductions of 96 % (Ruegg and Sigg 1992) and 97 % (Blumbach 1994) have been achieved. Activated carbon can also be injected with lime-slurry to neutralize HCl (Lerner 1997). The disadvantage in the entrained-flow method is the high consumption of activated carbon, which increases the costs of the method. In the fixed-bed method, flue gases pass over a fixed bed of active carbon, which is replaced at certain time intervals. Removal efficiencies of 83 % have been achieved with this process (Buekens and Huang 1998). In the moving bed method, the flue gases pass a bed of active carbon, and fresh carbon is fed to the top of the bed while spent carbon is removed from the bottom of the bed. Removal efficiencies of close to 99 % have been achieved with this method. (Yamaguchi et al. 1994).

A promising new technique for PCDD/F removal from flue gases is the catalytic decomposition of PCDD/Fs. Selective catalytic reduction (SCR) has previously been used for NO_x reduction in coal-fired power plants. The catalyst is mostly composed of Ti, V and W and is usually operated at 300-400 °C (Boos et al. 1992). Liljelind et al. (2001) studied PCDD/F removal with a Ti/V oxidative type catalyst also below 100 °C, and noted the PCDD/F removal to occur at these temperatures by adsorption and at temperatures between 100 and 230 °C by destruction (either by C-C bond breakage or loss of substituents), with efficiencies up to 99.9 %. Pt and Au supported catalysts have been claimed to be efficient at low temperatures as well. In municipal waste incineration, the SCR unit can be installed only after other flue gas cleaning devices (tail end), because high concentrations of heavy metals will poison the catalyst (Buekens and Huang 1998).

2.3.2 Prevention of PCDD/F formation in incineration process

Control of waste composition

The control of waste composition restricts the emission of PCDD/Fs during waste incineration if the compounds necessary for PCDD/F formation (metals and chlorine containing material) can be separated from the waste stream. Material from household waste can be processed into refuse derived fuel (RDF) in the waste treatment plant. During the separation phases metals and e.g. plastics (especially chlorine containing PVC) can be separated from the waste. The correlationship between PVC in municipal waste and the emissions of PCDD/Fs in MSWI has been a matter of debate, and some researchers have found a correlation between chlorine content of the waste or HCl in the flue gases and PCDD/F emissions (Takeshita and Akimoto 1992, Gullett et al. 1994, Wikström et al. 1996) while others did not (Fängmark et al. 1991, Lenoir et al. 1991). Manninen et al. (1996) did not find an increase in total PCDD/F emissions when PVC containing waste was co-combusted with peat or coal. However, multivariate analysis of the data revieled that chlorine concentrations of the fuel correlated with PCDFs. Probably, the most important factor with respect to PCDD/F emissions is the removal of metals catalyzing the PCDD/F formation and alteration of waste into more favourable combustion condition (dry pellets).

Improvement of combustion conditions

Combustion conditions have a major influence on PCDD/F formation in incinerators. Although PCDD/Fs are mainly formed in the post-combustion zone; the reactants or precursors are already formed in the furnace. Optimization of combustion parameters may thus play a major role in reducing the emissions of PCDD/Fs.

Several correlation studies between combustion parameters and PCDD/F formation have been conducted with quite contradictory results. Vogg et al. (1987), Addink et al. (1995) and Pekarek et al. (2001) all observed in laboratory conditions that the amount of PCDD/Fs formed increased when the oxygen concentration was increased from 0 to 10 %. Johnke and Stelzner (1992) concluded that in MSWIs excess oxygen levels (from 11 to 13 %) increase the PCDD/F formation. Gullett et al. (1994) suggested that according to their results from a pilot-scale combustor, intermediate levels of oxygen (4-7 %) yield larger concentrations of PCDD/Fs. Song et al. (1992) claimed that oxygen levels of 2-8 % did not affect the PCDD/F formation in tests conducted at a hazardous waste incineration plant. Similar conclusions were drawn by Fängmark (1993) and Fängmark et al. (1991, 1993) from their laboratory-scale fluidized-bed incinerator tests, where the O_2 concentrations varied from 5-7 %. Lenoir et al. (1991) described a negative correlation between levels of O_2 (2.7–11 %) and PCDD/Fs in fluidized bed incinerator. Their results could be attributed to incomplete combustion conditions at lower O_2 levels, which would favour formation of PICs and, finally, PCDD/Fs. In conclusion, it seems probable that different types of incinerators give varying results in this respect, and since formation of PCDD/Fs is a multivariate process, it is hard to define general correlationships of PCDD/Fs with oxygen concentrations.

A number of different incinerator designs exist, from grate-type incinerators to fluidized bed types, but in general, combustion is expected to be more efficient with proper mixing and high turbulance. Installation of nose sections and secondary air nozzles into a MSWI furnace had a major impact on reducing PCDD/F formation (Hiraoka and Okijama 1994). Even if the PCDD/F concentrations in the furnace outlet are arranged to be reduced to extremely low levels, formation of these compounds in the post-combustion zone is still possible (Kato et al. 1994). Therefore, special attention should be paid to the composition after the furnace. The heat exchange surfaces e.g may gather flue gas particles contributing the PCDD/F formation under favourable conditions, and during the soot blowing, considerable concentrations of PCDD/Fs may be released in the process (Johnke and Stelzner 1992).

As the temperature range for PCDD/F formation is quite broad (250-450 °C), the temperature and the residence time profile of the flue gases is crucial when considering reduction of PCDD/F formation in incineration. According to the studies of Fängmark et al. (1993) conducted in a laboratory-scale fluidized bed combustor, the flue gas temperature profile is the most important factor affecting the PCDD/F formation. If flue gas is rapidly cooled down to temperatures below 260 °C, the PCDD/F formation is notably suppressed. At water quenching, the stack gas is quickly cooled to temperatures below 200 °C by spraying water or steam (Reimann 1992). Water quenching has been found to be more effective in reducing PCDD/Fs compared to water cooling (Vogg et al. 1992). The key parameter, however, is the cooling rate of the flue gas. In a waste heat boiler, the flue gas cooling rates are in the range of 100-200 °C/s and PCDD/F concentration levels of 5 ng-TEQ/Nm^3. A cooling rate of 1500-1000 °C/s is required to achieve a PCDD/F level 1 ng-TEQ/Nm^3 (Buekens and Huang 1998). This might be difficult in practice, since with water quenching, much energy is lost.

Inhibitors of PCDD/F formation

Inhibitors can be used to reduce PCDD/F formation, and the problem of PCDD/F-containing waste can be avoided. A variety of chemicals, both inorganic (calcium oxide, ammonia, calcium cyanamid, ammonium sulfide, sodium sulfide, sodium thiosulfate, sodium ammonium hydrogen phosphate, hydrogen sulfide and sulfur) and organic compounds (pyridine and quinoline coal distillation fractions, hexamethyl silazane, ethylene glycol, amines and amino-group-containing compounds and mixtures of NaOH and KOH with amines) have been shown to inhibit PCDD/F formation (Dickson et al. 1989b, Gullett et al. 1992b, Naikwadi et al. 1993, Addink et al. 1993, 1996, Tuppurainen et al. 1999, Samaras et al. 2000).

Alkaline sorbents have been used for control of acidic gases in combustion. CaO inhibited PCDD/F formation in a laboratory scale test (Naikwadi and Karasek 1989), but in full-scale incinerators, the results have been contradictory: lime ($Ca(OH)_2$) and dolomite decreased PCDD/F concentrations, but $Mg(OH)_2$ and CaO increased them. The effect of these chemicals could be based on their effect on the Deacon reaction (4) e.g. $Ca(OH)_2$ would decrease HCl concentrations (5).

(5) $Ca(OH)_2 + 2\ HCl \rightarrow CaCl_2 + 2\ H_2O$

This decline in HCl has actually been observed in the tests, but since the PCDD/F concentrations were not subsequently decreased, HCl was obviously not a controlling factor with respect to PCDD/F formation in these tests (Buekens and Huang 1998).

Sulfur containing compounds have been widely studied as PCDD/F inhibitors. Stieglitz and Vogg (1987) studied hydrogen sulfide, Addink et al. (1993, 1996) tested sodium sulfide (Na_2S) and sodium thiosulfate ($Na_2S_2O_3$). Samaras et al. (2000) examined amidosulfonic acid (ASA), hydroxylamine-*O*-sulfonic acid (HOSA), sulfamide and elemental sulfur, and Ogawa et al. (1996) evaluated sulfur dioxide and elemental sulfur. They all found that decreasing amounts of PCDD/Fs were formed when there was an increasing amount of inhibitor present in their laboratory scale tests. Bechtler et al. (1996), however, noted that elemental sulfur actually increased the formation of PCDD/Fs in their laboratory tests. Object to the findings of Bechtler et al. (1996), Griffin (1986) suggested that low PCDD/F emissions from coal combustion would be a consequence of high sulfur concentrations in the coal, where the sulfur dioxide formed from the combustion of sulfur would react with chlorine to produce HCl which would chlorinate the aromatic compounds less effectively (6):

(6) $SO_2 + Cl_2 + H_2O \rightarrow SO_3 + 2\ HCl$

Gullett and co-workers (1992b) suggested that sulfur reduces the catalytic activity of Deacon reaction catalysts as follows (7):

(7) $CuO + SO_2 + \frac{1}{2}\ O_2 \leftrightarrow CuSO_4$

A third possible mechanism is that presence of SO_2 will sulfonate the phenolic PCDD/F precursors and in this way prevent the chlorination and biaryl synthesis or promote the formation of polychlorodibenzothiophenes and polychlorotrianthrenes, the sulfur analogues of PCDDs and PCDFs (Gullett et al. 1992b).

In full-scale incinerators, addition of sulfur compounds into the boiler section (SO_2 concentrations from 200 to 2000 mg/m^3, Johnke and Stelzner 1992) and S-containing lignite or S-containing coal among the fuel feed (Lindbauer et al. 1992, Frankenhaeuser et al. 1993, respectively) has resulted in a decline in the flue gas PCDD/F concentrations. However feeding SO_3 and SO_2 in the economizer sections of an incinerator did not reduce the amounts of already formed PCDD/Fs (Lindbauer et al. 1993).

Ammonia has been used for NO_x reduction, where it reduced NO into N; and its effect on the formation of PCDD/Fs has been studied both at the laboratory scale (Vogg et al. 1987) and in full-scale incinerators (Takacs and Moilanen 1991, Takacs et al. 1993). NH_3 proved to be an efficient PCDD/F formation inhibitor in the studies of Vogg et al. (1987), Takacs and Moilanen 1991 and Takacs et al. 1993. Johnke and Stelzner (1992), however, did not find any reduction when 3000 mg/m^3 SO_2 was injected into the boiler section. The mechanism of action has been postulated to be the suppression of the catalytic activity of fly ash with ammonium, but no mechanistic details have been offered so far.

Amines and amino-group-containing compounds (triethylamine, triethanolamine, ethanolamine, 3-aminopropanol, monoisopropanolamine, EDTA (ethylenediaminetetra-acetic acid), mixtures of sodium hydroxide and potassium hydroxide with triethanolamine, urea) have been especially successful in laboratory scale studies in inhibiting PCDD/Fs, especially from aromatic precursors (Dickson et al. 1989b, Naikwadi et al. 1993, Addink et al. 1993, 1996). These compounds have caused PCDD/F reductions of close to 100 % in laboratory scale studies. Some mechanisms have been proposed, i.e. they are thought to form complexes with metals in the fly ash, although precise mechanisms remain to be elucidated. In pilot scale tests, injection of urea into flue gases at 720 °C (0.5 % urea of the fuel feed) resulted in a 70 % reduction of PCDD/F concentrations (Tuppurainen et al. 1999).

In summary, various inhibitors have been successful in preventing the PCDD/F formation. However, only a few inhibitors have been tested in real scale incinerators. The ideal inhibitor for a real-scale waste incinerator would be a compound with low-cost, non-toxicity and easy to use. Such a compound has still to be discovered.

3 AIMS OF THE PRESENT STUDY

The aim of this work was to find suitable inhibitors for prevention of PCDD/F formation during waste incineration and to specify the role of the most important factors affecting the inhibition process.

The detailed aims covered in the present work were:

- to compare the effect of different inhibitors on PCDD/F formation during incineration in pilot plant
- to investigate the role of particle size distribution of flue gas on the inhibition of PCDD/Fs
- to find the most important parameters affecting the PCDD/F inhibition in waste incineration
- to clarify the relationship between chlorophenols and PCDD/Fs during formation and inhibition of PCDD/Fs

4 MATERIALS AND METHODS

4.1 Experimental set up

The tests were carried out in a 50 kW pilot scale plant (Figure 4), which consisted of an oil burner or stoker burner, and a furnace from which the flue gases were directed through a delay chamber and economiser to the stack.

The fuel in the first part of the tests was light heating oil, with a feeding rate of 4.7 l/h, and it was spiked with tetrachloroethylene as a chlorine source (0.5 % chlorine of fuel mass). Copper nitrate (also 0.5 % as copper of the fuel mass) as a source of copper was added to the flue gases just after the furnace. The addition of copper and chlorine was performed in order to increase the PCDD/F levels to the levels corresponding to MSW incinerator emissions.

In the second part of the tests, the fuel was pelletized refuse derived fuel (RDF) with a feeding rate of 10.5 kg/h. The pellets consisted of mixture of household waste and packaging waste from industry (1:1). RDF was analysed to have a heating value of 22 MJ/kg, a chlorine content of 0.5 % and a copper content of 0.54 %.

The four gaseous inhibitors used in the tests, i.e. sulfur dioxide (SO_2), ammonia (NH_3), dimethylamine (DMA) and methyl mercaptan (MM), were selected due to results from laboratory tests published in the literature and were all purchased from AGA with purity of >99.0 %. Gaseous inhibitors were sprayed into flue gases at two locations: after the furnace at 670 ° C and before the economizer at 410 °C. The solid inhibitor, urea, was selected due to our previous test results (Tuppurainen et al. 1999) and was purchased from Merck, with purity of > 99 %. In first part of the urea tests, urea was dissolved in de-ionized water and injected at different concentrations into the flue gases just after the furnace at approximately 700 °C. In the second set of tests, three different levels of concentrated urea-water solution were mixed into the RDF prior to incineration.

The residence time of the flue gas between the furnace and the stack could be adjusted by directing the flue gases through different routes in the delay chamber. For the longest residence times, detours were made for the flue gases using partitions in the delay chamber.

The flue gas temperatures at different locations of the pilot plant (Figure 4) were monitored through the tests.

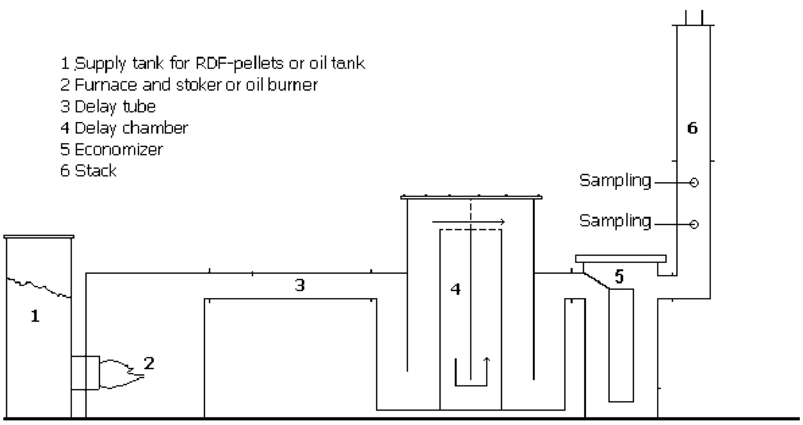

Figure 4. The pilot incinerator used in tests

4.1.1 Flue gas analysis

The flue gas parameters O_2, CO, CO_2, NO, and in some tests also SO_2, were analysed continuously during the tests. Additionally, in part of the tests, NO_2, HCl and hydrocarbons were also analysed. The amount of water was measured by condensing it at the PCDD/F sampling. Continuous flue gas sampling was adopted from Finnish SFS 3869 standard (1982). HCl-samples were absorbed into 0.1 M sodium hydroxide and analyzed by ion chromatography by Technical Research Centre of Finland (VTT). NO_2, HCl and hydrocarbon sampling (IV) was carried out with Gasmet FT-IR-analyzer by Technical Research Centre of Finland.

In one set of test runs, PCDD/F concentrations were analyzed in different particle size fractions. Particulate samples were taken with a five–stage modified Bird&Tole Cascade Centripeter, whose cut-off values varied from < 1.6 µm to > 52 µm. The filters for each stage were weighed before and after sampling, after conditioning them at constant temperature and humidity (21±2°C; 50±5 %, respectively), and analyzed by the procedure described later.

4.1.2 PCDD/F and chlorophenol sampling

Flue gas sampling protocol for chlorophenols and PCDD/Fs was modified from the European PCDD/F sampling standard EN 1948:1(1996). The most important difference between the sampling method described here and the European standard, was that no $^{13}C_{12}$ labelled sampling standards were spiked into our sampling device, since these $^{13}C_{12}$ labelled PCDD/F congeners were already present in our internal standard solution which is added during the extraction phase. Before each sampling, the burner was used for approximately 4 h at the stated conditions. After PCDD/ PCDF/chlorophenol sampling

(~3 h) the burner was further used without additives for 2 h to avoid possible memory effects. Particles of the flue gas sampling were collected isokinetically in a glass fiber filter (Schleicher & Schuell), which was kept at 120 °C during sampling to prevent water from condensing on the filter. Then condensation water was removed from the sample stream, and subsequently the gas phase was collected in XAD-2 resin (Amberlite, 20-50 mesh). All the PCDD/F and chlorophenol samples were taken in duplicate simultaneously from the stack, and the results were reported as mean values of these duplicates.

4.2 PCDD/F and chlorophenol analysis

The gaseous phase and particle phase were extracted separately in a Soxhlet apparatus for 20 h after addition of 16 $^{13}C_{12}$- labelled 2,3,7,8-substituted PCDD/F compounds and 2,4,6 –tribromophenol as an internal standard for chlorophenol analysis. Chlorophenols were then extracted with 0.1 M potassium carbonate, acetylated with acetic anhydride and, finally, extracted with hexane. Hexane was analyzed by gas chromatography/mass spectrometry (HP 5890 or 6890 gas chromatograph with HP 5970 or 5973 mass selective detector). PCDD/Fs were purified by shaking the extract with concentrated sulfuric acid and eluting through microcolumns (Al_2O_3, eluted with 2 % dichloromethane in hexane followed by 50 % dichloromethane in hexane). After evaporation and addition of recovery standard, the sample was analyzed with HRGC/HRMS (VG 70 250 SE), operating the MS at a resolution of 10000 (Ruokojärvi et al. 1995a,b).

4.3 Computational methods

Since the study composed of multivariate data, PLS (partial least-squares regression) was used as a method for relating two data matrices, which are usually described as X (independent variables) and Y (dependent variables), to each other by linear multivariate model. PLS breaks down X and Y data matrices into new latent variables (PLS components) and creates a predictive relationship between them. PLS is able to analyze data with many noisy, collinear and even incomplete variables in both X and Y matrices, and it has the property to improve its precision with the increasing number of relevant X variables (Geladi and Kowalski 1986, Wold et al. 1998).

The optimum number of PLS components is determined by cross-validation. Leave-One – Out crossvalidation proceeds by omitting one sample of the input data, and then developing a number of parallel models from reduced data with one of the samples deleted. The PLS model is then rederived, and Y values of the omitted sample are predicted. The cycle continues until all Y values have been predicted once. The cross-validated correlation coefficient Q^2 is calculated from predicted dependent variables, observed dependent variables and mean of observed dependent variables. The final, non-cross-validated model is derived using the optimum number of PLS components. The statistical significance of the model is evaluated with conventional parameters: correlation coefficient r^2, standard error SE, and F statistic.

PLS modeling was carried out using the Molecular Spreadsheet facility of the SYBYL molecular program package (SYBYL, Tripos, 1699 South Hanley Road, St. Louis, MO 63144) with the Leave-One-Out crossvalidation and Autoscaling options. Preliminary correlation analysis was performed with the MATLAB program package (The MathWorks, 24 Prime Park Way, Natick, MA 01760-1500).

4.4 Kinetic modeling of urea decomposition

The calculations for the conversion of urea were performed for ideal plug flow conditions at atmospheric pressure by Åbo Akademi University, Process Chemistry Group. Urea was represented by equal molar amounts of NH_3 and HNCO. The base reaction mechanism used consisted of 199 elementary gas-phase reactions describing the $CO/NH_3/HCN/NO/O_2$ system (Aho et al. 1995). The thermodynamic data for the elementary scheme were taken from Kee et al. (1990) and Glarborg et al. (1993).

5 RESULTS

5.1 Effect of different inhibitors

The effect of different inhibitors on PCDD/F flue gas concentrations during incineration can be seen in Figure 5. The feeding temperature of the inhibitor in these tests was 670 – 1050 °C (the latter figure for the furnace temperature when urea was added among the fuel). Only tests with higher feeding temperatures are included in Figure 5 to assure comparability. Both gaseous inhibitors (SO_2, NH_3, dimethylamine (DMA) and methyl mercaptane (MM)) and urea, either injected into flue gases or fed among the fuel, were successful in lowering the total PCDD/F concentrations in the flue gases and resulted in PCDD/F reductions of 50-90 %. Total PCDD/F concentration in the reference runs (no use of inhibitors) varied throughout the tests from 135 to 852 ng/Nm^3 (2-28 TEQ/Nm^3).

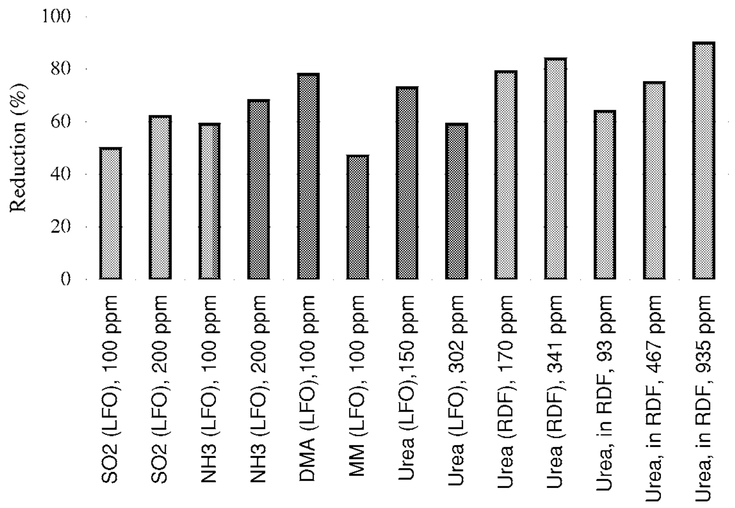

Figure 5. PCDD/F reductions with tested inhibitors (Papers I-IV).

The results are not fully comparable since the incineration conditions (temperatures of the inhibitor feeding point and concentrations of inhibitor) vary between the tests. It can, however, be noted that the PCDD/F reduction was considerable with all of the studied inhibitors.

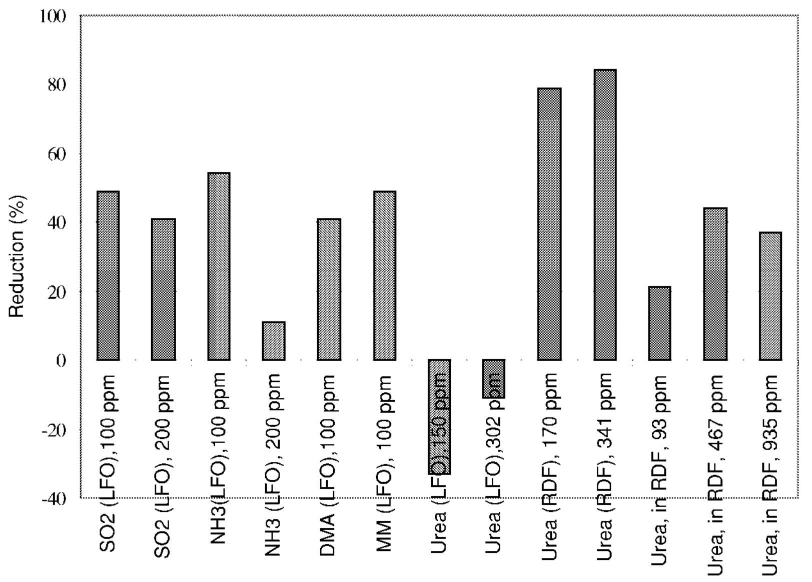

Figure 6. Chlorophenol reductions with tested inhibitors (Papers I-IV)

The effect of inhibitors on chlorophenols was somewhat more contradictory (Figure 6). The highest reductions were observed in the test series with RDF as the fuel and liquid urea as the inhibitor (chlorophenol reduction 79 and 84 %) whereas the test series with light fuel oil as fuel and liquid urea as inhibitor resulted in no reduction, or in fact even a slight increase in the chlorophenol concentrations.

5.2 Effect of feeding point temperature

In the first test series with gaseous inhibitors (Paper I) it was observed that as the inhibitors were injected earlier (i.e. at a higher temperature, 670 °C) into the flue gases, the PCDD/F reductions were higher compared to the tests where they were injected at a lower temperature, 410 °C. At 410 °C and 670 °C, the reductions were 15 and 50 % for sulfur dioxide, 56 and 59 % for ammonia, and 56 and 78 % for dimethylamine, respectively. The concentration of each gaseous inhibitor was 100 ppm in these tests.

The impact of inhibitors on the flue gases at different temperatures is also clear for the chlorophenols. Chlorophenol reductions at 410 °C and 670 °C were –13 and 49 for sulfur dioxide, 0 and 54 % for ammonia and 38 and 41% for dimethylamine, respectively. In conclusion, no inhibitory effect could be observed for chlorophenols with SO_2 and NH_3 when inhibitors were injected into the flue gases at the lower temperature. It can further be seen (Papers III, IV) that the PCDD/F reductions were of the same magnitude irrespective of whether urea was fed among the flue gases after the furnace at 730 °C or either into the furnace with the fuel at 900-1000 °C (Figure 5). At appropriate conditions , urea decomposes rapidly (< 1 s) into NH_3 and HNCO, which are then further broken down. When the conditions change enough (most importantly in this case: temperature decreases) urea molecules may stay intact through the process.

5.3 Effect of inhibitor concentration

The effect of inhibitor concentration on PCDD/F and chlorophenol concentrations was tested both with gaseous and liquid inhibitors (Papers I-IV). As seen in Figure 5, the PCDD/F reduction increased when the amount of inhibitor increased except in the urea tests with LFO as a fuel. In this case there was a slight decrease in PCDD/F reduction when the amount of urea fed into the flue gas was doubled.

For chlorophenols, the results were not as clear as for PCDD/Fs (Figure 6). An increase in the amount of the gaseous inhibitor did not necessarily lead to an increase in the chlorophenol reduction in flue gases. Only for tests with urea as inhibitor did the chlorophenol reductions increase as the amount of the inhibitor increased. However, the reductions in general were moderate compared with the PCDD/F reductions.

The tests with liquid urea sprayed into flue gases (with LFO as fuel) showed that no significant further reduction in PCDD/F levels was achieved when 0.5 % urea concentration was doubled to 1.0 % urea in the fuel feed. The predicted decomposition under the test conditions in the furnace is very fast (Papers III and IV). The lower the concentration of urea at the beginning of the decomposition, the faster the decomposition proceeds.

5.4 Effect of flue gas residence time

The effect of flue gas residence time on behaviour of urea inhibitor was investigated with three residence times (4, 7, and 9 s, referred to as shortest, medium and longest residence times)(Paper III). Refuse-derived fuel was used as the fuel in these tests. With the shortest residence time, no reduction in PCDD/F concentrations could be observed compared to the reference tests with plain water addition. With the shortest residence time, the reaction time and the amount of the inhibitor were apparently too short to reduce the amount of PCDD/Fs in the flue gases. In fact, the PCDD/F concentrations were higher after urea addition compared to with plain water addition. With medium residence, PCDD/F reduction occurred only with 0.24 and 0.5 % urea addition (reductions of 24 and 39 %, respectively), but was negative for the smallest urea addition, 0.05 %. With the longest residence time, the PCDD/F concentrations were remarkably lower with urea additions compared to the reference test (PCDD/F reductions 60-84 %). In conclusion, PCDD/F reductions were best when there was a high concentration of urea injected and a long reaction time in the flue gas.

5.5 Effect of inhibitor on gaseous phase and particle phase

The effect of inhibitors on the gaseous phase and particle phase varied throughout the tests. In tests with gaseous inhibitors, gas/particle distribution of PCDD/Fs was 0.5 for the reference tests, and with the use of inhibitors increased substantially, so that the gas/particle ratio of PCDD/Fs at highest was 43 for dimethylamine. In all of the other tests with urea, the PCDD/F concentrations were greatest in the particle phase: over 90 % of the PCDD/Fs were present in the particle phase. The gas/particle ratio of PCDD/Fs, however, increased with the use of inhibitors.

In the test with gaseous inhibitors (Paper I), the PCDD/F reduction occurred almost entirely in the particle phase and varied from 20 % (SO_2, 100 ppm, lower input temperature) to 98 % (DMA, 100 ppm, lower input temperature). The PCDD/F reductions in the gas phase were less than 20 %, except for 100 ppm DMA injected at the higher temperature, where the PCDD/F reduction was 42 %.

In tests with urea input into flue gas with LFO as fuel PCDD/F reductions were greatest in the particle phase (53-80%) and very moderate for the gaseous phase (11-29 %)(Paper II). In the tests with liquid urea input into flue gases with RDF as fuel, the PCDD/F reductions for the longest residence time varied from 54 to 67 % in the particle phase and 66 to 95 % in the gas phase (Paper III). When the urea was fed among the RDF, the PCDD/F reduction for the particle phase varied from 65 to 93 % and for the gas phase from 39 to 47 % (Paper IV).

Since it has been proved that fly ash particles of submicron size are the main contributors to the levels of chlorinated aromatics in the flue gases (Fängmark et al. 1994, 1995) and the role of the particle phase also proved to be of such importance in our tests, a series of tests were performed to investigate the effect of urea on PCDD/F particle size distribution (II). Over 50 % of the particle mass and over 50 % of the PCDD/Fs were found in the smallest size fraction with a particle diameter < 1.6 µm. Urea injections (0.1 % and 1.0 % of the fuel feed) resulted in PCDD/F reduction in all size classes. However, the reduction with 0.1 % urea in the smallest particle size class was not as good as for other size classes or for the particle size classes with 1 % urea. This indicates that if the amount of inhibitor is not high enough, the reduction is insufficient in the smallest particle sizes with the greatest surface area. No other significant differences could be observed in PCDD/F reductions between different particle size classes.

5.6 Effect of inhibitors on PCDD/PCDF ratio and PCDD/F congener distribution

The effect of inhibitors on PCDD/PCDF ratio and PCDD/F congeners is summarized in Table 2.

Table 2. The effect of inhibitors on PCDD/F ratios and congener patterns

TEST	**PCDD/PCDF ratio (reference tests/with inhibitors)**	**Dominating congeners: reference test**	**Dominating congeners: use of inhibitors**	**Effect of inhibitors on congener distribution**
Gaseous inhibitors (I):				
SO_2	0.6/0.4-0.5	HpCDF, TeCDF OCDF	OCDF, HpCDF, OCDD	no clear effect
NH_3	0.6/0.2-0.5	HpCDF, TeCDF OCDF	TeCDF, PeCDF	dechlorination of PCDFs
DMA	0.6/0.3-0.4	HpCDF, TeCDF OCDF	TeCDF, PeCDF	dechlorination of PCDFs
MM	0.6/0.4	HpCDF, TeCDF OCDF	TeCDF, HpCDF	dechlorination of PCDFs
Urea/LFO fuel (II)	0.2/0.2	HxCDF, HpCDF	TeCDF,HxCDF, HpCDF	dechlorination of PCDFs, slight dechlorination of PCDDs
Urea/RDF fuel (III):				
shortest residence	0.6/0.2-0.3	OCDF, OCDD, HpCDF	HxCDF, PeCDF, TeCDF	dechlorination of PCDDs and PCDFs
medium residence	0.5/0.3-0.4	OCDD, HxCDF, HpCDF,	HxCDF, HpCDF, OCDD	no clear effect
longest residence	0.4/0.5-0.8	HxCDF, PeCDF, TeCDF	OCDD, HxCDF, HpCDF	slight shift to higher congeners
Urea input with RDF (IV)	0.3/0.4-0.5	HxCDF, PeCDF	HxCDF, HpCDF, OCDD	slight shift to higher congeners

As seen in Table 2, with gaseous inhibitors, dechlorination of PCDFs occurred when inhibitors were used. With the use of urea (Papers II and III) the results were not as clear. Some indication of dechlorination was seen in two tests: in the urea/LFO tests and in the urea/RDF test when the shortest residence time was used. For the longest residence time and for the test with urea input in RDF, a slight shift in the congener pattern was seen towards higher congeners i.e. octachlorinated isomers.

5.7 Relationship between chlorophenols and PCDD/Fs during formation and inhibition of PCDD/Fs

The most abundant chlorophenol isomers found throughout the tests were 2-, 4-, 2,4-(+co-eluted 2,5-), 2,4,6-, 2,3,4,6- and pentachlorophenol. The isomeric distribution of PCDD/Fs was similar to that found in MSW incinerators (Brzuzy and Hites 1996), i.e. hexa- and heptachlorinated furans and highly chlorinated dioxins dominated the congener pattern. Typically, the PCDF to PCDD ratio was greater than one throughout the tests.

The relationship between chlorophenols and PCDD/Fs was examined with PLS analysis. This was first performed for the results from tests II and III (urea inhibitor with LFO and RDF as fuel, Papers II and III, respectively), and later for the results from test IV (urea inhibitor input in the RDF fuel, Paper IV).

For PLS analysis, the X-block matrix of the results from tests II and III consisted of all of the chlorophenol isomers and 10 operating parameters (temperatures at 3 different points in the pilot plant, O_2, CO, CO_2, particle concentration, amount of urea, amount of water, and residence time). For test IV, the X-block was extended with some parameters (more temperature measurement points and SO_2). The Y-block matrix from tests II and III consisted of I-TEQ related PCDD/F congeners and I-TEQ values of PCDDs, PCDFs and PCDD/Fs both in gaseous and in particle phase, resulting in 39 dependent variables. The Y-block matrix from the results from test IV consisted of combined particle and gas phases for I-TEQ related PCDD/F congeners, and the sum values for each isomer group.

For the PLS analysis from results from tests II and III, the correlation coefficients were calculated separately for the gas phase and particle phase. The results indicated that PCDD/Fs in gas phase correlated either closely (for PCDFs) or at least moderately (PCDDs) with chlorophenols whereas in the particle phase, the correlation was clearly worse. In the particle phase, 2,3,4,6- and pentachlorophenol correlated with the particle phase PCDD/Fs. The importance of process parameters seemed to be rather small for the gaseous PCDD/Fs, but of some importance for the particle bound PCDD/Fs. In the PLS derived from the results from test IV, a slightly clearer correlation could be seen with the process parameters (CO, CO_2, SO_2, temperature between delay chamber and economizer, O_2 and urea) and concentrations of PCDD/Fs in the flue gas. Otherwise, in both set of tests, chlorophenols correlated best with hexa- and heptachlorinated dioxin/furan isomers, whereas for tetra-, penta- and octachlorinated congeners, the correlations were poor.

For the results from tests II and III, the final PLS analysis was performed by fitting both gas and particle phase values in the same model. Almost all PCDD/F congeners could be fitted into the model. Only gas phase 2,3,7,8-TeCDD and OCDF had to be omitted from the model where chlorophenol concentrations were used as independent variables. In the PLS-analysis for the test IV, tetra- and octachlorinated congeners and total quantities of different isomer groups were omitted from the final model. In both of these PLS-analyses, predictive ability of the model was good for the hexa- and heptachlorinated congeners (Q^2 values 0.5- 0.9; R^2 values 0.7-0.9), but only fair or even poor for the other congeners. The influence of the process parameters was insignificant especially in the first PLS-analysis;

in the other PLS-model derived from the "urea in the RDF" (IV) the results of the temperature of the flue gas after the furnace seemed to have some importance on the final model.

6 DISCUSSION

6.1 Effect of inhibitor and concentration of inhibitor

6.1.1 Gaseous inhibitors

The gaseous inhibitors (ammonia, sulfur dioxide, dimethylamine and methyl mercaptan) as well as liquid urea were able to reduce PCDD/F concentrations in the flue gases in our tests, the highest PCDD/F reductions being 68 % for ammonia, 62 % for sulfur dioxide, 78 % for dimethylamine, 47 % for methyl mercaptan, and 90 % for urea. Laboratory scale tests published in the literature achieved similar PCDD/F reductions as found here. Vogg et al. (1987) studied the effect of ammonia on MSWI fly ash and noted that PCDD/F reduction after exposure for 3 h at 300 mg/m^3 NH_3 was 82 %. In this study NH_3 was reported to counteract the catalytic action of $CuCl_2$. Also Takacs et al. (1993) achieved PCDD/F reductions of the same magnitude (76 % for PCDDs and 52 % for PCDFs) as we did on a pilot scale plant. They suggested that the mechanism of action would be neutralization of HCl. In their test, the HCl concentration was considerably reduced, but in our tests, HCl was still present at reasonable quantities after NH_3 injection (190 mg/m^3). However, the theory of neutralization of NH_3 cannot be excluded in our tests, since only few measurements were performed for the HCl concentrations in our tests. One probable explanation for inhibition of PCDD/Fs by molecules with lone pair electrons, e.g. those containing nitrogen or sulfur, could be their ability to form stable complexes with metallic compounds (as an example, structure of strong urea-copper complex has been presented by Tuppurainen et al. (1999)) and thereby eliminate or reduce the catalytic properties of the metals. Formation of inactive complexes could also account for the inhibitory effect of dimethylamine and methyl mercaptan. In our tests, dimethyl amine was the most effective of the gaseous inhibitors in reducing PCDD/F concentrations in the flue gas. The same explanation can be offered for the other successful laboratory studies which have utilized compounds with functional amino groups as inhibitors (Dickson et al. 1989b, Naikwadi and Karasek 1989, Lippert et al. 1991, Naikwadi et al. 1993). A further possible mechanism of action of this group of inhibitors could be the formation of copper nitrides, and subsequently deactivation of catalytic surfaces by nitride layers as stated by Lippert et al. (1991).

Sulfur dioxide

Sulfur dioxide and other sulfuric compounds are probably the most widely studied PCDD/F inhibitor group. In our pilot scale tests, a considerable reduction in PCDD/F concentrations occurred when SO_2 was added to the flue gases at 670 °C, whereas when added at 410 °C the PCDD/F reductions were only minor. Gullett et al. (1992b) determined in their laboratory experiments that SO_2 had only little impact on PCDD/F concentrations at their test temperature range, 300-500 °C. The possible reaction mechanism could be reaction of SO_2 with Cu-based Deacon catalysts to alter the form of Cu-based catalysts (reaction 7, p. 25) and further to reduce the ability to produce Cl_2 (reaction 4, p 18). Addition of $CuSO_4$ actually resulted in lower PCDD/F concentrations in the tests of Gullett et al. (1992b), compared to the use of CuO, indicating that $CuSO_4$ had a reduced ability to promote biaryl synthesis. Reaction (7) is thermodynamically favourable towards $CuSO_4$ under temperatures below 870 °C, but $CuSO_4$ decomposes at temperatures around and over 600 °C, so at temperatures below 600 °C the reaction would proceed towards $CuSO_4$. While the thermodynamic calculation suggest that reaction (6) should be favourable towards formation of HCl over the total temperature range expected in MWIs, the explanation for the poor PCDD/F reduction in our tests with SO_2 input at 410 °C could at least partly result from the fact that PCDD/F formation has already started, and the ability of inhibitor to block the PCDD/F formation is no longer possible at that stage. Sulfur dioxide did reduce PCDD/F concentrations in pilot scale tests (natural gas or coal combustion) by Raghanuthan and Gullett (1996) and also in small-scale FBC tests (fired with wood saw dust and PVC pellets) by Ogawa et al. (1996). The reduction due to SO_2 was distributed evenly among all of the congener classes occurring at reaction temperatures between 400 and 850°C in the study of Raghanuthan and Gullett (1996) similar to this study. Ogawa et al. (1996) found a slight increase in the PCDD/PCDF ratio with the use of SO_2 .

Laboratory experiments by Addink et al. (1993, 1996) with municipal waste fly ash and Na_2S (sodium sulfide) or $Na_2S_2O_3$ (sodium hyposulfide) have proved that also these sulfur-containing compounds can act as PCDD/F inhibitors. Bechtler et al. (1996) studied the effect of elemental sulfur on PCDD/F concentrations on MSWI fly ash from ESP, and the use of sulfur did not reduce PCDD/F concentrations in their laboratory tests, whereas Samaras et al. (2000) achieved a 96 % PCDD/F reduction when 10 % sulfur was co-combusted with RDF in a laboratory reactor. Furthermore, the use of other sulfur-containing compounds (amidosulfonic acid, hydroxylamine-*O*-sulfonic acid and sulfamide) resulted in significant (over 98 %) PCDD/F reductions in their study as well. In the small scale FBC tests of Ogawa et al. (1996), the addition of sulfur containing coal to fuel (wood saw dust and PVC) resulted in a PCDD/F reduction of 99.8 %, which could be further increased to almost 99.9 % when extra elemental sulfur (0.68-1.5 %) was added. The PCDD/PCDF ratio increased clearly in these tests, indicating that PCDFs were more affected by the sulfur-inhibitors than PCDDs, a trend also observed by Samaras et al. (2000). This trend could, however, not be seen in our SO_2 tests. These discrepancies could arise from differences in temperature and residence time profiles after the furnace between the studies, or the different form of the S-containing inhibitor.

6.1.2 Urea

Highest PCDD/F reductions (90 % compared to the reference test) in our tests were achieved when 1 % urea was fed into the refuse derived fuel (RDF). Most of the PCDD/Fs detected in the tests were found in the particles present in the flue gas throughout the tests (PCDD/Fs' gas/particle ratio 0.5 or less in reference tests). Samaras et al. (2000) did not attain as good results in their laboratory scale tests at 1000 °C (PCDD/F reduction 28 %) even though the concentration of urea was as high as 10 % in the RDF fuel. Later the same research group (Samaras et al. 2001) repeated the laboratory scale experiments with urea, but the results are difficult to interpret because of the great fluctuation between parallel tests. However, they concluded that isomer profiles of the PCDD/Fs were not affected by the urea addition among the RDF fuel, while in our tests some differences could be seen between tests with different residence times. In our tests, the use of inhibitors had a greater ability to reduce particle-bound PCDD/Fs compared to the PCDD/Fs found in the gas phase, indicating that inhibitors function mainly on the particle phase. Overall, PCDD/F reductions were higher, the greater the amount of inhibitor used. As seen in tests with the urea inhibitor (Paper II), PCDD/F reductions did not increase, when the amount of urea was increased from 0.5 % to 1 % of the fuel feed. There is obviously a maximum concentration above which any further increase in the amount of inhibitor no longer produces any benefits.

On the basis of the extremely fast decomposition of urea under certain test conditions, it can be concluded that in addition to the urea molecule itself, also some of its decomposition products, or a combination of decomposition products, could be responsible of the actual inhibition reactions.

6.2 Particle size distribution and PCDD/Fs

In the study where the effect of urea inhibitor on PCDD/F concentrations in different particle sizes was examined (Paper II), it was noted that if the amount of inhibitor is not high enough, the reduction is poorer for those particle size classes with the greatest particle surface area, i.e. in most cases the smallest particle size fraction. When the amount of inhibitor was elevated 10-fold (1 % of the total fuel flow), the PCDD/F reduction occurred to the same extent in all particle size classes. Since the smallest particles have been proven to be most harmful for humans, and in addition, they are the ones that are difficult to capture in air protection equipment, care must be taken to ensure that the amount of inhibitor is high enough to prevent PCDD/F formation in even the smallest particles.

6.3 Feeding point of the inhibitor

The temperature of the feeding point of the inhibitor proved to be of crucial significance (Paper I). PCDD/F reductions were higher, when the inhibitor was fed into flue gases at 670 °C compared to the case where they were fed in at 410 °C. At 410 °C, it is possible that post combustion zone formation of PCDD/Fs has already started and the inhibitor is thus unable to block the PCDD/F formation. Especially in the experiments where SO_2 was used as inhibitor we observed a drastic increase in PCDD/F reductions when the feeding point was brought closer to the incinerator, i.e. to a higher feeding temperature. When urea was fed with the RDF, the PCDD/F reductions were comparable to previous tests where urea was fed into the flue gases. Since this is the most convenient input form, it is concluded that the best way to introduce the inhibitor to the system is with the fuel, if this is at all possible. As calculated with kinetic modeling (III, IV), urea decomposes more rapidly at higher input temperatures. Feeding the inhibitor into the furnace at temperatures where it decomposes in a fraction of a second but still inhibits the PCDD/F formation suggests that in addition to inhibitor itself, the decomposition products of the inhibitors may be responsible for the PCDD/F inhibition process.

6.4 Residence time of the flue gas

Urea reduced the PCDD/F concentrations in the flue gas notably only when the residence time of the flue gas was long enough, in this case 9 s (III). Irrespective of the feeding point of the inhibitor, the reaction time must be adequate for inhibition reactions to take place. This reaction time in the flue gases can, however, be compensated at least to a certain extent by higher amounts of inhibitor. It seems clear that residence time has a crucial effect on both the formation of PCDD/Fs (Fängmark et al. 1991) and on the extent of inhibition. *De novo* –inhibitor test results (involving inhibitor-impregnated fly ash heating in laboratory scale reactors) described in the literature cannot be compared with the pilot scale inhibitor tests as such, since the *de novo* tests involve reaction times of hours rather than seconds, and therefore probably involve different reaction mechanisms for formation and inhibition of PCDD/Fs. In full scale incinerators, flue gas residence times are in the range of seconds or minutes rather than hours which probably makes our results better applicable to full scale incinerators.

6.5 Congener patterns of PCDD/Fs

The effect of inhibitors on PCDD/PCDF ratios and congener patterns varied according to the prevailing circumstances, e.g. the inhibitor itself, residence time and feeding point of the inhibitor. The most evident effect was dechlorination of PCDFs, which could be seen in the tests with gaseous inhibitors and also in the tests with urea. Addink et al. (1993) also observed in their laboratory tests that inhibitors reduced the degree of chlorination, and stated that this was because less copper ions were available for catalysing PCDD/F chlorination. The observation of Stieglitz and coworkers (1989) that a decrease in copper concentration leads towards less chlorinated PCDD/F supports this theory. For the longest residence time in the urea/RDF test (Paper III) and in urea/LFO test (Paper II) there seemed to be a slight shift towards higher PCDD/F congeners in the congener pattern. As the reaction time of the PCDD/Fs in the flue gas becomes longer, this probably enables further chlorination reactions to occur.

As different inhibitors seem to have a different effect on the PCDD/F congener distribution, it seems reasonable to propose that different forms of inhibitors affect different routes and phases of formation, this being then expressed as different congener patterns after inhibition.

6.6 Relationship between chlorophenols and PCDD/Fs

The formation and inhibition of chlorophenols with the use of inhibitors varied in our tests, even between the tests where the same inhibitor (urea) was used. However, some clear trends between PCDD/F reductions and chlorophenol reductions (Figures 5 and 6) were seen throughout the tests, although it is clear from these figures that total PCDD/F concentrations (or reductions) cannot be unambiguously explained by the total concentrations (or reductions) of chlorophenols.

As the amount of data involving a variety of inhibitor tests was large, PLS- analysis was used to identify correlations between dependent (PCDD/Fs) and independent (chlorophenols and process parameters) variables. Two sets of PLS-analysis (results from Papers II and III, larger data set, and results from Paper IV, smaller data set) were performed. Similar results were obtained from both data sets. In the analysis of the larger data set (Paper V), it transpired that it was possible to fit almost all of the TEQ related PCDD/F congeners (excluding the gas phase 2,3,7,8-TeCDD and octachlorodibenzofuran) into a single PLS-model using chlorophenol concentrations as independent variables. The model for the smaller data set (Paper IV) included all the other, except tetra- and octachlorinated, TEQ-related PCDD/F congeners as dependent variables, gas and particle phase combined. Both of these models predicted well the concentrations of hexa- and hepta-PCDD/F congeners, but only fairly well the tetra- and pentachlorinated compounds. Of the various independent variables studied here, the most influential was the concentration of certain chlorophenol isomers, 2,4,6- and pentachlorophenols in particular. The role of the process parameters (flue gas temperatures, flue gas composition, concentration of flue gas particles etc.) was poor which could derive from the fact that variation of the process parameters was so small that their influence on the model was negligible, or their influence on PCDD/Fs is mainly mediated through the chlorophenols.

Since PCDD/Fs have unquestionably been proven to be formed from chlorophenols in several laboratory studies (Ballschmiter et al. 1988, Karasek and Dickson 1987, Altwicker and Milligan 1993, Rappe et al. 1996, Weber and Hagenmaier 1999), our work corroborates the fact that chlorophenols are precursors of PCDD/Fs in waste incineration, and that formation of PCDD/Fs from chlorophenols is an important formation route in flue gases produced in municipal waste incineration. The present results also suggest that measurement of chlorophenols in waste incineration flue gases could be used as surrogate for the emissions of TEQ-related PCDD/Fs. However, the possibility to generalize the present results to full-scale plants should be evaluated in further studies.

7 CONCLUSIONS

Chemical inhibitors can successfully be used to reduce PCDD/F concentrations in waste incineration. Gaseous (sulfur dioxide, ammonia, dimethylamine and methyl mercaptan) and liquid (urea) inhibitors caused clear reductions in the PCDD/F concentrations in the flue gases in a pilot scale incinerator. When the gaseous inhibitors were injected immediately after the furnace at 670 °C led to PCDD/F reductions varying from 50 to 78 %, with dimethylamine being the most effective tested gaseous inhibitor. Urea reduced PCDD/F concentrations by a maximum of 90 %.

The PCDD/F concentrations in the particle phase decreased clearly more than in the gaseous phase when inhibitors were used. The impact of the urea inhibitor on particle size distribution of PCDD/Fs was proved to be equivalent in all size classes when the amount of inhibitor was adequate. With a lower urea concentration, the smallest particles with greatest surface area did not show such a clear reduction.

The most important factors affecting the PCDD/F inhibition in pilot scale tests were the chemical itself, the concentration of the inhibitor, the feeding temperature of the inhibitor and the residence time of the flue gas between the furnace and the PCDD/F measurement point. The highest PCDD/F reductions were achieved with urea as an inhibitor, although when comparing urea tests at the same concentration level with the other tested inhibitors (approximately 100 ppm), also dimethylamine was a good inhibitor. Both gaseous and liquid inhibitors caused greater PCDD/F reductions with increased inhibitor concentrations. Residence time of the flue gas also had a major effect on PCDD/F reductions. With the shortest residence time, no reduction in the PCDD/F concentrations could be observed, but when the residence time was more than doubled, the reductions became notable. On the basis of our results, it seems probable that increasing the amount of the inhibitor can compensate for shorter residence times. The feeding temperature of the inhibitor is also of great importance because the inhibitor has to be introduced into the system at the stage where PCDD/F formation has not yet started. This is how the formation of these compounds can still be blocked.

There are probably several concurrent inhibition mechanisms prevailing in the flue gases of waste incineration. Evidence of this is seen in the variation of PCDD/F congener distributions between tests under different conditions. However, formation of inactive complexes on fly ash particle surfaces between inhibitor and transition metals could be one of the most important mechanisms. Molecules with lone pair electrons (including nitrogen and sulfur containing molecules) can easily form stable complexes with transition metals and thus block the active sites on the particle surfaces.

As proven here, good PCDD/F reductions were achieved also with urea added into the RDF fuel before incineration. Addition of this low-cost inhibitor prior to incineration could probably be readily adapted to full-scale incinerators, requiring only minor modifications to existing plants. The use of inhibitors could also provide a low-cost preventative method for reducing PCDD/F emissions in minor or hard to control-sources. When combined with other air cleaning devices, the method could lighten the dioxin burden in full-scale incinerators as the PCDD/F amounts in other air cleaning devices, e.g. consumption of activated carbon could be reduced or the frequency of the replacement of the carbon could be decreased since the formed PCDD/F concentration would be clearly reduced.

It is clear that chlorophenols play an important role in the formation of PCDD/Fs. The formation of PCDD/Fs through chlorophenols is probably one of the the main formation routes occurring in waste incineration. The present results suggest that since the prediction of PCDD/F concentrations in the flue gases is possible from the flue gas chlorophenol concentrations, measurement of chlorophenols in waste incineration flue gases could be used as surrogate for the emission of TEQ-related PCDD/Fs.

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