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ORIGINAL PAPER

The effect of distribution processes on the isomeric composition of hexachlorocyclohexane in a contaminated riverine system

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Abstract Various factors influence the isomeric composition of hexachlorocyclohexanes which are released to the environment. Original compositions in technical mixtures may vary slightly, but higher shifts are observable for transfer processes, bioaccumulation and microbial transformation. Consequently, the isomeric composition in environmental samples is a superposition of these processes. In this study, isomeric distributions and concentrations of hexachlorocyclohexanes were analyzed in water, sediment, and soil samples of a riverine system known to be highly contaminated by hexachlorocyclohexanes. To assess desorption of hexachlorocyclohexanes from particulate matter to water, batch shaking and percolation experiments were conducted complementary. Analyzed samples exhibited total hexachlorocyclohexane concentrations of up to 2.8 µg/g in sediments and up to 21 µg/L in river water predominated by the α-isomer. Downstream hexachlorocyclohexane pattern changed toward δ-isomer domination, while overall hexachlorocyclohexane concentrations decreased. Desorption experiments supported the assumption of discrimination by preferred association of the α- and β-isomers with particulate matter, showing elevated mobilization of γ-, δ- and ε-hexachlorocyclohexanes and lower mobilization of the α- and β-isomers. Soil samples of a riparian wetland exhibited elevated concentrations of hexachlorocyclohexanes exceeding 200 µg/g and predominance of α-hexachlorocyclohexanes in the top soil layer. Subjacent soil layers showed rapidly decreasing hexachlorocyclohexane concentrations and an isomeric shift toward the β-isomer. The assumed preferential mobilization of β-hexachlorocyclohexane was supported by desorption experiments. This study demonstrated firstly that transfer processes influence substantially hexachlorocyclohexane isomer distribution in the aquatic environment. Secondly, conditions of aging determine strength of association and remobilization potential of hexachlorocyclohexane residue down to an isomer-specific level.

Keywords Distribution processes · Hexachlorocyclohexane · Isomer-specific · Lindane · Persistent organic pollutant

Introduction

Hexachlorocyclohexanes (HCHs) represent a group of persistent organic pollutants (POP) consisting of the eight isomers of 1,2,3,4,5,6-hexachlorocyclohexane. Five of these isomers (see Figure S1, supplement material)—α-HCH, β-HCH, γ-HCH, δ-HCH and ε-HCH—are of high environmental relevance according to the Stockholm Convention Annex A. HCHs have been used for decades as pesticides. Although only γ-HCH exhibits insecticidal properties, isomeric mixtures as yielded by technical synthesis were applied dominantly in the initial time period

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after the Second World War. Later on after 1950, purified γ-HCH (trade name: Lindane) was produced and applied until its termination of production in the majority of countries [e.g., in West Germany (1984) and in East Germany 1989]. Currently, it is still used in some Asian and African countries, e.g., India (Ali et al. 2014; Sharma et al. 2014).

Technical synthesis of HCH by chlorination of benzene using UV radiation yields a mixture (technical HCH) of five stereoisomers with a typical composition of 60–70 % α-HCH, 5–12 % β-HCH, 10–12 % γ-HCH, 6–10 % δ-HCH and 3–4 % ε-HCH (Willett et al. 1998; Walker et al. 1999). In-depth examinations of structural properties of HCH are described by Li et al. (2011b). Different chemical and physical properties such as the environmentally relevant partition coefficient K_{OW} and water solubility S_{WL} are caused by the stereochemical orientation of the chlorine atoms around the cyclohexane ring (see Table 1). While α-HCH is much more soluble in water than the β- and γ-isomers, this difference is not visible in the corresponding K_{OW} value. Higher variation is observable for the Henry's law constants with a significant lower value for the β-isomer. The environmental fate of each HCH isomer is influenced by these differences in the partition coefficients and solubility.

HCHs are of high environmental relevance due to their high persistence, their tendency for bioaccumulation and their (eco-)toxicological effects (Bhatt et al. 2009; Olivero-Verbel et al. 2011; Stockholm Convention on POPs). Certain isomers (α-HCH and γ-HCH) are known for their global, air-bound migration (Wania and Mackay 1996), whereas other isomers (β-HCH but also α-HCH) tend to bioaccumulate due to their lipophilic character (Willett et al. 1998; Kumar et al. 2006). Some isomers exhibit elevated toxicity (γ-HCH) in aquatic environments (Oliveira and Paumgartten 1997) and even carcinogenic potential (Zou and Matsumura 2003). These diverse patterns of behavior are caused by slightly deviating physical–chemical properties, and therefore, an isomer-specific observation of HCHs in the environment is an important issue.

Numerous studies were performed on the occurrence of HCHs in various environmental compartments such as air (e.g., Karlsson et al. 2000; Ding et al. 2007), soil (e.g., Manz et al. 2001; Schwartz et al. 2006), sediment (e.g., Heim et al. 2005; Ricking and Schwarzbauer 2008; Li et al. 2011a), water (e.g., Heemken et al. 2000), plants (e.g., Abhilash et al. 2008) and animals (e.g., Marth et al. 1997; Willett et al. 1998). Most of these studies focused either on selected isomers or on reported cumulated concentrations of all HCH isomers. Individual quantitative data for all environmentally relevant isomers have been published to a minor extent only. In some studies, specific values were reported only for selected main isomers (e.g., Gandrass and Zoll 1996; Marth et al. 1997; Heemken et al. 2000; Franke et al. 2005), whereas other studies solely reported cumulative values of HCHs (e.g., Wilken et al. 1994).

However, it is known that isomeric patterns of HCH deviate between but also within environmental compartments (e.g., Manz et al. 2001; Heinisch et al. 2005; Abhilash et al. 2008). The variation in isomer patterns is related to different environmental processes. On the one hand, transfer and transport processes can be responsible for isomer discrimination. Several studies reported HCH patterns dominated by α-HCH or β-HCH in sediment and soil, whereas α-HCH and γ-HCH constitute the major isomers found in airborne particulate matter (e.g., Bhatt et al. 2009). These distribution trends are illustrated by HCH patterns detected in various environmental compartments at Lake Baikal (Iwata et al. 1995).

On the other hand, biotic transformation by bacteria discriminates HCH isomers by preferred transformation of certain isomers. Various studies on HCH transformation by bacteria showed β-HCH to be more resistant to degradation under aerobic conditions as compared to the other isomers (Bhatt et al. 2009).

Further on, the comparatively small concentrations of γ-HCH in terrestrial and freshwater environmental compartments are due to its fast transformation, isomerization (Bachmann et al. 1988; Wu et al. 1997) and its higher tendency to evaporate, respectively. Emissions from industrial waste derived from purification processes of raw HCH mixtures also have a very low γ-HCH content. Further on, due to its relatively short half-life compared to the other isomers, high concentrations of γ-HCH within HCH

Table 1 Physical–chemical properties of the most environmental prevalent HCH isomers as described by Xiao et al. (2004)

	S_{WL} (mol/m^3)	S_{OL} (mol/m^3)	logK_{OW}	logK_{OA}	H (Pa m^3/mol)	P_L (Pa)
α-HCH	1.44	2870	3.94	7.46	0.735	0.245
β-HCH	0.333	11,800	3.91	8.74	0.037	0.0529
γ-HCH	0.247	1680	3.83	7.74	0.306	0.0757

Data sets for δ- and ε-HCHs were not available for the author

S_{WL}, S_{OL} and P_L refer to liquid state

S_{WL} water solubility, S_{OL} octanol solubility, K_{OW} octanol/water partition coefficient, K_{OA} octanol/air partition coefficient, H Henry's law constant (air–water), P_L vapor pressure patterns detected in natural samples indicate recent emission but exclude historical contamination (Ding et al. 2007). Regarding the occurrence of γ-HCH, it has been suggested that Lindane may have been used preferentially in urban areas, while technical HCH was applied almost exclusively as an insecticide in agriculture (Venier and Hites 2014).

Various studies have been performed on metabolization (Macrae et al. 1967; Willett et al. 1998; Rodriguez-Garrido et al. 2004; Li et al. 2011b) and isomerization (Huhnerfuss et al. 1992; Wu et al. 1997; Phillips et al. 2005) of HCH isomers under different environmental conditions (redox environment, biotic/abiotic). Slightly different biotic transformations under aerobic and anaerobic conditions were proposed involving stepwise dechlorination to less chlorinated derivatives such as pentachlorocylohexene (e.g., Bachmann et al. 1988; Rodriguez-Garrido et al. 2004; Phillips et al. 2005; Ricking and Schwarzbauer 2008; Bhatt et al. 2009; Li et al. 2011b). Hydrolysis was reported as the dominant abiotic degradation pathway for HCHs (Bhatt et al. 2009).

In summary, various factors are influencing the isomeric composition of HCHs released to the environment. The original composition in technical mixtures may vary slightly, but higher shifts are observable for transfer processes, bioaccumulation and microbial transformation. Consequently, the isomeric composition in environmental samples is a superposition of these processes.

This study is a systematic analysis of the effect of environmental distribution processes on HCH composition in the aquatic environment. To achieve this objective, several environmental samples were taken from the riverine system of the Spittelwasser creek downstream of the former industrial area of Bitterfeld–Wolfen (Germany) in October 2012. Sediments, wetland soils, and surface water of this highly contaminated aquatic ecosystem were analyzed with respect to their isomer-specific HCH contamination. The water body, sediments, and wetlands of the Spittelwasser creek and the Mulde River system at Bitterfeld–Wolfen are well known for their high HCH pollution (Franke et al. 2005; Schwartz et al. 2006). At two chemical plants of the chemical–industrial complex *Elektrochemisches Kombinat Bitterfeld* upstream of the Spittelwasser creek Lindane was produced on an industrial scale from 1951 to 1982 at the times of the GDR (East Germany). Waste material from Lindane purification by recrystallization was dumped in former opencast pits creating a highly complex multipoint, almost diffuse source situation in this region. Until now, after 25 years of ceased production, high concentrations of HCH can be found in environmental compartments downstream of the industrial complex (e.g., Schwartz et al. 2006; Kolarikova et al. 2013). Being a tributary river to the Elbe River, the water quality of Germany's third largest river (Kolarikova et al. 2013), adjacent farmland as well as the North Sea (Huhnerfuss et al. 1997) has been affected by this contamination as well.

Complementary laboratory experiments were conducted to study the influence of isolated transfer and transport processes on HCH isomers and to simulate discrete natural processes such as flooding or remobilization of riverine sediments.

Materials and methods

Sample material

Samples were taken in October 2012 at various locations shown in Fig. 1 and Table 2 around Jeßnitz, north of Bitterfeld–Wolfen and the former industrial complexes. Three types of samples were taken to characterize the system: water samples, sediment samples, and soil samples from flooding areas. Two riverine systems are present in this area. The Schachtgraben canal is an approximately 3-km-

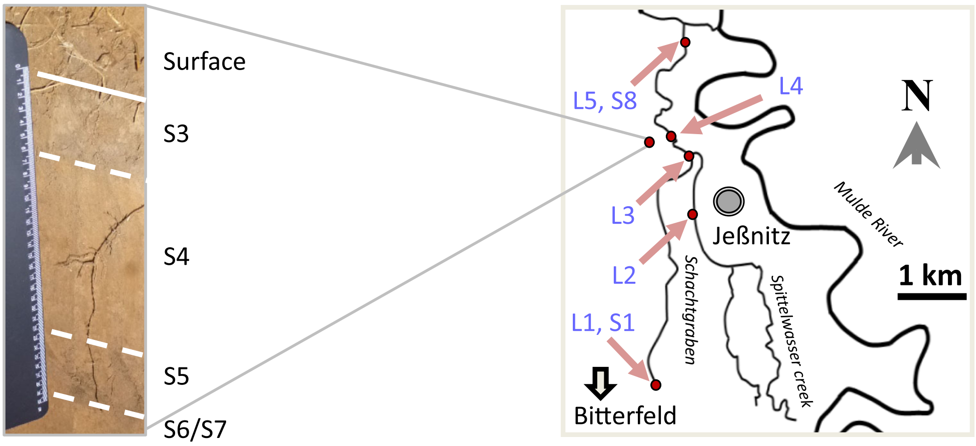


Fig. 1 Soil profile (*left*)—full scale indicates 30 cm, *continuous line* marks surface border, and *dotted lines* mark border between visual distinguishable soil layers. Map of sampling area (*right*)—*red dots* indicate sampling point and associated sample number (see Table 2)

Table 2 Samples of the area Bitterfeld–Wolfen and their characterization by TOC and dry matter content

	Sample no.	Description	TOC (%)	Dry matter (%)
Particulate matter	S1	Sediment—outlet Schachtgraben	13.4	21.6
	S2	Soil—riparian wetland	11.0	81.2
	S3	Soil—sampling depth 0–6 cm	10.0	83.3
	S4	Soil—sampling depth 6–24 cm	5.5	83.8
	S5	Soil—sampling depth 24–30 cm	4.2	82.6
	S6	Soil—sampling depth 30–40 cm	2.5	85.9
	S7	Soil—sampling depth 40 cm	2.3	85.8
	S8	Sediment—isolated pond	4.1	41.2
Water	L1	Outlet Schachtgraben		
	L2	Spittelwasser near Jeßnitz		
	L3	Schachtgraben prior joining Spittelwasser		
	L4	Spittelwasser near riparian wetland		
	L5	Isolated pond		
	W1	Industrial HCH waste		

long canal originally set up to drain opencast pits and industrial wastewater. Nowadays, drainage water from dumps and further unknown sources within the area of former chemical plants are discharged (Schmidt et al. 2008). The Spittelwasser creek was subject to a similar fate in the past, and both recipients of the Mulde River and later the Elbe River are therefore still affected by the chemical industry. Water samples were taken at five different locations. The Schachtgraben canal was represented by samples L1 and L3 located at the beginning, respectively, the end of the canal. Water from this canal exhibited a red-brownish color. In particular at the beginning, a high quantity of suspended particulate matter as a result of elevated iron hydroxide precipitation was observed. This observation pointed to a high contribution of anaerobic mine drainage water in the Schachtgraben canal water. The Spittelwasser creek was characterized by sample L2 prior the confluence with the Schachtgraben canal, sample L4 after inflow of the Schachtgraben canal, and sample L5, a pond fed by the Spittelwasser creek during flood events.

Two types of particulate matter were investigated in the Spittelwasser creek/Mulde River system: Sediment samples representing perpetual subaquatic particulate matter and soil samples only exposed sporadically to riverine water. The soils samples were included in this study, since during flood events remobilized sediment material can be deposited in large amounts on adjacent riparian wetlands. Sample S1 was a representative sediment from the Schachtgraben canal. At time of sampling, no fine-grained sediment was present in the Spittelwasser creek. Hence, sediment sample S8 was taken from a small, isolated pond next to the Spittelwasser creek, which is sporadically connected to the river. Thus, this sample can be characterized as a subaquatic deposit of the corresponding riverine sediments.

For batch desorption experiments, sample S2 was taken from the upper 20 cm of a test pit. To further investigate possible depth-dependent changes in HCH concentrations, a soil profile from a riparian wetland next to the Spittelwasser creek (samples S3–S7) was taken by sampling individual soil layers according to their color and texture shown in Fig. 1.

Soil and sediment samples were analyzed for TOC and dry matter content (see Table 2). Two representative samples were further characterized by their particle-size distribution (see supplement material Table S2).

Water samples L1–L5 were taken and stored in four 1 L glass flasks per sampling point at 4 °C in the dark. Soil profile samples S3–S7 were stored in 250 mL glass flasks with Teflon-lined screw caps. Sediment samples S1 and S8 and soil sample S2 were stored in sealable buckets. For comparison, a sample of matured industrial HCH waste W1 was provided by local authority. This waste was deposited for a prolonged period (minimum since ceased production of technical HCH in Bitterfeld–Wolfen over 25 years ago).

Extraction and fractionation

From each sampling point, 2 L water samples were processed in portions of 1 L, respectively. Each 1 L aliquot was extracted using sequential liquid–liquid extraction (according to Franke et al. 1995) with 50 mL of *n*-pentane, 50 mL of DCM and 50 mL of DCM after acidification to pH 2 using conc. HCl. After each extraction step, the organic phase was separated via separating funnel. For quantification, 50 µL of a surrogate standard mixture consisting of fluoroacetophenone (7.2 ng/µL), decafluorobenzophenone (7.0 ng/µL) and d_{34}-hexadecane (6.0 ng/µL) was then added to the first two extracts. To the third extract, 200 µL of a different surrogate standard mixture consisting of fluoroacetophenone (7.2 ng/µL), decafluorobenzophenone (7.0 ng/µL) and difluorophenylacetic acid (5.0 ng/µL) was added. Then, the extracts were concentrated to approx. 5 mL by a rotary evaporator at ambient temperature and dried by filtration over anhydrous sodium sulfate. Thereafter, each two aliquots per sequentially processed extract was combined and concentrated to a final volume of ca. 50 µL at ambient temperature.

Soil and sediment subsamples of 10 g were extracted by sequential ultrasonic agitation (according to Ricking and Schwarzbauer 2008) with 100 mL acetone and 100 mL *n*-hexane. Each extraction step involved 15-min treatment by ultrasonication followed by a stirring period of 1 h and a second 15-min treatment by ultrasonication. Then, the samples were stirred overnight. The organic phase was separated from the dispersed solid material by centrifugation. The organic extracts were combined in a separating funnel, subsequently concentrated to a volume of approx. 5 mL by a rotary evaporator at ambient temperature and then dried by filtration over anhydrous sodium sulfate. After further concentration to approx. 1 mL, activated copper powder was added and the sample was treated by ultrasonic agitation for 15 min and left overnight in a refrigerator.

Soil and sediment extracts were fractionated using glass microcolumns packed with approx. 2 g of activated silica gel (particle size 40 µm, dried overnight at 200 °C). The fractionation was carried out by stepwise elution of 5 mL *n*-pentane, 8.5 mL *n*-pentane/DCM 95:5 (v/v), 5 mL *n*-pentane/DCM 90:10 (v/v), 5 mL *n*-pentane/DCM 40:60 (v/v), 5 mL DCM and 5 mL MeOH, respectively. For quantification, 50 µL of a surrogate standard mixture consisting of fluoroacetophenone (7.2 ng/µL), decafluorobenzophenone (7.0 ng/µL) and deuterohexadecane (6.0 ng/µL) was then added to fractions 1–5. The fractions were then concentrated to 50 µL at ambient temperature. HCHs were detected in fractions 3–5 of soil and sediment samples and extracts 1 and 2 of water samples.

Batch desorption experiments

Batch desorption experiments were conducted using samples S2, S8 and W1. In a first setup, 0.5 L Spree river water (Berlin) water was added to 250 g of wet sample material (S2, S8). The mixture was shaken with 7 rpm in an end-over-end-tumbler at 22 °C. After 2 h, 24 h and 2 weeks, the samples were centrifuged (10 min at 670×*g*) and the liquid phase was replaced.

In a second smaller setup considering the much higher concentrations of HCH pollutants in the waste sample W1, 40 mL Spree river water (Berlin) was added to 50 mg (W1) and 40 g (wet S2) sample material, respectively, for the purpose of comparison to the first setup. The mixture was shaken with 7 rpm in an overhead shaker. After 4 h, 24 h, 1 week and 2 weeks, the samples were centrifuged and the liquid phase was replaced. This procedure was performed four times, and corresponding water samples were combined due to difficulties in separating solid waste and water phase resulting in approx. 150 mL water samples per sampling point. All experiments were conducted in PE flasks. No sorption effects were observed.

Resulting water samples were filtered through 0.45 µm filter (Macherey–Nagel MN GF-5, Germany) prior to analysis using the method described above. Results from the second-batch desorption experiment with soil sample S2 supported conclusions of first-batch desorption experiment using soil sample S2 and are therefore not described further.

Percolation experiments

Percolation experiments were conducted using samples S2 and S8. A column (stainless steel, 30 cm × 10 cm i.d.) was packed with fine stainless steel gauze, 200 g aquarium gravel and 200 g of wet sample material (S2/S8) on top. Elution was done by gravity using 1 L Spree river water (Berlin) as eluent (roughly equivalent to 1/10th of average local annual precipitation). The percolation experiment with waste sample W1 was conducted using 884 mg sample sealed with 100 g uncontaminated sand above 300 g aquarium gravel under the same conditions as sample S2 and S8. Portions of 100 mL eluate were taken and analyzed using the method described above.

Gas chromatographic mass spectrometric analyses, GC/MS

GC/MS analyses of soil profile samples S3–S7 were carried out on a double-focusing sector field mass spectrometer Finnigan MAT 95 (Finnigan MAT, USA) linked to a Modell 5890 Series II gas chromatograph (Hewlett Packard, USA) equipped with a 30 m × 0.25 mm i.d. × 0.25 µm ZB-1 fused silica capillary column (Phenomenex Inc., USA). One microliter of sample was injected as split/splitless injection with an injector temperature of 270 °C and a splitless time of 60 s. The GC oven was programmed from hold for 3 min and then heated to 310 °C with a rate of 5 °C/min. Final isothermal time was 20 min. The mass spectrometer was operated in electron impact ionization mode (EI^+, 70 eV) in low-resolution scanning from 35 to 700 amu at a rate of 1.0 scans/decade and an interscan time of 0.1 s. The source temperature was held at 200 °C. Helium carrier gas velocity was approximately 30 cm/s.

GC/MS analyses of water, sediment and non-profile soil samples were carried out on a Trace MS quadrupole mass spectrometer (ThermoQuest, Italy) linked to a Trace GC gas chromatograph (ThermoQuest, UK) with a 30 m × 0.25 mm i.d. × 0.25 µm ZB-XLB fused silica capillary column (Phenomenex Inc., USA) under the chromatographic conditions described above. The mass spectrometer was operated in electron impact ionization mode (EI^+, 70 eV) in low-resolution scanning from 35 to 700 amu at a scan rate of 1.5 scans/s. The source temperature was held at 200 °C. Helium carrier gas velocity was approximately 40 cm/s.

Quantification

HCH isomers were quantified by integration of the ion chromatograms 217 and 219 *m/z*. Retention order of HCH isomers were confirmed by a defined standard mixture of HCH isomers as following: α-HCH, β-HCH, γ-HCH, δ-HCH, ε-HCH (ZB-1-type column) and α-HCH, γ-HCH, β-HCH, δ-HCH, ε-HCH (ZB-XLB-type column). Quantification was carried out by an external four-point calibration using reference compounds (values for ε-HCH were derived from mean values of aforementioned HCH isomers). For correction of injection volume and sample volume inaccuracies, the results were corrected based on the surrogate standard d_{34} hexadecane. Reproducibility and analytical accuracy were tested by recovery experiments at least in triplicate (according to Dsikowitzky et al. 2002) to ensure analytical quality. Recovery rates for HCH in soil and sediment samples were determined by extraction of pre-extracted sediment samples spiked with HCH reference compounds and subsequent extraction and fractionation as described above (recovery rates and abs. STD: α-HCH (54 % ± 8), β-HCH (66 % ± 10), γ-HCH (60 % ± 10), δ-HCH (58 % ± 10), ε-HCH (59 ± 10); values for ε-HCH derived from mean values of aforementioned HCH isomers). Recovery rates of HCHs in water samples were determined by extraction of water spiked with HCH reference compounds and subsequent extraction as described above (recovery rates and abs. STD: α-HCH (113 % ± 19), β-HCH 111 % ± 26), γ-HCH (119 % ± 17), δ-HCH (104 % ± 32), ε-HCH (112 ± 20); values for ε-HCH derived from mean values of aforementioned HCH isomers). Recovery rates were considered for quantitative data reported. All data of particulate matter are given on dry matter basis.

Results and discussion

Sediment and water samples

All quantitative results obtained for sediment and water samples are summarized in Table 3. Maximum values of total HCHs were approx. 2800 ng/g in sediments and approx. 21 µg/L in water.

Analyses of water samples revealed diverse isomeric patterns of HCHs throughout the examined area (see Fig. 2). At the outlet of the Schachtgraben canal L1, the runoff HCH pattern was strongly dominated by α-HCH (87 %) accompanied by 10 % β-HCH. Occurrence of other isomers was negligible. Besides changes in isomeric patterns, also changes in HCH concentrations were observed. Concentrations of dominant isomers, especially α-HCH, were exceptionally high in comparison with the other investigated water samples (see Table 3). Prior to joining the Spittelwasser creek at L3, the isomeric pattern shifted dramatically to a dominance of δ-HCH (38 %) followed by α- and β-HCHs both with approx. 24 %. This change in the isomer pattern was the result of decreasing concentrations of α-HCH (by a factor of 100) and β-HCH (by a factor of 10), respectively. Complementary, the remaining three isomers γ-, δ- and ε-HCHs exhibited no decrease in concentration over the canal's distance.

The Spittelwasser creek at L2 showed only a negligible contamination of HCH (see Table 3) with low concentrations of δ-HCH and evenly distributed α- and β-HCHs. After the confluence of the Spittelwasser creek and Schachtgraben canal, only a minor shift in the HCH pattern toward a slight dominance of α-HCH and even distributed β- and δ-HCH isomers was observed in the combined water body at L4. Between sample points L3 and L4, no change in HCH concentration occurred. The isomeric pattern in the pond water L5 exhibited a completely different distribution. Here, the pattern was predominated by β-HCH (62 %) followed by 20 % of α-HCH and a significant percentage

Table 3 HCH concentrations in sediment and water samples from Schachtgraben canal and Spittelwasser creek (concentration in ng/L for water samples and ng/g for sediment samples)

Sample no.	α-HCH	β-HCH	γ-HCH	δ-HCH	ε-HCH	Σ-HCH
S1	210	130	4	13	11	368
S8	1800	740	110	61	120	2831
L1	18,000	2200	86	390	120	20,796
L2	28	25	n.d.	n.d.	n.d.	53
L3	130	130	24	200	45	529
L4	190	140	16	140	40	526
L5	48	150	n.d.	7	40	245

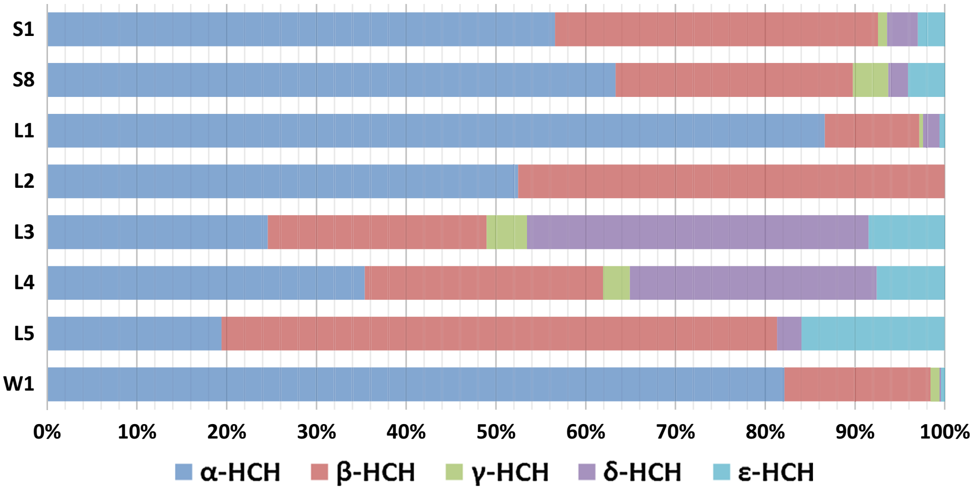


Fig. 2 HCH composition in water and sediment samples (*S1*, *S8*, *L1*–*L5* and *W1*)

of ε-HCH. It is worth mentioning that concentrations of β- and ε-HCHs were nearly constant in L3, L4 and L5, while there was a notable decrease in concentration of α-, γ- and δ-HCHs between L3/L4 and L5. Former studies have shown that a roughly equal outflow rate can be assumed for both water bodies (Jacobs et al. 2013) represented in our study by sampling locations L2 and L3. However, the accordingly expected decrease in HCH concentration by factor of 0.5 at sampling point L4, representing the combined water bodies, was not observed. The lack of dilution effects might be attributed to an incomplete mixing of both bodies even 450 m after their confluence.

Analyses of sediment samples revealed only minor differences in HCH isomer patterns. Both sediments S1 and S8 were dominated by α-HCH followed by β-HCH and minor percentages of the other isomers. Concentrations of total HCH increased by roughly a factor of 10 in S8 relative to S1.

Since the isomeric pattern at L1 (and to a lower extend at S1) was nearly identical to a pattern found in matured industrial HCH waste W1 (see Fig. 2), a close linkage can be assumed. A dramatic shift in the isomeric pattern was observed as the water body moves downstream. The clear decrease in α- and β-HCHs and simultaneously lack of decrease in the other remaining isomers between L1 and L3 points to a process primarily affecting the two dominant isomers of which α-HCH is reduced in amounts ten times higher than β-HCH. Interaction with particulate matter can be an explanation since the Schachtgraben canal exhibited elevated amounts of suspended matter in the form of iron hydroxides. Hence, adsorption or co-precipitation might lead to a favorable association of α- and β-isomers with the newly formed particulate matter.

As already mentioned, no fine-grained sediment was present in the Spittelwasser creek. Thus, the water–particle interaction is limited between L3 and L4 explaining the nearly unchanged isomeric pattern at L4. Contributions to a shift in the HCH pattern from contaminations of the Spittelwasser creek L2 prior to the joining of the Schachtgraben canal were negligible.

Although sediment of the stagnant water pond S8 exhibited the same pattern as the Schachtgraben canal sediment S1, the corresponding water sample L5 showed a completely different β-HCH-dominated isomeric pattern. This discrepancy is most likely caused by a steady runoff of fresh contamination from the Schachtgraben canal outlet and more extensive interaction with fluviatile sediment versus an almost equilibrium state between limnic sediment and corresponding water in the stagnant water pond.

To simulate the desorption processes, the transfer from particulate matter to surrounding water (mobilization), batch desorption experiments with material from sediment S8 were conducted. Results are shown in Table 4. Initially, only small amounts of α-, β-, γ- and δ-HCHs, but a noticeable amount of ε-HCH, were transferred to the liquid phase within the first 2 h. After 24 h, the amounts of mobilized α- and β-HCHs increased by a factor of 10, while the mobilization of γ-, δ- and ε-HCHs remained constant. Lastly, after 2 weeks, further increase in mobilization of α-HCH and to a lower extent of β-HCH and γ-HCH was observed, while δ- and ε-HCH still remained constant. Net mobilization values were calculated by dividing the sum of individual HCH isomer content in all water aliquots by the sum of the content in the residual sediment and all water aliquots. Thus, a percentage value of mobilized HCH throughout the experiment was obtained. In contrast to the mobilization of α-HCH and β-HCH (exhibiting comparatively low mobilization rates below 1 %), higher mobilization rates (between 1.8 and 6.1 %) for γ-, δ- and ε-HCHs were observed. Further on, a distinct dynamic behavior in mobilization of α-HCH and β-HCH was visible, while γ-, δ- and ε-HCHs showed a

Table 4 Results for batch desorption experiments from sediment sample S8 and soil sample S2

Sediment S8	HCH in water phases of the batch experiment				HCH in sediment after the batch experiments	Mobilization[a]
	2 h	24 h	2 weeks	Σ-HCH$_{water}$	Σ-HCH$_{solid\ residue}$	(%)
α-HCH	26	360	1800	2200	270,000	0.8
β-HCH	21	120	590	730	110,000	0.7
γ-HCH	12	65	130	200	11,000	1.8
δ-HCH	90	57	82	230	9700	2.3
ε-HCH	560	910	750	2200	34,000	6.1
Σ-HCH	709	1512	3352	5560	434,700	1.3

Soil S2	HCH in water phases of the batch experiment				HCH in soil after the batch experiments	Mobilization[a]
	2 h	24 h	2 weeks	Σ-HCH$_{water}$	Σ-HCH$_{soil\ residue}$	(%)
α-HCH	2100	2800	2400	7300	1,200,000	0.6
β-HCH	25,000	22,000	34,000	82,000	2,000,000	3.9
γ-HCH	190	240	230	650	120,000	0.5
δ-HCH	180	200	370	760	83,000	0.9
ε-HCH	470	530	780	1800	94,000	1.9
Σ-HCH	27,940	25,770	37,780	92,510	3,497,000	2.6

Values of HCH contents are given in ng

[a] Mobilization $= \Sigma\text{-HCH}_{water}/(\Sigma\text{-HCH}_{water} + \Sigma\text{-HCH}_{solid\ residue}) \times 100$

continuous mobilization rate. Opposing, a higher transfer rate from the water body to particulate matter for α-HCH and β-HCH as compared to the other HCH isomers can be deduced from the batch desorption experiments. This supports well the observed behavior of α-HCH and β-HCH between L1 and L3 in the Schachtgraben canal where these isomers were depleted to a higher extent from the water phase.

In water and sediment compartments, detected HCH patterns were subject to superimposition with other environmental processes. Physical processes such as evaporation are governed by physical properties of the individual HCH isomer (see Table 1). At the water–air-phase boundary, preferred evaporation of α-HCH and γ-HCH over β-HCH is implied by their higher vapor pressure and Henry's law constant. It can be assumed that additional HCH transfer processes at water–sediment-phase boundary are very similar to the water-suspended matter interaction previously described by the conducted laboratory experiments. Complementary chemical processes include degradation and isomerization of HCHs. Both abiotic and biotic degradation pathways of HCHs were observed (Bhatt et al. 2009). Briefly, isomers of lower chlorinated cyclohexane derivatives such as pentachlorocyclohexene are formed by hydrolysis of HCHs (Li et al. 2011b), the preferred abiotic degradation pathway. This hydrolysis is triggered by the potential of *anti*-elimination within the cyclic molecular system (Rodriguez-Garrido et al. 2004). Consequently, higher reactivity of α-HCH and γ-HCH over β-HCH can be assumed. Biotic degradation of HCHs was observed under aerobic (aqueous-phase) and anaerobic (sediment-phase) conditions (Phillips et al. 2005), and numerous pathways were proposed (Li et al. 2011b). General isomeric tendency to degradation is similar to abiotic reactions. Bioisomerization of γ-HCH to α-HCH or β-HCH was described (Walker et al. 1999). In addition, under laboratory conditions, isomerization by photolysis was observed (Malaiyandi et al. 1982). However, only minor contributions from these other processes to the overall isomeric HCH distribution is assumed according to our results. Physical processes and degradation within the aqueous phase were not able to change drastically the isomeric HCH pattern in the creek between sample points L3 and L4, as well as in sediments between sample points S1 and S8.

Industrial HCH waste

Sample W1 (see Fig. 2) consisted of HCH waste derived from the purification process of technical HCH and was therefore γ-HCH-depleted. Small amounts of the γ-isomer were still present in this sample. Theoretically, isomerization to γ-HCH from other HCH isomers is possible as a single study reported (Deo et al. 1980), but the applied condition in that study (shaking in distilled water) is unlikely to be found in natural systems. Further reports suggest α-HCH and/or β-HCH as preferred transformation products from bioisomerization of γ-HCH (Walker et al. 1999).

Table 5 Results for batch desorption experiments from waste sample W1

	HCH in water phases of the batch experiment					HCH in waste after the batch experiments	Mobilization[a]
	4 h	24 h	1 week	2 weeks	Σ-HCH_{water}	Σ-$HCH_{waste\ residue}$	(%)
α-HCH	170	86	72	66	394	50,300	0.8
β-HCH	17	9.6	6	5.6	38	15,300	0.2
γ-HCH	170	88	53	31	342	1040	24.7
δ-HCH	39	29	21	8	97	180	35.0
ε-HCH	10	4.8	2.7	2.2	20	680	2.8
	406	217	155	113	891	67,500	1.3

Values of HCH content are given in µg

[a] Mobilization = $\Sigma\text{-HCH}_{water}/(\Sigma\text{-HCH}_{water} + \Sigma\text{-HCH}_{waste\ residue}) \times 100$

Thus, traces of residual γ-HCH illustrate an incomplete separation of HCH isomers by the HCH purification process.

To simulate initial mobilization by water contact, batch desorption experiments with sample W1 were performed and results are shown in Table 5. Analyses of obtained water samples showed patterns dominated by α- and γ-HCHs, whereas α-HCH dominated the pattern of residual waste after the experiment. After 24 h, the highest amount of transferred HCH was observed in the α- and γ-isomers, whereas only small amounts of β-HCH, δ-HCH and ε-HCH were dissolved. Thereafter, all isomers exhibited decreased mobilization. Compared to the initial 4-h interaction with water, the following longer interaction periods removed less HCH from sample material. After 2 weeks, only 20–40 % of initial amount of HCHs were dissolved. Net mobilizations were calculated as described before. Highest mobilization rates were determined for γ-HCH and δ-HCH high (25 and 35 %, respectively). The other isomers exhibited much lower mobilization by a factor of 10 for ε-HCH and a factor of 100 for α-HCH and β-HCH. Therefore, it can be assumed that α-HCH and γ-HCH mobilize initially to a greater extent than β-HCH, δ-HCH and ε-HCH, although comparatively small amounts of δ-HCH are readily transferred to the interacting water. Longer wastewater contact (during flood events) can be assumed to result in α-HCH-dominated wastewater/leaching water by depletion of the higher mobile γ- and δ-isomers.

Soil samples and percolation

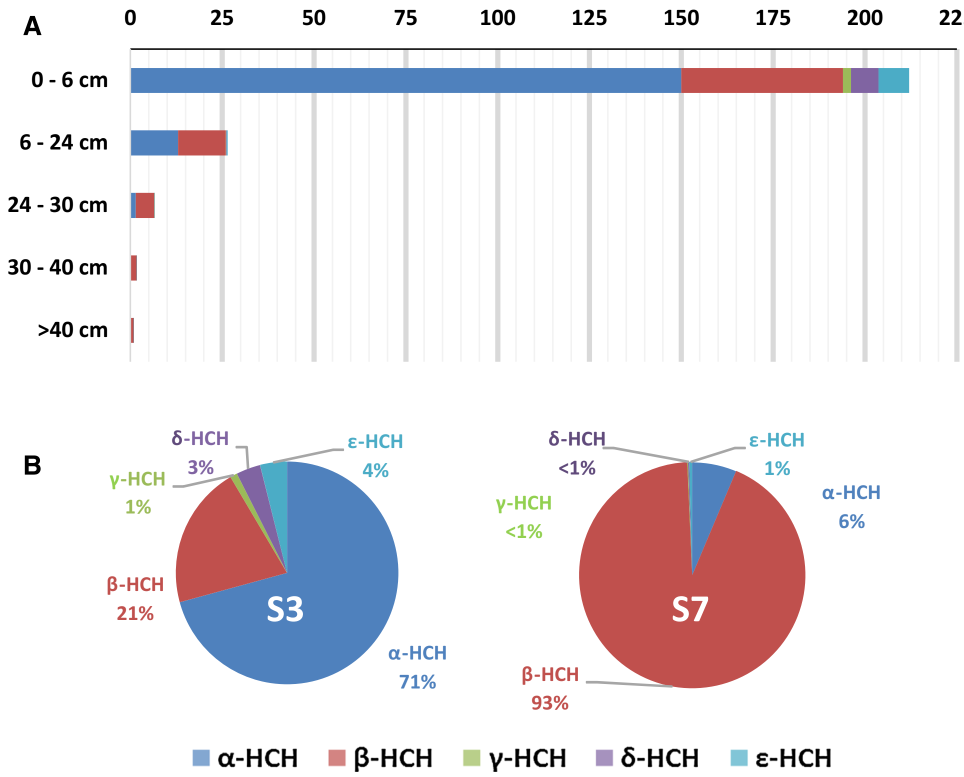
The status of HCH contamination with increasing depth was assessed by analysis of a taken soil profile S3-S7. Five soil layers were separated according to changes in color and texture. The overall HCH concentration in the top layer S1 was very high reaching over 200 µg/g soil. A rapid decrease in HCH concentration was observed toward subjacent layers (S4–S7) with values down to 30 µg/g soil in the second layer (see Fig. 3a).

A HCH pattern (see Fig. 3b) very similar to the industrial waste W1 and sediment samples S1 and S8 was exhibited in the top layer S3. Here, α-HCH predominated followed by β-HCH. With increasing depth, a shift in the isomeric pattern of the HCH contamination occurred. In the second layer S4, the β-isomer became predominant followed by α-HCH (see Fig. 3a). With increasing depth, the isomeric HCH pattern shifted toward β-HCH domination reaching more than 90 % in the bottom layers and only small amounts of the other HCH isomers shown in Fig. 3b.

An isomeric discrimination by preferred transport of β-HCH into deeper soil layers is indicated by both this noticeable isomers shift and the exponential depletion of HCH concentration with increasing depth. Aside from transport processes simulated by desorption and percolation experiments, HCH isomers in soil are subject to discrimination by other processes. The initial alluvial deposit is subject to evaporation and photolysis as described previously. Furthermore, metabolization/biodegradation of HCH isomers by soil bacteria was observed by various authors (Bhatt et al. 2009). Aerobic biodegradations of HCHs in soil are well investigated for the bacteria *Sphingomonadaceae* (Pal et al. 2005). Degradation of HCHs is enabled by the exoenzymes LinA and LinB (Nagata et al. 1999; Suar et al. 2005; Raina et al. 2007; Bala et al. 2012; Geueke et al. 2013). Degradation thereby forms isomer-specific metabolization products such as pentachlorocyclohexene for α-HCH and γ-HCH and pentachlorocyclohexane-1-ol for β-HCH and δ-HCH. Degradation of the most recalcitrant HCH isomer, the β-HCH, is only achieved by LinB, whereas LinA is able to degrade the other isomers. Therefore, a superimposition of the similar biodegradation pattern and percolation/mobilization pattern is suggested.

A second type of riverine particulate matter contaminated with HCHs in Bitterfeld–Wolfen area was represented by soils of riparian wetlands. This environmental

Fig. 3 **a** Isomeric HCH distribution and concentration in a soil profile of a riparian wetland near Bitterfeld–Wolfen. Values are given in µg/g d.w. **b** Comparison of isomeric HCH distributions in soil layers S3 (*left*) and S7 (*right*)



compartment is built up by deposition of contaminated sediments during flood events. In this particular system, wetlands and Spittelwasser creek are flooded frequently by the Mulde River. During rain events, wetland pollutants can be mobilized by percolating water through the unsaturated soil zone toward the groundwater.

The initial mobilization step was simulated by batch desorption experiments similar to sediment using sample S2 as representative (see Table 4). Significant mobilization of α-HCH and even to a greater extent of β-HCH was already observed after 2 h of interaction. Mobilization of β-HCH, δ-HCH and ε-HCH increased slightly over the course of the experiment, while α-HCH and γ-HCH remained constant. Mobilization was dominated by β-HCH and α-HCH with a factor of 100 and 10, respectively. Net mobilization values were calculated as described above. High mobilization rates were observed for β-HCH and ε-HCH, low rates for α-HCH, γ-HCH and δ-HCH. In contrast to batch desorption experiments involving sediment samples, much lower dynamic behavior was observed in mobilization of HCH from soil samples. After 2 h, the concentration of mobilized HCH already reached its maximum values. A distinct difference between mobilization in soil and mobilization in sediments is obvious. Therefore, water interacting with soil is likely to show a β-HCH-dominated HCH pattern. Further implication of this result will be discussed later.

For simulating the leaching of HCH contaminants into deeper soil layers, a percolation experiment with soil sample S2 was conducted. Over the course of the experiment, no significant change in the isomeric pattern of eluted water samples was observed (see Fig. 4a). Resulting patterns were strongly dominated by β-HCH (75–95 %) followed by a minor percentage of α-HCH (1–18 %) and ε-HCH (1–4 %). Other isomers were eluted to a lesser amount (<1 %). Results from the percolation experiment on soil indicate a preferred desorption of β-HCH and subsequent transport to deeper soil layers by water. This observation supports not only experimental data from batch desorption experiments (higher mobilization of β-HCH in soil) but also the analyses of HCH content in soil layers (β-isomer-dominated HCH patterns in deeper soil layers). The other HCH isomers were in contrast much less mobile and will therefore stay more adsorbed to particulate soil matter. Depletion of β-HCH in upper soil layers and a shift in the HCH pattern toward remaining isomers is implied.

After flood events, deposited contaminated sediments on riparian wetlands are also subject to rinsing out, e.g., by rainfall. These events were simulated by percolation experiment with sediment sample S8 (see Fig. 4b). Over the course of this experiment, HCH patterns of eluted water samples showed an increase in ε-HCH content (49–82 %), an almost constant leaching of δ-HCH (∼4 %), a slight decrease in β-HCH (15–7 %) and a stronger decrease in α-

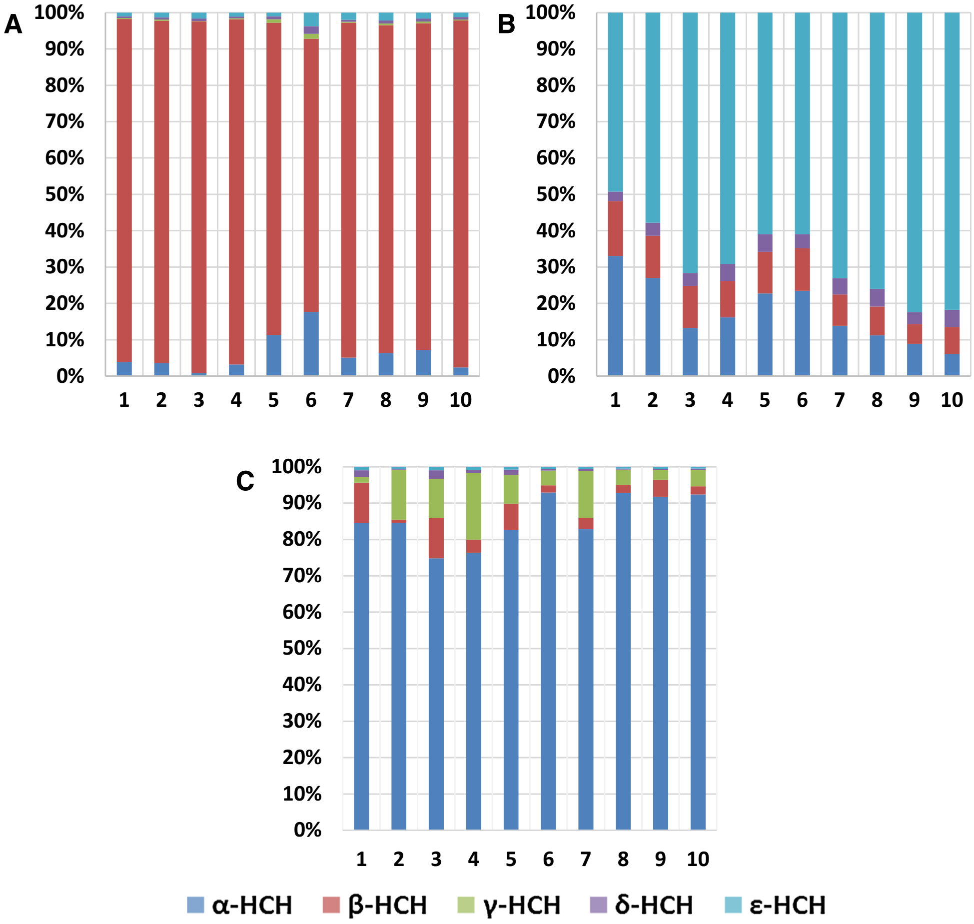


Fig. 4 Isomeric HCH distribution in eluted water samples of a percolation experiment using **a** soil sample S2, **b** sediment sample S8 and **c** waste sample W1. Each pattern represents a step of 100 mL eluted water for a total of 1 L

HCH (33–6 %). The γ-isomer was not detected in any of the eluates. Preferred desorption of ε-HCH increasing over time is suggested by the results from percolation experiment using sediment. A subsequent transport of ε-HCH in subjacent soil can be assumed. Initial mobilization of α- and β-HCHs decreased over time. These observations were different to the results obtained from percolation experiment applied to the soil sample.

Combined results point to an increased transport of ε-HCH from accumulated polluted sediments into subjacent riparian wetland soil after a flood event. Thereafter, further transfer of ε-HCH and β-HCH into groundwater may occur as indicated by elevated mobilization rates.

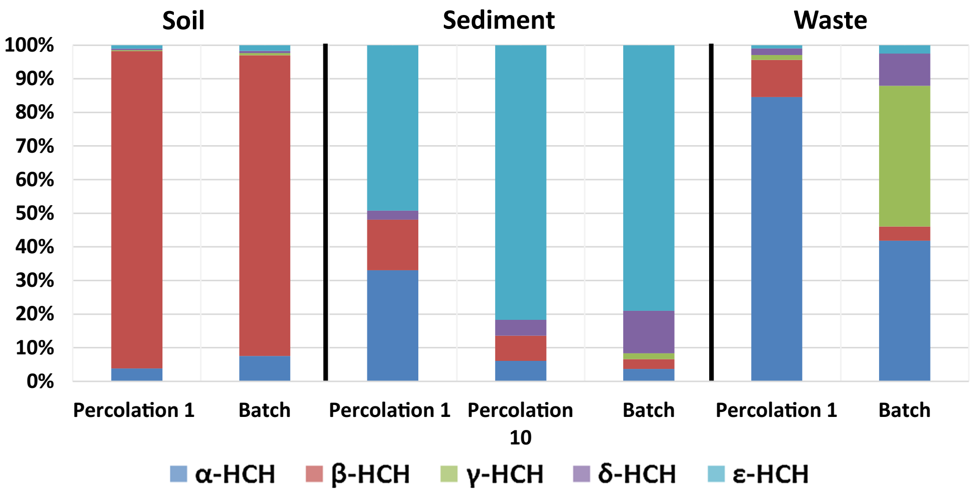
For simulating the leaching of HCH contaminants directly from buried industrial waste of HCH residues, a percolation experiment with waste sample W1 was conducted. Over the course of the experiment, no significant change in the isomeric pattern in eluted water samples was observed (see Fig. 4c). Resulting patterns were strongly dominated by α-HCH (75–93 %) followed by a minor percentage of γ-HCH (1–18 %) and β-HCH (1–11 %). Other isomers were eluted to a lesser amount (~1 %). Results from the percolation experiment on this matured HCH waste indicate a preferred desorption of α-HCH and subsequent transport to subjacent soil layers. In contrast to batch desorption experiments with waste sample W1, γ-HCH was eluted to a lesser extent. It can be assumed that much shorter interactions with water during elution in percolation experiments compared to batch desorption experiments impede equilibrium of HCH in water/waste and therefore discriminate desorption and solubility of γ-HCH.

In comparison with water sample L1, batch desorption experiments with waste sample W1 showed elevated amounts of γ-HCH transferred to the water phase. Patterns of leaching water from corresponding percolation experiment (see Fig. 4c) showed a similar α-HCH domination relative to water sample L1. However, amounts of the β- and γ-isomers did not match. Therefore, the water sample L1 does not represent direct leaching water from this composition of industrial HCH waste.

Comparison of HCH behavior in sediment, soil and waste

The conducted laboratory experiments revealed main differences in amount and distribution of HCH isomers as

Fig. 5 Comparison of the outcome of batch desorption and percolation experiments using different samples types: soil S2 (*left*), sediment S8 (*middle*) and HCH waste W1 (*right*)



well as temporal changes in mobilization rates between subaquatic sediment and terrestrial soil. This is astonishing since both environmental compartments originate from the same riverine particulate matter (see Fig. 5). On the one hand, experiments with the soil sample resulted in β-HCH-dominated patterns and no change in composition of eluted HCH patterns over the time course of the percolation experiment and fast increasing mobilization rates with time toward constant values. On the other hand, experiments with the sediment sample showed ε-HCH-dominated patterns with an increasing contribution of ε-HCH in the eluted HCH pattern and slow increasing mobilization rates with time toward constant values. A third experimental behavior was observed in the industrial HCH waste. Over the time course of the HCH waste percolation experiment, α-isomer-dominated HCH patterns were eluted with no change in isomeric distribution, whereas slow decreasing mobilization rates with time toward constant values were observed.

In summary, experimental setups with three types of sample material resulted in different HCH patterns as well as a different mobilization rate. Obviously, the observed differences are related to the type of sample and the corresponding interaction with the HCH contamination. Aging, describing changes in properties of environmental contaminants over time due to different environmental conditions (e.g., level of oxygen, pH value, exposure to light, type and quantity of microbacteria) strongly influences association and mobilization of HCHs. Prolonged aging under terrestrial conditions (e.g., with elevated levels of oxygen and higher exposure to light) results in a weaker association of HCH with particulate matter indicated by a faster mobilization toward a steady state than aging under subaquatic conditions. Despite differences in content and quality of TOC and particle size (Table 2, Table S2), no correlation was illustrated with Σ-HCH or selected isomers.

Conclusion

Results from desorption experiments support the observation in the natural system. In the Schachtgraben canal, a strong depletion of α- and β-HCHs was observed, whereas these isomers exhibit the weakest mobilization in the batch desorption experiments; thus, a strong adsorption to particulate matter can be assumed. Furthermore, as concentrations of HCH in water are much lower than in sediment, small changes in particulate matter composition (SOM, clay minerals, hydroxides) and amount have huge impact on the HCH isomer distribution in the corresponding water phase. Both analyses of the natural system and the batch desorption experiments revealed water-suspended matter interaction to be a dominant factor in composition of the isomeric pattern whereby adsorption of α- and β-HCHs is preferred over y-, δ- and ε-HCHs.

In soils, a depth-dependent decrease in concentration and a shift from α- to β-HCH predomination were observed. Laboratory experiments support the assumption of an isomeric discrimination by preferred desorption of β-HCH and subsequent leaching in subjacent soil layers resulting in a weaker adsorption of β-HCH to terrestrial particulate matter.

Environmental conditions seem to be responsible for the different behaviors of HCH contaminations in different environmental matrices. Variations in aging conditions (subaquatic, terrestrial) change the strength of association of HCH with particulate matter. This result not only in different mobilization rates in total but also in preferential mobilization of individual isomers depending on the type of matrix.

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