

Appendix A Background Information on PCDDs and PCDFs

This appendix has been compiled from a number of MfE reports (Buckland *et al.*, 2001, Buckland *et al.*, 1998, Smith and Lopipero, 2001).

A.1 Chemical Structure and Toxicity

The PCDDs and PCDFs are chemically classified as halogenated hydrocarbons. They are tricyclic aromatic compounds, comprising two benzene rings joined via either one or two oxygen atoms at adjacent carbons on each of the benzene rings, as shown in Figure A-1, below.

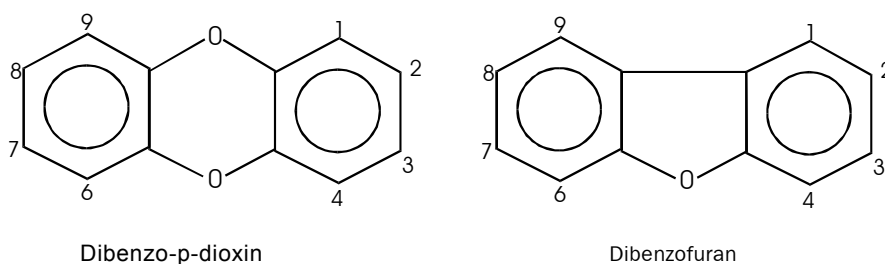


Figure A-1: Structures of dibenzo-p-dioxin and dibenzofuran

Both groups of chemicals may have up to eight chlorine atoms attached at carbon atoms 1 to 4 and 6 to 9. Each individual compound resulting from this is referred to as a congener. Each specific congener is distinguished by the number and position of chlorine atoms around the aromatic nuclei. In total, there are 75 possible PCDD congeners and 135 possible PCDF congeners. Groups of congeners with the same number of chlorine atoms are known as homologues. The number of congeners in each homologue group is shown in Table A-1. The most widely studied of the PCDDs and PCDFs is 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD). This congener is often generically referred to as 'dioxin', and is the reference compound for this class of chemicals.

Congeners containing one, two or three chlorine atoms are thought to be of no toxicological significance. However, 17 congeners with chlorine atoms substituted in the 2, 3, 7 and 8- positions are thought to pose a risk to human and environmental health. Toxic responses include dermal toxicity, immunotoxicity, carcinogenicity and adverse effects on reproduction, development and endocrine functions. Increasing substitution from four to eight chlorine atoms generally results in a marked decrease in potency.

Table A-1: Homologues and congeners of PCDDs and PCDFs			
Abbreviation	Homologue name	No. of possible congeners	No. of possible 2,3,7,8-chlorinated congeners
MCDD	Monochlorodibenzo-p-dioxin	2	0
DiCDD	Dichlorodibenzo-p-dioxin	10	0
TrCDD	Trichlorodibenzo-p-dioxin	14	0
TCDD	Tetrachlorodibenzo-p-dioxin	22	1
PeCDD	Pentachlorodibenzo-p-dioxin	14	1
HxCDD	Hexachlorodibenzo-p-dioxin	10	3
HpCDD	Heptachlorodibenzo-p-dioxin	2	1
OCDD	Octachlorodibenzo-p-dioxin	1	1
MCDF	Monochlorodibenzofuran	4	0
DiCDF	Dichlorodibenzofuran	16	0
TrCDF	Trichlorodibenzofuran	28	0
TCDF	Tetrachlorodibenzofuran	38	1
PeCDF	Pentachlorodibenzofuran	28	2
HxCDF	Hexachlorodibenzofuran	16	4
HpCDF	Heptachlorodibenzofuran	4	2
OCDF	Octachlorodibenzofuran	1	1

A.2 Toxic Equivalency Factors and Toxic Equivalents

In environmental media, PCDDs and PCDFs occur as complex mixtures of congeners, which therefore complicates any environmental or human health risk evaluation. However, because it is widely accepted that the toxicological action of PCDDs and PCDFs is via a common mechanism of action (in the initial stages, at least), these compounds have been assigned individual toxic equivalency factors (TEF) values, as agreed by international convention (see, for example, Kutz *et al.*, 1990; Van den Berg *et al.*, 1998). This mechanism of action is believed to involve the binding of a congener to a cellular protein known as the 'Ah receptor'. The importance of the TEF approach is that it allows the combined toxicity of a complex mixture of congeners to be represented in terms of a single numerical value, or 'toxic equivalents' (TEQ). The TEQ contribution of each congener is calculated by multiplying its concentration by the TEF for that congener. This approach facilitates risk assessment and regulatory control of exposure to these mixtures.

The TEQ method is based on toxicological and in vitro biological data, and knowledge of structural similarities among this group of chemicals. In essence, TEFs are estimates of the relative toxicities of individual PCDD and PCDF congeners compared to the toxicity of 2,3,7,8-TCDD, which, as the reference compound for this group of chemicals, is assigned

a TEF of 1. All 2,3,7,8-PCDDs and PCDFs have been assigned TEF values, which are generally less than 1, reflecting their lower toxic potency. Periodically, these TEFs are revised based on new toxicological data. The latest internationally accepted TEFs for the PCDDs and PCDFs, as agreed at a 1997 World Health Organization (WHO) consultation (Van den Berg *et al.*, 1998), are shown in Table A-2. The earlier "International" TEF (Kutz *et al.*, 1990) scheme (I-TEF) is also shown in Table A-2.

The use of TEFs assumes that the toxicity of the various congeners acts in an additive fashion. The toxic potency of a mixture of PCDDs and PCDFs (i.e. the TEQ) is the sum of the products of the concentration of each congener present in the mixture and that congener's TEF. Thus, the TEQ represents 2,3,7,8-TCDD toxic equivalents for mixtures of PCDDs and PCDFs.

Table A-2: Toxic equivalency factors for PCDDs and PCDFs		
PCDD and PCDF congener	WHO-TEF (Van den Berg <i>et al.</i> , 1998)	I-TEF (Kutz <i>et al.</i> , 1990)
2,3,7,8-TCDD	1	1
1,2,3,7,8-PeCDD	1	0.5
1,2,3,4,7,8-HxCDD	0.1	0.1
1,2,3,6,7,8-HxCDD	0.1	0.1
1,2,3,7,8,9-HxCDD	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.01	0.01
OCDD	0.0001	0.001
2,3,7,8-TCDF	0.1	0.1
1,2,3,7,8-PeCDF	0.05	0.05
2,3,4,7,8-PeCDF	0.5	0.5
1,2,3,4,7,8-HxCDF	0.1	0.1
1,2,3,6,7,8-HxCDF	0.1	0.1
2,3,4,6,7,8-HxCDF	0.1	0.1
1,2,3,7,8,9-HxCDF	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.01	0.01
OCDF	0.0001	0.001

A.3 Sources

PCDDs and PCDFs are not produced intentionally, but are released to the environment from a variety of industrial discharges, combustion processes and as a result of their

occurrence as unwanted by-products in various chlorinated chemical formulations. Historically the manufacture and use of chlorinated aromatic chemicals have been major sources of PCDDs and PCDFs in the environment. Most notable examples include the wood preservative and biocide pentachlorophenol (PCP), 2,4,5-trichlorophenoxy acetic acid (2,4,5-T) and the polychlorinated biphenyls (PCBs). Other processes, such as the production of chlorine-bleached pulp, have led to environmental contamination by PCDDs and PCDFs, as well as the trace contamination of pulp and paper products.

Combustion processes are recognised as being another important source of PCDDs and PCDFs. Most thermal reactions which involve the burning of chlorinated organic or inorganic compounds appear to result in the formation of these substances. PCDDs and PCDFs have been detected in emissions from the incineration of various types of wastes, particularly municipal, medical and hazardous wastes, from the production of iron and steel and other metals, including scrap metal reclamation, from fossil fuel plants, domestic coal and wood fires, and automobile engines (especially when using leaded fuels) as well as accidental fires. An extensive review of PCDD and PCDF sources has been published by Fiedler *et al.* (1990), and more recently by the United States Environmental Protection Agency (USEPA, 1998). Although natural, non-anthropogenic, combustion sources (like forest fires) have probably always been a source of PCDDs and PCDFs, the background levels associated with the pre-industrial processes (before the 1930s/1940s) are found to be negligible when compared to those resulting from more recent industrial activities (Kjeller *et al.*, 1991; Beurskens *et al.*, 1993; Jones and Alcock, 1996).

An inventory of dioxin emissions to air, land and water in New Zealand has been published (Buckland *et al.*, 2000)

A.4 Physical and Chemical Properties and Environmental Fate

In general, PCDDs and PCDFs have low water solubility, high octanol-water partition coefficients, low vapour pressure and are resistant to chemical degradation under normal environmental conditions. These properties mean that dioxin-like compounds are extremely persistent in the environment, and their highly lipophilic nature results in bio-concentration into biota and biomagnification through the food chain.

In soil, sediment, water and (to a lesser extent) ambient air, PCDDs and PCDFs are primarily associated with particulate and organic matter because of their high lipophilicity and low water solubility. The lower chlorinated congeners have a relatively higher vapour pressure, and more readily partition into the gaseous phase. Once adsorbed to particulate matter, PCDDs and PCDFs exhibit little potential for significant leaching or volatilisation. The available data indicate that these are extremely stable compounds under most environmental conditions, with environmental persistence measured in decades.

The only environmentally significant transformation process for PCDD/F congeners is considered to be photodegradation in the gaseous phase and at the soil-air or water-air

interface. PCDDs and PCDFs entering the atmosphere are removed either by photodegradation or by wet or dry deposition. Although some volatilisation of PCDDs and PCDFs on soil does occur, the predominant fate of these chemicals adsorbed to soil is to remain in place near the surface of undisturbed soil, or to move to water bodies with soil erosion. The scouring of surface soil through wind erosion may also lead to the re-suspension of particle-bound PCDDs and PCDFs into the atmosphere. PCDDs and PCDFs entering the water column primarily undergo sedimentation and burial. The ultimate environmental sink of these PCDDs and PCDFs is believed to be aquatic sediments.

A.5 References

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