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Chapter 15

SORPTION/DESORPTION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZO FURANS (PCDDs/PCDFs) IN THE PRESENCE OF CYCLODEXTRINS

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Abstract: The goal of this study was to investigate the usefulness of cyclodextrins (CDs) for the removal of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDDs/PCDFs) in soil and water. Five CDs having different molecular cavities and active functional groups were selected and evaluated for their ability to include (trap) PCDDs/PCDFs in soil and water. For the soil experiments, CDs were added to the soil on day one and the concentrations of unbound PCDDs/PCDFs were monitored over a 28-day period. Parallel control experiments were conducted to assist in the process performance evaluation. The ability of CDs to remove PCDDs/PCDFs from the contaminated soil was dependent upon the type of CD used and constituents of PCDDs/PCDFs. Among the five CDs investigated, hydroxypropyl- β -cyclodextrin (HPBCD) gave the highest removal efficiency for all components of PCDDs/PCDFs. The removal efficiency of total PCDDs/PCDFs was 81% one day after application of CDs and then increased to 96% after 28 days. The α -cyclodextrin (ACD) and β -cyclodextrin (BCD) removed only 45% and 50% of the total PCDDs/PCDFs after 28 days, respectively, whereas hydroxypropyl- γ -cyclodextrin (HPGCD) removed 80% of the total PCDDs/PCDFs.

Key words: PCDDs/PCDFs; Cyclodextrins; Inclusion; Removal; GC-ECD; Soil

1. INTRODUCTION

Polychlorinated dibenzo-p-dioxins and polychlorinated dibenzo furans (PCDDs/PCDFs) are persistent organic pollutants and have been determined to be toxic by many government agencies. PCDDs and PCDFs are formed as by-products from various combustion and chemical processes. They are produced during incomplete combustion of chlorine containing wastes like municipal solid waste, sewage sludge, and hospital and hazardous wastes and can become soil and water pollutants.

There are methods to remediate PCDDs/PCDFs including phytoremediation and thermal treatment (Kasai et al., 2000; Campanella et al., 2002; Kluyev et al., 2002). One of the technical challenges faced when remediating soil and sediments is the difficulty of leaching the sorbed (i.e. bound) PCDDs/PCDFs from the soil particles into the flushing medium. PCDDs/PCDFs, like other organic contaminants, tend to partition (sorb) onto suspended solid particles through various physico-chemical forces. Yoshii et al (2001) reported the high affinity of PCDDs/PCDFs with soil and the difficulty of the effective removal of the pollutants from the soil matrix. They used biphenyls to demonstrate the usefulness of cyclodextrins (CDs) to enhance the solubility of hydrophobic chemicals in the environment. Narita et al (2000) studied fluorescent molecular sensing for endocrine-disrupting chemicals (including PCDDs/PCDFs) and their analogs using regio-selective dansyl-tosyl-modified β -cyclodextrin (BCD) and γ -cyclodextrin (GCD) and found that these host compounds showed pure monomer fluorescence at 526 nm; the intensities of the guest-induced fluorescence either increased or decreased depending on PCDD/PCDF analogs. Otsuka et al (1999) carried out an on-line concentration of neutral analytes for CD assisted micellar electrokinetic chromatography (MEKC) in environmental analysis to enhance the UV detection sensitivity using several PCDD/PCDF compounds and found that the detection sensitivity increased 200 times.

PCDDs/PCDFs are hydrophobic and trapping them in the cavities of water soluble CDs may assist the desorption of these compounds from within the structure of the solid particle into the surrounding medium. The overall objective of this project was to investigate the efficacy of different CDs as enhancers for the outward diffusion of PCDDs/PCDFs from contaminated soil and sediments. Five CDs were selected for this study: (1) α -cyclodextrin (ACD), (2) β -cyclodextrin (BCD), (3) hydroxypropyl- α -cyclodextrin (HPACD), (4) hydroxypropyl- β -cyclodextrin (HPBCD), and (5) hydroxypropyl- γ -cyclodextrin (HPGCD). The diameter of the molecular cavity and presence of active functional groups were taken into account in the selection of these CDs. The PCDDs/PCDFs were brought into contact with CDs in soil and water and the free (unbound) PCDDs/PCDFs were

determined over time using gas chromatography – electron capture detector (GC-ECD).

2. APPROACH

The approach used in this study involved contacting CDs with PCDDs/PCDFs in aqueous medium and analysis of the unbound PCDDs/PCDFs using GC-ECD. Four essential steps were performed for the assessment of the process: a) mixing the PCDD/PCDF-contaminated soil with CDs, b) centrifuging the supernatant of the CD treated soil slurry to separate the liquid phase for analysis, c) extracting the sample with the organic solvent, and d) injecting the sample extract into the GC-ECD.

The GC-ECD measurements are used for investigation of the CDs capability to enhance desorption of PCDDs/PCDFs from the soil as well as for determination of the inclusion efficiency. The mixing step ensures that these pollutants are given enough contact time with CDs, whereas, the centrifugation is required to separate the liquid phase from the suspended solid particles and both of mixing and centrifugation should have no effect on the GC-ECD response. The extraction step provides important information on the inclusion as well as surface sorption since the included PCDDs/PCDFs may differ appreciably from that of the free PCDDs/PCDFs in terms of partitioning or diffusion from the water to the organic solvent.

The introduction of PCDDs/PCDFs in the hot injection chamber of the GC-ECD is interesting because the physico-chemical processes involved play a significant role in producing the signal profile. The fundamental processes that occur when the sample is injected include: (1) vaporization at 280°C inside the injector chamber, (2) purging the analyte vapour by the carrier gas to the GC column for separation, (3) detection with ECD, and (4) recording the signal.

The production of the GC-ECD signal of the free PCDDs/PCDFs is straightforward. The elevated temperature of the injection port causes the sample extract to vaporize (at least some of it). The vapour of the free PCDDs/PCDFs is carried out to the GC column where they are separated according to their physico-chemical properties and detected as they enter the ECD module. Regarding the bound PCDD/PCDF compounds, there are three scenarios as to what will happen when these compounds are deposited inside the hot injection port. These scenarios can be used as guidance for interpretation of the GC-ECD response to PCDD/PCDF-CD compounds, as follows:

Case I. The PCDDs/PCDFs-CD compounds vaporize and the vapor is carried out to the GC column. In this case, the included compounds may separate into peaks or overlap with the free PCDD/PCDF compounds. The

overlap of the included PCDDs/PCDFS with the free PCDDs/PCDFs may result in enhancement or depression of the ECD signal.

Case II. The PCDD/PCDF-CD compounds dissociate into PCDDs/PCDFs and CDs causing no discrimination between the free PCDDs/PCDFs and the included compounds. The decomposition of the included compounds into free PCDDs/PCDFs results in no distinction between the bound and free PCDD/PCDF compounds. The signal of the CD treated sample, as well as, the untreated sample will be identical providing no further information about the inclusion even if it happens. In this case, another chemical identification technique would be necessary.

Case III. The PCDD/PCDF-CD compounds deposit onto the inner surface of the injector liner, hence escape detection by the ECD module. This case entails that these compounds are thermally stable and non-volatile inside the injection port. The sample residue is not evaporated and the included compounds simply deposit on the inner surface of the injection port. This may result in loss of the ECD's response to PCDDs/PCDFs, which can be interpreted as a sign of inclusion with CDs.

3. MATERIALS AND METHODS

Three sets of experiments were designed to investigate the usefulness of CDs as enhancers for desorption of PCDDs/PCDFs from contaminated soil. First, CDs were added to the PCDD/PCDF-contaminated soil to bring the sorbed PCDDs/PCDFs from the soil matrix to the surrounding medium. Second, the PCDDs/PCDFs and CDs were added simultaneously to the clean soil of the same matrix to investigate the surface deposition onto soil particles in the presence of CDs. Third, inclusion of PCDDs/PCDFs was performed in water without the soil. Control experiments were run parallel to the test experiments for comparison.

3.1 Chemicals and Solvents

The CDs (ACD, BCD, HPACD, HPBCD and HPGCD) were obtained from Sigma-Aldrich Canada. The isooctane and dichloromethane were distilled in glass, purchased from Caledon Laboratories. Some of the PCDDs/PCDFs (OCDD, OCDF and 1,2,3,4-TCDD) were obtained from the Analysis and Air Quality Division of Environment Canada's Environmental Technology Centre. Reference standard solutions of PCDDs/PCDFs were acquired from Wellington Laboratories.

3.2 Stock Solution of PCDDs/PCDFs for Spiking the Soil

The stock solution of PCDDs/PCDFs was prepared in a 500 mL round bottom flask. The residue of solvents was evaporated to dryness using a rotary evaporator at 60 °C. Then, 100 mL of water was added to the flask and heated in a water bath at 60°C for 1 hour until most of the PCDDs/PCDFs dissolved. The hot solution was transferred to a 1 L volumetric flask and the volume was completed to the mark with water. The solution was left in the fumehood overnight prior to testing. Table 1 shows PCDD/PCDF components and concentrations of the stock solution used for spiking the soil.

Table 1. PCDD/PCDF solution used for spiking the soil

Component	Concentration (ppm)
1,2,3-TCDD	1.80×10^{-1}
1,2,3,4-TCDD	2.96×10^{-2}
2,3,7,8-TCDD	2.58×10^{-4}
1,2,3,6,7,8-HxCDD	5.44×10^{-4}
1,2,3,7,8,9-HxCDD	1.76×10^{-5}
OCDD	3.12×10^{-2}
OCDD	5.26×10^{-2}

3.3 Preparation of the PCDD/PCDF-Contaminated Soil

The soil used was from a heavy-metal contaminated site in Eastern Canada. It was homogenized and air-dried in the fumehood, then sieved to remove particles greater than 2 mm. About 250 g of the soil was slurried with PCDD/PCDF solution using a mechanical mixer (Kitchen Aid model 4K45SSWH) and placed in the fumehood for two weeks where it was air-dried to be used for the desorption testing, with and without CDs. The other part of the soil, which contained no PCDDs/PCDFs, was set aside for the sorption experiments, also with and without CDs.

3.4 Desorption of PCDDs/PCDFs from the Spiked Soil

Five CDs (ABD, BCD, HPACD, HPBCD and HPGCD) were used as enhancers for desorption of PCDDs/PCDFs from the soil to the surrounding aqueous medium. Table 2 details reagents and amounts of soil used. Three sets of reaction vessels were prepared: Set one involved the inclusion of PCDDs/PCDFs with CDs in water, without the soil; Set two was designed for deposition of PCDDs/PCDFs onto the clean soil in presence of CDs, i.e., both CDs and PCDDs/PCDFs were in water added to the non-contaminated soil matrix; and Set three was conducted to leach PCDDs/PCDFs from the

spiked soil, which was aged for two weeks. Samples were taken on days 1, 5, 8 and 28 for analysis using GC-ECD.

Table 2. Reagents and amounts of soil used

No	Sample ID	Water mL	Soil g	Stk, mL	ACD, g	BCD, g	HPACD, g	HPBCD, g	HPGCD, g
<u>Inclusion testing in water</u>									
1	WI-1	-	-	50	-	-	-	-	-
2	WI-2	-	-	50	1	-	-	-	-
3	WI-3	-	-	50	-	1	-	-	-
4	WI-4	-	-	50	-	-	1	-	-
5	WI-5	-	-	50	-	-	-	1	-
6	WI-6	-	-	50	-	-	-	-	1
<u>Sorption testing (clean soil)</u>									
1	ST-1	-	10	50	-	-	-	-	-
2	ST-2	-	10	50	1	-	-	-	-
3	ST-3	-	10	50	-	1	-	-	-
4	ST-4	-	10	50	-	-	1	-	-
5	ST-5	-	10	50	-	-	-	1	-
6	ST-6	-	10	50	-	-	-	-	1
<u>Desorption testing (spiked and aged soil)</u>									
1	DT-1	50	10	-	-	-	-	-	-
2	DT-2	50	10	-	1	-	-	-	-
3	DT-3	50	10	-	-	1	-	-	-
4	DT-4	50	10	-	-	-	1	-	-
5	DT-5	50	10	-	-	-	-	1	-
6	DT-6	50	10	-	-	-	-	-	1

Stk = stock solution of PCDDs/PCDFs

For each set of experiments, a control experiment was used. The control experiments contained all test reagents, but had no CDs. The response of GC-ECD to PCDDs/PCDFs in each vessel was documented over time.

3.5 GC-ECD Analysis

3.5.1 Calibration of GC-ECD

The calibration standard solution of PCDDs/PCDFs was prepared from reference solutions provided by Wellington Laboratories, shown in Table 3. The Gas Chromatograph used was HP 5800, Series II, equipped with electron capture detector (ECD) and HP Chemstation, both manufactured by Hewlett Packard Canada. The analytical setup of the system was as follows: The column was DB5-MS, 0.25 mm ID $\times$ 0.25 μ m $\times$ 30 m. The temperature program: initial column temperature was 90°C held for 2 minutes, ramped to

200°C at 3.5°C /minute, then to 280°C at 2.5°C/minute; and then to 300°C at 20°C/minute, held for 5 minutes. The injection volume was 5 µL.

Table 3. Reference standard solution of PCDDs/PCDFs used to calibrate the GC-ECD

Compound	ppm
1,2,3-TCDD	0.0015
1,2,3,4-TCDD	0.1
2,3,7,8-TCDD	0.5
1,2,3,6,7,8-HxCDD	1.1
1,2,3,7,8,9-HxCDD	0.1
OCDD	2.2
OCDD	2.0

3.5.2 Analysis of the Sample

The water sample was withdrawn of the supernatant of the test vessel using a syringe and transferred into a test tube. It was centrifuged for 1 hour and the supernatant was extracted with isooctane and injected to the GC-ECD. Samples were taken immediately after contacting CDs with PCDDs/PCDFs in the reaction vessel. The steps are summarized as follows: Using a syringe, a 7 mL water sample was withdrawn from the supernatant of the sample of the reaction vessel into a test tube and was centrifuged for 1 hour to ensure that fine soil particles were separated from the water sample. Then, 5 mL of the water was withdrawn from the centrifuged sample with an Eppendorff pipette into another test tube. The sample was extracted with 1 mL of isooctane by vortex for 10 seconds and then was left for 10 minutes to allow phase separation. The sample extract was taken out of the test tube using a Pasteur pipette, placed into a GC vial and injected into the GC-ECD.

4. RESULTS AND DISCUSSION

4.1 Desorption of PCDDs/PCDFs from the Spiked Soil

Table 4 summarizes the efficiency of desorption of PCDDs/PCDFs from the soil into the surrounding medium calculated over a period of 28 days from the time of inoculation with CDs. Eq.1 was used to calculate the percentage removal efficiency using CDs relative to that of the control experiment, without CDs.

$$\%D_{Soil} = \frac{C_{CD} - C_{RS}}{C_{CD}} \times 100 \quad (1)$$

Where,

$\%D_{Soil}$ = percentage of PCDDs/PCDFs removed from the contaminated soil using CDs relative to the control experiment without CDs.

C_{CD} = concentration of PCDDs/PCDFs in aqueous phase surrounding the CD-treated soil

C_{RS} = concentration of PCDDs/PCDFs in aqueous phase surrounding the control experiment

Initially, the desorption efficiencies of total PCDDs/PCDFs were almost nil for ACD and BCD, 16% for HPACD, 81% for HPBCD and 57% with HPGCD. On day 28 (end of testing), the removal efficiencies improved appreciably reaching 45%, 50%, 73%, 96% and 80% using ACD, BCD, HPACD, HPBCD and HPGCD, respectively. The effect of size of molecular cavity of the host molecule is evident in the inclusion efficiency obtained by these GC-ECD measurements. For the case of ACD and BCD the inclusion of total PCDDs/PCDFs increased only slightly (from 45% to 50%). The difference in the capability of CDs is noticeable using HPACD, HPBCD and HPGCD. The removal efficiency increased from 73% for HPACD to 96% for HPBCD and then decreased to 80% using HPGCD. Note that the existence of an active functional group to dissolve PCDDs/PCDFs into the surrounding medium is not enough for leaching these pollutants from the soil. In fact, it appears that the size of the cavity plays an important role in the desorption processes as demonstrated by the substantial difference in the removal efficiencies of HPACD, HPBCD and HPGCD, which have the same functional group ($-CHCH_2OH$), but different cavity sizes.

Not only the size of the molecular cavity of the host plays a role in the inclusion but that of the guest molecule is important as well. The contact time between the guest and host was found to be vital for the inclusion. A close look at the data in Table 4 it can be discerned that the PCDD/PCDF congeners had different affinities toward the same host. The inclusion improved over time suggesting that the inclusion process was not fast under experimental conditions. It was observed that at over a longer period of time some of the congeners had disappeared from the aqueous medium possibly because of surface deposition on the inner surface of the reaction vessel.

Table 4. Removal efficiencies of selected PCDDs/PCDFs from soil with different CDs over a period of 28 days

Day	Congener	$\%D_{Soil}$				
		ACD	BCD	HPACD	HPBCD	HPGCD
1	1,2,3-TCDD	-	-	17±3	82±9	58±13
	1,2,3,4-TCDD	-	-	-	66±6	55±8
	2,3,7,8-TCDD	-	-	-	-	-
	OCDD	-	51±5	83±9	10±4	31±7

	OCDF	-	-	44±3	37±7	45±5
	Total	-	-	16±	81±	57±
5	1,2,3 -TCDD	27±7	51±9	71±10	93±12	93±9
	1,2,3,4 -TCDD	-	50±6	82±8	91±9	92±7
	2,3,7,8 -TCDD	-	-	-	-	-
	OCDD	100±10	-	-	-	-
	OCDF	100±8	-	100±12	-	-
	Total	26±6	50±4	70±8	92±11	93±9
8	1,2,3 -TCDD	36±6	60±8	70±10	95±9	84±8
	1,2,3,4 -TCDD	49±8	59±4	65±5	94±6	90±9
	OCDD	-	-	-	-	-
	OCDF	-	-	-	100±9	100±13
	Total	25±5	53±4	64±7	94±8	81±6
28	1,2,3 -TCDD	45±8	51±5	73±8	96±12	80±9
	1,2,3,4 -TCDD	63±9	50±7	71±6	95±10	87±5
	2,3,7,8 -TCDD	-	-	-	69±6	-
	OCDD	-	-	-	-	-
	OCDF	-	-	-	-	-
	Total	45±5	50±3	73±8	96±12	80±10

“-“ indicates no removal

The behavior of the 2,3,7,8-TCDD was different. This congener did not show an appreciable affinity toward CDs investigated. Only at day 28, this congener demonstrated an inclusion efficiency of 69% with HPBCD. Other congeners did not show inclusion efficiencies and were excluded from data in Table 4. In some instances, these compounds caused either enhancement in the GC-ECD response or could not be detected at all. It is conceivable that these CD-included congeners were extracted into the organic solvent and interfered with that of the free congeners. This interference did not permit calculation of the inclusion efficiency but it could be used to indicate that a kind of interaction between the CDs and the PCDD/PCDF congener present.

Fig.1 depicts the GC-ECD response to the presence of total PCDDs/PCDFs leached from the contaminated soil to the surrounding water, normalized to the control test (i.e. all data points were divided by the highest value of the control). For illustration, the data were plotted in reverse order. The data of day 1 was obtained after one day of CD application; the other data were acquired on days 5, 8 and 28. As can be seen, HPBCD performed very well in leaching PCDDs/PCDFs from the contaminated soil relative to other CDs, reaching a maximum after 28 days. Note that in day 1, the GC-ECD response was higher compared to other sampled days, which is attributed to the presence of CDs causing signal enhancement. The HPGCD did not perform well in day 1 and then leveled off at day 8. This may be attributed to the stability of the PCDDs/PCDFs-HPGCD complex. The other three CDs showed some enhancement, but were not considered significant when compared to the HPBCD.

Figure 1. Desorption of total PCDDs/PCDFs from the contaminated soil with various CDs over a period of 28 days. The GC-ECD response is normalized to the control experiment "RS", which is contaminated soil slurried with water, without CDs.

It was observed that the GC-ECD response to 2,3,7,8-TCDD leached out from the soil using five different CDs, which is interesting because within HPBCD the behaviour of this congener was very different from the other congeners. It was detected initially in all tests except that of HPBCD, which did not show any appreciable removal until day 28 (end of testing). Other CDs did not show important leaching relative to the control experiment. This congener is the most toxic of the PCDD/PCDF compounds. So this result warrants further investigations. Fig.2 depicts chromatograms obtained using GC-ECD for the total PCDDs/PCDFs leached from the contaminated soil after 28 days, with and without HPBCD. As can be seen, HPBCD caused a significant enhancement in the removal of these pollutants from the soil matrix to the surrounding medium. Of the seven congeners of PCDDs/PCDFs investigated, 1,2,3-TCDD gave the highest GC-ECD response upon inoculation with HPBCD. Notice that OCDD and OCDF disappeared completely from the control and test experiments. This can be interpreted in terms of re-deposition onto soil and vessel surface because the

tests were in batch experiment (i.e., the leachate was in contact with the matrix through the duration of testing).

Figure 2. Typical GC-ECD chromatogram for desorption of PCDDs/PCDFs from HPBCD treated soil into the surrounding aqueous medium, after 28 days; 96% removal was obtained.

A = control (contaminated soil + water, no HPBCD) and B = HPBCD-treated soil.

Fig.3 delineates the concentration of 1,2,3,4-TCDD desorbed from the contaminated soil to the surrounding water medium under the influence of five CDs. In these experiments, the PCDD/PCDF-contaminated soil was treated with different CDs and the monitoring of PCDDs/PCDFs leached from the soil into the aqueous medium commenced immediately. The control experiment was the same contaminated soil matrix without CDs. Initially, the rate of desorption was high and then levelled off after 5 days demonstrating a typical first order reaction. In all cases, the levels of the leached PCDDs/PCDFs were dependent on the type of CDs added to the soil. Among the five CDs investigated, HPBCD was the most effective in dislodging the contaminants from the soil matrix, as illustrated by the prominent level of HPBCD relative to others. The PCDDs/PCDFs detected at the start of testing were from the labile type of PCDDs/PCDFs loosely attached to the surfaces of the soil particles. The HPGCD was also effective in desorption of target contaminants from the soil. It should be mentioned that HPBCD and HPGCD are very similar with only one difference, the size of the cavity. HPGCD has an extra glucose molecule. One may interpret the difference between the desorption capacities of these two CDs in terms of fitting the PCDD/PCDF molecule inside the CD molecular cavity. The best fit will result in more PCDDs/PCDFs pulled out of the soil into the aqueous medium where the CD is present. The reason for choosing CDs with hydroxyl groups was to render these extremely insoluble PCDDs/PCDFs into water-soluble substances so that they could be leached out of the soil. The CDs with hydroxyl groups appeared to be those that could include

PCDDs/PCDFs and render them into water soluble compounds. This proved that the inclusion of PCDDs/PCDFs with CDs did indeed occur as demonstrated by detection of these contaminants in water.

Figure 3. Concentration of 1,2,3,4-TCDD in water surrounding PCDD/PCDF-contaminated soil particles monitored using GC-ECD over a period of 28 days.

Fig.4 depicts the concentration of total PCDDs/PCDFs desorbed from the soil over a period of 28 days using different CDs. The rate of desorption decreased exponentially from the start of inoculation with the CDs to the end of testing (28 days) giving rise to different concentrations in the presence of CDs. As can be seen, again, the HPBCD performed very well with respect to other CDs in the removal of these contaminants from the soil over the entire period of testing. It was observed that HPGCD matched the efficacy of the HPBCD at day 5, but later, its capability decreased appreciably. One may advance a reason for this experimental observation in terms of stability of the HPGCD-PCDDs/PCDFs complex. It is conceivable that HPGCD formed a complex in a good yield at the time of sampling but that complex decomposed at later time thus releasing PCDDs/PCDFs and HPGCD. However, the performance of the HPBCD was far better than the HPGCD through the entire course of experiment (28 days). This performance may be explained in terms of the mechanism of inclusion with CDs. Although other CDs, like ACD, BCD and the HPACD were investigated, they could not match the capacity of HPBCD in terms of leaching capability of PCDDs/PCDFs from the soil. Notice that even though the HPACD has a

solubilizing group (-OH), it did not do much in terms of removal of PCDDs/PCDFs. It is of interest to mention that at the end of the study, it was observed that a type of biological growth existed on some of the soil inoculated with CDs. One may wonder if that biological activity was active during the testing.

Figure 4. Concentration of total PCDDs/PCDFs desorbed from soil over a period of 28 days.

When a water solution containing HPBCD and PCDDs/PCDFs was introduced to clean soil it appeared that HPBCD prevented PCDDs/PCDFs from travelling from the aqueous medium to the soil particles. Fig.5 delineates the concentration of total PCDDs/PCDFs plotted as a function of types of CDs after 28 days of application. As can be seen, without CDs, specifically HPBCD, the soil sorbed PCDDs/PCDFs from the surrounding water, whereas, in the presence of CDs, the contaminants preferred to stay in the complex form in surrounding medium. Note that the BCD and the HPACD showed similar effect, but the HPGCD was the second most effective after the HPBCD at inhibiting PCDDs/PCDFs from moving toward the soil matrix. This is consistent with desorption experiments, where the HPBCD was found the most effective in pulling out the sorbed PCDDs/PCDFs into the surrounding aqueous medium.

Figure 5. Prevention of PCDDs/PCDFs from sorption onto the soil matrix in presence of different CDs, after 28 days.

In water without soil, again different CDs had different effect on GC-ECD response. The ACD did not show any effect on the GC-ECD response, meaning no inclusion occurred. BCD and HPACD appeared to include PCDDs/PCDFs, whereas, HPBCD and HPGCD demonstrated an appreciable enhancement in the GC-ECD response (about 37 times). The difference in the GC-ECD response to the PCDDs/PCDFs in water, with and without CDs, can only be explained in terms of the physico-chemical properties of the included PCDDs/PCDFs. The PCDDs/PCDFs that bonded with the CDs behaved differently from those free of CDs, which was illustrated by the appreciable difference in the GC-ECD signals, specifically HPBCD. It is possible that during the GC-ECD analysis, the transformation inside the hot injection chamber and the detection with the ECD, the inclusion with CDs caused enhancement in the GC-ECD response. This is not a testing error because PCDDs/PCDFs are sparingly soluble in water and the phenomenon was observed repeatedly. It is also conceivable that the PCDDs/PCDFs may have deposited onto the inner surface of the test vessel and that the HPBCD dislodged them back into the water because the PCDDs/PCDFs are insoluble in water.

5. CONCLUSIONS

This work demonstrated the usefulness of CDs for the removal of PCDDs/PCDFs from the soil. Five CDs including ACD, BCD, HPACD,

HPBCD and HPGCD were investigated for inclusion of PCDDs/PCDFs. HPBCD gave the highest removal efficiency for the majority of PCDDs/PCDFs components, ranging from 69% to 96% for 2,3,7,8-TCDD and 1,2,3-TCDD, respectively. The removal efficiency of total PCDDs/PCDFs was estimated to be 81% at the start (one day after CD application) and 96% after 28 days. The ACD and BCD removed only 45% and 50% of the total PCDDs/PCDFs after 28 days, whereas, HPACD and HPGCD removed 73% and 80% of the total PCDDs/PCDFs from the contaminated soil, respectively. The results showed that the existence of a solubilizing active group in the CD molecular structure alone is not enough to leach PCDDs/PCDFs from the soil. The size of the cavity plays a significant role as demonstrated by the different removal efficiencies of HPACD, HPBCD and HPGCD, 73%, 96% and 80%, respectively. It was observed at the end of the study that some type of growth developed in the CD-treated soil, indicating that biological activity had occurred. The nature of this growth has not been investigated further.

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