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Hexachlorocyclohexane - Long term variability and spatial distribution in the Baltic Sea

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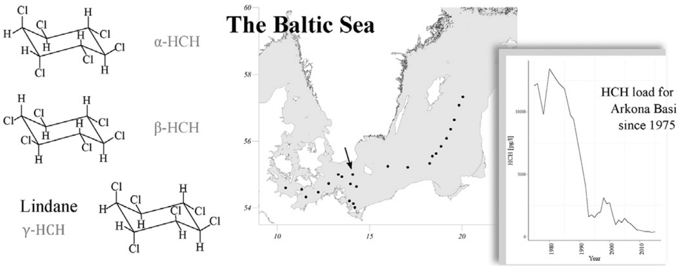
HIGHLIGHTS

- Substantial reduction of the HCH pressure for the Baltic Sea during the past 40 years.
- The β-isomer is currently the predominant HCH isomer (α/β/γ: 1/2/1) and will remain longest in the Baltic Sea.
- Inflow events from the North Sea temporarily influenced HCH concentrations of surface and deep water body of the Baltic Sea.

GRAPHICAL ABSTRACT



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ABSTRACT

In response to the HELCOM commitment the Leibniz Institute for Baltic Sea Research Warnemuende conducts a monitoring program on listed substances of concern for the Baltic Sea environment which comprises the isomers of technical hexachlorocyclohexane (HCH). After World War II the HCH compounds were applied globally in huge amounts as insecticidal formulation in which only γ-HCH is the effective agent. Monitoring was conducted in water samples from a large Baltic Sea area. Mostly, the HCH compounds were evenly distributed in the Baltic Sea. Data from 1975 to 2015 from the Arkona Basin depict a substantial reduction of the HCH pressure (12,500 to < 400 pg/L). Longest residence is shown for β-HCH, which is currently the predominant HCH isomer in the Baltic Sea (α/β/γ:1/2/1). Half lives were determined to be 4–8 years for α- and γ-HCH and 5–20 years for β-HCH.

1. Introduction

The Baltic Sea is a trap for discharges from industrial and agricultural activities in the catchment area due to its encapsulated geographical position, substantial riverine inflow and the strongly restricted water exchange with the North Sea. Long lasting and intensive exposure to hazardous substances since arise of the industrialization in the late 19th century changed the Baltic Sea to one of the most polluted seas in the world (HELCOM, 2010). Since 1998 and Germany's commitment to the Helsinki Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM) the Leibniz Institute for Baltic Sea Research Warnemuende conducts a monitoring program on a number of listed substances of concern for the Baltic Sea environment. These comprise, beside others, the group of hexachlorocyclohexane (HCH) isomers.

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Technical HCH is a mixture of isomers which are predominantly the α- (55–80%), β- (5–14%) and γ-HCH (8–15%) (see graphical abstract) which was applied after World War II as insecticidal agent. Usage of technical HCH in Europe was estimated with 382,000 t from 1970 to 1996 (Breivik et al., 1999; Willett et al., 1998).

However, with respect to insecticidal activity, the γ-isomer was most potent among the HCH compounds, but all HCH isomers exhibit severe toxic properties. Therefore, application of technical HCH in which the insecticidally effective HCH substance makes up only 15% led to a concomitant flood of non-effective, but severely toxic compounds. Therefore, the use of HCH formulations was restricted to sole γ-HCH; in Germany use of technical HCH was banned in 1977, but other countries applied it until the 1990s (Vijgen et al., 2011; Willett et al., 1998). Since then HCH formulations were purified from the non insecticidal α- and β-HCH to an isomeric purity of 99% of γ-HCH known as Lindane. Finally, in 2009 the three HCH isomers α-, β- and γ-HCH were added to the list of persistent organic pollutants (POP) of the Stockholm Convention leading to a ban on HCH production and use in most of the European Countries.

Reports on marine HCH depict higher HCH concentrations for the Northern than for the Southern hemisphere (Lakaschus et al., 2002; Weber et al., 2006; Xie et al., 2011), a fact that has been described as global distillation (Simonich and Hites, 1995). Highest HCH concentrations were found for Arctic seawater and concentrations reported for α-HCH were about 315 pg/L in 2001 (Lakaschus et al., 2002) and for γ-HCH up to 900 pg/L (1990–2001) (Lakaschus et al., 2002; Weber et al., 2006) while for the Southern Ocean about 10 pg/L were reported for α-HCH and 6 pg/L for γ-HCH (2001) (Lakaschus et al., 2002). Thus, the HCH isomers may serve as model compounds to understand the global fate of persistent contaminants as has been discussed before (Breivik and Wania, 2002b; Wania et al., 1999).

Processes that influence HCH concentrations and fate in the Baltic Sea are basically water exchange with the North Sea upon inflow events, runoff from the catchment area and interaction with the atmosphere. Earliest data for the HCH load of Baltic Sea water and highest concentrations ever reported are from 1975 with 8000 pg/L and 4000 pg/L for α- and γ-HCH, respectively for the Arkona Basin (Brügmann et al., 1991). HCH concentration analyses which covered the whole Baltic Sea area were reported for the years 1983 and 1988 (Brügmann et al., 1991; Gaul, 1984). The data presented there revealed a similar pattern as it was shown for the Arkona Basin (Brügmann et al., 1991) which was a clear reduction of α-HCH concentrations, but only to a minor extent for the γ-HCH and no reduction for β-HCH.

For North Sea water samples, generally lower HCH concentrations than for the Baltic Sea were found with a clear increase from the North-Western North Sea to the German Bight (Gaul and Ziebarth, 1983), which is basically determined by water inflow from the Atlantic Ocean and inputs of the large rivers from the European continent such as the Elbe and Rhine. Thus, in 1981 α-HCH concentrations ranged from about 600 pg/L in the North-West to about 3000 pg/L in the German Bight and for γ-HCH from about 200 pg/L to 1200 pg/L (Gaul and Ziebarth, 1983).

Today, the Leibniz Institute for Baltic Sea Research Warnemuende harbors a unique *quasi* time series data set that allows systematic analysis of the HCH pressure, the Baltic Sea was and still is exposed to. The goal of this study is a comprehensive analysis of the available long time data collection with respect to spatial distributions and temporal trends of HCH pressures and their possible transport routes. This includes analyses of the dissipation patterns of the individual isomers and a discussion on how occurrence of natural incidents may have influenced HCH concentrations in the Baltic Sea. Finally, these analyses for the Baltic Sea may serve as environmental model to understand the fate of the HCH compounds in other marine environments of the global ocean.

2. Experimental

2.1. Chemicals and material preparations

All standards were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). The standard mixture contained α-HCH, β-HCH and γ-HCH in a concentration of 10 pg/μL each. The internal standard solution contained the deuterated α-HCH-d6 and γ-HCH-d6 as well as the ε-HCH in a concentration of 100 pg/μL each.

Purified water was obtained through a Milli-Q water system from Merck Millipore (Schwalbach, Germany). Barreled acetone, dichloromethane and *n*-hexane (Walter-CMP, Kiel, Germany) were purified through distillation. Silica 60 (0.063–0.200 mm), alumina 90 (0.063–0.200 mm) and sodium sulfate (all from Merck KGaA, Darmstadt, Germany) were combusted at 400 °C, 800 °C and 450 °C, respectively and stored in a desiccator. Directly prior to use silica and alumina were deactivated by sonication of 1 g solid and 0.035 g or 0.15 g of Milli-Q water, respectively. All laboratory glass ware was baked at 250 °C for a duration of 12 h and rinsed with acetone and *n*-hexane and subsequently air dried. Solvents, silica, alumina and sodium sulfate were analyzed for their blank values before use.

2.2. Sampling sites and sample collection

The HCH monitoring program extended from Kiel Bight in the West to the Gotland Deep in the Eastern part of the Central Baltic Sea and covered the Mecklenburg Bight, Arkona Basin, Oder Bight and Bornholm Basin (Fig. S1, Tables S1–S4).

Additional information on sampling sites and descriptions of sampling procedures are provided in the supplemental data.

2.3. Sample preparation

Extraction and purification followed the procedures described before (Dannenberger and Lerz, 1995; Gaul and Ziebarth, 1983) and basically did not change during the observation period. Thus, the sampler drawn water samples were extracted on board not later than 6 h after collection. The volume of the sampled water was adjusted to 20 L and 200–300 mL of hexane and the internal standard solution were added. Subsequently, the sample was stirred with an electrical stirring device for about 10 min and was allowed to rest for phase separation. The hexane phase was collected by extrusion and dried on sodium sulfate. The samples were stored at −20 °C until analysis in the laboratory.

Samples drawn through solid phase extraction on C_8 were extracted in the laboratory. The C_8 columns were dried over nitrogen to remove excess water. The internal standard was added onto the column and the HCH compounds were extracted with 20 mL of a solution containing acetone/hexane (1:1). The eluate was collected, acetone was removed through rotary evaporation and the residual hexane was dried on sodium sulfate. Extracts were stored at −20 °C until further preparation in the laboratory.

The extracts were filtrated and concentrated to 200 μL by rotary evaporation at ambient pressure and 30 °C and, subsequently, conveyed to flash column and, thereafter, to high pressure liquid chromatography for purification. For this, a successive flash column chromatography system was prepared with alumina and silica that was conditioned with dichloromethane and hexane. The extract was applied onto the flash column system and eluted with 12 mL of hexane and 40 mL of dichloromethane/hexane (1:9). The eluate was collected, concentrated to a final volume of 200 μL and applied