Potential Contamination of Shipboard Air Samples by Diffusive Emissions of PCBs and Other Organic Pollutants: Implications and Solutions

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Air samples were taken onboard the RRS Bransfield on an Atlantic cruise from the United Kingdom to Halley, Antarctica, from October to December 1998, with the aim of establishing PCB oceanic background air concentrations and assessing their latitudinal distribution. Great care was taken to minimize pre- and post-collection contamination of the samples, which was validated through stringent QA/QC procedures. However, there is evidence that onboard contamination of the air samples occurred, following insidious, diffusive emissions on the ship. Other data (for PCBs and other persistent organic pollutants (POPs)) and examples of shipboard contamination are presented. The implications of these findings for past and future studies of global POPs distribution are discussed. Recommendations are made to help critically appraise and minimize the problems of insidious/diffusive shipboard contamination.

Introduction

Long-range atmospheric transport (LRAT) has made persistent organic pollutants (POPs) ubiquitous in the global environment. Their transport away from the source regions to remote and hitherto pristine environments has resulted in POPs being detected in the Arctic and Antarctic (*1*). For example, numerous persistent, bioaccumulating organic

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contaminants reach Arctic food chains. International treaties aim to address the emission of POPs into the environment through elimination of their production, use, and/or minimization of their unwanted release (*2, 3*). Polychlorinated biphenyls (PCBs) are a key group of POPs. PCBs are industrial products, which were produced until the mid 1970s before being banned in most industrialized countries. Concern about their environmental distribution, fate, and effects has spawned numerous research projects. PCBs are often considered as markers for tracers of environmental distribution and fate processes. On the basis of early observations of POPs accumulation in the Arctic, Wania and Mackay expanded on the 'global fractionation' and 'cold condensation' hypothesis, suggesting that POPs move different distances from source regions, dependent on their properties and response to global temperature differences (*4, 5*).

Over recent years, several workers have sought evidence for the global dispersal, redistribution, and cycling of POPs. PCBs are often the target compounds. A key approach in such studies is the collection of numerous spatially separated samples of air and other media, in remote/rural locations, away from sources. It would be very costly to install air samplers at many sites to determine concentrations simultaneously. Hence, ship-based air sampling is seen as a convenient and elegant way of measuring the global distribution of the compounds of interest, including PCBs and other POPs (e.g., *6−9*). Within a rather short period of time, samples can be collected from a variety of sampling sites with one operator responsible for handling the samples. Cruise data has been collected (i) to assess the relative distribution of PCBs and hexachlorocyclohexanes (HCHs) in the Northern and Southern Hemisphere, (ii) to test the cold condensation theory with sampling up into the Arctic and Antarctic regions, (iii) to assess the net direction of air−sea exchange and the role of the oceans in the global cycling of PCBs and other OC−pesticides, and (iv) to help determine how close to equilibrium POPs have come in the global environment. However, interpretation of ship-based data is complicated, potentially subject to the influence of many variables (see Figure 1) and needs to be undertaken with caution.

Typical Ship-Based Sampling Issues. Air sampling from ships needs to adhere to strict quality control measures to ensure that (i) the low levels of POPs present in remote regions can be reliably detected and (ii) any sample contamination onboard is avoided. Where PCBs have been used in buildings, they can have a major, long-term impact on indoor air quality and act as sources to the surrounding atmosphere (*10*). Older ships might have contained PCBs in sealants and paints or as flame retardants. The presence of electrical/mechanical workshops onboard ships provides the potential for additional PCB sources onboard (as electric fluids in transformers and capacitors, adhesives, dedusting agents, cutting oils, heat transfer fluids, hydraulic lubricants) (*11*), while the heat generated by running engines facilitates their evaporation and mobility. For example, Schulz-Bull et al. reported the contamination of water samples with PCBs during their onboard processing on the CSS Hudson, built in 1964 (*12*). Similar concerns would arise when sampling flame retardants such as polybrominated diphenyl ethers (PBDEs), pesticides, and other POPs that may have been used onboard ship. Air samplers are therefore usually mounted at or near the bow of the ship to sample 'clean' marine air.

Sample contamination can occur (i) during storage of the precleaned or deployed sample media onboard, (ii) during sampling of the ambient air due to mixing of the marine air
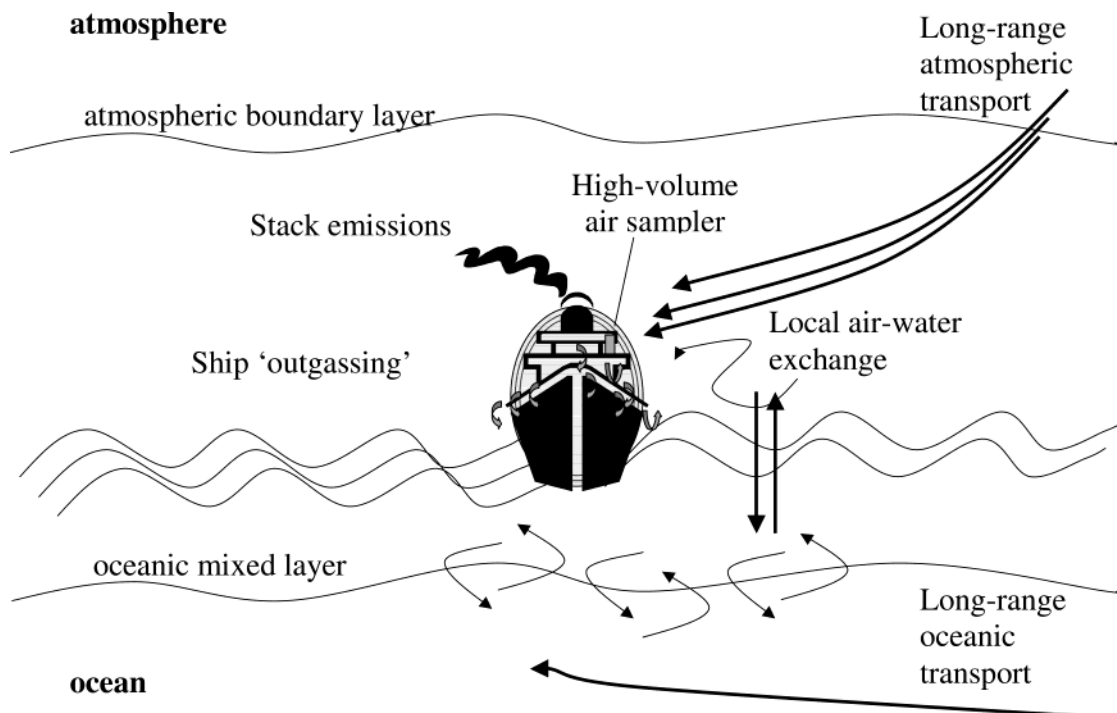
FIGURE 1. Schematic diagram depicting the main processes affecting organic pollutants being sampled onboard ship.

with ship-based, 'contaminated' air, and (iii) during handling of the sampling media prior to and after their deployment. The most obvious contamination problem is when samples are affected by the ship's stack emissions or, more generally, when air has moved over the ship before reaching the sampler. This would be particularly important for combustion-derived pollutants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), for example. This could be prevented/reduced by linking the sampler to a wind direction sensor, so that the air is only sampled when the wind is coming from clean sectors. However, a more insidious problem is where the ship 'outgasses', i.e., where there is the continuous diffusive emission from the body of the ship, via air vents and doors, etc. This could give rise to a 'halo' of high concentrations around the ship, which could potentially impact an air sampler installed on a higher deck as close to the bow as possible (Figure 1). Turbulent air movement created around a ship and the sampler could result in air being sampled from the lee of the sampler.

Field blanks and other QA/QC procedures are routinely included in sampling strategies to minimize the artifacts from sample storage and handling. Sometimes special 'clean labs' can be mounted on the ship to improve the handling of the samples. However, all these procedures only guarantee that pre- and post-collection contamination is minimized; they do not enable the researcher to assess whether insidious, diffusive sources of shipboard contamination have affected the sampling of apparently background/remote air.

Within the framework of attempts to determine the global atmospheric distribution of PCBs, we will judge the quality of a set of air samples taken onboard the RRS Bransfield for PCBs and PCDD/Fs. The data will be compared to those obtained by other ship-based sampling programs and to land-based air results. The feasibility of establishing time trends based on data obtained by different groups on different ships will be discussed.

Experimental Section

**Illustration of the Potential Problem.** Air samples were taken onboard the RRS Bransfield, on an Atlantic cruise from the United Kingdom to a research base operated by the British Antarctic Survey in Halley, Antarctica, from October to December 1998, ostensibly to establish oceanic background air concentrations and assess their latitudinal distribution. The cruise route, the sampling procedures, and PCDD/F and coplanar PCB data from the cruise have been reported previously (*8*). The air sampler was installed on the monkey deck, immediately above the bridge deck (ca. 20 m above sea level). The majority of air samples were taken while the ship was on the open ocean. Sampling modules were assembled and taken apart immediately prior to and after deployment. Once taken, samples were handled with nitrile gloves and rinsed pairs of tongs only. Particles were trapped by a glass fiber filter (GFF); gaseous compounds were retained by two polyurethane foam (PUF) plugs. PUFs and GFFs were stored in solvent-rinsed metal tins and amber glass vials, respectively. They were firmly sealed and stored at −25 °C until extraction. Of the 53 samples taken, 12 were blanks. Great care was taken to minimize contamination of the samples (see below). Samples were analyzed for PCBs by GC-MS, as described elsewhere (*13*). For every five samples, a field blank was taken by assembling two PUFs and a GFF in a module next to the air sampler. For every 10 samples, a laboratory blank was taken, representing the unopened PUFs and GFF.

Discussion

Atmospheric concentrations of Σ_7PCBs (sum of ICES PCBs-28, -52, -101, -118, -138, -153, -180) and of PCBs-52 and -138 are summarized in Table 1. Average values were calculated for sampling regions in the Atlantic Ocean, namely, samples taken in the Arctic (ca. 55−80°N), off the European coast (ca. 30−55°N), off Africa (ca. 0−30°N), off South America or Southern Africa (ca. 20−50°S), and the Antarctic circle (ca. 55−80°S). Higher concentrations of Σ_7PCBs were measured on the Bransfield in the Northern Hemisphere (NH) with Σ_7PCBs of around 400 pg/m³. In the Southern Hemisphere (SH), mean Σ_7PCBs concentrations were lower, under 200 pg/m³ (see Table 1). This concentration gradient was also mirrored in concentrations of PCBs-52 and 138; both were lower by a factor of ~2 in the SH than the NH. Higher concentrations had been expected in the NH, based on

latitude	mean Σ_7PCBs	mean PCB-52	mean PCB-138
Bransfield cruise, 1998			
European samples	60°N−30°N	411	53	9.5
African samples	30°N−0°N	424	84	15
South American	20°S−50°S	189	27	5.8
Antarctic	≥60°S	173	20	3.3
Polarstern, 1990 (7)			
European	48°N−39°N	33	11	4.5
African	35°N−24°N	63	29	3.0
mid-Atlantic	15°N−1°S	64	27	4.3
South American	6°S−48°S	64	20	8.4
South African	45°S−48°S	5.2	2.2	0.1
Polarstern, 1999 (16)			
Arctic	80°N−55°N	2.1	0.6	0.1
European	55°N−50°N	37	8.2	3.5
African	40°N−25°S	3.8	0.5	0.5
Cape Town	27°S	0.8	0.2	0.1
Antarctic	40°S−70°S	1.0	0.2	0.1
Pelagia, 2001 (17)			
Europe	50°N−30°N	18	3.6	1.5
Africa	30°N−5°N	45	8.5	3.6
African Ocean	5°N−20°S	21	4.2	1.6
South Africa	≥20°S	21	7.9	1.5
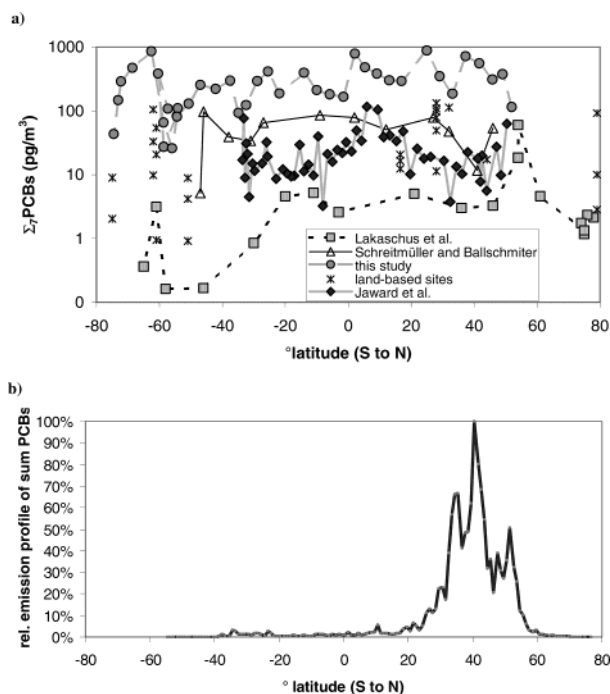
FIGURE 2. (a) Atmospheric Σ_7PCBs concentrations from different Atlantic cruises and land-based sites, and (b) relative PCB emission strengths (after refs 14 and 15).

production, usage, and emission data for PCBs (see Figure 2B) (14, 15). However, PCB sampling along a similar route in the Atlantic was undertaken by Schreitmüller and Ballschmiter in 1990, onboard the German research vessel, Polarstern (7). Their Σ_7PCBs concentrations were on the order of 60 pg/m³ for most samples, with lower concentrations measured in Capo Verde (5 pg/m³). Compared to the Bransfield data, their 1990 data was lower by a factor of ~3−10.

Comparison with more recent PCB measurements taken over the Atlantic, off the European and African coasts, further highlights anomalies in the Bransfield data. Results obtained

by Lakaschus et al. (16) onboard Polarstern in 1999 show much lower Σ_7PCBs concentrations, typically <5 pg/m³, except for samples taken close to the European continent (see Table 1). Finally, Jaward et al. (17) obtained data on a cruise from The Netherlands to South Africa, along the European and African coasts, made on a Dutch research vessel, the Pelagia. Their sample results were broadly comparable to those obtained by Schreitmüller and Ballschmiter in 1990, with Σ_7PCBs on the order of 20−50 pg/m³ (see Table 1). The results of these different Atlantic cruises are illustrated in Figure 2a (note logarithmic y-axis). From a comparison of different datasets it proves difficult to agree on a 'true value', as samples were taken by different workers at different times and analyzed in different laboratories. Indeed, in retrospect it is extremely difficult to judge which samples displayed 'correct' values and were not affected by contamination artifacts. This limits what we can conclusively say about the global distribution of PCBs in background oceanic air.

PCB Air Concentrations at Other Remote Sites. Some remote PCB sampling has been performed with land-based sampling equipment, minimizing contamination concerns (although the potential impacts of local sources of PCBs are always a concern). These published results are summarized in Table 2 and are included in Figure 2a. A latitudinal trend was evident: highest concentrations (Σ_7PCBs >100 pg/m³) were reported at Tenerife (18) and Bermuda (19), both around 30°N. Data from other remote land-based sampling stations at Ny-Alesund (79°N) (20), Sable Island (44°N) (21), and Capo Verde (16.5°N) (22) gave Σ_7PCBs data of ~10−30 pg/m³ with lower concentrations (~2 pg/m³) reported from the Antarctic (see Table 2).

In summary, results from four independent cruises resulted in a wide range of atmospheric concentrations, with Σ_7PCBs ranging from a few to hundreds of pg/m³ (see Table 1 and Figure 2). Measurements performed on the RRS Bransfield in 1998 displayed uniquely elevated PCB concentrations, mostly in the range of 100−1000 pg/m³, well above other ship cruise data and land-based measurements (see Figure 2). Measurements by Schreitmüller and Ballschmiter in 1990 (7) and by Jaward et al. (17) on 2001 samples resulted in Σ_7PCBs of ca. 10−100 pg/m³, roughly in-line with land-based measurements. Finally, measurements by Lakaschus et al. (16) on 1999 samples displayed the lowest concentrations, ranging mostly between 1 and 10 pg/m³, with even lower concentrations in the remote SH (see Figure 2). The divergent results for these different Atlantic cruises highlight the anomalous nature of the data obtained onboard the RRS Bransfield. In fact, this is the major reason that we are able to discount the results obtained on that ship, as the 'normal' QA/QC procedures did not highlight elevated concentrations in the field and laboratory blanks.

Latitudinal Trends. Other than comparing absolute concentrations, further clues about the potential contamination problem can be obtained by looking at absolute (i.e., latitudinal) and relative (i.e., PCB pattern) spatial trends within the data. Distinct changes in the PCB profiles are expected, and these can be used to check the 'internal' consistency of cruise data because, in general, the routes taken by each of the cruises cover a gradient from global 'source' to 'remote' regions (14, 15). Intuitively, one would expect to find higher ambient concentrations near the heavily industrialized countries of Northern Europe and America and lower concentrations further away from population/ industrial centers (e.g., 26). A strong ship-based contamination signal would tend to blur those differences, falsely indicating a more uniform distribution of PCBs and incorrectly implying an efficient transport of PCBs away from their usage areas to remote environments. Figure 2B shows the estimated relative emission profile of PCBs as a function of latitude, as calculated by Breivik et al. (14, 15).

TABLE 2. Σ_7PCBs (sum of ICES 7), PCB #52, and PCB #138 Concentrations from Remote, Land-based PCB Measurements (pg/m^3)

location	year	deg lat.	Σ_7PCBs			PCB 52	PCB 138	ref
			mean	min	max	mean	mean	
Ny-Alesund	1993	79	9.9	3	92	2.5	0.5	20
Sable Island, N.S.	1989	44	17			4.4	1.5	21
Bermuda	1994	32	110			18	3.2	19
Tenerife, 2400 masl	2002	28	49	11	97	10	5.0	18
Tenerife, 50 masl	2002	28	110	78	130	30	10.3	18
Capo Verde	1990	16.5	16	12	21	6.1	1.5	22
Falkland Islands	1999	−51	4.2	1	9	0.7	0.2	23
Signy Island	1994/95	−61	21	1	54	5.9	0.6	24
King George Island	1995/6	−62	33	10	100	8.6	2.6	25
Halley, Antarctica	1999	−75	2.0	0	9	0.0	0.2	23

If ambient PCB concentrations are still dominated by ongoing primary emissions (27), a consequence of their main usage in Europe and North America, higher PCB concentrations will be expected in the 30−60° N region, with concentrations lower in the SH. A minor increase could be expected around 30°S, with concentrations decreasing toward the Antarctic. This trend was observed by Lakaschus et al. (16) and Jaward et al. (17) (see Figure 2a). The results of land-based PCB samplers also follow that gradient (see Table 2). Again, the data obtained onboard the Bransfield was unique in not displaying a strong gradient from source to remote regions. Intriguingly, a north−south difference was observed in the Bransfield data (see Table 1). We note that wind speeds were, in general, higher in the SH, and that might have minimized the ship's halo and hence resulted in lower concentrations. Minor details such as renovations and paint jobs during the first part of the cruise might also have affected the sampled air.

PCB Patterns. Further clues can be gained by looking at the relative profile of different PCBs congeners in air samples. Profiles will vary with many factors, notably the vicinity to primary/secondary sources, air mass origin, and 'age' of the air mass. Again, a strong ship-based contamination will blur these differences on a cruise and make the PCB patterns more alike. Figure 3 in the Supporting Information shows the relative contribution of the individual PCBs to Σ_7PCBs calculated for different cruise results. The Bransfield data stand out, being strongly dominated by PCB-28 (60−70% of Σ_7PCBs) and showing remarkably constant PCB ratios across different air regions. This is in sharp contrast to results from the other cruises: PCB-28 accounted for only ∼10% of Σ_7PCBs in the samples taken by Schreitmüller and Ballschmiter (7) in 1990, in which PCB-52 (30−45%) and PCB-101 (∼30%) dominated. In the samples analyzed by Lakaschus et al. (16), PCBs-28 and -52 both contributed ∼10−25% to Σ_7PCBs, with PCBs-101 and -153 dominating (20−30% each). In the samples taken by Jaward et al. (17) on the Pelagia, PCBs-28 and -52 dominated again, accounting for ∼30−40% and ∼20−30%.

Various pattern analysis techniques have been developed to differentiate the PCB profiles of numerous samples. Using a combination of similarity indices and principal component analysis (PCA), Schreitmüller et al. (22) discerned a distinct marine air pattern for PCBs, with a preponderance of the lower chlorinated congeners. A higher proportion of PCBs-28 and -52 were also found in the Arctic and Antarctic samples by Lakaschus et al. (16). Different groups of samples can thus be explained by their proximity to land and different back-trajectories.

Implications. In summary, the Bransfield cruise results were far higher than those from the other cruises and from land-based studies. A distinct latitudinal gradient, with highest concentrations near Europe and decreasing concentrations toward the SH and remote regions, was not observed in the Bransfield data. No clear differences in the PCB pattern were observable between Bransfield samples taken near the source region of Europe and samples taken in the Antarctic region. Adequate QA/QC was undertaken to minimize pre- and post-collection contamination of the samples, as documented by laboratory and field blanks. It is therefore concluded that the Bransfield samples were contaminated by diffusive PCB emissions outgassing from the ship, even though the sampler was installed in a location designed to sample incoming marine air.

However, the samples taken on the RRS Bransfield were also analyzed for PCDD/Fs and coplanar PCBs. The Atlantic transect results for atmospheric PCDD/Fs and non-*ortho*-substituted PCB congeners PCBs-77, -126, and -169 were presented in an earlier publication (8). PCDD/F concentrations were, in general, extremely low and showed a marked change between the Northern and Southern Hemisphere. The lowest concentrations were found in Antarctica. Changes in the relative importance of the different homologue groups were also observed. All this information indicates no discernible influence of the ship's emission and/or outgassing on the PCDD/F concentrations. In addition, PCDD/Fs were never industrially manufactured; their only possible origin would be as incomplete combustion byproducts. PCB congeners -77, -126, and -169 are not routinely detected in PCB formulations or are minor constituents of them. However, correlations are apparent between PCBs-101, -118, -138, -153, -180 and PCBs-77, -126, and -169, respectively ($P < 0.01$). This suggests that even concentrations of PCBs-77, -126, and -169 may have been affected by the ship's outgassing.

Dachs et al. (28) recently assessed the biogeochemical control exerted by phytoplankton uptake and settling on the oceanic cycling of POPs using PCB and PCDD/F data collected on the RRS Bransfield. It is therefore important to evaluate the potential bias of this PCB data set. Their main conclusions were that there is a strong coupling of air−water exchange and settling fluxes, which exerts an important influence on the global cycling of POPs. They suggested that in high primary productivity regions, settling fluxes deplete water column concentrations, thus increasing the air−water gradient of some POPs. These conclusions were independent of the absolute values in the data set used (see Supporting Information of ref 28). However, use of the Bransfield dataset will overestimate the magnitude of predicted fluxes and water concentrations, especially for the lower chlorinated PCBs.

It is important to consider whether the Bransfield data are unique, as a sample set where shipboard contamination has affected the apparent 'ambient' trends, or if other shipboard datasets are subject to similar, though much less severe, insidious contamination. Bidleman and Leonard (29) questioned the validity of their PCB measurements taken onboard the Atlantis II in the Arabian Sea in 1976−78. In another study, Hinckley et al. (30) reported anomalously high

TABLE 3. Selected Ship-Based Air Sampling Programs for PCBs, DDT, Chlordane, and Short-Chain Chlorinated Paraffins (SCCPs) for Which Contamination Was Suspected

analytes	sampling location and time	ship	year released	ref
PCBs	Arabian Sea, 1976-78	Atlantis II	1962	29
DDTs, PCBs	Bering, Chukchi Sea	Akademik Korolev	1967	30
SCCPs	Arctic Ocean, 1994	Louis St. Laurent	1969	31
lindane	Antarctica, 1997	Agulhas	1977	32
chlordane	Antarctica, 1997	Agulhas	1977	33
chlordane	Arctic, 1996	Oden	1988	34
PCBs	Atlantic, 1998	Bransfield	1970	this study
PCBs	Baltic Sea, 2000-2	Alkor	1990	35
		A.von Humboldt	1967	
		Prof. Albrecht Penck	1951	

concentrations of PCBs and DDT, for samples taken in the Bering and Chukchi Sea. Several other reports highlight the perceived problem of onboard sample contamination (see Table 3). Potential problems are by no means limited to PCBs but also apparent for pesticides (chlordane, DDTs) and short-chain chlorinated paraffins (SCCPs), for example. Ship-based atmospheric sampling of organic pollutants has to be undertaken with the utmost caution as the sampling vessel can *potentially* be a prime source of contamination for many organic chemicals. This raises questions as to the measures researchers can take to ensure that their shipboard data have not been affected by onboard usage/emissions.

PCBs are now ubiquitous in the modern environment and exchange between different environmental compartments. Thus, for a given marine air sample taken onboard ship, PCBs could have originated from LRAT and/or air−sea exchange. PCB concentrations in ambient air display a day-to-day (and possibly hour-to-hour) variability at a given site (e.g., *36*, *37*). These factors make the *a priori* interpretation of patterns and concentrations difficult, and our current level of knowledge and understanding makes it hard to predict the likely ambient levels in oceanic air and their distribution. Hence, the onus is on researchers using ships as their sampling platform to prove that their samples are not contaminated. In light of the obvious difficulties just mentioned, we suggest several methods to improve the handling and quality of ship-based air sampling campaigns.

Recommendations for Ship-Based Sampling Campaigns. *Measuring the Ship's Outgassing.* Most importantly, evidence should be gathered to determine whether the ship has the *potential* to be a source of contamination. This can be tested by deploying passive air samplers onboard the ship. Typical profiles from different parts of the ship could be determined to aide with the interpretation of the ship's potential interference. Different designs of passive samplers exist and have been proven as source identification tools (e.g., *38−40*). Of course, active samplers could also be deployed in different locations in or onboard ship. In an ideal situation it can be demonstrated that the ship itself is not a source of the contaminants of interest, based on these sampling results. If the ship displays elevated concentrations of the contaminants of interest relative to the marine atmosphere, then further comparisons and measurements are needed to assess the degree to which the samples were affected by the ship's outgassing.

Comparison with Land-Based Measurements. The ship-based sampling results need to be compared to land-based measurements for at least one station. Ideally, simultaneous ship- and land-based sampling can be integrated in the sampling itinerary. If these samplers can be operated and analyzed by the same group, then concerns about data comparability can be minimized. However, it should be pointed out that current knowledge limits our ability to know *a priori* how similar land- and water-based samples should be. Variability could stem from (a) the natural heterogeneity

of ambient air masses, (b) different temperatures of the water surface versus the land and its influence on the partitioning of pollutants, and (c) the role of vegetation, surface soil, and water in the exchange of organic pollutants with the atmosphere at the microscale. Nevertheless, we assume that coastal air samples will give results sufficiently close to those obtained onboard ship in the absence of contamination through diffusive emissions.

Assuming Air−Water Equilibrium. If simultaneous air and water sampling is undertaken, the aqueous concentrations can be used to estimate atmospheric concentrations assuming equilibrium conditions (*35*). Of course, water and air need not be equilibrated at a given place and time, but atmospheric concentrations can be approximated. Recent model results suggest air and water to be in equilibrium for most PCBs across the oceans, with the exception of high primary productivity regions (*28*). This comparison is necessarily based on the assumption of 'clean', contamination-free water sampling. This becomes feasible using in situ water sampling equipment, such as the 'Kiel in situ pump' (*41*). Care has to be taken to either avoid any onboard processing of the samples or to have a designated 'clean' lab facility onboard (e.g., *12*).

Influence of Ship Stack Emissions. To assess the degree to which the ship's stack emissions have been integrated in atmospheric samples of marine air, certain tracers can be included in the analytical procedure. Examples of such tracers are trace gases, such as CO or NO_x, and combustion-derived POPs, such as certain PCN congeners or PAHs. While there was no discernible influence of stack emissions on PCDD/F concentrations sampled on the RRS Bransfield (8), this is of course relevant if PAHs are targeted (*17*).

Sampler Deployment. During stationary periods with low wind speed, the sampler can be attached to a moveable crane/arm and be hoisted away from the ship. Although not feasible at all times and on all ships, this would reduce the effect of the ship's halo. Ideally, simultaneous measurements onboard and beside the ship could be compared. This would also improve our understanding of the possible extent of the ship's diffusive emission halo.

Compatibility of Different Cruise Results. *Sampling Technique Development.* The remote sampling of PCBs and other trace organic contaminants requires sampling and analytical methods capable of reliably detecting as little as a few pg/m^3 (10^{-12} g/m^3) per sample. A combination of highly selective and sensitive analytical equipment is needed together with 'ultra' clean sampling procedures. 'Cleaner' sampling procedures will help research projects (i) by lowering their blank levels and hence increasing their analytical sensitivity for POPs in the environment and also (ii) in making it easier to detect a possible contamination problem. Hence, it seems worthwhile to develop a standard procedure for POPs sampling on ships, possibly using a standard material. A comparison of different sampling methods and matrices can be made to assess if there are

clear advantages for certain materials. For example, some groups have used XAD-2 (e.g., *7*) in a filter holder, while others have used PUFs (e.g., *8, 17, 21*) or PUFs in combination with XAD (*9, 16*). Different sampling devices were also used, which may influence their contamination during exposure and storage. This last point is more important for the comparability of data analyzed by different research groups. If implemented, it would enable the deduction of temporal and spatial trends based on data obtained by different groups.

Outlook. Ships will continue to be used as measurement platforms to study the distribution of chemicals. In view of the problems that were encountered by different groups sampling marine air for the analysis of trace organic contaminants, the need for extra QA/QC focused on assessing the ship's indoor atmospheric concentration of the targeted analytes becomes apparent. Even data gathered on the same research vessel need not be comparable as ships are routinely renovated and refitted. This also precludes us from deeming any ship built in or prior to the 1970s as 'contaminated' or any ship built recently as automatically 'clean' with respect to POPs (see also Table 3 for ship's ages). It is therefore suggested that any ship-based air sampling campaign should include the routine monitoring of the ship's outgassing/inner air. The comparison of different research cruises on the Atlantic (see Figure 2) does not allow the identification of time trends of PCBs in marine air. However, more stringent analytical procedures and QA/QC for both the ship and the laboratory can help provide trustworthy data to establish spatial and temporal trends.

In some cases, newer ships might be 'contamination-free' of the older generation of POPs. However, this depends on the type of contaminants targeted by the research project. Due to constant renovation and makeover of ships, it seems a necessary and worthwhile precautionary measure to sample its indoor air on any cruise.

Supporting Information Available

Figure 3a−d containing the relative contribution of atmospheric PCBs to Σ_7 PCBs from (a) Bransfield in 1998, (b) Polarstern in 1990, (c) Polarstern in 1999, and (d) Pelagia in 2001. This material is available free of charge via the Internet at http://pubs.acs.org.

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