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Analysis of Non-Extractable DDT-Related Compounds in Riverine Sediments of the Teltow Canal, Berlin, by Pyrolysis and Thermochemolysis

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Eighteen pre-extracted samples derived from a subaquatic riverine sediment core taken from the Teltow Canal, Berlin (Germany), were treated by off-line TMAH-thermochemolysis and subsequently analyzed by GC−MS to investigate release and thermodegradation of non-extractable anthropogenic organic compounds (bound residues). Furthermore, six selected samples from the lower core section were additionally treated by off-line pyrolysis. Due to former investigations of the extractable fraction of Teltow Canal sediments, high amounts of compounds structurally related to the pesticide DDT (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) were anticipated within the nonextractable fraction. It has been shown that DDT-related bound residues can be gathered by pyrolysis and TMAH-thermochemolysis. Among other compounds, the experiments revealed two DDT-related degradation products (DDPU (3,3-bis(4-chlorphenyl)-1-propene) and DDPS (1,1-bis(4-chlorophenyl)propane)) which were detected for the first time in the environment. The latter compounds may represent formerly unknown metabolites or hints for the existence of carbon−carbon incorporated DDT-metabolites. Both methods tend to produce artifacts which complicate the interpretation of the results. With more knowledge on mechanisms occurring during application of pyrolysis and thermochemolysis, both methods can serve as valuable tools for analyzing bound residues in sediments.

Introduction

Direct or indirect emission of anthropogenic organic compounds into aquatic systems results in a complex network of transport, transformation, and adsorption processes occurring in both water and particulate phases (*1*). Adsorption of anthropogenic organic compounds to particulate matter leads to the formation of an extractable fraction and a nonextractable fraction. The latter is characterized by interactions with geomacromolecules, e.g., humic compounds, covering the range from reversible adsorptive or van-der-Waals forces to reversible or irreversible covalent bonds (*2*−*6*). These associations prevent the extraction of such compounds, termed bound residues. Nonextractable compounds can also be encapsulated in humic matrices (*7*, *8*). Within the bound state, the compounds' environmental behavior change compared to the labile fraction. For example, bound residues are principally immobile and of a limited bioavailability. Further details concerning environmental chemical properties of incorporated organic xenobiotics are described elsewhere (*9*, *10*). Bound residues have been investigated extensively in relation to incorporation of pesticides and other organic xenobiotics in soils (*11*−*16*). However, corresponding investigations in aquatic sediments are rare (*10*, *16*). Generally, two types of approaches have been used to obtain information on bound residues in particulate matter. The first approach, nondestructive methods like NMR- and FTIR-spectroscopy, allow to determine covalent interactions between macromolecular organic matter and associated bound residues. This approach is appropriate when using isotope-labeled compounds (*17*−*19*). However, the application of spectroscopy to natural samples has limitations due to overlapping of specific and unspecific background signals and generally low relative amounts of xenobiotic constituents compared to natural compounds. The second approach relies on destructive methods, which bring about the degradation of macromolecular compounds or specific interactions to release associated bound residues for subsequent sensitive analysis by methods such as GC−MS. Destructive methods can be subdivided into chemical and thermochemical approaches. Chemical procedures target specific chemical bonds (e.g., cleavage of ester bonds by acidic or alkaline hydrolysis) providing information on chemical interactions between bound residues and geomacromolecules. More detailed information can be obtained by applying different chemical degradation procedures sequentially (*10*). Thermochemical degradation procedures, such as pyrolysis and thermochemolysis, can provide complementary insights by cleaving bonds that are not affected by chemical degradation techniques.

Schwarzbauer et al. (*10*) investigated bound residues of DDT-(1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) related compounds in sediments of the Teltow Canal, Berlin using both chemical and pyrolytic degradation. The chemical degradation methods revealed numerous DDT-related compounds within the bound fraction. However, on-line pyrolysis provided poor results due to the imperfect chromatographic separation accompanying this analytical technique. Consequently, the goal of the present investigation was to establish off-line pyrolytic methods with subsequent chromatographic fractionation of the solvent-extractable products for GC−MS analysis. Further aims were to screen comprehensively for released DDT-related analytes and to characterize interactions between macromolecular matter and bound residues through interpretation of the structural information obtained during the experiment. Sealed-vessel tetramethylammonium hydroxide thermochemolysis (SV-TMAH-thermochemolysis) and sealed-vessel pyrolysis were considered suitable analytical techniques to reach these objectives. Unlike conventional pyrolysis, TMAH-thermochemolysis facilitates methylation of acidic groups on degradation products generated during the experiment (*20*).

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This methylation facilitates analysis of acidic organic analytes by gas chromatography. Additionally, the alkalinity of TMAH supports thermochemical bond cleavage; consequently, this procedure has also been termed thermally assisted chemolysis (*21*).

TMAH-thermochemolysis was applied in this study for several reasons. First, the method has been successfully applied for degradation of geomacromolecules in organic geochemistry. Second, the method facilitates gas chromatographic detection of acidic compounds, such as bis(4-chlorophenyl)acetic acid (DDA), a quantitatively important metabolite of DDT. TMAH-thermochemolysis was formerly applied primarily in the field of organic geochemistry for the characterization of naturally occurring organic matter in aquatic sediments, peat, or natural waters (*22*−*26*) and also in biological systems (*27*). However, thermochemical degradation with TMAH increases the potential of secondary reactions that can result in artifact generation. Consequently, conventional pyrolysis was also applied in this study to evaluate the degradation characteristics of both methodologies. Heim et al. (*28*) previously investigated the extractable fraction of the same sample set. Dominating DDT-related compounds within this investigation were DDD (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane), DDMS (1-chloro-2,2-bis(4-chlorophenyl)ethane), and DBP (4,4′-dichlorobenzophenone).

Experimental Section

Sampling. The sampling site was situated within the Teltow Canal, Berlin, near a chemical plant which operated in the time of the German Democratic Republic. Production of high tonnages of the insecticide DDT took place at this plant until 1989. More details of the sediments and the sampling site are reported by Heim et al. (*28*). High concentrations of DDT-related compounds in the water and sediment phase of the canal have been described previously (*29*, *30*). Freeze probing facilitated sampling of an undisturbed sediment core of 36 cm length. More details of the sampling technique are described elsewhere (Supporting Information, *31*). The frozen core was cut vertically into 18 samples in 2 cm intervals which were freeze-dried and, thereafter, stored in glass vessels with PTFE seals at +4 °C until extraction.

Chemicals, Reagents, and Syntheses. All chemicals used as reference materials and for synthesis were purchased from Sigma Aldrich (Taufkirchen, Germany) and Merck (Darmstadt, Germany). Before using, solvents were distilled and purity was checked by reducing an aliquot of 50 mL of each solvent to 50 μL and subsequent analysis by GC. Distillation was achieved with a reflective coated 80 cm Vigreux column. The reflux condensor was tempered with a coolstar SC-500 cooling device (resona technics, Gossau, Switzerland) at 10 °C. The reflux ratio was 10:1 (reflux/distillate).

Three reference compounds (bis(4-chlorophenyl)methoxymethane, 3,3-bis(4-chlorophenyl)propene, and 1,1-bis-(4-chlorophenyl)propane) had to be synthesized. Details are given in the Supporting Information.

TMAH-Thermochemolysis, Pyrolysis, Extraction, and Fractionation. Prior to TMAH-thermochemolysis, the samples were extensively preextracted by a 5-step dispersion extraction with different solution mixtures of acetone and *n*-hexane, performed with an Ultra Turrax T25 dispersion device (IKA, Staufen, Germany) at 19 000 rpm. Details of the extraction procedure are described elsewhere (*35*, *36*). An aliquot of approximately 100 mg of each pre-extracted sample was transferred into a DURAN glass tube (8 mm i.d. × 200 mm length). Additionally, 200 μL of a 20% methanolic tetramethylammonium hydroxide (TMAH) solution was added, and the mixture was suspended by shaking the tube gently. Methanol and oxygen were removed by a gentle stream of nitrogen (Westfalengas, Münster, Germany, 99.999%). After sealing the tube by smelting the opening with a Bunsen burner, it was heated for 30 min at 250 °C and, thereafter, cooled to −18 °C. The tube was opened and 1 mL of *n*-hexane was added to the degraded sample residue. The mixture was sonicated for 3 min at 35 kHz with a 120 W Sonorex RK-52 ultrasonic device (Bandelin, Berlin, Germany). After washing the inner vessel surface with *n*-hexane, the extract was decanted into a glass flask. The sample and the vessel surface were washed again with 1 mL of *n*-hexane and the organic solutions were combined. The extraction procedure was repeated with acetone. To the combined solutions, approximately 5 mL of *n*-hexane was added, and acetone was removed by rotary evaporation, followed by drying the resulting *n*-hexane phase with anhydrous Na_2SO_4 (>99%). Before using, the sodium sulfate was Soxhlet-extracted for 12 h with acetone. Pyrolysis procedures were performed similary to the TMAH-thermochemolyses (30 min, 250 °C), but without introduction of TMAH into the glass tubes. The extracts were separated into four fractions on silica gel microcolumns, using mixtures of *n*-pentane, dichloromethane, and methanol as eluates according to Schwarzbauer et al. (*29*). Subsequently, 50 μL of an internal standard mixture, containing d_{34}-hexadecane (5.0 ng/μL), d_{10}-anthracene (5.0 ng/μL), and d_{12}-chrysene (5.0 ng/μL) in *n*-hexane, was added to each fraction. All methanol fractions derived from pyrolysis procedures were treated with a methanolic diazomethane solution to methylate acidic compounds (*10*). The procedure is illustrated in Figure 1, Supporting Information.

Degradation Experiments on Reference Compounds. In order to investigate the question of artifact generation, several reference compounds were treated by TMAH-thermochemolysis as well as pyrolysis in pure state and within a matrix of pre-extracted riverine sediments. DDT, DDD, DDE, DDA, DBP, and DDOH served as reference compounds (see Table 1, Supporting Information). Bis(4-chlorophenyl)methanol (BCMeOH) was additionally considered within thermochemolysis experiments as a potential precurser of bis(4-chlorophenyl)methoxymethane (BCMM) due to methylation by TMAH. Approximately 10 μg of each reference compound was dissolved in *n*-hexane and introduced into a pyrolysis tube. The solvent was evaporated by a nitrogen stream and pyrolysis or thermochemolysis procedures were performed as described above.

For experiments with sediment matrix, riverine sediment not affected by DDT-related compounds and similar in TOC-content and grain size distribution as compared to the Teltow sediment, was pre-extracted as described above. Approximately 100 mg of the preextracted sediment was then transferred into a pyrolysis tube. Thereafter, approximately 10 μg of each single reference compound dissolved in *n*-hexane was spiked on the sediment, respectively. After evaporation of the solvent under a gentle stream of nitrogen, the spiked sediments were treated by pyrolysis or thermochemolysis procedures.

For each degradation experiment, the relative abundance of the total measured analytes of the degradation products was determined under consideration of the compound-specific response factors. Consequently, these values do not represent absolute recoveries. Due to the fact that condensation and rearrangement reactions by pyrolysis are known processes, a significant portion of organic matter has not been considered by the analyses.

Within all four experimental series—thermochemolysis and pyrolysis on pure compounds and spiked sediments—additional blank experiments were performed, which revealed no relevant laboratory contamination.

Gas Chromatography−Mass Spectrometry (GC−MS). Qualitative and quantitative GC−MS analyses were performed on a Finnigan Trace MS single quadrupole mass spectrometer (ThermoElectron, Egelsbach, Germany), operating in impact ionization mode (EI^+, 70 eV) and linked to a HRGC 5160 gas chromatograph (Carlo Erba, Milano, Italy), which was equipped with a 30 m × 0.25 mm i.d. × 0.25 μm film BPX-5 fused silica capillary column (SGE, Australia). Chromatographic conditions were 1−3 μL splitless injection at 60 °C, 3 min hold, then programmed at 3 K/min to 310 °C. The limit of quantification (LOQ) was 0.05 μg/g while the limit of detection (LOD) was 0.01 μg/g. The limits are influenced by compound-specific response factors as well as by sample-specific matrix and noise effects, meaning that the limits differ from sample to sample and from analyte to analyte. For LOQ and LOD, signal-to-noise ratios of 10:1 and 2.5:1 were used, respectively. More details on the GC−MS analyses are given in the Supporting Information.

When using heated injectors for gas chromatography, a possible breakdown of DDT to DDD (1,1-dichloro-2,2-bis-(4-chlorophenyl)ethane) and DDE has been reported (*37*, *38*). In our calibration experiments we quantified the breakdown of DDT below 1%.

Results and Discussion

The experiments revealed several DDT-related compounds which will be presented and discussed. Identified structures are listed in Table 1, Supporting Information.

Degradation Products Obtained by TMAH-Thermochemolysis. Nine DDT-related degradation products were identified, of which some occurred as different structure isomers, mostly 2,4′- and 4,4′-substituted, resulting in detection of 17 different isomers. DDT was not detected. All quantitative data obtained from thermochemolysis experiments are given in Table 1.

The quantitatively most important degradation products were DDM and DDNU. DDM was present at concentrations up to almost 79 μg/g and DDNU was present up to about 20 μg/g. The amounts of DDM and DDNU relative to the total amount of quantified compounds were quite constant (81−93%), in spite of the large range of the total amount of degradation products. These results differ significantly from those of Schwarzbauer et al. (*10*). Within this investigation of subaquatic sediments, also taken from Teltow Canal, DDA (bis(4-chlorophenyl)acetic acid) and DBP were identified as major degradation products in the non-extractable fraction, whereas DDM and DDNU were quantitatively less important.

Other identified compounds were DDEt, DBP, and DDMU, which are all well-known metabolites of DDT. The monochlorinated 4-chlorodiphenylmethane (4-CDM) clearly also shows a structural relation to the DDT metabolites. BCMM, DDPU, and DDPS have not been previously described as DDT-related transformation products. It is reasonable to consider BCMM as a methylated artifact of oxygen-containing degradation products like DBP or bis(4-chlorophenyl)methanol (BCMeOH) due to the presence of TMAH during thermochemolysis. The methoxy group of BCMM indicates a former incorporation by an ether functionality. Generally, the overall distribution patterns of detected degradation products were similar in all 18 samples.

The concentration ranges of the extractable fraction of the samples, investigated by Heim et al. (*28*), are given in Table 2, Supporting Information. Apart from DBP and DDMU, the quantities of all other compounds in post-thermochemolysis extracts were within the same magnitude or higher than the corresponding concentrations in the extractable fraction. Hence, the detected amounts of DBP and DDMU might represent extractable residues.

Structure Elucidation of DDPU and DDPS. Due to the fact that mass spectra of DDPU and DDPS were not available within the digital libraries, structures for these compounds had to be elucidated from their mass spectra. Figure 1 shows the EI^+-spectra as well as the retention behavior of the synthesized reference compounds and the corresponding ones in a sediment sample. These data demonstrate the accordance of sample analytes and reference compounds. Mass spectra of both compounds show the molecular ions (DDPS, $M^+/z = 264$; DDPU, $M^+/z = 262$) and the fluorenyl cation ($m/z = 165$) which is characteristic for most chlorinated diphenylmethane derivates. Additionally, the mass spectrum of DDPS shows a fragmentation leading to the bis(4-chlorophenyl)methyl cation ($m/z = 235$) by loss of an ethyl group followed by loss of two chlorine radicals.

The mass spectra of 2,4′-DDPU and 4,4′-DDPU show no significant differences. They are characterized by sequential abstraction of two chlorine radicals from the molecular ion ($m/z = 227$, 192) and the subsequent loss of a vinyl radical ($\Delta m/z = 27$) resulting in the generation of a flourenyl ion. A distinct structural feature of DDPS and DDPU is the fact that those propane-based compounds contain one carbon atom more than the ethane-based structure of DDT. Possible reasons will be discussed below.

Artifact Generation During TMAH-Thermochemolysis. Synthetic reference compounds of DDT and the most important metabolites, namely 1,1-dichloro-2,2-bis(4-chlorophenyl)ethane (DDD), 1,1-dichloro-2,2-bis-(4-chlorophenyl)ethene (DDE), 2,2-bis(4-chlorophenyl)ethanol (DDOH), DDA, DBP, and additionally bis(4-chlorophenyl)methanol (BCMeOH), were treated by TMAH-thermochemolysis under the same conditions as the sediment samples in order to investigate artifact generation. A first experimental series was performed on pure reference compounds and a second series was performed on pre-extracted spiked sediments to investigate the influence of naturally occurring inorganic and organic matrices on the degradation behavior of the compounds. Results are listed in Table 2.

In order to check the degradation products with extended carbon chains that were found following thermochemolysis of the Teltow sediments, samples 17 and 18 were treated by thermochemolysis in the presence of tetraethlyammonium hydroxide (TEAH), instead of tetramethylammonium hydroxide (TMAH). Within those experiments, DDPS and DDPU were also generated, indicating that these compounds are not the result of transalkylation by TMAH.

With respect to experiments considering thermochemolysis of reference compounds without matrix, degradation products of the majority of compounds were dominated by DDM and DDNU. During thermochemolysis of DDT, DDD and DDE, DDM was generated as the major degradation product with relative contents of more than 70%, respectively. Degradation products of DDOH were dominated by DDNU with a relative content of 55%. Generation of DDNU is possibly preferred as it is a dehydration product of DDOH. DDA was almost quantitatively decarboxylated to DDM; negligible amounts of DDNU were found as a by product. Decarboxylation of several benzoic acid derivates with specific non-halogen ortho- and para-substituents during TMAH-thermochemolysis has been described by Joll et al. (*39*).

Significant amounts of DBP survived thermochemolysis. The main degradation product was BCMM, which was probably generated by electrophilic attack of TMAH on the carbonyl function of the substrate. Bis(4-chlorophenyl)-methanol (BCMeOH) was methylated to bis(4-chlorophenyl)-methoxymethane by transalkylation. BCMeOH has been described as a photodegradation product of DDT in laboratory experiments (*40*). Therefore, DBP as well as BCMeOH are possible precursors of BCMM in the Teltow sediments.

Because there was a general trend of DDT-related compounds (DBP and BCMeOH excepted) to degrade to DDM and DDNU during TMAH-thermochemolysis, the dominance of those compounds within the Teltow sediment thermochemolysis analyses is explainable. Because of their high relative amounts, quantities of the two main degradation

TABLE 1. Quantitative Results of Thermochemolysis Experiments in μg/g Based on Dry Weight (n.d. Means Not Detected)

	sample (depth [cm])																	
	1(2)	2(4)	3(6)	4(8)	5(10)	6(12)	7(14)	8(16)	9(18)	10(20)	11(22)	12(24)	13(26)	14(28)	15(30)	16(32)	17(34)	18(36)
2,2′-DDM	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.1	0.5	0.4	0.2	0.1	0.6	0.4	0.4	0.2	0.4
DDM isomer 2[a]	n.d.	0.1	n.d.	0.1	0.1	n.d.	0.1	0.1	0.1	0.2	0.2	0.1	0.1	0.2	0.2	0.2	0.1	0.2
2,4′-DDM	3	4	3	4	4	6	4	7	3	13	12	5	4	16	12	14	8	11
DDM isomer 4[a]	0.2	0.3	0.2	0.3	0.3	0.3	0.4	0.5	3.0	1	1	0.2	0.2	1	1	1	1	1
4,4′-DDM	13	15	16	20	20	28	22	35	18	57	51	15	12	61	63	58	51	42
Σ(DDM)	**16.3**	**19.5**	**19.3**	**24.5**	**24.5**	**34.5**	**26.6**	**42.8**	**24.3**	**71.7**	**64.6**	**20.5**	**16.4**	**78.8**	**76.6**	**73.6**	**60.3**	**54.6**
2,4′-DDNU	1	1	1	1	1	2	1	2	1	3	4	2	1	4	4	5	3	5
4,4′-DDNU	1	1	1	2	1	1	1	4	1	7	11	2	2	13	4	10	2	15
Σ(DDNU)	**2**	**2**	**2**	**3**	**2**	**3**	**2**	**6**	**2**	**10**	**15**	**4**	**3**	**17**	**8**	**15**	**5**	**20**
4,4′-DDEt	**1.2**	**1.1**	**1.2**	**1.5**	**0.7**	**3.0**	**1.3**	**1.0**	**1.3**	**1.8**	**1.7**	**0.8**	**0.7**	**5.3**	**2.8**	**2.8**	**2.9**	**1.9**
2,4′-DBP	0.1	<0.05	0.3	0.1	0.2	0.1	0.2	0.2	n.d.	0.2	0.1	0.1	0.1	0.2	n.d.	0.1	0.2	0.1
4,4′-DBP	1	0.5	0.5	0.5	0.7	0.1	3	2.0	3	3	3	0.4	0.6	2	0.2	0.4	2	2
Σ(DBP)	**1.1**	**0.5**	**0.8**	**0.6**	**0.9**	**0.2**	**3.2**	**2.2**	**3.0**	**3.2**	**3.1**	**0.5**	**0.7**	**2.2**	**0.2**	**0.5**	**2.2**	**2.1**
2,4′-BCMM	n.d.	0.1	n.d.	0.1	0.1	0.1	0.1	0.2	n.d.	0.3	0.1	0.2	0.1	0.3	0.1	0.4	0.1	0.1
4,4′-BCMM	0.3	0.3	0.2	0.4	1	0.5	1	1	0.3	2	0.7	1	1	2	1	2	1	1
Σ(BCMM)	**0.3**	**0.4**	**0.2**	**0.5**	**1.1**	**0.6**	**1.1**	**1.2**	**0.3**	**2.3**	**0.8**	**1.2**	**1.1**	**2.3**	**1.1**	**2.4**	**1.1**	**1.1**
4,4′-DDMU	**0.1**	**<0.05**	**0.2**	**0.2**	**0.1**	**0.5**	**0.1**	**<0.05**	**0.3**	**<0.05**	**0.2**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.3**	**0.2**	**0.2**
4-CDM	**0.1**	**0.1**	**0.1**	**0.1**	**0.2**	**0.1**	**0.1**	**0.2**	**0.2**	**0.3**	**0.2**	**0.1**	**0.1**	**0.2**	**0.3**	**0.2**	**0.3**	**0.2**
4,4-DDPS	**0.3**	**0.4**	**0.3**	**0.4**	**0.1**	**0.5**	**0.3**	**0.8**	**0.3**	**1.3**	**1.2**	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**0.6**	**1**
2,4′-DDPU	0.2	0.2	n.d.	0.2	0.2	0.3	0.2	0.3	0.2	0.5	0.6	0.2	0.2	0.6	0.5	0.5	0.3	0.4
4,4′-DDPU	1	0.2	0.4	0.4	0.1	n.d.	0.3	0.7	0.2	1	2	0.5	0.3	3	1	1	0.2	2
Σ(DDPU)	**1.2**	**0.4**	**0.4**	**0.6**	**0.3**	**0.3**	**0.5**	**1.0**	**0.4**	**1.5**	**2.6**	**0.7**	**0.5**	**3.6**	**1.5**	**1.5**	**0.5**	**2.4**
total	**22.3**	**24.3**	**24.3**	**31.5**	**29.9**	**42.6**	**35.2**	**55.1**	**32.2**	**92.1**	**89.5**	**27.3**	**22.9**	**109.2**	**90.0**	**95.9**	**73.2**	**83.5**
Σ(DDM+DDNU)/Total	**81%**	**88%**	**87%**	**88%**	**89%**	**88%**	**81%**	**88%**	**82%**	**89%**	**89%**	**88%**	**86%**	**88%**	**93%**	**92%**	**89%**	**89%**

[a] Structure unidentified.

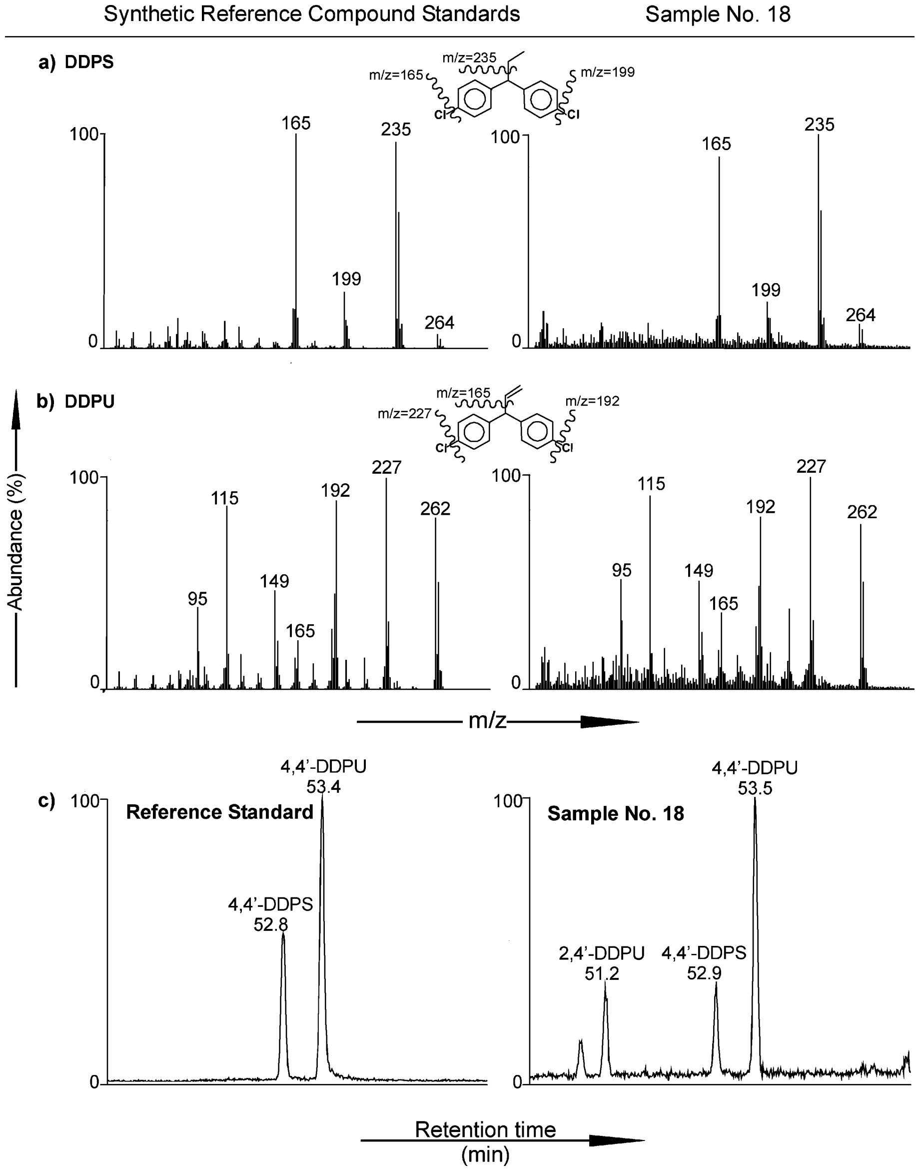

FIGURE 1. Mass spectra of reference compounds and corresponding analytes detected in sample 18 of (a) DDPS and (b) DDPU. (c) GC−MS chromatograms (*m/z* = 264) of the compounds.

TABLE 2. Degradation Products Generated by TMAH-Thermochemolysis of DDT and Important Metabolites (Relative Contributions of the Generated Degradation Products Are Given in Parentheses)

substrate	TMAH-thermochemolysis without matrix	TMAH-thermochemolysis with matrix
DDT	DDM (92%), CDM (3%), BCMM (5%)	DDM (100%)
DDD	DDM (72%), DDNU (24%), CDM (4%)	DDM (100%)
DDE	DDM (80%), DDNU (15%), CDM (4%)	DDM (100%)
DDA	DDM (98%), DDNU (2%)	DDM (100%)
DBP	DBP (15%), BCMM (85%)	DDM (10%), BCMM (95%)
BCMeOH	BCMM (100%)	DDM (5%), BCMM (95%)
DDOH	DDM (34%), DDNU (55%), DDEt (9%), CDM (2%)	DDM (90%), DDNU (10%)

products represent an estimation of the total quantity of DDT-related bound residues. However, detailed structural information is lost. In summary, TMAH-thermochemolysis on pure reference compounds induces artifact generation by abstraction, elimination, etherification, and addition reactions. DDPS and DDPU were not detected within any degradation experiment and, thus, would appear not to be artifacts.

Experiments with spiked sediments, representing an inorganic and organic matrix, revealed similar but more distinct trends concerning artifact generation than experiments on pure compounds (Table 2). DDT, DDD, DDE, and DDA were completely degraded to DDM. Matrix-associated degradation of BCMeOH resulted in products similar to those generated in experiments on pure compounds.

Degradation of DBP revealed no substrate residues. Regarding degradation of DDOH, loss of methanol to DDM dominates over dehydration. As in experiments on pure compounds, DDPS and DDPU were not detected as artifacts (Table 2).

Degradation patterns derived from matrix-associated experiments are characterized by a more intensive degrada-

TABLE 3. Quantitative Results of Pyrolysis Applied on Teltow Canal Sediments in μg/g Based on Dry Weight (n.d. Means Not Detected)

	sample (depth [cm])					
	13(26)	14(28)	15(30)	16(32)	17(34)	18(36)
2,2′-DDM	0.1	2	3	3	n.d.	2
DDM isomer 2[a]	<0.05	1	1	1	0.3	0.5
2,4′-DDM	3	52	50	63	6	42
DDM isomer 4[a]	0.1	3	2	3	n.d.	1
4,4′-DDM	8	150	133	170	16	130
Σ(DDM)	**11.2**	**208**	**188**	**239**	**22.3**	**175.5**
2,2′-DDNU	0.1	0.4	0.3	0.4	n.d.	n.d.
DDNU isomer 2[a]	1	5	4	7	1	5
2,4′-DDNU	2	10	6	10	0.5	4
DDNU isomer 4[a]	2	8	11	23	120	145
4,4′-DDNU	3	16	9	21	1	9
Σ(DDNU)	**8.1**	**39.4**	**30.3**	**61.4**	**122.5**	**163**
4,4′-DDEt	**7**	**40**	**33**	**61**	**9**	**42**
2,4′-DBP	10	20	20	29	8	24
4,4′-DBP	74	106	36	150	25	178
Σ(DBP)	**84**	**126**	**56**	**179**	**33**	**202**
2,4′-DDMU	1	5	2	4	n.d.	1
4,4′-DDMU	1	5	2	4	7	8
Σ(DDMU)	**2**	**10**	**4**	**8**	**7**	**9**
2,2′-DDPU	1	2	2	2	n.d.	1
2,4′-DDPU	1	3	2	2	0.3	2
4,4′-DDPU	2	2	5	4	18	25
Σ(DDPU)	**4**	**7**	**9**	**8**	**18.3**	**28**
2,2′-DDE	0.5	1	1	3	2	7
2,4′-DDE	n.d.	n.d.	n.d.	2	1	1
4,4′-DDE	3	4	6	22	4	34
Σ(DDE)	**3.5**	**5**	**7**	**27**	**7**	**42**
2,2′-DDCN	n.d.	0.5	0.4	0.5	n.d.	n.d.
DDCN isomer 2[a]	n.d.	n.d.	n.d.	0.1	n.d.	n.d.
2,4′-DDCN	1	10	10	12	4	6
DDCN isomer 4[a]	n.d.	0.2	0.2	0.3	n.d.	n.d.
4,4′-DDCN	2	20	23	28	8	9
Σ(DDCN)	**3**	**30.7**	**33.6**	**40.9**	**12**	**15**
total	**122.8**	**466.1**	**360.9**	**624.3**	**231.1**	**676.5**

[a] Structure unidentified.

tion. However, those patterns are not consistent with respect to the results of thermochemolysis experiments of the Teltow Canal sediments. These field sediment data, indicating relative contents of [DDM] + [DDNU] around 85%, are more similar to results derived from the experiments on pure compounds. Even those results are characterized by much higher contents of DDM and DDNU than the analytical results of Teltow Canal sediments.

Degradation Products Obtained by Pyrolysis. Pyrolysis was applied on the lower section of the sediment core (samples 13−18). The experimental results are listed in Table 3. Eight different DDT-related compound groups were detected, some including different isomers; 26 compounds were identified. Quantitatively most important were DDM (11−240 μg/g), DDNU (8−160 μg/g), and DBP (33−200 μg/g). DDEt, DDMU, DDPU, DDE, and DDCN occurred at concentrations between 2 and 41 μg/g. The total of all quantified compounds ranged between 120 and 670 μg/g. Similar to the thermochemolysis experiments, the overall distribution pattern was similar in all six samples. All quantities are higher than or in the same magnitude as the corresponding concentrations in the extractable fraction (see Table 2, Supporting Information) investigated by Heim et al. (*28*).

There are several differences between the results obtained by TMAH-thermochemolysis and pyrolysis. First, the concentrations of DDT-related compounds are significantly higher after pyrolysis, indicating a more effective release of incorporated compounds or less destruction of degradation products compared to the thermochemolysis experiments. Unlike the pattern found in the thermochemolysis experiments, there is no single dominating compound following pyrolysis. The three main degradation products DDM, DDNU, and DBP are quantitatively within the same range. Furthermore, the specific compounds generated by the two methodologies differ. Whereas DDM, DDNU, DDEt, DBP, DDMU, and DDPU were revealed by both techniques, DDE and DDCN were found only after pyrolysis, and BCMM, CDM, and DDPS were generated only by TMAH-thermochemolysis.

As production of BCMM is attributed to reaction of TMAH with oxygen-containing DDT-related structures, the absence of BCMM after pyrolysis is expected. The observation of DDPU in the post-pyrolysis extracts is further confirmation that this compound is not produced by transalkylation of TMAH.

Artifact Generation During Pyrolysis. Analogous to the thermochemolysis artifact generation experiments, degradation of DDT, DDD, DDE, DDA, DBP, and DDOH during pyrolysis was investigated, both as pure compounds and in association with sediment matrix. BCMeOH was not investigated because potential methylation reactions of alcohols are of no relevance when applying pyrolysis. The results are listed in Table 4. Regarding pyrolysis experiments on pure compounds, DDT, DDD, DDE, and DBP remained completely or largely stable. DDA and DDOH were completely degraded to DBP.

The degradation pattern of matrix-associated pyrolysis experiments was different. Whereas DDT, DDE, and DBP also remained largely or entirely unaltered, DDD was completely degraded to DDNU, DDMU, and DBP, and DDA was transformed to DBP. DDPU was not detected within any degradation experiment. As in the thermochemolysis experi-

TABLE 4. Degradation Products Generated by Prolysis of DDT and Important Metabolites (Relative Contributions of the Generated Degradation Products Are Given in Parentheses)

substrate	pyrolysis without matrix	pyrolysis with matrix
DDT	DDT (80%), DDE (20%)	DDT (93%), DBP (7%)
DDD	DDD (80%), DDMU (20%)	DDNU (37%), DDMU (55%), DBP (8%)
DDE	DDE (100%)	DDE (100%)
DDA	DBP (100%)	DBP (100%)
DBP	DBP (100%)	DBP (100%)
DDOH	DBP (100%)	DDNU (22%), DBP (78%)

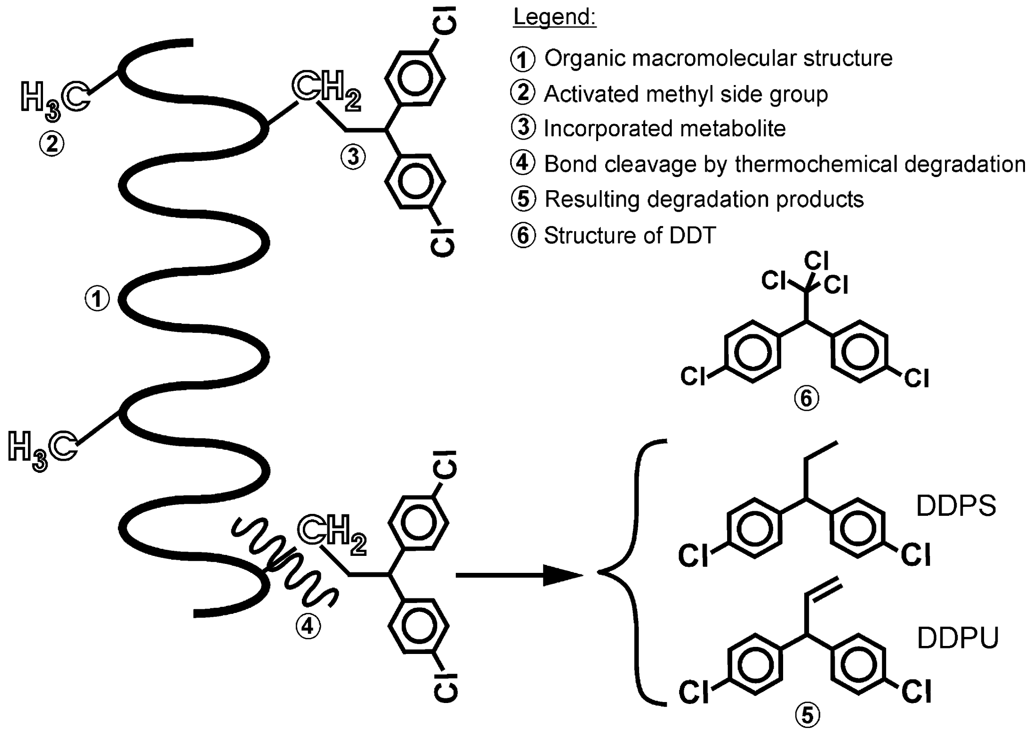

FIGURE 2. Proposed scheme of DDPS and DDPU generation during thermochemical degradation of carbon−carbon incorporated DDT-related metabolites.

ments, matrix-associated pyrolysis experiments are characterized by a more intensive degradation of the substrates.

Apart from the high amounts of DBP, the analytical results for pyrolysis treatments of Teltow Canal sediments (Table 3) are not congruent with the degradation experiments on reference compounds. For example, DDM and DDNU, both quantitatively important compounds in the Teltow sediment pyrolysis extracts did not occur as dominating artifacts within degradation experiments of the reference compounds. At the same time, DDT and DDE were reasonably stable in the reference compound pyrolysis experiments regardless of the presence or absence of the matrix. Therefore, those compounds could be regarded as unaltered bound residues when found in environmental samples. Taken together, the obtained facts indicate that analytical results derived from offline pyrolysis of Teltow Canal sediments are more realistic than those of TMAH-thermochemolysis.

Former investigations of Teltow sediments by Curie-point pyrolysis (*10*, *41*) revealed only two DDT-related compounds (2,4′- and 4,4′-DDM), superimposed by a huge amount of natural pyrolysis products. Other DDT-related compounds were supposably also yielded but not detected because of the complex pyrolysate. Because this pyrolytic approach differed signifficantly from the off-line sealed-vessel pyrolysis, different degradation reactions of DDT-related compounds have to be expected.

Interpretation of Pyrolysis Results. Because fewer artifacts were generated by pyrolysis compared to TMAH-thermochemolysis, the pyrolysis results of Teltow Canal sediments allow some interpretation. The above-mentioned absence of DDM as an artifact within degradation experiments indicates that the analyzed amounts are probably authentic. Similary, DDNU, a possible byproduct of DDOH-degradation, is considered to be dominately authentic. If DDNU was derived from degradation of DDOH in the Teltow sediment, the amount of DBP would be expected to be much higher than it is (Table 3). DDEt was not detected as an artifact and therefore can represent a genuine compound. Due to the artifact generation of DBP from DDA, DBP, and DDOH, DBP would appear to represent the sum of the oxygen-containing metabolites of DDT. DDMU is a potential byproduct of DDD. Due to the relatively low amounts of DDMU detected (Table 3), the authenticity of DDMU generated during pyrolysis cannot be assumed. DDPU, DDCN, and DDE were not recognized as potential artifacts, and can therefore represent authentic compounds. However, the experiments revealed no specific information regarding former modes of incorporation of these compounds.

Potential Origins of DDPU and DDPS. DDPU and DDPS were described for the first time as environmental contaminants within this study. By degradation experiments on reference compounds and by thermochemolysis experiments with TEAH the compounds were proven not to be artifacts. Regarding the structures of the compounds characterized by an additional carbon atom compared to the structure of DDT, two potential origins are conceivable. First, the compounds may represent formerly unrecognized metabolites. However, the potential position within the degradation pathway of DDT-metabolization cannot be acquired by the present information. If the compounds are metabolites, they should be detectable in extracts of DDT-contaminated sediments and also in corresponding nonextractable fractions investigated by chemical degradation procedures.

A second potential origin for the compounds is the possibility that DDPU and DDPS represent a portion of nonextractable DDT-related compounds which was formerly incorporated by carbon−carbon covalent bonds. With respect to this hypothesis, the additional carbon atoms are former moieties of associated macromolecules (Figure 2). Carbon−carbon incorporation is only conceivable on activated carbon atoms within macromolecular structures, near a heteroatom, most likely in α- or β-position. By applying pyrolysis or thermochemolysis on such molecular configurations, cleavage of the activated bond would result in generation of DDT-related species with extended carbon chains. This hypothesis is illustrated in Figure 2. The occurrence of DDPU only in the post-pyrolysis extracts can be a consequence of dehydrogenation of DDPS. The hypothesis concerning carbon−carbon incorporation can only be proven by long-term spiking experiments with isotope-labeled DDT and subsequent analysis by NMR spectroscopy.

Evaluation of the Degradation Methods Applied. Application of both methods, pyrolysis and thermochemolysis, revealed formerly bound residues within the sediment samples investigated. Pyrolysis revealed more detailed structural information due to less artifact production, and is therefore more suitable for analyzing DDT-related bound residues. This might not be the case when analyzing other compound classes. Both methods revealed indications for the existence of carbon−carbon incorporated DDT metabolites as well as for incorporations by ether functionalities. Therefore, both approaches should be applied within future studies. It has been shown that the foremost problems are difficulties of interpreting the results due to artifact generation.

More case studies on different compound classes, other sampling sites, and variable experimental conditions can yield a better understanding of the mechanisms responsible for the structure modifications induced by the methods as well as the influence of matrix effects.

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Supporting Information Available

Sampling, synthesis, and GC−MS details, schematic workflow diagram of the applied analytical procedure, table of quantitative data of extractable DDT-related contaminants, and table of names, structures, and ions used for quanitification of the detected compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Lichtfouse, E., Schwarzbauer, J., Robert, D., Eds. *Environmental Chemistry*; Springer: Heidelberg, 2005.
(2) Senesi, N. Binding mechanisms of pesticides to humic soil substances. *Sci. Total Environ.* **1992**, *123*−*124*, 63−76.
(3) Piccolo, A.; Celano, G.; De Simone, C. Interactions of atrazine with humic substances of different origins and their hydrolysed products. *Sci. Total Environ.* **1992**, *117*−*118*, 403−412.
(4) Kan, A. T.; Fu, G.; Hunter, M. A.; Tomson, M. B. Irreversible adsorption of naphthalene and tertrachlorobiphenyl to Lula and Surrogate sediments. *Environ. Sci. Technol.* **1997**, *31*, 2176−2185.
(5) Klaus, U.; Oesterreich, T.; Volk, M.; Spiteller, M. Interaction of aquatic dissolved organic matter (DOM) with amitrole: the nature of bound residues. *Acta Hydrochim. Hydrobiol.* **1998**, *26*, 311−317.
(6) Nanny, M. A. Deuterium NMR characterization of non-covalent interactions between monoaromatic compounds and fulvic acids. *Org. Geochem.* **1999**, *30*, 901−909.
(7) Lichtfouse, E.; Wehrung, P.; Albrecht, P. Plant wax n-alkanes trapped in soil humin by noncovalent bonds. *Naturwissenschaften* **1998**, *85*, 449−452.
(8) Lichtfouse, E. Temporal pools of individual organic substances in soil. *Analusis* **1999**, *27*, 442−444.
(9) Northcott, G. L.; Jones, K. C. Experimental approaches and analytical techniques for determining organic compounds bound residues in soil and sediment. *Environ. Pollut.* **2000**, *108*, 19−43.
(10) Schwarzbauer, J.; Ricking, M.; Littke, R. DDT-related compounds bound to the nonextractable particulate matter in sediments of the Teltow Canal, Germany. *Environ. Sci. Technol.* **2003**, *37*, 488−495.
(11) Boul, H. M.; Garnham, M. L. G.; Hucker, D.; Baird, D.; Alslable, J. Influence of agricultural practices on the levels of DDT and its residues in soil. *Environ. Sci. Technol.* **1994**, *28*, 1397−1402.
(12) Khan, S. U. Bound pesticide residues in soil and plants. *Residue Rev.* **1982**, 1−25.
(13) Liechtenstein, E. P. Bound residues in soils and transfer of soil residues in crops. *Residue Rev.* **1980**, *76*, 147−155.
(14) Liechtenstein, E. P.; Katan, J.; Anderegg, B. N. Binding of persistent and nonpersistent ^{14}C-labeled insecticides in an agricultural soil. *J. Agric. Food Chem.* **1977**, *25*, 43−47.
(15) Wheeler, W. B.; Stratton, G. D.; Twilley, R. R.; Ou, L. T.; Carlson, D. A.; Davidson, J. M. Trifluralin degradation and binding in soil. *J. Agric. Food Chem.* **1979**, *27*, 702−706.
(16) Richnow, H. H.; Seifert, R.; Hefter, J.; Kästner, M.; Mahro, B.; Michaelis, W. Metabolites of xenobiotica and mineral oil constituents linked to macromolecular matter in polluted environments. *Org. Geochem.* **1994**, *22*, 671−681.
(17) Berns, A.; Vinken, R.; Bertmer, M.; Breitschwerdt, A.; Schäffer, A. Use of ^{15}N-depleted artificial compost in bound residue studies. *Chemosphere* **2005**, *59*, 649−658.
(18) Knicker, H. Incorporation of ^{15}N-TNT transformation products into humifying plant organic matter as revealed by one- and two-dimensional solid state NMR spectroscopy. *Sci. Total Environ.* **2003**, *1*−*3*, 211−220.
(19) Käcker, T.; Haupt, E. T. K.; Garms, C.; Francke, W.; Steinhard, H. Structural characterization of humic acid-bound PAH residues in soil by ^{13}C-DPMAS-NMR-spectroscopy: evidence of covalent bonds. *Chemosphere* **2002**, *48*, 117−131.
(20) Challinor, J. M. The scope of pyrolysis methylation reactions. *J. Anal. Appl. Pyrolysis* **1991**, *20*, 15−24.
(21) Kralert, P. G.; Alexander, R.; Kagi, R. I. An investigation of polar constituents in kerogen and coal using pyrolysis-gas chromatography-mass spectrometry with in situ methylation. *Org. Geochem.* **1995**, *23*, 627−639.
(22) Pulchan, J.; Abrajano, T. A.; Helleur, R. Chrarcterization of tetramethylammonium hydroxide thermochemolysis products of near-shore marine sediments using gas chromatography/mass spectrometry and gas chromatography/combustion/isotope ratio mass spectrometry. *J. Anal. Appl. Pyrolysis* **1997**, *42*, 135−150.
(23) Pulchan, K. J.; Helleur, R.; Abrajano, T. A. TMAH thermochemolysis characterization of marine sedimentary organic matter in Newfoundland fjord. *Org. Geochem.* **2003**, *34*, 305−317.
(24) Garcette-Lepecq, A.; Largeau, C.; Bouloubassi, I.; Derenne, S.; Saliot, A.; Lorre, A.; Point, V. Lipids and their modes of occurrence in two surface sediments from the Danube delta and northwestern Black Sea: Implications for sources and early diagenetic alteration. *Org. Geochem.* **2004**, *35*, 959−980.
(25) Guignard, L.; Lemée, L.; Amblès, A. Lipid constituents of peat humic acids and humin. Distinction from directly extractable bitumen components using TMAH and TEAc thermochemolysis. *Org. Geochem.* **2005**, *36*, 287−297.
(26) Frazier, S. W.; Nowack, K. O.; Goins, K. M.; Cannon, F. S.; Kaplan, L. A.; Hatcher, P. G. Characterization of organic matter from natural waters using tetramethylammonium hydroxide thermochemolysis GC-MS. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 99−128.
(27) Briggs, M. K.; Desavis, E.; Mazzer, P. A.; Sunoj, R. B.; Hatcher, S. A.; Hadad, C. M.; Hatcher, P. G. A new approach to evaluating the extend of Micheal adduct formation to PAH quinones:

Tetramethylammonium hydroxide (TMAH) thermochemolysis with GC/MS. *Chem. Res. Toxicol.* **2003**, *16*, 1484−1492.
(28) Heim, S.; Ricking, M.; Schwarzbauer, J.; Littke, R. Halogenated compounds in a dated sediment core of the Teltow Canal, Berlin: Time related sediment contamination. *Chemosphere* **2005**, *61*, 1427−1438.
(29) Schwarzbauer, J.; Ricking, M.; Franke, S.; Francke, W. Halogenated organic contaminants in sediments of the Havel and Spree rivers (Germany). Part 5 of organic compounds as contaminants of the Elbe river and its tributaries. *Environ. Sci. Technol.* **2001**, *35*, 4015−4025.
(30) Heberer, T.; Dünnbier, U. DDT Metabolite bis(chlorophenyl)-acetic acid: The neglected environmental contaminant. *Environ. Sci. Technol.* **1999**, *33*, 2346−2351.
(31) Ricking, M.; Schulze, T. Deep-freeze sampling methods for soft sediments. In *Contaminated Sediments: Characterization, Evaluation, Migration/Restoration and Management Strategy Performance*; Locat, J., Galves-Cloutier, R., Chaney, R.C., Demars, K.R., Eds.; ASTM International: West Conshohocken, PA, 2003.
(32) Namboodiri, V. V.; Varma, R. S. Iron-catalyzed solvent-free conversion of alcohols and phenols into diphenylmethyl (DPM) ethers. *Tetrahedron Lett.* **2002**, *43*, 4593−4595.
(33) Schwarzbauer, J.; Franke, S.; Francke, W. Chlorinated di- and triphenylmethanes in sediments of the Mulde and Elbe rivers. *Fresenius' J. Anal. Chem.* **1999**, *365*, 529−536.
(34) Nystrom, R. F.; Berger, C. R. A. Reduction of organic compounds by mixed hydrides. II. Hydrogenolysis of ketones and alcohols. *J. Am. Chem. Soc.* **1958**, *80*, 2896−2898.
(35) Franke, S.; Schwarzbauer, J.; Francke, W. Arylesters of alkylsulfonic acids in sediments. *Fresenius' J. Anal. Chem.* **1998**, *360*, 580−588.
(36) Schwarzbauer, J.; Littke, R.; Weigelt, V. Identification of specific organic contaminants for estimating the contribution of the Elbe river to the pollution of the German Bight. *Org. Geochem.* **2000**, *31*, 1717−1731.
(37) Gferer, M.; Lankmayr, E. DDT degradation during enhanced solid-liquid extractions. A consideration. *J. Chromatogr., A* **2005**, *1072*, 117−125.
(38) Foreman, W. T.; Gates, P. M. Matrix-Enhanced Degradation of *p,p′*-DDT during Gas Chromatographic Analysis: A Consideration. *Environ. Sci. Technol.* **1997**, *31*, 905−910.
(39) Joll, C. A.; Huynh, T.; Heitz, A. Off-line tetramethylammonium hydroxide thermochemolysis of model compound aliphatic and aromatic carboxylic acids. *J. Anal. Appl. Pyrolysis* **2003**, *70*, 151−167.
(40) Llompart, M.; Lores, M.; Lourido, M.; Sinches-Prado, L.; Cela, R. On-fiber photodegradation after solid-phase microextraction of p,p′-DDT and two of its major photoproducts, p,p′-DDE and p,p′-DDD. *J. Chromatogr., A* **2003**, *985*, 175−183.
(41) Schwarzbauer, J.; Ricking, M.; Gieren, B.; Keller, R.; Littke, R. Anthropogenic organic contaminants incorporated into the non extractable particulate matter of riverine sediments from the Teltow Canal (Berlin). In *Environmental Chemistry, Green Chemistry and Pollutants in Ecosystems*; Lichtfouse, E., Schwarzbauer, J., Robert, D., Eds.; Springer: Heidelberg, 2005; pp 329−352.

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