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Hexachlorocyclohexane derivatives in industrial waste and samples from a contaminated riverine system

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HIGHLIGHTS

- HCH derivatives were detected in samples of a contaminated riverine system.
- PeCCH and HpCCH aggregate mainly in riparian wetland soil isomeric patterns found in soil were similar to patterns found in HCH waste.
- HpCCH proved useful as emission source tracer for industrial waste emissions.

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ABSTRACT

Side and initial degradation products of the persistent organic pollutant hexachlorocyclohexane (HCH) were largely neglected in environmental analysis so far. However, these compounds can be indicative for biodegradation or emission sources.

Thus, several samples from a contaminated riverine system in vicinity to a former HCH production site in Central Germany were analyzed. This area adjacent to the industrial megasite Bitterfeld-Wolfen is known for elevated concentrations of various organic industrial pollutants as legacy of decades of industrial activity and subsequent deposition of chemical waste and emission of waste effluents. In environmental compartments of this riverine system, several isomers of HCH related compounds were detected comprising the two lower chlorinated species tetrachlorocyclohexene (TeCCH) and pentachlorocyclohexene (PeCCH) and the higher chlorinated species heptachlorocyclohexane (HpCCH). Except for the uppermost soil of an analyzed riparian wetland, concentrations of these compounds were low. Detected isomers in sediment, water, and soil samples correlated and dominant isomers of PeCCH and HpCCH were observed in the alluvial deposits. Comparisons with industrial HCH waste revealed isomeric patterns similar to patterns found in soil samples. Therefore, the application of HpCCH as an indicator of industrial HCH pollution is suggested.

1. Introduction

Persistent organic pollutants are of major concern in environmental analyses and were target of numerous investigations in the past. Hexachlorocyclohexanes (HCH) are a group of compounds well known for their persistence in environmental compartments and toxicity to humans and animals (Bhatt et al., 2009). They have been classified as persistent organic pollutants (POP) by the Stockholm Convention (Stockholm Convention on POPs). Although, production and application were phased out in most countries beginning from the 1970s and 1980s, residues from manufacture and utilization still impact the quality of environmental compartments worldwide (e.g. Kolarikova et al., 2013; Ricking and Schwarzbauer, 2008; Schwartz et al., 2006; Venier and Hites, 2014; Walker et al., 1999; Wu et al., 1997a).

Technical synthesis of HCH on industrial scale involves chlorination of benzene catalyzed by UV radiation. The resulting mixture of eight isomers, technical HCH, contains around 10–12% of the desired isomer γ-HCH (lindane), the only isomer showing pesticidal properties. Pure lindane is obtained by subsequent

Abbreviations: HCH, hexachlorocyclohexane; TeCCH, tetrachlorocyclohexene; PeCCH, pentachlorocyclohexene; HpCCH, heptachlorocyclohexane; OcCCH, Octachlorocyclohexane.

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recrystallization of technical HCH. Thus, technical synthesis generates around 8–10 t waste isomers for every ton of target isomer. Investigations of HCH contaminations focused so far on quantification and isomeric distribution. By nature of the highly non-selective chlorination of the benzene ring, possible synthesis side products are either higher chlorinated cyclohexanes, such as up to 5% hepta- and octachlorocyclohexanes (Schulze and Weiser, 1983), or less chlorinated compounds like tetra- and pentachlorocyclohexenes. These side products of the lindane production were also removed during recrystallization and likely deposited alongside the HCH waste. In addition to contaminations originating from the application of lindane and technical HCH as pesticides e.g. in agriculture and forestry, these disposed waste isomers pose a significant risk to the environment (Wycisk et al., 2003). Noteworthy, the less chlorinated compounds tetra- and pentachlorocyclohexenes are thus far largely considered as anaerobic and aerobic degradation products of HCHs, respectively (Li et al., 2011; Phillips et al., 2005; Rodriguez-Garrido et al., 2010). Therefore, it can be assumed that the naturally occurring pollutant patterns of these compounds consist of a superimposition of originally synthesized compounds and products of biotic and abiotic degradation. To our knowledge lower and higher substituted HCH derivatives were not considered adequately in common environmental analyses so far. Occurrence of these compounds in environmental compartments (Barriada-Pereira et al., 2005; Ricking and Schwarzbauer, 2008) or in degradation experiments (Bala et al., 2012; Hamada et al., 1981; Quintero et al., 2005; Rodriguez-Garrido et al., 2004) were reported only rarely.

HCHs were produced on an industrial scale at numerous sites in the former German Democratic Republic. One facility located in Bitterfeld-Wolfen in Central Germany produced HCH from 1951 to 1982. Total amounts of HCHs produced at this site from 1967 until termination was estimated around 73,000 t (5400 t lindane). Disposal of waste isomers in former opencast pits and further depots formed heavily contaminated areas. Even after ceased industrial production at local chemical factories, several studies revealed elevated concentrations of various HCH isomers in environmental compartments of the adjacent riverine system (Barth et al., 2007; Franke et al., 2005; Heemken et al., 2000; Heinisch et al., 2005; Marth et al., 2000; Schwartz et al., 2006; Wilken et al., 1994). Pollution of the environment is not limited to the local area. This industrial legacy still severely impacts the quality of one of Germany's largest rivers further downstream, the Elbe River (Götz et al., 2007; Heininger et al., 2004).

For the industrially affected areas around Bitterfeld-Wolfen, the occurrence and pattern of especially lower but also higher chlorinated HCHs might be the result of technical waste disposal, transfer processes, or biotic transformation. In this study, we investigate polluted water, sediment and soil from a riverine system (environmental samples) downstream the industrial area as well as matured waste of HCH production. Main targets were higher chlorinated derivatives of HCHs, especially hepta- (HpCCH) and octachlorocyclohexane (OcCCH) and the lower chlorinated species tetra- (TeCCH) and pentachlorocyclohexene (PeCCH) as shown in Fig. 1. In addition, a lab experiment was conducted to investigate the occurrence of these compounds in the eluate of the matured waste created by e.g. rainfall on non-sealed HCH waste deposits, thus examining transfer processes. On the basis of isomeric patterns of the target compounds detected in industrial waste and samples of environmental compartments from the riverine system, we assessed whether occurrence of these compounds in the environment originated mainly from the industrial waste and related eluates or from formation in environmental compartments by degradation of HCHs. Similar patterns in industrial waste and environmental samples suggests an origin during the synthetic

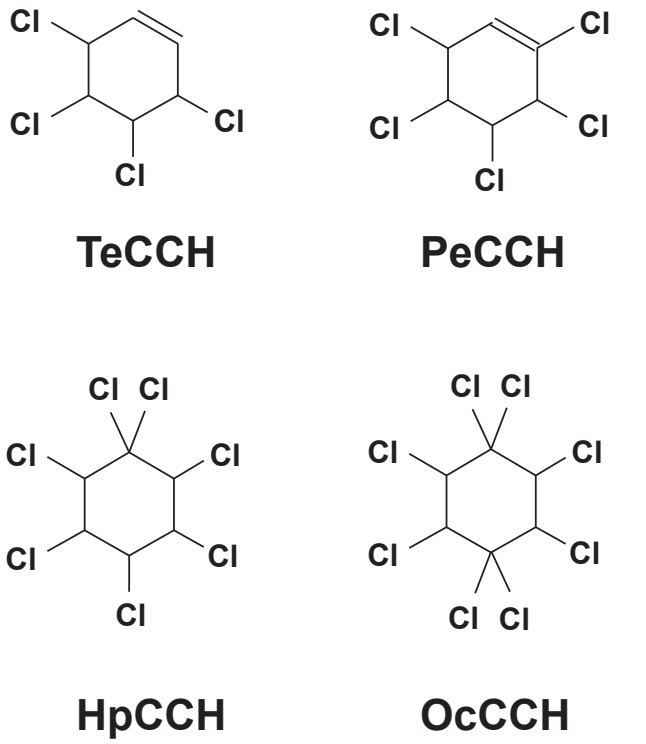

Fig. 1. Molecular structures of selected lower and higher chlorinated HCH derivatives potentially formed during technical synthesis of HCHs. For simplification only one isomer of each species is shown. It was pointed out that biotic degradation of HCH isomers results in different isomers of degradation products (Geueke et al., 2013; Li et al., 2011).

formation of HCHs and subsequent transportation to environmental compartments. Different isomeric patterns indicate an origin by degradation of HCHs in environmental compartments. HpCCH may act as reference point and tracer for the fate of these chlorinated cyclohexane derivatives in environmental compartments. Typical degradation processes of HCHs involve the removal of chlorine atoms from the benzene ring. Thus, formation of additional isomers of HpCCH during degradation processes is unlikely. In addition, a comparison with concentrations of the most recalcitrant HCH isomer (β-HCH) is included and indicates shifts in concentration of the derivatives due to depletion or accumulation in a certain sample.

2. Material and methods

2.1. Sample material

The analyzed sample materials are summarized in Table 1. In October 2012 water, sediment, and soil samples from the Spittelwasser creek, Germany, were taken. Sampling sites were located around Jeßnitz near the industrial area of Bitterfeld-Wolfen and the Mulde River in Saxony-Anhalt. Sampling, sampling methods and storage are described in detail previously (Berger et al. accepted). The following samples were analyzed for lower and higher substituted HCH derivatives: one water sample (**1**) at the beginning of the Schachtgraben drainage canal, one sediment sample (**2**) of the Spittelwasser creek further downstream, three soil samples from different depths of a testing pit of the adjacent flood plain (**3**–**5**), and a sample of matured industrial HCH waste (**6**). The industrial HCH waste represents HCH production waste deposited for at least 30 years. In addition batch shaking experiments with the