Atmospheric Environment 80 (2013) 41–49

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Atmospheric occurrence and deposition of hexachlorobenzene and hexachlorocyclohexanes in the Southern Ocean and Antarctic Peninsula

Cristóbal Galbán-Malagón, Ana Cabrerizo [1], Gemma Caballero, Jordi Dachs*

Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, Barcelona 08034, Catalunya, Spain

HIGHLIGHTS

- Concentrations of HCHs and HCB are low (few pg m^{-3}) in the Southern Ocean surrounding the Antarctic Peninsula.
- Antarctic snow is a secondary source of HCHs and HCB to the regional atmosphere.
- The biological and degradative pumps have an influence on the atmospheric deposition of HCH and HCBs to the Southern Ocean.

ARTICLE INFO

Article history:
Received 31 May 2013
Received in revised form
25 July 2013
Accepted 26 July 2013

Keywords:
Antartic Peninsula
Southern Ocean
HCH
HCB
Atmospheric deposition

ABSTRACT

Despite the distance of Antarctica and the Southern Ocean to primary source regions of organochlorine pesticides, such as hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs), these organic pollutants are found in this remote region due to long range atmospheric transport and deposition. This study reports the gas- and aerosol-phase concentrations of α-HCH, γ-HCH, and HCB in the atmosphere from the Weddell, South Scotia and Bellingshausen Seas. The atmospheric samples were obtained in two sampling cruises in 2008 and 2009, and in a third sampling campaign at Livingston Island (2009) in order to quantify the potential secondary sources of HCHs and HCB due to volatilization from Antarctic soils and snow. The gas phase concentrations of HCHs and HCB are low, and in the order of very few pg m^{-3} α-HCH and γ-HCH concentrations were higher when the air mass back trajectory was coming from the Antarctic continent, consistent with net volatilization fluxes of γ-HCH measured at Livingston Island being a significant secondary source to the regional atmosphere. In addition, the Southern ocean is an important net sink of HCHs, and to minor extent of HCB, due to high diffusive air-to-water fluxes. These net absorption fluxes for HCHs are presumably due to the role of bacterial degradation, depleting the water column concentrations of HCHs in surface waters and driving an air–water disequilibrium. This is the first field study that has investigated the coupling between the atmospheric occurrence of HCHs and HCB, the simultaneous air–water exchange, soil/snow-air exchange, and long range transport of organic pollutants in Antarctica and the Southern Ocean.

1. Introduction

Persistent and semivolatile organic pollutants can reach remote oceanic regions through atmospheric transport and deposition (Iwata et al., 1993; Dachs et al., 2002). The study of organochlorine pesticides (OCPs) and other persistent organic pollutants (POPs) in the northern hemisphere and Arctic Ocean has received more attention than the assessment of atmospheric deposition in the southern hemisphere, and especially to its remote regions such as Antarctica and the Southern Ocean (Jantunen et al., 2004; Bengtson-Nash, 2011). OCPs are ubiquitous in the environment and have been detected in all the environmental compartments (water, air, snow, ice and biota) of Polar Regions (Tanabe et al., 1983; Iwata et al., 1993; Cabrerizo et al., 2012; Macdonald et al., 2005). Although there are previous reports of the atmospheric concentrations of OCPs, such as hexachlorobenzene (HCB) and hexachlorocyclohexanes (HCHs), in the Southern Ocean (Tanabe et al., 1983; Larsson et al., 1992; Iwata et al., 1993; Bidleman et al., 1990; Kallenborn et al., 1998,Jantunen et al., 2004; Montone et al., 2005; Dickhut et al., 2005; Cincinelli et al., 2009; Baek et al.,

---

* Corresponding author.
E-mail address: jordi.dachs@idaea.csic.es (J. Dachs).

[1] Present address: Institute for Environment and Sustainability, European Commission, Via Enrico Fermi 2749, 21027 Ispra, Italy.

1352-2310/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.atmosenv.2013.07.061

2011; Xie et al., 2011), these studies usually cover a small subregion. Historical production of HCHs and HCB mainly occurred in the northern hemisphere (Breivik et al., 2004), and the occurrence and temporal trends of OCPs in the Arctic reflect its production and usage in the northern hemisphere. Conversely, the occurrence of OCPs in Antarctica reflects their efficiency for long-range atmospheric transport in addition to production trends due to the distance to potential sources and the lower magnitude of these sources in the southern hemisphere in comparison with the northern hemisphere (Li et al., 2000; Bengtson-Nash, 2011; Dickhutt et al., 2005). Since 1990 there was a restriction and reduction of the global production and usage of HCHs and HCB (UNEP, 2001). Consequently, the primary sources have been reduced during the last decades (Breivik et al., 2004), which have also lead to a decrease of OCPs seawater concentrations in the Southern Ocean (Galbán-Malagón et al., 2013).

Long range atmospheric transport and deposition are usually considered the main source of POPs to the Antarctic continent and Southern Ocean (Bengtson-Nash, 2011; Cabrerizo et al., 2012). Ultimately, these compounds may experience “cold-trapping” at polar regions, where the low temperatures further prolong persistence (Wania and Mackay, 1995) and enhance their deposition and accumulation in water, soil, snow or biota. Under the current decreasing primary sources, it has been suggested that remobilization of historical polar terrestrial reservoirs (snow, soil) of PCBs and HCB may also be feasible (Ma et al., 2011; Cabrerizo et al., 2013) due to changes in climate. Previous attempts to study the cycling of HCHs in Antarctic waters have revealed that net deposition predominates over net volatilization (Dickhut et al., 2005; Cincinelli et al., 2009; Jantunen et al., 2004; Xie et al., 2011). Conversely, close to air–water equilibrium conditions have been reported for HCB (Cincinelli et al., 2009). Regardless of these pioneering studies, there is a lack of comprehensive studies covering the atmospheric occurrence and deposition in a large region of Antarctica and Southern Ocean. Therefore, the objectives of the present work are: i) to study the occurrence of HCHs and HCB in the atmosphere over the South Scotia Sea, the Weddell Sea, Bransfield Strait and Bellingshausen Sea during two Antarctic oceanic campaigns in 2008 and 2009, ii) to assess the diffusive air–water exchange of HCHs and HCB and the factors driving the air–water cycling of OCPs in the Antarctic Region, and iii) to identify potential local sources of atmospheric HCHs and HCB due to volatilization from soil and snow.

2. Material and methods

2.1. Sampling and site description

Atmospheric sampling was conducted during the ESSASI and ATOS-II Antarctic cruises during the austral summers of 2008 and 2009, respectively, on board of R/V Hespérides. In addition, and simultaneously to the ATOS-II campaign, a field terrestrial sampling campaign was performed at Livingston Island (Southern Shetland Islands) in January–February 2009. The ESSASI campaign sampled the region of the South Scotia Sea between Elephant Island and South Orkneys islands (Fig. 1 and Figure S1 in Appendix A). The ATOS-II cruise covered the region around the Antarctic Peninsula including the Weddell Sea, the Bransfield Strait and the Bellingshausen Sea (Fig. 1 and Figure S1 in Appendix A). The terrestrial sampling campaign was carried out at Livingston Island, at the surroundings of the Spanish Research Station (Juan Carlos I) (62° 34′S, 61° 13′W, South Shetland Islands) (Figure S2).

During the cruises, simultaneous samples of air (gas and aerosol phase) and surface water (particulate and dissolved phases) were taken. The methods and occurrence of HCHs and HCB in seawater has been described previously in a companion paper (Galbán-Malagón et al., 2013), and we describe here only the sampling and analytical methods for the atmospheric samples and land samples. Ancillary data including physical and chemical characterization of air and water were obtained from the automatic continuous water system and the meteorological station on board of the ship. Samples’ ancillary data are reported in Table S1 in Appendix A of the supporting information.

Air samples (gas and aerosol phase) were collected using a high-volume air sampler (MCV: CAV-A/HF, Collbató, Spain) deployed over the vessel bridge connected to a wind direction sensor in order to avoid contamination from the ship. Air was sampled only when the wind direction was from the bow (90° to −90°). Sampling flow rate was set at 40 m^3 h^{-1} and the sampling volumes averaged 1000 m^3 and 1400 m^3 for the gas phase samples of the ESSASI and ATOS II cruises, respectively. During the ATOS-II cruise, a second high-volume air sampler was operated in parallel for the sampling of aerosol-phase only, with longer sampling periods, so higher volumes of air were sampled (around 1800 m^3). This was part of an attempt to determine POPs in aerosols, since aerosol concentrations are extremely low in Antarctica (Weller et al., 2012). The gas phase was collected on a polyurethane foam (PUF) plugs (100 mm diameter × 100 mm, Klaus Ziemer GmbH, Germany) and the aerosol phase was trapped on a quartz microfiber filters (QM/A) 203 × 254 mm (Whatman, England).

The fugacity of OCPs in soil and snow were measured using the fugacity sampler (Cabrerizo et al., 2009, 2011a, b, 2013) in which the air is forced to flow below a stainless-steel chamber with a surface of 1 m^2 and separated 3 cm from the soil/snow surface. This sampler allows the air to equilibrate with the surface soil/snow in terms of the chemical fugacity. Four soil-fugacity samplers were operating simultaneously and distributed above soil covered with lichens (*Usnea Antarctica*) in Pico Radio Hill (one sampler), bare soil at Polish beach (one sampler) and snow in Sofia Mountain (two samplers) (See Figure S2). In these samplers, the air, after it has been equilibrated with snow or soil, passes through a glass fiber filter to remove dust particles and a polyurethane foam plug (PUF) in which the compounds from the gas phase are retained. In addition to the air equilibrated from the surface (snow and soil), ambient air at a height of 1.5 m is also analyzed. The comparison of the fugacity in the soil/snow, and the fugacity in ambient air, provides the direction of the air-surface exchange. A high-volume air sampler was also deployed at Livingston Island in order to determine HCB and HCHs concentrations in the aerosol phase. Filters and PUFs used in the soil fugacity sampler were quartz fiber filters (GF/F) of 47 mm of diameter and the dimensions of PUFs were 10 × 2 cm. Details of the sampling strategy and conditions at Livingston Island are given elsewhere (Cabrerizo et al., 2013).

Prior to the sampling campaigns, PUFs were pre-cleaned using a Soxhlet extraction with acetone:hexane (3:1) for 24 h. They were then dried under vacuum, and kept well sealed until the sampling. QMA filters used for aerosol sampling were initially pre-combusted at 450 °C during 24 h, pre-weighed and wrapped in aluminum foil before sampling. After the sampling, PUF and QMA filters were kept at 4 °C and −20 °C, respectively, until chemical analysis.

2.2. Analytical methods

2.2.1. Atmospheric and aerosol extraction and fractionation of OCPs

Briefly, all samples were Soxhlet extracted for 24 h using acetone:hexane (3:1) for gas-phase samples collected on PUFs and using methanol:dichloromethane (1:2) for aerosol-phase samples collected by QMA filters. Prior to extraction, samples were spiked with PCB 65 (Dr Ehrenstorfer, GmbH, Germany), which was used