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When will α-HCH disappear from the western Arctic Ocean?

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ABSTRACT

Water column concentrations of α-HCH were measured in the southern Beaufort Sea as part of the Canadian Arctic Shelf Exchange Study (CASES; 2003–04), the Circumpolar Flaw Lead System Study (CFL; 2007–08), and in the Mackenzie River during the 2008 NAHIDIK program. Atmospheric α-HCH concentrations were measured during CASES program. Inventories of α-HCH in the Polar Mixed Layer (PML) and the Pacific Mode Layer (PL) of the Beaufort Sea were calculated between 1986 and 2007 based on the available data. Between 1986 and 1993, there was a significant loading of α-HCH to the Beaufort Sea *via* the ocean currents. About 12% of the loading to the PML could be explained by the combined effect of the air–water gas exchange and the river runoff. After 1993, α-HCH inventories started decreasing, and could be well predicted exclusively by degradation. Ice formation was shown to be a solvent depleting process leading to a significant increase in the α-HCH concentration in the water just beneath the ice. Associated low α-HCH concentrations in the ice and relatively low ice export from the Beaufort Sea resulted in negligible influence of this output route on the inventories in the PML. The majority of α-HCH in the Beaufort Sea could be eliminated due to degradation by 2020, with concentrations in 2040 dropping to <0.006 and <0.004 ng L^{-1} in the PML and PL, respectively. Elimination of α-HCH from sea water takes significantly longer than from the atmosphere, with a lag of about two decades.

1. Introduction

α-hexachlorocyclohexane (α-HCH) is the classical example of a volatile halogenated organic contaminant whose distribution in the world ocean is under the thermodynamic control of water temperature as reflected by Henry's Law (Li et al., 2002). About 6 Mt of α-HCH was released to the environment in the mid-latitudes and tropics between the 1940s and 2000 as a major constituent of technical HCH (Li and Macdonald, 2005). Due to its high vapor pressure, α-HCH readily entered the atmosphere where it underwent long-range transport, partitioning favorably into cold surface water in the Arctic Ocean (Iwata et al., 1993; Oehme et al., 1996; Wania and Mackay, 1993). α-HCH poses a risk for the environment and living organisms because it is persistent, bioaccumulative and toxic (Hargrave et al., 2000; Prasad et al., 1995; Willett et al., 1998). The spectrum of biochemical actions for HCH has been well documented and includes endpoints such as enzyme activation, calcium homeostasis, gap junctional intercellular communication, endocrine disruption, and cancer (Olivero-Verbel et al., 2011). The total loading of α-HCH to the Arctic Ocean was estimated at ~27 700 t between 1945 and 2000, approximately 0.4% of the total released, with highest concentrations found in the surface water of the Beaufort Gyre and the central Canada Basin (Carmack et al., 1997; Li et al., 2004; Macdonald et al., 1997, 2000).

With the banning of technical HCH use during the 1980s, atmospheric concentrations of α-HCH declined such that in about 1990, the Arctic Ocean switched from being a sink for atmospheric HCH to a source. Furthermore, the buildup of HCH concentrations in the cold, ice-covered surface waters of the western Arctic Ocean prior to the 1990s produced a large inventory, which continues to supply HCH to out-flowing waters in the Canadian Archipelago (Bidleman et al., 1995, 2007; Harner et al., 1999; Jantunen and Bidleman, 1995; Li et al., 2004; Macdonald et al., 2000; Shen et al., 2004; Wania and Mackay, 1999). In this process, the Arctic Ocean became the last refuge of α-HCH (Macdonald et al., 1997; Wania and Mackay, 1999).

Sea water in the southern Beaufort Sea exhibits strong layering reflecting density contrasts of source waters (riverine inflow, sea-ice melt, Pacific water, Atlantic water), which may be distinguished by chemical tracers like stable oxygen isotope composition ($\delta^{18}O$), salinity (S), temperature (T) and nutrients (Macdonald et al., 1989). The water mass in the top 30–50 m, often referred to as the Polar Mixed Layer (PML) (Macdonald et al., 1989), is re-formed annually in winter when cooling and brine rejection from ice formation lead to uniform mixing.

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In summer, this layer becomes strongly stratified by river inflow (predominantly the Mackenzie River) and sea-ice melt. Beneath the PML (40–225 m) is a halocline containing Pacific Ocean water which has been strongly processed during passage across the Chukchi Shelf. This layer, referred to as the Pacific Mode Layer (PL), has a residence time of about 10 years (Macdonald et al., 1989). Deeper still, the water masses originate in the Atlantic Ocean with the water undergoing processing during its long (~15–20 years) passage from Fram Strait and the Barents Sea (Macdonald et al., 1989). Since the Arctic is ice covered for the majority of the year, sea-ice cover which controls air–sea exchange must be considered when trying to understand α-HCH concentrations in arctic air and surface waters (Jantunen and Bidleman, 1996, 1997; Jantunen et al., 2005, 2008; Wong et al., 2011).

Here, we report levels of α-HCH in the southern Beaufort Sea region in 2003/2004 (CASES) and 2007/2008 (CFL/NAHIDIK), particularly emphasizing the influence of ice formation on the vertical distribution of α-HCH in the PML. Using these data together with historical data collected since 1986, we show the evolution of the α-HCH inventory in the PML and the PL of the Beaufort Sea. Major inputs and outputs responsible for the observed trends are discussed.

2. Material and methods

2.1. Sampling site

Water column samples were collected in the southern Beaufort Sea as part of the Canadian Arctic Shelf Exchange Study (CASES; 2003–04), the Circumpolar Flaw Lead System Study (CFL; 2007–08) and in the Mackenzie River during the 2008 NAHIDIK program (Fig. 1). Atmospheric samples were collected during the CASES program.

2.2. α-HCH concentrations

2.2.1. CASES 2003/2004

Water samples (~90 L) were collected using 10 L Teflon Niskin bottles mounted on a Rosette sampler/CTD system SBE 911*plus*, Sea-Bird Electronics, Bellevue, WA, USA. Samples were drained into 18 L stainless steel cans, spiked with d_6-α-HCH surrogate, and pumped through a 142 mm A/E Glass Fiber Filter, Pall Corporation, Port Washington, NY, USA, followed by a Teflon column containing Amberlite XAD-2 Resin, 20–60 mesh, Rohm and Haas Company, Philadelphia, PA, USA. Air samples were collected by pulling approximately 2500 m^3 of air through an EPM 2000 Glass Fiber Filter, Whatman, Kent, UK, followed by polyurethane foam (PUF) plugs of 7.5 cm i.d. and 6.5 cm in length (Tish Environmental, Cleves, OH, USA) using a Gast Regenair Blower (Cole-Parmer, Vernon Hills, IL, USA). The flow rate used was 7 m^3 min^{-1} with an average sampling time of 7 h. The blower was calibrated using the Sierra 620 Mass Flow Meter (Sierra Instruments, Monterey, CA, USA). Prior to further analysis, XAD-2 columns and PUF plugs were stored at 4 °C and −20 °C, respectively.

The XAD-2 columns were extracted by drawing 200 mL each of methanol and dichloromethane, respectively, through the column. Subsequently, the extracts were rotoevaporated and transferred into n-hexane (final volume was 1 mL). PUF filters were spiked with a recovery standard (PCB 30 congener), extracted using n-hexane on

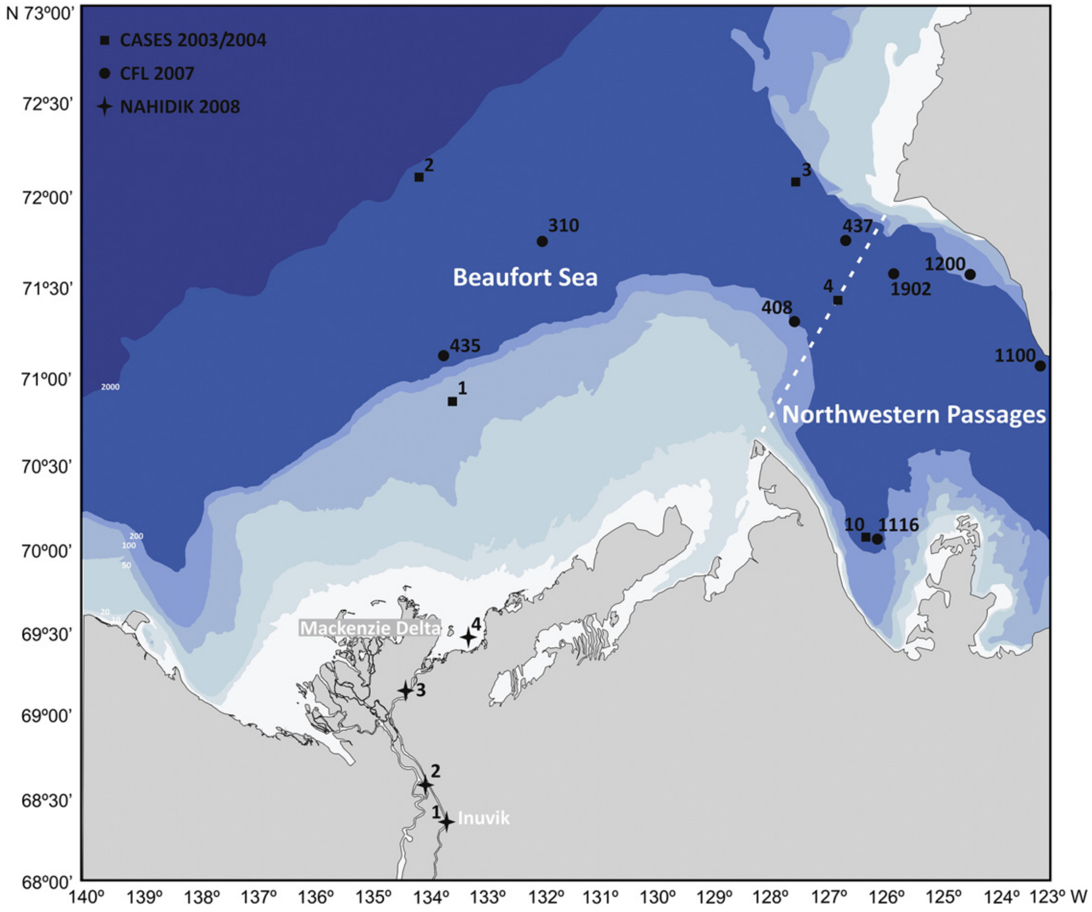

Fig. 1. Location of sampling stations during CASES (October 2003 — stations 1–4; 15 March–15 May 2004 — station 10), CFL (October–November 2007), and NAHIDIK (July 2008); dotted line shows the boundary between the Beaufort Sea and the Northwestern Passages defined by IHO.