Physical and chemical properties determining the fate of chlorinated dibenzo-p-dioxins and dibenzofurans

A literature review

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Report 35

The WINAND STARING CENTRE, Wageningen, The Netherlands, 1990

ABSTRACT

Bolt, F.J.E. van der, 1990. Physical and chemical properties determining the fate of chlorinated dibenzo-p-dioxins and dibenzofurans, a literature review. Wageningen, The Netherlands, The Winand Staring Centre. Report 35.
58 p., 11 fig., 21 tab.

A literature review has been carried out in order to outline the fate of chlorinated dibenzo-p-dioxins and dibenzofurans in the (natural) soil-water-plant system. Processes involved are adsorption, convection, diffusion, volatilization, non-homogeneous transport, chemical processes, microbial biodegradation and plant uptake. The studied compounds appear to be almost immobile due to the strong adsorption to soil organic matter and the low water solubility. In the soil the dioxins and furans are chemical inert, but in presence of ultraviolet light they decompose photochemically. There are strong uncertainties on the uptake by plants and on biodegradation. The overall half-lifes vary dependent on the occurance of photodecomposition and range from half a year to more then ten years.

Keywords: dioxin(s), furan(s), fate.

ISSN 0924-3062

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The WINAND STARING CENTRE is continuing the research of: Institute for Land and Water Management Research (ICW), Institute for Pesticide Research, Environment Division (IOB), Dorschkamp Research Institute for Forestry and Landscape Planning, Division of Landscape Planning (LB), and Soil Survey Institute (STIBOKA).

Project 4841 014/cis/10.90

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PREFACE

Because high polychlorinated dibenzo-p-dioxin (PCDD) levels have been detected in milk from cows grazing in the Lickebaert-area and the region Zaandam/Alkmaar, the Dutch Ministery of Agriculture, Nature and Fisheries in december 1989 started a research program on the applicability of proposed decontamination techniques. Results were expected in may 1990. In this short period the Winand Staring Centre had to map the soil in the Lickebaert-area, and to evaluate the proposed measurements on their agricultural and environmental consequenses. Because knowledge on the fate of these chemicals was lacking a literature research had to be done before environmental effects could have been studied. This report contains the results of the literature review. Also (poly)chlorinated dibenzofurans (PCDF's) have been considered because these chemicals have very similar physical and chemical properties.

I would like to thank the librarians of the Staring Centre for their enjoyable cooperation, and Pauline Sparenburg and Reinier van den Berg (RIVM), and Joop Harmsen and Koen Roest (SC) for their comments.

SUMMARY

The fate of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) has to be studied in order to get insight into the distribution of these contaminants in the soil-water-plant system. Therefore the fate of PCDD's and PCDF's has been outlined by a literature study.

The PCDD's and PCDF's enter the environment as waterborne or airborne particles. In the air released PCDD's and PCDF's are subject to rapid (gas-phase) photolysis. The components not affected by this degradation process will precipitate on plants, on the soil surface or in aquatic systems.

The chemicals of these families precipitated on plants are fast photodecomposed (half-lifes some hours) because of the presence of organic hydrogen donors at the waxy leaf surfaces, but in smaller quantities also volatilization will occur. In case of rainfall the at the plant adsorbed compounds partly wash off to the soil surface. Consequently precipitation on plants can be regarded as an interception process, retarding and diminishing effective precipitation. The compounds present at the soil surface are subject to slow photodegradation of the pure chemical and half-lifes vary from months to years. If organic solvents like oil or pesticides are present the half-lifes are in the order of some days. Photolysis of the pure compounds on the soil surface does not follow first order kinetics because the dioxins and furans are partly protected from irradiation by soil particles (shading) and because they are strongly sorbed to soil particles. In this part of the system (plants and soil surface) the PCDD's and PCDF's may be transported in horizontal direction by wind and water (runoff).

The PCDD's or PCDF's which remain at the soil surface dissolve into water and leach downward. The lipophylic character of these compounds makes them very sensitive to adsorption to (organic) soil particles and downward transport will be retarded. Due to the low water solubility and the huge adsorption leaching will be very small and the PCDD's and PCDF's remain almost immobile beneath the soil surface. Organic matter however, may be dissolved and can be transported downward, carrying the sorbed material. Diffusion due to concentration and temperature gradients leads to a slow redistribution of these chemicals in the soil profile and makes it neccessary to take both water and vapour phase into account. Volatilization-losses due to the diffusion through the soil surface and the watermediated evaporation, are concentration dependent and decrease with increasing organic carbon content of the soil (due to adsorption). The volatized compounds are either photodegraded in the gas-phase or will adsorb to plants. Uptake from the soil-water system and translocation by plants and also microbiological degradation seem to be very small. Preferential pathways, cracks and biological activity affect the distribution of chemicals in the soil and may result in a faster downward movement of the pollutants, and as a result in an earlier pollution of the groundwater.

Overall half-lifes of these chemicals in the soil-water-plant system are dominated by the processes at the surface, i.e.

volatilization and photodegradation. Therefore half-lifes after an incidental release vary from small immediately after contamination because photodecomposition is dominant, to very large after some months when volatilization becomes the main pathway of disappearance from the soil. Consequently reported values of half-lifes range from half a year to more than ten years.

1 INTRODUCTION

(Poly)Chlorinated dibenzo-p-dioxins (PCDD's) and dibenzofurans (PCDF's) form a group of chemicals with very specific properties. During the last decades much attention has been paid to these chemicals because of the extreme toxicity of some congeners. To assess the harmful effects on humans and other organisms the exposure to these chemicals as well as the toxicity of these chemicals have to be studied. To gain insight into the exposure, the amount released into the environment and the fate of dioxins and furans in the environment have to be investigated.

Recently in the Netherlands high PCDD levels have been detected in milk from cows grazing in the Lickebaertarea (Liem et al., 1989) and the region Zaandam/Alkmaar (De Jong et al., 1990). Sources of pollution are probably the chemical waste incinerator Rijnmond and the municipal waste incinerators at Alkmaar and Zaandam.

Because of the large economic implications some technical solutions have been proposed to rehabilitate the Lickebaert-area for continuous agicultural use (MLNV, 1989). In order to study the effect of the proposed measures on the pollution, the fate of the contaminant in the environment has to be known. This report contains the results of the literature study carried out to obtain qualitative insight in the behaviour of PCDD's and PCDF's in the soil-water-plant system. Also attention has been paid to the physical-chemical properties of dioxins and furans because of their importance for understanding and explaining the processes in the different compartments of the environment. In a next phase of the research-programm it will be attempted to get quantitative information on the proposed measures by modelling of the processes determining the fate of these chemicals in the soil-water-plant system.

2 CHARACTERISATION OF PCDD's AND PCDF's

2.1 General description of PCDD's and PCDF's

(Poly)chlorinated dibenzo-p-dioxins and dibenzofurans are tricyclic, planar, aromatic compounds with similar physical and chemical properties. The structures of PCDD's and PCDF's (Chemical Abstracts) are presented in Fig. 1.

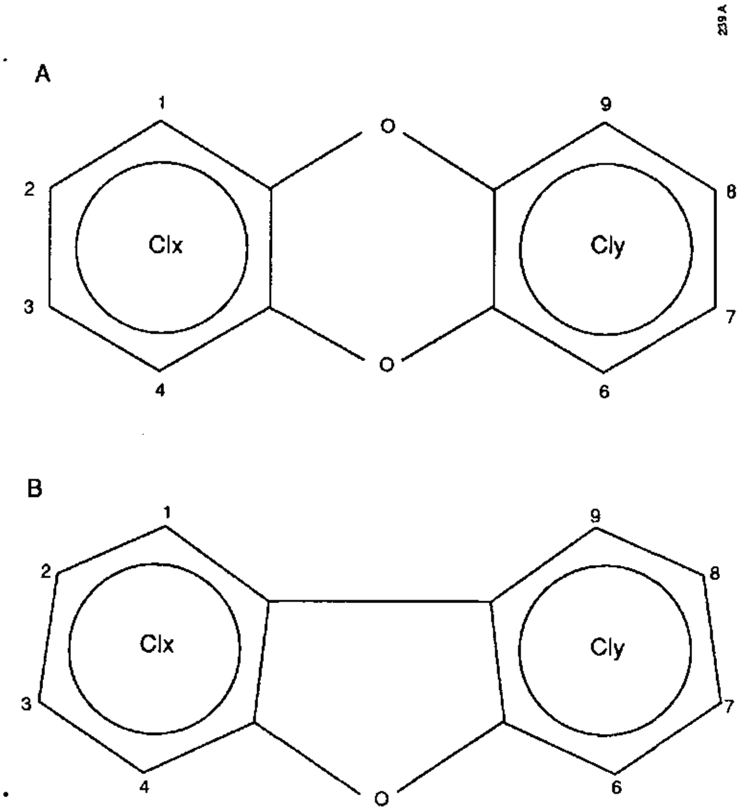

Fig. 1 Structures of PCDD's (A) and PCDF's (B).

Table 1 Number of positional PCDD and PCDF isomers.

Chlorine substitution	Number of isomers	
	PCDD's	PCDF's
mono-	2	4
di-	10	16
tri-	14	28
tetra-	22	38
penta-	14	28
hexa-	10	16
hepta-	2	4
octa-	1	1
total:	75	135

A large number of isomers exists (Table 1). Dioxins are generated thermally or photochemically (Crosby et al., 1973, Rappe, 1984). The formation of PCDD's by several mechanisms has been documented by Choudry and Hutzinger (1982).

2.2 Physical-chemical properties of PCDD's and PCDF's

From the structure (Fig. 1) it can be seen that PCDD's and PCDF's are nonpolar and lipophylic (the incorporation of chlorine in a molecule makes the compound more lipophylic, Hutzinger and Roof 1980), and that PCDD's and PCDF's have no labile functional groups.

In environmental studies often partition coefficients are used. These constants express the partition of the relative amounts of a chemical present in two phases at equilibrium. The partition coefficient between the solid phase of the compound and water equals the water-solubility. The partition of a chemical between octanol and water (K_{ow}) is a measure of the lipophylicity of the substance.

Sarna, Hodge and Webster (1984) calculated the Log(K_{ow}) of a number of dioxins and furans from retention times on reverse phase HPLC columns. Webster, Friesen, Sarna and Muir (1985) determined water solubilities, vapour pressures and Henry's law constant data by the same method. The minimum values presented by Webster et al. (1985) of Log(K_{ow}) are, as expected, comparable to the data of Sarna et al. (1984) for the same type of column and calculated in an identical way. The data given by Webster et al. (1985) have been evaluated and corrected by Burkhard and Kuehl (1986) by using experimental instead of estimated Log(K_{ow}) values of other (reference) chemicals in the derivation of the correlative relationship between Log(K_{ow}) and the retention time. Burkhard and Kuehl (1986) also published some measured values. Friesen, Sarna and Webster (1985) presented water solubilities and melting points of some other chlorinated dioxins. Shiu, Doucette, Gobas, Andren and Mackay (1988) evaluated these already reported data and presented new experimental data for aqueous solubility, octanol water partition coefficient, vapour pressure and Henry's law constant of PCDD's (Tables 2, 3 and 4).

Henry's law constant is defined as the partial pressure of a chemical in air above water divided by the mol fraction in the water. In fact this relationship is not linear but depends on temperature and concentration. For solutes with very low solubility the concentration effect can be ignored and the relation is simplified to the ratio of the vapour pressure of the pure compound to the water solubility at the same temperature. The variety in published water solubilities and the range in measured vapour pressures leads to a series of Henry's law constants.

With the increasing number of chlorine atoms both the solubility (Table 2) and the volatility (Table 4), decrease, whereas the Log(K_{ow}) (Table 3) increases.

The range in 2,3,7,8-TCDD water solubilities in Table 2 is remarkable. These data have been determined by Crummet and Stehl (1973), Webster et al. (1985), Marple et al. (1986) and Adams and Blaine (1986). Moreover Kearney et al. (1972)

presented the water solubility of TCDD to be 0.6 $\mu g\ l^{-1}$, whereas Lodge (1989) determined the water solubility to be 0.483 $\mu g\ l^{-1}$ at 17.3 °C and 0.013 $\mu g\ l^{-1}$ at 4.3 °C.

Table 2 Aqueous solubility of some PCDD's at 25 °C as presented by Shiu et al. (1988).

Species	Aqueous solubility		Molecular weight
	($\mu g\ l^{-1}$)	($mol\ l^{-1}$)	
dibenzo-p-dioxin	842	4.58E-06	184.0
	900	4.89E-06	
1-chloro-	417	1.91E-06	218.5
2-chloro-	278	1.27E-06	218.5
	318	1.46E-06	
2,3-dichloro-	14.9	5.90E-08	253.0
2,7-dichloro-	3.75	1.48E-08	253.0
2,8-dichloro-	16.7	6.60E-08	253.0
1,2,4-trichloro-	8.41	2.61E-08	287.5
1,2,3,4-tetrachloro-	.63	1.97E-09	322.0
	.47	1.46E-09	
1,2,3,7-tetrachloro-	.42(20 °C)	1.30E-09	322.0
1,3,6,8-tetrachloro-	.32(20 °C)	9.40E-10	322.0
2,3,7,8-tetrachloro-	.2	6.20E-10	322.0
	.317	9.84E-10	
	.0193	6.00E-11	
	.00791	2.46E-11	
1,2,3,4,7-penta	.118(20 °C)	3.31E-10	356.5
1,2,3,4,7,8-hexa	.0044(20 °C)	1.13E-11	391.0
1,2,3,4,6,7,8-hepta	.0024(20 °C)	5.64E-12	425.5
octachloro-	.0004(20 °C)	8.70E-13	460.0
	.00007	1.61E-13	

Table 3 Octanol-Water partition coefficients of PCDD's at 25 °C, data given by Shiu et al. (1988).

Species	$Log(K_{ow})$ (measured)		$Log(K_{ow})$ (selected)
	Burkhard	Shiu	
dibenzo-p-dioxin	4.20	4.37	4.3 +/- .1
1-chloro-	4.75	5.30	4.75 +/- .3
2-chloro-	5.08	4.94	5.00 +/- .2
2,3-dichloro-			5.60
2,7-dichloro-		5.75	5.75 +/- .3
2,8-dichloro-			5.60
1,2,4-trichloro-	6.45	5.57	6.35 +/- .2
1,2,3,4-tetrachloro-	7.13	6.20	6.60 +/- .5
1,2,3,7-tetrachloro-	6.91		6.90 +/- .5
1,3,6,8-tetrachloro-	7.16		7.10 +/- .5
1,3,7,9-tetrachloro-	7.16		7.10 +/- .5
2,3,7,8-tetrachloro-	7.02		6.80 +/- .2
1,2,3,4,7-penta			7.40 +/- .5
1,2,3,4,7,8-hexa	7.79		7.80 +/- .5
1,2,3,4,6,7,8-hepta	8.20		8.00 +/- .5
octachloro-	8.60	7.59	8.20 +/- .5

This variety in measured water solubilities is probably caused by differences in purity of the starting material and by differences in methods of preparing the solution and determining the concentrations. Problems in analysing compounds at such low levels are numerous. Harmsen (1990,personal communication) evaluated the range of 2,3,7,8-TCDD data presented by Shiu et al. (1988) assuming a linear relationship between the log of the aqueous solubility (mol l^{-1}] and the number (N) of chlorine atoms. Omitting the

2,3,7,8-TCDD values Harmsen calculated by linear regression (Log S = -0.896*N - 5.24) a 95%-confidence interval of TCDD ranging from 0.33 µg l^{-1} to 0.71 µg l^{-1}, with a mean of 0.48 µg/l. It must be noted that this method does not discriminate between isomers.

Table 4 Vapour pressure and Henry's law constant for some PCDD's at 25 °C summarized by Shiu et al. (1988).

Species	Vapour pressure (Pa)		H (Pa*m^3 mol^{-1})
	solid	liquid	
dibenzo-p-dioxin	5.50E-02	5.14E-01	12.29
1-chloro-	1.20E-02	1.00E-01	8.38
2-chloro-	1.70E-02	8.58E-02	14.82
2,3-dichloro-	3.90E-04	9.26E-03	6.61
2,7-dichloro-	1.20E-04	8.11E-03	8.11
2,8-dichloro-	1.40E-04	2.47E-03	2.13
1,2,4-trichloro-	1.00E-04	1.07E-03	3,84
1,2,3,4-tetrachloro-	6.40E-06	2.75E-04	3.77
1,2,3,7-tetrachloro-	1.00E-06	3.05E-05	0.77
1,3,6,8-tetrachloro-	5.37E-04	1.36E-02	
	7.00E-07	5.79E-05	0.71
2,3,7,8-tetrachloro-	4.50E-06	2.65E-03	
	1.51E-07	8.90E-05	
	9.80E-08	5.81E-05	1.63
	2.00E-07	1.18E-04	3.34
	6.20E-07	3.65E-04	10.34
1,2,3,4,7-penta	8.80E-08	4.31E-06	0.264
1,2,3,4,7,8-hexa	5.10E-09	1.45E-06	4.52
1,2,3,4,6,7,8-hepta	7.50E-10	1.77E-07	0.133
octachloro-	8.70E-06	8.13E-03	
	1.10E-10	1.19E-07	0.683

Until a few years ago the PCDF's were less investigated than the PCDD's because their toxicity is lower than the toxicity of dioxins and because their physical-chemical properties are expected to be familiar to those of PCDD's due to the identical molecule structure. As a consequence data on furans were rare. The Environmental Protection Agency (EPA) resumed available data (1978). Recent PCDF's became subject of several studies. Doucette and Andren (1988) determined the water solubility of some dioxins and furans by using a generator column technique (Table 5). Presented data of the dioxins are equal to the gas chromatography detected values of Shiu et al. (Table 2). Friesen et al. (1990) measured with the same method the solubilities of some other furans (Table 5).

Table 5 Aqueous solubility of (chlorinated) dibenzofurans measured by (a) Doucette and Andren (1988) and (b) Friesen et al. (1990).

Species	Water solubility (mol l)	Temp. (°C)	Ref.
dibenzofuran	2.51E-05	25	(a)
2,8-dichlorodibenzofuran	6.11E-08	25	(a)
2,3,8,7-TCDF	1.37E-09	22.7	(b)
2,3,4,7,8-PCDF	6.92E-10	22.7	(b)
1,2,3,6,7,8-HCDF	4.72E-11	22.7	(b)
1,2,3,4,7,8-HCDF	2.20E-11	22.7	(b)
1,2,3,4,6,7,8-H7CDF	3.31E-12	22.7	(b)
octachlorodibenzofuran	2.61E-12	25	(a)

Friesen et al. (1990) presented a first order lineair regression equation to relate aqueous solubility and the chlorine number of both PCDD's and PCDF's (Fig. 2). The relations for PCDD's obtained by Harmsen (personal communication) and by Friesen et al. (1990) are almost identical.

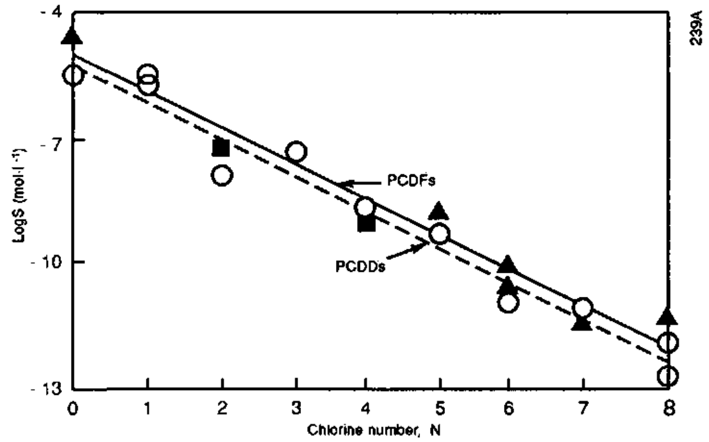

Fig. 2 Correlation of the Log (Solubility) with the chlorine number (N) for PCDF's and PCDD's at approximately 25 °C (after Friesen et al. 1990).

Sijm et al. (1989) published data of measured octanol/water partition coefficients (K_{ow}). The partition coefficients between octanol and water of PCDD's are lower than those of PCDF's with the same substitution pattern. Values are generally lower than reported by Shiu et al. (1988), according to Sijm et al. (1989) probably due to octanol micelles formation in the water phase, leading to an overestimation of the concentration in the water and consequently in a lower Log(K_{ow}).

Recently brominated and brominated/chlorinated dibenzo-p-dioxins and dibezofurans became subject of studies (Buser, 1987). If bromine and chlorine sources are present, bromo/chloro compounds (of the same toxicity as the chloro compounds, Buser, 1988) can theoretically be formed. Other halogenated products may be expected as well, but these are assumed to be less toxic (fluoro compounds) or chemically and thermally instable (iodo compounds).

Some of the PCDD's and PCDF's have extremely toxic properties (Table 6) and are subject of much concern. The toxicity is dependent on number and place of the chlorine substituents (Rappe, 1984). The bromine compounds seem to be equally toxic as the corresponding chlorine compounds. The most toxic compound is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). TCDD is acnegenic, teratogenic and embryotoxic. The toxicity of dioxins and furans is often related to the toxicity of TCDD and expressed in TCDD equivalents. TCDD has been studied extensively, and often TCDD is supposed to represent the complete group of PCDD's and PCDF's.

Table 6 Toxicity of some chlorinated dibenzo-p-dioxins according to Esposito et al., 1980.

Dioxin-isomer	LD_{50} (µg/kg)		
	rat	mouse	cavy
dibenzo-p-dioxin	$> 10^6$	$5*10^4$	-
2,7 - DCDD	$2*10^6$	-	$> 3*10^5$
2,3 - DCDD	$> 10^6$	-	-
2,3,7 - TriCDD	$> 10^6$	$> 3*10^3$	$3*10^4$
1,2,3,4 - TCDD	$> 10^6$	-	-
1,3,6,8 - TCDD	$> 10^5$	-	-
2,3,7,8 - TCDD	40	283.7	0.6-2
1,2,3,7,8 - PCDD	-	337.5	3.1
1,2,4,7,8 - PCDD	-	> 5000	1125
1,2,3,4,7,8 - HCDD	-	825	72.5
1,2,3,6,7,8 - HCDD	-	1250	70-100
1,2,3,7,8,9 - HCDD	-	> 1440	60-100
1,2,3,4,6,7,8 - HeptaCDD	-	-	> 600
1,2,3,4,6,7,8,9 - OCDD	$2*10^6$	$> 4*10^6$	-

3 FATE OF CHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS IN THE ENVIRONMENT

Environmental contamination with PCDD's and PCDF's can result from industrial and agricultural chemicals containing dioxins as impurities, from accidental formation and release into the environment, from incineration of industrial chemicals acting as precursors and by generation from suitable precursors under environmental conditions. Also leaching from dump sites is a well known source of contamination. Formation of PCDD's and PCDF's under natural conditions is possible, but seems to be of minor importance because the rate of degradation exceeds the rate of formation (Hutzinger et al., 1973). Several authors summarized the sources of release of PCDD's and PCDF's (Crosby et al., 1973, Rappe, 1984, Hutzinger et al., 1985). Chlorinated dioxins enter the environment as airborne or waterborne particles (Bumb et al., 1980). Townsend (1983) argues chemical equilibration by unknown redox-reactions tending to result in a steady distribution of dioxins on airborne particles at the moment of release. The final distribution is influenced by differences in photochemical decomposition-rate and volatilisation rates (Townsend, 1983, Eduljee and Townsend, 1987). The particles will move downward due to gravity or will be washed out by rainfall and will precipitate at the soil-surface or will be intercepted by and adsorbed to the vegetation. Hereby the dioxins become available for ingestion by animals and humans.

3.1 Transport in the soil

3.1.1 Adsorption

Adsorption is the adhesion of ions or molecules to the surface of soil solids, increasing the concentration at the soil surface and lowering the soil moisture concentration. Desorption is the reverse proces. Adsorption causes retardation of the migration of the substance in the soil. Adsorption is dependent on the kind of soil matrix and on the type of chemical. For organic compounds the partitioning between water and the organic carbon content appeared to be the most important adsorption mechanism. Adsorption to the soil organic material increases with increasing lipophilicity of the chemical. Therefore PCDD's and PCDF's are expected to adsorb strongly to organic matter.

Walters et al. (1988) studied the behaviour of 2,3,7,8-TCDD in water/methanol mixtures in several soil types in the linear range of the adsorption isotherm of TCDD. Adsorption was influenced by the fraction methanol in the liquid phase and the amount of soil organic matter. Adsorption equilibrium established faster with higher methanol contents. Equilibrium is reached instanteneously for most soils (i.e. within one day), but for one particular soil type equilibrium was attained after 30 days, probably because of differences in the composition of the soil organic matter. In a second study Walters et al. (1986) found adsorption of TCDD to soil in presence of methanol to be irreversible. Puri et al. (1989) detected linear desorption of TCDD from TCDD-contaminated soil to waste oil.

Esposito et al. (1980) suggested the adsorbtion of PCDD's and PCDF's to become more irreversible with increasing residence time in the soil. If so, the recovery of TCDD from soil will diminish after long term incubations. Hutter and Philippi (1982) reported problems with quantitative recovery of radioactively labeled material and argued that TCDD becomes irreversible adsorbed to or incorporated into biological or soil material during long-term incubations. Muir et al. (1985) determined the amount unextractable 1,3,6,8-TCDD in soil by combustion to be constant in time (during 500 days), ranging from 5 to 15%.

Partition coefficients for dioxins between total organic carbon and water (K_{oc}) have been presented by several authors:

- Kenaga (1980) calculated K_{oc} to be 468000 ($\log(K_{oc}) = 5.67$);
- Des Rosiers (1986) determined a $\log(K_{oc})$ for 2,3,7,8-TCDD in soils of 7.39, 7.58 and 7.55;
- Jackson et al. (1986) measured a mean $\log(K_{oc})$ of 7.39 for ten soil types;
- Walters et al. (1988) extrapolated from their measurements the $\log(K_{oc})$ to be 6.6 +/- 0.7;
- Lodge and Cook (1989) determined the partition coefficient of dioxin between sediment and water, taking into account solids concentration effects. The mean $\log(K_{oc})$ for sediments determined after 4 days ranged from 7.25 to 7.59, and the authors made the general statement that $\log(K_{oc})$ is always greater than or equal to 6.3;
- Using the relationship between $\log(K_{oc})$ and the aqueous solubility presented by Van der Meyden and Driessen (1986) and the solubilities of TCDD presented by Shiu et al. (1988) gives $\log(K_{oc})$ values ranging from 6.79 to 7.97;
- Combining the relationship presented by Van der Meyden and Driessen (1986) with the solubility of TCDD derived by Harmsen (paragraph 2.2) leads to a $\log(K_{oc})$ varying from 6.54 to 6.78 with a mean value of 6.66.

Summary

- The lipophylic character of chlorinated dibenzo-p-dioxins makes them very sensitive to adsorption to (organic) soil particles and transport will be retarded or even prohibited, dependent on the solution present.
- Adsorption equilibrium is reached fast, i.e. within some days.
- Adsorption seems to be (partly) irreversible.
- Measured $\log(K_{oc})$ values range from 6.6 to 7.6.

3.1.2 Convection

Convection refers to the transport of a compound by the bulk motion of the fluid flow. Generally water is the fluid present in soil systems and the compound will be in solution. The compound also may be adsorbed to soluted organic matter or to (solid) particles and can be transported by water in this (indirect) way. Sometimes other fluids (herbicides, pesticides, oil) are present in the soil system in noticeable amounts.

Few laboratory studies on convection have been carried out. Helling (1971) investigated the mobility of 2,7-DCDD and 2,3,7,8-TCDD in five soils with different textures and properties (organic matter content ranged from 0.14 up to

90.40%) by soil thin-layer chromatography. Both dioxins appeared to be immobile in all soils for convection by water and for diffusion and therefore tended to remain on the soil surface. Helling (1971) explained this with the low water solubility. Matsumura and Benezet (1973) deposited 1 µmole of TCDD on 1 gram of clean sea sand and put this on a column (10 * 1.5 cm) filled with a sandy loam. Water (2 ml h^{-1}) was added to the surface. Almost no transport of TCDD caused by convection has been found (Table 7). Therefore Matsumura and Benezet (1973) concluded that TCDD is translocated in the environment either by particle transport or by biological transfer. The leaching water however contained about 0.1 percent of the added amount TCDD. No data on soil properties or duration of the experiment were given.

Table 7 Vertical translocation of TCDD from sand to organic soil and the amount detected in the eluate expressed as percentage of the total applied amount (after Matsumura and Benezet, 1973).

Soil column:	top sand	90.41
	0 - 0.5 cm	7.32
	0.5 - 1.0 cm	1.04
	1.0 - 1.5 cm	.50
	1.5 - 2.0 cm	.26
	2.0 - 2.5 cm	.18
Water eluate:	1st 50 ml	.12
	2nd 50 ml	.08
	3rd 50 ml	.09

The absence of detailed experimental observations results in the use of theoretical models in order to investigate the supposed behaviour of contaminants in the soil-water system. Mobility in soils calculated by Des Rosiers (1986) with an one dimensional, convective dispersive, solute transport equation, appeared to be very small (average movement rate 388 y cm^{-1}, the data used in the calculations have not been mentioned). The results of the calculation seem to be consistent with the observations of Helling (1971) and Matsumura and Benezet (1973). The results of these two laboratory studies have often been cited, and TCDD was assumed to be immobile.

In addition to these laboratory experiments some authors measured at contaminated sites, others organized field experiments. Di Domenico et al. (1980a) described the vertical distribution of TCDD in the soil at Seveso. Samples have been taken at several sites in the contaminated area. For some sites sampling has been repeated at three time-intervals. Table 8 contains the data of two sites at three times. In general the amount of TCDD dropped sharply down below the soil surface. Investigations in the soil top layer showed the highest TCDD levels between 0.5 and 1.5 cm below soil surface, and not in the top layer of 0-0.5 cm. Only a smaller amount of TCDD was detected below 8 cm minus soil surface.

The data show a significant soil penetration after contamination. Because of the low solubility Di Domenico et al. (1980b) suggest this is to be caused by transport with particles to which TCDD has been adsorbed. The decrease of the total TCDD-content and the large concentrations found beyond 50 cm below soil surface in the third series of measurements are remarkable. The latter may have been caused by the presence of soil fissures and preferential pathways. Di Domenico et al. (1980b) also determined the relative distribution in the soil to be constant in time (Fig 3).

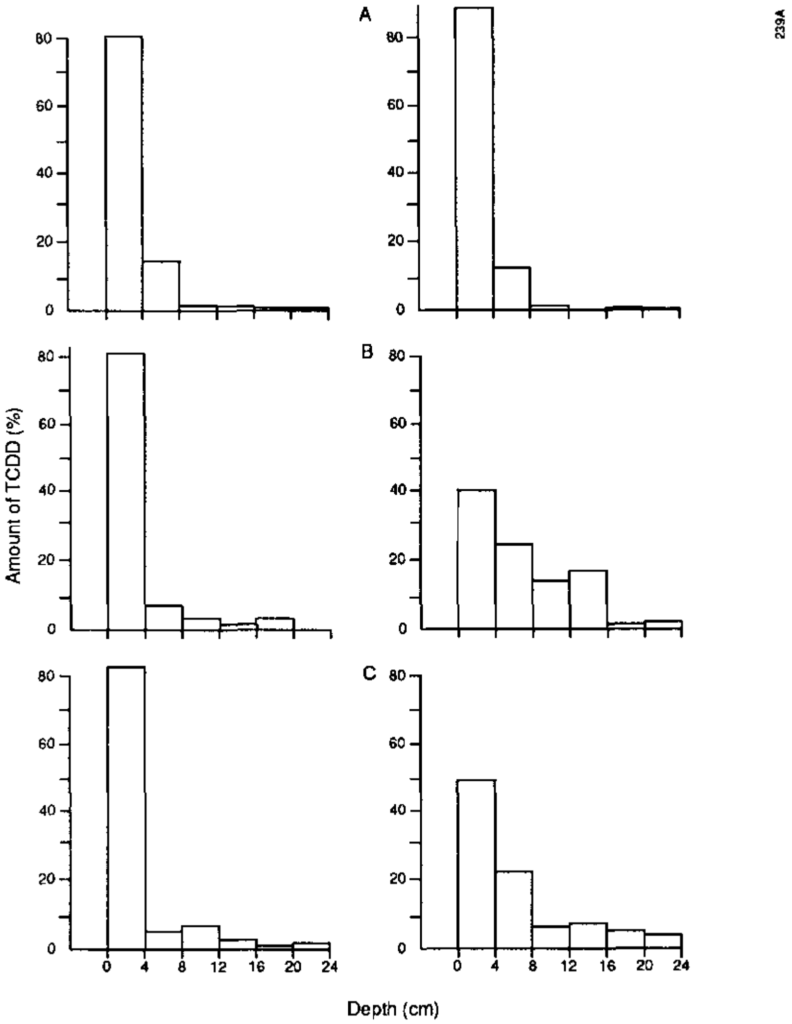

Fig. 3 Variation with time of vertical distribution of TCDD in the soil at site A11 (left) and A12 (right) at date 15-10-1976 (A), 1-4-1977 (B) and 1-12-1977 (C) after Di Domenico et al. (1980b).

Comparable data have been published by Young et al. (1983). In this case however transport processes are not comparable because organic solvents (having a higher solubility, Crummett and Stehl 1973, EPA 1978) were present. Young et al. (1983) measured low soil penetration of herbicides and very low though measurable soil penetration of PCDD at spill sites of herbicides containing TCDD two years after contamination (Table 9).

No appropiate data on soil, temperature, rainfall or drainage are given in this study (Young et al., 1983). Few years later, Young et al. (1987) presented data of a long-term study on Eglin Air Force Base in Florida (soil: 92% sand, 3.8% silt, 4.2% clay, organic matter content 0.17%, pH 5.6 and CEC 0.8; slope: 0% to 3%; rainfall: 150 cm y^{-1}; groundwaterlevel: 1.5 to 3 m; mean temperature: 19.7 °C; mean relative humidity:

70.8%). TCDD was applied (as impurity) with the herbicides 2,4,5-T and 2,4-D. Most of the TCDD was found in the top 15 cm of the soil profile (Table 10).

Table 8 Vertical distribution of TCDD in soil at different zone A-sites sampled at three times in 1976 and 1977 (after Di Domenico et al., 1980b).

Depth (cm)	TCDD levels (µg m^{-2})[a]					
	A11[b] (410/15/7)[c]	A11 (4/1/77)	A11 (12/1/77)	A12 (10/15/76)	A12 (4/1/77)	A12 (12/1/77)
0- 4	$1.2x10^{3}$	3.1x10	1.6x10	$1.4x10^{3}$	9.2x10	$3.4x10^{2}$
4- 8	$2.0x10^{2}$	3.0	$9.1x10^{-1}$	$1.4x10^{7}$	5.6x10	$1.5x10^{2}$
8- 12	3.3x10	1.1	1.2	2.5x10	3.7x10	5.1x10
12- 16	2.1x10	$2.3x10^{-1}$	$4.7x10^{-1}$	n.d[d]	4.2x10	5.7x10
16- 20	1.6x10	1.4	$1.9x10^{-1}$	6.4	4.1	4.2x10
20- 24	1.7x10	$1.9x10^{-1}$	$2.5x10^{-1}$	3.6	5.7	2.6x10
24- 28	2.0	2.5	$9.0x10^{-2}$	n.d.	3.0	9.7
28- 32	n.d.	$8.8x10^{-1}$	$1.3x10^{-1}$	2.5	2.5	7.4
32- 36	n.d.	1.0 x 10	$4.0x10^{-2}$	$6.0x10^{-1}$	2.6	1.1
36- 40	n.d.	n.t.[e]	$5.0x10^{-2}$	1.1	2.5	$7.3x10^{-1}$
40- 44	n.d	n.t.	n.t.	n.d.	n.t.	n.t.
44- 48	n.d.	n.t.	n.t.	n.d.	n.t.	n.t.
58- 62	n.t.	n.t.	5.9	n.t.	n.t	$4.3x10^{-1}$
78- 82	n.t.	n.t.	$5.0x10^{-2}$	n.t.	n.t.	$1.3x10^{-1}$
98-102	n.t.	n.t.	$4.0x10^{-2}$	n.t.	n.t.	$2.9x10^{-1}$

[a] estimated amount of TCDD in a parallelepiped of soil with base 1 m and height equal to the layer thickness (1.2). Samples with the same code were taken within a few months distance;
[b] site code;
[c] sampling date;
[d] n.d., nondetectable;
[e] n.t., not tested.

Table 9 Penetration of TCDD in soil. Cores collected August 1979 from the Herbicide Storage Area, Johnston Island (A, B), and the Herbicide Orange Storage Area, Gulfport Mississippi (C), where herbicide spills occured in 1977 (after Young et al., 1983).

Depth (cm)	TCDD content (ppm)		
	A	B	C
0- 8	0.119	0.116	0.325
8-16	0.044	0.011	0.340
16-24	0.049	0.008	0.021

Esposito et al. (1980) in 1976-1978 found at a site at the Eglin Air Force Base 275 ppt at the soil surface and 1/3 of this concentration was still detected at 1 m depth. Esposito et al. (1980) also presented the TCDD-concentrations of another site at Eglin AFB 282 days after after treatment with 0.448 kg m^{-2} TCDD contaminated Herbicide Orange (Table 11). Again TCDD appeared to be more mobile than could be expected based on the laboratory experiments on convection by water.

Table 10 Distribution of TCDD in soil. Cores collected 1974 and 1984 from the Test Area C-52A, Eglin AFB, Florida (after Young et al., 1987).

Depth (cm)	TCDD concentration (ppt)	
	1974	1984
0 - 2.5	150	460
2.5- 5	160	815
5 -10	700	2375
10 -15	44	1100
15 -30	-	35

Table 11 Distribution of TCDD in soil 282 days after contamination at Eglin AFB, Florida (after Esposito et al., 1980).

	Depth (cm)	TCDD concentration (ppt)
untreated	0-15	< 10
treated	0-15	15,000
	15-30	3,000
	30-45	90
	45-60	120

In order to get more insight recently laboratory experiments on convection in presence of solvents have been carried out. Palausky et al. (1986) conducted a laboratory experiment in order to determine the TCDD mobility in soil (11.4% sand, 55.2% silt, 33.4% clay and 2.0% organic matter) using six different solvents. In these experiments 9 ml of each solvent containing 900 ng of TCDD has been applied to soil columns. 90% of the amount of TCDD applied with a acetone/water mixture remained at the surface (first 1 mm section of the soil profile). The results of the organic solvents are presented in Fig. 4.

The movement appeared to be related to the solubility of TCDD in the solvent. Due to adsorption, volatility of the solvent and viscosity of the solvent no direct correlation between solubility and distance of transport could be derived by Palausky et al. (1986). Kapila et al. (1989) added a TCDD contaminated waste oil to homogenized soil (11.4% sand, 55.2% silt, 33.4% clay, 2.0% organic matter) in column studies under laboratory and field conditions. After adding TCDD-contaminated waste oil the soil columns were exposed to rainfall. After 3, 6 and 9 months additional applications of uncontaminated waste oil were made. Fast downward movement of TCDD occurred after rainfall, probably due to formation of a colloidal suspension and after the second and third application of waste oil (Fig. 5).

Integration of the concentration profiles (Fig. 6) showed no losses and consequently a decrease in TCDD-concentration in the upper layers of the soil columns is accompanied by an increase in the lower layers.

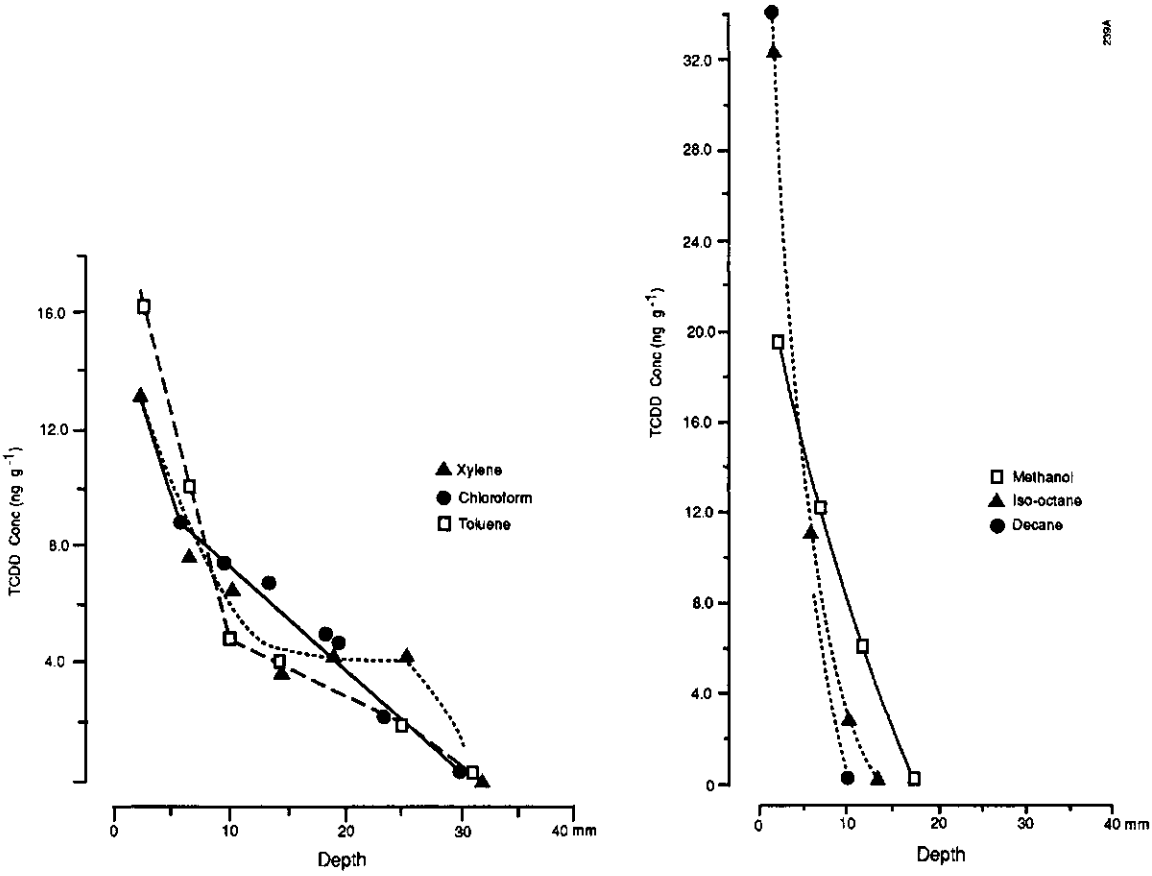

Fig. 4 Graphs showing the migration of 2,3,7,8-TCDD with six different solvents (after Palausky et al., 1986).

Convection in presence of a solvent appears to be faster then convection by water solely due to the higher solubility of TCDD's in solvents and the possibly higher rate of desorption for the solvents.

Arsenault (1976) determined concentrations (Table 12) in the leachate from soil composted with waste sludges containing PCP (pentachlorophenol) and OCDD (3.15, 7.94 and 11.6 ppm) in cilindrical glass vessels (ten inches diameter and eight inches deep). Water was applied at a rate of 2.5 inches/week during the first 121 days and at a rate of 5 inch/week during the last 84 days of the 205-day experiment. No soil physical data have been presented.

Table 12 Octachlorodibenzo-p-dioxin (OCDD) in leachate from waste sludges in soil after 20 days (after Arsenault, 1976).

Leachate volume (ml)	Concentration (µg/l)	Amount (µg)	Percent of original OCDD in soil (%)
3597	0.036	0.13	0.00026
3459	0.084	0.29	0.00021
3712	0.27	1.00	0.00049

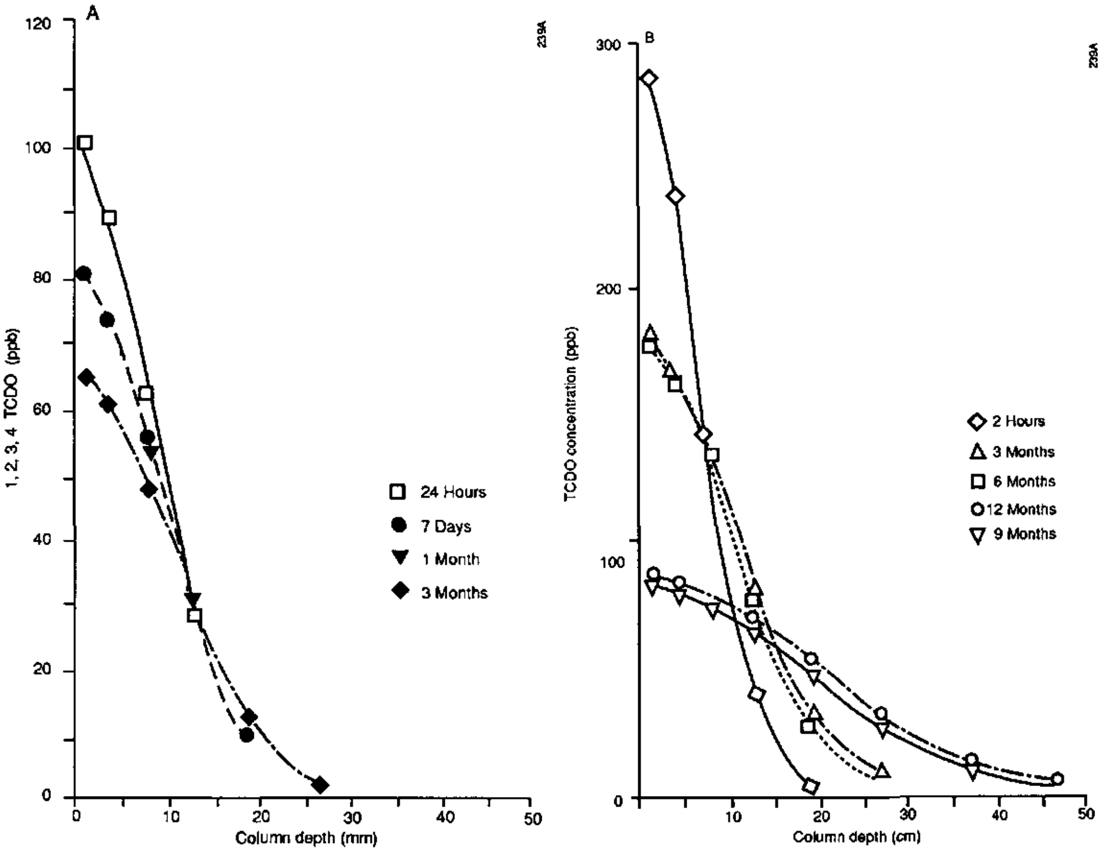

Fig. 5 Concentration profiles for 1,2,3,4-TCDD obtained during field experiments with rainfall at day 4 and 5 and in the thirth month (A) and concentration profiles of 2,3,7,8-TCDD (B) from soil columns in laboratory with waste oil applications after 3,6 and 9 months (after Kapila et al., 1989).

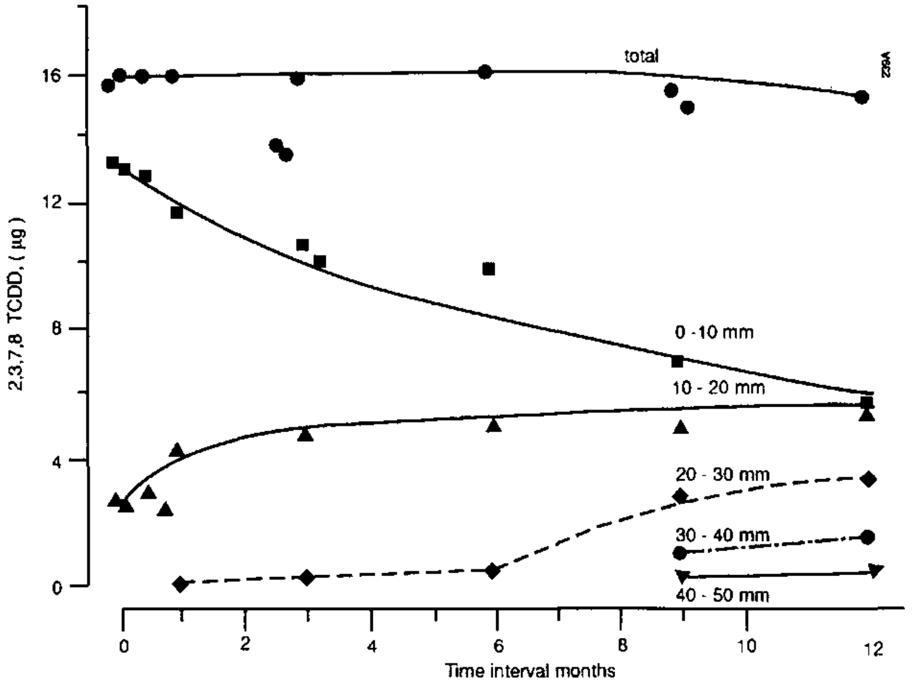

Fig. 6 Changes in total 2,3,7,8-TCDD in soil columns incubated for periods ranging up to twelve months (after Kapila et al., 1989).

Arsenault (1976) concluded that OCDD will not migrate significantly if soil contamination occurs and that OCDD cannot be leached into the groundwater. Concentrations of PCP in the leachate were 0.019, 0.067 and 0.103 mg l^{-1}. It can be concluded that OCDD in the soil system will move slower than TCDD because of the higher degree of chlorination of OCDD and the forthcoming lower solubility and higher lipophilicity.

Organic matter is partly mobile, leading to an indirect, particle-bound transport mechanism. Caron et al. (1985) mentioned the role of dissolved organic carbon in the process of pollutant adsorption. In addition, Webster et al. (1986) determined water solubility of some dioxins both in pure water and in the presence of dissolved humic acids. "Solubility" increased in presence of issolved humic substances. Log($K_{oc(mobile)}$) defined as the association constant between dissolved pollutant and dissolved organic carbon has been determined by these authors. Values of log($K_{oc(mobile)}$) for TCDD at 20°C varied with the kind of organic matter from 5.4 to 6.6 and are somewhat smaller than the log(K_{oc}) values.

Summary

- The PCDD's or PCDF's precipitated at the soil surface are expected to dissolve in small amounts into water and to be leached downward.
- Due to the low water solubility and the huge adsorption leaching will be very small and the PCDD's and PCDF's look immobile if organic matter is present.
- In presence of a significant amount of a co-contaminant with a higher solubility for dioxins then water, convection increases considerably.
- Some of the organic matter is dissolved and can be transported downward, carrying sorbed dioxins.
- Also downward movement by particle transport seems to be possible. No data on this phenomenon are available however.
- Under field circumstances transport of dioxins can not be explained fully by regular processes on convection and adsorption only, so non-homogeneous transport processes have to be taken into account.

3.1.3 Diffusion

Diffusion is the movement of ionic or molecular constituents in a uniform medium (gas or liquid) in the direction of the lowest concentration due to their kinetic activity.

Helling (1971) determined 2,7-DCDD and 2,3,7,8-TCDD to be immobile for diffusion in five soils with different textures and properties due to the low water-solubility.

Freeman and Schroy (1985) used a model based on the energy balance of the solid and vapour phase to simulate dioxin distributions in a sand soil. The temperature gradient acted as the driving force. The calculated rate of movement was very slow. TCDD diffused about ten cm both upward and downward from its initial position in 12 years. The good agreement of the (calibrated) results with measurements at Eglin Air Force Base (Fig. 7) indicates that vapour transport at least in this case is an important transport mechanism. No data on soil type or temperature gradients were presented.

Palausky et al. (1986) also found a temperature dependent TCDD profile in their experiments, suggesting transport by the liquid and the gas phase. Data produced by a model describing gas phase transport fitted well with the measured profiles. No change in TCDD-concentration has been found 30 days after application at temperatures ranging from 0 °C to 20 °C, at 40 °C however a significant change in the TCDD-concentration profile occured because of the increased vapour pressure at higher temperatures. Eduljee (1987) concluded from simulation studies with the model developed by Jury et al. (1983, 1984a, 1984b, 1984c) that diffusion of TCDD in soil (maximum moisture content 0.5, dry bulk density 1350 kg m^{-3}, temperature 25 °C, fraction organic carbon 0.0125) is a vapour-dominated process up to a certain volumetric water content, and liquid-dominated up to saturation. As a result diffusion decreases if pore spaces become filled with water, as long as the gas-phase diffusion is dominant, and increases again if liquid-phase diffusion dominates becomes dominant (Fig. 8).
An increase of soil organic matter content led to a decrease in the volatilisation flux.

Summary

- Diffusion due to concentration and temperature gradients leads to a slow redistribution of dioxins in the soil profile. Consequently both the water and vapour phase have to be taken into account.
- Temperature strongly influences diffusion because of the linear correlation between temperature and vapour pressure of TCDD.
- If organic matter is present in soil the diffusion will be hampered due to the strong adsorption of PCDD's and PCDF's to organic matter.

3.1.4 Volatilization

Volatilization is the transport from the solid or liquid phase to the gas phase and is driven by the kinetic energy of molecules. In environmental studies the term volatilization is often used to cover the mass fluxes through the soil/air boundary.

Crosby et al. (1971) found no volatilization of dioxins on bare surfaces of dry and wet soils and glass plates after 96 hours in their attempt to measure photodecomposition. Isensee and Jones (1971) tried to determine the volatilization of DCDD and TCDD from leaf surfaces of oat and soybean and from glass surfaces. After 48 hours a loss of 90% and 2% was measured for respectively DCDD and TCDD on glass surfaces, 84% and 8% for DCDD and TCDD on soybean leafs and 17% of TCDD on oat leafs. The residual amount on soybean leafs remained constant, the remaining amount on oat leafs decreased, indicating a difference in dioxin adsorption and consequently in an other volatilization rate. EPA (1978) estimated volatilization rates from PCDD's and PCDF's vaporizing from their own surfaces. Rates were in the order of 10E-11 to 10E-13 g cm^{-1} sec^{-1} which are obviously very low. Because the solubility and vapour pressure of TCDD and OCDD are roughly similar to those of DDT, PCDF's and PCDD's were expected to have the same volatility as DDT. DDT is known to volatilize readily from soil and rapidly from water. Crosby and Wong (1977) already mentioned that te losses measured by Isensee and Jones were induced more likely

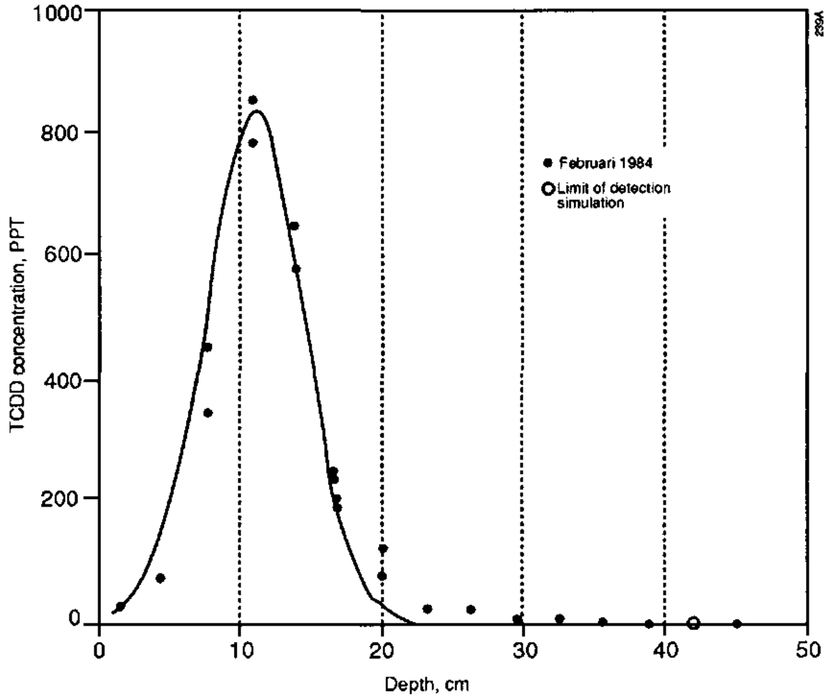

Fig. 7 Simulated (line) and measured (dots) TCDD-concentration of the field experiment at Eglin AFB 12 years after application (after Freeman and Schroy, 1985).

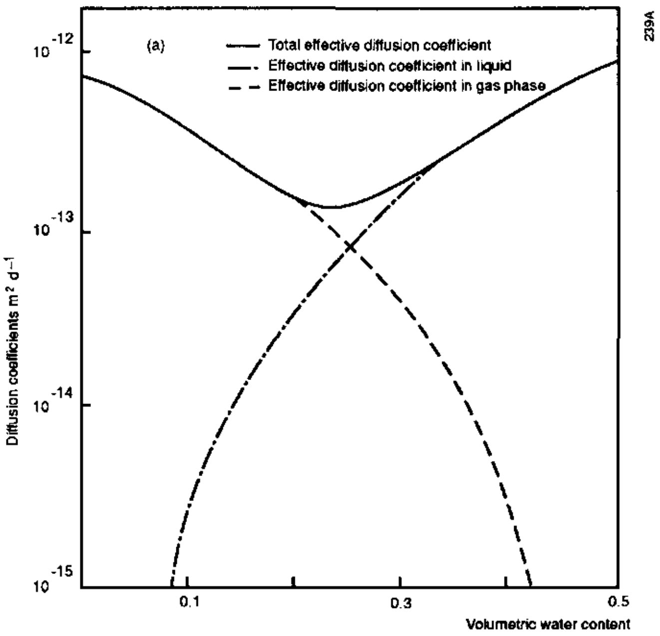

Fig. 8 Effective diffusion coefficient of TCDD calculated by Eduljee (1987).

by photodecomposition than by volatilization. Experiments confirmed this, because losses measured in a dark environment were zero. Facchetti (1986) found a spatially dependent distribution of TCDD content in the above ground parts of control plants around plants growing in contaminated soil (concentration 1 ppt, plants were grown in pots placed in outdoor and indoor greenhouses, duration of the experiment was 75 days) and concluded that evaporation from the contaminated soil had to be responsible. Kearny et al. (1972) suggested that TCDD would behave like DDT and volatilize by codistilling with water. Hutter and Philippi (1982) were not able to calculate volatilization on a theoretical base because of the numerous factors influencing this process, and therefore extrapolated experimental data of comparable chemicals. These authors pointed out that the volatilization of TCDD from a wet soil is around 3/4 the volatilization of DDT (i.e. 2-3 ng cm^{-2} d^{-1} for concentrations in the the 100 ppm-range). Volatilization fluxes observed by Nash and Beall (1980) are considerably lower but also suggest to be around 3/4 of the volatilization fluxes of DDT. Nash and Beall (1980) applied 44 ppb and 7.5 ppm of TCDD in 2.0 kg silvex per hectare to bluegrass turf. Concentrations of TCDD in air were in the femtogram per cubic meter (10E-15 g m^3) range, increasing with increasing soil and air temperatures (maximum temperature 50 °C and 30 °C in the shadow). Nash and Beall (1980) stated that volatilization is a major pathway of TCDD dissipation. A more sophisticated approach was presented by Eduljee (1987), assuming volatilization equal to the flux of TCDD through the soil surface. The volatilization flux then depends on the rate of diffusion through the air boundary layer and the partial vapour pressure of TCDD (which depends on the rate of desorption from the soil and the upward movement to the soil surface). The latter can be realized by diffusion due to a gradient or by mass transfer due to the upward movement of water. This theory has been incorporated into a mathematical model by Jury et al. (1983, 1984a, 1984b, 1984c). Eduljee concluded from studies carried out with Jury's model and input-parameters according to Schroy (1985) that volatilization increases with increasing water evaporation fluxes and that volatilization increases with increasing diffusion fluxes (see 3.1.3). The study showed a depressed volatilization flux due to an increased organic carbon content.

Summary

- Volatilization depends on factors such as organic carbon content, capillary rise, temperature and soil moisture content.
- Volatilization-losses decrease with increasing organic carbon content of the soil (due to adsorption).
- Volatilization increases with increasing temperature.
- In case of a equilibrium state between the gas, water and solid state the gasphase transport may be an important transport mechanism due to the high mobility of the gas phase, even at low concentrations.
- Volatilization under natural conditions seems to be negligible over short time periods.
- Although fluxes are small, volatilization of PCDD's and PCDF's on the long term possibly forms an important path of dissipation of PCDD's and PCDF's from soil.

3.1.5 Non-homogeneous transport

The range in concentrations detected in experiments by several authors indicates a spatial variability in the distribution of TCDD at the soil surface under (normal) field conditions. Most intensive monitoring program took place at Seveso. Di Domenico et al. (1980a) described the distribution of TCDD in the soil surface layer at Seveso to be very uneven with large differences in concentrations between closely spaced locations. Concentration factors of two close sites (< 100 m) varied as much as a factor > 100. The distribution of data collected at the same site (distance 1 m apart) fitted a lognormal Gausian distribution, the distribution over surface areas appeared to be of the Poisson-type (frequency maximum towards low-value concentrations). Freeman and Schroy al. (1986) found different TCDD-contents in soil cores from Missouri taken within 1 m of each other. Contamination occured by spraying the road with TCDD-containing oil.

Helling (1971) determined in a laboratory-experiment the dioxins 2,7-DCDD and 2,3,7,8-TCDD to be immobile in soil. He assumed that dioxins deposited to the soil-surface would not move further into the soil, but would remain at the soil surface and therefore, like other immobile pesticides, become subject to runoff or wind erosion transport. Monteriolo et al. (1982) found TCDD levels in dust samples to suggest that dust was transported from contaminated areas near Seveso into adjoining areas. Muir et al. (1985) suggested that measured losses of 1,3,6,8-TCDD from microplots were due to wind and water erosion of soil. Young et al. (1987) observed particle movement through wind and water erosion causing deposition of contaminated soil in lower parts of the study area and consequently resulting in a uneven redistribution of TCDD at the soil surface.

Di Domenico et al. (1980b) also observed the vertical distribution of TCDD in the soil profile and found unexpected (paragraph 3.1.2) high TCDD levels at depths greater than 30 cm. According to these authors the presence of soil fissures and preferential pathways may be responsible for these high contamination levels relatively deep below the soil surface. The same conclusion was presented by Monteriolo et al. (1982).

Summary

- The distribution of TCDD at the soil surface appeared to be uneven immediately after deposition in the Seveso area.
- Horizontal transport due to erosion and wind- or water transport (runoff) occurs at the soil surface. As a result the distribution of dioxins is non-homogeneous.
- The unequally distribution of dioxins at the soil surface gives problems in modelling the fate of dioxins in an area.
- The presence of preferential pathways or cracks and biological activity can result in transport to greater depths and makes the transport processes more complex.
- Due to this non-homogeneous transport processes dioxins appear to be more mobile under field-circumstances than expected based on the laboratory experiments and model-studies assuming homogeneous transport processes.
- No data are available to quantify the non-homogeneous transport mechanisms.

3.2 Transformation

3.2.1 Chemical processes

PCDD's are chemically stable due to their planar electropositive cycles. Under natural conditions there is no degradation by hydrolytic reactions. TCDD is almost complete decomposed after 21 seconds exposure to a temperature of 800 °C (Stehl et al., 1973, Table 13). Recently Sutton and Hunter (1989) in laboratory tests detected an exponential increase of (thermal) destruction with increasing solar radiant flux level.

Des Rosiers (1983) summarizes chemical methods to destruct PCDD- or PCDF-contaminated wastes. Most methods require artificial conditions and were not yet available for large-scale decontamination at that moment. Articles on the (non-photochemical) chemodegradation of PCDD's and PCDF's are scarce:

- Firestone (1977) reported first-order half-lifes of higher chlorinated PCDD's in an aqueous alkali solution. TCDD was found to be stable.
- Botre et al. (1979) applied micellar catalysis with chloroiodides to degrade pure TCDD and to decontaminate Seveso soil. The amount degraded was 70-90% and 40% respectively. Because this reaction takes place at ambient temperatures, in an aqueous solution and without the use of light energy it seems to be a promising decontamination technique.
- Des Rosiers (1986) mentioned the ability of alkali polyethylene glycolates (APEG's) to destroy TCDD in solution and within soils. However, no data or results are presented in this study.

Table 13 Decomposition of 2,3,7,8-tetrachlorodibenzo-p-dioxin after exposure to elevated temperatures (after Stehl et al., 1973).

Temperature (°C)	Decomposition (%)	
	21 sec exposure	50 sec exposure
500	39	42
600	40	59
700	50	53
800	99.5	

Exposed to light PCDD's and PCDF's loose their stability and become subject to photochemical reactions. For this reason the photochemical reactions of these compounds have been studied extensively. Photochemical reactions involve the adsorption of an amount of energy by a molecule. The molecule then reaches an excited state after which chemical reactions can take place. The needed amount of energy can be absorbed directly from radiation energy but it is also possible that an excited donor transfers his excitation energy to an acceptor-molecule which then reacts photochemically just as if it received the radiation energy directly. The latter process is called photosensitation. Research has been carried out for photochemical formation and especially for photochemical degradation of PCDD's and PCDF's.

3.2.2 Photochemical formation

PCDD's and PCDF's have been considered to be man-made chemicals for many years. This implied that measures on the release of these compounds would prevent further contamination. However recent research pointed out that these chemicals may also originate from environmental photochemical processes: parent materials being other man-made chemicals like PCB's (Crosby et al., 1973) and polychlorophenols (Plimmer et al., 1973, Stehl et al., 1973, Akermark, 1978, Lamparski et al., 1980). A review on reaction mechanisms is given by Choudry and Hutzinger (1982). Because these reactions are very inefficient (Akermark, 1978) and were found under idealized conditions the formation of PCDD's or PCDF's in the natural environment (low concentrations) is unlikely (at least two excited molecules are required for a reaction). Accumulation of dioxins and furans in the environment formed by photochemical processes therefore seems negligible. Moreover photolytic degradation processes act at the same moment with higher rates.

3.2.3 Photochemical degradation

Crosby et al. (1971) found that in methanol dissolved chlorinated dioxins are rapidly degraded by irradiation in natural sunlight and artificial light (half-lifes 3 to 6 hours). Under similar conditions the rate of decomposition of OCDD appeared to be slower than that of 2,3,7,8-TCDD, which again appeared to be slower than that of 2,7-DCDD, so the rate of decomposition seems to be dependent upon the degree of chlorination. Small amounts of a trichloro - and a dichlorodioxin were detected as breakdown products of TCDD (indicating a dechlorination reaction). This indicates that (sun)light can destruct dioxins in the presence of organic hydrogen donors. On bare surfaces of glass plates, on wet or dry sandy loam and silty clay, and in aqueous suspensions a negligible loss of TCDD was measured. The same results have been presented by Plimmer et al. (1973) and by Crosby et al. (1973). The photoreduction of TCDD proceeds stepwise to produce TCDD, and next DCDD, and eventually the nontoxic unchlorinated parent which is itself further decomposed by light (Plimmer et al., 1973). Crosby and Wong (1976) applied TCDD contaminated Agent Orange to glass plates, soil and leaves of rubber plants and exposed the samples to sunlight. Degradation rates from leaves were even faster than from glass, rates from soil were small (Fig. 9). It is not clear

Because losses from dark controls were zero, the losses were not caused by volatilization. The authors concluded that photochemical degradation is the principal factor causing dioxin to disappear from inert surfaces, soils and plants treated with TCDD-contaminated pesticides. Crosby et al. (1973) formulated three requirements for a significant photodecomposition of TCDD:

- dissolution in a light-transmitting film;
- the presence of an organic hydrogen-donor (solvent, pesticide);
- the presence of ultraviolet light.

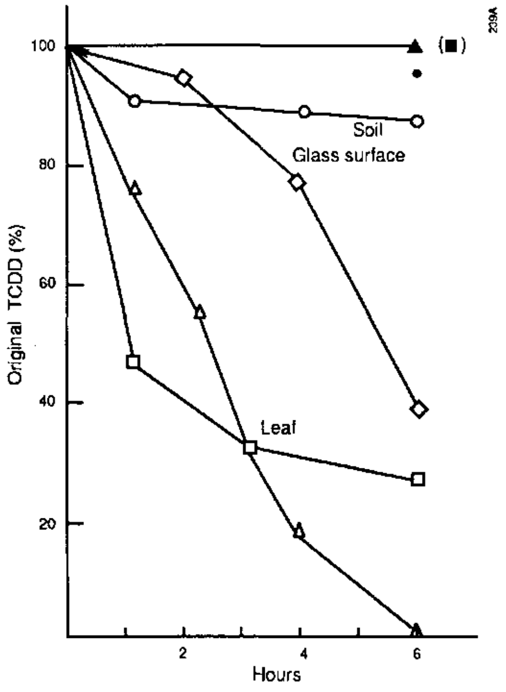

Fig. 9 Loss of TCDD from Agent Orange formulations on a glass surface (◇), leaves (6.7 mg/cm^2, △), leaves (1.3 mg/cm^2, □) and soil (○). Closed symbols are the dark controls (after Crosby and Wong, 1976).

wether this experiment deals with photodegradation of TCDD on (bare) surfaces or with TCDD photodecomposition in solution at these surfaces. Degradation in the soil is smaller than on glass because of the shading effect of the soil particles and the rapid adsorption to the soil particles. The degradation on the plant leaves occurs faster probably due to the presence of hydrogen donors in or at the waxy cuticula of the leaves.

The latter statement was confirmed by the photolytic profiles determined by Koshioka et al. (1989), showing an easy decomposition in the environment (wavelengths above 300 nm) for 2,3,7,8-TCDD, 1,3,6,8-TCDD and 1,2,3,4-TCDD in a 1,4-dioxane solution.

Liberti et al. (1978) stated that photochemical degradation of TCDD can be achieved in any material in the presence of a hydrogen donor. The autors applied a solution of 1:1 xylene and ethyl-oleate in field experiments on a grass-cutted soil and irradiated with a UV-lamp with an intensity of 2 mW cm^{-2}. A decrease in TCDD content of approximately 70% in the upper 3 cm of the soil has been determined after 2 months. In laboratory experiments (Liberti et al., 1978) the decomposition rate not only appeared to be dependent on the intensity of radiation, but also on the temperature (Fig. 10). Liberti et al. suggested the temperature effect to be caused by the higher activity of the oily layer at higher temperatures.

In an experiment (Liberti et al., 1978) with homogenized Seveso soil exposed to natural sunlight in Rome during 1 month (July 1977) again degradation was shown not only at the surface, but also below the surface, possibly due to a diffusion mechanism of dioxin in the oleate-solvent or because of a photolytic reaction occuring through radicals. In the

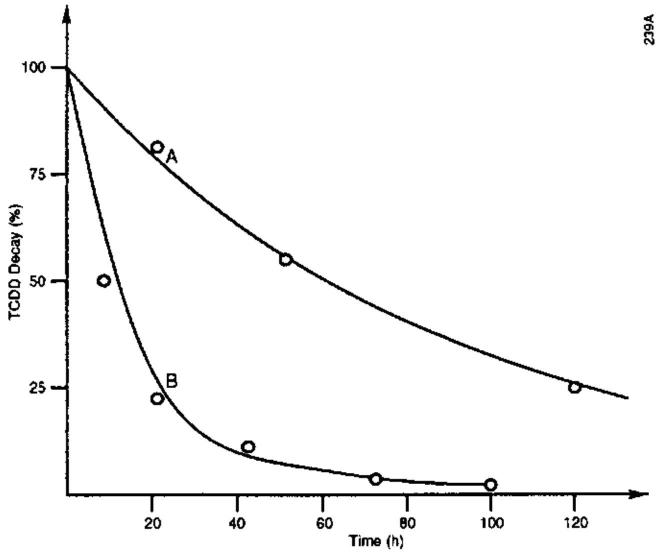

Fig. 10 Thermal effect on the photodecomposition rate of TCDD on glass plates (after Liberti et al. 1978). A, 23 °C; B, 30 °C.

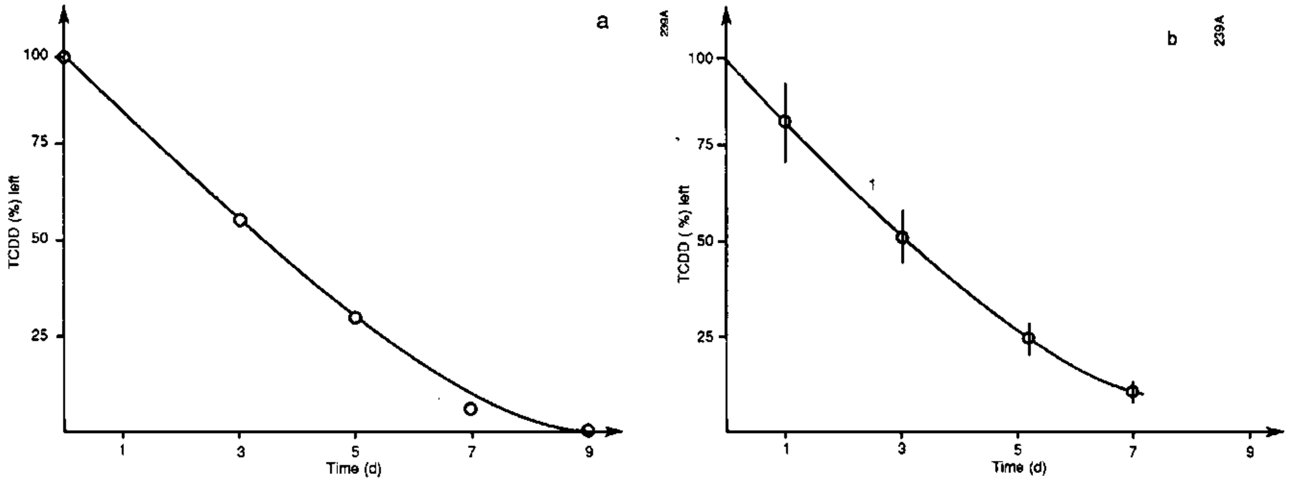

Fig. 11 Decontamination of TCDD polluted Seveso soil sprayed with ethyl-oleate and exposed to natural solar radiation. Results presented by (a) Liberti et al. (1978) and (b) Bertoni et al, (1978).

upper 1 cm soil no TCDD was recovered after 9 days exposure to natural sunlight (Fig. 11a). A decay of 40-60% has been measured in the lower layers. Bertoni et al. (1978) measured in an identical experiment that 90% of TCDD in a 1 cm soil sample was degraded by natural (Italian) sunlight within 7 days when spread with a mixture of ethyl-oleate and xylene (Fig. 11b). The decomposition rate appeared to be 1 microgram per kg soil per day. Spraying with a sufficient amount of a xylene/ethyl-oleate mixture in summer is supposed to result in a satisfactory decontamination of the Seveso-area (Bertoni et al., 1978). Ethyl-oleate is fully effective if used alone, xylene is added mainly as viscosity reducer.

Wipf et al. (1978) sprayed olive oil solutions at plants and soil in a (three) microplot experiment. Wash-off effects were found in both sprayed plots and control (unsprayed) plots and were not increased by adding olive-oil. A significant decrease in TCDD concentrations was detected for two plots, whereas no significant decrease was detected in the third microplot. From laboratory and field studies leaching from olive oil and TCDD appeared to be zero and Wipf et al. concluded that this decontamination method is effective and safe.

Botre et al. (1978) investigated the solubilization and photodecomposition of TCDD in aqueous solutions of cationic, anionic and nonionic surfactants. A cationic surfactant, 1-hexadecylpyridinium chloride (HPDC), proved to increase the decomposition rate of dissolved TCDD. The solubilizing agent is decomposed simultaneously with the TCDD by sunlight. It took only four hours to effect a total destruction of 8 $\mu g\ l^{-1}$ TCDD in 0.02 M HPDC, the half-life being smaller than 2.5 hour. The reaction mechanism is not known.

Plimmer (1978) studied photodecomposition of TCDD on silica and on soil. Control groups in the dark indicated volatilization. Measured photodegradation of TCDD on silica was approximately 28% after 8 hours of exposure and 63% after 20 hours of exposure. A polar metabolite was detected but not identified. In soil no metabolite was found, suggesting that no photolysis took place. Recovered amounts of TCDD on soil were smaller than on silica. Gebefugi et al. (1977) also investigated photolysis of TCDD on silicagel. They used two artificial light sources with wavelenghts above 290 nm and above 230 nm. In the latter case within four days total decomposition has been found, in the prior case after 7 days about 8% of the added TCDD was recovered. The half-lifes were one and two hours. The authors stated that photolysis occurs without organic protondonor. This conclusion is essentially wrong because silicagel irradiated with UV light has been shown to produce hydrogen (Tseng and Chang, 1975).

Buser (1976) and Koshioka et al. (1989) suggested that chlorine atoms at the 2,3,7 and/or 8 positions of chlorinated dioxins are photodegraded faster than those with chlorine atoms at the other positions. Busers hypothesis has been confirmed by Dobbs and Grant (1979). The latter even supposed that 2,3,7,8-TCDD is the most photolabile of the PCDD's. However all these authors studied pholoysis of PCDD's in solution. Lamparski and coworkers (1980) and Miller et al. (1989) in contrary observed a preferential photo-dechlorination at the 1,4,6,9-positions of OCDD in soils. These results indicate an essential difference in photochemistry of PCDD's at the soil surface and in solution and therefore confirm the findings of Nestrick et al. (1980).

Nestrick et al. (1980) measured rates of photodegradation of some PCDD's deposited on a glass surface and in solution of an hydrocarbon solvent (Table 14), and presented data on the half-life of the 22 TCDD-isomers for photolysis both on glass surface and in solution (Table 15a and 15b).

Table 14 PCDD half-lifes on glass surfaces and in hexane solution (data from Nestrick et al., 1980).

Isomers represented	Half-lifes (hr)	
	glass surface	hexane solution
TCDD (22 isomers)	2-140	1-140
PCDD (1 isomer)	1	8
HCDD (3 isomers)	131-735	6- 13
H7CDD (2 isomers)	40- 52	30- 53
OCDD	815	24

Table 15a Photolysis data of TCDD isomers at surfaces (data from Nestrick et al., 1980.

TCDD isomer	Amount of TCDD[a] exposed (ng)	Exposure time (min)	TCDD[b] remaining (%)	Absolute $t_{1/2}$[c] (min)	Relative $t_{1/2}$[d] (-)
1239-TCDD	1.03	180	35.7	121	0.014
1237/1238-TCDD	1.23	180	43.7	151	0.018
1378-TCDD	1.20	180	45.9	160	0.019
1379-TCDD	1.20	180	47.8	169	0.020
1236-TCDD	1.02	180	57.4	225	0.027
1237/1238-TCDD	1.04	180	59.0	236	0.028
1368-TCDD	0.71	480	28.3	264	0.031
1268-TCDD	0.96	480	31.0	284	0.034
1279-TCDD	0.98	480	33.2	302	0.036
1247/1248-TCDD	1.14	480	35.9	325	0.039
1267-TCDD	1.05	480	36.1	326	0.039
1246/1249-TCDD	1.06	480	37.2	336	0.040
1247/1248-TCDD	0.92	480	38.0	344	0.041
1278-TCDD	1.12	480	38.7	350	0.042
1246/1249-TCDD	0.99	480	44.1	406	0.048
1269-TCDD	1.05	480	46.7	437	0.052
1478-TCDD	1.06	480	47.8	451	0.054
1289-TCDD	1.20	480	51.5	501	0.060
1369-TCDD	1.02	480	52.0	509	0.061
1234-TCDD	1.00	480	55.2	560	0.067
1469-TCDD	1.16	1380	31.5	830	0.099
2378-TCDD	1.00	3780	80.3	8400	1.00

[a] Present on a clean soft glass surface.
[b] Percent of initial concentration remaining after exposure.
[c] Half-life as calculated by first-order reaction kinetics.
[d] Normalized with respect to 2378-TCDD half-life.

Table 15b Photolysis data of TCDD isomers in solution (after Nestrick et al. 1980).

TCDD isomer	Amount TCDD[a] exposed (ng)	Exposure time (min)	TCDD[b] remaining (%)	Absolute $t_{1/2}$[c] (min)	Relative $t_{1/2}$[d] (-)
2378-TCDD	3.00	60	48.0	56.8[e]	1.00
1378-TCDD	2.40	120	58.1	153	2.69
1279-TCDD	2.45	315	49.9	314	5.53
1289-TCDD	3.00	375	56.3	429[e]	7.55
1268-TCDD	2.40	545	43.0	482[e]	8.49
1278-TCDD	2.80	555	46.0	491[e]	8.64
1379-TCDD	3.00	300	65.9	499	8.79
1368-TCDD	1.80	330	63.7	507	8.93
1237/1238-TCDD	2.45	345	65.4	563	9.91
1239-TCDD	2.05	330	67.6	584	10.3
1267-TCDD	2.60	545	55.0	632	11.1
1237/1238-TCDD	1.55	315	71.6	653	11.5
1236-TCDD	1.55	330	76.2	841	14.8
1247/1248-TCDD	2.85	545	64.5	861	15.2
1478-TCDD	2.85	545	64.5	861	15.2
1478-TCDD	2.65	570	65.7	940	16.5
1247/1248-TCDD	2.30	570	68.9	1060	18.7
1234-TCDD	1.20	555	76.0	1294[e]	22.8
1269-TCDD	2.60	1260	50.2	1319	23.2
1246/1249-TCDD	2.00	540	75.9	1339[e]	23.6
1246/1249-TCDD	2.65	555	75.2	1349	23.8
1369-TCDD	2.55	540	78.3	1388[e]	24.4
1469-TCDD	2.90	1260	90.1	8400[f]	148

[a] Present in 50 µL of n-hexadecane.
[b] Percent of initial concentration remaining after exposure.
[c] Half-life as calculated by first-order reaction kinetics.
[d] Normalized with respect to 2378-TCDD half-life.
[e] Average value based on multiple
[f] Approximate value.

Table 15a shows that the majority of TCDD's are photodegraded faster on the glass surface than in the hydrocarbon solution. Because 2,3,7,8-TCDD compared to other TCDD-isomers is characterized by a larger half-life in hexane and a smaller half-time on a glass surface, Nestrick et al. (1980) conclude that 2,3,7,8-TCDD is unique in its photochemical behaviour. They also suggest that this photochemical behaviour correlates with some fundamental property of this dioxin making it the most toxic species of the PCDD's.

Arsenault (1976) measured photodegradation of OCDD in an oil solvent on filter paper. The following observations were made:
1. Decomposition was faster in sunlight than in laboratory UV-light (no wavelenghts and intensities of the light used were presented).
2. Degradation was faster in presence of oil than in the absence of oil.
3. After 16 hours outdoor exposure 66% of the OCDD was decomposed in presence of oil and 20% was degraded in absence of oil.
4. No 2,3,7,8-TCDD was detected as a breakdown product of OCDD.

Arsenault explains the latter observation by a more rapid decomposition of 2,3,7,8-TCDD under these circumstances than it could be formed from OCDD. Measurements on poles confirmed the results of the filter paper. Miller (1989) studied the photodegradation of OCDD on soil with and without ethyl-oleate (hydrogen-donor) added. The measured depth of photolysis of OCDD in soils was very small (0.06 to 0.13 mm), and the conversion of OCDD to toxic congeners was small but significant. Miller (1989) concludes that at the soil surface photodegradation of OCDD 2,3,7,8-TCDD formation is preferred, whereas photodegradation of OCDD in solution will result in small amounts of 2,3,7,8-TCDD.

Hutzinger et al. (1973) investigated photochemical degradation of di- and octochlorodibenzofuran. Both furans showed similar rates of decomposition in hexane due to dechlorination. After 20 hours of exposure no furans could be detected. Observed degradation of furans on a thin film exposed to sunlight was smaller. Neupert et al. (1988) studied the stability of (poly)brominated dibenzo-p-dioxins and dibenzofurans in a toluene solution. The furans were less stable than the dioxins, and the degree of bromination determined the rate of decomposition.

Orth et al. (1989) stated that (evaporated) gas phase 2,3,7,8-TCDD photodecomposes in the environment when sunlight is present. The half-life calculated from the data presented by
Orth (temperatures varying from 150 to 350 ^{o}C, irradiated by an UV-source of the same intensity as sunlight) is 76 sec.

Choudry and Webster (1985) calculated half-lifes and rate constants of two PCDD's in water by means of determined quantum yields of this compounds and measured absorption spectra and variable sunlight duration and intensity. Choudry and Webster (1986) published a table containing half-lifes of six PCDD's in aquatic bodies. In addition, Dulin et al. (1986) determined quantum yields, rate constants and half-lifes of TCDD. The latter concluded that not only dechlorination but also C-O cleavage may be an important photochemical process. Half-lifes presented by Choudry and Webster and by Dulin are summarized in Table 16.

Table 16 Calculated photolysis half-lifes [d] of PCDD's in aquatic bodies at 40° latitude (data from (a) Choudry and Webster (1986) and (b) Dulin et al. (1986)).

Compound	Spring	Summer	Fall	Winter	Source
21,2,3,7-	2.08	1.77	3.20	5.42	a
1,3,6,8-	0.35	0.31	0.53	0.84	a
2,3,7,8-		6.00			b
1,2,3,4,7-	18.29	15.16	28.59	52.37	a
1,2,3,4,7,8-	7.57	6.27	11.87	21.57	a
1,2,3,4,6,7,8-	56.46	47.33	87.86	155.79	a
OCDD	20.55	17.85	31.26	50.45	a

Summary

- Chemical reactions other than photolysis seem to be negligible under natural conditions.
- The wavelength required for photolysis of PCDD's and PCDF's belongs to the sunlight spectrum and therefore photochemical reactions occur under natural conditions.
- Photolysis leads to both formation and degradation of PCDD's and PCDF's.
- Formation seems of minor importance because concentrations of the parent-chemicals in the natural environment are very low and because degradation takes place at a higher rate.
- Degradation processes depend on the state of the compounds:
  1 In the gaseous phase photodecomposition is very fast.
  2 In the solid phase there is a preferential loss of chlorine from the 1,4,6 and 9 position (leading to more toxic compounds). In this case 2,3,7,8-TCDD is the most stable TCDD-isomer.
  3 In solution there is a preferential loss of chlorine from the 2,3,7 and 8 positions, resulting in less toxic compounds. Then 2,3,7,8-TCDD possesses the smallest half-life of the TCDD's.
- Photodegradation is influenced by the presence of a proton donor (acting as a photosensitizer), so two cases have to be distinguished:
  a Photolytic decay of the compound in absence of a H-donor, in this case degradation rates are slow.
  b Photodegradation in presence of a hydrogen donor, with fast degradation rates and small half-lifes.
- Half-lifes of TCDD calculated from the data presented by several authors or already published are summarized in Table 17.

Table 17 Half-lifes of 2,3,7,8-TCDD exposed to ultraviolet light calculated by first order kinetics.

Hydrogen donor		Absent	Present
gas phase		76 sec	–
solid state	glass surface	>> (Crosby) 6 d (Nestrick)	5-6 hr (agent o.)
	soil surface	>> (Crosby) >> (Plimmer)	3 d (ethyloleate) 3 d (olive oil) 2 d (agent o.)
	leafs		1-3 hr (agent o.)
soluted		6 d (water)	3-6 hr (methanol) 2.5 hr (HPDC) 1 hr (hexadecane)

- In the natural environment PCDD's and PCDF's at the soil surface are supposed to have half-lifes in the order of weeks to years.
- Oil and pesticides in the soil act as sensitizers and half lifes reduce to several days.
- PCDD's and PCDF's on leaf surfaces are supposed to have half lifes of some hours like in solution with a hydrogen donor present.
- It is not known whether PCDD's and PCDF's on leaf surfaces behave photochemically as if they are in solution or if they are in solid state attached at the surface.
- Photolysis of the compounds in the soil does not follow first order kinetics because the PCDD's and PCDF's are partly protected from irradiation by soil particles and because they are strongly sorbed to soil particles.
- If the fate of PCDDD's and PCDF's in the environment has to be studied it seems not correct to study the fate of 2,3,7,8-TCDD solely. This because of the photochemical "formation" of 2,3,7,8-TCDD from higher chlorinated dioxins at the soil surface.

3.2.4 Microbial biodegradation

Biodegradation is the transformation of chemicals by microbial metabolism to other (natural) compounds. Comparing the results of microbiological studies is difficult due to the heterogenity in the methods used. For this reason the articles dealing with biodegradation of PCDD's are summarized in chronological order.

- Kearny et al. (1972) measured the loss of radioactive labeled C from DCDD and TCDD in the form of CO_2 applied at three concentrations to two types of soil. The CO_2 evolution from the DCDD treated soils, caused by biological activity, showed to be concentration dependent. The soil physical properties and the organic matter content of the soil also influenced the biological activity. Metabolites were detected but could not be identified. Hardly measurable labeled CO_2 was detected from TCDD treated soil at any concentration, and no metabolites were found after 1 year of incubation.
- Matsumura and Benezet (1973) found five microbial strains to possess some ability to degrade TCDD. Because they studied almost 100 microbial strains which were known to degrade persistent pesticides, the authors concluded that microbial mediated degradation of TCDD is rather rare in nature. Uptake of TCDD by algae and yeasts has been detected.
- Arsenault (1976) assessed after 205 days a loss of 15, 29 and 37% (27% average) of OCDD (3.15, 7.94 and 11.6 ppm) in waste sludges containing PCP and OCDD composted with soil. Because leaching was negligible, the author concluded that losses were due to biodegradation. Volatilization and photodegradation were not taken into account by Arsenault.
- Klecka and Gibson (1979) found the bactery Pseudomonas sp. to degrade (non-chlorinated) dibenzo-p-dioxin by co-oxidation when grown on salicylate. Two metabolites could be identified, cis-1,2dihydroxy-1,2hydro-dibenzo-p-dioxin and 2-hydroxy-dibenzo-p-dioxin. Cell extracts from the parential strain grown with naphtalene oxidized the first metabolite under both aerobic and anaerobic conditions to 1,2 dihydroxy-dibenzo-p-dioxin.
- Klecka and Gibson (1980) studied the oxidation of dibenzo-p-dioxin and some chlorinated dibenzo-p-dioxins by

Beijerinckia sp. grown with succinate and biphenyl. Oxidation of dibenzo-p-dioxin resulted in the metabolites cis-1,2dihydroxy-1,2hydro-dibenzo-p-dioxin and 2hydroxy-dibenzo-p-dioxin, oxidation of two monochlorinated dibenzo-p-dioxins gave cis-dihydrodiols. No metabolites were detected from two dichlorinated dibenzo-p-dioxins. The rate of oxidation seems to decrease with increasing degree of chlorine substitution. The oxidation of 0.05% dibenzo-p-dioxin was shown to inhibit growth of the Beijerinckia sp. after four hours. The Beijerinckia sp. were not able to use any of the chlorinated dibenzo-p-dioxins as a source of carbon and energy for growth.
- Camoni et al. (1982) studied the influence of an organic compost addition at TCDD contaminated soil in the laboratory. After 480 days 73 to 77% of the originally present TCDD was recovered. The compost had no influence on the degradation rate of TCDD. The measured loss is the overall result of several processes (photolysis, volatilization, irreversible adsorption and biological degradation). The investigators could not distinguish (micro-)biological degradation.
- Hutter and Philippi (1982) found no significant metabolism of TCDD after one year of incubation in liquid nutrient media and in nutrient enriched moist soils at 28 °C. Up to one percent of a possible polar metabolite was detected. No carbon dioxide labeled by radioactivity was trapped in the air above the soil.
- Philippi, Schmid, Wipf and Hutter (1982) in addition identified the (polar) metabolite to be 1-hydroxy-2,3,7,8-tetrachlorodibenzo-p-dioxin. No rearrangement of the chlorine substituents occured.
- Young et al. (1983) analysed the presence of microbial strains in natural soil samples contaminated with TCDD both quantitatively and qualitatively. Some organisms found in polluted soils with high TCDD levels were not found in other samples.
- Quensen and Matsumura (1983) examined the degradation of TCDD by cultures of Bacillus megaterium and Nocardiopsis spp. Degradation in soil systems appeared to be small (experiments were shielded from light) and were up to 1% for long term experiments (8 months). Degradation only occured during the first two months. This was suggested to be before the TCDD became completely bound to the soil.
- Freeman and Schroy (1985) presented field data on the movement of TCDD applied in the soil at 11 cm depth after twelve years. Because it is suggested that all the applied TCDD is still remaining in the soil, biodegradation during this twelve year period should have been very small or zero.
- Muir et al. (1985) detected a polar degradation product in soil 131 and 321 days after contamination with 1,3,6,8-TCDD. The metabolite covered 0.7 to 2.5% of the amount applied. After 495 days no metabolites were detected. The metabolites were not identified.

Summary

- The lack of consensus of these observations is a consequence of the large number of variables influencing microbiological processes (e.g. pH, temperature, aeration, available moisture, nutrients, composition of microbial communities, concentrations of studied chemicals etc.).
- Microbial biodegradation of PCDD's has been proved to occur in laboratory.

- PCDD's seem to be co-oxidized, i.e. other substrates have to be present as a source of carbon and energy for growth.
- If microbiological metabolism occurs under laboratory conditions, only small amounts of the PCDD are transformed.
- The current knowledge on biodegradation of PCDD's indicates that it is not certain wether this process occurs under natural conditions, and if so it will affect only very small amounts of the PCDD's.
- Although some degrading microbial strains have been identified, degradation of PCDD's by micro-organisms under natural conditions is not likely, because these compounds are strongly adsorbed to particles, making them less available to microorganisms, and because the natural conditions are less optimal than the laboratory conditions.

3.3 Plant uptake

Plant uptake has to be studied because it is a possible pathway of exposure (via ingestion), but also because it forms a possible "technique" for extraction of TCDD from soil. Chemicals may enter plants either through leaf uptake after deposition at the plant foliage or by root uptake from the soil moisture. Compounds strongly adsorbed to soil particles are hardly available for uptake.

The studies on PCDD plant-uptake are reviewed briefly.
- Isensee and Jones (1971) measured the uptake of DCDD and TCDD from a sandy loam (low adsorptive capacity) by two crop species: oats and soybeans. A maximum of 0.15% and 0.10% of the original compounds was found after 10 days respectively in the tops of oats and soybeans. Thereafter levels dropped continuously for both species. Tops of mature oats and soybeans contained no detectable amounts of dioxins. No detectable amounts were found in oat grain and beans of soybean. From a nutrient solution the maximum measured uptake was considerably higher. Smaller quantities were translocated to the tops but the dioxin accumulated in the roots. To which degree adsorption or absorption contributed to the total root content is not known. Application of the dioxins to the leaves of young oat and soybean plants did not result in a translocation to other parts of the plant. However the amount of dioxins decreased in time, according to the authors possibly due to volatilization. Photodecomposition was not considered. The effect of rainfall was also examined. Leaves of oats and soybeans were washed with drops of water. Most of the dioxins were washed of in the first wash, less were removed in the second wash. The amount TCDD washed of appeared to be dependent on the time after application of TCDD to the leaves. The use of a solubilizing surfactant may have influenced the results of the "leaf-applications"; more TCDD was washed off than could have been expected based on the water solubility of TCDD. Wipf et al. (1978) found wash of effects in a field experiment after rainfall. Isensee and Jones (1971) concluded that accumulation of TCDD in plants from soil uptake in the environment is highly unlikely (extremely high concentrations of TCDD were applied in the study).
- Cocucci et al. (1978) took samples of plants growing in soil polluted with TCDD in the Seveso area. Samples from new formed (1 year after contamination) leaves, fruits, twigs and cork were all contaminated. The dioxin content ($\mu g\ kg^{-1}$ fresh weight) of the cherry tree was: leaves 1.01, fruits

0.40, twigs 13.14, cork 3.16. Results from other plants (fig, pear, apricot, peach and vine) were similar. Concentration is higher in leaves than in fruit due to a higher rate of transpiration, and higher in twigs (transport tissue) than in cork (inactive tissue). According to the authors these data show that dioxin is translocated in plants to the new formed tissues. Potato and carrot grown in spring 1977 contained more TCDD in the underground parts (at levels of the same order of magnitude as the TCDD level in the soil, Table 18) compared to the shoots, and the conductive tissues contained more TCDD than non-active tissues. This also proves translocation to the aerial parts, where volatilization or photodecomposition is likely to occur. After washing the plants and moving them to clean soil, TCDD levels were considerably decreased after four months. TCDD content of the wash water was not determined.

Table 18 Dioxin content of carrot, potato, onion and narcissus plants after Cocucci et al. 1978).

Plants	Aerial parts	Underground parts		Soil
		inner	outer	
carrot	2.150	4.462	9.203	5.310
potato	2.115	3.560	1.961	8.330
onion	0.835	1.798	1.763	2.680
narcissus	1.658	2.221	2.593	4.370

Values expressed as µg per kg fresh weight and as µg per kg fresh soil. Values are the mean of 2 determinations.

- Contrary conclusions were drawn by Wipf et al. (1982), who collected samples from plants growing in the Seveso area from 1976 through 1979. TCDD-content in plant material was up to 1 ppm in 1976, and decreased in time several orders of magnitude. Leaves grown in the spring of 1977 were not contaminated with TCDD. No traces of TCDD were detected in the flesh of fruits (Table 19) and in corn cobs grown in 1977. Translocation seems to be negligible in these experiments. The skin of the fruit (Table 19) and the husks of the corn cobs however contained TCDD, suggesting contamination from local dust.

Table 19 TCDD-distribution in fruit from zone A2/A3 (fall 1977), Seveso (after Wipf et al., 1982).

Fruit	Concentration (ppt) in				Amount on peels (%)
	soil	peeled fruit	peels	whole fruit	
apples	10,000	< 2.5	137	37	> 95
pears 1	10,000	< 1.5	95	25	> 98
pears 2	10,000	< 0.5	79	21	> 96
peaches	10,000	< 0.8	102	30	> 98

Measurements on carrots grown in polluted soil also showed that uptake is minimal. Presented data (Table 20) on carrots show 30% of the TCDD to be present in/at the root surface whereas almost 70% was found in the wash water. This TCDD-distribution indicates adsorption to the root surface.

Table 20 TCDD-distribution in carrots grown in a greenhouse in soil of zone A (estimated concentration: 1000-5000 ppt in soil) from Seveso (after Wipf et al. 1982).

Tissue	Amount of tissue (g)	Amount of TCDD		Amount of tissue (%)
		(ng)	(ppt)	
central cylinder	191	1.9	10	1
outer edible part	591	3.8	6.5	2
total edible part	782	5.7	7.5	3 (peeled)
peels	218	48.8	224	29
total scrubbed carrots	1000	54.5	54.5	32
wash water		112.5		68
total carrots, unwashed	1000	167	167	100

- Facchetti (1986) studied the uptake of TCDD from soil (1 to 752 ppt) by maize and beans under laboratory conditions. The total uptake proved to be low (a few ppt), the TCDD level of roots and washwater was higher than that of the surrounding soil. No increase of TCDD was detected in the shoots, neither in time nor as a function of concentration of TCDD in the soil. Therefore the contamination of the overground parts was suggested to occur mainly due to evaporation of TCDD from contaminated soil.
- Sacchi et al. (1986) determined TCDD concentrations in the aerial parts from bean and maize plants grown in pots filled with contaminated soil. The amount of TCDD in the shoots increased with increasing TCDD concentration of the soil and in time. When peat was added to the soil the accumulated amount of dioxin in the aerial parts was evidently smaller, this due to the strong adsorption of PCDD to the organic matter, and even decreased in time. Plants grown in uncontaminated soil contained about 5% of the radioactivity applied to polluted soil, suggesting contamination with vaporized TCDD. To investigate this, maize plants were grown in continuous light and in dark (transpiration flow resp. 0.6 g dm^{-2} h^{-1} and 0.04 g dm^{-2} h^{-1}). Incorporation of TCDD in the 3rd leave was considerable higher for maize grown in continuous light. According to the authors this suggests translocation through the vessels with the transpiration flow. When plants were grown in water, 90% of the present TCDD was found to be adsorbed at the root surface within 1 hour. The same result was observed when dead roots were applied to the solution. This proves passive adsorption.
- Briggs et al. (1982) posed a relation between lipophylic, non-ionized organic chemicals and uptake and translocation by plants with non-woody roots, expressed as a function of the octanol/water partition. For very lipophilic species the derived relation leads to very high RCF (root concentration factor = [concentration in roots]/[concentration in soil water]) due to accumulation of non-ionized organic chemicals to the lipophylic root solids, whereas translocation is very unlikely. Using a Log (K_{ow}) varying from 6 to 7 the RCF will

be 1250 to 7400. The TSCF (transpiration stream concentration factor = [concentration in transpiration stream]/[concentration in soil water] for Log(K_{ow}) ranging from 6 to 7 leads to a TSCF of 5.E-04 to 1.E-05.

- Ryan et al. (1988) used simple relations to evaluate potential plant uptake of organic chemicals. According to the results presented by these authors TCDD is no subject to plant uptake from soil but is subject to plant uptake via volatilization.
- Reischl et al. (1989) in addition concluded, based on fundamental theoretical considerations, that accumulation of PCDD's and PCDF's mainly results from deposition in the gaseous state. Particle bound deposition, except area's of extreme particle loading, is of secondary importance. Finally Reischl calculated bioconcentration factors between needles and air for some dioxins with the aid of the data presented by Shiu et al. (1988) and two relations derived by Reischl (1989) from available data on other chemicals (Table 21).

Table 21 BCF-values needle/air as calculated by Reischl et al. (1989) with data presented by Shiu et al. (1988).

Compound	Log(BCF) (1)	Log(BCF) (2)
TCDD	4.63	4.40
PCDD	5.47	5.69
HCDD	5.83	5.34
H7CDD	6.08	6.07
OCDD	6.33	5.85

(1) BCF calculated as a function of the vapour pressure of the solid at 25 °C.
(2) BCF calculated as a function of the vapour pressure of the solid at 25 °C and Henry's law constant.

Summary

To compare these studies is difficult for several reasons:

- the studies are focussed on different crops and different parts of the plants;
- differences in concentration of TCDD in the polluted soil;
- differences in sampling time after contamination;
- different treatment of the plant samples;
- the use of different analytical techniques;
- insufficient or no soil characterization;
- units based on dry weight versus fresh weight. Moreover, the studies done by Wipf et al. (1982) and Cocucci et al. (1978) in the same area, with the same soils and with identical plant species led to opposite conclusions regarding translocation in the plant.

However, some general conclusions have been drawn.

- Most of the available studies indicate adsorption at the root surface, but none or small uptake and translocation by plants.
- This implies that accumulation of PCDD's on leaf surfaces is caused mainley by deposition of vapourized gas phase PCDD.
- Adsorption to roots as a concentration effect is expressed in comparison to the soil concentration by several authors. It seems more correct to compare with the concentration in the soil solution because immobilized (adsorbed) PCDD is

ignored in the latter case .
- Because PCDD's are strongly adsorbed to soil organic matter, they are hardly available for plant uptake.
- The lipophylicity of the PCDD's and PCDF's theoretically causes adsorption to the root surface and a (very) small uptake.
- Because of these considerations uptake of PCDD's and PCDF's is expected to be very small to neglectable.

3.4 Overall half-lifes

Dissipation can be described with an experimentally determined half-life. Often this is an "overall half-life", i.e. the result of all acting (transport and transformation) processes.

Kearney et al. (1972) studied the persistence of TCDD in two soils at 30 °C and a moisture content near field capacity. After 360 days 56% and 63% of the TCDD was recovered in the sand and the silty clay loam respectively. Woolson et al. (1973) reported that no residues of TCDD applied with 2,4-D and 2,4,5-T were found six years after application during three years in an identical sand soil. Di Domenico et al. (1980d) analysed TCDD levels taken at exact the same sites in the Seveso area at three different dates. TCDD levels dropped within the first 5 months after contamination, but no further decrease was detected after this period. So half-life is dependent on the residence-time of TCDD in the soil. Calculated half-lifes (Di Domenico et al., 1980c) were 1 year 1 month after contamination and 10 year 17 months after contamination. Muir et al. (1985) determined the overall half-life of 1,3,6,8-TCDD applied to soil (4.6% organic matter) at 130-400 days.

Young et al. (1983) observed spill sites of herbicides containing TCDD during three years. TCDD showed trends to decrease during the observation period, but it was not possible to estimate the TCDD persistence from these studies. In 1987 Young stated, based on a 15 year long-term observation, that the half-life of TCDD certainly must be greater than 10 years. Yanders et al. (1989) presented data of Time Beach samples taken with a time interval of four years. No migration or losses of TCDD in the soil were found from twelve to sixteen years after contamination. Losses through photodecomposition or volatilization were hindered by the pavement of the streets.

Summary

Reported values of half-lifes range from half a year to more than ten years. The discrepance in results probably can be explained. After an incidental release of PCDD's and PCDF's into the air these compounds deposite at the soil or plant surface. When rain falls the species leach to the soil surface and into the soil (where they get sorbed if organic matter is present). At the soil and plant surface the pollutants can be photodegraded, resulting in a fast decrease in contaminant content at the soil surface. These processes continue until no more compounds are available for photodecomposition. So far the half-life has been small. The resulting profile contains little contaminant at the soil surface, more in the layers directly below the surface with decreasing amounts downward. Disappearance of PCDD's and PCDF's from the soil profile at this moment is only possible due to evaporation and subsequently photodegradation, and due to plant uptake or biodegradation, as far as these phenomenon occur. Moreover transport and transformation are possibly hampered by an irreversible adsorption which increases with time. At this stage the half-life will increase considerably. Depending on the time after release at which the measurements started and the period the measurements took place, different authors therefore determined different half-lifes.

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