Dioxins and Dioxin-Like Compounds in Soil

technical memorandum

Background

Dioxins and dioxin-like compounds are chlorinated organic pollutants formed as trace amounts of undesired impurities in the manufacture of other chemicals such as chlorinated phenols and their derivatives, chlorinated diphenyl ethers, and polychlorinated biphenyls (PCB) (WHO, 1988) and combustion of chlorine containing materials under some conditions. These compounds are also referred to as unintentionally produced persistent organic pollutants (UPOP).

The group dioxins comprise 75 polychlorinated dibenzo-p-dioxin (PCDD) congeners and 135 polychlorinated dibenzofuran (PCDF) congeners. There are no known technical uses for PCDD and PCDF (WHO, 1988).

Some PCB also have dioxin-like properties and are included as part of dioxin and dioxin-like compounds. PCB are a class of organic compounds with 1 to 10 chlorine atoms attached to the biphenyl molecule. There are 209 possible PCB congeners although only 130 were found in commercial PCB mixtures.

WHO (Van den Berg *et al.,* 2006) identified 29 dioxins and dioxin-like compounds of environmental concern based on similar toxicological profiles. These include seven PCDD, ten PCDF and twelve co-planar "dioxin-like" PCB.

Whilst these substances have similar toxicological profiles, they have differing toxicological potencies. Thus, their concentrations in environmental and biological media are reported using toxicity equivalence (TEQ) relative to a reference compound, which in this case is 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD). The relative toxicity of each compound is expressed as a toxicity equivalency factor (TEF) and the product of the concentration and the TEF for each substance in the mixture results in a TEQ concentration relative to 2,3,7,8-TCDD. The sum of the resultant TEQ for each substance yields a single concentration for the TEQ of the mixture. The following TEQ systems have been used historically:

- The International TEQ (I-TEQ) developed largely by the United States Environmental Protection Agency (US EPA) in 1990.
- The WHO modified the I-TEQ in 1998 by incorporating "dioxin-like" PCBs, this was known as the WHO_{98} TEQ.
- In 2005 the WHO_{98} TEQ system was updated to WHO_{05} TEQ (Van den Berg *et al.,* 2006).

Soil Contamination by Dioxin and Dioxin-Like Compounds – Summary of Findings

A conceptual model for the sources, environmental transport pathways and human exposure routes for dioxins and dioxin-like compounds is shown in Figure 1 (adapted from Weber *et al.,* 2008).

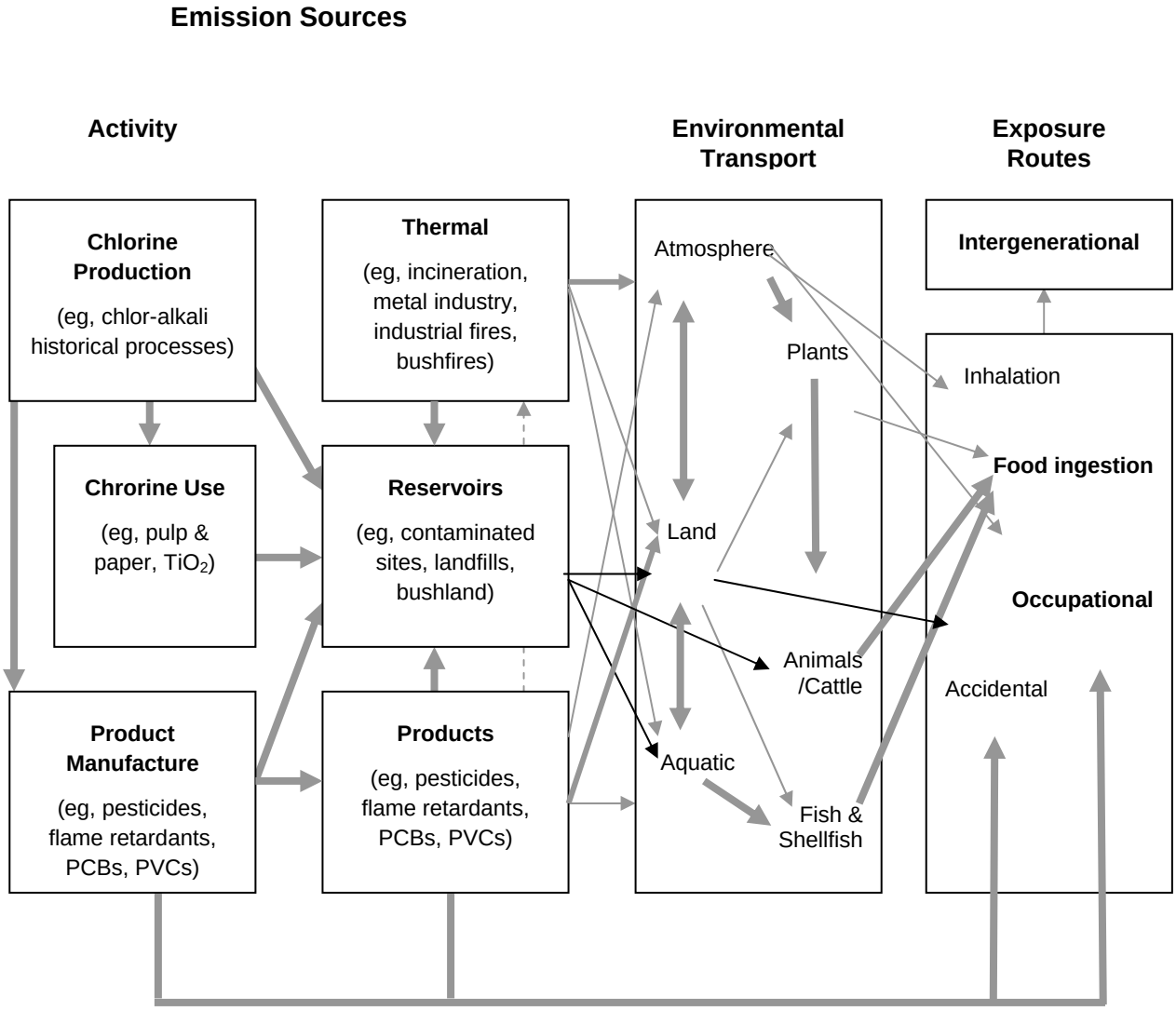

Figure 1: Adapted from: Sources, reservoirs, environmental transport and major human exposure pathways of PCDD/PCDFs (Weber et al., 2008)

The major causes of soil contamination by dioxin and dioxin-like compounds are from accidental or incidental spillages in the manufacture, transport, storage and use of various chlorinated compounds and past disposal of these compounds to unregulated landfill. Land uses associated with waste disposal, pulp and paper mills, chemical manufacturing and dry cleaning industry may have resulted in soil contamination by these compounds.

Other industrial sources of dioxin and dioxin-like compounds such as thermal or combustion sources and reservoir sources such as sludges may be less significant as contaminant sources for soil. Dioxins and dioxins-like compounds are also released into the atmosphere from forest fires and volcanoes. As for anthropogenic sources of dioxin in air, these may not be a concern with respect to deposition from air and soil contamination as they are isolated events, although they may be a concern for inhalational exposure during the events.

Conclusions from the four-year National Dioxins Program conducted in Australia were that the concentration of dioxin-like compounds were greatest in soils near centres along the populated south-east coastal region and were consistently low at inland locations and in Western Australia. The concentrations of dioxin-like compounds in urban and industrial locations sampled in their program were "*similar to those reported in previous Australian studies and in the New Zealand Organochlorines Program*". Concentrations in remote and agricultural areas were on average "*much lower*" compared to other industrialised countries and among the lowest background concentrations internationally. In industrial and urban locations the levels of dioxin-like compounds were "*more variable*" and the contribution of PCB to WHO_{98}-TEQ concentrations was often more relevant. In general, levels of dioxin-like compounds in urban and industrial soils were relatively low compared to results from overseas.

Soil Contamination by Dioxin and Dioxin-Like Compounds – Support for Findings

Industrial Sources of Dioxins

Industrial Sources of dioxin-like compounds can be classified into three main groups (Fiedler *et al.*, 1996):

- chemical/industrial sources;
- thermal/combustion sources; or
- reservoir sources.

A summary of the industrial land uses that are potential sources of dioxins and dioxin-like compounds in soil is outlined in Table 1.

Table 1: Industrial Land Uses Associated With Release to Soil of Dioxins and Dioxin-Like Compounds

Source/Land Use	Examples and Comments
Chemical/industrial	
Pulp and paper mills	■ Manufacture of bleached pulp and paper
Chemical manufacturing	■ Manufacture of chlorinated compounds e.g. PCB, phenoxy herbicides, chlorinated benzenes chlorinated aliphatic compounds, chlorinated catalysts and halogenated diphenyl ethers ■ Storage of chlorinated compounds
Dry cleaning industry	■ Dry cleaning distillation residues
Thermal/Combustion	
Cement kilns	■ When hazardous waste is used as an auxiliary fuel
Crematoria	■ Source of chlorine and organic material
Coal-fired utilities	■ Source of chlorine and organic material

Source/Land Use	Examples and Comments
Municipal solid waste incinerators	■ Municipal solid waste commonly contains chlorinated compounds and organic polycyclic hydrocarbons ■ Modern municipal waste incinerators have less dioxin emissions
Hospital waste incinerators	■ Low-level technologies, high numbers, and burning of high chlorine waste
Hazardous waste incinerator	■ Hazardous organic compounds such as chlorinated phenols can be incinerated using this method
Metals industry	■ High temperature steel production ■ Smelting operations ■ Scrap metal recovery furnaces ■ Sintering of iron ore
Recycling facilities	■ Sintering plant ■ Rolling mills
Reservoirs	
Sewage sludge	■ Used as fertiliser

Chemical/Industrial Sources

Chemical/industrial sources include the manufacture of chlorinated compounds such as PCB, phenoxy herbicides, chlorinated benzenes, chlorinated aliphatic compounds, chlorinated catalysts and halogenated diphenyl ethers, the pulp and paper industry, and dry cleaning distillation residues.

Manufacture of chlorinated phenolic intermediates and products and PCBs occurred until 1990; however, continued limited use and disposal of these compounds can cause the release of dioxins into the environment (Kulkarni *et al.,* 2008).

Organochlorine production processes generally improved from the 1960s to the 1980s in relation to PCDD/PCDF formation and release. Consequently higher levels of PCDD/PCDF may be present in pesticides and associated wastes from early operation of the organochlorine industry.

Weber *et al.* (2008) describe sites used for the "*production, storage and use of PCBs, together with the sites of fires or disposal activities involving PCBs*" as being likely to be significant and frequently encountered examples of soil contamination by dioxins and dioxin-like compounds.

Historically the pulp and paper industry was an important source of PCDD/PCDF from the chlorination of phenolic compounds present in wood (Weber *et al.,* 2008). These compounds were described as often being discharged in wastewater and sludge. Currently, most major industrialized countries have discontinued the use of elemental chlorine for bleaching; however, contamination from past activities may persist.

Weber *et al.* (2008) describe several recent publications in which chlorine processing in the production of titanium dioxide has been associated with the generation of significant amounts of PCDD/PCDF. Production of nylon in Japan using a nitrosyl chloride intermediate step has been associated with "*environmentally relevant*" amounts of PCDD/PCDF.

Soil contamination by dioxin and dioxin-like compounds may be significant in and around sites used for the production, storage, use and disposal of:

- PCB
- POP pesticides
- other chlorinated compounds.

Thermal or Combustion Sources

PCDD/PCDF are produced when organic compounds containing chlorine are burned and a series of chemical reactions take place under specific conditions.

Thermal sources include incinerators for municipal solid waste and hazardous waste, steelworks, metal refinery factories, power stations, coal and oil industries, sintering plants, cement, lime, glass and brick production, and recycling plants (Fielder *et al.* 1996; Zheng *et al.* 2008).

Emissions to air are an important potential source of environmental pollution. Fielder (1996) reported limited accumulation of dioxins in air by deposition in soil in urban areas in Germany, except for areas close to point sources where deposition could be up to ten-fold higher than urban areas in general. Current industrial combustion sources in Australia operate under licence conditions imposed by environmental protection jurisdictions and permitted emissions are unlikely to result in significant land contamination near or distant from the point source.

Reservoirs

Sewage sludge, compost and contaminated soils are reservoirs of dioxins. Agricultural land on which chlorinated pesticides that may have contained trace dioxins and dioxin-like impurities is also a reservoir for these compounds. However, as the levels of impurities were likely low and regulated, persistent contamination from the pesticide itself is likely to be of more concern than contamination from the POP impurities as shown by Fielder (1996).

Sewage sludge is often used as a fertiliser but can be contaminated by dioxin-like compounds. Clarke *et al.* (2008) concluded that the burden of dioxin-like compounds in Australian sewage sludge is low and its land applications as biosolids is not likely to pose a problem. Similarly, Fielder (1996) concluded that the use of sewage sludge and compost is unlikely to pose a risk to humans or grazing animals. Clarke *et al.* (2008) reported little variation to concentrations of dioxin-like compounds in sewage sludge in Australia during the years of their study, 2002-2006. The range of concentration of dioxin-like compounds in sewage sludge in Australia during 2002-2006, the period of their study, was 2.5 to 20.6 ng WHO_{05} TEQ $\cdot kg^{-1}$ and declined by an average of 1.40 ng $\cdot kg^{-1}$ per year.

Estimated Contribution on Various Activities to Dioxin Emissions to Soil

Dyke *et al.* (1997) provided the following examples of industrial processes and the associated releases of PCDD/PCDF to land in the United Kingdom (Table 2). These may assist in assessing the importance of land use and anthropogenic activities in contributing to soil contamination.

Table 2: Releases of PCDD/PCDF to Land from Industrial Processes in the United Kingdom

Process	Release to Land (g TEQ year^{-1})
Combustion Processes	
Coal combustion	
Power stations	1.6-81
All industrial	0.15-4.3
Oil combustion	
All industrial	NQ but low
Waste oil combustion	
All processes	NQ
Wood combustion	
All industrial	0.4-4.4
Tyre combustion	1.9-2.7
Crematoria	NQ
Refuse derived fuel combustion	3.7-6.4
Poultry litter combustion	0.26
Metal Processes	
Iron ore sinter plants	0.02-0.06
Electric arc furnaces	59
Primary aluminium	0.082
Secondary aluminium	29-230
Secondary magnesium	0.38-3.2
Copper	24
Secondary lead	95-220
Mineral Processes	
Cement	0.0004-12
Lime	0.00006-1.8
Other processes	NQ
Chemical Processes	
Chlorine production	6
PVC/EDC production	25-80
Per/trichloroethylene production	350-630
Pesticides production	8.9-2000
Chlorophenol production	NQ
Waste Incineration	
Old municipal solid waste plants	510-2400
New municipal solid waste plants	14-38
Chemical waste	0.0058-2
Clinical waste	12-37
Sewage sludge	0.98
Miscellaneous Industrial Processes	
Carbonisation	0.023-0.85

Process	Release to Land (g TEQ ·year^{-1})
Paper and pulp processes	2.8-11
Textile treatment	NQ
Manufacture of dyes	NQ
Timber treatment	0.011-0.32
Non-Industrial Processes	
Accidental fires	7.5-2400
Sewage sludge disposal	14-56*
Waste oil disposal	NQ
Bonfires and incidental fires	0.075-42
Disposal of municipal solid waste to landfill	150
Compost from municipal solid waste	1.7*
Dredging	29*
Open use of PCP and disposal of PCP-treated use	100-3000*
Open use of other pesticides	4.8-240*
Surface run-off	NQ
Dry cleaning	0.68-9.8
PCBs	0.31-0.38*
NQ, not quantified	

Dioxins in Soil in Australia – National Dioxins Program

A four year National Dioxins Program was established by the Australian Government in 2001.The publication by Müeller *et al.* (2004) is one of twelve technical reports presented on the program. The study involved the collection of several thousand soil cores from 76 locations in Australia representative of air-sheds and catchments based on the National Pollutant Inventory, and ten samples from remote Australia.

Dioxin-like compounds were detected in most of the 116 (composite) soil samples analysed. PCDD/PCDF and PCB concentrations (expressed as middle bound WHO_{98}-TEQ) ranged from less than 0.05 pg ·g^{-1} (the limit of detection; 0.05 ng ·kg^{-1}) to 43 pg ·g^{-1} dm. Median concentrations of dioxin-like compounds reported in the North, South-east and South-west regions were 0.98 pg ·g^{-1}(0.98 ng ·kg^{-1}), 0.74 pg ·g^{-1} (0.74 ng ·kg^{-1}) and 0.21 pg ·g^{-1} dm (0.21 ng ·kg^{-1}), respectively.

Samples from industrial and urban land uses contained approximately ten-fold higher WHO_{98}-TEQ concentrations of dioxin-like compounds (expressed in pg ·g^{-1} dm) compared with agricultural and remote land uses samples. Soils from sugarcane areas showed "*substantially greater concentrations compared to all other agricultural soils*". Müeller *et al.* noted that other studies showed no specific link between dioxins and sugarcane, and while other studies suggested that natural formation processes may be involved, the evidence was indirect.

Müeller *et al.* (2004) concluded that the concentration of dioxin-like compounds were greatest in soils near centres along the populated south-east coastal region and were consistently low at inland locations and in Western Australia. The concentrations of dioxin-like compounds in urban and industrial locations sampled in their program were "*similar to those reported in previous Australian studies and in the New Zealand Organochlorines Program*".

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