

# Spatial distribution of atmospheric PAHs and PCNs along a north–south Atlantic transect<sup>☆</sup>

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**“Capsule”:** Proximity to source regions and air mass origin influence broad trends in oceanic air POPs concentrations, while diurnal cycling occurs in remote regions.

## Abstract

Ship-board air samples collected between The Netherlands and South Africa in January–February 2001 were analysed for polycyclic aromatic hydrocarbons (PAHs) and polychlorinated naphthalenes (PCNs). The highest PAH concentrations occurred in the European samples, and in samples close to West Africa and South Africa. Consistently low PAH concentrations were measured in the southern hemisphere open ocean samples (190–680 pg/m<sup>3</sup>). The highest PCN concentrations occurred in the European samples, but high values were also detected off the West African coast, and in the sample taken closest to South Africa. Data are presented for diurnal cycles taken in the remote South Atlantic. The day:night ratios of phenanthrene, 1-methylphenanthrene and fluoranthene were typically ~1.5–2.5:1. The mechanism(s) causing this observation is/are not understood at present, but dynamic environmental process(es) is/are implicated.

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## 1. Introduction

The atmosphere transports persistent organic pollutants (POPs) to terrestrial and aquatic systems, both close to point sources and to remote areas. POPs span a wide range of vapour pressures ( $10^{-4}$ – $10^{-11}$  atm. at ambient air temperatures) and are consequently available for atmospheric transport in both the gas and particle phases (Jones and de Voogt, 1999; Klecka et al., 2000). The distribution of compounds between these phases controls their depositional behaviour. Partitioning between aerosol and gas phases is controlled by several factors, including compound vapour pressure, ambient temperature, and the nature, size and

concentration of particles (Pankow and Bidleman, 1991). Their susceptibility to atmospheric transport, coupled with their persistence, has made POPs ubiquitous. Their global distribution is therefore the result of local and regional emissions (including their re-emission from environmental compartments), coupled with horizontal and vertical transport processes, and influenced by the physical and chemical properties of the compounds (Schreitmuller and Ballschmiter, 1994).

PAHs and PCNs are subject to long-range atmospheric transport (LRAT). They have been measured in the atmosphere of remote regions. PAH emissions are subject to international regulations, with the stated objective for signatory countries to reduce their emissions to 1990 levels (European Commission, 2001). Production, usage and emission information is available for some PAHs from European and national inventories (e.g. European Commission, 2001; Pacyna et al., 2003). PCNs are being considered as ‘candidate POPs’ under the international POPs protocol (van de Plassche and Schwegler, 2002).

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PAHs are by-products of incomplete combustion and have many current sources, including motor vehicles, domestic burning of coal and wood for space heating, power generation via combustion of coal and oil, incineration, wood burning, cooking, smoking and burning of natural gas (Wild and Jones, 1995; Lohmann et al., 2000; European Commission, 2001). The highest ambient levels occur in winter months (consistent with the increase in combustion-derived PAH emissions in colder periods) and tend to be concentrated in urban areas, which can in turn influence the PAH concentrations in rural areas. PCNs have both combustion and industrial/formulation sources. Technical mixtures of PCNs have been used in similar applications to PCBs, such as capacitor fluids, engine oil additives, cable insulation and wood preservation. PCNs have also been found in incinerator emissions, as contaminants in PCB formulations, and metal refining. Recently Helm and Bidleman (2003) reported combustion related PCNs in air.

There are several possible sinks for POPs: reaction in the atmosphere, degradation in soils and sediments, and deposition into the oceans (Dachs et al., 2002; Wania and Daly, 2002; Mandalakis et al., 2003; Meijer et al., 2003). The last of these, oceanic sinks, is traditionally viewed as an ultimate sink for pollutants. However, it has been suggested that, as primary POP sources are reduced, remobilisation from previous repositories can act as secondary sources to the environment. Studies monitoring POPs in open ocean air and water have still been rather limited in temporal and spatial terms, often because of practical or analytical constraints (Iwata et al., 1993; Schreitmuller and Ballschmiter, 1994; Schulz-Bull et al., 1998; Lakaschus et al., 2002; Tsapakis et al., 2003). The role of oceans as an exchanging compartment and/or permanent sink for POPs is therefore yet to be fully understood. Certainly only limited data are available on PAHs and PCNs in oceanic air and remote locations. This paper therefore presents PAH and PCN data from samples collected on board the Pelagia Research Vessel owned by The Netherlands Institute of Sea Research, as it sailed from The Netherlands to South Africa in January–February 2001. PCBs and organochlorine compounds were also studied in the same campaign and are available elsewhere (Jaward et al., 2004). Such large-scale spatial/latitudinal surveys have proved useful in the past, to identify global source areas, elucidate transport processes and highlight potential losses of other POPs (e.g. Lohmann et al., 2001; Lakaschus et al., 2002).

## 2. Materials and methods

### 2.1. Air sampling, extraction and analysis

A total of 55 12-h day–night air samples were taken from 4th January to 11th February 2001 as the Pelagia

travelled from the Netherlands (1.06° N, 1.43° E) to South Africa (33.88° S, 18.3° E). Samples were generally collected from 06:00 to 18:00 h GMT (day samples) and from 18:00 to 06:00 h GMT (night samples). The sampling route is shown in Fig. 1. The high volume (Hi-Vol) air sampler was placed windward on the uppermost deck of the ship, about 20 m above sea level, to minimise contamination from emissions from the ship's exhausts. Air (~110–190 m<sup>3</sup> per sample) was aspirated through a glass fibre filter (GFF) to remove particles from the air stream and the gaseous phase compounds were trapped on two polyurethane foam plugs (PUF) contained in an aluminium cylinder. After sampling, the PUFs and GFFs were transferred into solvent rinsed glass jars and stored at <−20 °C until analysis. Sampling intervals and meteorological information during the sampling period are given as Supplementary Information (Table SI-1).

Samples were spiked with a range of <sup>13</sup>C<sub>12</sub>-labelled PCB congeners (<sup>13</sup>C<sub>12</sub> PCB 28, 52, 101, 138, 153, 180, 209) and deuterated PAH (1-methylnaphthalene-*d*8, fluorene-*d*10, anthracene-*d*10, pyrene-*d*10, *p*-terphenyl-*d*14, benzo[*a*]pyrene-*d*12, indeno[123-*cd*] pyrene and benzo[*ghi*]perylene-*d*12) recovery or surrogate standards to monitor the extraction and cleanup procedures. The samples were extracted for 18 h with dichloromethane (DCM) in a Buchi extraction unit, rotary evaporated and transferred with hexane to a 15 ml amber vial. This was blown down under a gentle stream of nitrogen to about 0.5 ml and cleaned on a 9 mm id chromatography column with 1 g alumina (BDH neutral Alumina), 2 g silica gel (Merck Silica 60) and 1 cm sodium sulphate (all

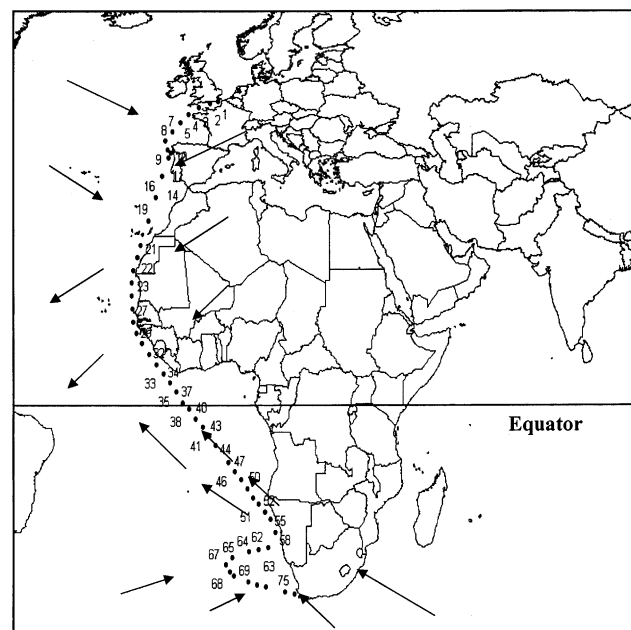


Fig. 1. The ship's route, mean sample locations and broad origins of the air masses.

baked at 450 °C overnight) and then passed through gel permeation chromatography (GPC) using 6 g of Biobeads SX 3. Deuterated PAH internal standards (naphthalene-*d*8, acenaphthene-*d*10, phenanthrene-*d*10, fluoranthene-*d*10, benzo[*a*]anthracene-*d*12, perylene-*d*12 and 1,3,5-triphenylbenzene) were added to the fractions and the volume of sample reduced to 500 µl hexane for PAH analysis.

PAHs were analysed with an HP 5890 series II GC equipped with a 30 m HP5MS column (0.25 mm i.d., 0.25 µm film thickness) and 3 m long deactivated HP retention gap (0.53 mm i.d.). This was connected to a HP 5972 MSD operating in selected ion monitoring mode. Details of the GC temperature programme and monitored ions are given elsewhere (Smith et al., 2001a; Smith et al., 2001b). Eight PAHs (fluorene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, chrysene, benzo[*e*]pyrene and benzo[*ghi*]perylene) were regularly detected from a much more comprehensive range of 16 compounds present in the standards (Smith et al., 2001a; Smith et al., 2001b) and were quantified. The sum of these constitutes the  $\sum_8$ PAHs reported later. After checking that the chromatograms were satisfactory, the samples were reduced to a final volume of 25 µl under a gentle stream of nitrogen and solvent exchanged to 25 µl of dodecane containing PCB-30 and <sup>13</sup>C<sub>12</sub> PCB-141 as internal standards. The samples were analysed for PCNs by GC-MS on a Fisons MD800 operated in electron ionisation mode using selected ion monitoring. A total of 13 PCN congeners (PCN-19, 24, 15, 17/25, 23, 42, 33/34/37, 47, 36/45, 28/43/29, 35, 38/40 and 46) were identified according to Helm et al. (1999), detected in samples and quantified using dilutions of a Halowax 1014 mixture. The sum of these constitutes the  $\sum_{13}$ PCNs.

## 2.2. Quality assurance/quality control (QA/QC)

All analytical procedures were monitored using strict quality assurance and control measures. Laboratory and field blanks consisted of pre-extracted PUF plugs and baked out GFFs, which were extracted and analysed in the same way as samples. Laboratory blanks constituted 10% and field blanks 20% of the total samples. There was no significant difference (*t*-test significance < 95%) between analyte concentrations in the laboratory and field blanks, indicating contamination was minimal during transport, storage and analysis. Method detection limits (MDLs) were derived from the blanks and quantified as 3 times the standard deviation of the mean blank concentrations. MDLs ranged from 13 to 47 pg m<sup>-3</sup> for PAHs (depending on compound) and from 0.3 to 1.5 pg m<sup>-3</sup> for PCNs (depending on congener). In addition, peaks were only integrated if the signal:noise ratio was ≥ 3, otherwise they were considered non-detects. Average PUF recoveries were 76–90% for individual PCNs and 69–110% for PAHs while the average GFF

recoveries were 69–84% for PCNs and 71–98% for PAHs. Reported values are not recovery corrected. A quality control standard was included to monitor instrument efficiency after every six samples.

There is always the potential for contamination of air from ship-board samples. Visual observations were therefore made throughout the cruise to see when prevailing winds were such that emissions from the ship's funnel could have been sampled, i.e. when the predominant wind direction was from the stern of the ship. The mixture of compounds was also investigated. The PAH and combustion-related PCN concentrations in samples 21–26 were affected and are therefore not reported. Statistical analysis (*t*-test significance > 95%) showed a significant difference between these 'contaminated' and the 'uncontaminated' samples.

## 2.3. Back trajectories

Air mass origins were determined for the cruise samples using the HYSPLIT transport and dispersion model from the NOAA Air Resources Laboratory (Draxler and Rolph, 2003). Two back trajectories (BTs) were performed for each sampling episode, that is, one at the start and one at the end. BTs were traced for 5 days with 1 h steps at 00:00 co-ordinated universal time (UTC) and 12:00 UTC at 500 and 1000 m above sea level to reduce the effect of turbulent mixing and convection in the atmosphere (Stohl et al., 2002). Samples are shown with a general indication of the direction of their air mass origin/surface wind patterns in Fig. 1. In the northern hemisphere (NH) between 50°N and 32°N (samples 1–16), air was generally coming from the NW to the ship. Between ~30°N and 11°N, the winds came mainly from the NE. Samples 19–29 were thus affected by this wind pattern. Further south towards the equator, a high-pressure subtropical anti-cyclonic system (the inter tropical convergence zone—ITCZ) was encountered. The ITCZ is a high reaching air curtain that divides the troposphere of both hemispheres and is caused by the counter flowing NE and SE trade winds. These are rather constant wind systems throughout the year and generally lie between ~6° N and the equator (Schreitmuller and Ballschmiter, 1994). The air in the trade winds is generally well mixed and influenced by the surface water layer up to the height of the trade wind inversion at 1500 ± 500 m. The wind patterns are shown in Fig. 1. BTs showed some air samples arriving at the sampler had crossed the Atlantic Ocean for at least 5 days prior to being sampled. These are clearly 'oceanic' samples (numbers 38–55, 58, 62, 68–71). For others, air came predominantly over the land before being sampled (samples 21–33 and 75). Others were partly continental and partly oceanic (1–3, 5–7, 9–20, 34–37, 73, 76). Samples with a 'continental' origin had filters containing notably more particulate matter. Samples 27–33 contained large quantities of

Saharan dust, for example. It should be noted that there is some uncertainty associated with the BTs since the ship is changing location (Subhash and Honrath, 1999; Stohl et al., 2002). There is additional uncertainty caused by the changing location of the ship.

### 3. Results and discussions

#### 3.1. General remarks on gas/particle phase distribution and compounds detected

The gas (PUF) and particle (GFF) phase samples were analysed separately. However, the  $\sum$ PAH and  $\sum$ PCN occurred primarily (>90%) in the gas phase, heavily influenced by the dominance of the lower molecular weight species. Mean air temperatures during the cruise ranged from 9.5 °C to 29 °C. Out of the 55 samples taken, 40% are oceanic, 25% continental and 35% mixed (continental/oceanic). Maritime air is generally low in particles and a high contribution from the gas phase component has been noted in previous studies of POPs in the Arctic Ocean, especially during summer months (Halsall et al., 1997; Stern et al., 1997). Most of the GFF samples in the southern hemisphere (SH) gave non-detect values for most compounds. Tsapakis et al. (2003) in their recent study in the Eastern Mediterranean marine environment reported a substantial decline in particulate PAH concentrations with increasing distance of the sampling sites from urban centres. This is probably due to the fact that removal processes of particulate PAHs (e.g. wet and dry deposition) are faster than those of gas phase PAHs (Halsall et al., 2001). The gas phase (PUF) data were therefore used in the interpretations in the remaining parts of the paper.

Of the 13 PCN congeners quantified, 11 (PCN-24, 17/25, 23, 42, 47, 36/45, 33/34/37, 28/43/29, 35, 38/40 and 46) were detected in >30% of samples, while PCN-19 and PCN-15 were detected in <20% of samples. Five of the 8 PAHs (fluorene, phenanthrene, 1-methylphenanthrene, fluoranthene and chrysene) were detected in >50% of samples, while anthracene, benzo[e]pyrene and benzo[ghi]perylene were detected in <20%. Summary data on the mean, median, minimum and maximum atmospheric concentrations are given in Table 1.

#### 3.2. Levels and trends of PAHs

The mean and median  $\sum_8$ PAH concentrations measured in the cruise samples were  $\sim 960$  and  $\sim 650$  pg/m<sup>3</sup>, respectively, but the range varied by a factor of 20 (190–3730 pg/m<sup>3</sup>) (see Table 1). Not surprisingly, all these values are generally lower than literature data for urban locations in Europe. Some are the same order as those from European rural/remote locations (see Table 2). It is note worthy that the number of PAHs making up

Table 1

Summary of results (concentrations in pg m<sup>-3</sup>) (minimum values occurred in SH oceanic samples and maximum values in European samples and samples close to West Africa)

Compound	% >DL	Mean	Median	Minimum	Maximum
Fluorene	63	170	80	<13	930
Phenanthrene	100	480	300	46	1590
Anthracene	24	60	37	<13	190
1-Methylphenanthrene	100	100	78	22	450
Fluoranthene	96	230	160	<47	890
Chrysene	51	40	37	<21	70
Benzo(e)pyrene	16	30	27	<13	47
Benzo(ghi)perylene	14	35	35	<13	52
$\sum_8$ PAH		960	650	190	3730
PCN 19	22	1.0	0.7	<0.4	2.3
PCN 24	29	7.5	5.6	<3	19
PCN 15	12	0.7	0.7	<0.4	1
PCN 17/25	43	0.7	0.6	<0.2	1.7
PCN 23	43	4.8	3.3	<1.5	13
PCN 42	31	0.8	0.6	<0.3	2
PCN 33/34/37	47	4.8	3	<1.4	15
PCN 47	43	1.4	1	<0.5	4
PCN 36/45	41	0.9	0.8	<0.3	2.7
PCN 28/43/29	67	2.3	1.4	<0.6	8
PCN 35	51	1.9	1.5	<0.6	5.4
PCN 38/40	78	3.2	2	<0.6	11
PCN 46	65	1.3	0.8	<0.3	4.3
$\sum_{13}$ PCN		16	7.7	0.3	86

$\sum$ PAHs is different for the different studies. Phenanthrene was the dominant compound, contributing  $\sim 50\%$  to the  $\sum_8$ PAH. The other compounds contributed broadly as follows: fluoranthene,  $\sim 20\%$ ; 1-methylphenanthrene and fluorene,  $\sim 10\%$  each; anthracene, chrysene, benzo[e]pyrene and benzo[ghi]perylene  $\sim 5\%$  in total.

Fig. 2 shows how the  $\sum_8$ PAH concentrations varied along the cruise. The highest concentrations (2270–3730 pg  $\sum_8$ PAH/m<sup>3</sup>) occurred in European samples and samples close to West Africa (samples 2, 9, 27–33) and considerably exceeded the values of the southern oceanic samples (38–55, 58, 62, 68–71). Recent efforts by the United Nations Environment Programme highlight the discrepancies in the amount of information available for different regions of the world (UNEP, 2002a; UNEP, 2002b). Although emission inventories have been developed for Europe (European Commission, 2001; Pacyna et al., 2003), almost no data are available for Africa (UNEP, 2002b). However, these few cruise data highlight an important issue: despite the general focus on urbanised, developed countries as key global sources of PAHs, less studied regions such as Africa may well be equally important to the global inventory. This observation was also made previously, for PCDD/Fs in air sampled close to West Africa (Lohmann et al., 2001). PAH levels in European and North American air have generally declined over the last few decades (e.g. European Commission, 2001), reflect-



Table 2

Comparison of recent measurements of  $\sum$ PAHs and  $\sum$ PCNs ( $\text{pg m}^{-3}$ ) in air from various studies

Location/year	Site type	PAH	PCN	Reference
North–South Atlantic Cruise	Remote/rural	190–3730	0.3–86	This study
Augsburg, Germany, 1992–1993	Urban	2170		Dorr et al. (1996b)
Augsburg, Germany, 1992–1993	Rural	1140		Dorr et al. (1996b)
London, UK, 1992	Urban	121,000		Halsall et al. (1994)
Manchester, UK, 1992	Urban	76,000		Halsall et al. (1994)
Augsburg, Germany, 1992–1993	Urban		60	Dorr et al. (1996a)
Augsburg, Germany, 1992–1993	Rural		24	Dorr et al. (1996a)
Downsview, Canada, winter 1995	Urban		17	Harner and Bidleman (1997)
Chicago, USA, 1995	Urban		68	Harner and Bidleman (1997)
East Arctic, summer 1996	Remote		12	Harner et al. (1998)
Manchester, 1998–1999	Urban		150	Harner et al. (2000)
Barent Sea, 1996	Remote		40	Harner et al. (1998)
Norwegian Sea, 1996	Remote		7	Harner et al. (1998)
Lancaster, UK, 1994	Semi-rural		66	Lee et al. (2000)
Lake Superior, 1996/1997	Remote		1.5–1.8	Helm et al. (2003)
Lake Ontario, 1998/2000	Rural		5.5–5.6	Helm et al. (2003)
East Mediterranean, 2001	Marine air affected by urban sites	20,000–83,200		Tsapakis et al. (2003)

ing general improvements in combustion technology and broad shifts in energy/space heating (e.g. coal, replaced by gas/electricity). In contrast, numerous lower temperature—and hence relatively inefficient—combustion sources may be contributing to relatively high emissions in Africa. These may include bush fires and open burning of domestic wastes (Lohmann et al., 2000; Kakareka and Kukharchyk, 2003).

For many POPs, emissions in the SH are lower than those in the NH and—because of the slow rates of inter-

hemispheric mixing of ca. 1–2 years (Schreitmuller and Ballschmiter, 1994)—the net result is that air concentrations in the SH are lower than those of the NH. NH PAH concentrations were generally higher than those in the SH, where samples 38–55, 58, 62, 68–71 were in the 190–680  $\text{pg } \sum_8\text{PAH/m}^3$  range. These samples were generally ‘aged’ air masses taken some distance away from land.

### 3.3. Levels and trends of PCNs

The mean  $\sum_{13}\text{PCN}$  concentrations ranged between 0.3 and 86  $\text{pg/m}^3$  (Table 1). Fig. 3 shows that the highest PCN concentrations occurred in the European samples, but—as for PAHs—some high values were also detected off the West African coast, and in the sample taken closest to South Africa. The lowest values measured over the SH oceans—typically 0.3–5  $\text{pg/m}^3$ —are the lowest so far reported globally. Values of a few  $\text{pg/m}^3$  have been reported for the remote east Arctic and Barents Sea and Lake Superior (Harner et al., 1998; Helm et al., 2003); highest values in the literature ( $\sim 150 \text{ pg/m}^3$ ) have been reported for urban centres (see Table 2). It should be noted that the number of PCN congeners making up  $\sum$ PCNs is different for the different studies.

Little or no information is available on regional or global usage and emission of the PCNs. However, as noted in Section 1, two broadly different sources have been identified—emissions from the technical PCN products (e.g. Halowaxes) and emissions from high temperature combustion processes. The technical PCN products had similar usage patterns to the PCBs. It has been estimated that  $\sim 90\%$  of the global usage and emissions of PCBs were in the NH (Breivik et al., 2002a;

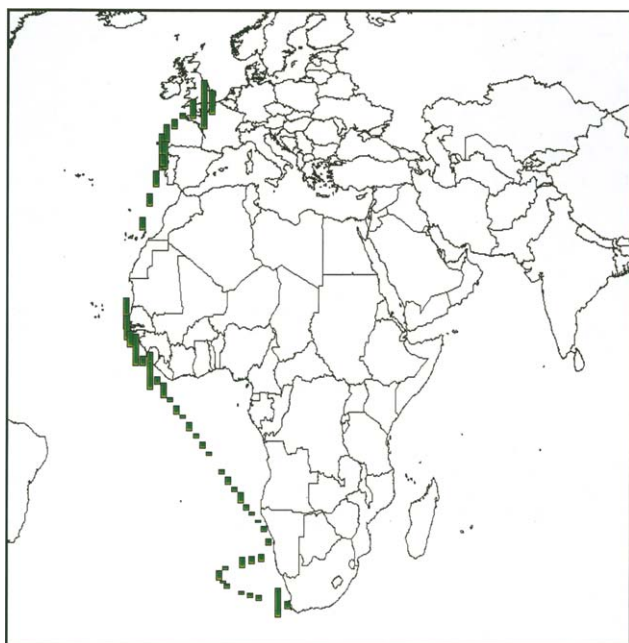


Fig. 2. Spatial distribution of  $\sum_8\text{PAH}$  ( $\text{ng/m}^3$ ) along the cruise. Note: the bars center on the sample site in all figures. Key: Largest bar = 3.7  $\text{ng m}^{-3}$  (site 2).

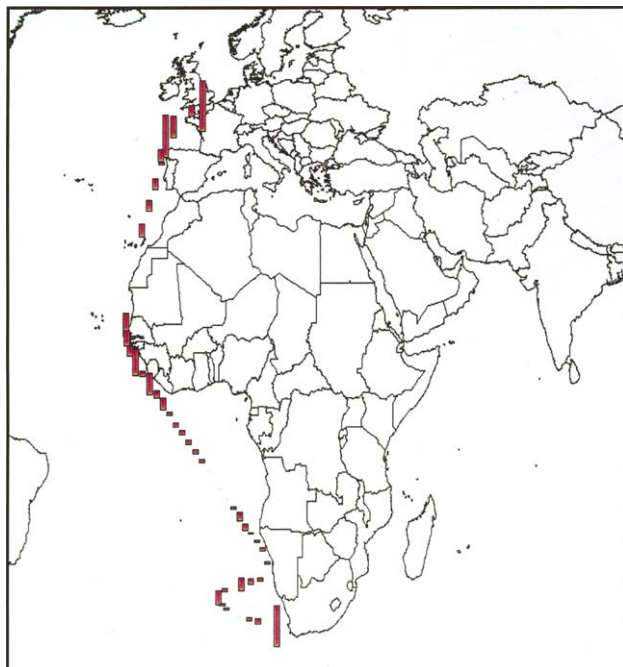


Fig. 3. Spatial distribution of  $\Sigma_{13}\text{PCN}$  ( $\text{ng}/\text{m}^3$ ) along the cruise. Note: the bars center on the sample site in all figures. Key: Largest bar =  $86 \text{ pg m}^{-3}$  (site 2).

Brevik et al., 2002b). Generally, the PCN concentrations measured on the cruise were higher in the NH and in samples of ‘continental’ air masses. Unsurprisingly the ‘maritime background’ of the SH (e.g. samples 38–55, 58, 62, 68–71) was considerably lower (typically  $0.3\text{--}5 \text{ pg}/\text{m}^3$ ) than that of the NH (typically  $1\text{--}30 \text{ pg}/\text{m}^3$ ).

#### 3.4. Comments on the effects of temperature

As noted in Section 1, it is important to establish whether re-supply of POPs from the oceans to the overlying air controls ambient concentrations, or whether the net flux is from air–surface waters–deeper waters–sinks, ultimately driven by continuing primary sources to the atmosphere from land-based sources. If there were substantial re-emission from surface waters to the atmosphere, the flux would vary between different regions of the ocean, because it would be affected by the ‘holding capacity’ of the surface waters. This is a strong function of the productivity/biomass in different regions of the world (Dachs et al., 2002). It would also be a function of temperature.

Fig. 4 summarises the latitudinal variations in air concentrations, together with the air and surface water temperatures logged during the cruise. It is clear that neither air nor surface water temperature are the dominant controlling variables for the broad latitudinal ambient PAH or PCN trends. Rather, as noted in the previous sections, proximity to potential source regions and air mass origin influenced where high concentra-

tions were observed. This clearly implies that primary (rather than secondary) sources broadly controlled the air concentrations observed over the cruise as a whole.

#### 3.5. Composition of the SH background oceanic air

Some compounds were always detected, even over the remote SH Atlantic Ocean. These were lower molecular weight PAHs (phenanthrene, fluoranthene and 1-methylphenanthrene)—compounds that also commonly dominate the mixture of PAHs in air over land (e.g. Halsall et al., 1997). Interestingly, these compounds are the most susceptible of the PAHs to reactions in the atmosphere with the OH radical. Reaction half-lives of tens of hours at  $25 \text{ }^\circ\text{C}$ , based on chamber studies have been reported (Mackay et al., 1992; Brubaker and Hites, 1998). As noted earlier, many of the samples taken in the SH were from ‘aged’ air masses, where they had not seen land for 5 days or more.

#### 3.6. Diurnal variations in air concentrations over the SH ocean

As just argued, the broad trends in ambient levels on the cruise appear to be controlled by primary emissions and air mass origins. The lack of an over-riding relationship with air or seawater temperature along the latitudinal transect supports this contention. However, in the most remote of the samples taken in the SH—far from land and where the ambient concentrations were lowest—a diurnal pattern was noted in the data with daytime concentrations higher than nighttime concentrations. This implies that some dynamic environmental process(es) is/are exerting an influence on the air concentrations in this region—far from global source regions.

Several factors can vary diurnally, which could potentially affect ambient POPs concentrations. These include: atmospheric OH radical concentrations (and hence atmospheric reaction rates of POPs), ambient temperature and wind speed/direction, surface temperatures, the atmospheric boundary layer (ABL) height, light penetration, stratification, and possibly features of the ocean surface waters (e.g. phytoplankton production; diurnal zooplankton migration) (Millero and Sohn, 1992). Substances coupled to biological processes,  $\text{O}_2$ ,  $\text{CO}_2$ , dimethyl sulphide and biogenic volatile organic compounds (VOCs), for example, exhibit diurnal cycles in production and emission from ocean waters.

Mandalakis et al. (2003) have previously presented results from a study where they measured PCBs in air sampled on the coast of the island of Crete in the Mediterranean. For part of their campaign, they observed daytime concentrations that were lower than nighttime concentrations and argued that this was evidence of a daytime depletion of air concentrations caused by OH

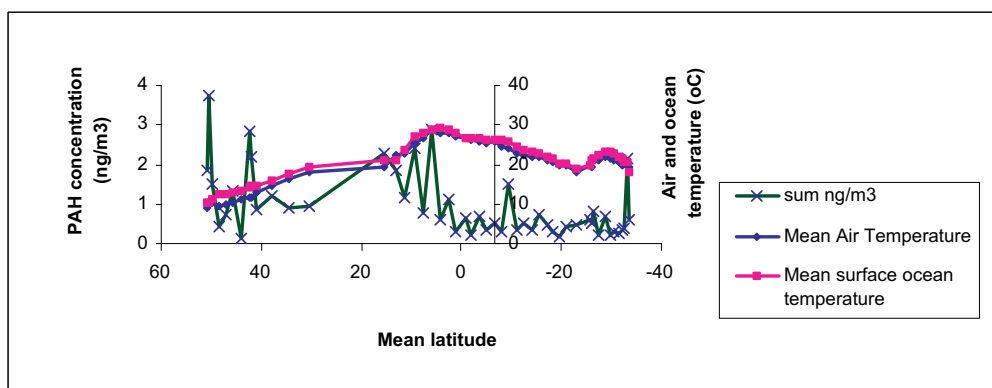
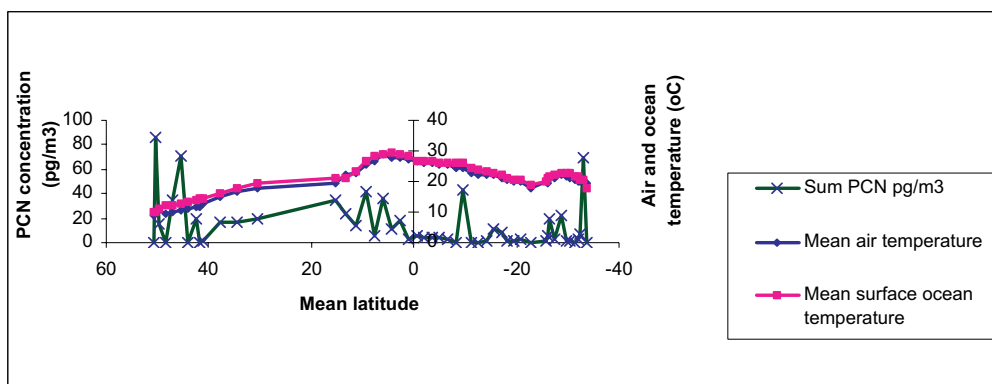
4a.  $\sum_8$ PAHs4b.  $\sum_{13}$ PCNs

Fig. 4. Air and surface ocean temperature and compound data versus mean latitude. (a)  $\sum_8$ PAHs, (b)  $\sum_{13}$ PCNs.

radical destruction. Other studies reporting diurnal cycling over vegetated surfaces have also been reported, where temperature drives up daytime concentrations (Hornbuckle and Eisenreich, 1996; Lee et al., 1998). Diurnal cycling can also be observed in coastal zones, where there can be a complex interplay between the variables noted above, plus land–sea breezes and emissions (e.g. Lohmann et al., 2003).

Fig. 5 shows the trends in concentrations of phenanthrene, 1-methylphenanthrene and fluoranthene in aged air samples, taken between 1° and 32°S (samples 38–55, 58, 62, 68–71) (see also Fig. 2). Daytime concentrations exceeded nighttime concentrations typically by a factor of 1.5–2.5 for the PAHs. The data are consistent with a close coupling of air–open ocean concentrations (Lakaschus et al., 2002; Bruhn et al., 2003). As far as we are aware, this is the first report of such a trend for POPs. It is inconsistent with expectations, based on OH radical reactions (although the atmospheric half-lives of the light PAHs are probably rather too long to expect a clear pattern based on enhanced daytime reactions; Brubaker and Hites, 1998). These trends are the complete reverse of those observed for

PCBs by Mandalakis et al. (2003) in part of their study. There is no evidence of day:night differences in the ABL height from the HYSPLIT trajectory information. Air and water (at ca. 3 m depth) temperatures were monitored continuously on the Pelagia during the cruise; however, they did not fluctuate more than a degree or

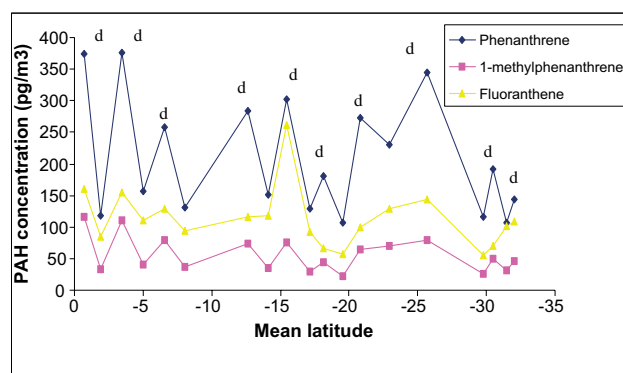


Fig. 5. Diurnal variations of selected PAHs ( $\text{pgm}^{-3}$ ) in remote southern hemisphere oceanic air samples (1–32° S). Key: d = day samples.

two diurnally over this part of the transect, which is insufficient to explain the changes in ambient concentrations purely through a temperature effect on air–water partitioning.

It is clear that these observations of diurnal fluctuation are potentially very important with regard to the air–water exchange and global cycling of POPs (Jaward et al., 2004). Further studies are urgently required to confirm the trends observed and to investigate their cause.

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