Persistent Organic Pollutants in the Equatorial Atmosphere over the Open Indian Ocean

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Twelve air samples collected over the Indian Ocean by a high volume air sampler between August 2004 and August 2005 were analyzed for selected polychlorinated biphenyl (PCB) congeners and organochlorine pesticides. The region of the Indian Ocean and adjacent countries is likely to be acting as a source of selected POPs to the global environment. Data were compared with those reported for the last 30 years to examine historical trends of selected persistent organic pollutants (POPs) over the Indian Ocean. Compound concentrations were influenced by the proximity to land and air mass origins. Higher concentrations of atmospheric ΣPCBs (50−114 pg m^{-3}) were found on the remote islands of Chagos Archipelago and Gan, Maldives, and in the proximity of Jakarta, Indonesia, and Singapore. Military activities and unregulated waste combustion were identified as possible sources for atmospheric PCB contaminations at the more remote areas. The highest concentrations of organochlorine pesticides were found adjacent to the coastline of Sumatra and Singapore, where ΣDDTs (dichlorodiphenyl-trichloroethane) and ΣHCHs (hexacyclohexanes) were as high as 30 and 100 pg m^{-3}, respectively. A comparison study for the last 30 years over six regions of the Indian Ocean showed that the concentrations of organochlorine pesticides have declined significantly, by a magnitude of two, since the mid 1970s, but were highest at the beginning of the 1990s. The time trend of PCB contamination in the atmosphere over the Indian Ocean is less apparent. The decline of atmospheric POPs over the Indian Ocean may be due to international regulation of the use of these compounds.

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Introduction

Persistent organic pollutants (POPs) are globally distributed through the environment (*1*) and are of great concern due to their persistence, carcinogenicity, and endocrine-disrupting effects (*2*). POPs include a wide range of xenobiotic chemicals, such as the polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), e.g., hexachlorocyclohexane (HCH), dichlorodiphenyltrichloroethane and related compounds (DDTs), and chlordanes. These chemicals have even been detected in remote polar regions with no historical usage, including the atmosphere (*3*, *4*), water (*5*), and biota (*6*). Recently POPs have been reported to have an effect on the endocrine system of polar bears, thereby indicating the potential of these chemicals to impact mammals at the top of the food chain (*7*, *8*). The atmosphere can be considered as a mobile phase for the long-range transport of POPs toward the polar regions, where cold condensation of POPs to the ocean occurs. In addition to primary sources, the atmosphere receives input of POPs via evaporation processes from soil and the ocean, which occurs intensively in tropical regions. Wania and Mackay (*9*) suggested that POPs may migrate to higher latitudes in a series of "jumps" characterized by evaporation and condensation steps, aligned by seasonal temperature changes at mid-latitudes, known as the "grasshopper effect". The collection of atmospheric data for POPs over the open oceans is challenging, and reports in the literature are sparse, even though such data are of primary interest for a better insight into the global distribution of POPs. The tropical regions of Asia are considered to be a prime source of many POPs of strategic geographical importance due to their extensive use and associated global atmospheric dispersion (*10*). Available data for prevailing concentrations of atmospheric POPs over the Indian Ocean now date back over a decade (*1*). However, data for the Atlantic Ocean atmosphere were reported more recently (*11*, *12*). Primary emissions of POPs to the atmosphere have changed over the decades, particularly after the establishment of international regulations on reducing emissions (*13*, *14*). However, there is mounting evidence that POPs are still widely used in the developing countries of tropical regions (*15*, *16*), where the enormous usage of DDTs and HCHs in India and China in recent decades (*17*) is likely to act as a long-term source to the atmosphere. For example, the pesticide Dicofol is manufactured in China and contains DDT compounds as impurities of unknown content, as reported by Qui et al. (*18*). Dicofol is still widely used in several countries of Southeast Asia and China and is likely to be a source for DDT contamination in these regions (*15*, *19*), even though actual DDT is banned. In the past, PCBs were mainly used as dielectric fluids in transformers and large capacitors, as plasticizer in sealants, heat exchange fluid, hydraulic lubricants, cutting oil, and paints (*20*). PCB production in most countries was banned in the 1970s and 1980s, but the ship-breaking industry in India and Bangladesh continues to be a major emission source of PCBs to the Indian Ocean, with up to 0.25−0.8 metric tons of PCBs generated per scrapped merchant ship (*21*). Many gaps in the inventory data of PCB-containing equipment exist for many countries adjacent to the Indian Ocean (*22*).

This study reports the concentration of PCB congeners, HCH isomers, DDT and its metabolites, and chlordanes in atmospheric samples collected over the open Indian Ocean between August 2004 and August 2005, and suggests sources of atmospheric contaminations of POPs. We have compared these data with three similar studies conducted over the last 30 years (*1*, *23*, *24*) to establish temporal trends of contami-
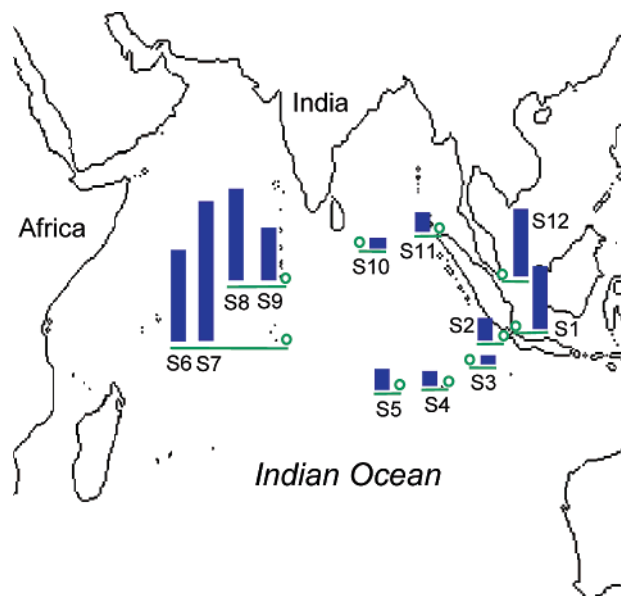
FIGURE 1. Spatial distribution of ΣPCBs at Stations S1−S12. Key: Largest bar = 114.3 pg m^{-3} (Station S7); smallest bar = 6.8 pg m^{-3} (Station S10).

nation. We have also investigated the influence of prevailing air mass direction on the prevailing atmospheric concentrations using air trajectory models.

Materials and Methods

Sample Collection. In contrast to other similar studies conducted on research vessels, the sample collection was conducted on an 18 m long fiberglass sailing vessel named *Jocara*. Samples were collected under sail to reduce possible contamination from combustion sources to an absolute minimum. Samples collected at Station S12 (Singapore) were collected from a small research vessel named *Hammerhead* anchored 4 km offshore of Singapore's main island. All samples were collected at 4 m above sea level and into the prevailing wind. In total, 12 samples were collected in duplicate between August 2004 and August 2005 during a cruise which circumnavigated the Indian Ocean from Singapore to Sumatra, Cocos Keeling, Madagascar, Seychelles, Chagos Archipelago, Maldives, and back to Singapore—a distance of approximately 8000 nautical miles. The sampling route is shown in Figure 1 and at each station one air sample in duplicate was collected. Sample stations S6 and S7, as well as S8 and S9, were located near each other. A 12-V DC high-volume air pump (H8400B, F&J Specialty Products, Inc.), with a fixed flow rate of 55 L/min, was used for sample collection at Stations S1−S5. Due to a 30% decline in the power of the air sampler, it was replaced by a 220-V AC H8400TE air sampler with a variable flow rate and a thermally protected motor for onward sample collection. The flow rate of the H8400TE air sampler was set to 400 L/min, resulting in a range of total collected air volume of between 60 and 260 m^3. However, as described in the Quality Assurance section, the breakthroughs of POPs from the polyurethane foam (PUF) plugs were within an acceptable range for all samples collected. The decline in power of the H8400B air sampler and inaccuracy of air flow measurements during collection of samples at Station S1−S5 was accounted for in data processing (see Error Analysis section). Air was aspirated through a glass fiber (GF) filter to remove particles from the air, and gaseous compounds were captured on two PUF plugs contained in dual stainless steel cartridges. The GF filter and PUF plugs were precleaned and stored prior to sampling as described in ref *25*. After sampling, the GF filters were stored

in solvent-rinsed glass jars, and the PUF plugs were stored in a solvent-rinsed tin container. Glass jars and tin containers containing samples were kept in air- and moisture-tight plastic containers and stored at −18 °C prior to extraction.

Sample Treatment and Analytical Procedure. The PUF plugs were extracted according to a quality assured microwave assisted extraction (MAE) procedure reported previously (*25*). Prior to MAE, each sample was spiked with a $^{13}C_{12}$ PCB surrogate standard containing the congeners CB 28, 52, 101, 138, 153, and 180. The exposure of samples to ambient laboratory air was avoided by using a purified nitrogen atmosphere. Sample extracts were subjected to cleanup on a silica gel column. Sample extracts were reduced to 100 μL under a gentle nitrogen stream.

Sample analysis was conducted using a Varian 4000 GC-MSMS equipped with a CP 8400 auto sampler, DB 5 fused silica capillary column (60 m × 0.32 mm i.d., film thickness 0.25 μm), and ion trap. Purified helium was used as the carrier gas with a flow rate of 1.5 mL/min. A 3-μL portion of sample was injected into the GC-MSMS in splitless mode with an injection time of 1 min. Manifold, injection, ion trap, and transfer line temperatures were set to 60, 260, 220, and 280 °C, respectively. The oven temperature was programmed from 70 to 140 °C at a rate of 25 °C min^{-1}, 140 to 179 °C at a rate of 2 °C min^{-1}, 179 to 210 °C at a rate of 1 °C min^{-1}, 210 to 300 °C at 5 °C min^{-1}, and held for 10 min. The ion trap was operated in internal EI-MS/MS mode. The multiplier offset was +300 V. The filament emission current was 80 μA for the internal EI mode. A resonant waveform (collision-induced dissociation, CID) was selected for all compounds. Three quality control criteria were used to ensure correct analyte identification: (a) signal-to-noise ratio greater than three, (b) GC retention times matched (±0.1 min) those of standard compounds, and (c) the threshold match calculated by GC-MSMS software using library and sample spectrum was greater than 600. The lower value of 600 for positive identification was derived from a comparison of the threshold match of both standard solution and samples. 38 PCB congeners (CB 17+31, CB 18, CB 28, CB 33, CB 44, CB 49, CB 52, CB 70, CB 74, CB 82+110, CB 87, CB 95, CB 99, CB 101, CB 118, CB 128, CB 132, CB 138, CB 149, CB 151, CB 153, CB 156, CB 169, CB 170, CB 171, CB 177, CB 180, CB 183, CB 187, CB 191, CB 194, CB 199, CB 205, CB 206, CB 208, and CB 209), HCH isomers (α-, β-, γ- and δ-HCH), DDT compounds (p,p'-DDT, p,p'-DDD, and p,p'-DDE), and chlordane isomers (cis- and trans-chlordane) were quantified using an internal standard method.

Quality Assurance. Analytical procedures were subjected to strict quality assurance and control procedures. The analytical procedure was routinely checked by the analysis of standard reference material (SRM) for organic contaminants in sediments and generally yielded recoveries between 72 and 112%. Samples were collected in duplicate and in general yielded coefficients of total variance of between 7 and 32%. A few analytes detected closer to the method detection limit (MDL) yielded coefficients of variance as high as 55%, which was considered to be acceptable for the low concentrations measured. The breakthrough of POPs trapped on two PUF plugs in series was assessed by analyzing the plugs separately and comparing the concentrations in each plug. The breakthrough was below 20% among all samples and highest for HCH isomers. The error of breakthrough was compensated, as described below in the section on error analysis. Field blanks and analyte-spiked PUFs plugs constituted each 10% of the total number of samples in order to identify any contamination or losses of analytes during the transport and storage of samples. Field blanks and spiked PUF plugs were analyzed using the same procedure as the samples. Procedural blanks were obtained by following the extraction and cleanup procedure without the PUF plug.

Analytes were not detected in the procedural and field blanks. MDLs were derived from the field blanks and calculated as average peak area ($n = 5$) plus 3 times the standard deviation. MDLs were in the same range as reported in our previous study (25). The recoveries of analytes from spiked PUF plugs were in the range of 72 to 95%. The entire analytical procedure was validated using $^{13}C_{12}$-labeled PCB congeners, where mean recoveries were between 64 and 105% among all samples. $^{13}C_{12}$-labeled PCB congeners (CB 32, 141, 208) were used as internal standards. Control calibration standards were analyzed for every six samples to check instrument performance during analysis.

Error Analysis. Uncertainties in the estimated atmospheric concentrations of POPs were derived from uncertainties occurring during sample treatment and analysis, and uncertainties in the flow rate of the air sampler. The uncertainty originated from breakthrough of POPs from the PUF plugs was not included in the error assessment, but atmospheric concentrations of POPs were corrected by a correction factor S, as calculated using an infinite Taylor Series as follows:

$$S = 1 + \frac{1}{k} + \frac{1}{k^2} + \frac{1}{k^3} + ...\frac{1}{k^n}... \quad (1)$$

where k is the multiplier factor that relates the concentration levels found in the first and second PUF plugs exposed to the sampled air flow. Equation 1 can be manipulated to give

$$S = \frac{k}{k-1} \quad (2)$$

For the highest breakthrough of 20% ($k = 5$) as observed in this study, S is therefore calculated as 1.25. All measured concentrations have been multiplied with the corresponding correction factor S.

To assess the uncertainty in the atmospheric concentrations measured, a propagation of random errors (26) was performed.

$$\sigma^2(c_{air}) = \left(\frac{\delta c_{air}}{\delta F}\right)^2 (\sigma F)^2 + \left(\frac{\delta c_{air}}{\delta c_{measured}}\right)^2 (\sigma c_{measured})^2 \quad (3)$$

where c_{air} is the atmospheric concentration. Total propagated variance [$\sigma^2(c_{air})$] is the linear combination of the weighted contribution of the variances (σ^2) of the flow rate F and measured concentrations $c_{measured}$.

Uncertainties in the quantification of POPs were estimated from the standard deviation of the analysis of duplicate samples. The uncertainty of the flow rate from the air sampler H8400B was estimated at 15% due to the gradual decline of the flow rate from 55 to 38 L/min. The uncertainty in the flow rate of the air sampler H8400TE was estimated to be ±20 L/min at a sample rate of 400 L/min. The overall error for the measurement of atmospheric concentrations of POPs was between 18 and 63% (mean 29%), and between 6 and 55% (mean 24%) for the H8400B sampler (Stations S1−S5) and H8400TE (Stations S6−S12) air sampler, respectively. The highest errors originate from compounds present at the lowest concentrations among samples, thereby resulting in relatively high standard deviations between duplicate samples.

Air Mass Back Trajectories. Air mass back trajectories have been performed to assess the origin of air masses collected at each station and to evaluate their travel time over the open ocean. Air mass origins were determined for the duration of each sampling event using the models Metrological Data Explorer (METEX), as obtained from the Centre for Global Environmental Research, Japan (27), and the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (28). Both air trajectory models

TABLE 1. Mean, Minimum, and Maximum of Results (pg m^{-3}) ($n = 12$)

compound	mean	minimum	maximum
CB 18	3.1	<0.3	20.2
CB 44	2.1	0.2	5.2
CB 49	1.1	0.2	2.4
CB 52	7.7	1.0	21.5
CB 70	2.4	0.4	4.9
CB 74	0.9	0.1	2.4
CB 87	1.8	0.2	3.7
CB 95	4.1	0.3	9.4
CB 101	4.4	0.3	10.6
CB 110/82	3.7	<0.1	16.3
Σ38PCB	40.9	6.8	114.3
α-HCH	3.2	<0.2	19.2
γ-HCH	13.8	2.3	80.0
ΣHCHs	18.4	2.4	105.6
p,p′-DDE	2.2	<0.2	6.3
p,p′-DDD	1.3	<0.2	4.8
p,p′-DDT	5.9	<0.2	26.7
ΣDDTs	10.4	2.5	33.2
trans-chlordane	1.2	0.3	2.7
cis-chlordane	0.5	<0.1	2.4
Σchlordane	1.7	0.3	4.5

were needed to perform calculations for all atmospheric samples collected over the Indian Ocean since the 1970s. The HYSPLIT model was used to perform air trajectory analyses for samples collected by Tanabe and Tatsukawa (23), and Bidleman and Leonard (24) in the 1970s (see section Temporal Trends of Atmospheric POPs over the Indian Ocean). Back trajectories were performed for the start and end of each sampling event at 500 and 1000 m above sea level for 5 days.

Results and Discussion

Origins of air Masses. Back trajectories were traced for 5 days and are shown in Figure 4 for the sampling events conducted during this study. Samples collected at Stations S1 and S2 originated from the northern and eastern coastal regions of Australia, but those collected at Station S3 and S5 are oceanic in origin, crossing the open ocean for 5 days prior to sampling. Air masses sampled adjacent to the coast of the southern tip of Sumatra (Stations S1 and S2) and Singapore (Station S12) were partly continental and partly oceanic, being derived from over the land of Java, Indonesia. Other air masses sampled were predominantly of oceanic origin. There is some uncertainty associated with the back trajectory analysis due to the changing position of the ship, which was significant for some of the back trajectory data collected both in the 1970s and 1989/1990 due to a relatively long sampling period of 3 days. In such cases, the origin of air masses is given for both the start and end of the sampling event in Figure 4.

PCBs. The atmospheric concentration of Σ_{38}PCBs ranged between 7 and 114 pg m^{-3} (Figure 1) with 13.1, 37.7, 43.6, 5.0, and 0.6% representing the fraction of the tri-, tetra-, penta-, hexa-, and hepta-homologues, respectively. The major congeners detected were CB 18, 44, 49, 52, 70, 74, 95, 101, and CB110+82. Mean, minimum, and maximum atmospheric concentrations are given in Table 1.

The concentrations of PCBs measured in the atmosphere over the Indian Ocean are lower than similar measurements reported for the Atlantic Ocean (11). Higher values were observed for samples collected adjacent to coastlines of Indonesia (Stations S1 and S2), and were probably affected by the proximity of Jakarta, and Singapore (Station S12). Surprisingly, however, the highest concentration of atmo-
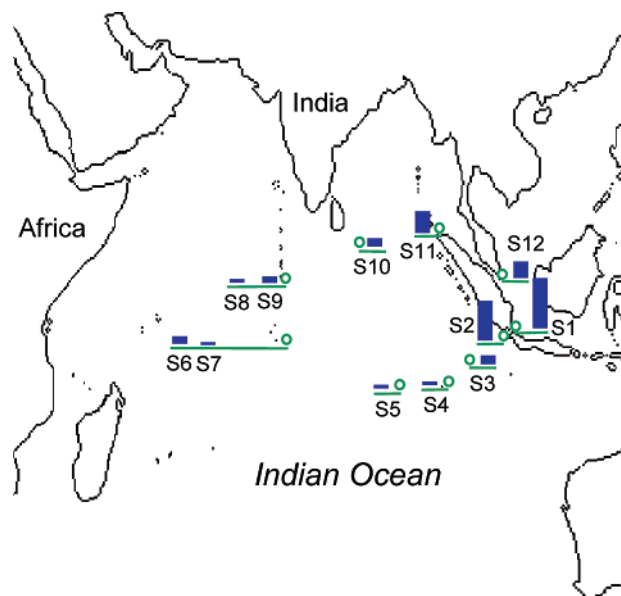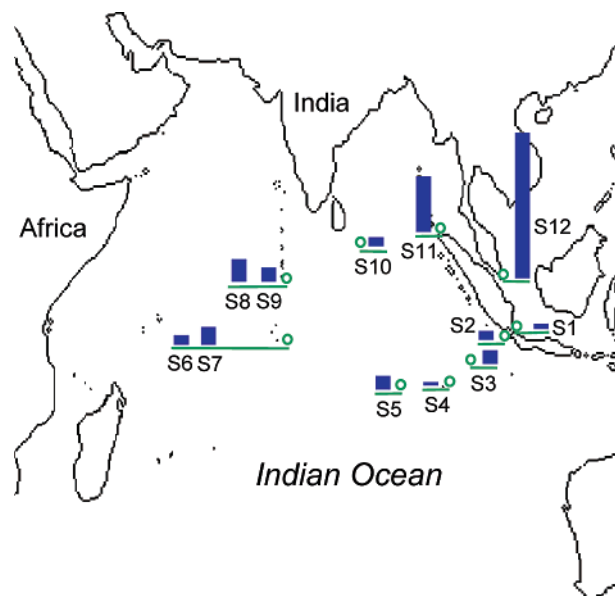
FIGURE 2. Spatial distribution of ΣDDTs at Stations S1−S12. Key: Largest bar = 33.2 pg m^{-3} (Station S1); smallest bar = <0.5 pg m^{-3} (Station S7).

FIGURE 3. Spatial distribution of ΣHCHs at Stations S1−S12. Key: Largest bar = 97.4 pg m^{-3} (Station S12); smallest bar = 2.4 pg m^{-3} (Station S4).

spheric PCBs was found at the remote Chagos Archipelago. The largest of the islands, Diego Garcia, contains a large joint UK−US naval support facility with about 1500 UK and US military personnel and 2000 civilian contractors, whereas all other islands are uninhabited (29). Air masses reaching Chagos Archipelago traveled at least 5 days over the open ocean and therefore it is suggested that the activities on Diego Garcia are likely to be a local source of atmospheric PCBs, which is supported by previous reports of high PCB contamination detected around military bases (30, 31). Concentrations of PCBs in air samples collected on the Addu Atoll, the most southerly atoll of the Maldives, with a population of approximately 28 000, were as high as in those collected at Singapore. A former UK military base on the island Gan of the Addu Atoll, which closed in 1976, is unlikely to be a significant source of PCBs when compared with concentrations measured on the Chagos Archipelago. Air masses reaching Gan during the sampling event originated from a southeast to south-southeasterly direction from the open ocean. A local source of atmospheric PCB contamination is likely to be a result of unregulated waste management practices on the atolls of the Maldives. It is known, for example, that an average of 0.66 kg of waste is generated per capita per day on the atolls, and burning of combustible household waste is a common practice (32) which leads to the emission of 0.13 mg PCBs kg^{-1} of burned material per day (33). Assuming that only half of the generated waste is combusted from the population (i.e., 28 000 × 0.66 × 0.13/2 = 1.2), a release of approximately 1.2 g of PCBs per day on the Addu Atolls may occur. On the basis of this calculation, the measured atmospheric PCB concentration over the atoll is comparable when based on the use of a simple fix-box model using this emission rate, an average wind speed of 2 m/s prevailing during sampling, and a background concentration of 20 pg m^{-3}—as detected at Station S5. The calculated value of approximately 50 pg m^{-3} is comparable with our findings (Figure 1).

DDT, DDD, and DDE. The highest concentrations of atmospheric DDT and its metabolites were detected in samples collected adjacent to the coastline of Sumatra (at Stations S1, S2, and S11), Indonesia, and Singapore (Station S12) and were in the range of 11−33.2 pg m^{-3} (Figure 2).

The concentrations of ΣDDTs over the open oceans were significantly lower, ranging from <0.5 to 5.8 pg m^{-3}. DDTs

in samples collected over the open Atlantic Ocean were frequently below the limit of detection of <1.5 pg m^{-3}, but the metabolite DDE was as high as 47 pg m^{-3} in samples influenced by a proximity to Africa and western Europe (11). The ratio of DDT:DDD+DDE ranged between 0.2 and 6.2 (mean 1.9), with the highest values in samples derived from terrestrial land masses of Southeast Asia (i.e., Stations S1, S2, and S11). This suggests that there are current sources of DDT still entering the atmosphere of the Indian Ocean. DDT: DDD+DDE ratios were in the range of 0.8−5.2 in air samples collected over a period of 6 weeks in Singapore (25). These samples were highly influenced by air masses derived from terrestrial areas of Indonesia, where the highest atmospheric concentrations of p,p'-DDT were found during this study (Stations S1 and S2). Indeed, one of the highest levels worldwide of p,p'-DDT in human milk has been found in Indonesian women (34). The restricted usage of DDT on Mauritius, Madagascar, and in East Africa is reported (35), but air trajectory analysis showed that no air mass originated form these regions during sampling events of this study. The ratios in samples collected at Stations S9 and S10 on the Chagos Archipelago were 3.8 and 0 (p,p'-DDT below MDL), respectively. Air trajectory analysis for 10 days prior to sampling reveals that air masses were derived from the northern coastline of Australia and the South Atlantic Ocean for these samples, respectively. The photooxidative half-life for DDT has been reported as between 17 and 177 h in the atmosphere (36), and it is therefore possible that long-range atmospheric transport of DDT from continental land masses, several thousands of kilometers away, results in the degradation of DDT and its derivatives to below LOD over the Indian Ocean.

HCH Isomers. The most common HCH isomers usually detected in atmospheric samples are α-HCH and γ-HCH. The highest concentrations of ΣHCHs of 37 and 97 pg m^{-3} were detected at the northern tip of Sumatra (Station S11) and Singapore (Station S12), respectively (Figure 3).

In a previous study, higher concentrations of HCH isomers were detected in atmospheric samples over Singapore when air blew partly over Malaysia (25), where lindane (γ-HCH) is still used as a pesticide (16). The lowest concentration of ΣHCHs was detected on Cocos Keeling Island (Station S4) at 2.4 pg m^{-3}, which was lower by a factor of 6 compared to
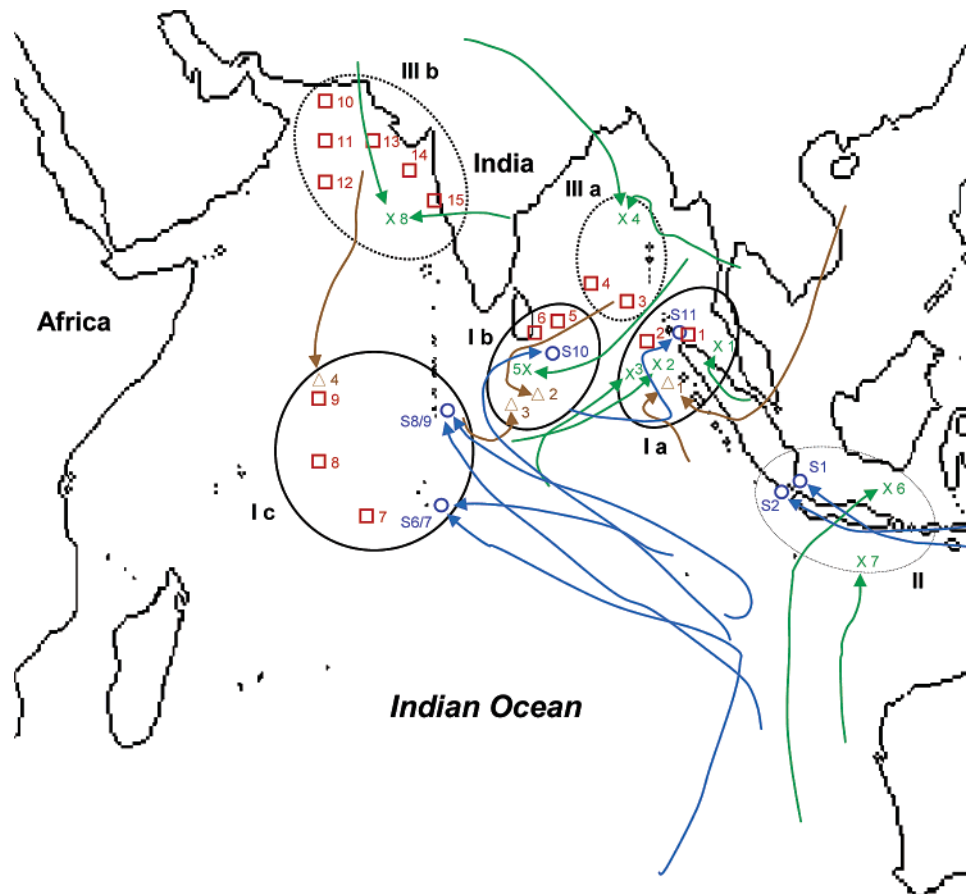
FIGURE 4. Cluster formation using sample locations from Tanabe and Tatsukawa (□), Bidleman and Leonard (△), Iwata et al. (X), and this study (O) and air mass trajectories. Air mass trajectories for sample stations S3, S4, S5, and S12 are described in the text.

levels measured at the Addu Atoll, Maldives, and the Chagos Archipelago. Agricultural activities on the Chagos Archipelago ceased 30 years ago, and contaminated soils are unlikely to be the source of atmospheric HCH contaminations. Long-range transport from continental sources is more likely. There are no data available for the usage of HCH compounds on the Maldives.

The ratio of the α- to the γ-isomer can be used to identify the source of HCH contaminations, and may be also used as an indicator of long-range atmospheric transport. In technical grade HCH mixtures, this ratio is between 3 and 7, whereas sources of lindane (γ-HCH), mainly derived from emissions during its application in agricultural areas, will show a ratio close to or below unity (37). This ratio is suggested to increase with distance from the source due to possible phototransformation of γ-HCH to α-HCH, and the higher reaction rate of γ-HCH with OH radicals compared to that of α-HCH. This results in an atmospheric lifetime of 96 and 120 days, respectively (37). The α:γ-HCH ratio varied between 0.05 and 0.21 among the samples, except for those collected at Station S11, where a ratio of 1.08 was observed. It is suggested that the primary source of atmospheric HCH contamination over the Indian Ocean is the pesticide lindane. The low α:γ-HCH ratios measured indicate that sampling events were conducted close to the source of lindane, or that γ-HCH was transported rapidly from the source to the air sampler with little transformation and/or degradation of γ-HCH in the atmosphere. However, the origin of air masses may also play a critical role in the α:γ-HCH ratio. For example, Iwata et al. (1) reported α:γ-HCH ratios of 4.8−9.6 in the Bay of Bengal and Arabian Sea, and 0.65−2.4 for the Eastern Indian Ocean. The higher values in the northern hemisphere may be a result of air masses that originate from India, where

use of the technical HCH mixture was relatively high until recent restrictions on usage were imposed. The samples from Eastern Indian Ocean of the southern hemisphere of Iwata's study were affected from more "oceanic" air masses, as shown for sample X7 in Figure 4.

Chlordanes. Measured atmospheric concentrations of Σchlordane (sum of trans- and cis-chlordane) were low among all samples. The highest concentrations were detected at Stations S1 and S4 (Cocos Keeling) at 3.8 and 4.5 pg m⁻³, respectively.

Temporal Trends of Atmospheric POPs over the Indian Ocean. To evaluate the historical trend of atmospheric concentration of POPs in the atmosphere over the Indian Ocean, previously reported data from studies conducted by Tanabe and Tatsukawa (23), Bidleman and Leonard (24), and Iwata et al. (1) have been compared with our data. The data cover the period from 1976 to 2005 and include periods of peak usage of HCHs and DDTs in Asian countries, e.g., in India in the early 1980s. It should be noted that the quality and accuracy of the analysis of POPs have risen substantially since the mid-1980s due to the availability of more sophisticated analytical techniques and greater awareness of possible contamination sources. Selected sample locations for all four studies are shown in Figure 4 and are represented as clusters comprising six regions of the Indian Ocean in order to assess time trends in atmospheric levels of POPs. Clusters I a, I b, and I c include data from 1976 to 2005, Cluster II data are from 1989 to 2005, and data for Clusters III a and III b are from 1976 to 1990. All available atmospheric concentration data of POPs reported for these time periods are summarized in Table 2. No concentration data have been reported for chlordanes from the 1970s, and the concentrations of Σchlordanes were in the same range in Cluster II (X6

TABLE 2. Historical Trends in Atmospheric Concentrations of POPs (pg m⁻³) in Six Clusters over the Indian Ocean (□, △, X: _n_ = 1; O: _n_ = 2)

	month/year	ΣDDT	_p,p′_-DDT	ΣHCH	α-HCH	γ-HCH	ΣPCBs
Cluster I a							
□1	10/1976	270		360			
□2	10/1976	160		160			
△1	12/1976		4.4	32	30	<2	
X1	05/1989	580	220				30
X2	05/1989	263					34
X3	05/1989	241					57
O11	08/2005	14.5	12.5	37	19	18	16.1
Cluster I b							
□5	10/1976	150		200			
□6	12/1976	220		140			
△2	12/1976		5.4	208	170	38	
△3	12/1976		4.7	85	79	6.3	
X5	02/1990	57		827			710
O10	08/2005	5.2	4.2	5.6	0.9	4.7	6.8
Cluster I c							
□7	11/1976	160		280			
□8	11/1976	130		180			
□9	11/1976	100		240			
△4	12/1976		16	1078	922	156	
O6	06/2005	5	3.8	12.1	1.3	10.8	75
O7	06/2005	<0.5	0	6.6	0.8	5.8	114
O8	06/2005	2.6	0	15.2	2	13.2	75
O9	07/2005	4.5	0.8	9.6	0.9	8.7	43
Cluster II							
X6	11/1989	5.6	3.4	58	46	12	22
X7	11/1989	10		181			136
O1	09/2004	33	27	3.2	0.4	2.8	51
O2	09/2004	27	18	6.6	0.7	5.9	18
Cluster III a							
□3	10/1976	190		950			
□4	10/1976	170		370			
X4	02/1990	240		2880			260
Cluster III b							
□10	11/1976	400		3300			
□11	11/1976	240		2100			
□12	11/1976	200		2500			
□13	12/1976	10900		2000			
□14	12/1976	1300		9100			
□15	12/1976	1100		10000			
X8	02/1990	1000		32000			500

and X7) compared to the results from this study (O1 and O2) (_1_). For the data collected between October and December 1976 by Tanabe and Tatsukawa (_23_) (indicated with (□1−15) in Figure 4), the day of sampling was not reported (only month and year), and therefore no air back trajectory analysis could be conducted for these samples. However, air back trajectory analysis was performed with a 24 h interval for the locations of samples □1−15 to obtain typical wind flows patterns during these months.

In Cluster I a, the concentration of ΣDDT was in the same range of approximately 250 pg m⁻³ in both 1976 and 1989, but has since decreased by a factor of about 15 in 2005. The higher concentration of ΣDDT of 580 pg m⁻³ in sample X1 may have originated from Sumatra, whereas samples □1 and □2 were likely more "oceanic" in origin. In Clusters I b and I c, the decline in atmospheric ΣDDT levels between 1976 and 2005 is evident, with a reduction factor of about 40. In contrast to Cluster I a, a substantial decrease in ΣDDT in the atmosphere over Cluster I b between 1976 and 1990 from approximately 200 to 50 pg m⁻³ is apparent. All air masses sampled in Cluster I b were of oceanic origin, but the location of sample □6 is likely to have been affected by air masses originating from North India during the last week of

December 1976. An increase of atmospheric ΣDDT in Cluster II by a factor of 3 occurs from 1990 to 2005. However, the samples O1 and O2 (2005) were partly terrestrial in origin, but samples X6 and X7 were of more oceanic character. No significant decline or increase of atmospheric ΣDDT can be detected for Clusters III a and III b. Cluster III b was clearly affected by air masses derived from Pakistan and India, as indicated for sample X8 in Figure 2. High concentrations found in both 1976 and 1990 in Cluster III b are consistent with extensive usage of DDT in India. The air at stations nearer to the coastline (□13−15) was substantially more contaminated than stations located offshore (□10−12). In general, atmospheric DDT concentrations have declined over the past 30 years, but to a greater extent over the oceanic Clusters I b and I c. The increase of DDT levels in the atmosphere over Cluster II may be due to the varying origin of air masses during the sample period of 1990 to 2004, but may also indicate the continued release of DDT and derivatives into the atmosphere over Indonesia.

Li et al. (_38_) reported a link between global usage of ΣHCHs and measured air concentrations over the Arctic. Two significant decreases in the air concentrations of α-HCH occurred in the Arctic in 1983, and between 1990 and 1992, which were consistent with corresponding decreases in global usage of technical HCH. The first restriction in 1983 was associated with the ban of this insecticide in China; and the latter in the early 1990s coincided with a ban in India and Russia of technical HCH. Tanabe and Tatsukawa (_23_) reported a 10 times higher concentration of ΣHCHs than Bidleman and Leonard (_24_) in the atmosphere over Cluster I a, which cannot be readily explained by different air mass origins or the fact that Tanabe and Tatsukawa defined ΣHCH as the sum of four isomers (α-, β-, γ-, and δ-HCH), and Bidleman and Leonard used only the two most common isomers in the atmosphere (i.e., α- and γ-HCH). However, due to the high historical usage of HCHs in Southeast Asia and India, the values reported by Tanabe and Tatsukawa may be regarded as more representative of ΣHCHs concentrations over Cluster I a in 1976. In Cluster I b, the concentration range of ΣHCHs reported by Tanabe and Tatsukawa (_23_), and Bidleman and Leonard (_24_), are in the same range with an average value of 160 pg m⁻³, which increased to 827 pg m⁻³ in 1990 (_1_). After 1990, a sharp decrease to 5.6 pg m⁻³ has been observed measured in this study. An increase of atmospheric ΣHCHs by a factor of 3−8 between 1976 and 1990 is apparent within Cluster III a and III b, which is consistent with the peak usage of technical HCH mixture in India in the early 1980s (_38_).

The elevated concentrations of ΣHCHs over the atmosphere in Cluster III a and III b were clearly affected by the usage of these compounds in India and in the Middle East. A declining trend of atmospheric ΣHCHs is apparent within the "oceanic" Cluster I c by a factor of 180 over the last 30 years. This shows that in the 1970s and 1980s even remote oceanic regions were highly influenced by atmospheric POPs originating from the continent. This phenomenon is likely to have become less significant in recent years due to international regulation controlling the usage of POPs. In Cluster II, atmospheric concentrations in 2004 were between 10 and 30 times lower compared to values from 1989, which is consistent with the ban of HCHs isomers in several countries of Southeast Asia (_16_). Overall, an increase of HCH isomers in the atmosphere over the Indian Ocean can be observed from the mid 1970s to the early 1990s, but has since decreased over all clusters, by a magnitude of up to two, in 2005. The decrease of atmospheric ΣHCHs is likely to be related to the restricted usage of these compounds in India since the early 1990s. A change of the ratio α:γ-HCH is also apparent between the studies conducted in 1976 and 1989/1990, and our study (Table 2). This may be explained

by the declining usage of technical HCH mixture in India and the oceanic air masses originating from the southern hemisphere during our study.

Data of ΣPCBs are only available for 1989 and 2005. However, Tanabe and Tatsukawa (23) reported that PCBs were below a limit of detection of <500 pg m^{-3} in all air samples collected over the Indian Ocean in 1976. From 1990 to 2005, ΣPCBs declined by a factor of 2 and 100 in the Clusters I a and I b, respectively. A concentration of 710 pg m^{-3} reported in Cluster I b (X5) in 1990 was the highest measured among all samples during a global survey (1) with a range of 19−710 pg m^{-3} (mean 270) reported for the Arabian Sea and Bay of Bengal. No clear trend of atmospheric ΣPCBs over the Cluster II can be ascertained, and a decline is unlikely to have occurred over the last 15 years (see X6, X7, O1, and O2 in Table 2). The concentration of ΣPCBs over Clusters III a and III b in 1976 were below 500 pg m^{-3} at Stations □1 and □2, and □10 to □15, respectively, and it can be concluded that there was no significant decline of atmosphere ΣPCBs between 1976 and 1990. Overall, the atmospheric concentration of ΣPCBs has not significantly declined in the clusters over Indonesia, but has been relatively low since the 1990s. The mean concentration for the Arabian Sea and Bay of Bengal from 1990 was 40 times greater than the concentration measured in 2005, but only 2−3 times higher than the concentrations measured at the Chagos Archipelago in this study.

The atmospheric concentrations of organochlorine pesticides measured in this study were generally in the same range as those reported for the tropical region of the Atlantic Ocean, but lower by a factor of up to 3 for atmospheric PCBs (11). Overall, it can be concluded that the contemporary atmosphere over the Indian Ocean is substantially less contaminated with atmospheric POPs when compared to available data from the 1970s and 1990s, due to restricted usage of major classes of POPs. However, countries bordering the Indian Ocean continue to be a source for the global atmospheric distribution of POPs and are likely to be so well into the future.

Acknowledgments

Supporting Information Available

Further details on sampling locations and concentrations in Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

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