

Metals as Catalysts during the Formation and Decomposition of Chlorinated Dioxins and Furans in Incineration Processes

Kees Olie, Ruud Addink, and Mirjam Schoonenboom

Department of Environmental and Toxicological Chemistry, Amsterdam Research Institute for Substances in Ecosystems, University of Amsterdam, Amsterdam, The Netherlands

ABSTRACT

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are found on fly ash and in flue gas of municipal waste incinerators. Municipal waste incinerators seem to be the most important source for PCDDs and PCDFs emitted into the air during the last decades. PCDD/F formation takes place in the cooler zones (250 °C–450 °C) of a municipal waste incinerator, at the electrostatic precipitator. Copper is an important component of the fly ash that can catalyze the formation of PCDDs and PCDFs. Inhibition of the formation can be done by complexation of the metals (Cu) with EDTA or NTA.

INTRODUCTION

Properties of PCDDs and PCDFs

Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are a group of tricyclic compounds substituted with one to eight chlorine atoms. This results in 210 different compounds: 75 PCDDs and 135 PCDFs. Seventeen congeners are more toxic than the others. These toxic congeners all have chlorine atoms at the 2,3,7 and 8 positions. PCDDs and PCDFs are very stable compounds and have very long residence times in the environment and in organisms, including humans. Their hydrophobicity promotes accumulation in sediments and organisms, resulting in high concentrations in both sediment and organisms. Physical chemical properties of PCDDs and PCDFs are reported in Table 1. In a substantial number of studies the effects of PCDDs and PCDFs on various animals are determined. Among toxicological effects reported are teratogenicity, reduced reproduction, liver toxicity, decreased growth rate and behavioral changes.¹ Toxicological effects were also reported for humans: chloracne, enlargement and tenderness

IMPLICATIONS

PCDDs and PCDFs are very toxic compounds that can enter the foodchain after being emitted into the air. Because of the toxicity, emission levels are set as low as 0.1ng TEQ/m³ for waste incinerators.

of the liver, decreased libido or sexual dysfunction, personality changes, tiredness, hirsutism, and neurological disorders.² Some studies also suggested soft tissue sarcoma, stomach cancer, nasal cancer, and cancer of the respiratory tract. In other studies of these cancers, no correlation was found.²

Sources

PCDDs and PCDFs have never been produced intentionally, but are formed as trace contaminants in various processes. One of the first known sources was in the production of 2,4,5-T, a herbicide. The production of pentachlorophenol has also been long established as a source. Restrictions to production have eliminated these sources to a large extent, at least in some countries. Sources of PCDD/F emission into the air are reported in Table 2. Municipal waste incineration is responsible for most of the PCDDs and PCDFs emitted into the air during recent decades.^{4,5} In 1977, they were found on fly ash and in the flue gas of municipal waste incinerators.⁶ Related compounds, like chlorobenzenes and chlorophenols, were also found. New technologies of flue gas cleaning in waste incineration will reduce the amount of PCDD and PCDF in the flue gas and, therefore, the contribution of municipal waste incineration in PCDD/F emission into the air. The total amount of PCDD and PCDF formed can be reduced by using filter systems that work at higher or lower temperatures than the optimum temperatures for the formation of PCDD/Fs. Waste from the cleaning section contains the larger part of the

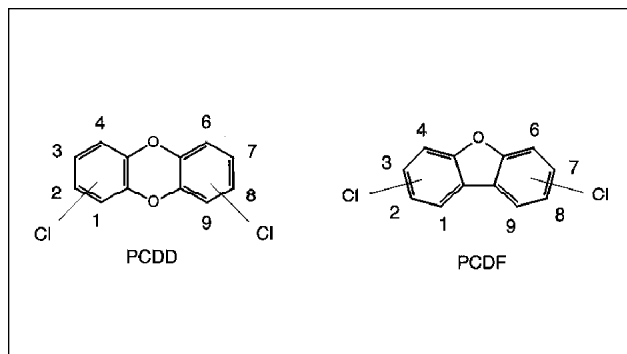


Figure 1. Molecular structures of PCDD and PCDF.

Table 1. Some physical chemical properties.³

	MP ^b (°C)	BP ^c (°C)	P ^s (Pa)	S ^e (mg/m ³)	Log K _{ow} ^f	Half Life Air	Half Life Water	Half Life Soil	Half Life Sediment
PCDDs ^a	89- 322	284-510	1.1*10 ⁻¹⁰ - 0.017	74*10 ⁻⁶ - 417	4.3-8.2	2 days- 3 weeks	2 days- 8 months	2 months- 6 years	8 months- 6 years
PCDFs ^a	184-258	375-537	5*10 ⁻¹⁰ - 3.9*10 ⁻⁴	1.16*10 ⁻³ - 14.5	5.4-8.0	1 - 3 weeks	3 weeks- 8 months	8 months- 6 years	2 - 6 years

^a Range for mono- to octa-chlorinated congeners, ^bMP = melting point, ^cBP = boiling point, ^dP^s = vapour pressure, ^e = solubility, ^fK_{ow} = octanol water partition coefficient.

PCDD/Fs formed.

Most of the reported PCDD/F sources are high-temperature processes. In addition to waste incineration, these include iron ore sintering in the steel industry,⁷ aluminium recycling,⁸ copper ore melting,⁹ nickel refinery, magnesium production,¹⁰ electrical cable splicing,¹¹ catalyst regeneration in the petroleum refining industry,¹² fossil-fueled powerhouses,¹³ automobile exhausts,^{13,14} fireplaces, charcoal grills, and cigarettes.¹³ Slag from copper ore melting was used at one time as covering material for sportsgrounds and playgrounds,⁹ resulting in PCDD/PCDF contamination of these areas.

Although not reported in Table 2, pulp bleaching in the paper industry is a source of PCDD/Fs in other countries.¹⁵⁻¹⁹ From the chemical production processes, the production of chlorophenols is the most important one;²⁰⁻²² it leads to PCDD/F contamination in wood impregnated with pentachlorophenol,²² and to contamination of chemicals formed from chlorophenols, like 2,4,5-T (2,4,5-trichlorophenoxy acids).²⁰ Other chemical production processes reported as sources of PCDDs and PCDFs are the production of chlorobenzenes, chlorobi-phenyls,²¹ chlorobenzoquinones,²⁴ and dyes (phthalocyanines and dioxazines).²⁵

PCDD/F formation during any natural or human activity requires three basic ingredients: an organic starting material, a chlorine source, and, in processes with relatively low temperatures, a metallic catalyst. These compounds can be present in different amounts; the metallurgic industry,

Table 2. Emissions of PCDDs and PCDFs in The Netherlands (g TEQ/year), 1991.⁴

Municipal solid waste incineration	382
Other incineration processes	18.4
Burning of cables and electromotors	1.5
Asphalt-mixing plants	0.3
Combustion of oil, coal, lignite and wood	16.7
Traffic	7.0
Sintering processes	26
Metal industry	4.0
Chemical production processes	0.5
Use of wood preservatives	25
Various high temperature processes	2.9

for example, has high amounts of metals available, but low amounts of carbon and chlorine. In the paper industry, large amounts of chlorine and carbon are available, but low amounts of metals.

MUNICIPAL WASTE INCINERATION

Incineration Parameters

The CO concentration in flue gas is an indicator of combustion conditions. CO also correlates to some extent with PCDD/F concentrations.²⁶⁻²⁸ Important parameters in CO control are oxygen concentration and furnace temperature. Excess oxygen and low furnace temperatures yield high CO and high PCDD/F concentrations. An oxygen concentration that is too low, however, will cause other problems, like formation of PAHs.^{29,30} Good control of oxygen is therefore very important. The residence time in the cooling section is also an important parameter. Long residence times means high PCDD/F concentrations. The residence time in a small temperature window around 340 °C is very decisive.³¹ HCl, sulfur oxides, and nitrogen oxide concentrations in the flue gas do not correlate with the PCDD/F concentrations. Also, the percentage of moisture in the flue gas has no effect.^{28,32} Adding PVC to the feedstock will give higher HCl concentrations. As there is no correlation between HCl concentration and PCDD/F concentration, this has no direct influence on the PCDD/F concentration.³³ There is a correlation between the elemental composition of fly ash and PCDD/F concentrations. Chlorine, copper, sodium, potassium, and zinc have a positive correlation with PCDD/F concentration, with copper being the most effective. Aluminum and silicon have a negative correlation.³⁴ In Table 3, the average concentration of some metals in fly ash from a large number of municipal waste incinerators is reported.

Mechanism of Formation

Since the discovery of PCDDs and PCDFs in Municipal Waste Incinerator (MWI) fly ash and flue gas in 1977, much attention has been paid to the formation of these compounds. Theoretical calculations by Shaub and Tsang showed that formation is unlikely to take place through homogeneous gas phase reactions.^{36,37} They instead proposed a heterogeneous fly ash catalyzed mechanism of formation in the

Table 3. Average metal concentration in fly ash (mg/g).³⁵

Al	96	Cr	1
Ca	50	Cu	1
Fe	45	Ni	0.46
Zn	42	As	0.05
Pb	9.3	Hg	0.02
Cd	2.3		

post combustion zone of the incinerator. It was experimentally verified that the PCDD/F concentration in the flue gas passing the downstream region before the electrostatic precipitator is very low.^{5,38} Since 1982, a large number of experiments have been performed in which the formation on fly ash has been modelled on laboratory scale. A review of the results is given by Addink and Olie.³⁹

Chlorinated aromatic compounds can be intermediates in the formation of PCDDs and PCDFs. The correlation between some chlorinated compounds and PCDD/Fs present in a municipal waste incinerator support this route of formation. Chlorophenols, however, might play only a minor role in PCDD/F formation according to the lack of correlation between chlorophenols and PCDD/Fs in a municipal waste incineration. The isomer pattern found for the PCDD/Fs formed from chlorophenols during laboratory experiments also does not support the role of chlorophenols.

A rather good correlation between the chlorinated benzenes and PCDD/Fs is found. Chlorinated benzenes can be formed from benzene during model experiments, but it is not possible to form PCDD/Fs from benzene under realistic model conditions.^{40,41}

Model experiments support the idea that carbon on the fly ash plays an important role during the formation of PCDD/Fs.

MUNICIPAL WASTE INCINERATION FLY ASH AS A CATALYST FOR THE FORMATION OF PCDDs AND PCDFs

Shaub et al.³⁶ have calculated that homogeneous gas-phase formation of PCDDs and PCDFs from (chlorophenol) precursors is not likely to occur. They suggested a surface reaction where the fly ash surface can promote reactions at relatively low temperatures.

Chlorination Reactions on Fly Ash

Fly ash is known to catalyze chlorination of aromatic compounds such as toluene, biphenyl, diphenylether, PAHs, dibenzodioxin, and lower-chlorinated PCDD congeners. The products found point to an electrophilic aromatic substitution reaction.⁴²⁻⁴⁶ This electrophilic aromatic substitution reaction can also take place on model fly ash systems, like silica gel,

activated carbon, Tenax GC polymer, and a silica-alumina support impregnated with copper chloride.^{47,48}

Dechlorination Reactions

Fly ash is also able to catalyze the dechlorination of PCDDs and PCDFs. Heating fly ash in absence of oxygen leads to a decrease of PCDD/F concentration. This decrease is totally due to a decrease of higher chlorinated congeners, the amount of lower chlorinated congeners increases. This has led to the assumption that a dechlorination/hydrogenation reaction occurs under these reaction conditions, leading to the formation of lower chlorinated congeners.⁴⁹⁻⁵³

Formation of PCDDs and PCDFs

A third reaction catalyzed by fly ash is the formation of PCDDs and PCDFs. The amount of PCDDs and PCDFs increased when the fly ash was heated at temperatures around 300 °C in an oxygen atmosphere.^{49-51,54} PCDDs and PCDFs are in this case probably formed from residual carbon present on the fly ash surface. Ions of heavy metals or of the transition metal group are essential for this formation reaction.⁵¹ Copper has been identified as the strongest catalyst.⁵⁰ The catalytic action of CuCl₂ is poisoned by NH₃, which results in lower PCDD/F amounts in the presence of NH₃. As already noted in the preceding section, the amount of oxygen present can influence the formation of PCDDs and PCDFs. Already 1% oxygen present in the carrier gas causes formation of PCDD/Fs.⁶⁰

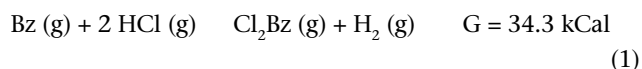
FORMATION OF PCDDs AND PCDFs FROM CARBON

The molecular structure of carbon consists of layers of aromatic rings of the type existing in graphite.⁵⁵ This ordered structure can be disturbed by oxygen and hydrogen atoms.⁵⁶ Part of the layer can also contain aliphatic chains.

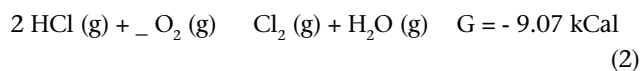
Formation of PCDDs and PCDFs from carbon starts with the chlorination of the surface of carbon. During oxidation of the carbon afterwards, PCDDs and PCDFs are released. The following knowledge is available on the mechanism of chlorination, the effect of water and carbon sources, temperature dependence, and inhibition with respect to the mechanism of formation of PCDDs and PCDFs.

The Deacon Reaction

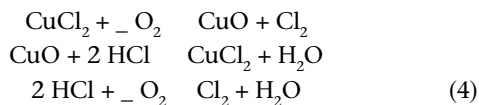
Chlorination of aromatic ring structures with HCl is a thermodynamically unfavored reaction: chlorination of benzene (Bz) with HCl, for example, proceeds with a positive Gibbs free energy of formation.⁵⁷



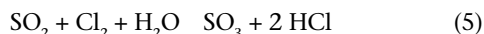
When HCl is first converted to Cl₂ a favored reaction is obtained.



Reaction 2 can be catalyzed by copper, as can be seen in reaction 4.⁴⁹

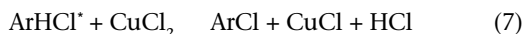
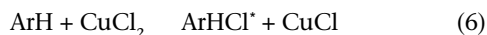


This reaction is called the Deacon Reaction and could play a role in the chlorination of carbon.^{49,50,57,58} The chlorine formed in the Deacon Reaction can react back to hydrogen chloride with sulfur dioxide (reaction 5). This reaction will inhibit the chlorination of carbon and, hence, the formation of PCDDs and PCDFs.^{57,58}



Chlorination via Direct Transfer

Stieglitz et al.⁵⁸ have looked at the influence of HCl and SO₂ on the formation of PCDDs and PCDFs. When the Deacon reaction plays an important role in the formation of PCDD/Fs, HCl would stimulate the formation of PCDDs and PCDFs, and SO₂ would inhibit PCDD/F formation. HCl and SO₂ concentrations, however, were found to have no influence on the formation of PCDDs and PCDFs. Elemental chlorine gas without copper chloride does not yield PCDDs and PCDFs at 300 °C. It also does not give oxidation of carbon at that temperature.⁵⁸ In other studies,⁵⁹ no correlation is found between the surface area of the carbon and the formation of PCDDs and PCDFs. This means that a direct interaction carbon-gas phase (as in the Deacon Reaction) is not the rate determining step. These facts suggest that the Deacon process plays only a minor role in the formation of PCDDs and PCDFs. Stieglitz et al.⁵⁸ have proposed a mechanism of direct transfer of halogen instead.



Cu(I) is oxidized to Cu(II) by oxygen. Hoffman⁴² also suggested a direct transfer of chlorine for the chlorination of aromatic compounds at the surface of fly ash. Aromatic compounds are adsorbed to the fly ash surface and chlorinated by an electrophilic aromatic substitution reaction. He suggests that iron is the chlorinating agent.

Carbon Source

The origin of carbon used for PCDD/F formation is

important.^{59,60} Soot and sugar coal, for example, are less reactive than charcoal. Graphite produces only minor amounts of PCDD/Fs.⁶⁰ The crystal lattice of graphite is probably more resistant to an attack of chlorine/oxygen than the already disturbed graphite structure of the other carbon samples. There is no correlation between the surface area of the carbon and the formation of PCDD/Fs,⁵⁹ so the variance of PCDD/F formation from different kinds of carbon is not caused by variance in surface area. In a recent study, Eichberger et al.⁶¹ found that formation of PCDDs, PCDFs, and PCBs is correlated with the activity of the carbon.

Role of Metals

Copper is very reactive in the formation of PCDDs and PCDFs. Various metal chlorides—such as MgCl₂, ZnCl₂, FeCl₂, MnCl₂, HgCl₂, CdCl₂, NiCl₂, SnCl₂, PbCl₂, and CuCl₂—have been tested for their ability to catalyze the formation of PCDD/Fs. From these metal chlorides, only CuCl₂ made a significant contribution to the PCDD/F formation.⁶⁰ Without metal chlorides, only trace amounts of PCDD/Fs were found. The addition of only 0.08% Cu²⁺ gives rise to significant amounts of PCDD/Fs. The addition of 0.24 and 0.4% Cu²⁺ gives rise to an overproportional rise in PCDD/F formation.⁶⁰ It was later found that FeCl₃ can catalyze the formation of PCDD/F too, but only when it is present in high amounts.⁵⁸

Inhibition

Inhibition of the formation of PCDDs and PCDFs from carbon was studied by Addink.⁵³ Ethylenediamine-tetra acetic acid (EDTA), nitrilo-tri-acetic acid (NTA), and Na₂S were found to inhibit the formation of PCDDs and PCDFs from carbon. Na₂S₂O₃ also inhibits PCDD/F formation, but less effectively. The inhibition is proposed to proceed by formation of stable complexes with transition metals, especially copper.

Formation of Other Chlorinated Aromatic Compounds

Chlorinated aromatic compounds other than PCDDs and PCDFs are formed during the municipal waste incineration process. In laboratory studies, many of those compounds are found to be formed from carbon. The most important group of compounds are chlorobenzenes, which are also dominant in municipal waste incineration.⁶ Besides chlorobenzenes, chloronaphthalenes, -biphenyls and -phenols, and a large number of trace compounds are formed from carbon.^{60,62-66} It is suggested that those compounds are formed when the carbon is degraded similarly to the formation of PCDDs and PCDFs.^{60,64,65} Some of these products, together with the compounds present or formed in the gas stream, could act as precursor compounds for the formation of PCDDs and PCDFs.

The complexity of the formation is also found from experiments where ¹⁸O₂ is used in model experiments.⁴⁰ The amount of ¹⁸O found in the PCDD/Fs formed is not constant

for all the compounds. Some compounds have relatively large amounts of ^{16}O due to oxygen, which is already present in the carbon.

CONCLUSIONS

Formation of PCDD/Fs during incineration of municipal waste is promoted by the catalytic properties of metals which are found in the waste itself. All types of carbon can serve as a carbon source. Chlorine can also be used in the different forms as it is present. Prevention of the formation can be done by poisoning the catalysts with complexing compounds. The formation of the PCDD/Fs is a complex of reactions in which chlorination of carbon and dechlorination of the initially formed PCDD/Fs are the most important.

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About the Authors

Kees Olie is with the Department of Environmental and Toxicological Chemistry, Faculty of Chemistry, Amsterdam Research Institute for Substances in Ecosystems, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV, The Netherlands. Mirjam Schoonenboom and Ruud Addink prepared their theses at this University.