

Nature and Fate of Dioxin in Soil Environment

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The chlorinated dioxins and furans have attracted considerable scientific and public concern because of their environmental persistence and super-toxicity through the foodchain. Recent dioxin scandals in several military bases have also contributed to a higher awareness on the side of food consumers as well as foodwaste combustion. However, there is continuing uncertainty over the relative importance of different sources of dioxins and furans to the soil environment. In difference to those awareness there is a main influence of potential soil contamination on the dioxin contents in groundwater. It is, therefore, important to provide a sound scientific framework and basis by which to evaluate the significance of the presence of dioxin in soils. Consequently, we have to identify the characteristics and nature of dioxin released into the soil environment, especially in agricultural aspect.

Key words: Dioxin, Structure, Toxicity, Adsorption and Transport

Introduction

Dioxins and furans that are produced during combustion processes and as unwanted byproducts of various chemical manufacturing and bleaching processes are ubiquitous environmental contaminants. They were first brought to the public's attention as impurities in the defoliant Agent Orange, which was named from the color of the orange-striped barrels used during the Vietnam War (Jones and Sewart, 1997).

The 2,4,5-T to produce Agent Orange was later discovered to be contaminated with 2,3,7,8-Tetrachlorodibenzodioxin (TCDD), an extremely toxic dioxin compound (Alastair, 2007). Several dioxin scandals in the past have contributed to a higher awareness in foodwaste combustion as well as on the side of food consumers. In difference to those awareness in foodwaste treatment there is a main influence of potential soil contamination on the dioxin contents in groundwater. Especially in cases of food contamination it is necessary to find out the way and cause, not neglecting the potential role of the contaminated soil.

Dioxin is the name generally given to a class of super-

toxic chemicals known to science, the chlorinated dioxins and furans. The word "dioxins" may also refer to a similar but unrelated compound, the polychlorinated dibenzofurans of comparative environmental importance (USEPA, 1994a, b). Dioxins and dioxin-like compounds which are formed as an unintentional by-product of many industrial processes are commonly regarded as highly toxic compounds that are environmental pollutants and persistent organic pollutants (Pohjanvirta and Tuomisto, 1994). Among the examples of dioxins polychlorinated biphenyls (PCBs) was commercially produced in large quantities until production was stopped in 1977 while polychlorinated dibenzo dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) were classified as unintentional byproducts of combustion and several industrial chemical processes (U.S. EPA 1994a).

Dioxins are of concern because of their highly toxic potential. Among the dioxin like compounds the most toxic compound is TCDD. A report released in September 1994 by the U.S. Environmental Protection Agency clearly describes dioxin as a serious public health threat which may rival the impact that DDT had on public health in the 1960's (U.S. EPA. 1994a, c, 2007). Dioxin exhibits serious health effects when it reaches as little as a few parts per trillion in the fatty tissues, where they may persist for months or years. Humans are primarily

exposed to dioxins by eating food contaminated by these chemicals. Experiments have shown they affect a number of organs and systems (U.S. EPA, 1984, 2007; Mukerjee et al., 1985; Fiedler, 1999).

It is clearly important for scientific, public reassurance, and economic reasons to provide a sound scientific framework and basis by which to evaluate the significance of the presence of dioxin in soils. Consequently, we need to identify the characteristics and nature of dioxin released into the soil environment, especially in agricultural land. In order to meet these objectives, a thorough review of the literature was undertaken.

Structures and properties of Dioxins Dioxins, called as PCDDs and PCDFs, are compounds with similar chemical properties. Each compound comprises two benzene rings interconnected by oxygen atoms. In the case of PCDDs, the benzene rings are joined by two oxygen bridges, and in the case of the PCDFs, the benzene rings are connected by a carbon bond and an oxygen bridge. Fig. 1 shows the generic structures of PCDDs and PCDFs, respectively (Mckay, 2002).

There are 75 PCDDs and 135 PCDFs, each differing in the number and position of the chlorine atoms. All PCDDs and PCDFs which are organic solids are all poorly

water soluble, possess high octanol-water coefficients K_{ow} and consequently will partition strongly to soils/sediments as opposed to readily entering the aqueous phase in environmental systems. Some of the key properties of the dioxins are presented in Table 1 (Mackay, 1991, 1992).

PCDD and PCDF congeners with chlorine atoms in the positions 2, 3, 7 and 8 are of particular environmental concern, especially the tetrachloro-CDD congener 2,3,7,8-TCDD. 2,3,7,8-Tetrachlorodibenzo-p-dioxin (TCDD or dioxin), the most potent toxicant of the halogenated aromatic hydrocarbons, is an environmental contaminant that is believed to pose serious human health concerns (Holsapple et al., 1991). Each individual PCDD or PCDF is termed a congener (giving 210 in total) and the number of congeners in each homologue group is shown in Table 2.

Sources and Environmental Distribution PCDD/Fs have been detected in anthropogenic emissions from waste incinerators, fossil fuel power plants, domestic coal and wood fires, vehicles, scrap metal reclamation and metal smelting, and accidental fires. However, the mechanisms of PCDD/F formation during combustion processes are not completely understood. (DoE, 1989b;

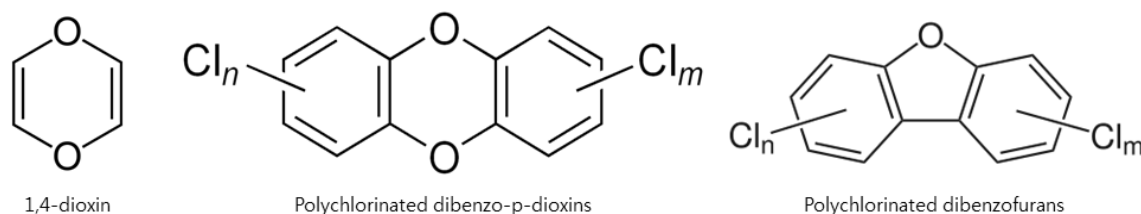


Fig. 1. The generic structures of PCDDs and PCDFs.

Table 1. Physico-chemical properties for selected PCDD/Fs.

Homologue group	Vapour pressure (mmHg at 25°C)	log K_{ow}	Solubility (mg L ⁻¹ at 25°C)	Henry's constant
TCDD	8.1×10^{-7}	6.4	3.5×10^{-4}	1.35×10^{-3}
PeCDD	7.3×10^{-10}	6.6	1.2×10^{-4}	1.07×10^{-4}
HxCDD	5.9×10^{-11}	7.3	4.4×10^{-6}	1.83×10^{-3}
HpCDD	3.2×10^{-11}	8.0	2.4×10^{-6}	5.14×10^{-4}
OCDD	8.3×10^{-13}	8.2	7.4×10^{-8}	2.76×10^{-4}
TCDF	2.5×10^{-8}	6.2	4.2×10^{-4}	6.06×10^{-4}
PeCDF	2.7×10^{-9}	6.4	2.4×10^{-4}	2.04×10^{-4}
HxCDF	2.8×10^{-10}	7.0	1.3×10^{-5}	5.87×10^{-4}
HpCDF	9.9×10^{-11}	7.9	1.4×10^{-6}	5.76×10^{-4}
OCDF	3.8×10^{-12}	8.8	1.4×10^{-6}	4.04×10^{-5}

Table 2. Homologues and congeners of PCDDs and PCDFs.

Homologue	Number of congeners	
	PCDDs	PCDFs
Monochloro (M)	2	4
Dichloro (D)	10	16
Trichloro (Tr)	14	28
Tetrachloro (T)	22	38
Pentachloro (Pe)	14	28
Hexachloro (Hx)	10	16
Heptachloro (Hp)	2	4
Octachloro (O)	1	1
Total	75	135

Harrad and Jones, 1992; Fiedler, 1994).

The polychlorinated aromatic chemicals which are another environmental burden as a result of their occurrence as unwanted byproducts in various chlorinated chemical processes include chlorophenols and derivatives such as biocide pentachlorophenol, chlorobenzenes and substituted chlorobenzenes, aliphatic chlorine compounds, and wood preservative of the pulp and paper industry. Chlorinated phenoxyacetic acid herbicides such as 2,4,5-T and 2,4-D and polychlorinated biphenyls (PCBs) all contain PCDD/Fs. PCDD/Fs formed by these processes, have a greater potential to be released to water and land than to atmosphere, either via the wastestreams from the process, subsequent use of the chemical formulation (e.g., PCP treatment of timber), or via secondary entry into the environment through the disposal of sewage sludge (Jones and Sewart, 1997).

MAFF (1992) estimated that municipal incinerators accounted for ~20% of the emission in 1990, with ~30% from the manufacture and use of organic chemicals primarily as PCP. Domestic coal fires contributed ~13% and "other sources" such as fires and metallurgical processes, ~27%. Harrad and Jones (1992) estimated the annual emissions of PCDD/Fs from various combustion processes to be a few tens of kilograms per year. They also noted that volatilization of PCDD/Fs from PCP-treated wood and secondary releases following the burning of PCP-treated products were likely to be of a similar order, although these sources are much more difficult to quantify.

It is necessary to understand the distribution of PCDD/Fs and the processes influencing their fate and behavior in the environment. There are two main routes by

which PCDD/Fs enter the environment. Emissions to the atmosphere from combustion processes result in subsequent aerial deposition onto soil, plants, and water bodies. Other discharges are via effluent from factories or sewage treatment works, by the application of sewage sludge and other wastes to land and via the use or disposal of contaminated chemicals (Jones and Sewart, 1997). Because of their very low solubility in water and strong sorption to soil and organic matter, PCDD/Fs are very persistent in soils and sediments. MAFF (1992) commented that "the persistence of these compounds means that it will probably be decades before there is any major fall in the overall levels found in the environment."

Atmospheric deposition has been the primary means of supply of PCDD/Fs into surface soils, where they become firmly bound by soil constituents. Kjeller et al. (1991) presented evidence that the concentrations of PCDD/Fs in rural U.K. soils have increased over the last century as a result of cumulative atmospheric deposition. The bulk of the PCDD/Fs present in soil probably therefore resides in the top few centimeters of the soil profile (Di Domenico et al., 1980a). Plants do not efficiently take up soil-borne PCDD/Fs because the compounds are bound too strongly to soil to be rapidly desorbed, enter the soil solution, and be available for uptake (Wild and Jones, 1992; Wang and Jones, 1994a, b; Duarte-Davidson et al., 1995).

Fate, Behavior, and Persistence of PCDD/Fs in Soils

Terrestrial environments may receive PCDD/Fs from input sources either via atmospheric deposition onto soils or vegetation, or via additions to soils of sewage sludge and impurities in chemicals, and their subsequent transfers to other environmental compartments, such as crop plants, animals, and groundwater. Several fates can affect the persistence of organic contaminants in soils (Wild and Jones, 1992; Beck et al., 1993a).

Once an organic contaminant (e.g., a PCDD/F) comes into contact with soil, it has an affinity for the organic matter and may migrate into the lattice of the organic macromolecules (Pignatello, 1993). The rapidly desorbed component of the compound is held near to the surface of organic matter, while the recalcitrant portion has to migrate out of the bulk of the organic matter before it is accessible for desorption. A hypothetical model suggested by Jones and Sewart (1997) shows that the portion remaining can potentially be separated into a component

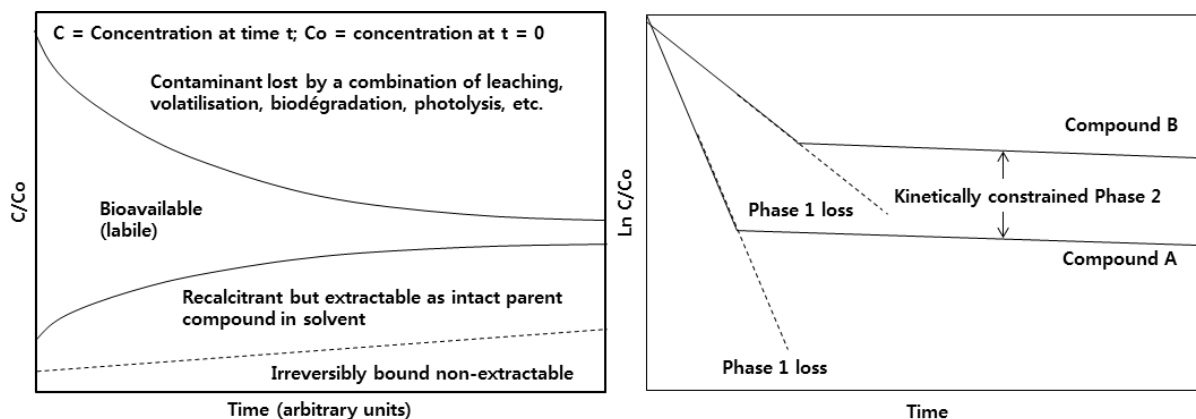


Fig. 2. Hypothetical schematic representation of the different forms of an organic compound present in soil. Two compounds (A and B) both exhibit loss from soil. A is less persistent and has a greater proportion of the total lost in Phase 1. PCDD/Fs are analogous to compound B.

that is relatively bioavailable (labile), a relatively firmly bound (recalcitrant but extractable) component, and an irreversibly bound (nonextractable) component (Fig. 2). The relatively labile proportion of compound is envisaged as decreasing over time, while the nonextractable proportion is envisaged as increasing with time.

Jones and Sewart (1997) represented various potential loss processes of organic contaminants introduced into surface soils: (1) volatilization from the soil to air, (2) leaching from surface soil to groundwater, (3) biodégradation, (4) photolysis and chemical reactions, (5) physical transport processes, and (6) "apparent loss" through the formation of irreversibly bound, nonextractable residues. The overall loss of organic compounds from soils is usually biphasic, with an initial period of relatively rapid loss followed by a longer, slower period of chemical release by desorption of compound from the soil solid phase (Beck et al., 1995). The kinetic constraints to desorption arise because of the slow rate of diffusion of nonpolar organic substances out of soil organic matter (Beck et al., 1993a, b, 1995).

Leaching, pure aqueous-phase transport, can be negligible for PCDD/Fs due to their extremely low aqueous solubility (Wild and Jones, 1992; Duarte-Davidson et al., 1995). However, some studies have shown that PCDD/Fs can be transported down through soils in the presence of nonpolar cocontaminants, such as oils and surfactants (Puri et al., 1989, 1990; Kapila et al., 1989; Jones and Sewart, 1997).

Physical transport processes include mixing of soil to depth by animal activity, channelling through soil macropores, cracks, and fissures, and runoff and wind erosion removal. PCDD/Fs are highly adsorbed to soil

and are considered persistent and non-leachable (Freeman and Schroy, 1986; Yanders et al., 1989). However, because movement of PCDD/Fs through soil can be enhanced under the presence of organic phases as a free phase such as wood-preserving oil.

Conclusions and Implications

Studies in the international literature provide evidence for declining inputs and changing sources of PCDD/Fs to the environment over recent years. However, there is still a lack of reliable long-term data on PCDD/Fs in soils, especially sludge-amended soils in Korea, resulting in that considerable uncertainties remain in the pathway. Therefore, the relative importance of different loss mechanisms and fate from soils needs to be clearly established, together with behavior for the full range of PCDD/Fs. Furthermore, questions about the long-term form and bioavailability of PCDD/Fs in soils need to be addressed.

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