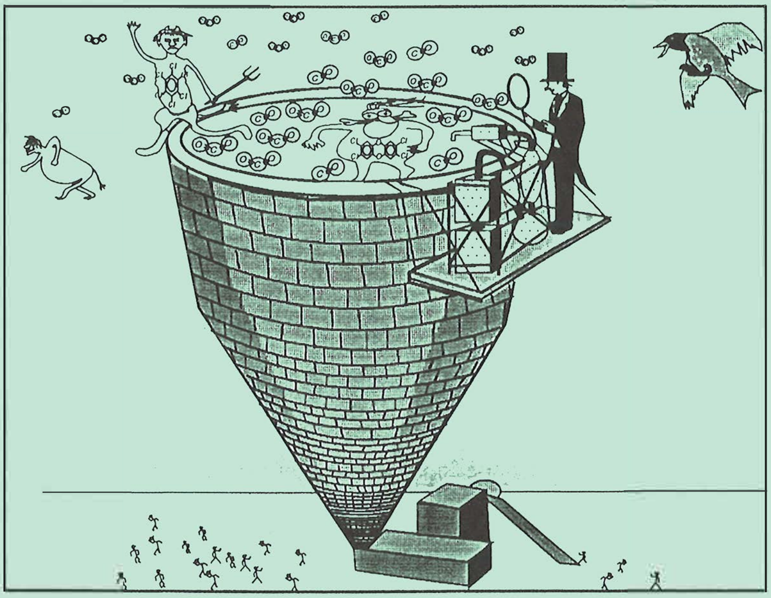
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF JYVÄSKYLÄ
RESEARCH REPORT No. 51

ORGANOCHLORO COMPOUNDS IN THE STACK EMISSION

BY

JUSSI-PEKKA AITTOLA

Academic Dissertation
for the Degree of
Doctor of Philosophy



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Abstract

To dispose of industrial and municipal wastes and residues without contaminating the environment is one of the major problems today. The most widely used technique for the disposal of this refuse is efficient, controlled incineration or thermal treatment.

The aim of the work has been to validate and improve the sampling methods for organochloro compounds, to study, to establish and to compare the emission of the above-mentioned oganochloro compounds in different municipal and hazardous waste combustion processes as well as to examine and establish emission of these compounds in a metal reclamation process. The effect of flue gas cleaning devices as a method to reduce the emission of organochloro compounds has been studied in the process of setting achievable technical design criteria for both stack gas emissions and combustion conditions in different thermal treatment processes of waste.

Validation of a number of different sampling systems against the more traditional SNV-sampling method proved successful and showed that all methods tested for measuring the emissions of PCDD's and PCDF's are reliable. However, sampling procedures and methods were and still are time consuming and complicated. Rapid concentration changes of organochloro compounds in the flue gases due to changes in the combustion processes or fuels can not be followed with sampling methods used. Faster sampling and analysis technologies with sufficient accuracy must be developed for the very low concentrations of different types of persistent chlorinated organic compounds in the off-gases from MSW- and HW-incineration and other thermal processes. The results obtained from these analyses must be such that they can be used in process control and development and simultaneously clearly show that the limit values for the impurities applicable in each particular case have been observed.

Co-combustion of waste or waste derived fuels with other fuels immediately showed an increase of PCDD's, PCDF's, PCP's and PCBz's in the flue gases when either less efficient combustion technology or high portioning of waste fuels were used in combustion. The data available in the context of present the work suggest that parameters reflecting good combustion conditions, optimization of the general process conditions and efficient process control are likely to result in low organochloro compound emission in MSW- and HW-incineration and metal reclamation. Observed data show that the application of efficient acid gas and particulate emission control facilities will significantly reduce organochloro compound emissions from studied thermal processes. The observed reductions in the combustion and metal reclamation process indicate that more particle-bound (higher molecular size, less volatile, more chlorine-containing) substances were recovered to a higher degree.

The analyses which focus only on PCDD/F's and PCB's in different thermal processes may underestimate the range and scale of the PCP- and PCBz-emission and the significance of the emission. Thus far, no commonly accepted TeCDD/TeCDF-type toxicity estimation method has been developed for these compounds. The present results indicate that, in addition to PCP, PCB and PCDD/F emission, emission of chlorobenzene, chloronaphthalene and polychlorinated dibenzothiophenes from thermic metallurgical processes might be of serious environmental concern.

Preface

I am grateful to my adviser and friend, Professor Jaakko Paasivirta, for his constructive, encouraging and stimulating discussions and suggestions, proposals and guidance throughout the years of this work.

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List of Original Publications

This thesis is based on the following publications which will be referred to in the text by Roman numerals I - IX.

I. Aittola, J-P., Korhonen, P., Vänni, P. and Helminen, L. (1991).
Treatment Options of MSW in Helsinki Area - Combustion or Materials Recovery and Recycling. Conference Papers and Abstracts of the Second Annual International Speciality Conference "Municipal Waste Combustion", pp. 590-607. April 15 - 19, 1991. Hyatt Regency Hotel. Tampa, Florida, USA. Organized by the U.S. EPA & Air and Waste Management Association. Air & Waste Management Association. P.O. Box 2861, Pittsburgh, PA 15230. USA

II. Aittola, J-P. (Finland), Hogland, W. (Sweden), Nagelhout, D. (Nertherlands), Poll, A. J.(England), Rosvold, H. (Norway), (1991).
Methodology for Size and Category Classification of MSW and the Downstream Effects. Conference Papers and Abstracts of the Second Annual International Speciality Conference "Municipal Waste Combustion", pp. 841-860. April 15 - 19, 1991. Hyatt Regency Hotel. Tampa, Florida, USA. Organized by the U.S. EPA & Air and Waste Management Association. Copyright 1991 Air & Waste Management Association. P.O. Box 2861, Pittsburgh, PA 15230. USA

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The Emission of PCDD/PCDF's and related Compounds from Co-Combustion of RDF with Peat and Wood Chips. Chemosphere 1989; Vol. 19, Nos. 1 - 6, 353 - 359.
https://doi.org/10.1016/0045-6535(89)90335-4

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"Internordic" Method Calibration for Sampling and Analysis of Dioxins and other Chlorinated Organic Compounds. Conference Proceedings of "The International Conference on Municipal Solid Waste Combustion, pp. 4C-1-14". April 11 - 14, 1989. The Diplomat Hotel. Hollywood, Florida, USA. Organized by the United States Environmental Protection Agency and Environment Canada. Minister of Supply and Services Canada 1989. Cat No. En 40-11/14-1989E. ISBN 0-662 16891-7.

VI. Aittola, J-P., Wihersaari, M., Kartano, J. (1990). The Emission of PCDD/PCDF's, Related Compounds and Heavy Metals from Combustion of MSW with Wood Chips in a Gasifier. 10th International Symposium on Chlorinated Dioxins and Related Compounds, "Dioxin 90". Short Papers, Volume 3, pp. 21 - 26. September 10 - 14, 1990, Bayreuth, Germany.

VII. Aittola, J-P. and Vänni, P. (1992). Effect of Combustion Optimization on Emissions of Chloroaromatics from a Semimodern Municipal Solid Waste (MSW) Combustion Plant. 12th International Symposium on Chlorinated Dioxins and Related Compounds, "Dioxin 92". Short papers, Volume 3, pp. 21 - 26. August 24 - 28, 1992, Tampere, Finland.

VIII. Aittola, J-P., Paasivirta, J. and Vattulainen, A. (1993) Measurements of Organochloro Compounds at a Metal Reclamation Plant. Chemosphere 1993; Vol. 27, Nos. 1-3, pp. 65 -72.

https://doi.org/10.1016/0045-6535(93)90277-C

IX. Aittola, J-P., Paasivirta, J., Vattulainen, A., Sinkkonen, S., Koistinen, J. and Tarhanen, J. (1995) Formation of Chloroaromatics at a Metal Reclamation Plant and Efficiency of Stack Filter in their Removal from Emission. (forthcoming in Chemosphere 1995).

https://doi.org/10.1016/0045-6535(95)00236-7

List of Abbreviations

PCB's	polychlorinated biphenyls
PCBz's	polychlorinated benzenes
PCP's	polychlorinated phenols
PCDD's	polychlorinated dibenzo-p-dioxins
PCDF's	polychlorinated dibenzofurans
TeCDD	2,3,7,8-tetrachlorinated dibenzo-p-dioxin, 2,3,7,8-TeCDD
TeCDF	2,3,7,8-tetrachlorinated dibenzofuran, 2,3,7,8-TeCDF
PCN's	polychloronaphthalenes
PCDT's	polychlorinated dibenzothiophenes
TEQ	Toxic Equivalent
I-TEQ	International Toxic Equivalent
TEF_i	Toxic Equivalent Factor of i_{th} isomer of PCDD's and PCDF's
P-	poly-
m-	mono-
D-	di-
Tri-	tri-
Te-	tetra-
Pe-	penta-
Hx-	hexa-
Hp	hepta-
O	octa-
FB-Boiler	Fluidized Bed Boiler
MSW	Municipal Solid Waste
MSWI	Municipal Solid Waste Incineration (plant)
HW	Hazardous Waste
HWI	Hazardous Waste Incineration (plant)
MRP	Metal Reclamation Process
WTE	Waste-to-Energy (plant)
ESP	Electro Static Precipitator
MRP	Metal Reclamation Process
Å	Ångström, 10^{-10} m
ng	10^{-9} g
pg	10^{-12} g
PE	Polyethylene
PET	Polyethylene terephtalate
PVC	Polyvinyl chloride
PS	Polystyrene

1. Introduction

1.1 General

The total amount of different types of wastes generated in Finland is nearly 80 Mt/a. Of this, c. 3.3.Mt/a comes in the form of municipal solid wastes and hazardous wastes /1/. In Finland, practically all municipal waste and also a large part of the industrial waste, is disposed of at the landfills. The landfill register maintained by the Ministry of the Environment lists a total of c. 1100 dumps, over 500 of which are used at the moment for disposal of municipal wastes /1/.

To dispose of industrial and municipal wastes and residues without contaminating the environment is one of the major problems of today's waste management. The most widely used technique for the disposal of this refuse is efficient, controlled incineration. Inefficient incineration, however, may allow some combustible material to remain unburned, which causes harmful end products (ashes) and gaseous emissions.

Incineration of municipal solid wastes (MSW) and hazardous wastes (HW) is used to reduce the volume of refuse, to destroy pathogenic organisms and to eliminate different disease vectors as well as to produce a hygienic end product, destroy toxic organic compounds, and to recover and recycle the energy component of the waste. In Finland, c. 50 000 t/a of MSW is burned at one old plant and c. 50 000 t/a HW is burned at a modern plant.

1.2 Historical Perspective

The findings of toxic and persistent aromatic chlorohydrocarbons such as chlorinated benzenes and phenols (PCBz's, PCP's) and later also polychlorinated dibenzo-p-dioxins (PCDD's), polychlorinated dibenzofurans (PCDF's), as well as other polychlorinated aromatic compounds in the ashes and flue gases generated by the incinerators have raised at least the following questions /2,3/: Are chlorinated organic compounds produced thermally in the incinerators? What are the mechanisms for the thermochemical formation of these pollutants? What is the source of chlorine? Are the organochlorine species present in the waste mixtures solely responsible for the appearance of the chloro-organics in the incineration process or does inorganic chlorine also act as a source of chlorine?

PCDD's and PCDF's do not occur naturally to any significant degree, and, as yet, they have not been manufactured as commercial products /4/. The PCDD's and PCDF's are two series of almost planar tricyclic aromatic compounds with very similar chemical properties. There are 75 and 135 congeners of PCDDs and PCDF's, respectively. With modern analytical methods, the PCDD's and PCDF's, and many other organochloro compounds, can be found as impurities in a variety of chlorinated and other compounds.

PCDD's and PCDF's have been identified in biological samples, particular in the Northern hemisphere. They can be detected in sediment, soil and air samples, with higher levels to be found in urban areas. Variable levels of PCDD's and PCDF's have also been found in human samples, even at background areas /5,6,7/.

PCDD's and PCDF's, and particularly the most toxic 2,3,7,8-tetrachlorinated isomer (TeCDD), were present in the herbicide mixture known as Agent Orange used during the Vietnam war. Agent Orange consisted of a mixture of the chlorphenoxy herbicides 2,4-D and 2,4,5-T butyl esters /8/.

These compounds have also been involved in accidents and massive intoxications such as the Yusho accident in Japan in 1968 /9/, the Yu-cheng disease in Taiwan in 1979 /10/, the Seveso accident in Italy in 1976 /11/ and the fire in the Binghamton Office State Building in Binghamton, NY, USA /12/ in 1981.

PCP's, PCBz's and PCB's, as well as PCDD's and PCDF's have been identified in emissions from all studied municipal solid waste (MSW) and hazardous waste incineration (HWI) plants in the world. Study groups in Scandinavia, other European countries and the USA have been using a variety of sampling methods, spiking protocols and analytical techniques in the measurement of PCDDs/PCDFs in combustion emissions. There has, however, been little validation or intercomparison of the different sampling and analysis techniques.

Measurements and discussions have concentrated on PCDD's and PCDF's, and in-depth studies on the emissions of PCP's and PCBz's have usually been omitted. However, for example, recent experiments have shown that PCDD's and PCDF's can be formed under controlled conditions in experiments using chlorophenols, hydrogen peroxide and various peroxidases in vitro /13,14/. Consequently, more attention should be paid to the environmental hazard caused by PCP's and their precursors, such as PCBz's.

1.3 Aim of the Present Study

The present study is focused on investigating the PCDD's and PCDF's, as well as the PCP's and PCBz's found in MSW- and HW-combustion emissions. In addition, emissions of these compounds in a metal reclamation process (MRP) are also examined.

The main factors which contributed to launching of this research were as follows:

- Occurrence of PCDD's, PCDF's, PCB's, PCP's and PCBz's in the stack gases of MSW- and HW-incineration, as well as in the exhaust gases in the MRP.

- Environmental hazards caused by PCP's, PCBz's, PCB's, PCDD's, PCDF's and other related anthropogenic organochloro pollutants.

- The possibility to use PCP's and PCBz's as markers for PCDD's and PCDF's, as well as the use of PCDD's and PCDF's as markers for a great number of micropollutants in emissions from different combustion and thermal processes.

- The possibility to sample and detect PCP's, PCBz's and PCB's as well as PCDD's and PCDF's, in very low concentrations with a great degree of accuracy by using a variety of sampling methods.

The main aims of this research work have been to:

- Examine the stack gases formed in the combustion of MSW and HW as well as MRP, which cause emission of PCP's, PCBz's, PCB's, PCDD's and PCDF's into the environment.
- Establish the emission from those sources, and improve and validate the sampling and analysis of organochloro compounds.
- Compare different combustion conditions and fuel mixtures, as well as flue gas cleaning devices, as an attempt to reduce the emission of organochloro compounds.
- Set achievable technical design criteria for both stack gas emissions, and combustion conditions in a MSW-combustion plant, in order to achieve and guarantee very low PCP, PCBz, PCDD and PCDF emissions into the environment.

2. Review of Literature

2.1 Chemical and Physical Properties

PCDD- and PCDF - Compounds

The PCDD's and PCDF's are two series of almost planar tricyclic aromatic compounds. The structures and numbering of the PCDD and PCDF ring systems are given in Figure 1. The number of chlorine substitutions can be from one to eight, resulting in 75 PCDD and 135 PCDF congeners /15/.

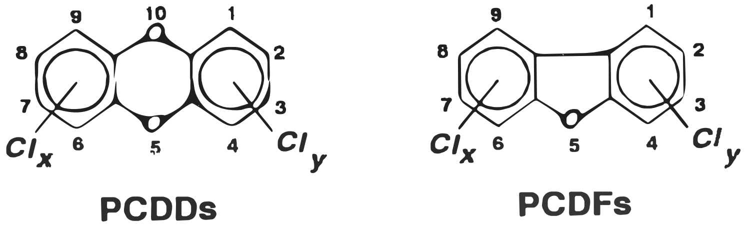

Figure 1. Structures of PCDD's and PCDF's /15/.

Both PCDD's and PCDF's consist of eight groups of isomers. Table 1 gives the numbers of isomers in each group and the numbers of 2,3,7,8-substituted (lateral) isomers /16/.

PCDDs and PCDFs are extremely lipophilic molecules. They are only slightly soluble in most organic solvents and almost insoluble in water (2,3,7,8-TeCDD, 10-20 ng/l at 25°C) /7/. Log octanol-water partition coefficients (log Kow) are high: from 6.1 for TeCDF to 13.8 for OCDF /17/. These compounds are solids at room temperature and their melting points are between 200°C-300°C. The melting points of 2,3,7,8-TeCDD and 1,2,3,7,8,9-HxCDD are ca. 305°C and 244°C, respectively. They also have a tendency to fasten on particulates.

The approximate molecular dimensions of the active species (Van der Waals surfaces) are 0.68 x 1.37 nm /18/. The vapor pressure is very low for these types of compounds, and has been calculated to be 2 x 10^{-7} Pa for 2,3,7,8-TeCDD at 25°C /16,19,20/. All PCDD's and PCDF's are rather stable and tend to resist heat, acids and alkalies. However, the PCDD's are susceptible to photodegradation in the presence of UV light. They also undergo photoreductive dechlorination in the presence of an effective hydrogen donor /7/.

In thermal treatment, PCDD's and PCDF's begin to decompose at 500°C, but at a temperature of 1000°C, a considerable amount of PCDD/PCDF-compounds can still be found in the flue gases (even after a residence time of 2 s in the active combustion zone)/16/.

Table 1. Numbers of isomers in each PCDD and PCDF group /16/.

Isomer group	PCDD total	PCDD lateral	PCDF total	PCDF lateral
Mono-	2		4	
Di-	10		16	
Tri-	14		28	
Tetra-	22	1	38	1
Penta-	14	1	28	2
Hexa-	10	3	16	4
Hepta-	2	1	4	2
Octa-	1	1	1	1
Total number of congeners	75	7	135	10

In general, the properties of PCDD/PCDF compounds have the following patterns /17,20/:

- the vapor pressure of PCDD's and PCDF's decreases with the increasing degree of chlorination of the molecule
- the solubility in water decreases as the degree of chlorination increases. For example the solubility of 2,3,7,8-TeCDD in water is 0.02 ug/L
- Kow increases steeply as the degree of chlorination increases.

Chlorinated Benzenes and Phenols

PCP's are formed from phenol by substitution of 1-5 hydrogen atoms in the benzene ring with chlorine atoms. A total of 19 different isomeric configurations of PCP's exist. Mono- and dichlorophenols are often used as starting chemicals in organic synthesis. Practically all of the PCP's are solids (except 2-chlorophenol).

Different PCP's can be found throughout the environment. They originate from wood preserving industries (tri-, tetra- and pentachlorphenol), from bleaching of pulp with chlorine chemicals and from different combustion processes. PCP's (mostly mono- and dichlorophenols) are also formed from dissolved organic impurities in the chlorodisinfection of tap water and waste water /21/.

PCBz's are formed by substitution of the hydrogen atoms in the benzene ring by chlorine. There are altogether 12 different PCBz-structures /21/. PCBz's can be used as, for example, solvents (mono-, di- and trichlorobenzens) and insecticides, as well as fungicides (hexachlorobenzene). More often, however, they are used as starting chemicals in different organic syntheses. In general, these compounds are relatively stable and concentrated in adipose tissue and in different food chains. The lipophilic nature of chlorobenzene congeners increases when the chlorination grade increases. Mono-, di- and trichlorinated benzenes are relatively volatile and soluble in water, which means that they can be found in air and water. The heavier tetra-, penta- and hexachlorinated congeners, on the other hand, can be found mostly in soil and in food.

2.2. Toxic Properties

Toxic Properties of PCDD- and PCDF-compounds

The dioxin which causes greatest toxicological concern is the 2,3,7,8-TeCDD. In general, the high toxicity is attributed to the congeners possessing the chlorine substitution in positions 2,3,7 and 8, with tetra- or pentachloro congeners being the most toxic, followed, in decreasing order, by hexa- and hepta-chlorinated congeners. The toxicity of the octachlorinated congener is reported to be comparatively low /22, 23/. However, repeated doses of OCDD have been reported to cause similar effects to those following low dose exposure to 2,3,7,8-TeCDD /24/.

The information available on 2,3,7,8-TeCDD has shown this isomer to be more lethal for certain laboratory animals at lower levels than any other man-made chemical. However, both the lethal dose levels and toxicological effects vary considerably among different animal species. The median oral lethal dose (LD50) ranges from 1 ug/kg for a guinea pig to 5000 ug/kg for hamsters /23,25/.

A number of comprehensive reviews have been published which deal with the health effects of PCDD's and PCDF's, and several risk evaluations have been made in various countries /22,23,25,26,27, 28,29/.

Toxic Properties of PCBz- and PCP-compounds

PCBz's

The study of the general toxic effect of PCBz's in chronical or subchronical animal studies has generally focused on the liver and the kidneys, and when higher doses have been used, on the nervous system. These substances also induce enzymes in the liver /21/.

Absorption of PCBz's via inhalation is about 70 - 80% (mono- and dichlorobenzens) in several species. Absorption of PCBz in the gastrointestinal tract is variable (penta- and hexachlorobenzens). If PCBz's are adsorbed on some particulate matter such as activated carbon, absorption can be decreased. Distribution occurs mainly to tissues high in lipid content, but also to the bone marrow. PCBz's are removed from the body via urine and/or milk. The available data indicate that the metabolites are reactive /21,30/.

Many studies have been performed on the elimination of PCBz's in animals indicating great variation between different isomers, from a few days for di- up to several months for hexachlorinated compounds. The elimination time can vary considerably between different species (rat, ape, etc.). In general, the highest toxicity and also carcinogenity is found for hexachlorobenzene, followed, in decreasing order, by penta-, tetra- and trichlorinated isomers. Liver cancer could be observed after a hexachlorobenzene dose of 4 - 5 mg/kg of body weight per day. Important biological effects of PCBz's also include teratogenic, reproductive and skeletal effects and carcinogenity /21,30/.

PCP's

The acute toxicity of PCP's is based on the release of oxidative phosphorylase in the cells. Interpretation of the results from toxicological studies concerning PCP's is very often difficult because of the small amounts of PCDD/PCDF's present as impurities in these substances. Important biological effects of PCP's include teratogenic and reproductive effects, skeletal effects, and carcinogenity /21,31/.

Absorption of PCP's via inhalation is about 70-100% (pentachlorophenol) in several species. Absorption of PCP's in the gastrointestinal tract can vary. Distribution occurs to blood, liver and the kidneys. PCP's do not concentrate in the body to the same degree as PCBz's do. The biological half-life for humans has been estimated to be less than 40 h for pentachlorphenol. Close to 90% of these compounds is eliminated in urine in about seven days /21/.

2.3 The Concept of Toxic Equivalents

In order to estimate the toxicological effects and risk of many of the PCDD/PCDF congeners, the concept of TeCDD-equivalents has been introduced. In this way a cumulative assessment can be made of the estimated toxicity rating of all the congeners with respect to the most toxic one, 2,3,7,8-TeCDD.

The toxic equivalence-concentration (TEQ) of a substance "i" is :

$$TEQ_i = TEF_i * c_i,$$

where

TEF_i = factor value given to each substance (for 2,3,7,8-TeCDD: $TEF_i = 1$)

c_i = concentration of the substance

The total toxicity of all PCDD/PCDF congeners analyzed in a sample is:

$$TEQ = \sum_{N1=i} TEF_i * c_i$$

The application of 2,3,7,8-TeCDD equivalents requires a detailed analysis of the emission sample in respect to PCDD's and PCDF's. Recently, some polychlorinated biphenyls PCB's (capable of taking a planar or nearly planar conformation) have been included in dioxin-type toxicants, and TEF-values have been given to them /32,33/. In the same way as other environmentally important chloroaromatic pollutants, PCP's and PCBz's could also be added to the TEQ evaluations in the near future.

The TEF/TEQ approach obviously poses at least three levels of uncertainty /23/:

- The evaluation of TeCDD itself.
- The determination of the fractional value (TEF_i) given to each isomer compared to the most potent 2,3,7,8-TeCDD.
- The assumed additivity of the effects of components in a mixture might not be valid. Some congeners may possess synergism or antagonism. Consequently, the effect calculated as the sum of TEQ's might be lower or higher than the actual effect caused by the congener mixture.

Despite these uncertainties, the approach has its merits, and it has consequently been used for evaluating and comparing the toxicity of samples obtained from different processes and from the environment /23/.
The concept is based on acknowledging the fact that although 2,3,7,8-TeCDD has been established as the most toxic isomer, in some cases the low level of this isomer can be overshadowed by the presence of a larger quantity of some less toxic compounds /15/. The most commonly used methods at the moment are the Eadon-model, Nordic-model and I-TEQ-model /15,27,34-36/.

Toxic equivalence factors (TEF-coefficients) have also lately been developed for co-planar PCB's /32,33,37/. For PCBz's and PCP's, no commonly accepted TeCDD/TeCDF-type toxicity estimation method has been developed, thus far.

3. **Methods**

3.1 Sampling

A carefully designed sampling strategy is always needed when MSW-, HW-combustion or other exhaust gases are studied. In the studies described in Paper V the analysis was based on simultaneous sampling with different sampling systems in the same smoke pipe. In Paper VII two similar sampling systems in two different combustion lines were used, and in papers III, VIII and IX two similar sampling systems were employed prior and after the flue gas cleaning procedure, respectively.

The sample validation aspect in Paper IV can be seen as a parallel analysis of samples at different laboratories. In Paper IX validation is done through optimization and control of the combustion process of waste (MSW) and successive sampling in two existing parallel combustion lines. In Papers III, VIII and IX the validation of sampling lines and the simultaneous study of the efficiency of the flue gas cleaning system are performed.

The SNV-sampling Method

The Swedish Environmental Protection Agency has recommended a sampling technique which is based on a glass fiber filter held at 160°C (+/-15)°C followed by a condenser which decreases the temperature of the flue gas to at least 20°C, "*the SNV Sampling method*" /38/.

This method is now frequently used in Finland and in Sweden. In Finland the sampling temperature has, however, been slightly lowered, to 120 - 140°C, because of the risk of formation and/or breaking down of PCDD/PCDF's or losses of sampling spike during routine measurements, cf. Figure 2, Paper V, and /39,40/.

In "the SNV sampling method", the condensate is collected in a glass bottle (container) and the cooled and dry sample gases pass an adsorbent cartridge containing more than 5g of "Ambrelite XAD-2-resin" per m^3 flue gas sampled. The gas flow through this sampling train is typically 2 - 3 m^3/h, and the total gas volume collected is usually 6-10 m^3. In Paper V, for example, a major part of the samples taken were pre-spiked with sample spikes from the laboratory which was going to carry out the analysis /39,41/.

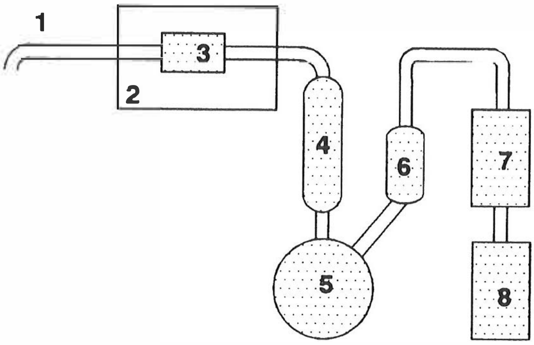

Figure 2. Sampling equipment. Schematic drawing of "the SNV system" /III, IV, V, VI, VII, VIII, IX/

1. Glass tube for isokinetic sampling
2. Oven held at 140(+/-15)°C
3. Glass fibre filter
4. Condensor (below 20°C)
5. Condensate (H_2O) bottle
6. Adsorbent column >5 g XAD-2/m^3 resin per sample)
7. Pump
8. Gas meter

The University of Umeå Sampling Method

The sampling system used in a number of validation experiments conducted, cf. Paper V, is presented in Figure 3 /39,41/.

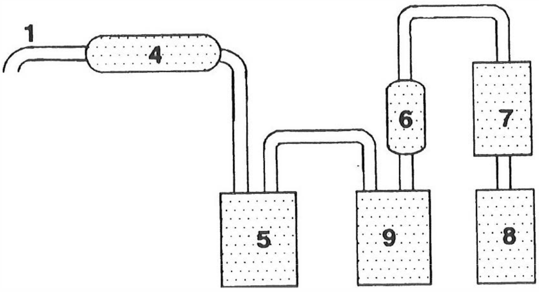

Figure 3. Schematic drawing of the modified sampling train /V/.

A water-cooled glass probe (1,4) ensures the cooling of the sample down below 20°C within seconds. In addition to the cooled probe an ice-cooled condensate collector (5) is used, followed by an impinger filled with toluene (9). After the impinger, the sample gases pass a poly-urethan foam plug (6). The gas flow rate can be adjusted by a pump (7), for example to 2 m^3/h, and the total sample volume depends on the sampling time. A preferable sample size is 6-10 m^3 (8).

The sampling done in different thermal processes, was mainly carried out by using "the SNV-method". In the validation, however, the SNV-method, the Umeå-method, the high volume sampler and the Norwegian standard system were all used /V/.

3.2 Analysis

The analysis of PCP's has normally been done by the GC-EC, and the analysis of PCBz's, PCB's, PCDD's and PCDF's as well as other analyzed organochloro compounds, by the GC-LRMS and/or the CG-HRMS /V,IX/. A typical sample treatment and analysis procedure used at present is given in Figure 4 /IX,42-44/.

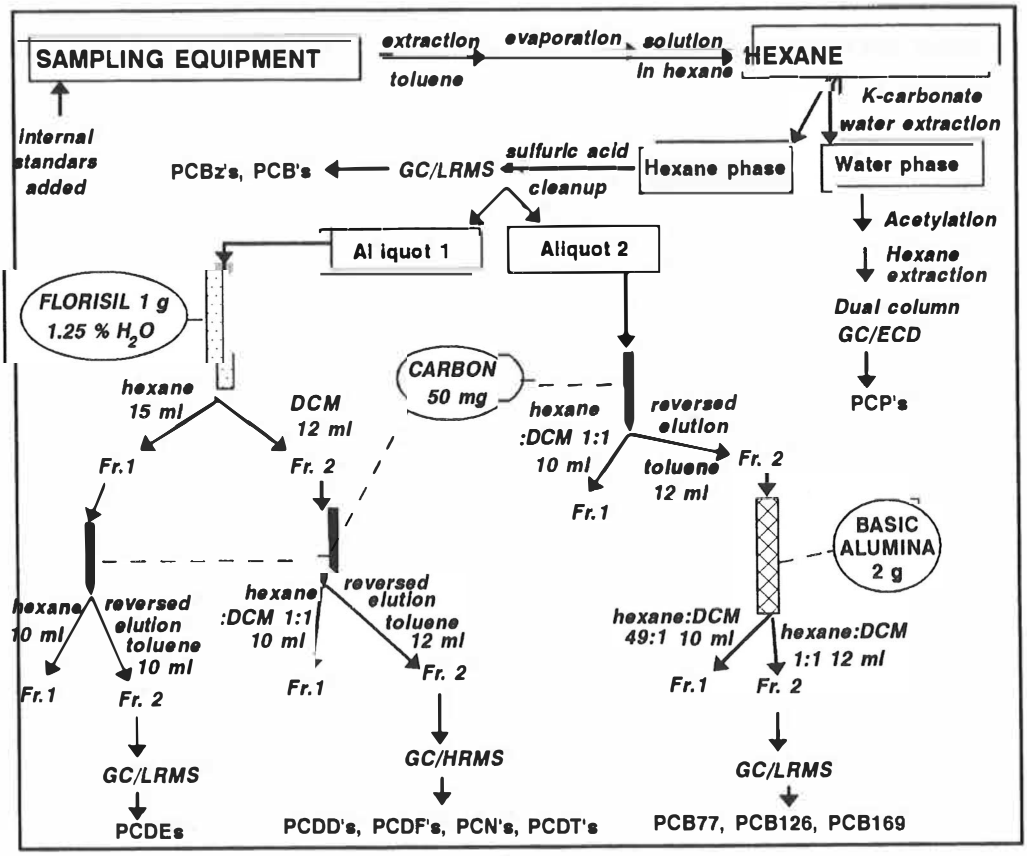

Figure 4. A typical treatment and analysis procedure for flue gas samples containing different organochloro compounds /42-44,IX/.

The sample treatment and analytical procedure may vary to some extent, depending on the nature and expected concentration of different organochloro compounds in the sample. However, this analytical procedure is rather complicated and very time-consuming, which means that the laboratory result is usually not available until some 4 - 6 weeks after, for example, the flue gas sampling.

4. Results and Discussion

4.1 Emission Guidelines

The high toxicity of some PCDD and PCDF congeners, as well as the low toxicity of the other congeners, require an efficient sampling technology and very sensitive and highly specific analytical methods in order to allow quantification of these chemical species. The detection level can vary within the sample matrices, but must be under the stipulated guideline- or the limit values given by authorities or set by the industry by at least one order of magnitude /38/. At the moment, the Commission of the European Communities is in the process of preparing and developing guidelines and a standardized procedure for MSW- and HW-combustion, as well as for the sampling and measurement methods for dioxins and furans emission in exhausted gas /45-47/.

Guidelines for Flue Gas Impurities in Waste Combustion

The present regulations on municipal solid waste combustion are concerned with the quality of the cleaned flue gas and combustion conditions. Less attention has been devoted to the solid and liquid residuals, such as bottom-ash, residuals from the flue gas cleaning and treated waste water(s). For flue gas emissions of PCDD's and PCDF's from a modern or renovated MSW-plant, the present guideline is in many European countries 100 pg/m^{3}n (calculated on the basis of I-TEQ/89). This means a detection level which is less than, or equal to, 1 pg/m^{3}n per isomer /47,48/. In Finland, however, the guideline for PCDD's and PCDF's is 1 ng/m^{3}n (calculated on the basis of I-TEQ/89) /49/. This approach, namely, stringent emission restrictions and control of combustion conditions, will increase the need for validated sampling and analytical techniques, as well as the reporting practices for PCDD's, PCDF's, PCP's, PCBz's and PCB's.

These guidelines for emissions from MSW-combustion in Europe can be compared with the technical emission requirements presented in Paper I for a big MSW-combustion plant for the Helsinki Metropolitan Area. The suggested guidelines in Paper I are very strict and quite comparable to those accepted as guidelines in Germany in 1990 /48/. The discussion in Paper I and Table 4 shows that the emission requirements and combustion restrictions will in the near future become more stringent in all European countries, where MSW-combustion is used as an integrated part of waste disposal /I,45-49/. This will also increase the need of more appropriate and detailed data on the wastes to be burned in all European countries /II/.

The validation of the sampling and of analysis of these compounds was studied extensively in an Inter-Scandinavian study (Finland, Sweden, Norway), presented in Paper V. Papers III,IV,VI and VII report studies of the applicability of the SNV-sampling method in the emission control for HW-combustion, for typical power plants and at a MSW-combustion plant in the City of Turku. The suitability and usability of the SNV-sampling method was also studied at a metal reclamation plant in Finland. This work has been reported in Papers VIII and IX. In the tables below (Table 2, Table 3) some recent European guidelines for flue gas emissions from MSW- and HW-combustion are summarized /II,21,45-50/.

Table 2. Emission guidelines for MSW incineration in Europe. Concentrations are given in mg/m^3n dry gas 11% O_2 (N.B. PCDD/PCDF-compounds in ng-eq TeCDD/m^3n).

Emission compound	Nether-lands 1993	Sweden 1992	Germany BImSchV 1990	Finland (new plants) 1994*
Particulates	5	18	10	10
Hydrochloric acid	10	90	10	10
Fluoric acid	1	0,9	1	1
Sulphur dioxide	40	180	50	50
Nitric oxides[1]	70[3]	360	100	-
Carbon monoxide	50	90	50	50
Organic carbon	10	-	10	10
PCDD/PCDF-comp.[5]	0.1	0.1	0.1	1.0
Heavy metals:				
- Cadmium, Cd	0.05	0.1	0.05	
- Mercury, Hg	0.05	0.07[2]	0.1	0.05
- Others	1[4]	1[4]	1-5[4]	0.5[4]

1) In Sweden defined as NO_x
2) For old plants
3) For new plants, 1997
4) Element sum
5) ng-eq TeCDD/m^3n
*) 24 h average

Table 3. Emission guidelines stipulated or proposed by the European Communities for MSW- and HW-incineration. Concentrations are given in mg/m^3n dry gas 11% O_2 (N.B. PCDD/PCDF-compounds in ng-eq TeCDD/m^3n).

Emission compound	MSW, >3t/h 1989	HW 1994[d]	MSW proposal 1994[d]
Particulates	30	10	5
Hydrogen chloride	50	10	5
Hydrogen fluoride	2	1	1
Sulphur dioxide	300	50	25
Nitric oxides (NO_2)			80
Carbon monoxide	100	50	50
Organic carbon	20	10	5
PCDD/PCDF-comp.	-	0.1[*]	0.1[*]
Heavy metals:			
- Cadmium, Cd		0.05[**]	0.05[**]
- Mercury, Hg	0.1	0.05	0.05
- Others	0.5	0.5	0.5

*) along I-TEQ scale, minimum 6h sampling
**) Sum of Cd and Tl
d) Daily average

4.2 Organochloro Compound Emission from Selected Combustion and Thermal Processes

At present, there are basically three theories or alternative ways for the formation of organochloro compounds in combustion, and particularly PCDD's and PCDF's /51-58/:

- PCDD and PCDF occur as trace constituents in the waste itself, and one proportion simply survives the incineration process.
- PCDD and PCDF are produced at some point during combustion and pyrolysis (high or/and low temperature region) from precursors such as PCB's, PCP's, PCBz's, chlorinated diphenyl ethers, etc.
- PCDD's and PCDF's (and also other organochloro compounds) are produced through "de novo" synthesis.

In these studies PCP's, PCBz's, PCDD's and PCDF's were sampled and analyzed from a number of different thermal processes, namely

- from MSW- and HW-combustion
- from co-combustion of MSW and biofuels (peat, wood chips)
- from gasification of MSW and co-gasification of MSW and wood fuels
- from scrap aluminium recovery.

Municipal Solid Waste Incineration, Co-Combustion of MSW and Biofuels

Four general factors can be considered when looking at the formation and production of chlorinated aromatics during waste and/or waste plastic (PVC, other chlorine containing plastics) incineration, cf. Papers III, IV, V, VII and IX and /55,57/.

These are:

- The availability and chemical form of chlorine during incineration (HCl, PCBz's, PCP's, PCB's)
- Combustion efficiency (furnace temperature, residence time, concentrations of CO, CO_2, O_2)
- Energy density in the furnace and the turbulent mixing of combustion gases in the system
- The secondary catalytic formation of PCDD/PCDF compounds in the boiler at some low temperature (200°C - 400°C) region, "de novo-synthesis".

Emission of PCDD's and PCDF's

Most papers in these studies include data on PCP, PCBz, PCB and PCDD/PCDF-emissions from different thermal processes. The sensitivity of the sampling procedure and the subsequent use of the analysis results for optimization purposes of the different combustion and thermal processes has also been a focus of study.

Table 4 shows the emission of chlorinated aromatics from the combustion and thermal systems included these studies in comparison to some typical Scandinavian MSW-combustion plant and other emissions /III,V,VII,VIII,IX/.

The observed typical emission level, if these incinerators and thermal processes are operating properly, is within the range of 0.05 - 10 ng/m³n, depending on the standard of combustion technology and flue gas cleaning equipment.

Table 4. Emission of PCDD- and PCDF-compounds (TEQ's, Eadon) in some incineration systems and scrap metal handling /III, V, VII, VIII, IX, 39, 55-58/.

Place	Combustion process	Average emission TEQ, ng/m³n	Reference paper
Umeå (S)	MSW, gross grate*	5.6	
Avesta (S)	MSW, gross grate*	2.0	
Turku (FIN)	MSW, gross grate*	3.0 - 8.0	VII
Högdalen (S)	MSW, gross grate	< 0.05	V
Malmö (S)	MSW, gross grate	< 0.05	
Linköping (S)	MSW, gross grate	< 0.05	
Quebec City (C)	MSW, gross grate	< 0.05	
SAKAB (S)	HW, rotary kiln,	0.1 - 6	III
EKOKEM (FIN)	HW, rotary kiln,	0.1 - 5	/58/
Nyborg (DK)	HW, rotary kiln,	3 - 10	
Degerhamn (S)	Cement kiln (PCB oil)	0.1 - 2	
Norcem (N)	Cement kiln (PCB oil)	< 1.5	
Rönnskär (S)	Industrial copper smelter	11	
Avesta (S)	Industrial steel mill	0.8 ng/g dust	
Kuusakoski(FIN)	Scrap aluminium smelter	3 - 30	VIII, IX

* Prior to modernization (retrofitting) of stack gas cleaning systems.

These emissions can be compared to those observed in the from experiments, Table 5, where MSW- and MSW-derived fuel or plastics are burned as an additional fuel with peat, wood chips or demolition debris in different types of semimodern or modern combustion systems (co-combustion) /IV,VI,59/.

Table 5. Emission comparison of PCDD's and PCDF's expressed in TCDD-equivalents (Eadon) in some co-combustion systems, ng/m^{3}n /IV,VI,59/.

Place	Combustion process	Emission, ng/m^{3}n
Laukaa[1]	20 - 40 % MSW-pellets	0.04 - 0.08
(Grate)	Wood chips only	ND*
Kitee[2]	65 % and 85 % crushed MSW	0.8 - 1.1
(Gasifier)	Wood chips only	ND*
Iisalmi[3]	20 - 40 % MSW-pellets	ND
(FB-boiler)	Peat only	ND*
Residential furnace[4]	wood fuel, 5 - 20 % mixed plastics	ND**
	Wood fuel only	ND**

ND* Detection limit 0.03 ng$_{eq}$/m^{3}n
ND** Detection limit between 1 - 2 ng$_{eq}$/m^{3}n
1 MSW pellets /wood chips, 20 - 40/80 - 60% by weight, Paper IV
2 Woodchips/crushed MSW, 20 - 40 /80 - 60% by weight, Paper VI
3 MSW pellets/peat, 20 - 40/80 - 60% by weight. No PCDD/PCDF's detected in analysis, Paper IV
4 Wood fuel and wood fuel mixed with 5 - 20 % of different plastics (PE, PET, PVC, PS) /59/

Emission of PCP's and PCBz's

The emission levels of PCP's and PCBz's generated by different combustion systems and thermal processes are presented in Papers IV, V, VI, VII, VIII and IX. A summary of these results is presented in Table 6. Sampling was most often carried out by using the SNV-system.

Table 6. Emission of PCP's and PCBz's, (expressed as a sum of measured isomers) in the flue gases created in different combustion systems and a thermal process.

Combustion system	PCP's (ug/m^{3}n)	PCBz's (ug/m^{3}n)	Reference paper
Counterflow gasifier, 6 MW			
Test 3[1]	1.8	1.1	VI
Test 2[2]	1.3	0.9	VI
Gross grate, 5 MW			
Test 4[3]	4.50	0.07	IV
Fluidized bed, 20 MW			
Test 4[4]	1.00	0.30	IV
Gross grate 5 t/h, MSW-combustion[5]			
Grate 1	4.9 - 12.5	5.0 - 7.4	VII
Grate 2	10.4 - 11.1	7.2 - 8.9	VII
Gross grate 15 t/h, MSW-combustion[6]	0.6 - 7.1	0.3 - 2.4	V
Hazardous Waste Combustion			
Plant 1, 6.8 t/h	1.9 - 3.7	1.8 - 2.5	/58/
Plant 2, 5 t/h	---	---	III
Residential furnace 35 kW, Wood fuel and mixed plastics[7]	NA	<50	/59/
Scrap aluminium smelter	37	52	IX

1 wood chips/MSW, 15/85 % by weight
2 chopped wood waste/MSW, 40/60 by weight
3 wood chips/MSW pellets, 70/30 % by weight
4 peat/MSW pellets, 60/40 % by weight
5 MSW, 100 % by weight
6 MSW, 100 % by weight
7 wood fuel/mixed plastics, 80/20 % by weight

Hazardous Waste Incineration

In hazardous waste incineration, the rotary kiln combustor, followed by a secondary afterburner chamber is the most commonly employed device /III, 58,60/. These rotary kilns are generally categorized as slagging or non-slagging. The distinction is based on the working temperature used: If the temperatures in the kiln are maintained high enough to convert inorganic salts into a molten form, the rotary kiln is a slagging kiln. On the other hand, if the temperatures are not high enough to convert the salts into the molten form, the incinerator is non-slagging. In this work, both HWI's studied were molten kiln type combustion units. A comprehensive description of the HW's and HWI's (slagging type) and of its operation is given in /58,60/.

Table 7 presents a summary of the results obtained from the emission measurements of PCDD's, PCDF's and PCP's and PCBz's at a HW-incinerator /58/. In the experiments, the combustion temperature, waste composition, chlorine content and chlorine source of the waste were varied in order to see the respective effect in the emission of organochloro compounds, as well as their effect in the combustion conditions.

Table 7. Chlorinated organic compounds in cleaned flue gases (PCDD/PCDF's, PCBz's and PCP's) from one hazardous waste incineration plant. Congener sum for PCBz's and PCP's in µg/m³n dry gas. PCDD/PCDF's are expressed as toxic equivalents, ng/m³n dry gas (along Eadon scale) /58/.

Sampling/test run	1*	2**	$3^{1,2}$	4^{1}	5^{3}	6^{1}
PCBz's, ug/m³n	2.5	2.5	2.5	2.4	3.7	1.8
PCP's, ug/m³n	3.5	2.9	1.9	1.1	10.2	3.7
PCDD/PCDF's, ng/m³n	1.8	2.0	4.1	1.3	0.6	0.2
Temperature, °C[4]	960	980	970	960	1010	1080

* "Normal HW", no waste drums or PCB in the waste feed
** "Normal HW", no PCB in the waste feed
1) PCB-containing condensators burned in drums in the experiment
2) Test and sampling interrupted due to difficulties in maintaining good combustion conditions
3) High chlorine content in the waste burned in experiment, no PCB in the waste feed
4) Temperature in secondary (afterburning) chamber during the experiments

The experiments and analysis indicate that the combustion temperature and a high chlorine feed (either PCB containing or chlorine containing other waste) to the kiln are important but not the only factors in the formation of emission of chlorinated aromatic compounds /III,58/. The unstable combustion conditions, test run 3, seem to have an immediate effect on the emission of different organochloro compounds, in this case PCDD's and PCDF's, in the flue gases. Furthermore, the experiments indicate that a slagging rotary kiln can be safely operated at a wide range of combustion conditions /III,58/. In another specific study on hazardous waste combustion /III/, emission of chlorinated aromatics was found to correlate closely with the chlorine input to the kiln, as well as with waste feed and air ratio.

The removal of different organochloro compounds from flue gases in the flue gas cleaning system at a HWI-plant was also investigated /III/. The results show that the less chlorinated PCDF-isomers can be removed more readily than the PCDD-isomers. The removal of PCDD/PCDF compounds also seems to increase with the increasing number of chlorine atoms in the molecule. In this study, a recovery from about 48% for tetra- to 89% for octachlorinated PCDD-congeners and from about 65% for tetra- and penta- to 85% for octachlorinated PCDF-congeners was observed in the flue gas cleaning unit.

The removal of different PCDD and PCDF isomers via the flue gas cleaning system was shown to correlate to some extent with the boiler load, expressed as steam production (t/h). Removal efficiency tends to decrease when the boiler load increases /III/.

When the formation of PCBz's was studied, a correlation was found between the formation of hexa-, penta and tetrachlorinated benzens and the chlorine load to the kiln. On the other hand, the correlation between the formation of PCP's and chlorine load was weak or non existing. The removal of different PCP and PCBz congeners in the flue gas cleaning was also analyzed and found to be low, 37% for PCBz's and 42% for PCP's.

The samplings and experiments done at two HWI-plants show that under normal operating conditions with high combustion efficiency, the production of chlorinated aromatics can be influenced by varying, for example, the combustion temperature, the total chlorine input and the load of the combustor, the kiln. High recovery (separation) of PCDD's and PCDF's and low recovery of PCBz's and PCP's can be achieved in the flue gas cleaning system at a design load of the combustion system /III, 61/.

Metal Reclamation Processes

Metal waste itself may contain harmful compounds, such as heavy metals and organic impurities (phenols, chlorine containing compounds, PCB, etc.), plastics, paints and solvents. Chemicals, e.g. NaCl, KCl and other salts are used as flux in aluminium reclamation processes. This may cause special emission problems in connection with the formation of organochloro compounds. Of special concern in the process are the formation and emissions of a number of chlorinated compounds /62-64/. At a metal reclamation plant, the sampling and emission analysis of PCP's, PCBz's, PCB's, and PCDD/PCDF's were performed from aluminium-, lead- and zinc-smelting, car shredder turnings drying, sink and float drying, aluminium dross-line and "ring crusher". The gas samples were taken from the flue- or ventilation gas ducts after the last gas cleaning equipment by using the sampler recommended by the Swedish National Protection Board (SNV-method) and modified as described in Paper V. The findings regarding aluminium smelting, car shredder and turnings dryer are discussed and presented in more detail in Papers VIII and IX.

The results show that metal reclamation processes are and can still be a substantial source for all types of polychlorinated aromatic compounds /VIII,IX/.

The removal of different organochloro compounds from flue gases in the flue gas cleaning system (baghouse filter) in aluminium smelting was also investigated /IX/. The removal of different isomers by the flue gas cleaning system was shown to correlate clearly with the less volatile and higher chlorinated compounds and compound groups, e.g. for PCB's, PCDD's and PCDF's, Table 8.

The obtained removal efficiency of the gas cleaning system for different PCDD- and PCDF-congeners also seems to follow clearly the chlorination grade, ranging from about 85% for tetra- to 99% for octachlorinated congeners. The TEQ-removal of 93 % was obtained /IX/.

Table 8. Gas cleaning system recovery for PCP's, PCBz's, PCB's, PCN's, PCDD/F's and PCDT's /IX/.

Compound	Filter Recovery (%)
PCP	43
PCBz	51
PCB	73
PCN	78
PCDT	90
PCDD/F	92
TEQ	93

This result is very similar to the PCBz, PCP, PCDD and PCDF removal observed and presented earlier /III,61/. The lower recovery, from about 48% for tetra- to 89% for octachlorinated PCDD-congeners and from about 65% for tetra- and penta- to 85% for octachlorinated PCDF-congeners, observed in that study is due to different flue gas cleaning technology: the electrostatic precipitator was used for dust removal.

4.3 Possibilities to Reduce and Remove Organochloro Compounds in Combustion

PCDD's, PCDF's, PCP's and PCBz's cannot be produced without chlorine in incineration and other thermal processes. Therefore, it would appear that, as a first step, elimination of most part of chlorine should result in reduced levels of formation and emission of chloroaromatics. Another possibility to avoid the formation of chloroaromatics in incineration is to cool down the flue gases from incineration so fast that the secondary formation by the "de novo"-synthesis does not occur or is of secondary importance. It has also been suggested and reported that the formation of these compounds could be suppressed by using additives in combustion and in the boiler /65,66/.

There are, in principle, four possible areas where reduction of harmful components in the incineration system or at least partial removal of these compounds from the flue gases can be done:

- Waste and waste fuel input to combustion
- Combustion process
- The low and/or medium temperature region in the boiler (control of the secondary formation mechanisms, rapid cooling of the combustion gases or use of additives)
- Flue gas cleaning region

Control of waste is directed towards the control of, in the first place, chlorine-containing waste fractions, such as PVC-plastics and impregnated wood residuals. The PCDD/F content of municipal solid waste has also been recently analyzed, and the results show that considerable amounts of these compounds can be found in the waste to be burnt /67/.

It has also been shown that even effective removal of waste containing chlorine (PVC, salts, etc.) does not substantially decrease the PCDD/PCDF emission from MSW-plants /II,39,68/. This is because even small amounts of chlorine in the waste are sufficient for the formation of the minimal amounts of chlorinated organic compounds.

In the combustion, the overall goal is to achieve as complete burning of the waste fuel as possible under carefully controlled combustion conditions.

On the basis of the conducted experiments and findings and results presented in the research literature, typical acceptable combustion conditions can be summarized as follows /I,III,IV,V, VI,VII,VIII,IX,39,68-71/:

- Good design of the furnace and effective combustion control system (facilities, instrumentation)
- Sufficiently high combustion temperature, ca. 850-1100°C
- Air ratio (excess oxygen) ca. 1.4 - 1.8
- Intense turbulent mixing of combustion gases in the burning space and sufficiently long residence times (> 2s) for the gas mixture in the active combustion zone
- Combustion efficiency > 99.9 % gives a measure for the completeness of burning. Combustion efficiency defined as $CE = (1-CO/CO_2)*100\%$.

Poor combustion conditions which usually lead to relatively high PCDD/PCDF concentrations in the flue gases can be summarized as follows /III,IV,VII,39,66,67,70,71/:

- "High" carbon monoxide concentration in the off gases
- Low combustion temperature, usually below 800 °C
- Partial load (low waste fuel feed) or too high a load (high waste fuel feed) in the furnace.
- Poor combustion conditions, out of control situations.

Control of the secondary formation mechanisms, the possibilities to reduce the "de novo" synthesis and dechlorination/hydrogenation reactions in the post flame region of the boiler can be summarized as follows:

- The catalytic action, primarily by copper (Cu) and also by other metals on chlorine, can be counteracted effectively by using different additives (PCDD/PCDF suppressants) in the post flame or flame region such as NH_3, triethyl amine, ammonium carbonate, calcium oxide etc. /IX,65,66/
- Use of the catalytic activity of fly ash from incinerators to dechlorinate PCDD/PCDF compounds under oxygen-deficient conditions with an additional heat treatment /72-74/
- Use of fast and deep heat recovery, until a final flue gas temperature of 150-170°C can be achieved
- Hot particulate and agglomerate removal, e.g. by means of a silica bed enhanced ESP /68/.

Air pollution control is directed towards the control of stack gas emissions, namely, to solid and gaseous effluent.

The data observed in this work /I,III,V,VIII,IX/, as well as the data collected in the literature indicate that modern waste-to-energy (WTE) plants using a properly designed flue gas cleaning system can remove from the stack gases over 99.9 % of the particulate matter, up to 99 % of the acid gases, 95 % - 99.9 % of the heavy metals and 40 % - 99 % of the different chlorinated hydrocarbons. The operational flue gas cleaning systems are currently capable of removing toxic stack gas emissions down to very low levels, for PCDD's and PCDF's below 0.05 ng_{eq}/m^3 standard dry gas. The levels of other organochloro compounds, PCBz's and PCP's are very low, usually below 5 ug/m^3n /III,V,VII,IX/.

5. Summary

This work covers a period from 1985 to 1995. Emission data gathered from the sampling and analysis experiments in the metal reclamation process, different waste combustion processes, burning of different wastes and waste fuels as such or as an additional fuel with peat, wood chips or chopped wood waste, are discussed and presented. PCDD's and PCDF's, as well as PCP's and PCBz's, have been identified in the emissions from all MSW- and HW-incineration studied, as well as from metal reclamation processes. The general emission guidelines set for MSW- or HW-combustion plants are very stringent in comparison to those set for other energy production plants.

For flue gas emissions of PCDDs and PCDFs the guideline found in many European countries is at present 100 pg/m^3n (I-TEQ/89), which means a detection level in analysis which is lower than or 1 pg/m^3n per isomer. The low concentrations PCDD- and PCDF-isomers require a very sensitive and highly specific sampling and analytic method. The prerequisites for the analyses are efficient and clean sampling, as well as professional sample extraction and sample purification, isomer-specific detection of PCB's, PCP's, PCBz's and the seventeen 2,3,7,8-substituted PCDD/PCDF-isomers with a sensitivity essential for the sample matrix. The detection level can vary within the matrices, but must be under the stipulated guidelines or limit values by at least one order of magnitude.

Most countries use their own sampling procedure for measuring PCDD's and PCDF's in the flue gases from combustion sources. All these different sampling systems contain a sampling probe, sample filtration, cooling and/or heating unit and some adsorbing material to trap chlorinated organic compounds and other organic microimpurities. The testing and validation of a number of different sampling systems against the more traditional SNV-sampling method proved successful and showed that all methods tested for measuring the emissions of PCDD's and PCDF's are reliable.

Some features in the existing sampling trains and analysis practices can be pointed out on the basis of this work:

- Sampling procedures and methods were and still are time-consuming, complicated and of "research equipment" type, as well as unpractical in "field conditions".

- Rapid concentration changes of organochloro compounds in the flue gases due to changes in the combustion processes or fuels cannot be followed with the sampling methods used.

- Sampling trains were used in which a substantial part of the PCDD's and PCDF's can be found in the rinsing fraction (for example the SNV-train). Losses of sample can occur during the rinsing procedure.

- Use of the sampling train, especially the front end (filter) at high temperatures (SNV-sampling train, > 160°C), can cause formation and/or degradation reactions of the collected compounds thus causing erroneous results. A lower sampling temperature of 120°C - 140°C was used in the present and preferred in future experiments.

- Only one of the sampling methods used was optimized for the collection of aerosols, too. The efficiency of the other methods for aerosols collection in sampling can be improved by adding an aerosol filter in the system.

- The long sample preparation and analysis time required does not allow efficient optimization of the combustion systems as regards the emission of PCDD's, PCDF's or PCB's, PCP's and PCBz's.

Fluctuations in the PCDD/PCDF concentrations due to absorption in the particulates and to nonisokinetic sampling will increase in significance when the levels of organochloro compounds are very low in the stack gases. This indicates that considerably longer sampling times and replicate sampling procedures are recommended when PCDD/PCDF levels are expected to be extremely low in the samples. This will also lead to a careful planning of the sampling and analysis strategy, based on more accurate knowledge of the process to be analyzed.

The data available in the context of the present work suggest that parameters reflecting good combustion conditions, sufficiently high temperature, adequate retention time, high turbulence and excess oxygen, and the plant load together, are likely to result in low PCDD-, PCDF-, PCBz- and PCP-emissions. Simultaneous poor combustion control and combustion conditions were observed to increase the emission of chlorinated compounds. Optimization of the general combustion conditions and efficient combustion control reduced noticeably the emission of chlorinated compounds in both MSW- and HW-incineration.

Co-combustion of waste or waste-derived fuels (RDF) with domestic fuels showed an immediate increase of PCDD's and PCDF's as well as PCP's and PCBz's in the flue gases when either less efficient combustion technology or high portioning of waste fuels were used in combustion. The data observed show that the application of efficient acid gas and particulate emission control facilities will significantly, from 65% to 99%, reduce PCDD- and PCDF-emissions from the thermal processes studied. The observed reductions for PCP's and PCBz's in the combustion and metal reclamation process were much lower, for PCP's 37-43 % and for PCBz's 42-51 %.

Some observations and research literature data indicate that there may be a possibility to use PCBz's and PCP's as markers for PCDD/F's. More research results as well as a comprehensive statistical analysis of the results and combustion conditions, are needed to verify this.

In the mid 80's, the incineration plants were not generally equipped with efficient flue gas or process gas cleaning equipment. At present, practically all plants are using very efficient and well working gas cleaning systems. This together with the new design criteria for MSW-plants will efficiently reduce the emission of harmful chlorinated organic compounds to the environment.

Fast sampling and analysis technologies with sufficient accuracy must be developed for the measurement and analysis of the very low concentrations of chlorinated organic compounds, including PCDD's, PCDF's, PCB's, PCP's and PCBz's in particular, as well as other either chlorinated or brominated toxic and persistent compounds generated in the off-gases from MSW- and HW-incineration and thermal processes. The results obtained from these analyses must be such that they can be used in process control and development, and simultaneously clearly show that the limit values for the impurities applicable in each particular case have been observed.

The analyses which focus only on PCDD/F's and PCB's in thermal processes may underestimate the range and scale of the PCP- and PCBz-emission and the significance of this emission. At present, no commonly accepted TeCDD/TeCDF-type toxicity estimation method has been developed for these compounds. The present findings indicate that, in addition to more traditional PCP, PCB and PCDD/F emission, emission of chlorobenzene, chloronaphthalene and polychlorinated dibenzothiophenes from thermic metallurgical processes might also be of serious environmental concern.

6. Conclusions

There is no question that incineration of waste materials including municipal solid waste and hazardous waste is a mature and proven technology for safely destroying a variety of wastes at various scales of operation, both with and without energy recovery. Incineration is capable of meeting virtually any environmental regulation, although equipment costs increase rapidly as regulatory limits tighten.

Validation of a number of different sampling systems proved successful and showed that all methods tested for measuring the emissions of PCDD's, PCDF's and other organochloro compounds are reliable. However, sampling procedures and methods were and still are time consuming, complicated and of research equipment type. Rapid concentration changes of different organochloro compounds in the flue gases due to changes in the combustion processes or fuels can not be followed with any sampling method used.

Sampling and analysis technologies with sufficient accuracy to follow the process fluctuations must be developed for the very low concentrations of different types of persistent chlorinated organic compounds in the off-gases from different thermal processes. The results obtained from these analyses must be of such quality that they can be used in process control and development and simultaneously clearly show that those by authorities stipulated limit values for the impurities in each particular case have been observed.

Co-combustion of waste or waste derived fuels with other fuels showed immediately an increase of PCDD's, PCDF's, PCP's and PCBz's in the flue gases when either less efficient combustion technology or high portioning of waste fuels were used in combustion. The data available in context of present work suggest that parameters reflecting good combustion conditions, optimization of the general process conditions and efficient process control are likely to result in reduced and low organochloro compound emission in MSW- and HW-incineration and metal reclamation.

Observed data show, that the application of efficient acid gas and particulate emission control facilities will reduce significantly organochloro compound emissions from studied thermal processes. The observed reductions in combustion and in one metal reclamation process indicate that more particle-bound (higher molecular size, less volatile, more chlorine-containing) substances were recovered to a higher degree.

The sampling and analyses made from different thermal processes, suggest that PCBz's and PCP's are the major chlorinated compounds emitted even when an efficient flue gas cleaning process was used. Thus, the analyses which focus only on PCDD/F's and PCB's in different thermal processes may underestimate the range and scale of the PCP- and PCBz-emission and the significance of that emission. Thus far, no commonly accepted TeCDD/TeCDF-type toxicity estimation method has been developed for these compounds. The present results indicate also that, in addition to PCP, PCB and PCDD/F emission, emission of chlorobenzene, chloronaphthalene and polychlorinated dibenzothiophenes from thermic metallurgical processes might be of serious environmental concern.

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