Stabilization of chlorinated dibenzo-*p*-dioxins, dibenzofurans and chlordecone in soils from three former industrial areas.

Leaching behavior of chlorinated dibenzo-*p*-dioxins, dibenzofurans and chlordecone from three soils

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Abstract

Chlorinated dibenzo-*p*-dioxins, dibenzofurans (together abbreviated as CDD/Fs) and chlordecone (CLD) are persistent organic pollutants in the environment and have deleterious health effects on humans and wildlife. These pollutants contaminate various soils throughout the world and they can leach out to contaminate other environmental compartments. The aim is therefore to find a cost-effective and environmentally friendly method to prevent leaching of CDD/Fs and CLD out of soils. Biochars were proven to be efficient to immobilize several pollutants in soil to prevent their leaching. Horse manure and rice husk torrefied at 230 °C were mixed separately (2%) to soil samples to test their efficiency at immobilizing CDD/Fs and CLD contaminated soils. Soils from three former industrial areas in Sweden (soil A, soil B and soil C) were put to the test. The results show the different leaching behaviors of CDD/Fs depending on the soil. The stabilization treatment was not sufficient enough to prevent their leaching. Soil A was spiked with CLD to test its leaching behavior but no result was obtained for CLD due to analytical issues.

List of abbreviations

BLK	Blank
CDDs	Chlorinated dibenzo-*p*-dioxins
CDFs	Chlorinated dibenzofurans
CLD	Chlordecone
DCM	Dichloromethane
GC-MS	Gas Chromatography-Mass Spectrometry
HM	Horse Manure
IS	Internal Standard
LP	Leaching Percentage
LT	Leaching Test
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-*p*-dioxins
PCDFs	Polychlorinated dibenzofurans
PLE	Pressurized Liquid Extraction
RH	Rice Husk
RS	Recovery Standard

Author contributions

The work presented in this thesis was performed by the author except for the running of the GC-MS and PLE instruments. The GC-MS and the PLE were run by Per Liljelind and Lisa Lundin, respectively.

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1. Introduction

1.1 Chlorinated dibenzo-*p*-dioxins and dibenzofurans

Chlorinated dibenzo-*p*-dioxins and -furans (CDDs and CDFs), see **Figure 1**, are a class of compounds structurally and chemically related aromatic hydrocarbons, which often occurs as a mixture of congeners. They include mono- and polychlorinated dibenzo-*p*-dioxins and dibenzofurans. CDDs constitute a group of 75 congeners with 7 considered as toxic, including the well-known 2,3,7,8-tetrachlorodibenzo-p-dioxin. There are 135 possible CDF congeners and among them, 10 have dioxin-like toxicity. They are formed unintentionally as by-products in production of herbicides and during incineration of waste. CDD/Fs are non-volatile compounds with a high $\log K_{ow}$ which means they are not soluble in water and have a high affinity to soil, sediment and biota. Those compounds present a high risk for the environment because they are very persistent, they bioaccumulate and biomagnify in the food chain causing health effects among animals and humans. CDD/Fs are related to health issues such as cancer, chloracne and birth defects. They are also affecting the immune, nervous and digestive systems among animals and humans.[2]

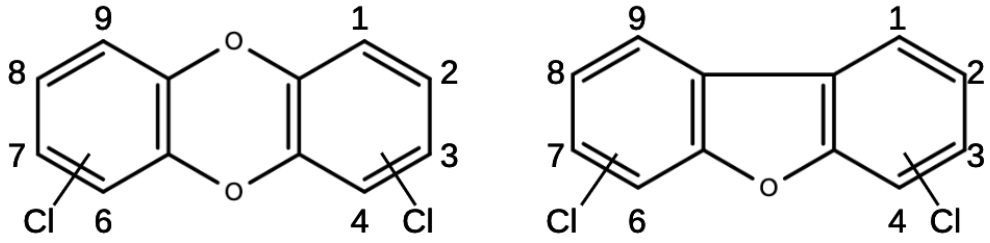

Figure 1. CDDs and CDFs general structures.

1.2 Chlordecone

Chlordecone (CLD, also known as Curlone or Kepone), see **Figure 2**, was a pesticide used mainly in banana plantations between 1972 and 1993 to kill the banana black weevil *Cosmopolites sordidus* in Guadeloupe and Martinique.[3] This compound is slightly soluble in water (3.0 mg/L), it can therefore be found in water in very small amounts, especially as bound to particles. CLD is non-volatile but can be transported through air by binding to dust. However, it rapidly deposits to surface water and soil. It binds strongly to organic-rich soils and sediment and has a half-life of 10 years in those compartments.[4] Although the molecule is highly immobile in those compartments, it can undergo long-range surface water transportation via erosion and water runoff. Surface water, sediment and about 25% of the soil in each island are highly polluted with CLD.[5] This molecule was proven to be very persistent in the environment, its high lipophilicity and poor metabolization in animals and humans make it bioaccumulative and biomagnifying. CLD is responsible of many health issues such as neurotoxicity, developmental problems in children and oligospermia; it

potentially gives prostate cancer. It has been classified as a POP in the Stockholm Convention since 2009.[4,6,7]

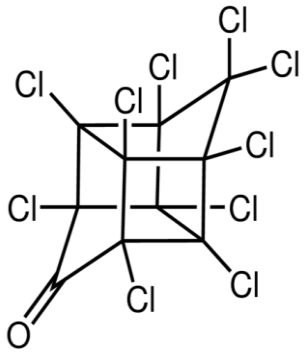

Figure 2. Chlordecone structure.

1.3 Solidification/Stabilization

CDD/Fs and CLD share similar physico-chemical properties and tend to have a similar distribution pattern in the different compartments of the environment. As discussed previously, those compounds constitute a high risk for the environment and human health. Therefore, solutions should be implemented to reduce exposure and eliminate them.

Solidification/Stabilization (S/S) is a cost-effective common method used to remediate sites (soil, sludge and sediment) contaminated with heavy metals and organic pollutants. This remedial technique reduces the leaching of contaminants in the environment by immobilizing them within the treated material. S/S is a versatile, effective and extensive method because it effectively treats numerous different contaminants within the same media; the polluted material can be treated ex-situ as separated waste or in-situ as excavated material.[8] Solidification consists of making the pollutants into a solid by changing their physical properties: it includes a decrease of permeability, an augmentation of compressive strength and encapsulation of hazardous constituents.[8,9] Stabilization makes the contaminants of concern less mobile after changing them chemically.[9] In this case, the contaminants are converting into a less mobile, soluble and toxic form. S/S treatment consists in mixing a binding reagent (cement, lime, limestone, fly ash, gypsum, slag, phosphate mixtures…) into a contaminated media or waste.[8] S/S efficiency can be evaluated by both leaching tests and volatilization measurements to assess environmental mobility.[10]

1.4 Aim of the diploma work

The aim of the project was to investigate if stabilization of contaminated soil with biochars could immobilize both CDD/Fs and CLD in three soils. The content of CDD/Fs in the soils and the content of CDD/Fs and CLD in the leachates from the soils were also investigated. Biochars from horse manure (HM) and rice husk (RH) were used in this study.

2. Popular scientific summary

2.1 Popular scientific summary

Dioxins and chlordecone are persistent organic pollutants in the environment and are a threat to human health. They are both found in high quantities in different places around the world. Chlordecone is found in Guadeloupe and Martinique (French Caribbean), Ivory Coast, Cameroon, Equator, Nicaragua, Honduras, Panama, the USA and Asia. Dioxins are ubiquitous around the world and are formed mainly as by-products in production of herbicides and during combustion of waste whereas chlordecone is an insecticide. Dioxins and chlordecone contaminate soils and tend to leach in water streams and oceans. Consequently, they also highly contaminate grazing animals, fish and shellfish. The most significant human exposure to dioxins and chlordecone is through food consumption, especially animal products.
It is therefore very important to implement solutions to avoid the release of dioxins and chlordecone into the environment as well as solutions to eliminate them.

The aim of this project was to test a cost-efficient, safe and environmentally-friendly solution to avoid the release of dioxins and chlordecone from contaminated soils to the rest of the environment. Stabilization is a remedial technique to achieve this goal. Biochars such as carbonized horse manure and rice husk were shown to be efficient into the removal of some contaminants (i.e pharmaceuticals) from the environment by adsorption. Therefore, horse manure and rice husk torrefied at 230°C were used in this study to test their efficiency at immobilizing both dioxins and chlordecone in polluted soils in Sweden. These biochars (2%) were incorporated separately into soil samples.The results from the leaching tests showed that these biochars were not sufficient enough to prevent the release of dioxins from the soil to the water compartment. There was no result with chlordecone due to experimental issues. Other approaches should therefore be implemented in the future.

2.2 Social and ethical aspects

2.2.1 Chlorinated dibenzo-*p*-dioxins and dibenzofurans

Chlorinated dibenzo-*p*-dioxins and dibenzofurans are persistent organic pollutants in the environment and are found throughout the world.[13,14] They are very toxic for both wildlife and humans causing cancer, hormonal, developmental and reproductive issues, as well as damage to the immune system. According the World Health Organization in 2016, more than 90% of human exposure to CDD/Fs is through consumption of contaminated food, especially meat, fish, shellfish and dairy products.[14] CDD/Fs accumulate in body fat and women can detoxify from them by having children and through breastfeeding. The deleterious health effects of CDD/Fs are therefore transmitted to future generations. Yet, everyone should have the right to be healthy. The World Health Organization constitution (1946) considers « the highest attainable standard of health as a fundamental right of every human being. »[17] Developing fetuses are the most affected by CDD/Fs. Therefore, it is necessary,

especially for girls and young women that want to have children later on in their life, to reduce their exposure to CDD/Fs by at least limiting their consumption of animal products.[14] Besides, sources of CDD/Fs should be reduced; cost-effective and environmentally friendly methods should be implemented to eliminate and avoid the release of CDD/Fs further into the environment. Such methods (i.e. photolytic destruction and thermal desorption) already exist but it is still crucial to investigate more efficient ones.[18]

2.2.2 Chlordecone

Chlordecone is also a persistent organic pollutant according to the Stockholm Convention.[15] Surface water, sediment and about 25% of the soil in Guadeloupe and Martinique are highly polluted with the insecticide. It is also found on the African, American and Asian continents.[5,15] A chronic exposure increases risk of prostate and liver cancer, neurotoxicity, hepatotoxicity, developmental problems in children and pregnancy complications.[16,19,20] Human exposure to chlordecone occurs mainly through dietary intake (ie. seafood, animals, root vegetables grown on contaminated soils…).[3,5,21,22] Vegetables that are grown in soil and near to the soil such as root vegetables and cucurbits uptake high amounts of chlordecone. However, fruits and vegetables that are grown further from contaminated soils do not seem to uptake the pollutant. The strategy to reduce human exposure is therefore to grow root vegetables and cucurbits on non-contaminated soils and the aerial fruits and vegetables can be grown anywhere. Nevertheless, the best solution is to eliminate and avoid further release of chlordecone in the environment.

3. Experimental

3.1 Materials

CDD/F-contaminated soils were collected from three former industrial locations (soils A, B and C). Soil A is from a former industrial property, where wood was treated with pentachlorophenol and arsenic. The soil is composed of natural sedimentary materials, morains and organic filling masses (chips, bark, ect) contaminated by CDD/Fs and arsenic.

Soil B and soil C are both sandy soils with elements of brick crust and smaller organic elements such as roots and bark. The level of contamination by CDD/Fs of these two soils is not the same.

The soils were stored in plastic containers at room temperature.

The solvents used for the PLE were n-hexane, toluene (provided by SupraSolv) and acetone (provided by HiPerSolv CHROMANORM). The hydromatrix used for the extraction cells was dispensed from Agilent Technologies. Internal standards were provided by Cambridge Isotope Laboratories.

Tetradecane and dichloromethane were dispensed from Aldrich Chemistry and Fisher Scientific, respectively.

A mixture of 32 chemicals including CLD (Kepone) diluted in dichloromethane (DCM) was also used for the experiments and was provided by Restek (EPA 8270, Appendix IX Mix 2). Concentration of each chemical: 138 µg/mL.
Carbonized HM and RH torrefied at 230°C for 3 hours were used for the stabilization experiments.

3.2 Pressurized liquid extraction (PLE)

3.2.1 Cleaning of the PLE cells

Cleaning of 10 stainless steel PLE extraction cells was performed to remove possible undesirable compounds. First, the extraction cells (internal volume of 34 mL) were assembled. After placing a paper filter at the bottom of the extraction cells, hydromatrix was added and compacted to fill each of them. The cells were then sealed properly for PLE.
The solvent mixture used for the cleaning were n-hexane and acetone (1:1). Temperature: 120°C; 1 cycle.

3.2.2 Extraction of the soils

Three CDD/F-contaminated soils from different locations, named A, B and C soils, were sieved through a 2.0 mm width mesh to remove plant debris and stones. Each soil was mixed using a big spoon to get representative samples and 2 g of each soil were extracted. Assays were performed in triplicates.
The soil samples were then mixed with hydromatrix and added to extraction cells. The cells were filled and compacted with additional hydromatrix. A blank extraction cell sample (BLK) containing only hydromatrix was also prepared. Tetra-to-octa-PCDD/F (40 µL) and mono-to-tri PCDD/F (40 µL) were added to each extraction cells as internal standards (IS). Internal standard is added to be able to compensate for losses during cleanup of the sample. A known amount of IS was added to all the samples as early as possible. During the many steps of the experiments, errors and volumetric losses can occur but they should affect IS and analyte proportionally so that the ratio of analyte to IS stays constant throughout the whole process.
PLE was then performed under the following conditions: Temperature: 120°C; Heat: 6 min; Static time: 5 min; 3 cycles; Rinse volume: 100%; Purge: 60 seconds; Solvent: toluene. Those are optimized conditions for exhaustive and simultaneous extraction of CDFs and CDDs.

3.2.3 Concentration of the extracts

N-tetradecane (100 µL) was added to each extract and the solvent was evaporated. N-tetradecane was used as a “keeper” to prevent a too fast evaporation of the solvent and helps prevent the chemicals from evaporating with the solvent. The samples were concentrated to about 1 mL. After evaporation, about ¼ of a teaspoon of copper granules were added to each sample to remove possible sulfur.

3.3. Multi Layer Silica Gel Column

Multi Layer Silica Gel Column was the cleanup method used to remove polar interferences. Ten columns were prepared as shown in **Figure 3A**, and washed with 30 mL of hexane. Then, each sample was added to a column, eluted with 100 mL of hexane and collected in a 250 mL pear-shaped flask. The solvent was then evaporated to 2 mL. The columns prepared as shown in **Figures 3B and 3C** were used after the batch leaching experiments (section 3.7.2).

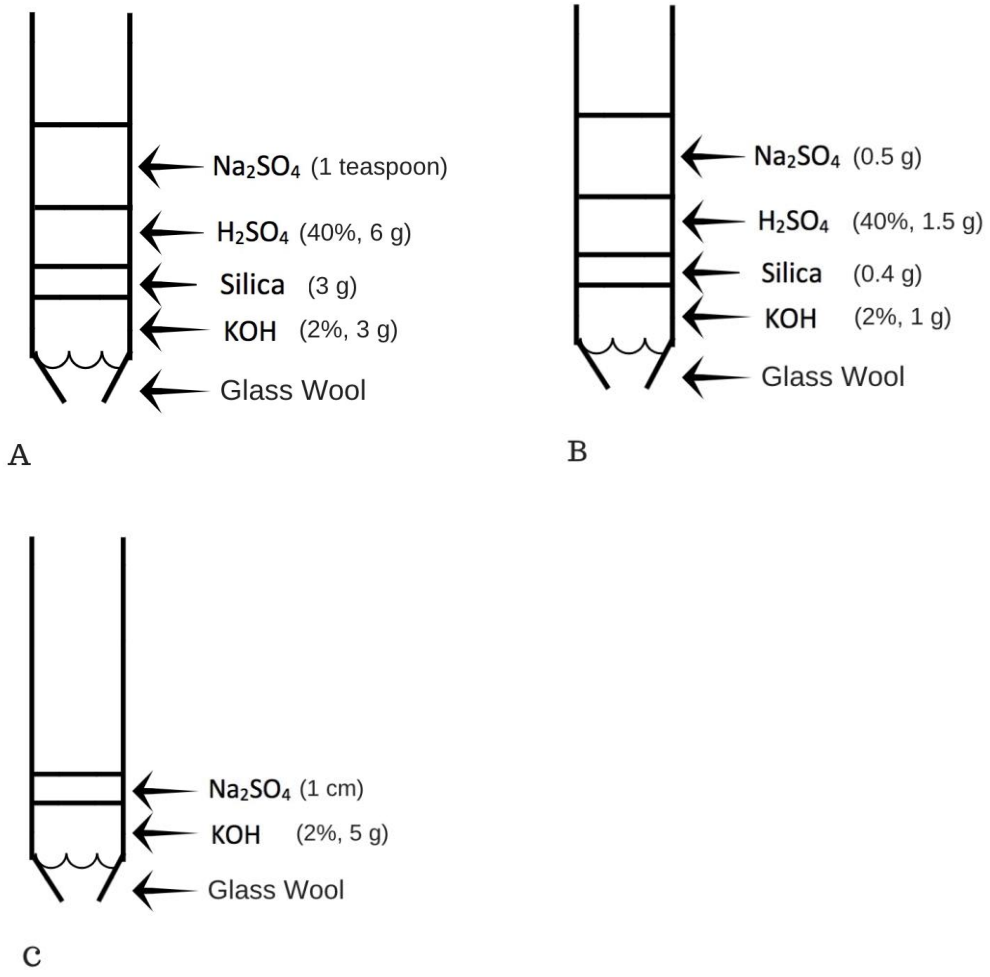

Figure 3. Multi Layer Silica Gel Column Schematic
A. Four -layer silica gel column for analysis of the initial CDDF-contaminated soils; the column was packed with 2% potassium hydroxide-impregnated silica gel (3 g), silica gel (3 g), 40% sulfuric acid-impregnated silica gel (6 g) and anhydrous sodium sulfate (1 teaspoon).
B. Four-layer silica gel column to analyze CDDF-contaminated soil after S/S and LT; the column was packed with 2% potassium hydroxide-impregnated silica gel (1 g), silica gel (0.4 g), 40% sulfuric acid-impregnated silica gel (1.5 g) and anhydrous sodium sulfate (0.5 g).
C. Two layer silica gel column to analyze CLD in dioxin-contaminated soil after S/S and LT; the column was packed with 2% potassium hydroxide-impregnated silica gel (5 g) and anhydrous sodium sulfate (1 cm).

3.4 Carbon Column

The carbon column was used to separate CDDs and CDFs from polychlorinated biphenyls (PCBs).

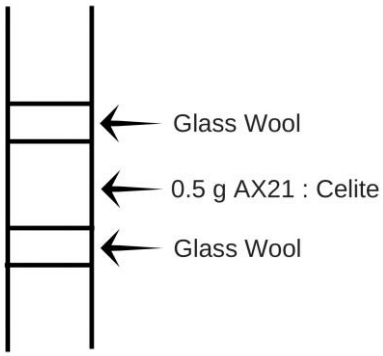

Figure 4. Carbon Column Schematic

Each carbon column was first washed with 10 mL of a solution mixture of DCM:methanol:toluene (15:4:1 mL v/v), followed by a second wash with 5 mL of DCM:n-hexane (1:1) and a third wash with 10 mL of n-hexane.
Each sample was added to a carbon column (AX21 Carbon mixed with celite) as shown in **Figure 4**, and eluted with 50 mL of DCM : n-hexane (1:1). Each column was then turned upside down and the samples were eluted with 40 mL of toluene into flasks. Thereafter, 40 µL of CDD/F and 100 µL of n-tetradecane were added to each flask. The sample was concentrated and each sample was analyzed with high resolution GC-MS.

3.5 GC-MS

The GC-MS instrument separates chemical mixtures into individual substances. Those substances are then detected and identified at a molecular level.
GC-MS was performed to analyze the composition of the initial CDDF-contaminated soil samples and the composition of the leachate samples after stabilization and leaching tests.
All GC-MS analyses were conducted by an expert analyst in the lab. The data was evaluated using MassLynxV4.1 software.

3.6 Stabilization of CDD/Fs and chlordecone

Carbonized HM and RH (both torrefied at 230°C for 3 hours) were used and milled with a pilar and mortar to obtain powders. At least 300 g of each soil B and C were dried in an oven at 105°C for 24 hours. About 400 g of soil A was also dried in the same conditions. Thereafter, tap water was added in each soil sample to reach 17.5% of moisture.[3] The aim was to be as close to reality as possible, therefore, tap water was chosen instead of deionized or miliQ water to mimic natural spring water; The solution mixture (7.25 g) with CLD (138 µg/mL) was added to 100 g of soil A. After 3 weeks of maturation, five samples of 20 g of soil A were prepared for the

stabilization treatment. As described in **Table 1**, fifteen samples of 100 g and five samples of 20 g of dioxin-contaminated soils were prepared. Only one replica was chosen for the non-stabilized soil samples to simplify the experimental steps. Additional soil samples were still available to replicate the experiments later outside of the Master's project.

Table 1. Stabilization experiments of soil A, B and C.

	Amount of soil (g)	HM carbon (g)	RH carbon (g)	CLD (µg)	Replicates
A, B, C	100	2			2
A, B, C	100		2		2
A, B, C	100				1
A	20	0.4		151	2
A	20		0.4	151	2
A	20			151	1

3.7 Batch leaching tests

3.7.1 Sample preparation

Batch leaching tests were performed to evaluate the efficiency of the stabilization experiments. Five leaching test experiments were scheduled after 1, 2, 3, 4 and 5 week(s) of maturation with the carbonized RH and HM (named respectively LT1, LT2, LT3, LT4, LT5). Twenty samples were prepared (**Table 2**) and frozen after each week of maturation so that the batch leaching tests could be performed at the same time no matter the week of maturation.

Table 2: Soil samples prepared for each leaching test.

Soils	A,B,C (HM)	A,B,C (RH)	A,B,C (BLK)	A & CLD (HM)	A & CLD (RH)	A & CLD (BLK)
Mass (g) for each leaching test	10	10	10	2	2	2
Replicates	2	2	1	2	2	1

3.7.2 Batch leaching experiments

Batch leaching tests were performed with a soil-to-water ratio of 1:10. Tap water (20 mL) was added to samples with 2g of soil and 100 mL of tap water was added to samples with 10g of soil. The samples were put on a shaking table (120 shakes/minute) during 24 hours at room temperature.

The solids of each sample were separated from the liquid by filtration and the aqueous phase was extracted by DCM ($50\,mL \times 3$ for samples with 100 mL of tap water and $20\,mL \times 3$ for samples with 20 mL of water). The organic phases were combined and 20 µL of PCDD/F internal standard and 20 µL of mono-, di- and tri-PCDD/F internal standard were added to the organic phases of each sample analyzed for CDD/Fs whereas 20 µL of dechlorane was added to the organic phases of each sample analyzed for CLD. Once all the organic phases were collected, 40 µL of n-

tetradecane was added to each sample and the solvent was evaporated. To finish, the samples were cleaned up with multi-layer silica gel columns as shown in **Figure 3B and 3C**, organic phases with hexane were collected, 20 µL of RS were added to each sample and the solvent were evaporated.
The samples were then analyzed by GC-MS.
Batch leaching tests and analysis of the water phase composition were performed on all samples (soils A, B, C and soil A with CLD) after 1 week of maturation with HM and RH carbons. The amount of time required for the project was not sufficient to perform all the batch leaching tests and their analysis. Soil C was found to be the most contaminated soil. It was therefore selected for additional leaching tests (LT3 and LT5) and analysis.

3.7.3 Leaching percentage (LP)

A leaching percentage was calculated for each individual furan and dioxin, as well as each type of furans and dioxins to find out what compounds or groups of compounds leach the most from soil to water.

$$LP(\%) = 100 \times \frac{C(water)}{C(soil)}$$

C(water) is the concentration in water and *C(soil)* is the concentration of soil. The concentrations of PCDD/Fs are in ng/g of soil.

4. Results

4.1 Content of CDD/Fs in soils A, B and C

The content of furans (CDFs) and dioxins (CDDs) in soils A, B and C is illustrated in **Figure 5**. The same figure is shown in **Appendix 1** with error bars. Legend for small bars was not displayed to simplify the graphs and focus on the most significant results. Soil C had the highest amount of CDD/Fs and soil A had the lowest amount of CDD/Fs. The most abundant furans and dioxins homologs in soils A, B and C were octa-CDF (OCDF), hepta-CDFs (HpCDFs), hexa-CDFs (HxCDFs), octa-CDD (OCDD), hepta-CDDs (HpCDDs) and hexa-CDDs (HxCDDs). The most abundant furans and dioxins isomers were OCDF, 1234678-HpCDF, OCDD, 1234678-HpCDD and 123678-HxCDD. The concentration of dominant furans and dioxins in soils A, B and C are presented in **Table 3**. A furan or dioxin homolog represents a group of isomers with the same number of chlorine atoms.

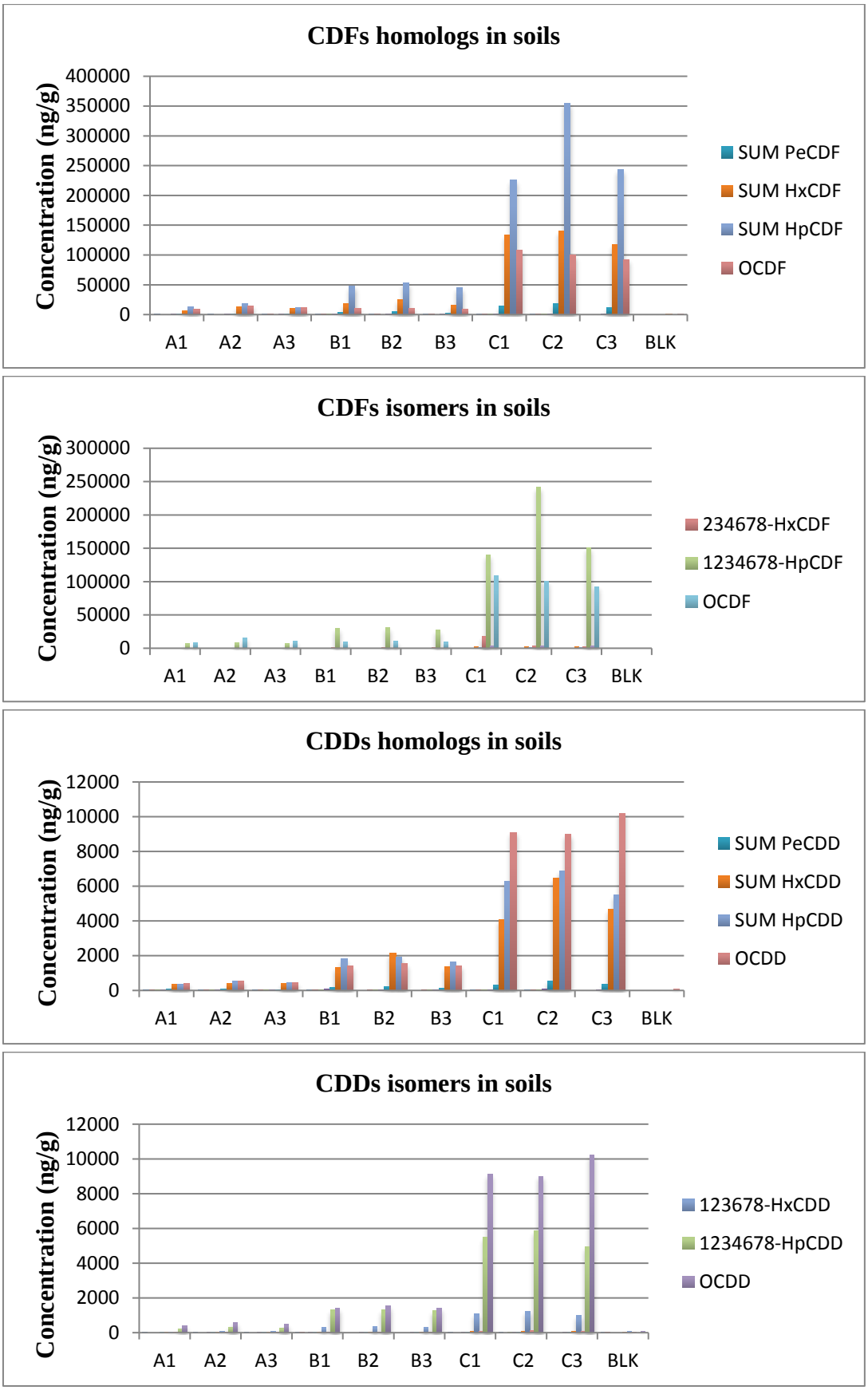

Figure 5. Concentration (in ng/g) of dioxins and furans in soils A, B and C.

Table 3. Concentration (in ng/g) of the dominant furans and dioxins in soils A, B and C.

PCDD/Fs	**Concentration in Soil A (ng/g) (10^3)**	**Concentration in Soil B (ng/g) (10^3)**	**Concentration in Soil C (ng/g) (10^3)**
OCDF	12	10	101
HpCDFs	15	49	275
HxCDFs	10	20	131
PeCDFs	0.70	4	15
1234678-HpCDF	8	29	178
234678-HxCDF	0.16	0.70	8
OCDD	0.50	2	9
HpCDDs	0.45	2	6
HxCDDs	0.40	2	5
PeCDDs	0.07	0.16	0.40
1234678-HpCDD	0.25	1	5
123678-HxCDD	0.06	0.30	1

4.2 Content of CDD/Fs in water after LT1 of soils A, B and C

The principal furans and dioxins found in water after LT1 of soils A, B and C treated with HM, RH or nothing (BLK) are displayed in **Figures 6 and 7**. Their concentrations (in ng/g of soil) are presented in **Table 4**. Many of the main CDD/Fs found in each soil were also found in the water samples in high quantities. All of the dioxins and furans found predominantly in soil B were also part of the main ones in water samples after LT1. In leachate samples of soil A, HxCDFs was by far the most abundant furans type among the others in all three samples. Furan isomers seemed more predominant in the leachate sample with carbonized HM than in sample with carbonized RH and the blank one. 2378-tetra-CDF (2378-TCDF) was the most found in the leachate sample with carbonized RH. It seemed to be less CDD/Fs in the water samples of soil C treated with carbonized HM compared to the other ones. However, by comparing HM and RH samples with their blank ones, it can be suggested that the stabilization treatment was not efficient.

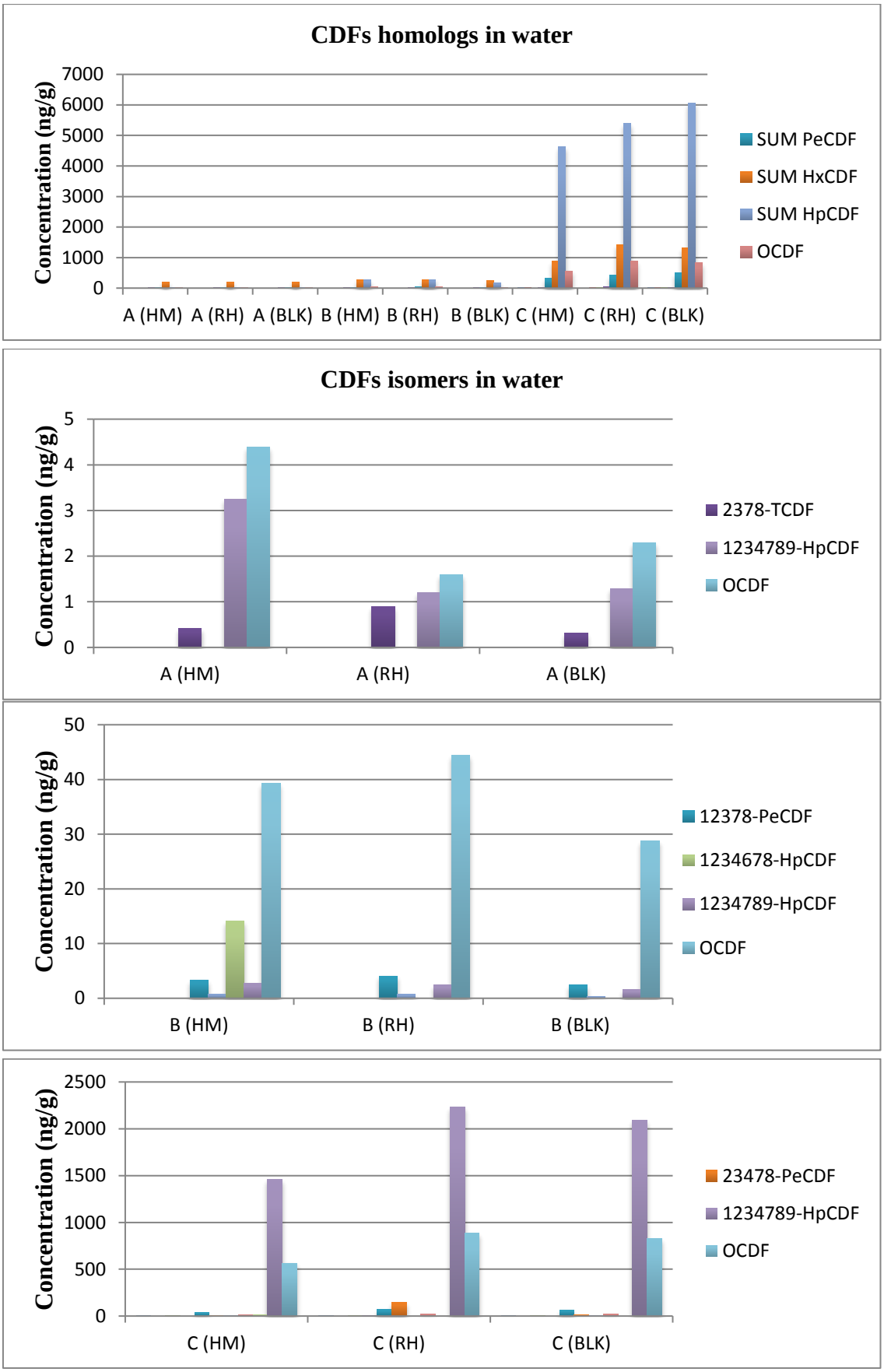

Figure 6. Concentration (in ng/g of soil) of furans in water after LT1 of soils A, B and C treated with HM, RH or nothing (BLK).

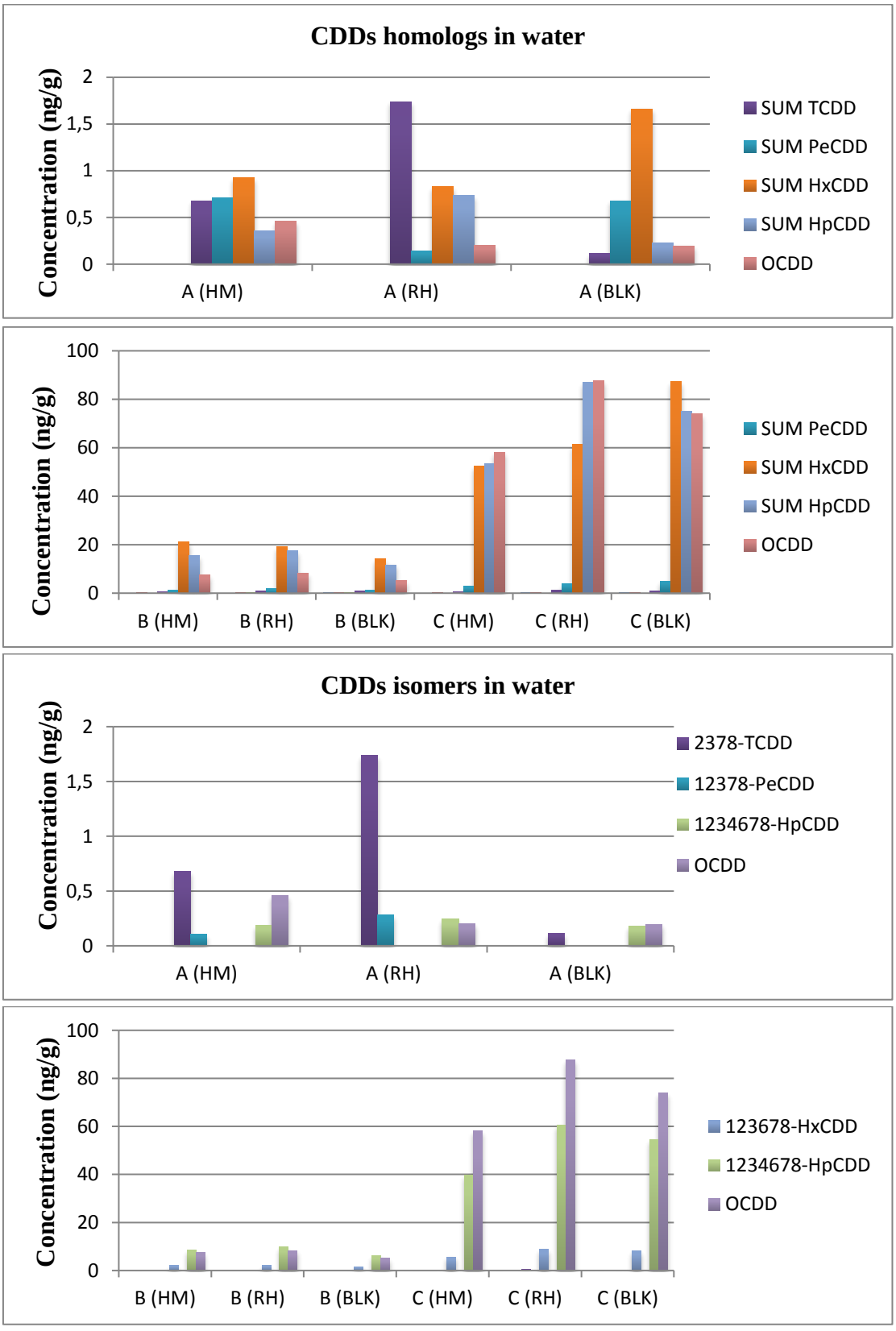

Figure 7. Concentration (in ng/g of soil) of dioxins in water after LT1 of soils A, B and C treated with HM, RH or nothing (BLK).

Table 4. Concentration (in ng/g of soil) of the dominant furans and dioxins in water after LT1 of soils A, B and C treated with HM, RH or nothing (BLK)

PCDD/Fs	**Concentration (ng/g of soil)**			**Concentration in Soil B (ng/g)**			**Concentration in Soil C (ng/g)**		
	HM	**RH**	**BLK**	**HM**	**RH**	**BLK**	**HM**	**RH**	**BLK**
OCDF	4.4	1.6	2.3	39	44	29	565	887	825
HpCDFs	8.9	3.2	3.9	264	285	179	4621	5406	6049
HxCDFs	204	202	201	274	279	248	896	1427	1316
PeCDFs	0.6	0.3	0.7	30	37	23	317	415	498
1234789-HpCDF	3.3	1.2	1.3	2.8	2.5	1.6	1462	2230	2088
1234678-HpCDF				14					
12378-PeCDF				3.3	4.1	2.4			
23478-PeCDF							4.2	144	14
2378-TCDF	0.4	0.9	0.3						
OCDD	0.5	0.2	0.2	7.5	8.4	5.1	58	88	74
HpCDDs	0.4	0.7	0.2	16	17	12	53	87	75
HxCDDs	0.9	0.8	1.7	21	19	14	52	61	87
PeCDDs	0.7	0.1	0.7	1.2	1.8	1.1	2.8	3.9	5
TCDDs	0.7	1.7	0.1						
1234678-HpCDD	0.2	0.3	0.2	8.6	9.9	6.2	40	61	55
123678-HxCDD				2.2	2.3	1.6	5.7	8.7	8.1
12378-PeCDD	0.1	0.3							
2378-TCDD	0.7	1.7	0.1						

4.3 Leaching percentages of CDD/Fs in water after LT1 of soils A, B and C

Although the results from section 4.2 show the main CDD/Fs in water after LT1, they do not indicate which CDD/Fs leached the most from the soils. That is why leaching percentages were calculated. The leaching percentages of furans and dioxins in soils A, B and C are presented in **Figures 8 and 9**. The results from **Figure 8** were quite homogeneous for the three samples of soil. However, the leaching pattern among the soils was not the same (see **Discussion** for explanation). In other words, some compounds leach more or less depending on the soil. The leaching percentages of furans and dioxins that leached the most from each soil are presented in **Table 5**.

The most leached homologs from soil A were HxCDFs, DiCDDs, TriCDDs and tetra-CDDs (TCDDs). The most leached compounds from soil A were 1234789-HpCDF, 12378-penta-CDF (12378-PeCDF), 2378-TCDF, 237-TriCDD, 2378-TCDD and 12378-penta-CDD (12378-PeCDD). Among CDFs homologs, HxCDFs were by far the most abundant in water. 2% of HxCDFs leached in water and around 0.5% or less of the other PCDFs leached in water. It may be suggested from the leaching percentages of CDFs homologs (**Figure 8**) that HpCDFs were retained by the soil and

did not leach easily but the contrary was showed for 1234789-HpCDF. It was found that 1234678-HpCDF was the furan that leached the less among the others (only 0.002% of leaching); therefore, the percentage of leaching of HpCDFs in total was drastically diminished. Among CDDs homologs, the compounds that leached the most were DiCDDs in all three samples (**Figure 9**). 2378-TCDD appeared to be the dioxin isomer that leached the most but the percentages of leaching exceeded 100% in samples treated with HM and RH. Apart from that, 12378-PeCDD was the most leached dioxin. It can be concluded that the heavier dioxins such as OCDD and HpCDDs were more retained in the soil whereas the most leached dioxins seemed to be DiCDD, TriCDD, TCDD and PeCDD.

The most leached homologs from soil B were HxCDFs, TriCDDs and TCDDs. The most leached compounds from soil B were 123478-HxCDD and 12378-PeCDF. The most leached furan isomer was by far 12378-PeCDF in all three samples. The rest of furans had a leaching percentage lower than 1% (**Figure 8**). TriCDDs leached the most among CDDs homologs in the sample treated with RH and the blank one with leaching percentages of 4% and 8% respectively (**Table 5)**. The leaching of TriCDD was not shown for the sample treated with HM. The second most leached was TCDD for the sample with RH and the blank one. The first and second most leached dioxins homologs for sample with HM were DiCDDs and HxCDDs. The dioxin compound with the highest leaching percentage was by far 123478-HxCDD for all three samples. The other compounds had a leaching percentage lower than 1% (**Figure 9**). The most leached homologs from soil C were HpCDFs, PeCDFs, TCDFs, Mono-CDDs (MoCDDs), DiCDDs, TCDDs. The most leached isomers from soil C were 2-MoCDD, 2378-TCDD, 123478-HxCDD Leaching of PCDFs seemed to occur less for soil C treated with carbonized HM after 1 week of maturation. However, MoCDFs leached more in the sample treated with HM compared to what was seen in sample with RH and the blank one. The results showing leaching percentages of dioxins from soil C were heterogeneous (**Figure 9**). In the blank sample, the dioxin homologs that leached the most were MoCDDs. In samples treated with HM and RH, DiCDDs leached the most. OCDD, HpCDDs and HxCDDs had leaching percentages smaller than 2% (see **Figure 9 and Table 5**). In that case, it was the lower dioxins (MoCDDs and DiCDDs) that seemed to leach the most.

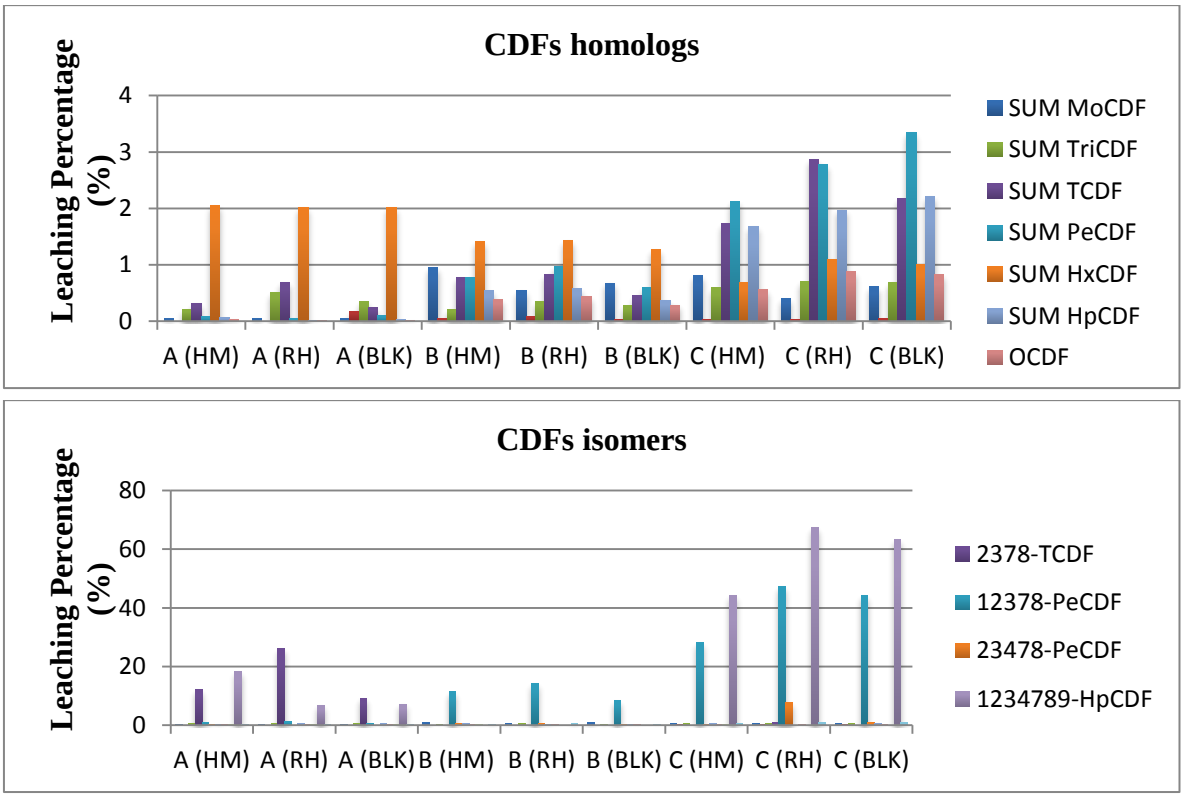

Figure 8. Leaching percentage of furans after LT1 from soils A, B and C treated with HM, RH or nothing (BLK).

Table 5. Main CDD/Fs with leaching percentages above 1% from soils A, B and C.

PCDD/Fs	LP (%) Soil A			LP (%) Soil B			LP (%) Soil C		
	HM	RH	BLK	HM	RH	BLK	HM	RH	BLK
HpCDFs							1.7	2.0	2.2
HxCDFs	2.0	2.0	2.0	1.4	1.4	1.3			
PeCDFs							2.1	2.8	3.3
TCDFs							1.7	2.9	2.2
1234789-HpCDF	18.1	6.7	7.2				44.2	67.4	63.1
12378-PeCDF	1.0	1.1		11.4	14.2	8.4	28.2	47.2	44.0
2378-TCDF	12.2	26.3	9.3						
MoCDDs								1.6	9.7
DiCDDs	2.1	12.1	7.8				5.6	2.7	1.3
TriCDDs		4.3	2.7		4.1	8.4			
TCDDs	2.1	5.4	0.4	1.0	1.9	1.9		2.2	1.6
2-MoCDD							2.8	12	2.0
237-TriCDD			2.4						
2378-TCDD	183	470	31				1.5	24.2	2.4
12378-PeCDD	1.4	3.7							
123478-HxCDD				4.5	3.7	2.4	2.0	3.1	2.2

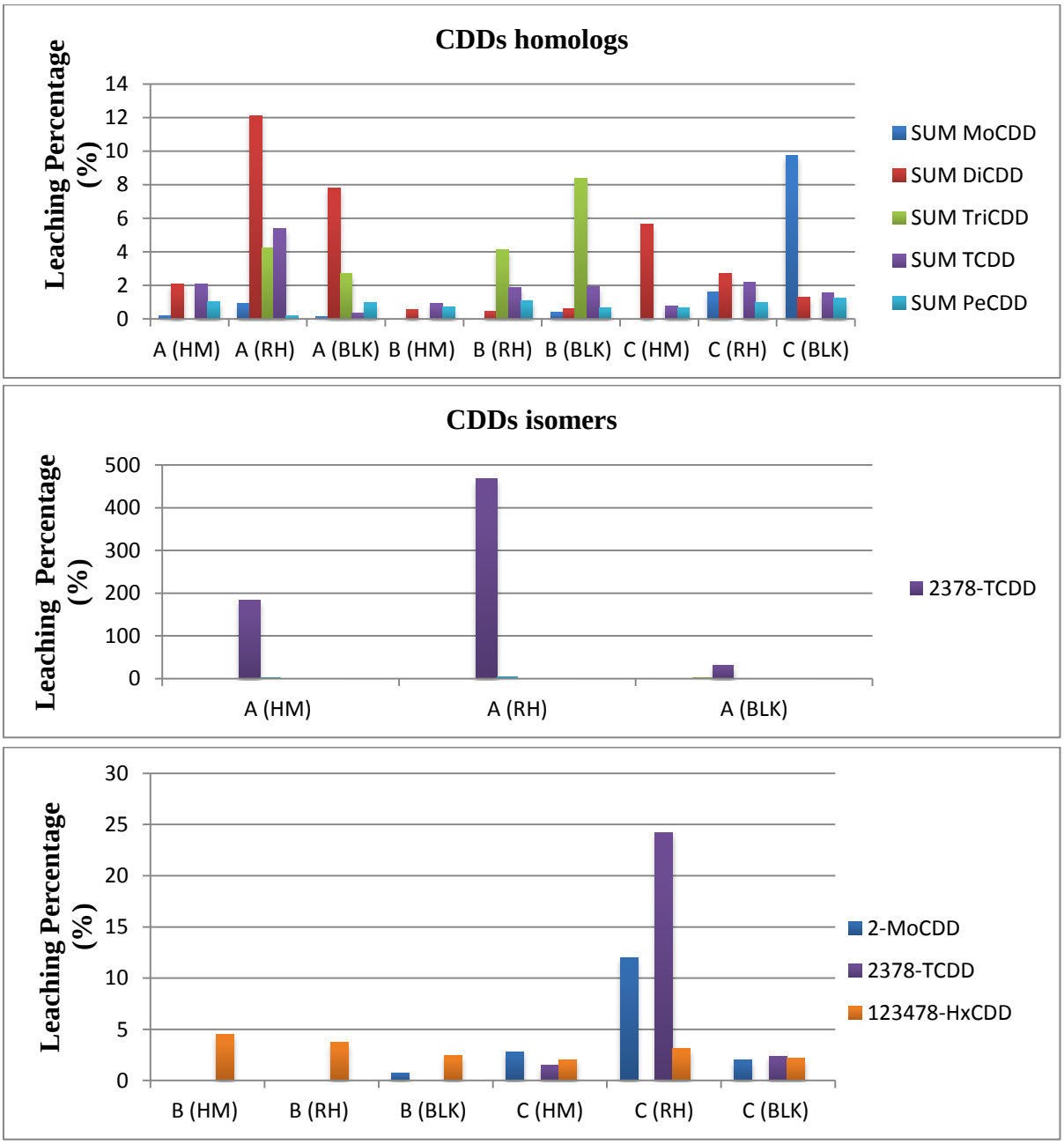

Figure 9. Leaching percentage of dioxins after LT1 from soils A, B and C treated with HM, RH or nothing (BLK).

The leaching percentage of 2378-TCDD for soil A(HM) and A(RH) (**Figure 9**) is much higher than 100%, which is absurd. This means that the concentration of 2378-TCDD in the water samples was much higher than the concentration found in soil samples. Even if the soil samples were mixed to be representative, the concentration of CDD/Fs can still vary in different part of the soil samples. Besides, more experimental steps are involved for the analysis of the content of CDD/Fs in soils A, B and C. Therefore, quantitative losses of CDD/Fs are more likely to happen in this case than during the batch leaching tests. Mistakes could have also be made during the evaluation of the final data.

Overall, more leaching was occurring from soil C and less leaching resulted from soil A. However, as it was shown previously, the leaching behavior of CDDFs was different among soils A, B and C. The furans that tend to leach the most in all three soils were "intermediate" ones such as HxCDFs, PeCDFs and TCDF. The dioxins that tend to leach the most in all three soils were low dioxins such as DiCDDs and TriCDDs. The leaching results showed that the stabilization treatment with either carbonized HM or RH after 1 week of maturation was not efficient even if less leaching of CDFs was observed for soil C samples treated with HM.

4.4 Content of CDD/Fs in water after LT1, LT3 and LT5 of soil C

Additional leaching tests (LT3 and LT5) were performed and analyzed to find out if the results varied depending on the week of maturation after the stabilization treatment with either carbonized HM or RH.

The proportions of furans and dioxins found in water after LT1, LT3 and LT5 were displayed in **Figure 10**. The main CDD/Fs found in soil C and the main ones found in water after LT1, LT3 and LT5 are the same except for 1234678-HpCDF that was found in soil whereas 1234789-HpCDF was found in water.

Less leaching was observed for soil C after 3 and 5 weeks of maturation and the results from LT3 and LT5 looked very similar (**Figure 10**).

In samples after LT1, it seemed like there was less furans that leached after the stabilization with carbonized HM compared to the blank (**Figure 8**). On the contrary, the soil samples with carbonized RH seemed to retain furans and dioxins somewhat more compared to the blank samples for both LT3 and LT5. Besides, the leachate of the sample treated with HM had the most CDD/Fs.

However, the result differences were not significant to confirm that the stabilization treatment was efficient in that case.

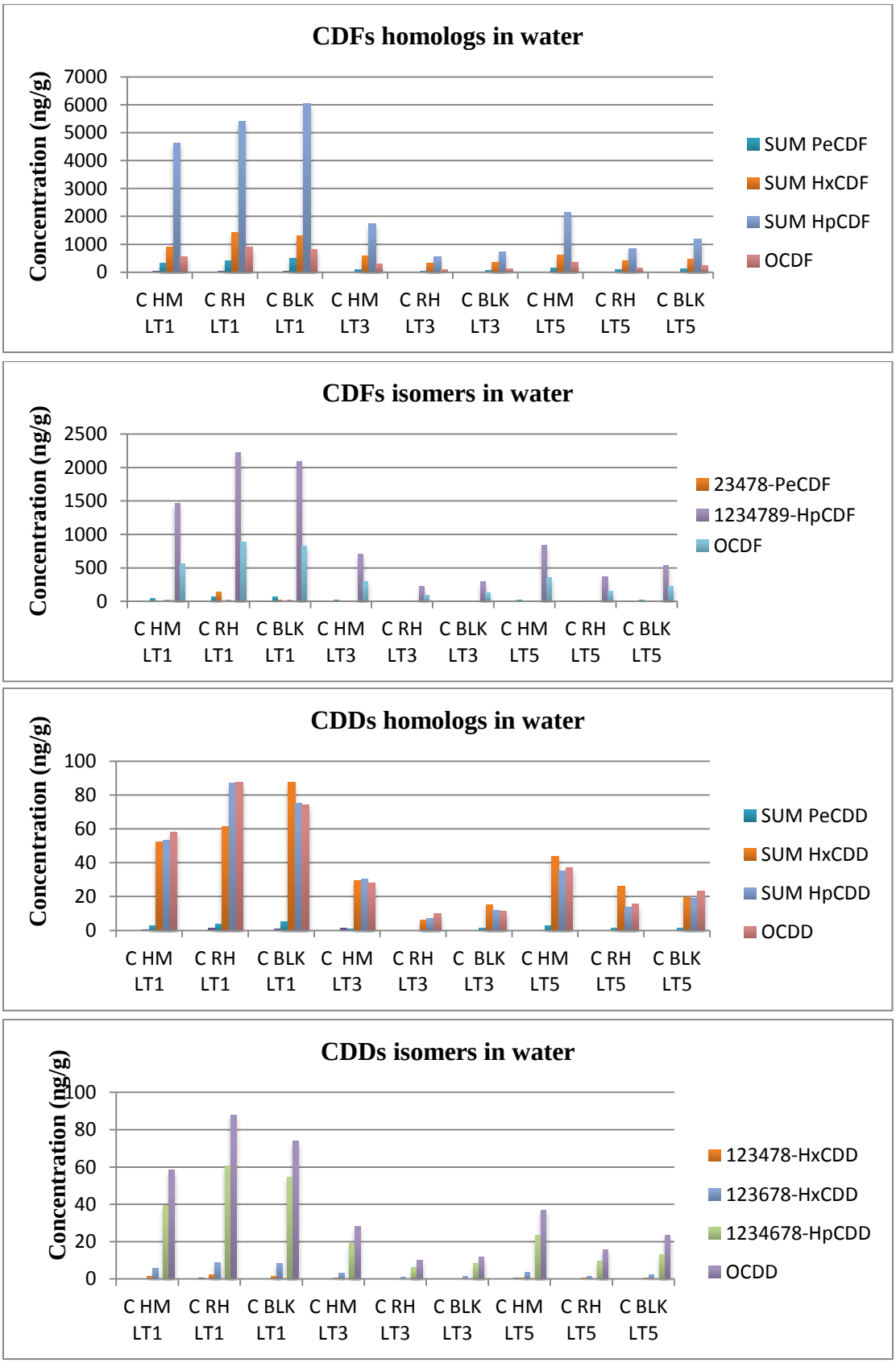

Figure 10. Concentration (in ng/g of soil) of furans and dioxins in water after LT1, LT3 and LT5 of soil C treated with HM, RH or nothing (BLK).

4.5 Leaching percentages of CDD/Fs in water after LT1, LT3 and LT5 of soil C

The leaching percentages of furans and dioxins in soil C are displayed in **Appendix 2** and the leaching percentages of furans and dioxins that leached the most from C soil are presented in **Table 6**. About 3 times more leaching of furans was occurring for LT1 compared to LT3 and LT5. However, the leaching behavior of furans and dioxins were almost the same after LT1, LT3 and LT5 (with some exceptions with dioxins). Intermediate to higher furans tend to leach the most (TCDFs, PeCDFs and 1234789-HpCDF) and lower dioxins such as MoCDDs, DiCDDs and TriCDDs tend to leach the most. Leaching of furans seemed less important in (FA RH) samples for both LT3 and LT5 but the contrary was observed in the case of dioxins. Even after 3 and 5 week of maturation, the stabilization treatment with carbonized HM and RH was not efficient. There are two HpCDFs isomers: 1234678-HpCDF and 1234789-HpCDF. The isomer that contributed the most to the concentration of HpCDFs was by far 1234689-HpCDF (**Table 6**).

Table 6. Furans and dioxins with leaching percentages above 1% after LT1, LT3 and LT5 from soil C.

PCDD/Fs	**LP (%) LT1**			**LP (%) LT3**			**LP (%) LT5**		
	HM	RH	BLK	HM	RH	BLK	HM	RH	BLK
HpCDFs	1.7	2.0	2.2						
HxCDFs		1.1	1.0						
PeCDFs	2.1	2.8	3.3						
TCDFs	1.7	2.9	2.2				1.0		
1234789-HpCDF	44.2	67.4	63.1	21.2	6.6	8.9	25.4	11.2	16.2
12378-PeCDF	28.2	47.2	44.0	10.7	3.5	5.2	12.7	7.1	9.0
23478-PeCDD		7.8							
2378-TCDF									
MoCDDs		1.6	9.7		67.2	87.4			
DiCDDs	5.6	2.7	1.3	12.8			6.9	17.2	8.3
TriCDDs				3.2				1.0	
TCDDs		2.2	1.6						
HxCDDs	1.0	1.2	1.7						
HpCDDs		1.4	1.2						
2-MoCDD	2.8	12	2.0			89.2		7.9	
237-TriCDD				3.9					
2378-TCDD	1.5	24.2	2.4						
12378-PeCDD							1.0		
123478-HxCDD	2.0	3.1	2.2	1.0			1.0		
1234678-HpCDD		1.1	1.0						

4.6 No result for CLD after LT1 of soil A

Initially, there was no chlordecone in the soil samples but a known quantity (7.55µg/g) was added to soil A. The results from LT1 are shown in the **Appendix**. The selected masses for CLD are 272, 274 and 355 based on its mass spectrum (**Appendix 3, Figure E**). CLD was not detectable (**Appendix 4**). Signals were seen at 15.7 min. They corresponded to the IS (13C-Dechlorane, m/z 277, 279) but it was hardly visible (**Appendix 4, Figures H and I**). Chlordecone was not detectable by the GC-MS instrument but bis(2-ethylhexyl) phthalate was recognized (m/z 149), as shown in **Appendix 5**. It should be noted that this molecule was not part of the 32 compounds mixture described in section 3.1. The lack of result for CLD is due to analytical issues: quantitative losses might have occurred during the preparation of the samples before GC-MS analysis. A development method specific to CLD was not possible at the time. Therefore, a method working for other compounds was tested but it did not work in that case.

5. Discussion

The leaching behavior of furans and dioxins in A, B and C soils was compared only after 1 week of maturation with torrefied HM and RH. The stabilization treatment was overall not efficient even if less leaching of furans was observed for (C HM LT1), (C RH LT3) and (C RH LT5) samples. The soils B and C were similar and less leaching for (B HM LT1) was not observed so the positive results with some samples from soil C might just be random. However, furans and dioxins from soils B and C did not have the same leaching behaviors. It can be explained by the fact that soil C were more heavily contaminated than soil B. Besides, leaching in water and air, as well as degradation of various types of furans and dioxins might have occurred differently before collection of the soil samples. It should also be noted that it can happen that the proportions of contaminants varied from samples to samples even if they were taken from the same batch of soil. Concerning soil A, a different leaching behavior was observed compared to the other soils. The previous explanation for this pattern is also valid for soil A. Moreover, soil A was a completely different type of soil; therefore, a different leaching behavior of CDD/Fs was expected. Furthermore, it was observed that the results of leaching appeared very different between the furans homologs and the furans isomers. For instance, in the case of soil A, it was displayed that HxCDFs leached the most but no HxCDF isomer was among the most leached individual furans. There are 4 HxCDFs homologs so if they are put together, they increase the concentration of the HxCDFs group. However they might hardly be seen if they are separated from each other. After the analysis of the results regarding the furans homologs, it was concluded that HpCDFs and OCDFs might have been retained by the soil because they were hardly present in the results of the leaching percentages even if they were found in higher quantity in the soil and water. However, still in the case of soil A as an example, 1234789-HpCDF was the second most leached individual furan. HpCDFs were among the less leaching group of furans because 1234678-HpCDF had the lowest leaching percentage (0.002%). That is why it was so important to have results from the furans or dioxins homologs separated

from the results of the individual furans or dioxins. In the case of dioxins, for soils A, B and C, it was the lower dioxins that leached the most. It can be explained by the fact that lower dioxins have a lower $\log K_{ow}$ than higher dioxins so they will not bind to the soil as tightly as higher dioxins.[23]

6. Conclusions and Outlook

It was shown in this study that furans and dioxins in soils A, B and C have a different leaching behavior. Nevertheless, in all three soils, lower dioxins leach the most. The stabilization treatment with carbonized horse manure and rice husk torrefied at 230°C was not proven to be efficient. The soils were treated with only 2% of carbon; a higher amount could be tested with a longer time of maturation in the polluted soils. Another approach with more effective carbons or mixing of carbons could also be tested. The experiments with CLD should be repeated in order to confirm or not the efficiency of the stabilization treatment in this specific case. However, it is best to find a method that could work on both dioxins and CLD and could be implemented to a larger amount of contaminants. After stabilization, the next step would be to apply a technique to eliminate the contaminants. A mechanochemical dechlorination has been proved to be efficient on dioxins and destroyed 93.2 % of dioxins in fly ash (FA).[24] This treatment could also be tested on chlordecone and other chlorinated pollutants to eliminate them.

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Appendix 1 – Content of CDD/Fs in soils A, B and C

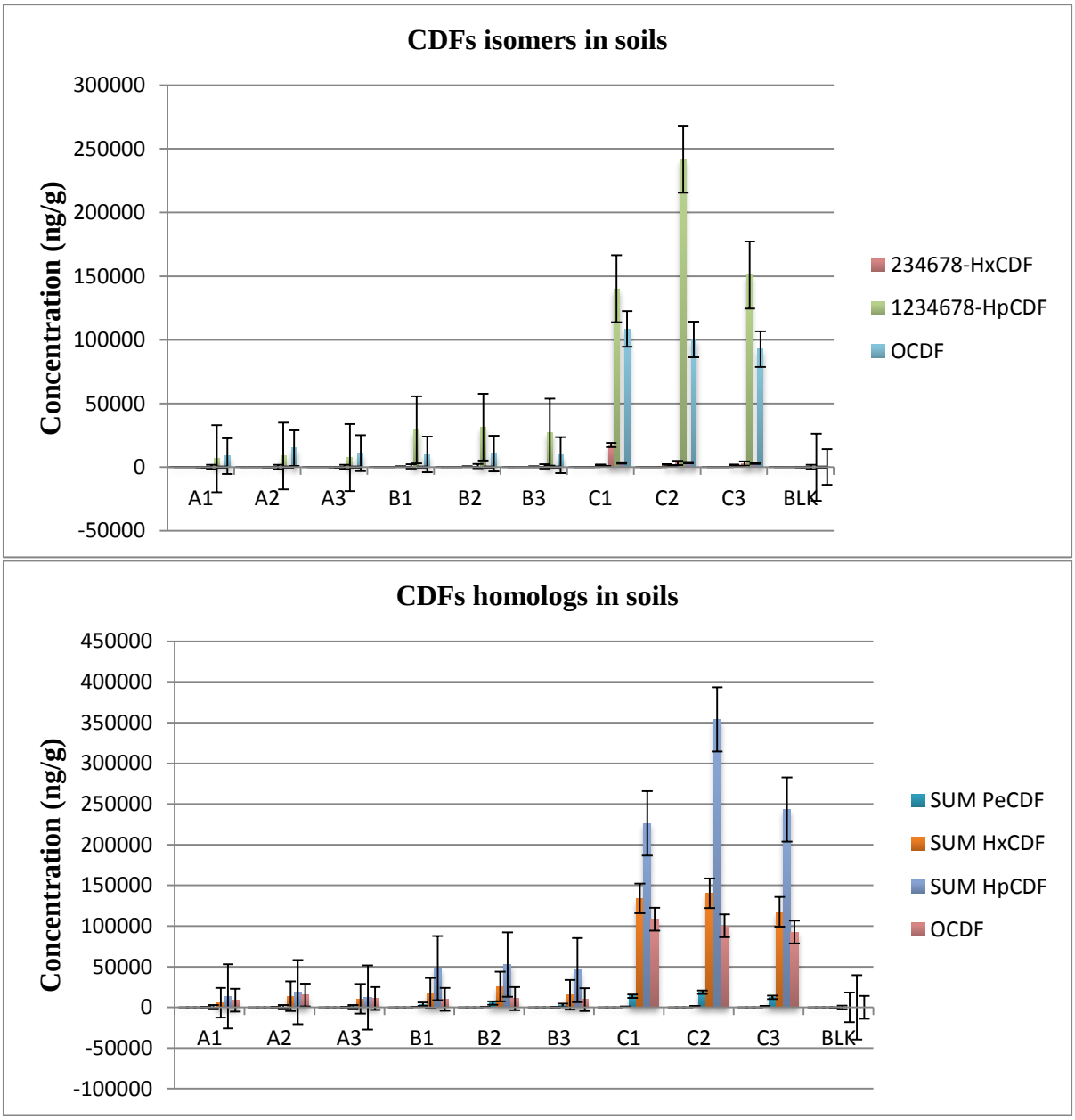


Figure A. Concentration (in ng/g) of furans in soils A, B and C. The error bars correspond to the standard errors. The smaller the error bar, the more liable the data is. The uncertainty of the data is the same among triplicates.

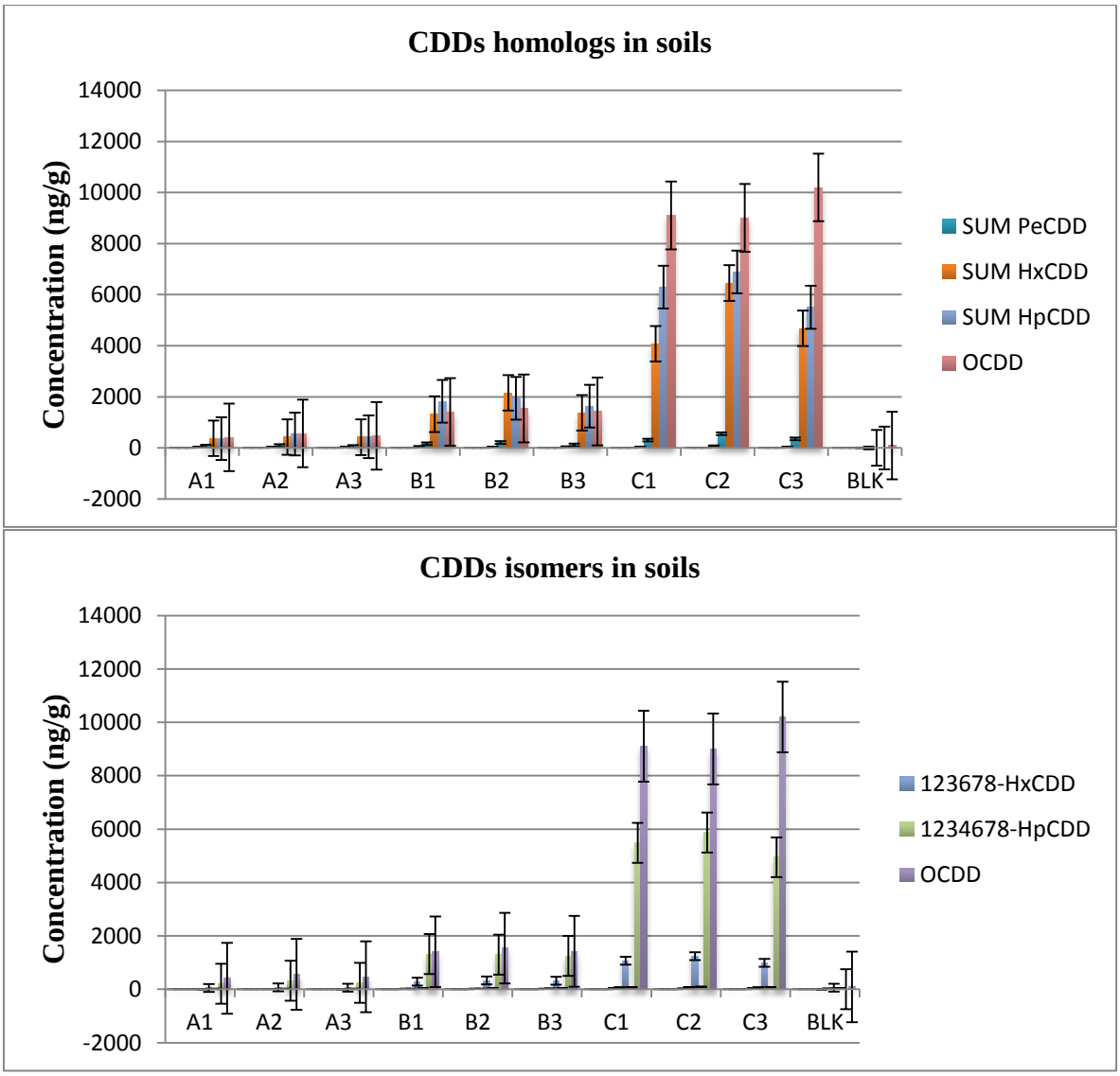


Figure B. Concentration (in ng/g) of dioxins in soils A, B and C with error bars representing standard errors.

Appendix 2 – Leaching percentage of furans and dioxins from soil C

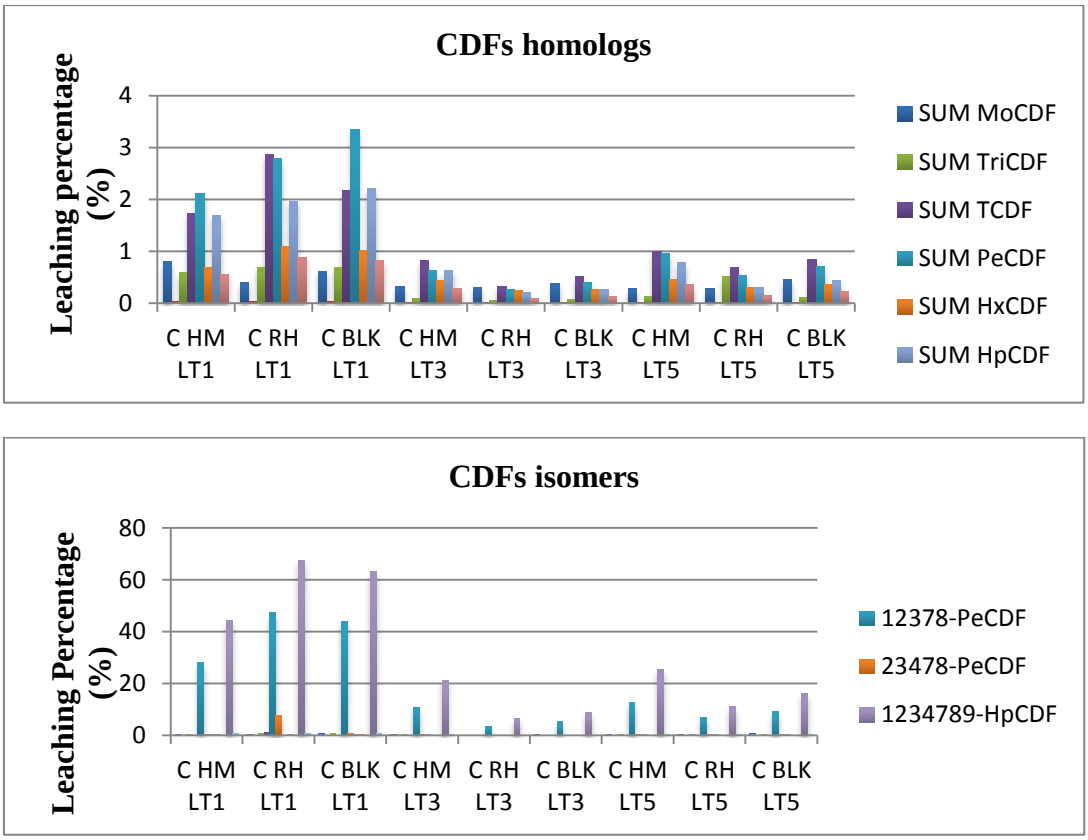


Figure C. Leaching percentage of furans after LT1, LT3 and LT5 from soil C treated with HM, RH or nothing (BLK).

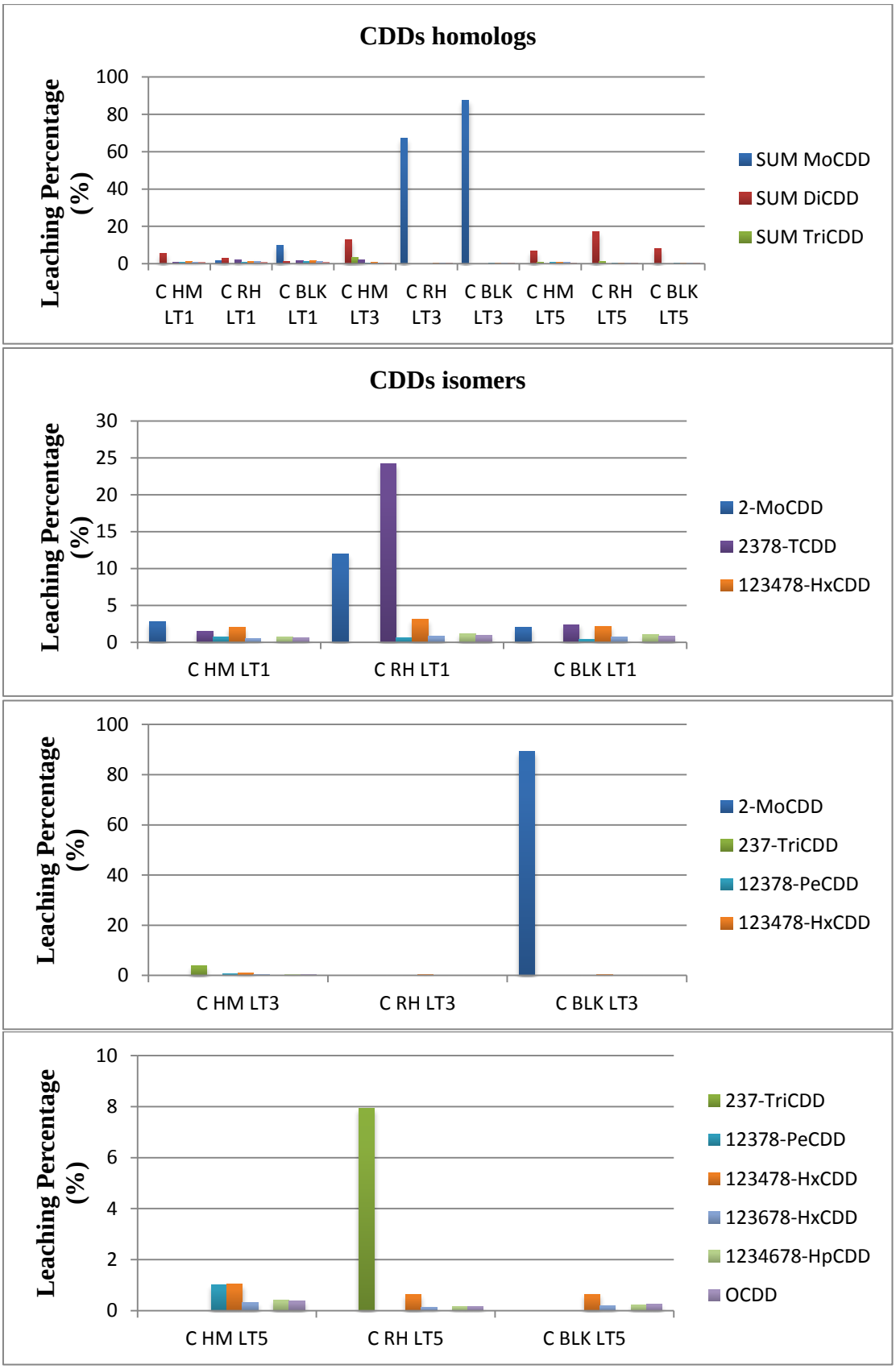


Figure D. Leaching percentage of dioxins after LT1, LT3 and LT5 from soil C treated with HM, RH or nothing (BLK).

Appendix 3 - Mass spectrum of chlordecone

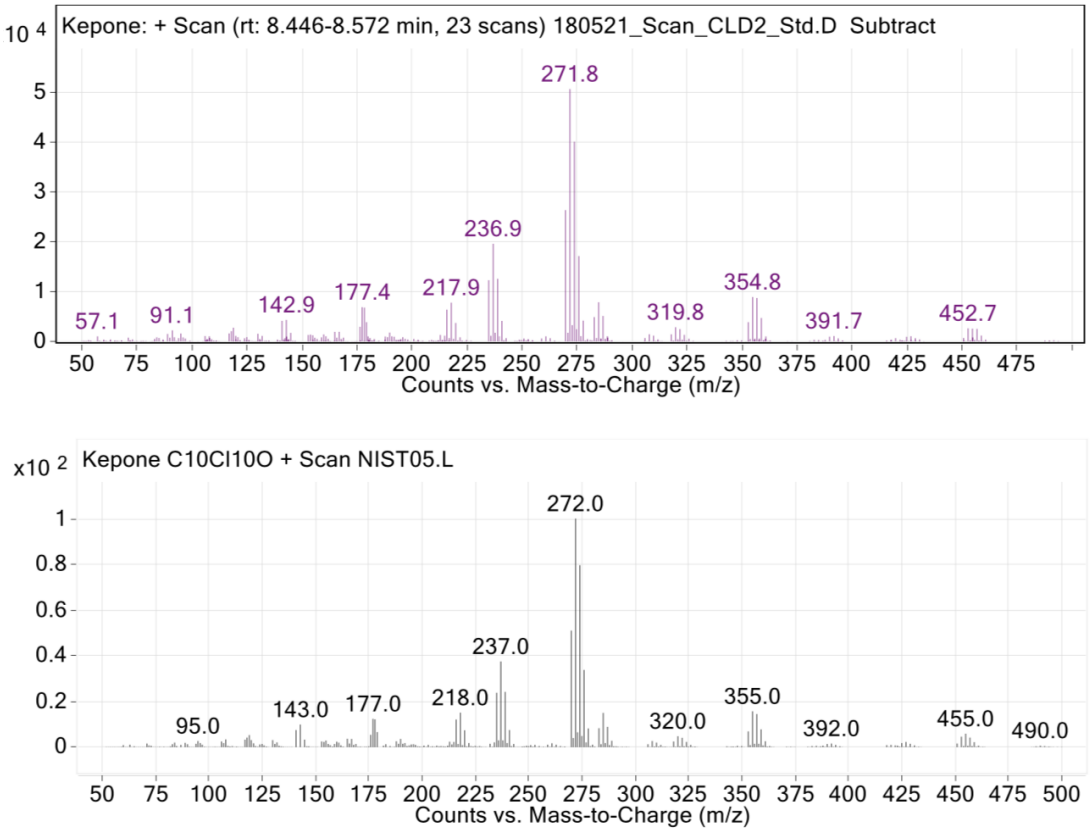
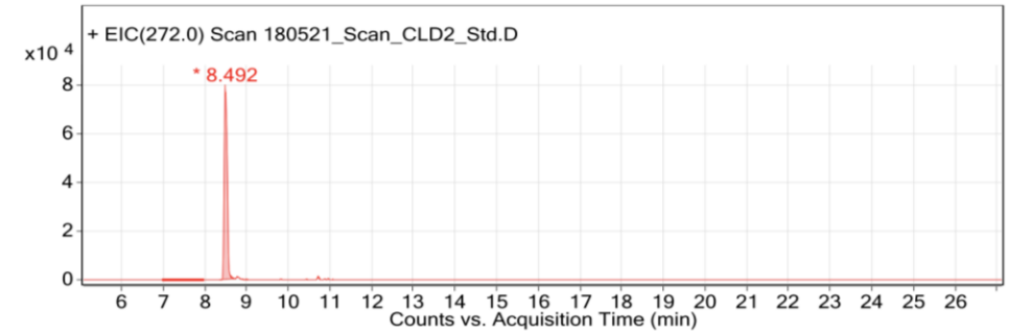


Figure E. Mass Spectrum of chlordecone. The mass spectrum from the standard run is compared to the NIST library. A good match is seen. Chlordeone, also known as Kepone, has a molecular weight of 490.636 g/mol. The masses 272, 274 and 355 were selected for quantification (in the samples after LT1 of soil A).

Appendix 4 - Analysis report. Chlordecone in LT1 of soil A



Integration Peak List

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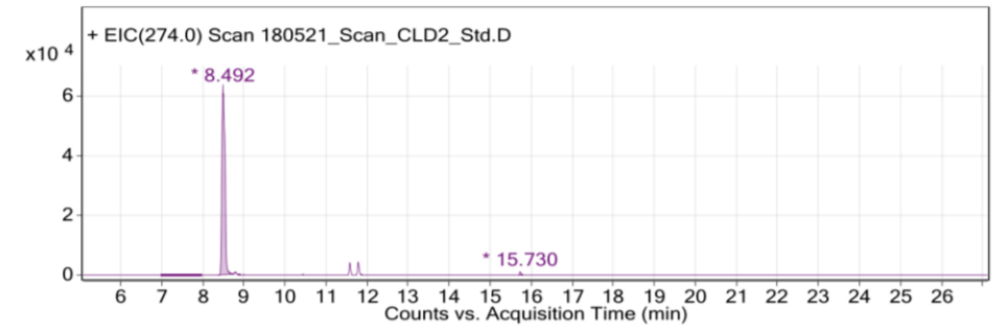
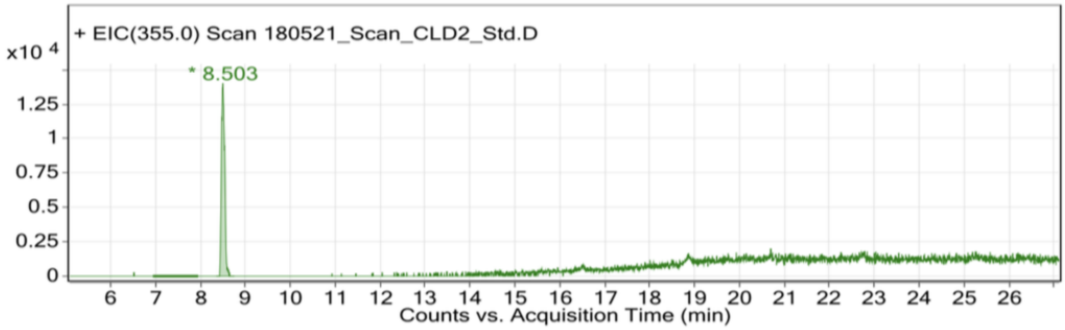


Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	8.366	8.492	8.743	63540.67	328395.06	100	Infinity
2	15.696	15.73	15.81	1081	2689.39	0.82	Infinity



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	8.354	8.503	8.755	14015	73371.9	100	Infinity

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Height	1	0

Figure F. Extracted Ion Chromatogram (EIC) of the selected masses 272, 274 and 355 for chlordecone. Result from standard run.

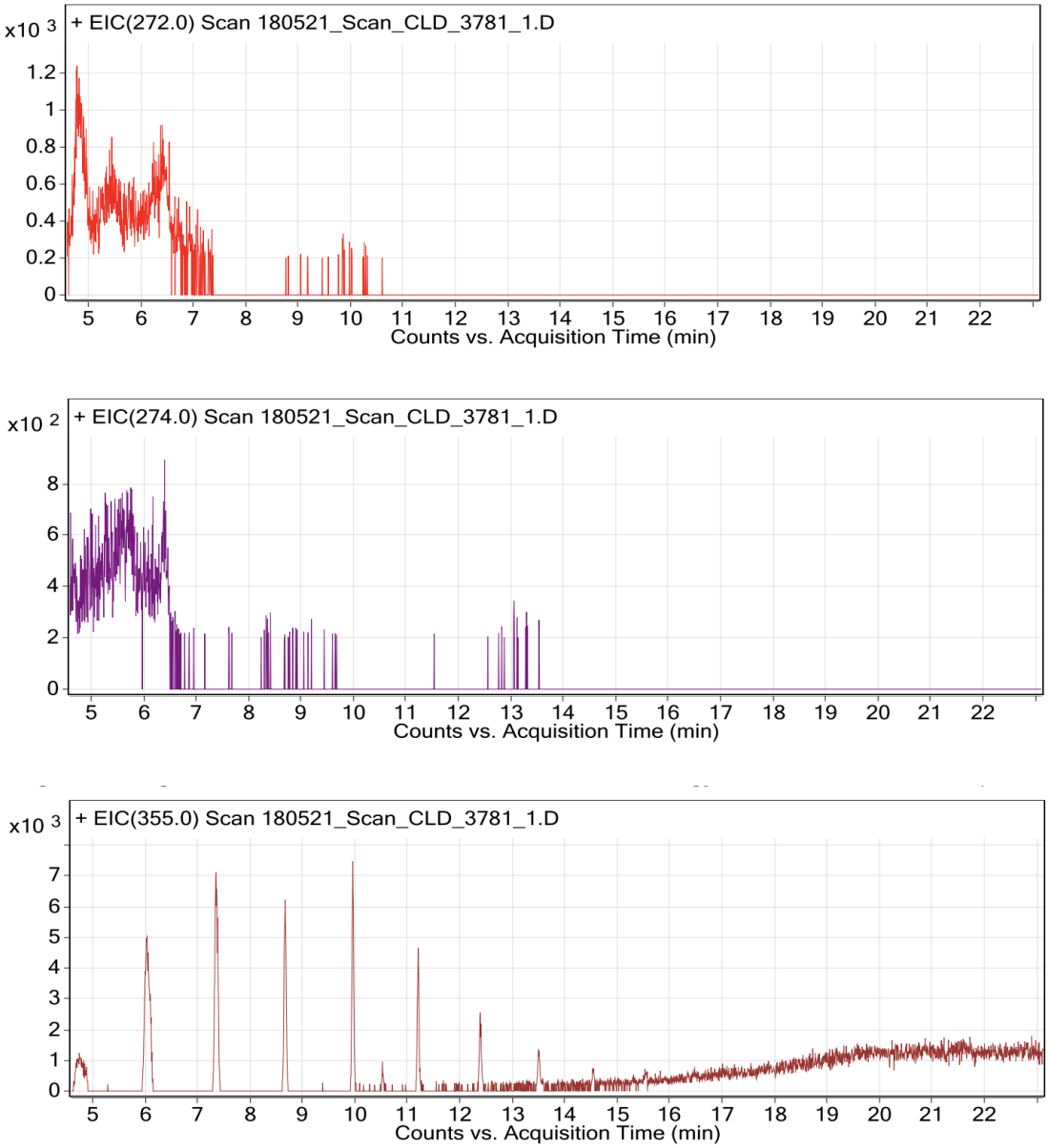
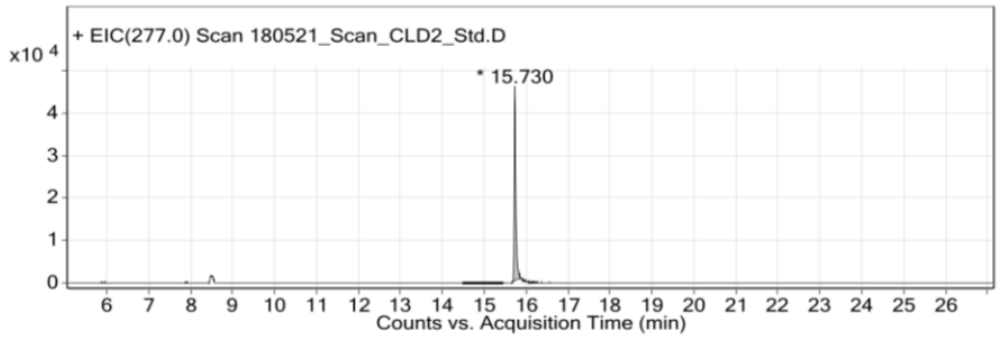


Figure G. Extracted Ion Chromatogram (EIC) of the selected masses 272, 274 and 355 for chlordecone. Chlordecone was not detectable in the sample.



Integration Peak List

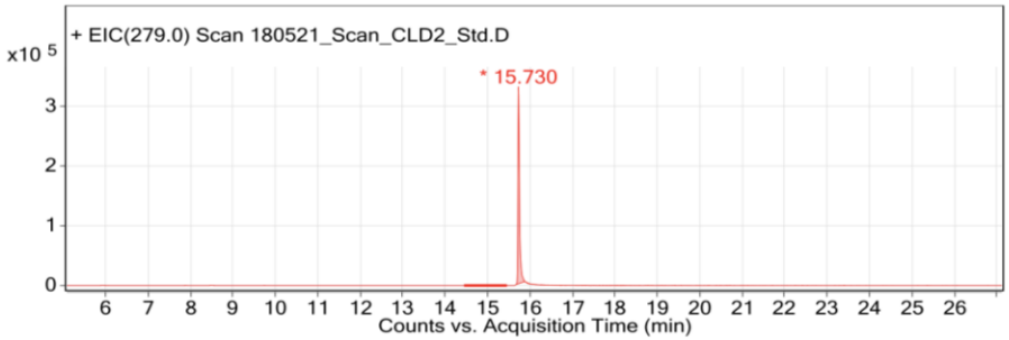
Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	15.667	15.73	15.867	45672.35	119832.76	100	Infinity

Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Height	1	0

Noise Regions

Start	End
14.46663333	15.46663333



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %	Signal To Noise
1	15.673	15.73	15.89	330777.69	847132.74	100	Infinity

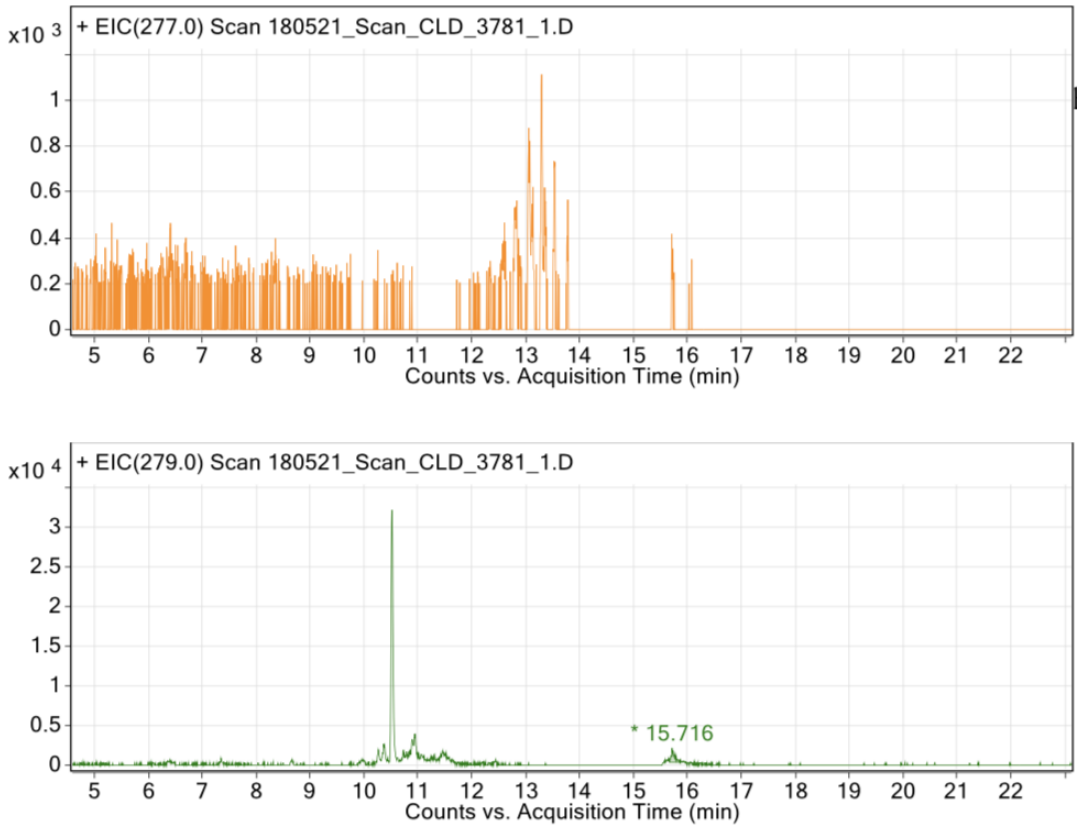
Noise Measurements

Noise Type	Signal Definition	Noise Multiplier	Noise Value
Peak-to-Peak	Height	1	0

Noise Regions

Start	End
14.45518333	15.45518333

Figure H. Extracted Ion Chromatogram (EIC) of 13C-dechlorane (IS). 13C-dechlorane (m/z, 277, 279) was the IS used for the analysis of chlordecone. Signals at 15.73 min corresponds to 13C-dechlorane. Result from standard run.



Integration Peak List

Peak	Start	RT	End	Height	Area	Area %
1	15.665	15.716	15.859	1823.25	7720.33	100

Figure I. Extracted Ion Chromatogram (EIC) of 13C-dechlorane (IS). 13C-dechlorane (m/z, 277, 279) was the IS used for the analysis of chlordecone. Signals at 15.73 min corresponds to 13C-dechlorane. The IS is almost not detectable in the sample.

Appendix 5 - **Bis(2-ethylhexyl)-phthalate**

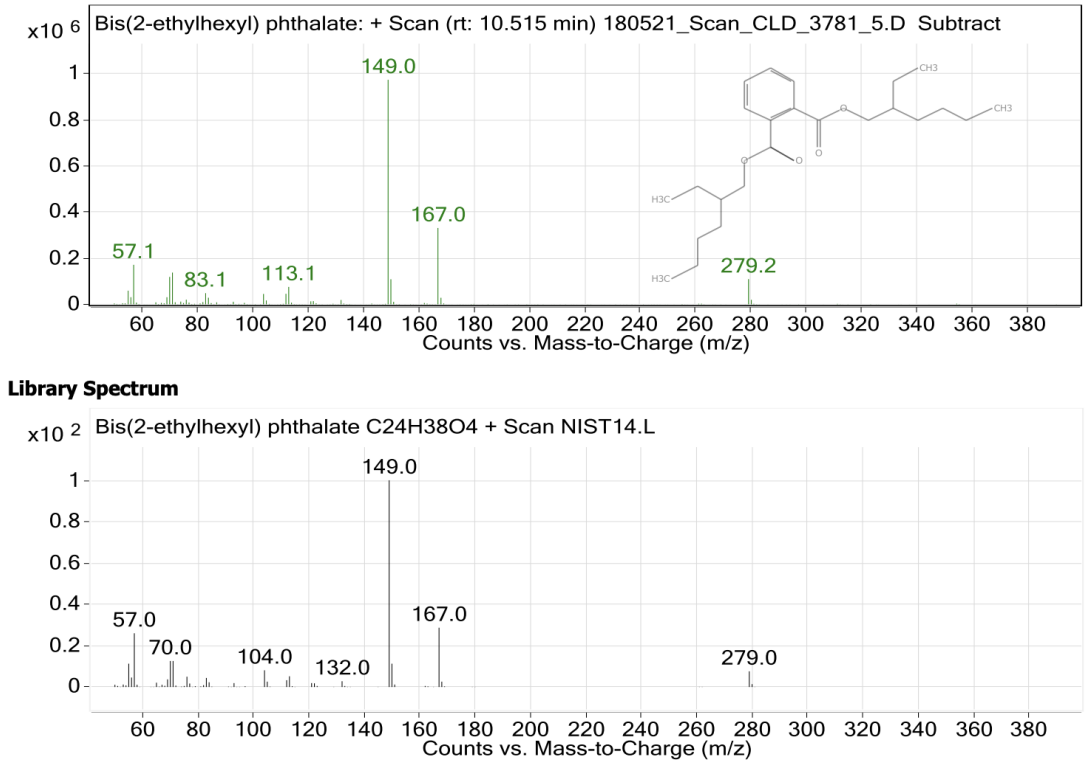


Figure J. Mass spectrum of bis(2-ethylhexyl)-phthalate.

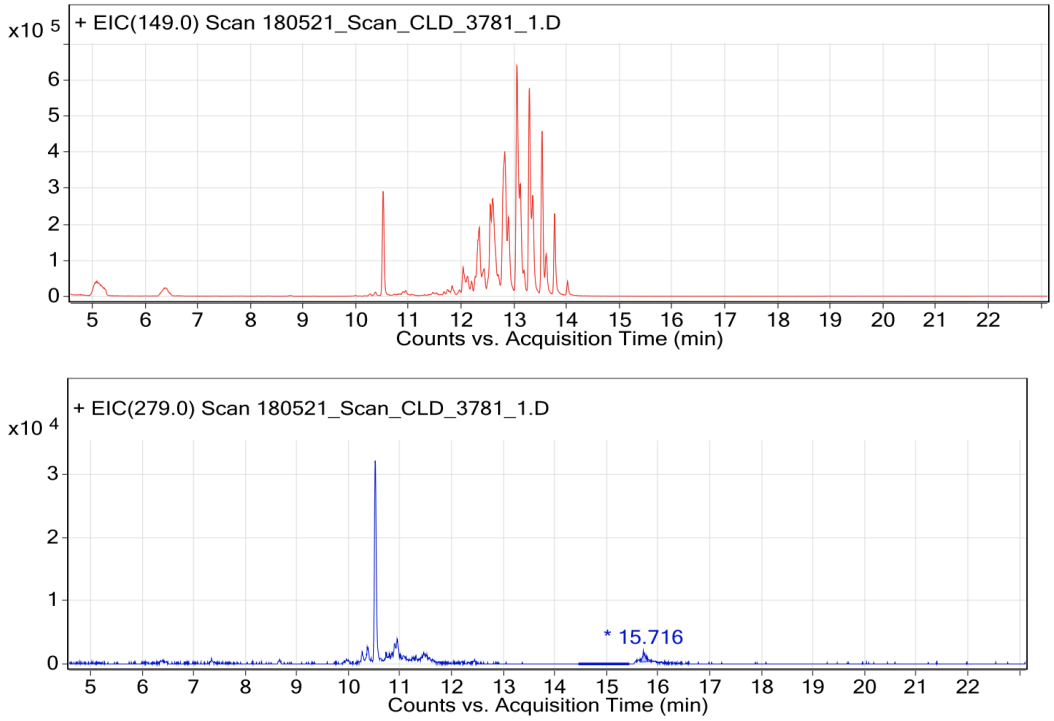


Figure K. Extracted Ion Chromatogram (EIC) of bis(2-ethylhexyl)-phthalate. The retention time for this compound was 10.515 min. The retention time detected at 15.716 min corresponds to the IS, 13C-dechlorane.