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

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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.,

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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

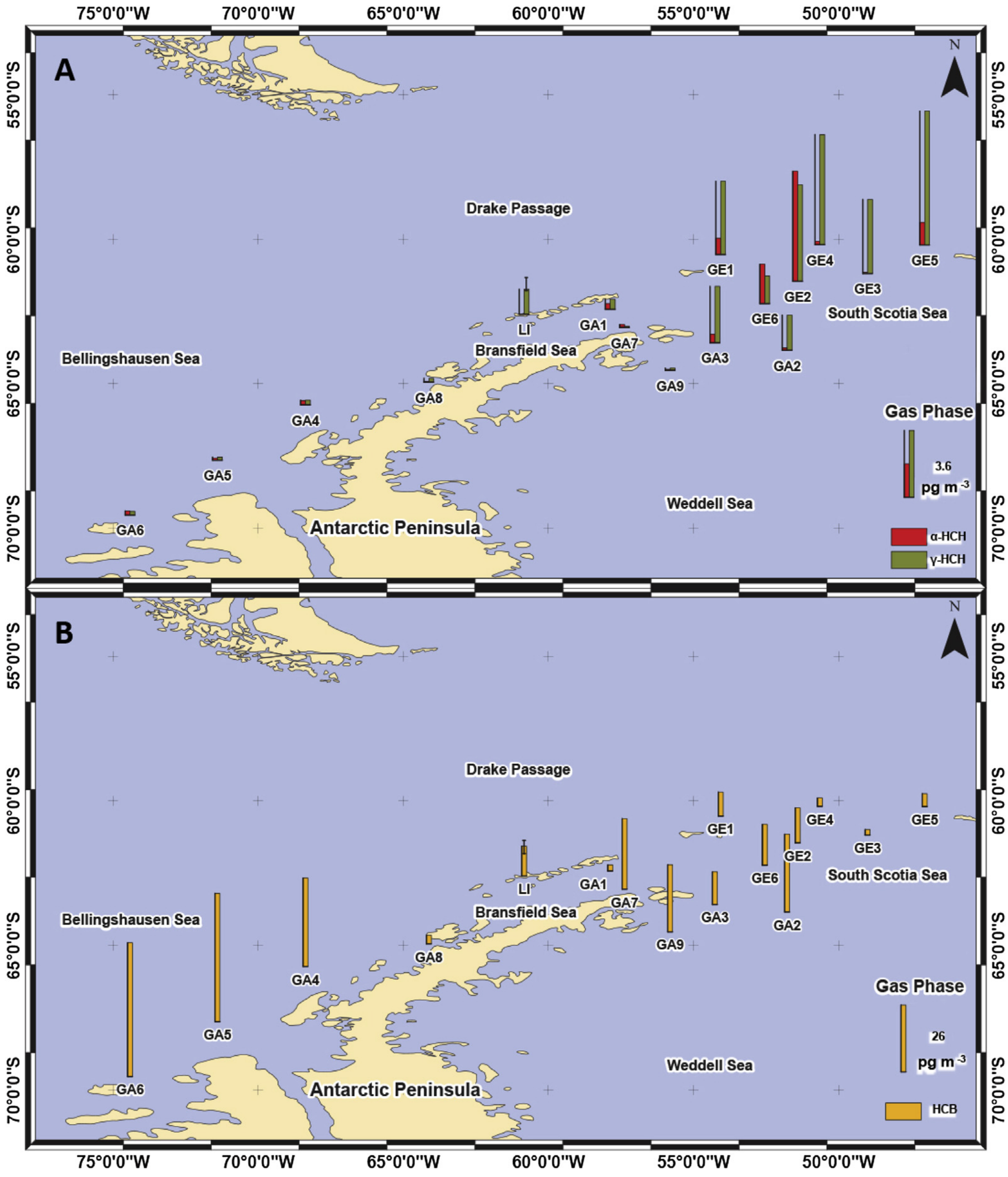

Fig. 1. Gas phase concentrations (pg m^{-3}) of HCHs (A) and HCB (B) in samples taken during the ESSASI (GE) and ATOS II (GA) cruises in 2008 and 2009, respectively. Average and range is also shown for the gas-phase samples taken at Livingston Island.

as a recovery standard. Extracts were reduced in a rotary evaporation unit (R-200, Büchi, Italy) until 0.5 ml and fractionated on a 3% deactivated alumina column (3 g), with a top of 1 g of anhydrous sodium sulphate. The first fraction containing PCBs and some OCPs was collected using 12 mL of hexane, while the second fraction containing PAHs and the rest of OCPs was collected using 15 mL of hexane: dichloromethane (1:2). All fractions were concentrated until 1 mL by rotary evaporation and solvent exchange to isooctane under a purified N_2 stream until a final volume of 150 μL. α-HCH, γ-HCH and HCB were analyzed in the merged first and second fraction for the gas and dissolved phase. For the aerosol phase samples, only the first fraction was analyzed. Identification and quantification was done using the retention time of the α-HCH, γ-HCH and HCB peaks. The details of the methodology used for analyzing the PUFs from the sampling of the fugacity in soil/snow and ambient air using the fugacity sampler at Livingston Island have been described elsewhere (Cabrerizo et al., 2013).

2.2.2. OCPs identification and quantification

OCPs were analyzed by a gas chromatograph coupled to a μ-ECD detector (Agilent Technologies, model 7890), provided with an HP-5MS 60 m capillary column (inner diameter 0.325 μm, film thickness 0.25 μm). The instrument was operated in splitless mode (close for 1.5min). The oven programmed temperature started from 90 °C (hold for 1 min) to 190 C at 20 °C min^{-1} and then to 310 °C (3 °C min^{-1}) (holding time 18 min). Injector and detector temperatures were 280 and 320 °C, respectively. Helium and nitrogen were used as carrier (1.5 ml min^{-1} and makeup (60 ml min^{-1}) gases respectively. Prior to injection, 5 ng of PCB 30 was added as internal standard to all samples.

2.3. Quality control and quality assurance

All analytical procedures were monitored using strict quality assurance and quality control measures. Sampling equipment were cleaned rigorously prior to sampling and between samples to avoid sample cross contamination. Laboratory and field blanks constituted 20% of total number of samples processed at a rate of one blank for every five samples. Blank signal accounted for an average of 5(±8)% of the amount detected in samples and was subtracted after quantification for all samples. Limits of detection (LODs) and quantification (LOQs) were estimated from the average plus three times the standard deviation, and average plus ten times the standard deviation from blanks, for LOD and LOQ, respectively. The estimated LODs and LOQs for α-HCH, γ-HCH and HCB were 0.059–0.16, 0.15–0.46 and 0.14–0.37 pg on column. Instrumental detection limits were also calculated from the lowest standard detected and considering the average sampling volumes, resulting in a value of <0.001 pg m^{-3} for the ESSASI samples, and <0.002 pg m^{-3} for the ATOS II samples. The recoveries of PCB 65, used as surrogate standard, ranged from 53 to 78% for ESSASI samples, and from 67 to 76% for ATOS II samples. Quality control and quality assurance parameters regarding samples taken during the terrestrial campaign are reported elsewhere (Cabrerizo et al., 2013).

2.4. Statistical analysis

Differences in concentrations were analyzed using a non-parametric statistical approach using the *Mann Whitney U test* for the comparison of the ESSASI and ATOS II atmospheric concentrations of α-HCH, γ-HCH and HCB (Fig. 2A–C). The influence of air-mass back trajectories on OCP atmospheric concentrations was discerned using the *Kruskal–Wallis test* for 3 or more groups followed by a post hoc *Dunn's Multiple Comparisons test* (Fig. 2D–F).

3. Results and discussion

3.1. Atmospheric occurrence of HCHs and HCB

3.1.1. Gas phase concentrations of α-HCH and γ-HCH

During the ESSASI cruise (January–February 2008), gas phase concentrations of α-HCH and γ-HCH ranged from 0.06 to 5.8 pg m^{-3} and from 1.5 to 7.1 pg m^{-3}, respectively. Conversely, the

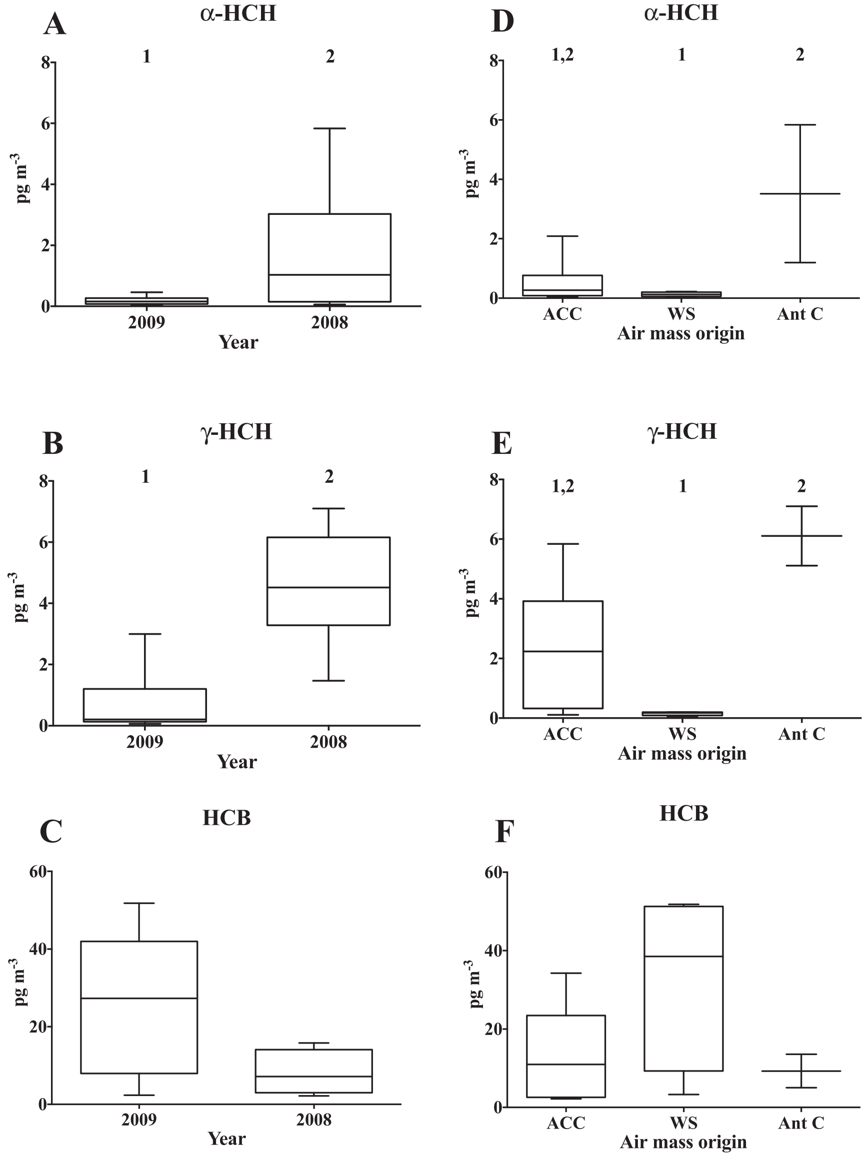

Fig. 2. Box-Plot comparing gas-phase concentrations during the ESSASI (2008) and ATOS II (2009) cruises for α-HCH (A), γ-HCH (B) and HCB (C). Box-Plot comparing the influence of the air mass origin (based on back trajectories analysis) for α-HCH (D), γ-HCH (E) and HCB (F). For figures A, B and C differences ($p < 0.05$) are marked numbers **1** and **2** over the box in the case of the figures D, E and F. **1,2** over the box means that there are no statistical differences with **1** and **2**. **ACC**: Antarctic Circumpolar Water Current influence, **WS**: Weddell Sea origin and **Ant C**: Antarctic Continent Influence.

gas phase concentrations from the ATOS II cruise (February 2009) ranged from 0.04 to 0.5 pg m^{-3}, and from 0.07 to 3 pg m^{-3} for α-HCH and γ-HCH, respectively (see Fig. 2). The concentrations of α-HCH and γ-HCH in 2008 were higher (*Kruskal Wallis test*, $p < 0.05$) than in 2009. These inter-annual differences may be due to the different regions sampled in the different cruises, to differences in the air mass trajectories, or to other factors as discussed below. In general, the concentrations of γ-HCH were higher than those of α-HCH in both cruises (see Table 1 and Table S4). During the sampling campaign performed at Livingston Island, only γ-HCH was detected with ambient air concentrations ranging from LOQ (0.14 pg m^{-3}) to 2.73 pg m^{-3} (Table S5). α-HCH was always below LOQ (0.14 pg m^{-3}) due to the low sampled volumes of the land-based samples (around 70 m^3). These concentrations are in agreement with previous reported studies for the atmosphere over the coastal Antarctic continent and Islands (Dickhutt et al., 2005; Cincinelli et al., 2009), or over the Southern Ocean (Jantunen et al., 2004; Dickhut et al., 2005; Montone et al., 2005; Xie et al., 2011). However, the concentrations reported in this study are significantly lower than the concentrations reported over Antarctic land and waters during early sampling efforts in the 1980s and 1990s (Tanabe et al., 1983., Larsson et al., 1992; Iwata et al., 1993; Bidleman et al., 1990) (See Table 1 for a comparison of HCHs and HCB concentrations reported in this study in comparison to previous reports), suggesting a decrease in atmospheric concentrations in agreement with the reported temporal trends for seawater concentrations of HCH (Galbán-Malagón et al., 2013). This decrease in atmospheric concentrations reflects the restriction in the use/emissions of these chemicals from source regions.

3.1.2. Gas phase concentrations of HCB

Over the Southern Ocean, ambient air concentration of HCB were in the range of 2.2–15.8 pg m^{-3}, 2.4–30.1 pg m^{-3}, 25.9–51.8 pg m^{-3} and 12.6–49.7 pg m^{-3} in the South Scotia, Weddell, Bransfield and Bellingshausen Seas, respectively. The highest concentrations were found in the Bransfield and Bellingshausen Seas, while the lowest concentrations were found in the Weddell Sea during the ATOS II cruise. The results of the *Kruskal Wallis test* indicate that there are no significant differences between the concentrations measured in 2008 and 2009 (Fig. 2). At Livingston Island, the HCB gas phase concentrations ranged from 4.19 to 15.73 pg m^{-3} (Table S5), comparable to those determined over the ocean. The gas-phase concentrations of HCB reported here are in the same range than those reported in the atmosphere from the open and coastal Southern Ocean (See Table 1) (Montone et al., 2005; Bidleman et al., 1990; Dickhut et al., 2005), and from the Antarctic continent and islands (Dickhut et al., 2005; Cincinelli et al., 2009). HCB concentrations are also comparable to those measured in the Arctic Ocean (Galbán-Malagón et al., 2013; Lohmann et al., 2009; Su et al., 2006; Wong et al., 2011). Gas phase concentrations over the ocean were not correlated with temperature (See Figure S4).

3.1.3. Aerosol phase concentrations of α-HCH, γ-HCH and HCB

The aerosol phase concentrations over the Southern Ocean during the ATOS-II cruise ranged from 0.01 to 0.1 pg m^{-3}, from 0.03 to 0.1 pg m^{-3} and from 0.04 to 0.08 pg m^{-3} for α-HCH, γ-HCH and HCB, respectively (Table 1). At Livingston Island, the aerosol-phase HCB concentration was in the range of 0.0035–0.004 pg m^{-3}. To the best of our knowledge, there are no previous studies reporting aerosol-phase concentrations of HCHs and HCB for the Southern Ocean or Antarctica. However, these concentrations were lower than the aerosol-phase concentrations measured in the Arctic and Subarctic atmosphere (Galbán-Malagón et al., 2013b).

3.2. Influence of the air-mass back trajectories on atmospheric concentrations of HCHs and HCB

The air-mass back-trajectories were assessed using the NOAA HYSPLIT model (Draxler and Rolph, 2011). The back trajectories were estimated at 25 m height and were computed for the initial, middle and final time of the sampling period to ensure clear and coherent information about the air mass origin during sampling, since air masses can be highly variable close to the Antarctic continent. The three characteristic air mass back trajectories encountered are shown in Fig. 3 (all the back trajectories are shown

Table 1
Atmospheric concentrations (gas-phase) of HCH and HCB reported for the Southern Ocean and Antarctic region (pg m^{-3}).

Location	Year	α-HCH		γ-HCH		HCB		Reference
		Mean	SD	Mean	SD	Mean	SD	
Sabrina Coast	1981	120		120				Tanabe et al., 1983[a]
Balleny Islands	1981	170		170				
Syowa Station	1982	49		49				
Amundsen Bay	1982	44		44				
Cape Evans (Ross Island)	1989			66.75	43.69			Larsson et al., 1992
	1990			72.00				
Southern Ocean (Daisan-Nisin Maru Cruise	1990	26.00		12.00				Iwata et al., 1993
Gondwana cruise (New Zealand to Antarctica)	1990	4.15	1.19	5.80	5.60	62.60	20.00	Bidleman et al., 1990
Signy Island	1995	3.50	2.44	33.01	20.13			Kallenborn et al., 1998
Transect Brazil-Antarctica	1995	3.77	0.64	3.00	4.60	23.90	1.79	Montone et al., 2005
Agulhas Cruise (South Africa-Antarctica)	1997–1998	1.01	0.31					Jantunen et al., 2004
Antarctic Peninsula	2001–2002	0.32	0.10	0.78	0.80	20.59	6.51	Dickhut et al., 2005
Terra Nova Bay	2003–2004	0.22	0.08	0.56	0.32	11.36	5.35	Cincinelli et al., 2009
King George Island	2005							Baek et al., 2011
	2006	2.28	0.27	2.85	0.46			
	2007	1.72						
Southern Ocean Cruise	2008	0.75	0.21	0.70	0.28			Xie et al., 2011
South Scotia Sea	2008	1.70	2.16	1.63	1.52	49.71	8.19	This study
Bellingshausen	2009	0.26	0.18	1.14	1.61	32.19	18.63	
Bransfield	2009	0.14	0.09	0.12	0.07	35.03	14.55	
Weddell	2009	0.16	0.14	0.87	0.88	11.93	15.77	
Livingston Island (Polish Bluff)	2009			0.93	0	11.97	2.67	
Livingston Island (Radio Peak)	2009			2.27	0.68	10.30	4.81	
Livingston Island (Sofia Mountain)	2009			0.79	0.77	11.79	1.82	

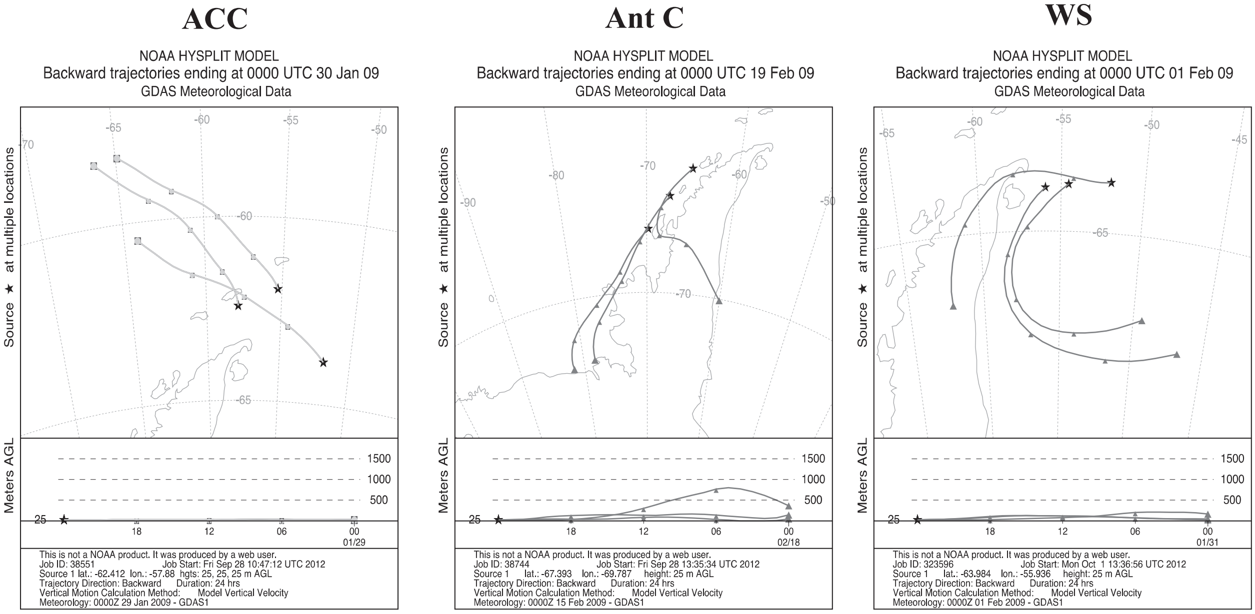

Fig. 3. Characteristic air-mass back trajectories for sampling periods influenced by the Antarctic Circumpolar water Current (**ACC**), the Weddell Sea (**WS**) and the Antarctic Continent (**Ant C**).

in Figures S5 and S6 in Appendix B) and belong to the Antarctic Circumpolar Water Current (ACC) accompanying air masses, those coming from the Antarctic Continent (AntC), and air masses coming from the Weddell Sea (WS). Non-parametric tests were performed to establish differences in gas phase concentrations between the sampling events dominated by the three air masses. Gas phase concentrations of α-HCH and γ-HCH were significantly higher ($p < 0.05$) for those samples influenced by the AntC air masses in comparison to those coming from the Weddell Sea (WS). However, the concentrations of α-HCH and γ-HCH when the sampling events were influenced by the ACC air masses were not significantly different than those sampling events dominated by the WS and AntC air masses (right panels of Fig. 2). Generally, concentrations of HCHs were higher when the air mass was coming from the Antarctic continent or they came from the NW seawater in the ACC, while concentrations were lower when the air mass came from the Weddell Sea. In the case of HCB, there were no significant differences between the gas-phase concentrations for the different air mass back trajectories (right panels of Fig. 2). The analysis of the air-mass back trajectories did not allow to discern a direct source of HCHs or HCB originating in South America, thus affecting the Antarctic atmosphere as a result of a lack of direct transport from mid-latitudes to higher-latitudes (Dickhut et al., 2005). This result agrees with the trends described recently for perfluorinated compounds (Del Vento et al., 2012).

3.3. Antarctica as a secondary source of HCHs and HCBs

The potential influence of the Antarctic continent as a secondary source of HCHs and/or HCB inducing higher gas phase concentrations, as observed in the AntC dominated air masses in comparison to WS air masses, require further attention. Recently, it has been suggested (Ma et al., 2011; Cabrerizo et al., 2013; Kang et al., 2012) that Arctic and Antarctic seawater, snow and/or soils are becoming important secondary sources, remobilizing POPs and modulating the trends of legacy pollutants in the Arctic and Antarctic atmosphere. Indeed, this process could be more intense during periods of high wind speeds influenced by the katabatic winds coming from the continents (speed >10 m s^{-1}), enhancing the release of contaminants to the atmosphere (Halsall et al., 2004). The deployment of fugacity samplers at Livingston Island allows determining the soil-air and snow-air fugacity ratios and thus the determination of the occurrence of local sources of atmospheric HCHs and HCB from Antarctica. The ambient air fugacity (f_a, Pa) and the snow or soil fugacity (f_s, Pa) were calculated by (Mackay, 1979):

$$f_A = \frac{10^{-12} C_{\mathrm{Gas}} RT}{\mathrm{MW}} \qquad (1)$$

$$f_S = \frac{10^{-12} C_{\mathrm{SA}} RT}{\mathrm{MW}} \qquad (2)$$

where C_{Gas} is the measured ambient air gas-phase concentration at 1.5 m height (pg m^{-3}), R is the gas constant (8.314 Pa m^3 mol^{-1} K^{-1}), T is the air temperature (K), MW is the chemical molecular weight (g mol^{-1}), and C_{SA} (pg m^{-3}) is the gas phase concentration that has been equilibrated with the soil or snow surface (Table S5 in Appendix C) as measured using the fugacity sampler (Cabrerizo et al., 2009, 2013). The re-volatilization of HCHs and HCB from the surface reservoirs can be confirmed by comparing f_A and f_s. When f_s is higher than f_A there is a net volatilization of the chemical. In contrast, if f_A is higher than f_s there is a net deposition of the chemical. However, since there is an uncertainty in the measurements, equilibrium would be represented by ln $f_s f_A^{-1}$ in the range of +0.53 and −1.20 (Cabrerizo et al., 2009, 2011b, 2013). Fig. 4 shows that HCB and γ-HCH in snow and soil were close to equilibrium with the over-lying atmosphere but with a tendency for a net volatilization for more than half of the sampling periods. These results suggest that during the austral summer, Antarctica is a secondary source of γ-HCH and HCB to the atmosphere, especially due to volatilization from snow. The “signal” from the Antarctic secondary sources may be more important for HCHs than HCB, as suggested by the comparison of gas-phase concentrations for different air-mass back trajectories, because HCB is more persistent in the atmosphere than γ-HCH and thus long-range atmospheric transport may be more effective in comparison to secondary sources.

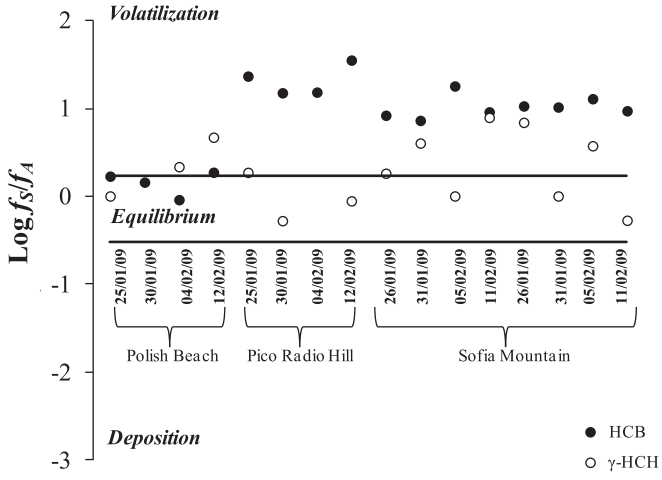

Fig. 4. Surface/Air fugacity ratio ($f_S f_A^{-1}$) of HCB and γ-HCH for the different sampling sites and periods at Livingston Island (Antarctica). The black lines indicate the surface–air equilibrium range for $f_S f_A^{-1}$ (+0.23, −0.52).

3.4. Air-sea diffusive exchange and dry deposition processes

The low concentrations over the Weddell Sea, and the high variability of concentrations when the air-masses come from oceanic regions, suggest that atmospheric deposition may be an important removal process for atmospheric HCHs and HCB. The net direction of the diffusive air–water exchange can be determined by comparing the chemical fugacity in water (f_W, Pa) and air (f_A, Pa).

$$f_W = \frac{10^{-12} C_{\mathrm{Dis}} H' R T_W}{\mathrm{MW}} \tag{3}$$

Where C_{Dis} is the truly dissolved concentration estimated from the measured dissolved concentrations corrected by dissolved organic carbon (DOC) as reported elsewhere (Galbán-Malagón et al., 2013), R is the ideal gas constant (8.314 Pa mol^{-1} K^{-1}), T_W is the water surface temperature (K), H' is the surface temperature and salinity corrected dimensionless Henry's Law Constant (*HLC*) for each compound (Table S2 in Apendix C), and MW is the molecular weight of the studied compound. f_A over the ocean was estimated from equation [1] using the C_{Gas} measured during the cruises. More information about the truly dissolved concentration and HLC corrections is given in the supporting info (Appendix C).

Fugacity ratios ($f_W f_A^{-1}$) should be considered with caution due to the uncertainties associated with the C_{Gas}, C_{Dis} and HLC. The uncertainties associated to C_{Gas} and C_{Dis} were estimated to be 0.15 (15% error in analytical measure). Another source of uncertainty is the estimation of HLC, and a factor of 3 was chosen (Li et al., 2003). Following the approach of Bruhn et al. (2003), if $f_W f_A^{-1} < 0.76$ indicates net deposition, $f_W f_A^{-1} > 3.23$ indicates net volatilization, and $0.76 \le f_W f_A^{-1} \le 3.23$ indicates that the gas-phase and dissolved-phase are close to equilibrium. $f_W f_A^{-1}$ are shown in Fig. 5A. During the ESSASSI cruise, the fugacity ratios indicate a net deposition for α-HCH and γ-HCH, while HCB showed conditions of close to air–water equilibrium to net deposition (South Scotia Sea). In the case of the sampling events during the ATOS II cruise (Weddell, Bransfield and Bellingshausen seas), there was a net deposition of HCHs and HCB for all the sampling events except for 2 samples (Table S5 on Appendix C). The fugacity ratios reported here for HCHs agree with those reported in the Antarctic Peninsula coastal waters (Dickhut et al., 2005), the Ross Sea (Cincinelli et al., 2009) and Southern Ocean (Jantunen et al., 2004; Xie et al., 2011) indicating that there is a strong disequilibrium between the air and water in the Southern/Antarctic Ocean. Conversely, HCB has been reported to be close to equilibrium in the Ross Sea (Cincinelli et al., 2009) but this study shows that there is significant air–water disequilibrium in some areas, especially for those samples from the ATOS II cruise that covered the marine regions around the Antarctic Peninsula (Weddell Sea, Bransfield Strait and Bellingshausen Sea).

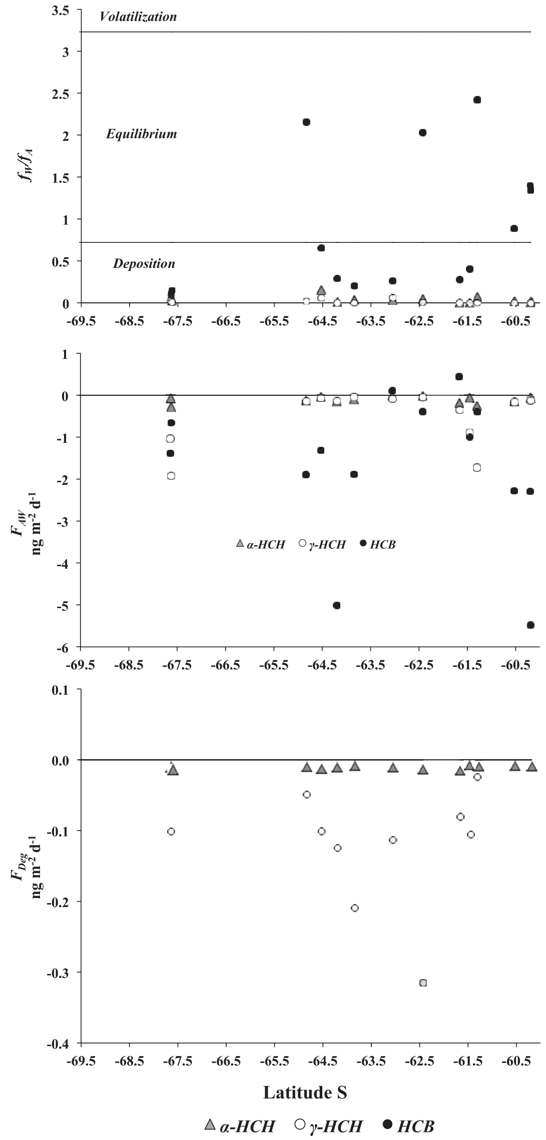

Fig. 5. (Upper panel) Water-air fugacity ratio ($f_W f_A^{-1}$), (Middle Panel) air–water diffusive exchange fluxes (ng m^{-2} d^{-1}) for the air–water pairs of samples obtained during the ESSASI and ATOS II cruises against latitude for α-HCH (grey triangles), γ-HCH (white circles) and HCB (black circles). $f_W f_A^{-1}$ values over 3.23 means volatilization, $f_W f_A^{-1}$ values under 0.72 means deposition, and $f_W f_A^{-1}$ values between 3.23 and 0.72 means that concentrations in the gas and dissolved phases were close to equilibrium. The Lower panel shows the degradative fluxes for α-HCH and γ-HCH in seawater.

The magnitude of the net diffusive air–water fluxes (F_{AW}, ng m^{-2} d^{-1}) were estimated using the Whitman two-film model (Withman, 1923) as follows

$$F_{\mathrm{AW}} = k_{\mathrm{AW}} \left(\frac{C_{\mathrm{Gas}}}{H'} - C_{\mathrm{Dis}} \right) \tag{4}$$

Where k_{AW} (m d^{-1}) is the estimated air–water mass transfer coefficient. The diffusive air–water fluxes are shown in Fig. 5B. The highest depositional fluxes of α-HCH and γ-HCH were estimated for the Bransfield Strait (0.3 ng m^{-2} d^{-1} and 1.9 ng m^{-2} d^{-1}, respectively) and the lowest were found in the Weddell Sea for α-HCH (0.02 ng m^{-2} d^{-1}) and in the Bellingshausen Sea for γ-HCH (0.04 ng m^{-2} d^{-1}). HCB fluxes were significantly higher than those measured for HCHs (Kruskal–Wallis $p < 0.05$) in the South Scotia and the Bellingshausen Seas. The highest HCB diffusive flux was obtained in the South Scotia Sea samples (5.5 ng m^{-2} d^{-1}) and the lowest in the Bransfield Sea (0.1 ng m^{-2} d^{-1}).

The dry deposition was calculated from the aerosol-phase concentrations by:

$$F_{DD} = 10^{-3} C_A v_D \tag{5}$$

Where C_A is the aerosol-phase concentration (pg m^{-3}) and v_D is the particle deposition velocity of 258 m d^{-1} (or 0.3 cm s^{-1}) measured in Antarctica (Grönlund et al., 2002). Dry deposition fluxes ranged from 0.003 to 0.009, from 0.008 to 0.03, and from 0.01 to 0.02 ng $m^{-2}d^{-1}$ for α-HCH, γ-HCH and HCB respectively (see Table S7 on Appendix C).

The seawater around the Antarctic Peninsula has low concentrations of POPs due to the distance from sources and isolation of Antarctic waters by the Antarctic Circumpolar Current (ACC) (Bengtson-Nash et al., 2010; Rintoul., 2000). The low concentrations of POPs in surface waters can also be due to loss processes in the water-column like the biological pump (Dachs et al., 2002; Galbán-Malagón et al., 2012) and the degradative pump (Galbán-Malagón et al., 2013b). Fig. 6 schematizes the major processes affecting the occurrence of HCH and HCB in the Antarctic atmosphere and waters. The biological pump occurs when the settling flux of organic matter-bound POPs depletes the dissolved concentrations at sea surface, inducing higher air–water diffusive exchanges (Dachs et al., 2002; Galbán-Malagón et al., 2012). This process is highly efficient for the transport of hydrophobic POPs, such as some PCBs (Dachs et al., 2002; Galbán-Malagón et al., 2012), but is not very efficient for the less hydrophobic PCBs and compounds like HCHs and HCB (Zhang et al., 2012; Berrojalbiz et al., 2011; Galbán-Malagón et al., 2013b). Conversely, in the degradative pump, the depletion of the dissolved phase concentrations is due to degradation. Degradation of HCHs is driven by hydrolysis and bacterial degradation (Harner et al., 1999, 2000, Helm et al., 2002) and it is the most important removal process in the Arctic water column (Li et al., 2004a, b), followed by ocean currents. A recent modeling study has also suggested that microbial degradation and hydrolysis could be the responsible of α-HCH depletion in surface waters from the Beaufort Sea (Pucko et al., 2011), and it has been demonstrated that degradation is an important process in the cycling of HCHs in the upper water column of the North Atlantic and Arctic Oceans (Galbán-Malagón et al., 2013b). Degradation constants have been reported for α-HCH and γ-HCH in the Arctic Ocean (Harner et al., 1999 and Harner et al., 2000) at a 1000 m depth, and these constants can be scaled for surface waters using the bacterial biomass as reported elsewhere (Galbán-Malagón et al., 2013b; see Appendix C for estimation of degradative fluxes). Degradation fluxes accounts, on average, for 12% and 28% of α-HCH and γ-HCH atmospheric inputs to the open Southern Ocean (Fig. 5), but this percentage is higher in areas near to coast line, where up to 40% for α-HCH, and around 100% of γ-HCH of atmospheric inputs are lost by degradation in the photic zone (See tables S6, S7 and S8 Apendix C). Therefore, in the Southern Ocean, the strong net diffusive fluxes are driven in part by the degradative pump depleting the dissolved phase concentrations. It has been reported that bacterial production is strongly correlated with the phytoplankton biomass in the Southern Ocean (Ortega-Retuerta et al., 2008), thus during periods of high phytoplankton growth and abundance, the degradative pump would be more efficient in the depletion of HCHs in the water-column. This loss process occurs in parallel to the losses due to the biological pump which are small for compounds such as HCHs. In the case of HCB, there is not any known process that could degrade HCB in the surface waters. So depletion of HCB concentrations in surface waters could be related to the exportation of HCB associated to particles (Barber et al., 2005; Lohmann et al., 2009) but this removal process is considered small for HCB due to its low K_{OW}, consistent with air and water fugacities closer to equilibrium.

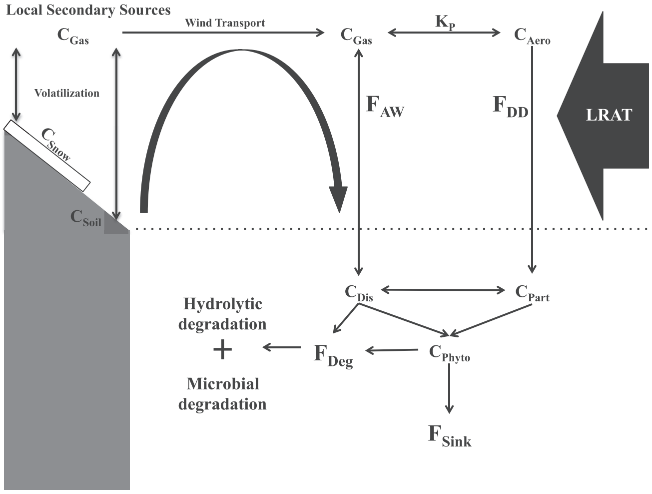

Fig. 6. Scheme of POPs cycling in Antarctica and Southern Ocean showing the influence of local secondary sources, such as soils and snow (C_{Soil} and C_{Snow}), and the long range atmospheric transport (LRAT), to gas-phase (C_{Gas}) and aerosol phase (C_{Aero}) HCB and HCHs. Main input fluxes to the surface waters are the diffusive air–water exchange (F_{AW}) and to lower extent dry deposition (F_{DD}). Ultimate sinks are the transportation trough the water column by settling particles (F_{Sink}, Biological Pump) and the microbial and hydrolysis degradation (F_{Deg}). C_{Dis} is the dissolved phase concentrations, C_{Part} is the particulate phase concentration and C_{Phyto} is the Phytoplankton concentration.

4. Conclusions

This work describes and discusses the first comprehensive study of the atmospheric occurrence and transport, soil/snow-air exchange and water–air exchange of HCHs and HCB for the Antarctic Peninsula and Southern Ocean (Fig. 6). Despite the importance of secondary sources of HCHs from land-compartments (soils, snow) affecting the levels of some sampling events, long range atmospheric transport is the main input of HCHs and HCB to the Antarctic Peninsula region. The high air–water net diffusive deposition of HCHs to the Southern Ocean is enhanced by the role of the degradative pump depleting the water column concentrations. Conversely, for HCB, which is persistent in the water column, air and water are closer to equilibrium conditions. Further research is needed to close the mass balance of these compounds in the region, and assess the role of zooplankton and macrozooplankton in Antarctic waters which recently has been revealed as an important transport pathway trough the water-column in Arctic waters (Pucko et al., 2013).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2013.07.061.

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