



Distribution of organochlorine pesticides in surface and deep waters of the Southern Indian Ocean and coastal Antarctic waters[☆]

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ABSTRACT

Antarctica is a remote and pristine region. Yet it plays a vital role in biogeochemical cycles of global anthropogenic contaminants, such as persistent organic pollution (POPs). This work reports the distribution of legacy and new POPs in surface and depth profiles/deeper water of the Southern Indian Ocean (SIO) and the coast of Antarctica (COA). Samples were collected during the 10th Indian Southern Ocean expedition (SOE-10) in the year 2017. Concentrations of \sum HCH (hexachlorocyclohexane), \sum DDT (dichlorodiphenyltrichloroethane), and \sum ENDO (endosulfan) in surface seawater from the SIO region ranged between not detected (ND) to 1.21 pg/Liter (pg L^{-1}) (average. \pm s.d.: $0.35 \pm 0.42 \text{ pg L}^{-1}$), ND to 1.83 pg L^{-1} ($0.69 \pm 84 \text{ pg L}^{-1}$), and ND - to 2.06 pg L^{-1} ($0.56 \pm 0., 88 \text{ pg L}^{-1}$), respectively. The concentrations of \sum HCH, \sum DDT, and \sum ENDO in COA ranged from ND to 0.98 pg L^{-1} ($0.25 \pm 0.27 \text{ pg L}^{-1}$), ND to 3.61 pg L^{-1} ($0.50 \pm 1.08 \text{ pg L}^{-1}$), and ND to 2.09 pg L^{-1} ($0.45 \pm 0.84 \text{ pg L}^{-1}$), respectively. Concentrations of isomers of endosulfan, and largely of HCHs, suggested an aged source. Some concentration ratios of α -to γ -HCH were close to 1, indicating a contribution from ongoing sources. Results indicate the important role of ocean currents in mediating the transport and detection of OCPs. As such, OCPs dynamics in deeper oceans may play an important role in OCPs cycling in the marine environment.

1. Introduction

Persistent organic pollutants (POPs) are organic compounds, well known to be ubiquitous in the environment, bioaccumulative, and toxic to organisms. Primary sources of POPs in the polar marine environment include fossil fuel combustion, aerosols from airplanes, industrial effluents, oil spills, and plastic debris (Rios et al., 2007; Xie et al., 2022). The increasing trends of POPs in the tropical regions suggest contributions from ongoing usage, and their detection in pristine environments suggests contributions from secondary emission sources (Chakraborty et al., 2021, 2015; 2010; Iwata et al., 1994; Pokhrel et al., 2018; Syed et al., 2013; Zhang et al., 2008). POPs are known to migrate across latitudes by two well-known processes, (i) long-range atmospheric

transport (LRAT) (Jones and Voogt, 1999; Kallenborn et al., 2015) and (ii) ocean currents-mediated transport (Ilyina et al., 2006; Ma et al., 2018).

Colder regions favor the condensation of volatile organic compounds. Snow acts as an efficient scavenger for atmospheric POPs and is responsible for the deposition of more than 80% of atmospheric POPs (Burkow and Kallenborn, 2000). During the winter season, coastal Antarctica is covered with seasonal sea ice, known for carrying POPs (Bigot et al., 2017; Chiuchiolo et al., 2004). Polar regions are highly susceptible to a slight rise in the annual average temperature. Due to the rising temperature, trapped POPs repositories, also known as polar sinks, act as secondary sources of POPs (Bigot et al., 2017; Casal et al., 2019; Geisz et al., 2008; Macdonald et al., 2005). This may enhance the

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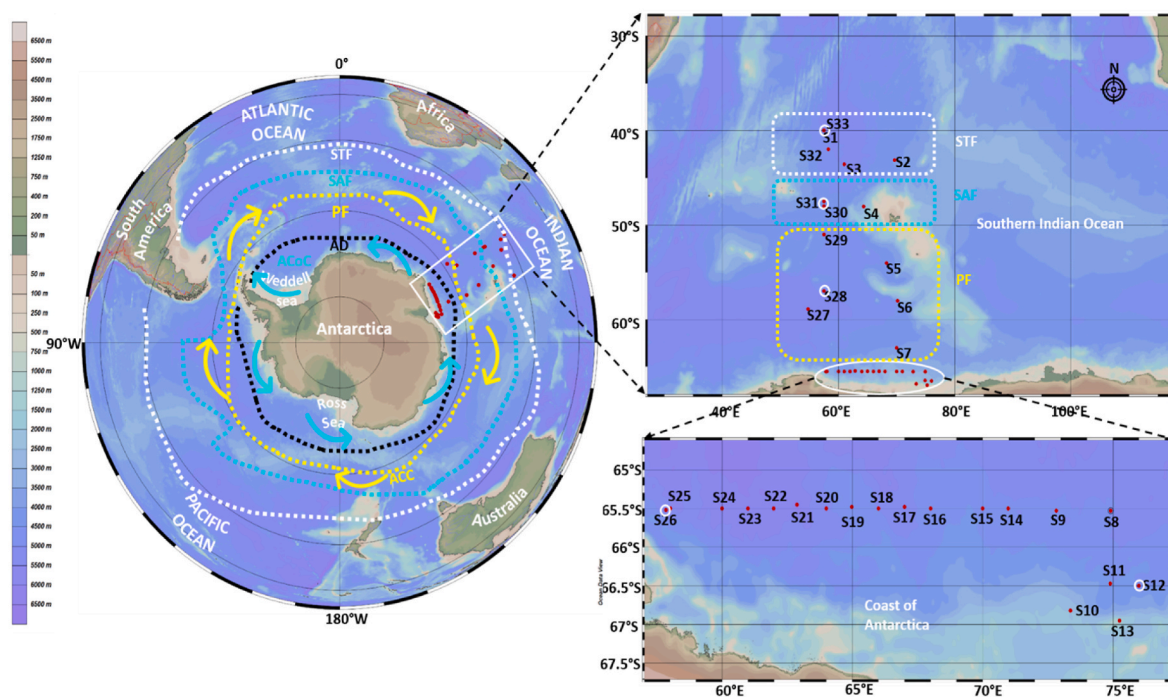


Fig. 1. Study map STF = Sub-Tropical Front, SAF = Sub-Antarctic Front, PF = Polar Front. AD Antarctic Divergence Red Antarctic Coastal Current (ACoC) Yellow Antarctic Circumpolar Current (AAC), the white circle indicates that vertical sampling location and the red dot indicates the surface sampling location. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

distribution of POPs in the polar regions as well as in the adjacent oceans. The leached organic pollutants can be harmful to the environment (Bhardwaj et al., 2018; Faruqi and Siddiqui, 2020) and add to the 'active pool' of POPs. Moreover, the air-sea exchange of POPs influences their occurrence in the marine boundary layer (Dachs et al., 2002; Iwata et al., 1993; Pozo et al., 2009, 2006).

Studies on POPs in open oceans are generally limited by issues such as sample collection, preservation, contamination during transportation, non-detectable data, cruise logistics, and the cost of expeditions (Gioia et al., 2013). Despite these challenges, several studies have reported the occurrence of legacy POPs in the North Pacific, Arctic, and North Atlantic Oceans (Cai et al., 2012a; Carrizo and Gustafsson, 2011; Gioia et al., 2008; Lohmann et al., 2009) Antarctic and Southern Oceans (Bigot et al., 2016; Cristóbal et al., 2013; Galbán-Malagón et al., 2013; Luek et al., 2017; Tanabe et al., 1983). In general, oceanic measurements are restricted to surface seawater (Booij et al., 2014; Gioia et al., 2013). A very limited number of studies have investigated POPs in the deep ocean. An early study from the eastern Arctic analyzed the advective outflows of HCHs, (Harner et al., 1999). Increasing concentrations of DDTs in the vertical profiles in the Arctic Ocean basin were reported in the early 2000s (Carrizo et al., 2017; Sobek and Gustafsson, 2014). More recently, diffusion of OCPs from the surface ocean to the deep ocean was reported for the tropical Atlantic and the North Atlantic Oceans (Sun et al., 2016). Other studies have inferred that the deep ocean can contribute a substantial amount of POPs to surface water through water mass mixing (Booij et al., 2014; Schulz et al., 1988). Previous works have thus suggested that OCPs dynamics in deeper water masses play an important role in their overall cycling in the marine environment. The Southern Ocean is the connecting link between the Atlantic, Indian, and Pacific Oceans and acts as a major source and sink for several intermediate and deep-water masses (Carter et al., 2008; Talley, 2013). The Atlantic, Indian, and Pacific Oceans also transport the dissolved phase POPs to the Southern Ocean (Li et al., 2020; Zhang et al., 2022). Hence, it is imperative to investigate the deeper water POPs particularly OCPs that have been extensively used across the globe in the Southern Ocean region.

Previous studies on POPs in the Southern Ocean region (Bigot et al., 2016) and Southern Ocean (Weddell, South Scotia, and Bellingshausen Seas) (Cristóbal et al., 2013; Luek et al., 2017) have focused on matrices such as air, plankton, and surface seawater. In the present study, we add to this knowledge by measuring POPs/OCPs in deeper and surface water in more locations with a specific focus on depth profiles. This work focused on the following objectives: (i) to elucidate the current levels of legacy and new organochlorine pesticides (OCPs) in the surface and deep waters collected from different fronts of the southern sector of the Indian Ocean and near the Coast of Antarctica, and their comparison with levels of OCPs from different oceans and polar regions, (ii) to understand the sources of these POPs vis-a-vis new or aged sources, and (iii) to assess the potential eco-toxicological risk associated with the quantified POPs.

2. Methodology

2.1. Study area

The present study was conducted onboard during the 10th Indian Expedition to the Southern Indian Ocean and coastal Antarctic waters by the polar research vessel SA Agulhas. Sample collection was carried out between December 2017 and February 2018 (Antarctica summer). Sampling stations were categorized into two regions: (1) the Southern Indian Ocean (SIO), transected between longitudes 40°S–65°S (stations S1–S7, S27–S33), and (2) the Coast of Antarctica (COA) (Fig. 1), transected between the latitudes 52°E–77°E (stations S8–S26). The oceanic fronts of the SIO region were divided into the Subtropical Front (STF), Sub-Antarctic Front (SAF), and Antarctic Polar Front (PF) (Belkin and Gordon, 1996; Orsi et al., 1995; Rintoul and England, 2002).

2.2. Sample collection

The 10th Indian Expedition was a multi-disciplinary oceanographic cruise to understand the various biogeochemical processes and biological productivity potential in the SIO and COA waters. Our sampling

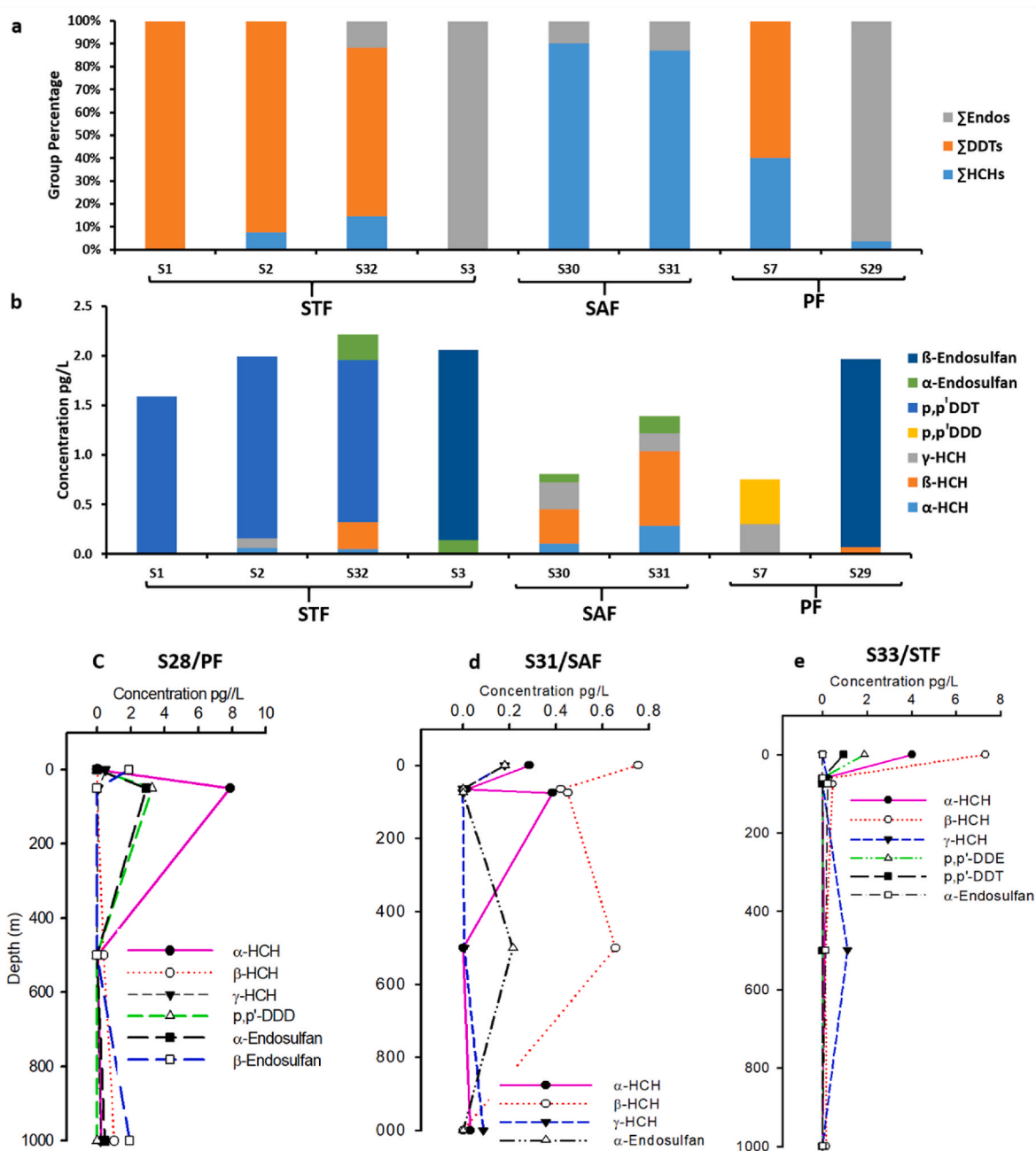


Fig. 2. OCPs congeners from the SIO region. a) Group-wise percentages and b) concentration profiles of OCP congeners from surface waters. Depth profiles of OCPs from c) PF, d) SAF, and e) STF stations.

strategy was devised to fall within the scope of the cruise. Thus, we measured OCPs in the dissolved phase. Depth profiles were limited to 1000 m. Likewise, sediment sampling, using a corer at 4000–5000 m depth, was outside the scope due to logistical limitations.

Thirty-three composite surface seawater samples were collected from SIO ($n = 14$) and COA ($n = 19$) using a pre-cleaned polypropylene bucket, rinsed three times each with type-1 Milli Q water and then by sample water (UNEP, 2017). In addition, samples were taken at different depths in photic and aphotic zones (10 m, at deep chlorophyll maxima (DCM, 30–60 m), 100 m, 500 m, and 1000 m) from three stations in SIO: S33 located in the STF, S31 located in the SAF, and S28 located in the PF. The location of S33 is the same as S1; S33 was sampled on the return journey. From the COA region, two depth profile stations were selected: S12 and S26. Depth samples were collected using Niskin water samplers connected with a conductivity temperature depth (CTD) unit. Samples

were collected in pre-cleaned 2-L Wheaton wide-mouth glass bottles with polytetrafluoroethylene (PTFE)-lined lids. Bottles were pre-cleaned with analytical grade hydrochloric acid (HCl) followed by copious amounts of ultrapure (type-1) water. After sample collection, each sample bottle was stored immediately in separate double zip-lock plastic bags at 4 °C temperature until further analysis.

2.3. POPs analysis

Sixteen OCP congeners: α -HCH (hexachlorocyclohexanes), β -HCH, γ -HCH, p,p' -DDD (dichlorodiphenyltrichloroethane), p , p' -DDE (dichlorodiphenyldichloroethylene), p,p' -DDT, α -endosulfan, β -endosulfan, endosulfan sulfate, dieldrin, heptachlor, heptachlor epoxide, methoxychlor, *cis*-chlordane, and *trans*-chlordane were analyzed. OCPs were segregated as legacy and new POPs, (UNEP, 2022, 2001; Vijgen

et al., 2011). New pesticidal POPs included α -HCH; β -HCH; γ -HCH; α -endosulfan; and β -endosulfan and the rest are legacy pesticidal POPs.

Seawater samples were extracted for OCPs according to the method given elsewhere (Khuman and Chakraborty, 2019). Briefly, 1-L of water was filtered using 0.45 μ m pore size filter papers and extracted via solid phase extraction unit using Bond Elute C18 cartridges. All samples were spiked with 20 ng of 2, 4, 5, 6-tetrachloro-m-xylene (TCmX) as a surrogate standard prior to extraction to check recovery. 10 mL of n-hexane: dichloromethane (1:1 v/v) was used as the eluting solvent. The eluates were reduced to 2 mL and cleaned up using a packed alumina-silica column (15 mm internal diameter \times 150 mm). OCPs were eluted using 10 mL of n-hexane: dichloromethane (1:1 v/v) and concentrated to 0.5 mL using a gentle stream of nitrogen. 20 ng of pentachloronitrobenzene (PCNB) was used as an internal standard

before instrumental analysis.

2.4. Instrumental analysis

An Agilent 7890 B Gas Chromatograph (GC) equipped with an electron capture detector (ECD) is used for the quantification of OCPs using the method given elsewhere (Rex and Chakraborty, 2022). Briefly, an HP-5 capillary column (30 m, 0.25 mm, 0.25 μ m) was used with nitrogen (99.9% purity) as the carrier gas, with a flow rate of 1.2 mL/min. The oven temperature was set initially at 120 $^{\circ}$ C and was rammed to a final temperature of 290 $^{\circ}$ C with a hold time of 3.5 min. The split-less injection was performed with an injection volume of 1 μ L.

GC-ECD has been shown to be an effective method for analyzing OCPs and validated with GC-MS (Jan et al., 2022; Tsygankov et al.,

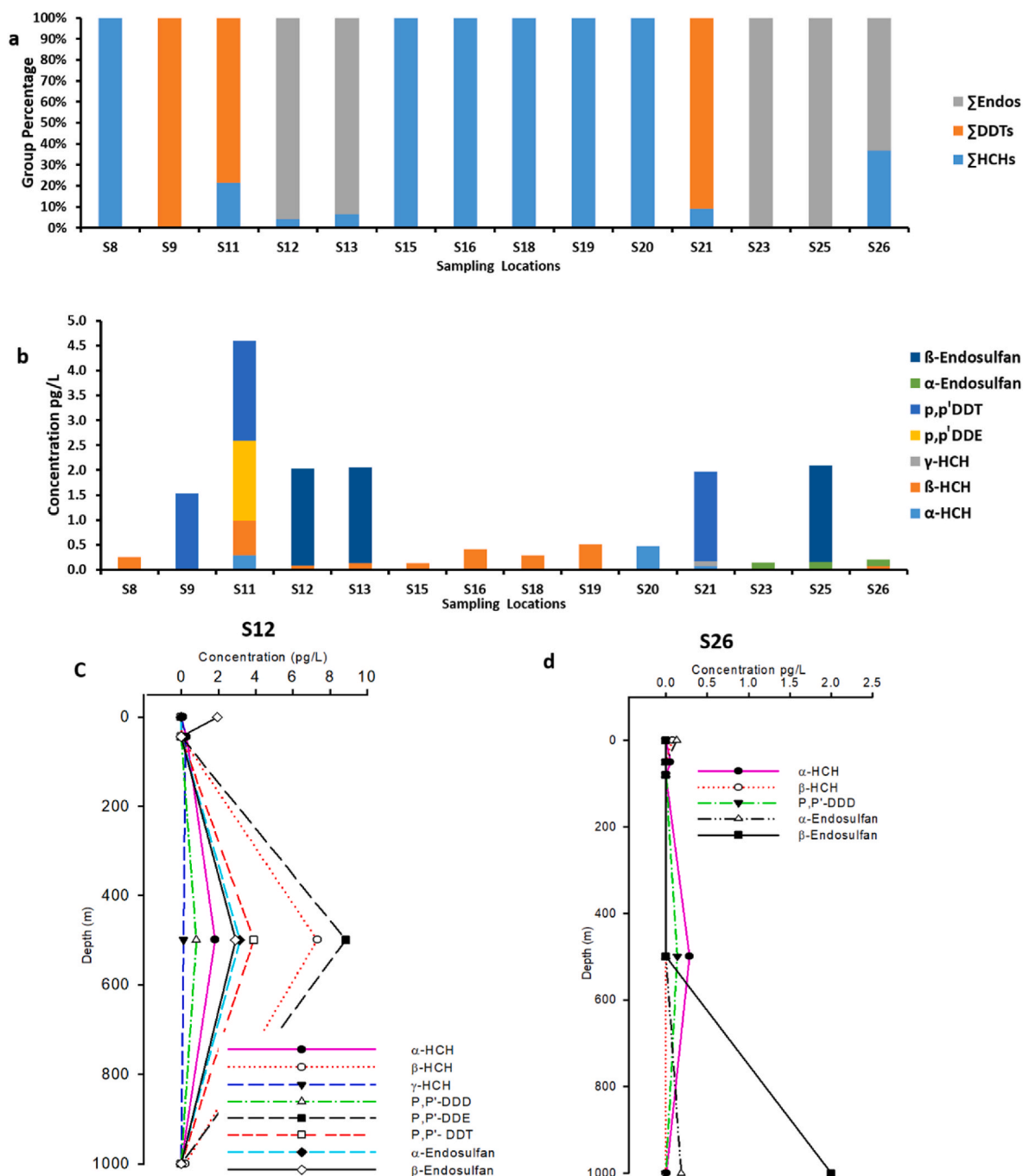


Fig. 3. OCPs congeners from the COA region. a) Group-wise percentages and b) concentration profiles of OCPs. Depth profiles of SIO region c) S12, and d) S26.

2022) including riverine and estuarine water (Rex and Chakraborty, 2022). We have provided a comparative chromatogram for 10 ppb of selected OCPs obtained from GC-ECD and GC-MS analysis of riverine and estuarine waters in the Supporting Information (SI-Figs. 1 and 2) which supports the use of GC-ECD as a highly sensitive and robust technique for analyzing OCPs.

2.5. Statistical analyses

All statistical analyses were performed using the IBM SPSS (Version 22) software. Principal component analysis (PCA) was used to evaluate the clustering between OCPs distributed in SIO and COA. Ocean Data View (ODV) was used for developing maps. The data presented in this study are an average of duplicate samples. Errors are indicated along with the average values.

2.6. Quality assurance and quality control

All the chemicals used in the study were of HPLC grade (FINAR). All chemical standards were procured from Wellington Laboratories (Sigma Aldrich, USA). Method recoveries ranged between 61 and 118% for OCPs with percent R.S.D. < 7%. Surrogate recoveries for TCmX ranged from 64 to 72%. For every set of 9 samples, one method blank was analyzed. One instrumental blank was analyzed for every five samples. No detectable levels of OCPs were observed in procedural blanks. The limits of detection (LOD) and instrumental detection limit (IDL) for each compound are given in Table SI 1. LOD was calculated as three times the standard deviation of method blanks and the limit of quantification (LOQ) was calculated as 10 times the standard deviation of method blanks.

2.7. Risk assessment

In chemical substance risk assessment, the hazard quotient (HQ) and risk quotient (RQ) are very important concepts (Arisekar et al., 2022). They are used by regulatory authorities such as US EPA to describe the risk category of a chemical substance. In this study, both were used, RQ and HQ for ecological and ecotoxicological risk assessment.

2.7.1. Hazard quotient (HQ)

A hazard quotient is the ratio of potential exposure to a substance and the level at which no adverse effects are expected on the marine ecosystem.

Hazard Quotient (HQ) = Exposure Concentration/Reference Concentration.

Ecotoxicological risk assessment was done for HCHs, DDTs, and endosulfan by estimating the HQ using USEPA protocols (USEPA, 1998):

$$HQ = EC/PNEC$$

where EC is the environmental concentration i.e. the concentrations of individual OCPs detected in surface seawater and PNEC is the predicted no-effect concentration of aquatic species. PNEC values were calculated for five tropic level groups (phytoplankton, zooplankton, molluscs, insects, and fishes); each group contains five species based on toxic endpoint value. The PNEC values for various tropic level has been summarized in Table SI 2. An HQ value > 1 infers the vulnerability of species at the given environmental concentration posing risk.

2.7.2. Risk quotient (RQ)

A risk quotient is the ratio of a point estimate of exposure and a point estimate of effects. It is primarily used by the USEPA to assess the ecological risk of pesticides.

Risk Quotient (RQ) = Estimated Environmental Concentration (EEC)/Ecotoxicity Endpoints.

Here, RQ was calculated according to USEPA guidelines (USEPA,

2006) and is briefly described below:

$$RQ = CTC/CQV$$

where CTC = Concentration of targeted contaminant. CQV = Corresponding quality values.

Further, risk quotients due to continuous criteria concentrations and maximum criteria concentrations were calculated using the equation

$$RQCCCs = CTCs/CQV(CCCs) \quad (1)$$

$$RQCMCs = CTCs/CQV(CMCs) \quad (2)$$

whereas RQCCCs = risk quotient for continuous criteria concentrations (CCCs), and. RQCMCs = risk quotient for maximum criteria concentrations (CMCs).

3. Results & discussions

3.1. General remark on OCPs in surface and depth profiles from SIO and COA regions

The OCPs were detected in only 23 out of the 33 stations, with the highest detection frequency for HCHs (54%), followed by endosulfan (30%) and DDTs (24%). Seven out of the 16 targeted OCPs, were detected with the following concentration ranges α -HCH: ND – 0.47 pg L⁻¹ (mean \pm s.d. = 0.06 \pm 0.14 pg L⁻¹), β -HCH: ND – 0.75 pg L⁻¹ (0.18 \pm 0.27 pg L⁻¹), γ -HCH: ND – 0.3 pg L⁻¹ (0.11 \pm 0.13 pg L⁻¹), p, p'-DDE: ND – 1.61 pg L⁻¹ (0.11 \pm 0.43 pg L⁻¹), p, p'-DDT: ND – 2.0 pg L⁻¹ (0.38 \pm 0.76 pg L⁻¹), α -endosulfan: ND – 0.26 pg L⁻¹ (0.08 \pm 0.10 pg L⁻¹), and β -endosulfan: ND – 1.92 pg L⁻¹ (0.48 \pm 0.88 pg L⁻¹). Principal component analysis revealed that most of the analyzed OCPs showed highly similar concentrations, and formed a single cluster.

Surface seawater in the SIO region showed a decreasing trend of OCPs contributions in the following order: \sum DDT (40.77%) > \sum HCH (30.33%) > \sum ENDO (28.90%) (Fig. 2a). On the contrary, \sum DDT contributions (19.26%) were lower in the COA region, whereas the contribution of \sum HCH (48.42%) was higher (Fig. 3a). In general, obtained data is consistent with the observations of endosulfan and HCH being widespread in remote regions such as the Arctic, high mountains, and across the globe (Weber et al., 2010). Excluding endosulfan sulfate, dieldrin, Heptachlor, Heptachlor Epoxide, Methoxychlor, cis-Chlordane, and trans-Chlordane, all other OCPs detected contributed to 50% of targeted OCPs. This observation was consistent with a previous study conducted in the Southern Ocean (Bigot et al., 2016). In the SIO region, individual OCP concentration profiles were p, p'-DDT > β -endosulfan > β -HCH > p, p'-DDD > α -HCH > α -endosulfan, and in COA were p, p'-DDT > β -Endosulfan > β -HCH > γ -HCH > α -HCH > α -endosulfan, respectively (Figs. 2b & 3b).

Depth profiles of OCPs were measured for five stations. In the SIO region, different OCP congeners were detected in three stations (α -HCH, β -HCH, γ -HCH, p, p'-DDD, α -endosulfan, and β -Endosulfan). In the COA region, OCP congeners were detected at two stations (α -HCH, β -HCH, γ -HCH, p, p'-DDD, p, p'-DDE, p, p'-DDT, α -endosulfan and β -Endosulfan) concentration profiles. The depth profiles were comparable with other deep ocean profile studies from the Atlantic Ocean (Sun et al., 2016) and the Arctic Ocean (Ma et al., 2018). Elevated concentrations of different OCP congeners were observed at lower depths (at 500 m). This might be an indication of the partitioning of particulate organic matter and subsequent mineralization and release in the remineralization zones, leading to the detected deeper water peaks. The depth profiles of individual OCPs congeners detected from Antarctica fronts in SIO (PF, SAF, and STF) (Fig. 2c – e) and COA stations (S12 & S26) (Fig. 3c & d) are discussed in detail in sections 3.1-3.3 along with surface profiles of individual OCP groups.

Table 1
Dissolved phase concentrations (pg L⁻¹) of OCPs in surface seawater at different locations of the world.

Location	Year	Concentration pg L ⁻¹					∑DDTs	References
		α-HCH	β-HCH	γ-HCHs	α-Endo	β-Endo		
Southern Ocean (SO)								
Coast of Antarctica	2018	ND-0.28 (0.06 ± 0.10)	ND-0.70 (0.19 ± 0.22)	ND-0.10 (0.01 ± 0.03)	ND-0.16 (0.03 ± 0.06)	ND-1.95 (0.41 ± 0.82)	1.54–3.61 (0.50 ± 1.08)	This Study
Southern Indian Ocean	2018	ND-0.47 (0.06 ± 0.14)	ND-0.75 (0.18 ± 0.27)	ND-0.03 (0.11 ± 0.13)	ND-0.26 (0.08 ± 0.10)	ND-1.92 (0.48 ± 0.88)	0.45–1.83 (0.69 ± 0.84)	This Study
Antarctic seawater	2015	1.0 to 1.3						Bigot et al. (2017)
Antarctic Sea-ice meltwater	2015	<0.63						Bigot et al. (2017)
SO between Australia and Antarctica	2014	2.0–4.4	<0.029–4.2	0.74–1.9	<0.42–0.87	<0.31	0.59–5.61	Bigot et al. (2016)
Bellingshausen	2009	0.198	0.261	0.876				(Cristóbal et al., 2013)
Brans field	2009	0.189	3.132	2.26				(Cristóbal et al., 2013)
Drake Passage	2009	0.953	0.929	0.787				(Cristóbal et al., 2013)
Weddell	2009	0.26	2.885	2.148				(Cristóbal et al., 2013)
Terra Nova Bay	2003	1.41		2.9				Cincinelli et al. (2009)
Western Antarctic	2001–2002	1.6–4.54		0.90–11				(Rebecca M. Dickhut et al., 2004)
Palmer Vicinity	2002	3.1		3.8				(Rebecca M. Dickhut et al., 2004)
Southern Ocean(30.2° S–66.2° S)	1999–2000	2.9–9.6		0.7–5.5				Lakaschus et al. (2001)
Southern Ocean	1990	18–43		4.9			0.6–1.5	Iwata et al. (1993)
Tottuki Point	1981	570 ^b	570	570				Tanabe et al. (1983)
Langhovde	1981	210 ^b	210	210				Tanabe et al. (1983)
Kitano-Ura Cove	1982	570 ^b	570	570				Tanabe et al. (1983)
Arctic Ocean								
Arctic sea-ice meltwater	2015	34.7–48.2						Bigot et al. (2017)
Arctic seawater	2015	224–253						Bigot et al. (2017)
Arctic Ocean (>70 N)	2010	67.2–536.0	23.7–88.7	16.0–134.2				Cai et al. (2012b)
Arctic (2007–08)	2008	250–1300		55–340				Wong et al. (2010)
Arctic (1993–94)	1994	230–2700						Jantunen and Bidleman (1998)
Canadian Archipelago	1999	1100–5400	56–160	190–450				Jantunen et al. (2007)
Atlantic Ocean								
South Atlantic (1.6° S–67.3° S)	2008	0.33–5.0	0.11–0.84	0.02–0.30				(Zhiyong Xie et al., 2011)
North Atlantic (8.5° N–50.1° N)	2008	1.4–47	0.18–9.5	0.09–7.2				(Zhiyong Xie et al., 2011)
Northeast Atlantic and Arctic	2004	1.1–65		0.4–21				Lohmann et al. (2009)
Atlantic (46.9° N–30° S)	1999–2000	2–69		1.4–130				Lakaschus et al. (2001)
ANT XVII Cruise/ Atlantic	1999	4.3		0.8				Lakaschus et al. (2001)
Atlantic (54.05° N–55.8° S)	1993	6.1–110		0.7–560				Lakaschus et al. (2001)
Atlantic (52.75° N–63.66° S)	1997	3.6–100		0.9–740				Lakaschus et al. (2001)
Atlantic (50° N–50° S)	1990–1991	6.7–70		21–75				Schreitmüller and Ballschmiter (2002)
Atlantic (53.9° N–63.4° S)	1991	5.0–140		0.9–570				Lakaschus et al. (2001)
Atlantic (51.1° N–29.3° S)	1987	10–470		2.6–1240				Lakaschus et al. (2001)
ANT IX/Atlantic	1991	15 ^d		21 ^d				Schreitmüller and Ballschmiter (1995)
Atlantic (50.6° N–30.8° S)	1989	15–530		3.6–1970				Lakaschus et al. (2001)
Gulf of Mexico	1989	44		14			2.2	Iwata et al. (1993)
North Atlantic and Arctic	1999–2000	59–690		72–504				Lakaschus et al. (2001)
North Atlantic	1989	70–140		10–27			0.7–0.9	Iwata et al. (1993)
North Sea (54° N)	1999, 2001	98		330				Lakaschus et al. (2001)
Caribbean Sea	1989	180		36			3.9	Iwata et al. (1993)
Pacific Ocean								
North Pacific (50–66°N)	2010	65.4–136.8	5.3–44.3	6.7–30.3				Cai et al. (2012b)
Celebes Sea	1990	240		43			2.6	Iwata et al. (1993)
Java Sea	1990	46		12			5.6	Iwata et al. (1993)
Strait of Malacca	1990	360		120			6.4	Iwata et al. (1993)

(continued on next page)

Table 1 (continued)

Location	Year	Concentration pg L ⁻¹					∑DDTs	References
		α-HCH	β-HCH	γ-HCHs	α-Endo	β-Endo		
South China Sea	1990	62–740		62–740			3.5–12	Iwata et al. (1993)
East China Sea	1990	100–1100		11–150			1.5–41	Iwata et al. (1993)
Northern North Pacific	1989	330–1400		43–320			0.6–5.5	Iwata et al. (1993)
North Pacific	1989	65–460		9.5–90			0.3–2.8	Iwata et al. (1993)
Gulf of Alaska	1989	1500–1800		200–310			0.9–1.6	Iwata et al. (1993)
Bering Sea	1989	1200–1900		160–230			0.2–2.9	Iwata et al. (1993)
Chukchi Sea	1989	1300–1600		150–220			0.2–0.4	Iwata et al. (1993)
Indian Ocean								
Eastern Indian Ocean	1990	40–130		14–39			1.3–4.3	Iwata et al. (1993)
Bay of Bengal and Arabian Sea	1990	100–1200		27–190			1.6–24	Iwata et al. (1993)

3.2. Concentration profiles and distributions of OCPs in SIO and COA

3.2.1. Endosulfan

The concentration of ∑ENDO (α-endosulfan + β-endosulfan + endosulfan sulfate) in SIO and COA ranged from ND - 2.06 pg L⁻¹ (0.56 ± 0.88 pg L⁻¹) and ND - 2.09 pg L⁻¹ (0.45 ± 0.84 pg L⁻¹). The metabolite endosulfan sulfate of endosulfan was not detected in any of the samples. Concentrations of detected α-endosulfan were higher but β-endosulfan was lower compared to the 2014 cruise by Bigot et al. (2016). In their cruise (Bigot et al., 2016), α-endosulfan concentrations were <0.42–0.87 pg L⁻¹, whereas in our study they were, ND - 0.16 pg L⁻¹ (COA) and ND - 0.26 pg L⁻¹ (SIO). β-Endosulfan concentrations were lower (<0.31 pg L⁻¹) (Bigot et al., 2016) than in COA (ND - 1.95 pg L⁻¹) and SIO (ND - 1.92 pg L⁻¹) in our work. ∑ENDO concentrations of SIO and COA were much (445 fold) lower than the Chukchi Sea (<MDL-1.39 ng L⁻¹; 0.25 ± 0.39 ng L⁻¹) (Gao et al., 2020). The low frequency of detection is a reflection of the overall reduced emissions of endosulfan in the study region, as observed elsewhere (Bigot et al., 2016; Cristóbal et al., 2013; Gao et al., 2020). Among endosulfan isomers, β-endosulfan was dominant. While the vapor pressures of α- and β-endosulfan are similar, the solubility of β-endosulfan is about 10 times higher than that of α-endosulfan thereby more likely to be scavenged by precipitation with higher proportions in seawater. This observation (Weber et al., 2010) is consistent with the observation made in the present study.

The α-endosulfan was detected at S3, S30, S31, and β-endosulfan at S3 and S29, and S32 stations in SIO. Concentrations of α-endosulfan decreased between STF to PF portions of SIO (with no α-endosulfan detected in PF) and were low in stations S23, S25, and S26 of COA. β-endosulfan was detected up to 2 pg L⁻¹ in station S3 of STF and PF. The range ratio of α/β endosulfan in the SIO surface waters was 0–0.072 and in the COA was 0–0.084. Commercial technical grade endosulfan contains α-endosulfan and β-endosulfan in the ratio 2:1 to 7:3 depending on the technical mixture (Herrmann, 2002) and a lower ratio is indicative of legacy use and no fresh source (Gao et al., 2020).

Similar to SIO, lower concentrations of α-endosulfan and higher concentrations of β-endosulfan were detected from locations S12, S13, S23, S25, and S26 in COA. In COA, β-endosulfan was detected in three stations S12, S13, and S25 closer to the Antarctic coasts. Global modeling based on global emissions, and latitudinal transport in air and water (Becker et al., 2011), predicted seawater α- and β-endosulfan concentrations to be between approximately 0.5 pg L⁻¹ and 1 pg L⁻¹, with a drop in concentrations of β-endosulfan close to the Antarctic coast. Sea ice is a reservoir of endosulfan and would act as a source of endosulfan to coastal waters during melting (Bigot et al., 2017; Gao et al., 2020; Potapowicz et al., 2020) This, along with the higher solubility β-endosulfan (Weber et al., 2010) could explain its presence at higher concentrations at stations near to the coasts.

Depth profile samples detected the highest concentration of β-endosulfan at 1000 m (1.93 pg L⁻¹) depth in station S28 of the PF region (Fig. 2c). α-Endosulfan were detected at all the frontal systems depths at PF (S28-60 m: 2.92 pg L⁻¹ and 1000 m: 0.19 pg L⁻¹); SAF (S31-

500 m: 0.21 pg L⁻¹) (Fig. 2d) and STF (S33: 75 m: 0.24 and 500 m: 0.15 pg L⁻¹) (Fig. 2e). Depth profiles in COA showed the highest concentration of α-endosulfan at station S26 (surface: 0.13 pg L⁻¹ and 1000 m: 0.18 pg L⁻¹) (Fig. 3d) and S12 (500 m: 3.16 pg L⁻¹) (Fig. 3c).

Depth profiles of α- and β-endosulfan at stations S28 in SIO, and S12 and S26 in COA, reveal elevated levels at lower depths, 1000 m at S28 and S26, and 500 m at S12. Based on their octanol-carbon partition coefficient (*K*_{OC}) values, α- and β-endosulfan are expected to partition to particulate matter. Lower depths are often the locations of particulate remineralization. Elevated concentrations at lower depths might be an indication of the partitioning of endosulfan to particulate matter and subsequent mineralization and release in the remineralization zones, leading to the detected deep water peaks.

3.2.2. HCHs

The concentrations of ∑HCH in the surface water of SIO ranged from ND -1.21 pg L⁻¹ (0.35 ± 0.42 pg L⁻¹). The concentrations of α-, β-, and γ-HCH were 0.06 ± 0.10 pg L⁻¹, 0.18 ± 0.27 pg L⁻¹, and 0.11 ± 0.13 pg L⁻¹, respectively (Fig. 2b). The range of HCH isomers (Table 1) observed from SIO was relatively lower compared to previous studies from the Southern Ocean (between Australia and Antarctica) (α-HCH; 2.0–4.42 pg L⁻¹, β-HCH; 0.02–4.2 pg L⁻¹, and γ-HCH; 0.74–1.9 pg L⁻¹) (Bigot et al., 2016), and Antarctic Peninsula (1.2–12.3 pg L⁻¹) (Cristóbal et al., 2013). ∑HCH concentrations in COA (0.25 ± 0.27 pg L⁻¹) were relatively lower (0.4 folds) compared to SIO (0.35 ± 0.42 pg L⁻¹), and other parts of the Southern Ocean (6.6 pg L⁻¹) (Bigot et al., 2016) and (0.46–82 pg L⁻¹) (Zhiyong Xie et al., 2011), indicating a decreasing trend of HCHs concentrations in the surface waters of the oceans in the last decade (Table 1).

The concentrations of α-, β-, and γ-HCHs were 0.06 ± 0.14 pg L⁻¹, 0.19 ± 0.22 pg L⁻¹ and 0.01 ± 0.03 pg L⁻¹, respectively. β-HCH was the most detected isomer (Figs. 2b and 3b) with a detection frequency of 42%. Higher levels of β-HCH are likely attributable to its lower vapor pressure and lower *K*_{AW} (air-water partition coefficient), and higher stability (Li et al., 2020).

β-HCH was the dominant congener in the both SIO and COA region. This observed dominance is consistent with observations in a Northern-to-Southern Hemisphere transect in the Western Atlantic Ocean (Lohmann et al., 2021). Overall, our values signify a consistent decreasing trend in HCH concentrations since the 1980s, similar to measurements in the South Atlantic Ocean (Zhiyong Xie et al., 2011) (Table 1), and is likely a reflection of the global decrease in the emission of these compounds. It is noteworthy that only α-HCH was detected during our first sampling at station S1 (on December 15, 2017). However, both α- and β-HCH were detected at station S1 (labeled as S33) when the ship returned to the same sampling point on January 29, 2018. This indicates a possible role of ocean currents in mediating the transport of OCPs and their detection in the study region.

α- and γ-HCH are more volatile and amenable to long-range transport in air, and are deposited in polar regions via cold condensation. The ratio of α-to γ-HCH which is close to the ratio in technical HCH,

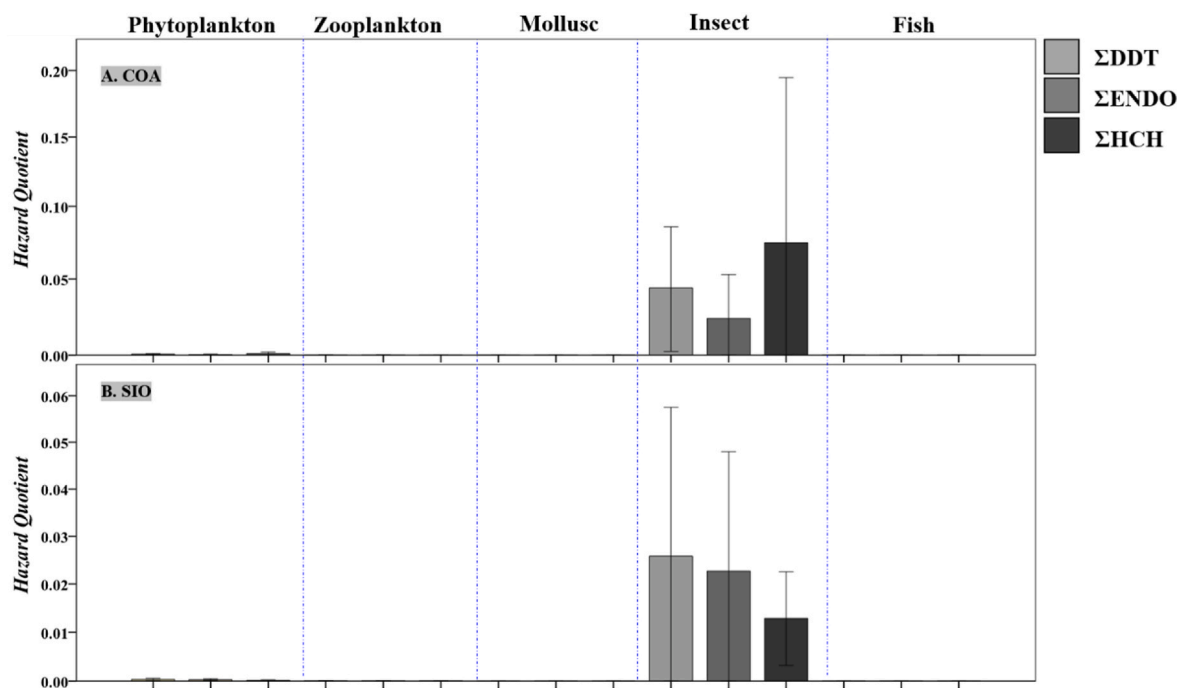


Fig. 4. The Error plots are showing ecotoxicological risk assessed from surface seawater concentrations of the sum of isomers and metabolite of HCH, Endosulfan, and DDT in the A. Southern Indian Ocean and B. Coast of Antarctica.

approximately 3–7, is indicative of global sources and long-range transport, whereas a ratio close to or lower than 1 is indicative of a lindane source (Willett et al., 1998). α/γ -HCH ratio close to one was observed at specific sites (S2, S30, and S7), indicating a more recent lindane source. Although station S7 is located at the southernmost latitude and closer to the Antarctic coast, the surface waters of S7 may still represent those from lower latitudes since colder Antarctic water would sink beneath the warmer lower latitude waters in an Antarctic Convergence zone (Bigot et al., 2016).

Depth profiles from station S31 in SAF showed a higher detection frequency of β -HCH (80%) than α -HCH (40%) and γ -HCH (40%) (Fig. 2c). Increased concentrations of β -HCH were detected at 75 m (0.45 pg L^{-1}) and 500 m (0.66 pg L^{-1}), which may be due to particulate mineralization at lower depths, where particulate matter-associated organic compounds can dissociate and enter the dissolved phase (Baltar et al., 2021). γ -HCH congener was increased at 1000 m depth. Likewise, there was a peak in γ -HCH in station S33 at 500 m, indicating some contribution from terrestrial sources (Vijgen et al., 2011) and transport (Z. Xie et al., 2011) to deep water masses via water masses mixing (Jurado et al., 2007; Lohmann et al., 2006). Station S28 in the polar front (PF) had very low concentrations of HCH at all depths and indicated the presence of old water masses without any new HCH source.

The α -HCH, β -HCH, and γ -HCH were detected at the highest levels at the 500 m depth at station S12 of the COA region (Fig. 3c). Additionally, in COA depth profiles, β -HCH existed at higher concentrations than α - and γ -HCH, and the ratio of α -to γ -HCH was much higher than 1. This indicates an aged source. This could be due to the contribution of melted sea ice containing old HCH which was transported by long-range transport, and the subsiding of this cold water mass under the warmer surface water (Bigot et al., 2016), followed by mineralization. HCH in particular is dependent on the movement of ocean masses and requires a better and more comprehensive understanding of their behavior and movement in the global environment (Li et al., 2020).

3.2.3. DDTs

The concentrations of \sum DDT (p, p' -DDT + p, p' -DDD + p, p' -DDE) in

SIO ranged from ND - 1.83 pg L^{-1} ($0.69 \pm 0.84 \text{ pg L}^{-1}$). The concentrations of \sum DDT in COA ranged from ND - 3.61 pg L^{-1} ($0.50 \pm 1.08 \text{ pg L}^{-1}$). \sum DDT in COA (ND - 3.61 pg L^{-1}) and SIO (ND - 1.83 pg L^{-1}) were higher compared to earlier studies from the Arctic Ocean (0.16 – 0.31 pg L^{-1}) (Cai et al., 2012a) and European Arctic (0.17 – 0.96 pg L^{-1}) (Lohmann et al., 2009). However, they were lower than those observed in other parts of the Southern Ocean (0.59 – 5.61 pg L^{-1}) (Bigot et al., 2016). While DDT has been banned in many regions, its use is allowed in tropical countries for malaria control. Additionally, it can be present in compounds such as dicofol (Turgut et al., 2009). The diagnostic ratio of p, p' -DDT/ p, p' -DDE was < 1 (0 – 0.5) at surface SIO indicating a past usage of DDT. On the contrary, in the surface COA region the diagnostic ratio of p, p' -DDT/ p, p' -DDE was > 1 (0 – 1.2) which indicates most legacy DDT might have degraded sources of DDT.

Deep water profiles in SIO (S33/STF and S31/SAF) showed the negligible presence of p, p' -DDT or its metabolites p, p' -DDD or p, p' -DDE (Fig. 2d and e). In S28/PF at 50 m p, p' -DDT metabolite p, p' -DDD was detected (3.36 pg L^{-1}) (Fig. 2c). However, all three were detected in deep water profiles in station S12 of COA, and p, p' -DDD was detected in S26 of COA. In both stations, peaks occur at 500 m, which coincides with peaks of other studied OCPs and are likely due to the remineralization of particulate matter. The diagnostic ratio of p, p' -DDT/ p, p' -DDE was < 1 (0.4) at 500 m of S12 in COA which suggests that p, p' -DDT at S12 aged source/past usage of DDT. However, a low p, p' -DDT to p, p' -DDE ratio also suggests the contribution of aged sources (Cipro et al., 2011).

3.3. Risk assessment

Ecotoxicological risks showed the impact of different OCPs (such as HCH, ENDO, and DDT) for the different group organisms in different trophic levels (phytoplankton, zooplanktons, molluscs, insects, and fishes) for the study sites SIO and COA (Fig. 4.). The error plots in Fig. 4 represent the calculated hazard quotient showed moderate risk only for insects for HCH, DDT, and ENDO. Mosquito was the significant contributor towards higher HQ among insects and other marine organisms and did not have any serious impact due to any of the OCPs.

In addition to the impact on different trophic level organisms, risk

Table 2
RQ (CCC_s) and RQ (CMCs) for OCPs and PCBs in surface water (pg L⁻¹) of SIO.

Criteria Guidelines by USEPA, 2006.	α -HCH	β -HCH	γ -HCH	α -Endosulfan	β -Endosulfan	<i>p, p'</i> -DDE	<i>p, p'</i> -DDD
CMC ^a (pg L ⁻¹)	–	–	950000	220000	2400000	1100000	1100000
CCC ^b (pg L ⁻¹)	–	–	–	56000	4300	1000	1000
MEC ^c	ND - 0.28 pg L ⁻¹ (0.06)	ND - 0.75 pg L ⁻¹ (0.18)	ND - 0.3 pg L ⁻¹ L ⁻¹ (0.11)	ND - 0.26 pg L ⁻¹ L ⁻¹ (0.08)	ND - 1.92 pg L ⁻¹ L ⁻¹ (0.48)	ND - 1.83 (0.63)	ND - 0.45 pg L ⁻¹ (0.06)
^{RQ} CMC	–	–	1.2E-07	3.6E-07	3.6E-07	5.7E-07	5.5E-08
^{RQ} CCC	–	–	–	1.4E-06	1.1E-04	6.3E-04	6.0E-05

Table 3
RQ (CCC_s) and RQ (CMCs) for OCPs in surface water (ng L⁻¹) of COA.

Criteria Guideline by USEPA, 2006	α -HCH	β -HCH	γ -HCH	α Endosulfan	β -Endosulfan	<i>p, p'</i> -DDE	<i>p, p'</i> -DDT
CMC ^a (pg L ⁻¹)	–	–	950000	220000	2400000	1100000	1100000
CCC ^b (pg L ⁻¹)	–	–	–	56000	4300	1000	1000
MEC ^c	ND-0.47 pg L ⁻¹ (0.06)	ND- 0.7 pg L ⁻¹ (0.19)	ND-0.1 pg L ⁻¹ (0.01)	ND-0.16 pg L ⁻¹ (0.03)	ND-1.95 pg L ⁻¹ (0.41)	ND-1.61 pg L ⁻¹ (0.11)	ND-2 pg L ⁻¹ (0.38)
^{RQ} CMC	–	–	1.1E-08	1.4E-07	1.7E-07	1.0E-07	3.5E-07
^{RQ} CCC	–	–	–	5.4E-07	9.5E-05	1.1E-04	3.8E-04

a) Criteria Maximum Concentration: is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed briefly without resulting in an unacceptable effect (USEPA, 2006)

b) Criteria Continuous Concentration: is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (USEPA, 2006).

c) Range of Measured Concentration for OCPs and PCBs and average in parenthesis. Criteria Continuous Concentration: is an estimate of the highest concentration of a material in surface water to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (USEPA, 2006)

Table 4
Comparison of present study concentrations (pg L⁻¹) of OCPs with safe levels of POPs determined by NOAA.

Compound Name	NOAA Standards		This Study
	Acute	Chronic	Range (average.)
Lindane	0.08(1/2)	–	0–5.79 (5.0)
<i>p, p'</i> DDD	3.6×10^6	0.36×10^5	0–4.14 (0.26)
<i>p, p'</i> DDE	14×10^6	1.4×10^5	0–1.87 (0.12)
<i>p, p'</i> DDT	$0.065(1/2) \times 10^6$	$0.065(1/2) \times 10^6$	0–2.0 (0.40)
Dieldrin	$0.355(1/2) \times 10^6$	$0.00095(1/2) \times 10^6$	0–6.06 (0.75)
Endosulfan Sulfate	–	–	–
α -Endosulfan	$0.017(1/2) \times 10^6$	$0.00435(1/2) \times 10^6$	0–4.19 (0.32)
β -Endosulfan	$0.017(1/2) \times 10^6$	$0.00435(1/2) \times 10^6$	0–6.09 (0.56)

quotients due to continuous criteria concentrations and maximum criteria concentrations for water quality assessment have been calculated and presented in Tables 2 and 3. Risk Quotients for criteria continuous concentration (RQ_{CCC_s}) of OCPs did not exceed the limit (RQ_{CCC_s} > 10) in both SIO and CAO regions. The concentrations of OCPs detected at SIO and COA was below the water quality criteria (USEPA, 2006) recommended by the Environmental Protection Agency (EPA) as well as the acute and chronic levels set by NOAA (Table 4). This suggests that these concentrations are not harmful to the marine organisms in the polar regions.

4. Conclusions

This work provides new baseline data that adds to the global dataset on OCPs in the open oceans. This data can contribute to the general understanding of the distribution and sources of POPs in open oceans and provide valuable input and validation data for global models. Results indicated that OCPs concentrations in both SIO and COA regions were lower compared to OCPs concentrations reported previously from the Arctic, Antarctic, Atlantic, Pacific, and Southern Oceans. This comparison indicated a decreasing trend of OCPs concentrations since the 1980s, which is owing to the global decrease in the use of OCPs. We recommend long-term monitoring of OCPs in the open oceans, which

can provide new insights into the complex cycle of these pesticidal POPs, and the impacts of long-range atmospheric transport, global ocean currents, and the water mass movements in the polar regions on pollution at high latitudes in the global south.

Author contribution

Krushna Vudamala: Investigation, Writing – original draft; Paromita Chakraborty: Resources, Writing – review & editing; Ramesh Chatharagadda; Formal analysis; Anoop Kumar Tiwari: Resources; Asif Qureshi: Conceptualization, Resources, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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