A COMPARATIVE STUDY OF THE PHOTOLYTIC DEGRADATION OF OCTACHLORODIBENZOFURAN (OCDF) AND OCTACHLORODIBENZO-P-DIOXIN (OCDD)

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ABSTRACT

Photolysis at 290 nm and higher wavelengths of octachlorodibenzofuran (OCDF) and octachlorodibenzo-p-dioxin (OCDD) was studied in three organic solvents hexane, 1,4-dioxane and methanol. It appeared that the degradation kinetics strongly depended on the type of solvent. OCDD degraded fastest in hexane, whereas OCDF degraded fastest in methanol. Less than 5% of the total loss of OCDD degraded by reductive dechlorination, with preferential loss of chlorine atoms at the 1 or 9 positions. 35 to 50% of the total loss of OCDF degraded via reductive dechlorination, with preferential loss of lateral chlorine. OCDF degraded faster than OCDD in all studied solvents.

Photolysis at 290 nm and higher wavelengths of OCDD and OCDF adsorbed onto alumina impregnated with copper (alumina/Cu) in the presence of natural and distilled water was also investigated. Under these more relevant environmental aquatic conditions, photolysis of OCDD and OCDF was much slower than photolysis in the studied organic solvents. Significant loss was only found for OCDF. A part of the loss of OCDF could be explained by reductive dechlorination; the results suggested that other mechanisms of degradation occurred in addition to reductive dechlorination.

All photolysis experiments showed that OCDF was photochemically less stable than OCDD.

INTRODUCTION.

In general, polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are considered as compounds that degrade poorly in the environment. Because of their strong adsorption properties, PCDDs and PCDFs tend to accumulate and persist in soils and sediments. For some compounds, significant

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differences have been found in isomer and groups patterns between known sources and environmental samples taken in the vicinity of these sources. For OCDF and heptachlorodibenzofurans (HpCDFs), several authors (1-5) have found surprisingly low environmental concentrations near to industrial sites from which these congeners were emitted. In general, background levels of these congeners found in air, water, sediments and in human tissues are lower than their corresponding dioxin congeners OCDD and heptachlorodibenzo-p-dioxins (HpCDDs) (6,7).

Two hypotheses can be put forward as possible explanations:

1   lower chemical stability of these congeners leading to environmental degradation and/or degradation during sample storage and analytical procedures;

2   particularly strong adsorption properties of OCDF and HpCDFs compared to their dioxin counterparts leading to low biological uptake and/or an analytical artefact due to low extraction efficiencies from environmental samples.

We have only examined chemical stability of OCDF compared to OCDD. Results concerning degradation of OCDF during analytical procedures have been presented elsewhere (8). These results showed that an analytical artefact could occur due to degradation of OCDF during Soxhlet extraction with toluene. To check whether OCDF is less stable than OCDD in the environment, we performed a comparative study of the photodegradation of these compounds under laboratory conditions. Photochemical reactions are considered to be suitable modelling reactions for other types of transformation routes and are said to be less complex to study. In this paper, two types of experiments were performed:

1 photolysis of OCDD and OCDF in the organic solvents methanol, hexane and 1,4-dioxane.

2 photolysis of OCDD and OCDF spiked onto alumina impregnated with copper (alumina/Cu) in the presence of sterilised distilled water and in the presence of sterilised natural water, to evaluate the potential influence of organic matter. An alumina/Cu matrix was used because this is a part of the catalyst applied in the production of 1,2-dichloroethane, a known source of OCDF (9).

Previous investigations have shown that OCDF and OCDD are photodegradable (10-20). In our experiments, a direct quantitative comparison between degradation rates of these compounds was performed. Furthermore, photolysis of OCDF and OCDD adsorbed onto a matrix in natural water adds a new aspect to the photodegradation studies of these compounds. This paper presents data indicating a significant difference in photochemical stability between OCDD and OCDF.

EXPERIMENTAL

Chemicals

Alumina, basic activity I, was purchased from Woelm.

Alumina impregnated with 62 g/kg copper; supplied by Solvay S.A., Brussels, Belgium, particle size 48 μm

Copper(II) nitrate, iron(III) nitrate, sodium bicarbonate, sodium sulphate anhydrous and pyridine were purchased from JT Baker.

p-Nitroacetophenone (PNAP) was purchased from Aldrich-Europe, art 61094. Purity 97%.

Distilled, sterilised water was purchased from Lamsberg; natural water was obtained from the "Municipal Water-Works Amsterdam" (MWA). The sample was taken on June 30, 1993 from lake Loenderveen. The water was characterised by MWA for the period 1 January - 30 June 1993: the organic carbon content was 6.1 mg/l, the chemical oxygen demand (COD) was 27 mg/l, the colour intensity Pt/Co scale: 10 mg/l and the UV extinction at 254 nm was 17.4 m^{-1}. Prior to use, the water was sterilised for 20 min at 120 ° C in an autoclave from Sanoclav.

Solvents

Acetic acid, acetonitrile, benzene and n-tetradecane were purchased from JT Baker and acetone, cyclohexane, dichloromethane, hexane, methanol, pentane and toluene were all nanograde quality from Mallinckrodt. 1,4-Dioxane (Lichrosolv) came from Merck.

Standards

OCDD, $^{13}C_{12}$-OCDD, OCDF, $^{13}C_{12}$-OCDF, tetra- to hepta-2378-congeners were purchased from Cambridge Isotope Laboratories. The purity of all standards was $\geq$ 98%.

$^{13}C_6$-1234-TeCDD was manufactured by the Department of Isotopic Analysis, Solvay Duphar at a purity of 98%.

UV Absorption Spectrophotometry

The absorption spectra of $^{13}C_{12}$-OCDD and OCDF in hexane and in methanol were obtained in a quartz cell with 1 cm optical pathlength (Hellma) using a double-beam spectrophotometer from Shimadzu (UV 2101 PC).

Laboratory photolysis equipment

For all laboratory photolysis experiments, an Original Hanau Suntest with Xenon lamp, type 7011 no. 0923 was used. The Xenon lamp has a spectrum comparable to sunlight (21). With this lamp, the samples were irradiated from above (surface light exposure). The photolysis tubes were made of borosilicate glass. Photolysis with solvents were performed at a surface temperature varying between 25-40 °C.

During photolysis with water, the temperature of water inside a photolysis tube was $47 \pm 2°$ C. This was continuously recorded with a thermocouple (Newport) for one tube.

Photolysis of OCDF and OCDD in organic solutions

Solutions of 60 ml, containing about 20 ng/ml $^{13}C_{12}$-OCDD and 20 ng/ml $^{12}C_{12}$-OCDF, were prepared in methanol, hexane or 1,4-dioxane and transferred into a photolysis tube, one tube per solvent.

About 60 ml actinometer solution of 0.011 mmol l^{-1} PNAP/0.1 mol l^{-1} pyridine was transferred into a photolysis tube. All tubes were placed at the same angle under the Xenon lamp. Samples from the methanol and 1,4-dioxane solutions were taken from the tubes after 0, 2, 4, 8, 16 and 136 minutes. Samples from the hexane solution were taken from the tube after 0, 8, 16, 32, 64 and 184 minutes. Samples were taken from the actinometer solution after 0 and 184 min. Actinometry was based on the methodology of Dulin and Mill (22) and Weerasinghe et al. (23).

A dark control was stored at 25 °C and the sample was taken after 184 min for each solvent and actinometer solution.

We calculated the quantum yields (moles degraded per einstein of light absorbed) for degradation of OCDF in hexane, 1,4-dioxane and methanol and the quantum yield for degradation of OCDD in hexane according to the method reported by Weerasinghe et al. (23). For all calculations concerning OCDF and OCDD we used the UV absorption data obtained with hexane. The rate constant for photolysis, K_{pa} , found for the actinometer was 0.0042 min^{-1}. The quantum yield of the actinometer which we used in our calculations (Φ_a = 0.00169 mol Einstein^{-1}) was adapted from Dulin and Mill (22).

Photolysis of OCDD and OCDF adsorbed onto alumina/Cu in the presence of water.

About 10 µg $^{12}C_{12}$-OCDD and 10 µg $^{12}C_{12}$-OCDF were dissolved in 5 ml dichloromethane and transferred to a slurry of 2.2 g alumina/Cu in pentane. The solvents were removed under reduced pressure at about 35 °C by rotary evaporation followed by air drying in the dark with an open stopcock for two days. It was then divided into 20 portions of 0.1 g which were transferred into photolysis tubes. To ten portions, 10 ml distilled water were

added; to the other ten portions, 10 ml natural water were added. The adsorbent was distributed as a film on the bottom of the tube. Ten sets of one natural water sample and one distilled sample were made. The two samples of each set were placed next to each other under the Xenon lamp together with one photolysis tube, filled with an actinometer solution of 0.011 mmol l^{-1} PNAP/0.01 mol l^{-1} pyridine. A set, consisting of one natural and one distilled water sample and a sample of the actinometer solution were taken at 0.5, 1, 3, 5, 7, 23, 28, 46 hours. The dark control samples were stored at 25 °C and samples were taken after 46 hours to determine the contents of OCDF and OCDD at time zero.

Analysis of PCDF and PCDD

Before the analytical procedure, all samples were enriched with internal standards. For the photolysis experiments with organic solutions, we used $^{13}C_{12}$-OCDF as internal standard for OCDF and HpCDF. $^{12}C_{12}$-OCDD was used as internal standard for $^{13}C_{12}$-HpCDD and $^{13}C_{12}$-OCDD (test compound). $^{13}C_6$-1,2,3,4 TeCDD was used as internal standard for tetra- to hexa-PCDF and PCDD.

The samples of the hexane solutions were concentrated to keeper volume (40 µl n-tetradecane) and analysed using GC-MS. The samples of 1,4-dioxane and methanol were mixed with 2% sodium bicarbonate in water and extracted with hexane. The hexane was passed through anhydrous sodium sulphate and concentrated to keeper volume (40 µl n-tetradecane) and analysed using GC-MS.

Except for $^{12}C_{12}$-OCDD, we used the same internal standards as described above for the photolysis of OCDF and OCDD on alumina/Cu in the presence of water. In this experiment, we used $^{12}C_{12}$-OCDD as test compound and $^{13}C_{12}$-OCDD as internal standard for HpCDD and OCDD.

The contents of the tubes were transferred by pouring, followed by rinsing with acetone onto a paper filter, which was placed directly on a separation funnel. The adsorbent was successively washed with 50 ml acetone and 100 ml dichloromethane. After liquid/liquid extraction with 100 ml 2 % sodium bicarbonate water solution, the lower layer was collected. The upper layer was successively extracted with 100 ml dichloromethane and 200 ml cyclohexane. All organic layers were collected through a filter filled with anhydrous sodium sulphate and concentrated to keeper volume (1 ml n-tetradecane) under reduced pressure using a rotary evaporator. This extract was subjected to a basic alumina clean up and concentrated to 40 µl n-tetradecane before analysis using GC-MS.

OCDD, OCDF and the photodegradation products formed by reductive dechlorination were measured using a GC-MS (HP 5890- HP 5970) from Hewlett Packard with a DB-5 CB column (df 0.25 µm, length 60 m, ID 0.25 mm). The samples were injected using a Programmable Temperature Vaporising (PTV) injector CIS 502 from Gerstel.

Quantification of the tetra- to octa chlorinated isomer groups was done by an internal standard procedure.
The concentrations of 2378-congeners were established using a DB-5 column. On this type of column not all 2378-congeners can be completely separated. Due to co-eluting isomers the actual concentrations of some 2378-congeners may be lower than apparent concentrations, which leads to a possible overestimation of Toxic Equivalence.

Analysis of actinometer

The actinometer (PNAP) was analysed using HPLC with a Zorbax ODS column, particle size 7.5 µm, length 250 mm, ID 4.6 mm. The mobile phase consisted of acetonitrile:water:acetic acid (35:64:1v/v). PNAP was detected at

280 nm using an UV detector (Kratos Spectroflow 757). 100 µl of the solution was injected using an auto sampler. Quantification was established using an external standard method based on duplicate injections.

RESULTS AND DISCUSSION.

UV Absorption spectra.

We measured the absorption spectra of the test compounds in methanol and hexane to check whether these solvents had an influence on the molar extinction coefficients and, thus, on the degradation rate.

The spectral data in Figures 1 and 2 clearly show that OCDF in contrast to OCDD has distinct absorption bands in the sunlight range from 290 nm and higher wavelengths.
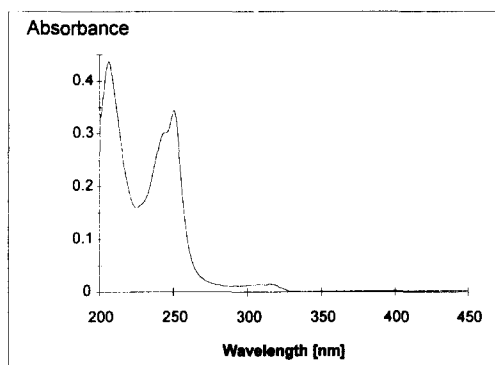

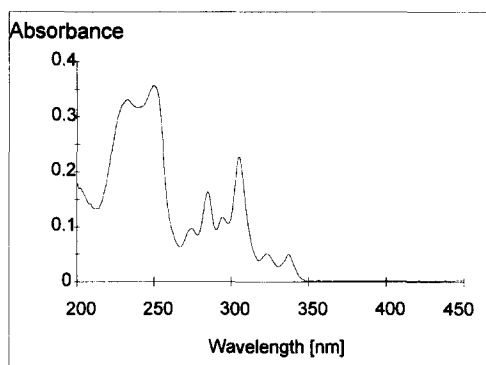**Figure 1**: Absorption spectrum of 7.31x 10^{-3} mmol/l $^{13}C_{12}$-OCDD in hexane

Figure 2: Absorption spectrum of 8.11x10^{-3} mmol/l OCDF in hexane

Below 280 nm, different molar extinction coefficients were found between OCDD in methanol and in hexane. However, there was no difference in the position of the wavelength bands and their relative intensities. The lower extinction coefficients in methanol were not due to peak broadening.

Some selected wavelengths above 280 nm with corresponding molar extinction coefficients are shown in Table 1. In this Table these data are compared with literature data. The difference between the experimental data of OCDD and the data of Choudhry and Webster (19) might be due to the low signal/noise ratio in this wavelength region.

Table 1: Selected maxima λ [nm] with corresponding molar extinction coefficients $\varepsilon[10^3 \times 1 \, mol^{-1} \, cm^{-1}]$ of experimental data of OCDD and OCDF in different organic solutions .

OCDD						OCDF					
Solvent	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	Solvent	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3

Solvent	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3	Solvent	λ_1	ε_1	λ_2	ε_2	λ_3	ε_3
Hexane	297.5	1.6	305	1.8	337	0.14	Hexane	297.5	12	305	27	337	5.4
Methanol	297.5	2.0	305	2.0	337	0.81	Methanol	297.5	12	305	23	337	5.2
Acetonitrile[1]	297.5	5.3	305	4.7	337	0.48	Toluene[2]	288.6	18	309	30	339	6.7

[1] Data of OCDD in acetonitrile taken from Choudhry and Webster (19).
[2] Data of OCDF in toluene taken from Tysklind et al (24).

Photolysis experiments of OCDD and OCDF with solvents

The solvent plays a role in the kinetics of photodegradation of PCDDs and PCDFs. Figures 3 to 5 show typical first-order reaction kinetics for OCDF in all solvents and for OCDD in hexane. The quantum yields and half-lives are shown in Table 2.

Table 2: Quantum yields and half-lives of OCDF and $^{13}C_{12}$-OCDD in three organic solvents.

Solvent	$^{13}C_{12}$-OCDD		OCDF	
	Half-life [min]	Quantum yield [mol Einstein^{-1}]	Half-life [min]	Quantum yield [mol Einstein^{-1}]
hexane	73.8	14.9E-04	30.7	5.15E-04
1,4-dioxane	n.o.	n.o.	8.4	1.89E-03
methanol	n.o.	n.o.	5.5	2.85E-03

n.o. = not observed in studied time interval of 136 min
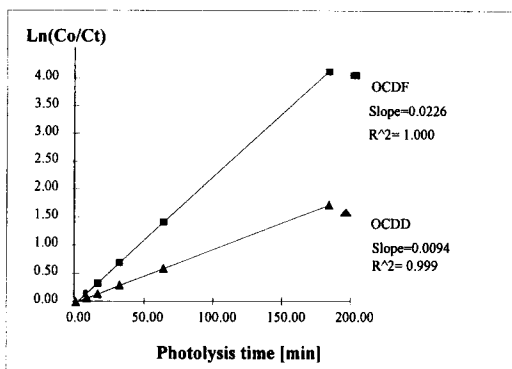
Figure 3: First-order kinetics plots of photolysis data of OCDF and $^{13}C_{12}$-OCDD in hexane.
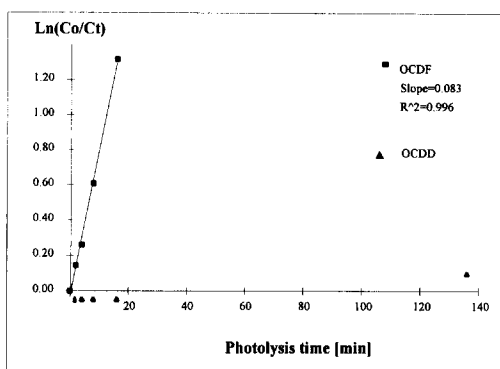
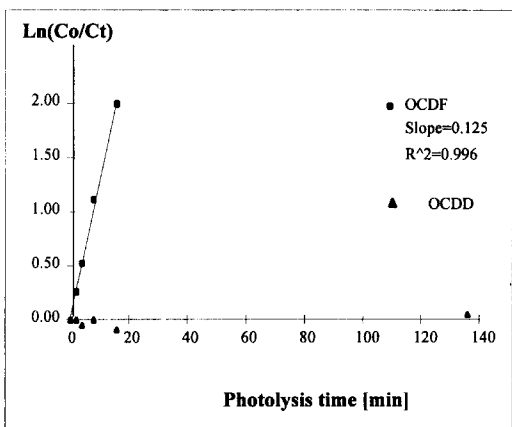**Figure 4**: First-order kinetics plots of photolysis data of OCDF and $^{13}C_{12}$-OCDD in 1,4-dioxane.

Figure 5: First-order kinetics plots of photolysis data of OCDF and $^{13}C_{12}$-OCDD in methanol.

Photolysis of OCDD in hexane was much faster than in 1,4-dioxane or methanol. Considering the fact that the molar extinction coefficients (from 290 nm and higher wavelengths) of OCDD in methanol were about the same as those in hexane (see Table 1), we expected some degradation of OCDD in methanol or in 1,4-dioxane at these time intervals. These latter solvents decreased the degradation kinetics for OCDD by an unknown mechanism. The quantum yield of OCDD (see Table 2) in hexane is in reasonable agreement with the quantum yields reported by Hung and Ingram (20), which is 12.6E-04 mol Einstein^{-1}.

OCDF degraded fastest in methanol, which is in agreement with the results of Hutzinger and Safe (13).

The photolysis of OCDF in methanol was about 1.5 times and 5 times more efficient than in 1,4-dioxane or hexane, respectively. The degradation kinetics for OCDD and OCDF strongly depended on the type of solvent used; OCDF was more sensitive for photodegradation than OCDD in these organic solvents.

We determined the photodegradation products formed via reductive dechlorination (see Table 3 and Figures 6 to 8). Congeners and groups not shown in Table 3 and Figures 6 to 8 were below the limit of quantification (0.03 ng/ml).

Table 3: Contents (ng/ml) of 2378-congeners of PCDFs and PCDDs in dark control, samples taken after last irradiation of OCDF and $^{13}C_{12}$-OCDD in hexane, 1,4-dioxane or methanol.

SOLVENTS	*HEXANE*		*1,4-DIOXANE*		*METHANOL*	
Photolysis time [min]	**dark**	**184**	**dark**	**136**	**dark**	**136**
1234678-HpCDD	0.24[1]	0.64	0.26[1]	0.29	0.23[1]	0.25
OCDD	22	4.0	22	19	21	20
23478/12369/12489/12679-PnCDF	< 0.02	0.07	< 0.03	0.03	< 0.03	0.18
123478/123467-HxCDF	< 0.02	0.05	< 0.03	< 0.03	< 0.03	< 0.03
123678/123479-HxCDF	< 0.02	0.26	< 0.03	< 0.03	< 0.03	0.17
234678/123689-HxCDF	< 0.02	0.82	< 0.03	< 0.03	< 0.03	1.5
123789/123489-HxCDF	< 0.02	< 0.02	< 0.03	< 0.03	< 0.03	< 0.03
1234678-HpCDF	0.03[1]	1.3	0.04[1]	< 0.03	0.03[1]	0.18
1234789-HpCDF	< 0.02	< 0.02	< 0.03	< 0.03	< 0.03	< 0.03
OCDF	22	0.37	23	< 0.03	22	< 0.03
TE (NATO/CCMS)	0.047	0.17	0.048	0.037	0.046	0.28

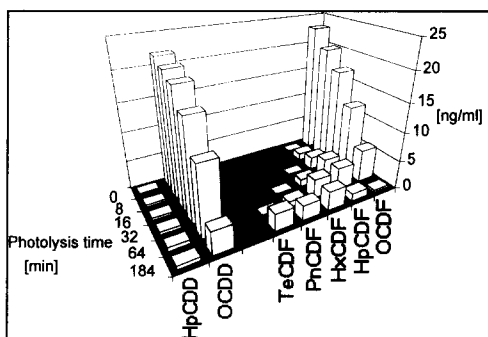1) These levels reflect background of HpCDD and HpCDF in standards used for test solutions.

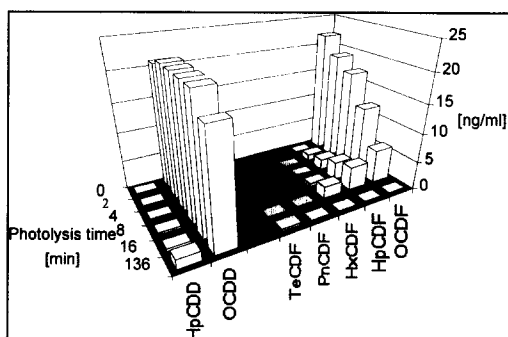**Figure 6**: Group profiles of photolysis products of OCDF and $^{13}C_{12}$-OCDD in hexane.

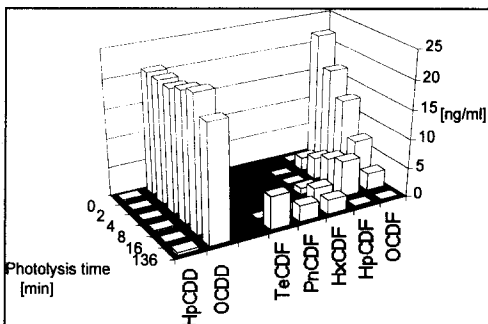**Figure 7**: Group profiles of photolysis products of OCDF and $^{13}C_{12}$-OCDD in 1,4-dioxane.

Figure 8: Group profiles of photolysis products of OCDF and $^{13}C_{12}$-OCDD in methanol

Less than 5 % of the OCDD which was degraded, was lost by reductive dechlorination in hexane after 136 min irradiation. This result is in agreement with those reported by Dobbs and Grant (15). The preferential loss of the lateral chlorine positions observed for OCDD is in agreement with the results of photolysis of OCDD in hexane:benzene (95:5 v/v) reported by Buser (14).

At about the half-life of OCDF, 35-50% of the loss of OCDF had degraded via reductive dechlorination. Preferential loss of the chlorine atoms at the 1 or 9 positions occurred, which resulted in formation of 1234678-HpCDF, as also found by Buser (14). Furthermore, the chromatograms showed that the same congeners were formed in hexane, 1,4-dioxane or methanol.

In conclusion, reductive dechlorination is partly an explanation for the loss of OCDF and especially for the loss of OCDD in hexane. Other degradation pathways may also be involved (e.g., furan ring cleavage) but, these were not investigated in this study.

Photolysis of OCDD and OCDF adsorbed onto alumina/Cu in the presence of natural water and in the presence of distilled water.

Initial experiments demonstrated that no hydrolysis of OCDF or OCDD occurred in distilled water under the conditions: pH 3.6 at 50°C and in the presence of Fe(III) and Cu(II) ions.

The results of photolysis in water show a larger variation than the results of photolysis in solvents. More parameters may have influenced the results, for instance:

- Heterogeneity of the intensity of the Xenon lamp:

  The samples were divided over more photolysis tubes (ten tubes compared to one used for the experiments with organic solvents) which were all placed at different positions under the Xenon lamp. Heterogeneity of light exposure as a partial explanation for the less consistent results is confirmed by the results obtained for the sample sets consisting of one natural and one distilled water sample. Figure 9 shows a correlation between the results of distilled water and natural water.

- Total variance due to spiking of the adsorbent and the more complicated analytical procedure is larger compared to photolysis in the organic solvents.

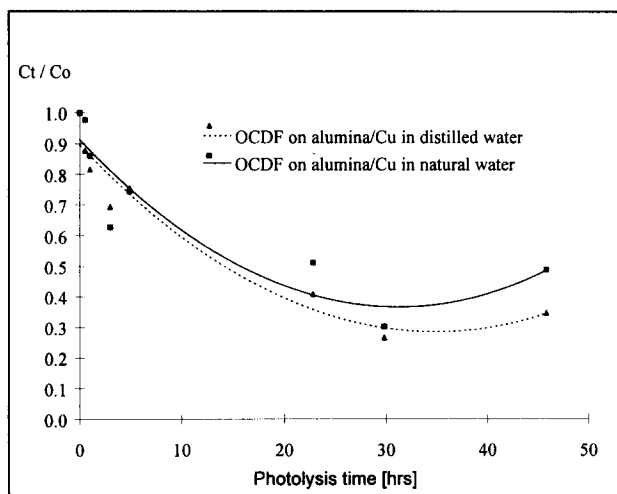- Low solubility of OCDD and OCDF in water.

Figure 9: Photolytic degradation plot of OCDF adsorbed on 0.1 g alumina/Cu in presence of distilled water and in presence of natural water.

We found significant loss for OCDF in the studied time interval (Figures 9 and 10). The half-life of OCDF was about 24 hours; no significant difference was observed between distilled and natural water. The very low solubilty of OCDF in water is a possible explanation. The copper was probably a limiting factor also, because alumina/Cu, when brought into water, resulted in a solution which absorbed light in the range 300 nm to 400 nm. It cannot be excluded that copper may also have acted as a catalyst (25). However, this cannot be conclusively proved from these experiments. Photolysis of OCDF under environmentally relevant aquatic conditions is much slower than in hexane, 1,4-dioxane or methanol.

We did not observe significant loss of OCDD, due to the large variation in the results of the experimental method. From minor formation of HpCDDs, we conclude that some photolysis had occurred. 1234678-HpCDD and 1234679-HpCDD were both formed in the ratio of about 1:1. This dechlorination route was also observed for photolysis of OCDD adsorbed on soil (17). This is in contrast with the photolysis of OCDD in hexane, in which preferential dechlorination of the lateral chlorine atoms was found, resulting mainly in 1234679-HpCDD.

The contents of 2378-congeners and groups of some representative samples are shown in Table 4 and in Figure 10. Congeners and groups not shown were below the limit of quantification (3 ng/g).

Table 4: Contents (ng/g) of 2378-congeners at time zero and for sample taken after 29.8 hour irradiation[1] of OCDF.

TYPE OF WATER	DISTILLED		NATURAL	
Photolysis time [hrs]	0	29.8	0	29.8
1234678-HpCDD	3.3[2]	58	3.9[2]	64
OCDD	4800	4900	4400	4200
123478/123467-HxCDF	< 3	6.8	3	6.7
123678/123479-HxCDF	< 3	8.4	3	8.9
234678/123689-HxCDF	< 3	23	3	20
123789/123489-HxCDF	< 3	< 4	3	4
1234678-HpCDF	19[2]	670	21[2]	550
1234789-HpCDF	6.0[2]	< 4	5.3[2]	4
OCDF	4900	1200	4300	1300
TE (NATO/CCMS)	10	17	9	15

1) At this time, about 70- 75 % of OCDF had disappeared
2) These levels reflect background of HpCDD and HpCDF in standards used for test solutions

After 29.8 hours, about 30 % of the total loss of OCDF (see Figure 10) resulted from reductive dechlorination. Preferential loss of the chlorine atoms at the 1 or 9 positions was observed. However, other HpCDF isomers were also found. A significant amount of 1234689-HpCDF was also found in contrast with photolysis in the studied organic solvents. Although the lower 2378-chlorinated congeners have Toxic Equivalence factors at least 10 times higher than OCDD and OCDF, the Toxicity Equivalence (TE-NATO/CCMS) increased less than a factor of 2 after photolysis. The results suggest other mechanisms of degradation than reductive dechlorination may have been taken place.
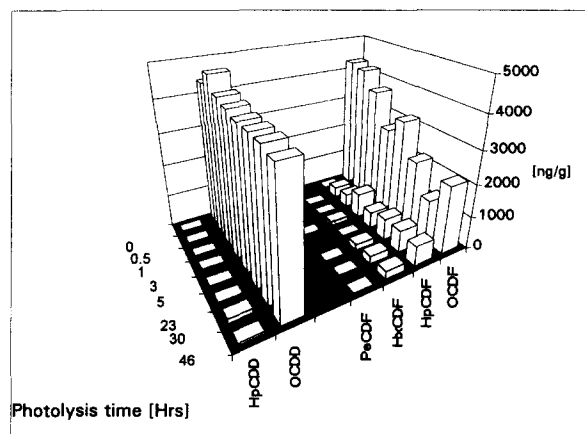

Figure 10: group profiles for photolysis products of OCDD and OCDF on alumina/Cu in the presence of 10 ml sterilised natural water. This group profile is also representative for distilled water sample.

CONCLUSIONS

The experiments performed under various conditions including in sterilised natural water at about 47 °C, showed that OCDF was photochemically less stable than OCDD. This may be an indication that OCDF is less chemically stable than OCDD under environmental conditions.

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