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**EXPOSURE OF MAN TO DIOXINS:
A PERSPECTIVE ON INDUSTRIAL
WASTE INCINERATION**

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**EXPOSURE OF MAN TO DIOXINS:
A PERSPECTIVE ON INDUSTRIAL WASTE INCINERATION**

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EXPOSURE OF MAN TO DIOXINS: A PERSPECTIVE ON INDUSTRIAL WASTE INCINERATION SUMMARY AND CONCLUSIONS

The current knowledge of the occurrence, mechanism of formation and environmental fate of polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) is reviewed. Emissions of these materials originating from industrial waste incinerators (IWIs) are placed into perspective relative to their global emissions. Exposure levels, toxicological properties and human health impact are also addressed.

At present the major sources of atmospheric contamination by PCDDs and PCDFs are hospital and municipal waste incinerators and metallurgical processes. In contrast, industrial waste incineration (IWI) has lower emissions representing only about 1% of the total known sources. Atmospheric PCDD and PCDF emissions from industrial waste incinerators are strongly adsorbed on particles, i.e. dust and fly ash. The levels of PCDDs and PCDFs in soil and grass close to IWIs in the U.K. and Germany were found to be indistinguishable from urban background levels. The local contribution from an IWI is low with regard to PCDD and PCDF emissions when compared to other sources.

Atmospheric PCDDs and PCDFs emitted from all sources are deposited on soil, grass, vegetation and surface water. Subsequent absorption by animals and bioaccumulation make the food chain the most important route of exposure (>90%) for man; fish, dairy produce, meat products, and vegetables all being important. Global human exposure to PCDDs and PCDFs has been estimated in various European countries as an average daily intake of about 120pg/d, expressed as 2,3,7,8-TCDD toxic equivalents (TEQ). Conversion to an average body weight of 60kg results in a daily burden of 2pg/kgbw/d. Because of mothers milk contamination, a higher food intake in respect to body weight and the larger proportion of dairy products consumed by children, values up to 10pg TEQ/kgbw/d for their body burden may be expected.

Based on a combination of experimental toxicology and epidemiological data, an assessment was made of the health risk to man resulting from such exposure. The lowest effect level in animal studies is between 100 and 1,000pg TEQ/kgbw/d, and recent mechanistic studies support the existence of a threshold level below which there is no toxic effect. In man, the only clearly established toxic effect of these compounds is a severe form of acne called chloracne, which is observed after high accidental exposure to 2,3,7,8-TCDD. Data on other effects, including cancer, are inconclusive and remain controversial. By applying a safety factor of 100, which is commonly

used in Europe, it can be assumed that man would not be affected by a lifetime exposure to PCDDs and PCDFs corresponding to a daily intake of 1 to 10pg TEQ/kgbw/d.

Thus the total uptake of PCDDs and PCDFs from all known sources by man (adults and children) is within the range for this tolerable daily intake. Emphasis should be placed upon further minimisation or elimination of emissions from remaining major sources of contamination by PCDDs and PCDFs.

Although IWIs are a minor source of PCDD and PCDF emissions, further improvements are being sought. These include optimisation of waste preparation and loading rate, residence time, turbulence, temperature and waste/oxygen ratio. Better knowledge of the nature of the precursors and the mechanisms of formation of PCDDs and PCDFs are taken into consideration in designing modern IWIs, permitting the emissions of PCDDs and PCDFs to be reduced to 0.1-1ng TEQ/m³. Even more advanced technologies which are presently being evaluated may reduce these emissions still further, but the technical effort and cost will be considerable for relatively little benefit.

Incineration avoids dangerous dumping of industrial waste, which may result in leachate and landfill gas problems for many years. The risk to human health from exposure to PCDDs and PCDFs originating from well studied industrial waste incineration processes using present state-of-the-art technology can be regarded as insignificant.

SECTION 1 INTRODUCTION

Halogenated tricyclic aromatics are members of a large family of substances with some congeners (Appendix A) notable for their toxic behaviour. Within this family two main groups exist, the polyhalogenated dibenzo-p-dioxins (PXDD) and the polyhalogenated dibenzofurans (PXDF). The chlorinated and brominated dioxins and furans are the most significant and have been the subject of much investigation. The major emphasis in this report will be on the chlorinated compounds as their presence is considered of most importance. This does not preclude the possible importance of other halogenated compounds, especially the brominated and mixed chlorinated and brominated compounds (Buser, 1987a, b).

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are known to be ubiquitous contaminants in ecosystems. In recent years considerable attention has been given to the formation of PCDDs and PCDFs as unwanted by-products in combustion processes involving chlorine-containing compounds and in some chemical manufacturing processes.

Public concern about risks to human health from exposure to PCDDs and PCDFs originating from industrial waste incinerators (IWIs) has led to many questions about the standards of performance of such incinerators regarding the control of PCDD and PCDF formation. The purpose of this report is therefore:-

- to review the knowledge of the formation and fate of dioxins and dibenzofurans during the incineration of chemical waste in relation to their occurrence from other sources;
- to review the approaches adopted for controlling emissions from industrial waste incineration;
- to review exposure to dioxins and dibenzofurans of toxicological significance and to assess the relevance of such exposure to man.

SECTION 2 BACKGROUND

PCDDs and PCDFs, popularly referred to as dioxins and furans, or even simply as "dioxins", are a group of closely related tricyclic aromatic chemical compounds. None of these compounds has any commercial use and they are not manufactured intentionally except on laboratory scale for research or analytical standards. Nevertheless, PCDDs and PCDFs are formed occasionally in extremely low concentration as by-products, or may be present as trace impurities in certain chemical processes involving chlorine and organic compounds. They are also produced in trace quantities in the combustion of organic materials whenever chlorine or chlorine compounds are present. The existence of these compounds as contaminants in products from a variety of processes and their consequent widespread distribution in the environment became evident as a result of advances in analytical techniques. PCDDs and PCDFs can now be detected below the parts per trillion (ppt) level.

2,3,7,8-Tetrachlorodibenzodioxin (2,3,7,8-TCDD) was the toxic contaminant in the defoliant Agent Orange used in the Vietnam war and was identified in emissions from chemical plant accidents, most notably the Seveso incident in 1976. Against this background, "dioxin" has been popularised as "the most dangerous substance known to man". When it became widely known that PCDDs and PCDFs could be produced in any combustion process where chlorine compounds as well as organic compounds were present, public concern about the environmental effects of waste incineration, and particularly industrial waste incineration, focused on the potential for these processes to generate and release PCDDs and PCDFs.

In recent years, largely in response to these concerns, regulatory authorities, research institutes and industry have studied the generation of PCDDs and PCDFs in combustion and manufacturing processes using organic compounds with chlorine or chlorine compounds. Numerous measurements have been made of the amounts of PCDDs and PCDFs emitted from such processes in flue gases, waste water discharges and solid wastes. Municipal and industrial waste incineration processes have been studied extensively in attempts to understand the mechanism of formation, and thereby methods for control, of PCDDs and PCDFs, both in combustion chambers and in flue gas cleaning systems. Surveys have been undertaken to determine the distribution of these substances in the immediate vicinity of known sources and in the environment generally.

A number of regulatory authorities and other organisations have used the available information on occurrence, distribution, environmental fate and toxicological properties of PCDDs and PCDFs to make assessments of the likely hazards to human health. Various proposals have been made about "acceptable daily intakes" and these have been used to assess hazards to public health associated with individual sources or types of sources.

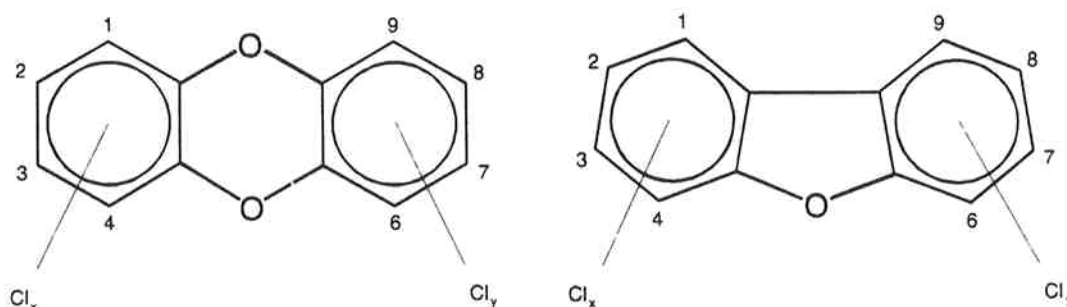
A comprehensive investigation of these compounds has been made including studies of their formation and evaluation of their ecological pathways from technical processes to the environment.

ECETOC has now carried out a critical review of the current knowledge of the occurrence, formation, distribution, environmental fate and toxicological properties of PCDDs and PCDFs. Available methods for estimating human exposure have been used and an assessment made of the relevance of such exposure to health. The approaches adopted by regulatory authorities and plant operators for controlling emissions from industrial waste incineration have also been examined. Plant performance criteria are recommended and a risk assessment approach put forward that can be used as the basis for the design and control of chemical waste incinerators in order to minimise discharges of PCDDs and PCDFs to the environment and to provide an adequate safeguard for public health.

SECTION 3 CHARACTERISATION OF PCDDs AND PCDFs

3.1. CHEMICAL IDENTITY

PCDDs and PCDFs are chlorinated tricyclic aromatic compounds. Each of these compounds has a triple ring structure consisting of two benzene rings inter-connected to each other by respectively two or one oxygen atoms. The number of chlorine atoms can vary between 1 and 8. The general formulae are:



Seventy five PCDD and 135 PCDF "congeners" are theoretically possible (cf Appendix A for definitions and abbreviations). Mixed halogenated substitution increases the number of congeners drastically, for example the number of congeners of chloro- and bromosubstituted dibenzo-p-dioxins and PCDFs is about 4,600 (Buser, 1987b).

The crystal structures of several chlorinated PCDDs have been reported (Boer *et al.*, 1972; Cantrell *et al.*, 1988). The molecules of the 2,7-dichloro, 2,3,7,8-tetrachloro and octachloro structures are all located on crystallographic centres of symmetry and are very nearly planar in each case (Cantrell *et al.*, 1989). The correlation between the chemical structure of the compounds and their acute toxicity is shown in Table 1. The 17 PCDD and PCDF congeners substituted at least on all four positions 2,3,7 and 8 appear to be more toxic than the others by several orders of magnitude.

The toxic potential of each congener is expressed by a factor ("toxicity equivalency factor" or TEF) which relates the toxic potential of a given congener to the toxic potency of 2,3,7,8-TCDD as a reference (NATO/CCMS, 1988a, b, c; Kutz *et al.*, 1990; Safe, 1990). These factors allow the toxic potential of each congener present in any source to be expressed as an equivalent concentration of 2,3,7,8-TCDD. The total toxic equivalent (TEQ) of a given environmental sample is calculated by multiplying the amount of each congener present in the sample by its specific "toxic equivalency factor" and by adding up the total (cf Section 5).

Table 1

Correlations between Chemical Structure and Acute Toxicity,
 expressed as LD₅₀ in Guinea Pigs[†]
 (McKinney and McConnell, 1982; Schlatter, 1985)

Name of Compound	LD ₅₀ (µg/Kg)
2,3,7,8-Tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD)	2
2,3,7,8-Tetrachlorodibenzofuran (TCDF)	7
3,3',4,4',5,5'-Hexachlorobiphenyl	223
2,3,7-Trichlorodibenzo-p-dioxin (TrCDD)	29,444
2,3,3',4,4',5,5'-Heptachlorobiphenyl	> 3,000
4,4'-Dichloro-3,3',5,5'-tetrafluorobiphenyl	> 3,000
3,3',4,4'-Tetrachlorobiphenyl	<552
3,3',4,4'-Tetrachlorobiphenyl ether	NDb
2,3,6,7-Tetrachloronaphthalene	> 3,000
1,2,4,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	1,125
1,2,3,7,8-Pentachlorodibenzo-p-dioxin (PeCDD)	3
2,3,4,7,8-Pentachlorodibenzofuran (PeCDF)	< 10
3,3',4,4',5-Pentachlorobiphenyl	NDc
2,3,7,8-Tetrabromodibenzo-p-dioxin (TBDD)	NDc
2,3,7,8-Tetrabromodibenzofuran (TBDF)	< 15
2,3,7-Tribromodibenzo-p-dioxin (TrBDD)	NDc
2,3,6,7-Tetrabromonaphthalene	242
1,2,4,6,7-Pentabromonaphthalene	200
1,2,3,4,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	73
1,2,3,6,7,8-Hexachlorodibenzo-p-dioxin (HxCDD)	70-100
1,2,3,7,8,9-Hexachlorodibenzo-p-dioxin (HxCDD)	60-100
1,2,3,4,6,7,8-Heptachlorodibenzo-p-dioxin(HpCDD)	> 600
Octachlorodibenzo-p-dioxin (OCDD)	NDb
2,3,4,6,7,8-Hexachlorodibenzofuran (HxCDF)	120
1,2,3,4,7,8-Hexabromonaphthalene	361
1,2,3,5,6,7-Hexabromonaphthalene	> 3,610
2,3,6,7-Tetrachlorofluoren-9-one	> 100

† Hartley strain guinea pigs given a single oral dose (gavage) and observed per 30 days.

NDb Not determined in guinea pig, but compound was inactive as inducer of cytochrome P-448 and associates enzymes in one or more biological test systems.

NDc Not determined in guinea pig, but compound was very active as inducer of cytochrome P-448 and associates enzymes in one or more biological test systems.

3.2. PHYSICO-CHEMICAL PROPERTIES

All PCDDs and PCDFs are organic solids with high melting and boiling points and low vapour pressures (Rordorf, 1985). They are characterised by extremely low water solubilities (Friesen *et al*, 1985; Shiu *et al*, 1988), and high n-octanol/water partition coefficients (Shiu *et al*, 1988). They have a tendency of being strongly adsorbed on surfaces of particulate matter (Walters and Guisleppe-Elle, 1988). The water solubility of PCDDs and PCDFs decreases and the solubility in organic solvents and fats increases with increasing chlorine content.

3.3. ANALYTICAL DETECTION OF PCDDs AND PCDFs

Details of the techniques used for the collection of samples from various environmental media together with state of the art of analytical techniques are fully discussed in Appendix B.

Results are usually expressed as TEQ. This necessitates the addition of at least 17 ¹³C PCDDs and PCDFs as internal standards, and these materials are coincidentally used to provide quality assurance during the sampling and analysis procedure. In this report analytical results will be expressed in TEQ whenever possible.

The most important sampling points associated with IWIs are stack gases, water effluents, ash, slag and sludge from gas cleaning activities. The method for analysis of PCDDs and PCDFs is high resolution capillary gas chromatography interfaced with mass spectrometry, following sample clean-up by liquid chromatographic techniques. Detection limits of 0.01ng TEQ/m³ in stack gases can be achieved, depending on sampling systems used. The accuracy largely depends on the sampling procedures, the efficiency of extraction and the instrumental analysis. Consequently, the results from different laboratories may differ by as much as one order of magnitude, particularly at low levels.

SECTION 4 ORIGIN, DISTRIBUTION AND FATE OF PCDDs AND PCDFs

4.1. ORIGIN

4.1.1. Natural

The known natural sources of PCDDs and PCDFs are related to fires and combustion processes. Thus, these toxic compounds may be produced from forest fires, by lightning or volcanic action. Bumb *et al* (1980) in their study on trace chemistry of fire have shown that hydrocarbon combustion in the presence of chlorine compounds can give rise to PCDDs and PCDFs in small amounts.

The pre-industrial existence of PCDDs and PCDFs has been demonstrated by analysis of ancient human Eskimo tissues (Schechter *et al*, 1988; Tong *et al*, 1990). Octachloro dibenzo-para-dioxin (OCDD) was found at concentrations of about 30pg/g with an analytical technique with a detection limit of less than 3pg/g and HeptaCDD (HpCDD) at a level of 10pg/g with a detection limit better than 1pg/g. The OCDD concentration is 25 times less than the levels found in adipose tissues of modern man (Schechter and Ryan, 1988). PCDDs and PCDFs were also found in 9 Chilean mummies (Ligon *et al*, 1989).

Hashimoto *et al*, (1990) confirmed that historical pollution by PCDDs and PCDFs occurred at least 6,100 years B.C. The total concentrations of PCDDs in sediment cores from Osaka Bay showed values of 8ng/g at a depth of 0.3m and 3ng/g dry sediment at a depth of 2.0m. They found PCDDs even at a soil depth of 8.75m on Harima-Nada with concentrations of 1,2,3,4,6,7,9-HpCDD at 0.05ng/g and OCDD at 0.3ng/g in dry sediment. The corresponding concentrations of PCDFs were at least one order of magnitude lower. The concentrations in historical sediments do not differ very much from those in a modern industrial landfill site (Stern *et al*, 1989). Similar levels of PCDDs and PCDFs compared to the values in historical sediments were also reported in urban soil samples from British cities in 1989 (Creaser *et al*, 1990):

PCDD (ng/g soil)		PCDF (ng/g soil)	
TCDD	0.07	TCDF	0.23
PeCDD	0.07	PeCDF	0.19
HxCDD	0.15	HxCDF	0.16
HpCDD	0.82	HpCDF	0.15
OCDD	10.0	OCDF	0.20

The natural or pre-industrial combustion sources produce PCDDs and PCDFs in low yields. The synthesis route is extremely complex and reaction kinetics are generally not favourable in open burning conditions. The generally low availability of halogens in the combustion of natural biomass will also limit the amount of PCDDs and PCDFs formed. Nevertheless, even at very low yields these primitive combustion processes could be significant sources of the compounds; a million tonnes of wood may be burned in a large forest fire.

4.1.2. Origin from Technological Sources

PCDDs and PCDFs have never been produced deliberately as commercial products. There are two main sources of PCDDs and PCDFs in the environment: industrial by-products and combustion processes.

Industrial Sources. The formation of PCDDs/PCDFs in a chemical reaction process is very dependent on the presence of oxygen, carbon, chlorine and heat. The presence or formation of precursor compounds with closely related molecular structures will greatly enhance the formation of these substances. The following sections of this section review a number of processes in which PCDDs and PCDFs can be produced as unwanted by-products.

Industrial Chemical Processes. Many manufacturing processes involving halogenated (particularly chlorinated and brominated) aromatic or aliphatic compounds are likely to involve side reactions leading to the production of halogenated polyaromatics. Processes involving chlorophenols, chlorobenzenes, chlorine substituted aliphatic compounds and chlorine containing catalysts are all potential sources of PCDDs, PCDFs and related compounds (Esposito *et al*, 1980; Heindl and Hutzinger, 1986). Other compounds are less likely to lead to dioxin formation because they would require an unusual combination of reaction steps to produce PCDDs (Esposito *et al*, 1980).

Hagenmaier and Brunner (1987) detected PCDDs and PCDFs as contaminants in pentachlorophenol (PCP) and sodium pentachlorophenate (PCP-Na) in amounts up to the mg/kg range. These compounds were widely used materials for pest control and wood preservation but their use is now restricted.

Another example of a process leading to significant production of PCDDs was the manufacture of Agent Orange, which achieved attention through its use as a defoliant in the Vietnam war. It was a 1:1 mixture of the n-butylesters of 2,4,5-T (2,4,5-

trichlorophenoxyacetic acid) and of 2,4-D (2,4-dichlorophenoxyacetic acid). Tetra- and higher chlorosubstituted dibenzodioxins were directly generated during the process via radical reactions of 2,4,5-T or the trichlorosodiumphenolate as intermediate compound. Analysis of 200 samples of Agent Orange (Kearney *et al*, 1973) showed a wide range of 2,3,7,8-TCDD content from 0.5mg/kg to 47mg/kg. It has been estimated that in the early 1970's manufacture of Agent Orange led to the formation of about 50kg of 2,3,7,8-TCDD per year.

2,4,5-T was also used as a herbicide in agriculture in the form of its esters or salts. For such products Smith and Pearce (1986) reported for 2,4,5-T average levels of 950ng/kg of 2,3,7,8-TCDD/kg in 1971. Subsequent improvements of the chemical processes brought a considerable reduction to a few ng 2,3,7,8-TCDD/kg. 2,4,5-T is no longer used in Western Europe and in the USA.

The potential PCDD and PCDF formation in certain manufacturing processes increases greatly if temperatures and pressures increase well beyond the normal operating conditions. Although such incidents are not common, Bruppacher and Reggiani (1986) have reported 16 accidents associated with the production of chlorophenols. Of these the best documented is the Seveso accident in 1976. The process in Seveso was the manufacture of 2,4,5-trichlorophenol (TCP), an intermediate for the production of the bactericide hexachlorophene. It was later estimated that some 300g of 2,3,7,8-TCDD had been discharged and spread over an area of about 2.2km². A further 600g were found in the remaining reactor mass and other parts of the plant (Kuenzi, 1982; Salomon, 1982; Sambeth, 1982; Krum, 1985; Hutzinger *et al*, 1985).

PCDDs and PCDFs were also detected as impurities in polychlorinated biphenyls and terphenyls used as dielectric fluids in transformers in the electricity supply network (UBA, 1984). They can also be formed during the production of halogenated diphenylethers and during the extrusion of thermoplastics containing such compounds (EEC, 1989; BASF, 1990).

Halogenated polyaromatics, in a wide range of chemical manufacturing processes, can give rise to PCDD and PCDF formation in waste streams, in recycled streams and as contaminants in intermediates and finished products.

Processes of the Pulp and Paper Industries. Manufacture of wood pulp and paper by processes using chlorine gives rise to PCDDs and PCDFs in products (Beck *et al*, 1989a) and in process sludge and waste water streams. It was demonstrated in a study of 104 paper mills in the USA (Whittemore *et al*, 1990) that the median values of