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# Persistent organic pollutants in the Atlantic and southern oceans and oceanic atmosphere

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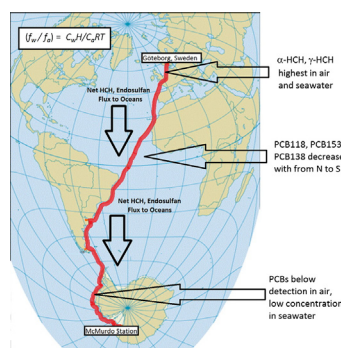
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## HIGHLIGHTS

- Samples were collected between Sweden and Antarctica aboard R/V Oden in 2007.
- Air and seawater samples were analyzed for persistent organic pollutants (POPs).
- Air and seawater POP concentrations were higher in the northern hemisphere.
- Net fluxes for  $\alpha$ -HCH,  $\gamma$ -HCH, and Endosulfan were from air to seawater.
- Ocean continues to act as a sink for legacy pesticides.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Persistent organic pollutants (POPs) continue to cycle through the atmosphere and hydrosphere despite banned or severely restricted usages. Global scale analyses of POPs are challenging, but knowledge of the current distribution of these compounds is needed to understand the movement and long-term consequences of their global use. In the current study, air and seawater samples were collected Oct. 2007–Jan. 2008 aboard the Icebreaker Oden en route from Göteborg, Sweden to McMurdo Station, Antarctica. Both air and surface seawater samples consistently contained  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH),  $\gamma$ -HCH, hexachlorobenzene (HCB),  $\alpha$ -Endosulfan, and polychlorinated biphenyls (PCBs). Sample concentrations for most POPs in air were higher in the northern hemisphere with the exception of HCB, which had high gas phase concentrations in the northern and southern latitudes and low concentrations near the equator. South Atlantic and Southern Ocean seawater had a high ratio of  $\alpha$ -HCH to  $\gamma$ -HCH, indicating persisting levels from technical grade sources. The Atlantic and Southern Ocean continue to be net sinks for atmospheric  $\alpha$ -,  $\gamma$ -HCH, and Endosulfan despite declining usage.

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## 1. Introduction

International regulation of persistent organic pollutants (POPs) is controlled by the Stockholm Convention of the United Nations

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Environment Programme (UNEP, 2016), which originally identified twelve pollutants to be monitored globally and their emissions to the environment reduced. This list included organochlorine pesticides including chlordane, hexachlorobenzene, and DDT, as well as polychlorinated biphenyls and polychlorinated dibenzo-*p*-dioxins and -furans. Additional chemicals identified as POPs continue to be added to this international treaty, including hexachlorocyclohexane (HCH) and Endosulfan (UNEP, 2016). POPs are distributed worldwide by various partitioning processes across interfaces between, e.g., air, water, and biota in aquatic and terrestrial environments (Jones and De Voogt, 1999; Wania and Mackay, 1996). Global scale studies of the atmospheric transport and air-sea exchange of POPs have had a major impact on our understanding of POP movement in the environment and the impact of POPs on remote locations (Dachs et al., 2002; Iwata et al., 1993; Pozo et al., 2009, 2006). According to the hypothesis of cold condensation, semi-volatile organic pollutants are constantly cycled from the gaseous phase in warmer latitudes to the cooler polar regions and deposited in aquatic and terrestrial environments where revolatilization is minimal (Wania and Mackay, 1996). Such chemicals have been found to accumulate in polar regions where they bioaccumulate in biota and may reach concentrations in top predators that potentially have adverse effects (Braathen et al., 2004; Brault et al., 2013; Goerke et al., 2004; Oskam et al., 2004; Sonne, 2010). Although substantial work has been done in the Arctic to monitor these compounds and their impacts, studies on POPs distribution and movement in the Southern hemisphere and particularly the Antarctic have been much more limited. Changes in polar regions are of particular interest as legacy use compounds may be released to the aquatic environment and atmosphere during the melting of ice sheets and general warming (Cabrerizo et al., 2013; Cincinelli et al., 2016; Geisz et al., 2008; Goerke et al., 2004).

Information on air-sea fluxes of individual POPs is important to understand if a particular area of the sea acts as a sink or a source, which, in turn, is essential for the understanding of the global distribution and environmental fate of these contaminants. Without environmental distribution and fate information, environmental risks cannot be estimated. A particular advantage of long geographical transects is that information from a wide range of environmental conditions and distances from anthropogenic sources can be collected.

This study took place during the expedition “Oden Southern Ocean 2007–2008” (OSO 07–08). The objective was to collect information on the distribution and air-sea fluxes of several POPs in a north-south transect of the Atlantic Ocean and a west-east transect in the Southern Ocean between the Western Antarctic Peninsula and the Ross Sea.

## 2. Methods

### 2.1. Sample collection

Air and surface seawater samples were collected aboard the Swedish Icebreaker Oden on a transect between Göteborg, Sweden and McMurdo Station, Antarctica from 23 October through 4 January 2008 (Fig. 1, Table S1). Samples were analyzed for 26 current and past-use organochlorine pesticides and 21 polychlorinated biphenyls (PCBs) using gas chromatography combined with mass spectrometry (Table S2). Gas and dissolved phase concentrations were then used to calculate air-sea fluxes.

Air samples were collected using two high volume samplers consisting of 150 mm diameter glass fiber filters (GFFs) to collect aerosol samples and two polyurethane foam (PUF) plugs (8 cm diameter  $\times$  7.6 cm) to collect gas phase samples of approximately 500 m<sup>3</sup> air. The air samplers were deployed in front of Deck 5, approximately 18 m above the sea surface with the bulk of the bridge shielding the samplers from the stack and, except during storms, out of the sea spray. Sampling took place only while under way, but regardless of wind direction. Prior to use, the GFFs were baked for 4 h at 400 °C and

the PUFs Soxhlet extracted with acetone and petroleum ether (24 h each). GFFs were stored in envelopes of aluminum foil baked at 400 °C and PUF plugs were stored in precleaned glass jars, both at –20 °C after sampling, until extraction.

To increase sample volume, some PUF gas phase samples were composited such that sample volumes ranged from ~500–1400 m<sup>3</sup> for Atlantic samples and ~600–2000 m<sup>3</sup> for Antarctic samples. Only Atlantic aerosol samples were analyzed as part of this study and were also composited prior to extraction to increase sample volumes (3500–6500 m<sup>3</sup>). Antarctic aerosol analyses from this study have been previously reported (Dickhut et al., 2012). A surrogate standard mixture of perdeuterated  $\alpha$ -hexachlorocyclohexane ( $d_6$ - $\alpha$ -HCH) and PCB 204 was added and PUF plugs were Soxhlet extracted with acetone and petroleum ether (24 h each). Anhydrous sodium sulfate was added to the sample extracts to remove residual water, and extracts were reduced to 10 mL using rotary evaporation (Buchi) and/or a Turbopap II (Zymark), exchanged into hexane, and further reduced to 3 mL using a gentle stream of ultra-high purity N<sub>2</sub>. Aerosol extracts and approximately half the gas phase extracts were acid treated using concentrated sulfuric acid. The sample extracts were then cleaned up using silica column chromatography (Chiuchiolo et al., 2004), and an internal standard ( $d_6$ - $\gamma$ -HCH) was added prior to volume reduction to ~100  $\mu$ L using ultra high purity N<sub>2</sub>.

Seawater samples were collected via a direct inlet line from the bottom of the ship (app. 8 m depth) into the laboratory. The entire inlet system was made of acid resistant stainless steel with the exception of PTFE pump impellers. Large volume seawater samples (~110 L for Atlantic Ocean and ~150–160 L for Southern Ocean) were collected in steel holding tanks and treated according to Dickhut et al. (2005). The water was extracted by passing through a column (35 cm  $\times$  25 mm i.d.) of Amberlite XAD-2 resin (Sulpeco, Bellefonte, PA). The XAD-2 resin columns were stored at 4 °C until extraction. For analyses, the XAD-2 resin was Soxhlet extracted with acetone and hexane (24 h each) after the addition of the surrogate standard mixture described above. The acetone fractions were back-extracted using hexane and hexane-extracted water three times via agitation for 3 min, and the resulting hexane was combined with the hexane extract and reduced in volume by rotary evaporation. The hexane extracts were then cleaned and analyzed as described above.

### 2.2. Quantification

Samples were analyzed on a Hewlett-Packard 6890 Gas Chromatograph with a 5973 Mass-Selective Detector in negative chemical ionization mode using a J&W DB-35MS capillary column (30 m  $\times$  0.25 mm i.d., 0.25  $\mu$ m film thickness) and selective ion monitoring. Method parameters for analysis were as follows: 70 °C initial hold time of 1 min; 70–150 °C at 20 °C min<sup>–1</sup>; 150–280 °C at 4 °C min<sup>–1</sup>, hold for 15 min; 280–295 °C at 5 °C min<sup>–1</sup>, hold for 2 min; source temperature 150 °C. The carrier gas for both methods was helium at 1.0 mL min<sup>–1</sup> with a velocity of 39 cm s<sup>–1</sup> (Chiuchiolo et al., 2004).

### 2.3. Quality assurance and quality control

Quality control procedures included the collection and analysis of laboratory and field blanks, selected duplicate samples, and breakthrough on PUF plugs, non-sequential sample extraction ordering, quantitation of surrogate standard and internal standard recoveries, and the use of a conservative method detection limit.

Laboratory and field blanks were collected and analyzed as quality control procedures. One laboratory blank of baked GFF filters was extracted alongside composite particulate filters (1 laboratory blank to eight samples), as were two laboratory blanks of cleaned PUF not taken in the field. Paired air and seawater field blanks were collected across the Atlantic leg every seven samples (three total), and four air field blanks (30 s on high volume air sampler) and two seawater field

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