

The spatial distribution and potential sources of polycyclic aromatic hydrocarbons (PAHs) over the Asian marginal seas and the Indian and Atlantic Oceans

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[1] Gaseous and particle-bound polycyclic aromatic hydrocarbons (PAHs) were analyzed in air samples taken on a voyage of the Scholar Ship from January 16th to March 14th, 2008. Samples were taken from the Asian marginal seas and the Indian and Atlantic Oceans, providing an opportunity to assess spatial trends and potential sources of atmospheric PAHs over those oceans. The results show that continental sources were still responsible for some high concentrations of PAHs measured over the oceans. The Σ_{15} PAHs in the gaseous phase were elevated on the approach to China and India, while the highest Σ_{15} PAHs in the particulate phase were found at Chennai Harbor and close to Guinea. The high proportion of fluorene in the gas phase over the East and South China Sea could be a marker of coal and coke related combustion emission from Mainland China. The elevated high-molecular-weight PAHs in particles close to Guinea might be related to biomass burning in Africa. These results are consistent with previous PAH emission inventories and highlight the potential impact of continental PAH sources in China, India and Africa on the adjacent marine atmosphere.

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1. Introduction

[2] Polycyclic aromatic hydrocarbons (PAHs) of natural and anthropogenic origin are ubiquitous environmental contaminants in the atmosphere. They have been of scientific concern for several decades due to their ubiquity in the environment and adverse effects on human health. Atmospheric PAH concentrations vary globally. The highest levels often occur in densely populated and industrialized areas [Gupta *et al.*, 2011; Ma *et al.*, 2011; Mohanraj *et al.*, 2010; Sharma *et al.*, 2007]. However, atmospheric circulation is an important vector for transporting pollutants, therefore emitted PAHs not only impose risks to local areas but also contaminate remote regions through long-range atmospheric transport.

[3] Oceans, which are relatively far from PAH emission sources, are traditionally viewed as an ultimate sink for pollutants [Jaward *et al.*, 2004]. To date, several PAHs

monitoring programmes in the marine atmosphere have been conducted over the Atlantic, Indian, Pacific and Arctic Oceans [Crimmins *et al.*, 2004; Ding *et al.*, 2007; Jaward *et al.*, 2004; Lohmann *et al.*, 2009; Nizzetto *et al.*, 2008] to identify global source areas and elucidate transport processes. Crimmins *et al.* [2004] found that fossil fuel combustion from the Indian sub-continent is the predominant source of PAHs in the atmosphere over the Northern Hemisphere part of the Indian Ocean. Jaward *et al.* [2004] observed high PAH concentrations near Europe and West Africa. Ding *et al.* [2007] indicated that biomass or coal burning in Asia influences the atmospheric PAHs over the North Pacific Ocean and the Arctic Ocean in the summer. Their measurements are consistent with an inventory estimation [Zhang and Tao, 2009] that PAH emission densities in East and South Asia, West Europe and Central Africa were higher than in other regions. However, the emission inventory continues to change because of the increasing energy efficiency of developed countries and the rapid growth of energy demand in developing countries, such as biomass, peat and coal. PAH concentrations also vary with the seasons. Previous studies took samples at different times or from different areas, so it is difficult to compare the levels over various oceans. Currently the existing data are not sufficient to evaluate the current spatial distribution of PAHs on a global scale. Further research is needed to assess how these toxic chemicals are transported from the surrounding source regions to remote marine atmosphere.

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[4] The voyage of the Scholar Ship in 2008 from Shanghai to Bangkok, Chennai, Cape Town and Cape Verde, provided an opportunity to establish an updated data set of PAHs and other inorganic components in the more recent marine atmosphere [Moreno *et al.*, 2010; Pérez *et al.*, 2010]. In this study, marine boundary layer air samples were collected and analyzed for the occurrence of PAHs over the Asian marginal seas and the Indian and eastern Atlantic Oceans i) to extend our knowledge of the remote marine atmosphere PAH burden and ii) to identify potential source areas of PAHs using back trajectories and hence characterize the types of potential sources during this voyage.

2. Materials and Methods

2.1. Sampling

[5] Diel atmospheric samples of $\sim 220 \text{ m}^3$ were taken onboard the MV Oceanic II (The Scholar Ship, http://en.wikipedia.org/wiki/The_Scholar_Ship) from January 16th to March 14th, 2008. The cruise route and air mass back trajectories (at the time of sampling) are shown in another study [Li *et al.*, 2011]. Sampling started from Shanghai, crossed the following ports of Bangkok, Chennai, Cape Town and Cape Verde and ended at Cape Verde Islands. A high volume air sampler was placed at the front of the ship to avoid contamination from ship exhausts. Particles and gas phase samples were collected on pre-combusted (450°C , 12 h) quartz fiber filters (Grade GF/A, $20.3 \times 25.4 \text{ cm}$, Whatman, Maidstone, England) and pre-cleaned polyurethane foam (PUF)/XAD-2 resin composite cartridges (3-cm-thick packing of XAD-2 adsorbent resin sandwiched between 5 and 2.5 cm foam plugs, 6.5 cm diameter, 7.5 cm length). Field blanks were obtained by the respective sampling method, but were exposed to the atmosphere only for a few seconds. After sampling, all the samples were wrapped with clean aluminum foil, sealed in clean jars, and kept at -18°C until analysis. The aerosol samples from January 16th to 24th were unavailable, so only samples in the gas phase are present for those days.

[6] Many meteorological factors could influence PAH concentrations in the atmosphere. The weather was commonly cloudy during the daytime, except during four samples (Feb-28D, Feb-29D, Mar-5D and Mar-10D). The effects of pressure, wind speed, rainfall, mixed layer height, relative humidity, solar radiation flux and hydroxyl radical concentrations (calculated according to the equation of Beyer *et al.* [2003]) were investigated. No statistically significant correlations were found between those meteorological factors and the gas-phase concentrations of PAHs, indicating those were not the key factors influencing the atmospheric concentrations of PAHs in most samples. The temperature dependence was also investigated by plotting the natural logarithm of the partial pressure versus $1/T$ [Nizzetto *et al.*, 2008]. The correlations were not significant ($p > 0.05$) or yielded low r^2 values (Ace, $r^2 = 0.134$, Acy, $r^2 = 0.077$) in this study. We will therefore not discuss these factors further.

2.2. Analytical Procedure

[7] The samples were spiked with a mixture of surrogate standards containing deuterium labeled PAHs and Soxhlet-extracted with dichloromethane (DCM) for 24 h. Activated

copper granules were added in excess to the collection flask to remove elemental sulfur. Half of each sample extract was concentrated with a rotary evaporator and solvent-exchanged into hexane. Purification was accomplished with an 8 mm i.d. alumina/silica column containing anhydrous sodium sulfate (1 cm), neutral silica gel (3 cm, 3% deactivated) and neutral alumina (3 cm, 3% deactivated). The PAH fractions were eluted with 15 ml of a mixture of dichloromethane and hexane (1:1, V/V). The eluent solvent was blown down to a final volume of 25 μL in dodecane under a gentle stream of nitrogen. Before analysis, 1000 ng of hexamethyl benzene was added as internal standards.

[8] The PAHs were analyzed on an Agilent 7890 gas chromatograph equipped with a capillary column (DB-5MS, 30 m, 0.25 mm, 0.25 μm) and a mass spectrometric detector (MSD, Agilent 5975). Each extract (1 μL) was injected in splitless mode with a 10 min solvent delay time. High purity helium was used as the carrier gas, with a flow rate of 1.83 ml/min. The temperature of the injector and transfer lines was 290°C and 300°C , respectively. The initial oven temperature was set at 60°C for 1 min, raised to 290°C at a rate of 3°C min^{-1} and then held for 20 min. Fifteen individual PAHs were quantified: acenaphthene (Ace), acenaphthylene (Acey), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flur), pyrene (Pyr), benzo[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), dibenzo[a,h]anthracene (DahA), benzo[g,h,i]perylene (BghiP) and indeno[1,2,3-c,d]pyrene (Ind).

2.3. QA/QC

[9] The instrument stability was checked daily using PAH standards, and the deviation was less than 10%. Isotope-labeled PAHs were added to samples and field blanks to monitor the analytical and sampling procedure. The recoveries were $64 \pm 14\%$, $79 \pm 17\%$, $85 \pm 19\%$ and $97 \pm 13\%$ for acenaphthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12, respectively. All the target compounds in the laboratory blanks were below method detection limits (MDL). Seven field blanks were taken at harbors (Shanghai, Bangkok, Chennai and Cape town) and at sea (the Bay of Bengal, Indian Ocean and Atlantic Ocean). The method detection limits (MDL) were defined as the average concentrations of target compounds in field blanks plus three times the standard deviation. Levels of BbF, BkF, BaP, Ind, DahA and BghiP in PUF samples were below the MDL, therefore only Ace, Acey, Flu, Phe, Ant, Flur, Pyr, BaA and Chr in the gas phase are discussed throughout the text. Nearly all target compounds were collected in the first PUF sandwich in the breakthrough tests during the sampling procedure, and thus breakthrough of gas phase PAHs was insignificant. The reported data in this study were not recovery corrected.

[10] Ship-based emissions could contaminate air samples, so the high volume air sampler was kept away from the ship's smoke stack to avoid this contamination. The vessel traveled at a speed of 17 knots for the samples we discussed, and the wind speeds were generally lower than 14 knots. Contamination by downwind ship smoke should be insignificant. The ratio of methylphenanthrene to phenanthrene (ranged from 0.26 to 0.65) also confirmed that petrogenic emission were not the major source [Hwang *et al.*,

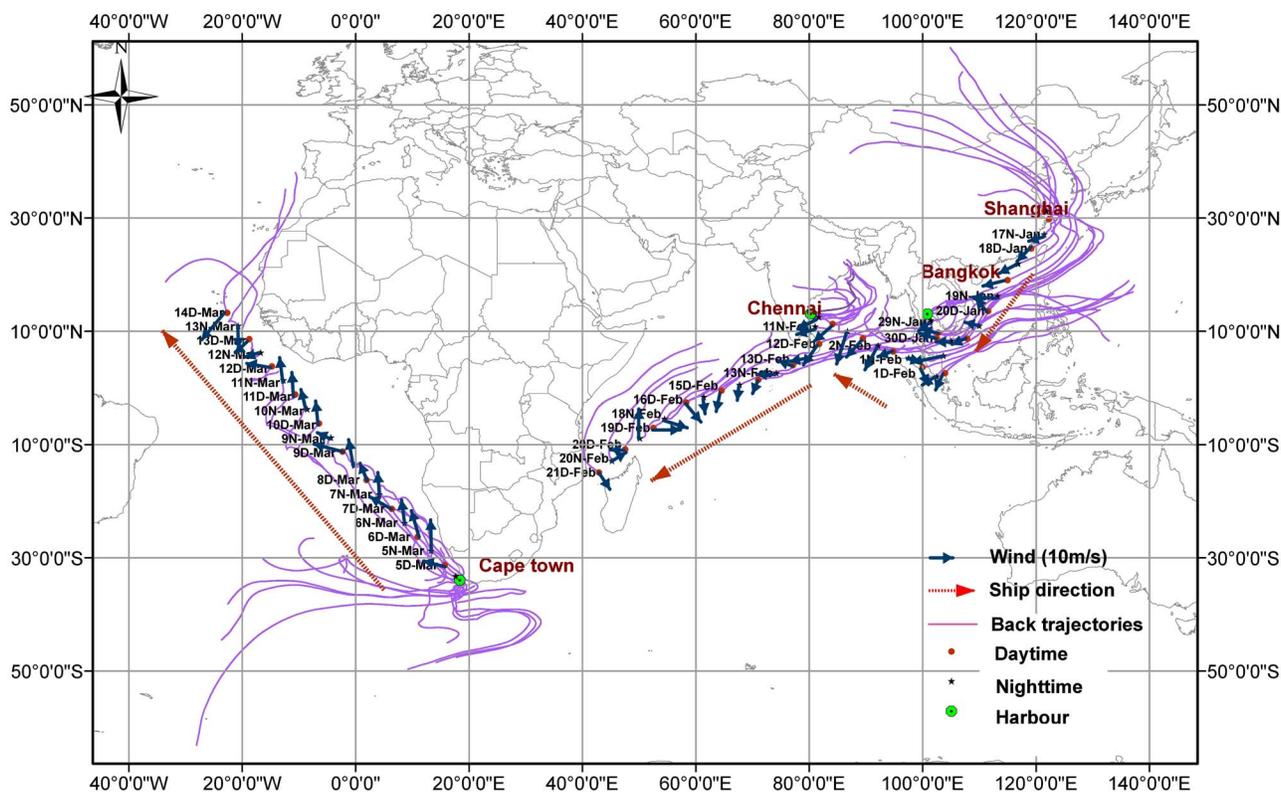


Figure 1. The sampling information and air mass back trajectories.

2003] during the whole voyage. In addition, the PAH concentrations exhibited spatial variations that resembled those found in previous studies. High and low concentrations were observed during both favorable and unfavorable wind conditions. *Nizzetto et al.* [2008] discussed similar experimental conditions. They suggested that if ship contamination had been the cause of the high concentrations observed, the PAH concentrations would have been recorded only in samples affected by favorable wind conditions. For these reasons,

PAH measurements are believed to be not affected by ship-based emissions in this study.

2.4. Back Trajectory Analysis

[11] One of the common ways to locate the potential source of atmospheric pollution is air mass trajectory analysis. Five-day air parcel back trajectories were calculated at 6-h-intervals for sampling days by the Hybrid-Single Particle Integrated Trajectories (HYSPLIT 4.8)

Table 1. Distribution of Atmospheric PAH Concentrations (pg m⁻³) in the Particulate Phase Over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean^a

	MDL	East and South China Seas (n = 4)			Bay of Bengal and the Andaman Sea (n = 10)			Indian Ocean (n = 12)			Atlantic Ocean (n = 18)		
		Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD
Ace	6.8	13 ± 15	n.d-35	2	4.9 ± 2.4	n.d-9.9	3	3.8 ± 1.5	n.d-8.5	1	4.5 ± 3.5	n.d-17	2
Acey	6.6	7.4 ± 5.5	n.d-15	2	4.1 ± 1.9	n.d-8.3	2			0	4.0 ± 3.2	n.d-17	1
Flu	12	18 ± 14	n.d-31	2	12 ± 9.1	n.d-28	4	7.0 ± 3.5	n.d-18	1	8.2 ± 4.7	n.d-21	4
Phe	40	58 ± 44	n.d-100	2	55 ± 27	n.d-91	7	31 ± 24	n.d-100	3	45 ± 30	n.d-110	10
Ant	3.6	4.0 ± 2.6	n.d-7.1	3	3.9 ± 2.0	n.d-6.8	6	2.3 ± 1.2	n.d-5.1	2	3.2 ± 2.6	n.d-12	5
Flur	10	19 ± 23	n.d-53	2	53 ± 65	n.d-180	7	38 ± 32	n.d-110	9	69 ± 68	n.d-290	17
Pyr	14	16 ± 17	n.d-42	1	49 ± 60	n.d-160	5	34 ± 30	n.d-99	8	71 ± 69	n.d-300	16
BaA	12	11 ± 3.9	n.d-15	3	16 ± 13	n.d-41	4	10 ± 5.9	n.d-21	5	14 ± 21	n.d-92	8
Chr	3.4	28 ± 14	9.2-42	4	56 ± 50	19-150	10	34 ± 23	9.0-86	12	52 ± 59	n.d-86	17
BbF	1.0	16 ± 8.2	7.1-27	4	71 ± 88	1.3-240	10	8.2 ± 11	1.8-41	12	28 ± 96	n.d-400	15
BkF	0.90	6.5 ± 2.9	3.9-10	4	30 ± 38	n.d-100	9	3.5 ± 5.5	n.d-20	8	9.6 ± 31	n.d-130	10
BaP	0.98	6.6 ± 1.9	5.1-9.3	4	25 ± 31	n.d-70	8	2.2 ± 3.8	n.d-13	4	9.6 ± 36	n.d-150	4
Ind	1.2	7.7 ± 0.5.1	2.7-14	4	58 ± 73	n.d-190	8	4.3 ± 9.2	n.d-30	2	18 ± 66	n.d-270	3
DahA	0.35	0.75 ± 0.80	n.d-2.0	1	3.2 ± 4.1	n.d-11	4	0.41 ± 0.22	n.d-1.1	1	1.2 ± 3.0	n.d-13	2
BghiP	1.1	9.4 ± 3.0	6.8-13	4	59 ± 72	n.d-180	8	6.1 ± 12	n.d-33	4	17 ± 64	n.d-270	5

^aMDL, method detection limit; Mean, arithmetic mean; NAD, number above detection limit.

Table 2. Distribution of Atmospheric PAH Concentrations (pg m^{-3}) in the Gaseous Phase Over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean

MDL	East and South China Sea (n = 18)			Bay of Bengal and Andaman Sea (n = 11)			Indian Ocean (n = 13)			Atlantic Ocean (n = 18)		
	Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD	Mean	Range	NAD
Ace	1200 ± 1700	150–5500	18	120 ± 33	67–160	11	220 ± 270	63–1000	13	120 ± 52	75–310	18
Acey	1300 ± 840	370–3100	18	300 ± 81	190–410	11	340 ± 190	120–870	13	260 ± 54	160–350	18
Flu	8100 ± 4200	2800–21000	18	2400 ± 1000	1100–4200	11	2100 ± 1300	880–5400	13	1100 ± 340	700–1900	18
Phe	17000 ± 8800	5500–41000	18	9300 ± 3800	4100–16000	11	13000 ± 9600	5800–37000	13	8000 ± 4400	2700–19000	18
Ant	2100 ± 870	750–3600	18	1300 ± 490	580–2900	11	1800 ± 1400	780–5500	13	1200 ± 710	340–3100	18
Flur	2000 ± 1100	250–5000	18	850 ± 420	250–1700	11	1900 ± 1400	540–4500	13	1400 ± 1000	410–4600	18
Pyr	1400 ± 840	130–3700	18	670 ± 370	190–1600	11	1500 ± 1000	430–3400	13	1100 ± 890	330–4000	18
BaA	14 ± 12	n.d.–52	8	11 ± 13	n.d.–48	2	14 ± 11	n.d.–41	6	23 ± 48	n.d.–210	6
Chr	91 ± 45	34–180	18	48 ± 42	13–170	11	45 ± 33	18–120	13	58 ± 97	9.2–430	18

developed by the National Oceanic and Atmospheric Administration (NOAA) Air Resource Laboratory (<http://www.arl.noaa.gov/HYSPLIT.php>). Each trajectory was estimated at 100 m, 500 m and 1000 m above ground level, respectively. The trajectories are presented in Figure 1.

3. Results and Discussion

3.1. Air Concentration Profiles of PAHs in Open Oceans

[12] To better illustrate the concentrations over the open ocean, PAH concentrations are compiled into four categories, namely, the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean (Tables 1 and 2).

[13] Nine PAHs (Ace, Acey, Flu, Phe, Ant, Flur, Pyr, BaA and Chr) were commonly detected in gas phase samples. BaA concentrations were above the MDL in 37% of the samples during this voyage. Concentrations of the other eight PAHs were all above the MDL. The average concentrations of total gaseous PAH were 33,000, 15,000, 21,000 and 13,000 pg m^{-3} over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Ocean, respectively. Phe, Flu, Flur, Ant and Pyr occurred predominantly in the gas phase throughout the whole voyage, contributing more than 80% of the total gaseous PAHs.

[14] The particulate-bound PAHs above MDL were detected in a few samples only (Table 1). Concentrations of Ace, Acey, Flu, Ant, DahA and BghiP were infrequently above the MDL (in <50% samples), while Flur, Chr, BbF and BkF concentrations were above the MDL in more than 50% samples. The median concentrations of Σ_{15} PAHs in the particulate phase were 230, 200, 170 and 260 pg m^{-3} over the East and South China Seas, the Bay of Bengal and the Andaman Sea, the Indian Ocean, and the Atlantic Oceans, respectively, 1–2 orders of magnitude lower than gaseous PAH concentrations. The predominant PAHs in the particulate phase were 3–4 ring compounds, accounting for more than 50% of the total PAHs. Phe, Flur, Chr, Pyr were the major components, although the relative abundance of these compounds was different over the four regions.

[15] The geographical distribution of gaseous PAHs reported in Table 2 show that their concentrations were significantly higher over the East and South China Seas ($p < 0.05$) than the other three regions, except for BaA. Lang *et al.* [2008] reported that of the PAHs transported out of Mainland China, 69.9% remained in the offshore environment. Therefore, it is not surprising that high levels of PAHs were observed over these seas. The magnitudes of individual PAHs in the gas phase exhibit the following sequence in the atmosphere of the East and South China Seas: Phe (~51%) > Flu (~25%) > Ant and Flur (~6% each) > Acey and Pyr (~4% each) > Ace (~3%). (Detail of the compound profiles can be found in Figures S1 and S2).¹ When the vessel passed through this area, the concentrations were lower than those of some adjacent coastal cities, such as Guangzhou [Li *et al.*, 2006] and Ho Chi Minh city [Hien *et al.*, 2007], and were comparable to those in Xiamen [Zhao *et al.*, 2010] and those in the marine atmosphere along Far East Asia [Ding *et al.*, 2007] but higher than those at Okinawa,

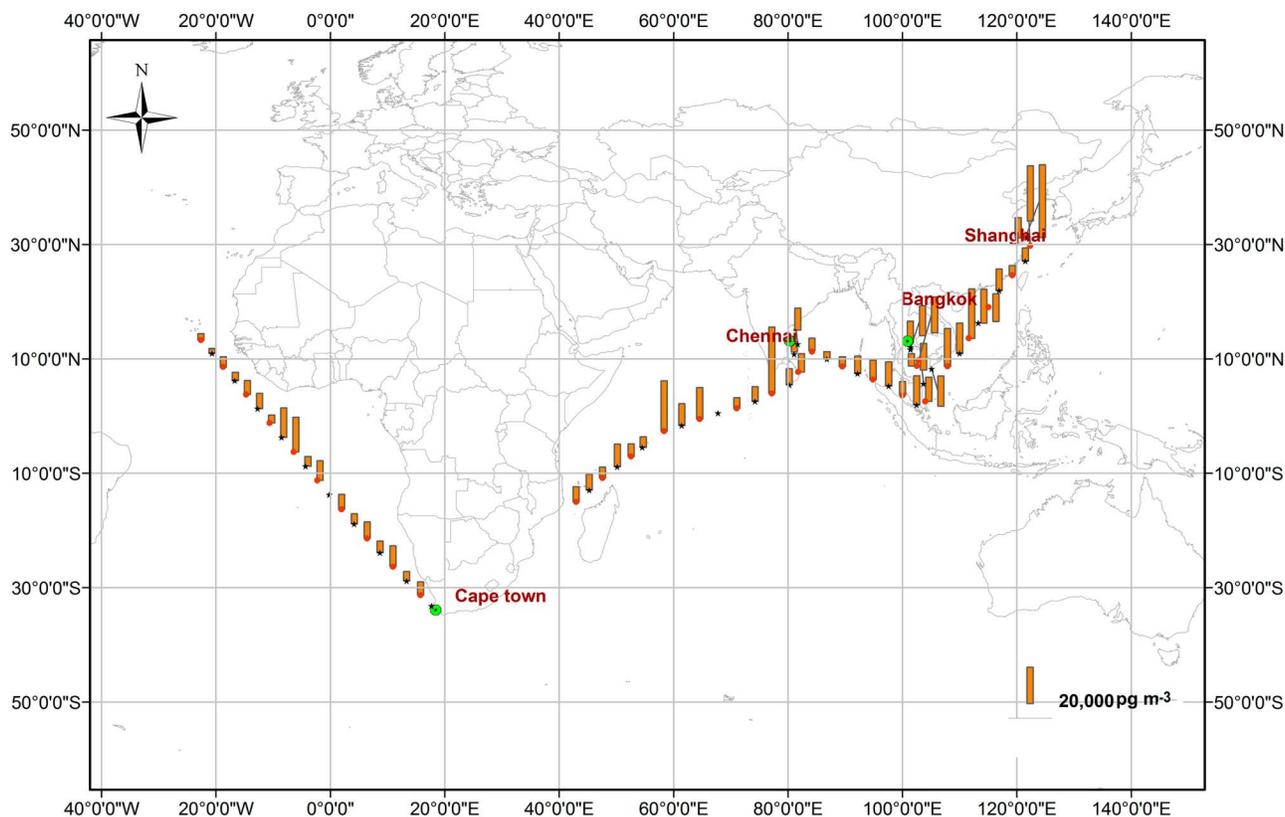


Figure 2. Spatial distribution of Phe concentrations in the gaseous phase.

~800 km away from the coast of China [Primbs *et al.*, 2007]. The relatively high abundance of Flu over the East and South China Seas detected in this study is different from the compound patterns in those above mentioned coastal areas, which have intensive anthropogenic activities, but is similar to the measurements at a remote continental site in China [Cheng *et al.*, 2006]. Anthropogenic activities could influence PAH congener profiles in local areas, so the observation at remote sites could reflect regional background levels in China. Our observation suggests that the regional atmosphere in China is enriched with Flu.

[16] Over the Bay of Bengal and the Andaman Sea, levels of heavy PAHs in the particulate phase (molecular weight ≥ 252) were elevated. Unlike the profiles over the East and South China Seas, the relative proportion of Flu of the total gaseous PAH decreased to $\sim 11\%$, while the major contributors to total PAHs in the particulate phase were still Phe ($\sim 17\%$), Flu ($\sim 17\%$), Chr ($\sim 16\%$) and Pyr ($\sim 15\%$). Previous reports of the atmospheric PAHs around the Bay of Bengal and Andaman Sea are limited. Omar *et al.* [2006] reported the average concentration of Σ_{13} PAHs in the particulate phase was 3.10 ng m^{-3} at the University of Malaya, Kuala Lumpur. Mohanraj *et al.* [2010] found that the annual average value of Σ_{11} PAHs in fine particulates ($\text{PM}_{2.5}$) was 517 ng m^{-3} at four sites in Chennai. These results are several orders of magnitude above the atmospheric levels in the Bay of Bengal and the Andaman Sea. However, the pattern

was consistent with that of the atmospheric aerosols of Kuala Lumpur [Omar *et al.*, 2006] when passing by Kuala Lumpur (31N- Jan, collected at the nighttime of January 31st), although the PAH concentrations were lower. This resembled the earlier profiles in Chennai [Mohanraj *et al.*, 2010] and Kolkata [Karar and Gupta, 2006]. It was possibly due to dispersion of continental point-sources around those urban areas.

[17] In the Indian Ocean, low particulate PAH concentrations were commonly detected. Less than 50% of the samples collected in this region contained Acey, Ace, Flu, Phe, Ant, BaA, BaP, Ind, DahA or BghiP. The air mass back trajectories suggested those samples were relatively far away from influences of continental sources. However, the concentrations were not significantly lower than other samples collected during the voyage, even though the average concentrations were the lowest among the four regions. The pattern of gaseous PAHs was similar to those over the Bay of Bengal, the Andaman Sea and the Atlantic Ocean. The major contributing PAHs in the particulate phase were the same as those over the Bay of Bengal and the Andaman Sea but with a higher proportion of Phe ($\sim 20\%$). Compared with the values over the Indian Ocean in 1999 [Crimmins *et al.*, 2004], the high-molecular-weight PAHs were at similar levels, but low-molecular-weight compounds increased in the particulate phase over the Indian Ocean in this study.

[18] The PAH concentrations over the Atlantic Ocean were not the highest in this study with the exception one particulate sample. The congener profile in the gaseous phase was similar to that over the Bay of Bengal and the Andaman Sea and the Indian Ocean. In contrast, the PAHs

¹Auxiliary materials are available with the HTML. doi:10.1029/2011JD016585.

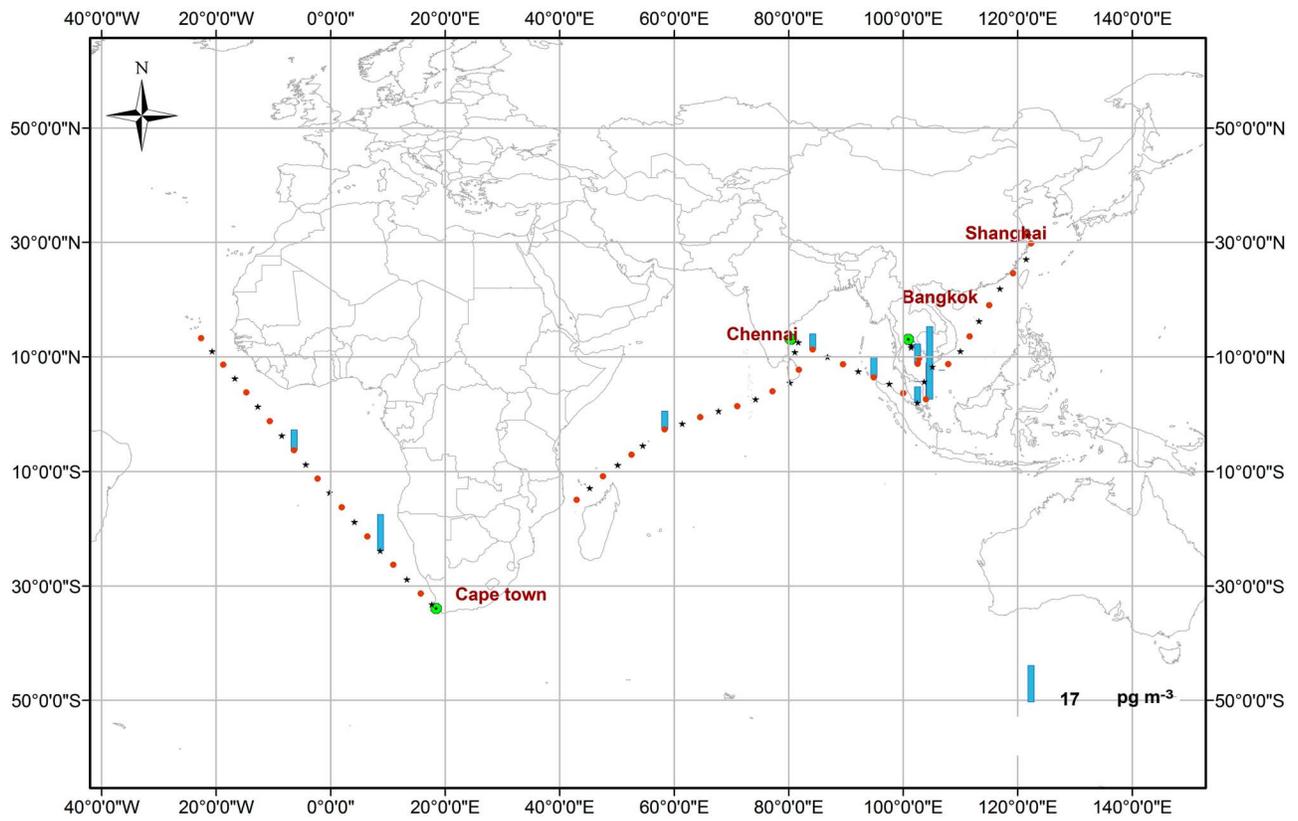


Figure 3. Spatial distribution of Ace concentrations in the particulate phase.

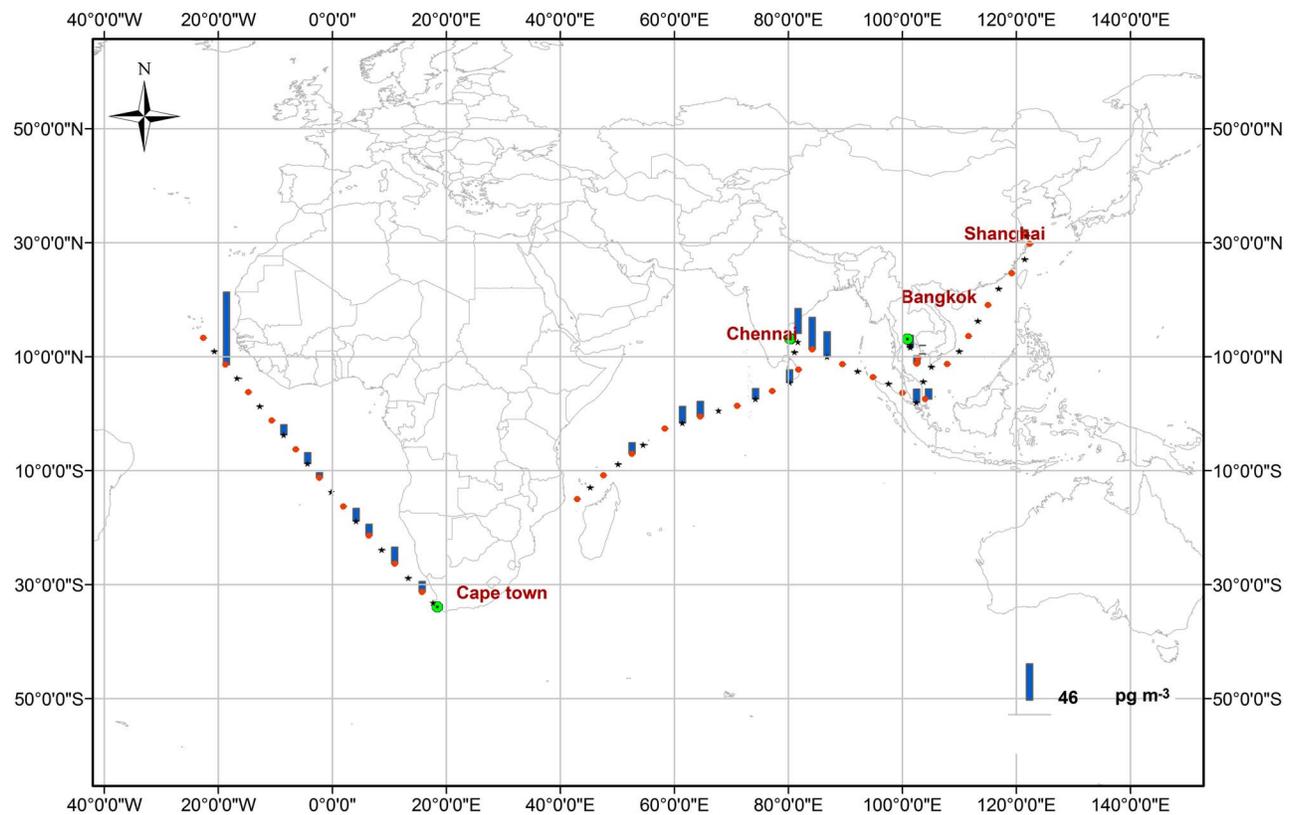


Figure 4. Spatial distribution of BaA concentrations in the particulate phase.

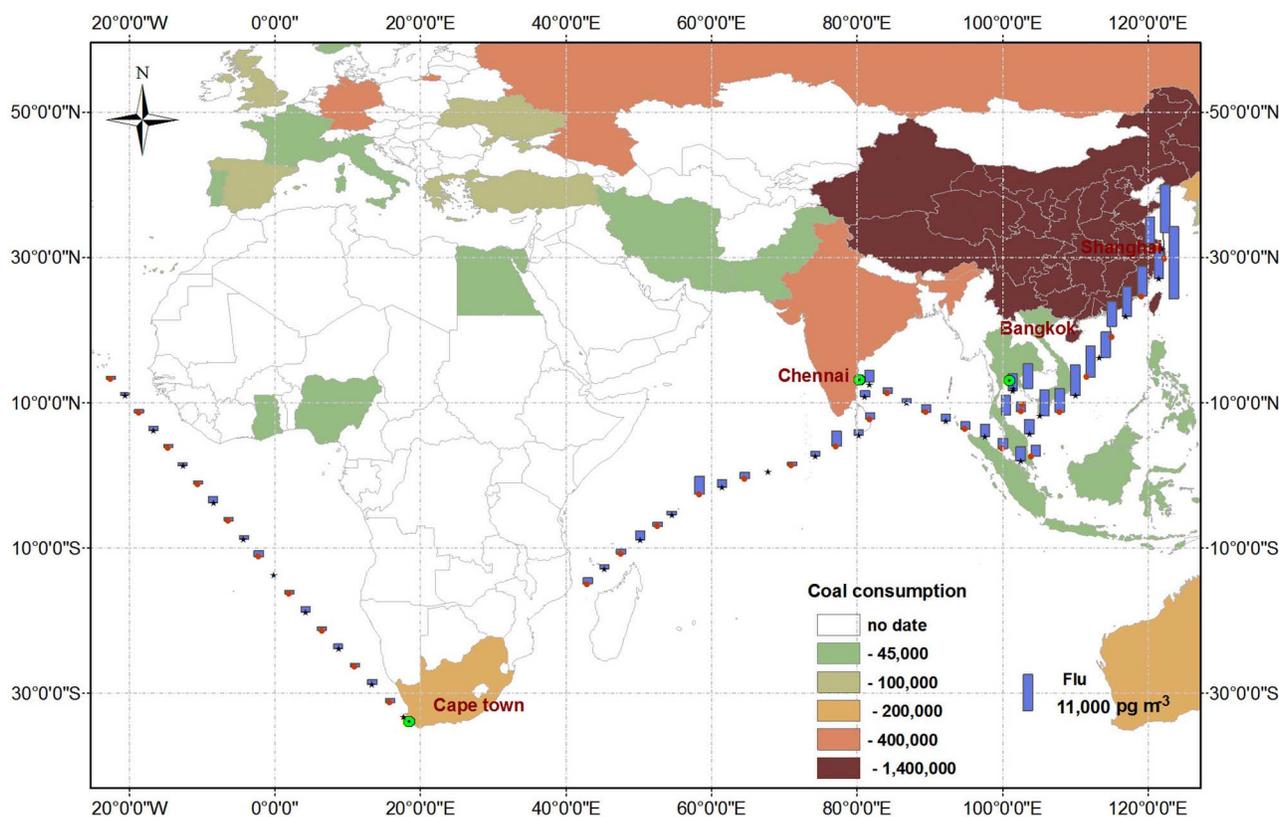


Figure 5. Spatial distribution of Flu and the coal consumption by selected countries.

in the particulate phase were characterized by a high proportion of Pyr ($\sim 23\%$), which was different from the congener pattern in filter samples over the other oceans in this study. Compared with reports in the past, the concentrations were about an order of magnitude greater than the levels observed from January to March, 1999 [Crimmins *et al.*, 2004], January to February, 2001 [Jaward *et al.*, 2004], and October to November, 2005 [Nizzetto *et al.*, 2008], but consistent with the reported levels obtained from May to June, 2003 [Del Vento and Dachs, 2007]. However, Del Vento and Dachs [2007] took samples in the northeast tropical and subtropical Atlantic Ocean, where elevated levels of POPs (Persistent Organic Pollutants) were found, while most of the samples in this study were taken over the Southern Hemisphere Atlantic where PAH concentrations are low [Jaward *et al.*, 2004]. Therefore, as Jaward *et al.* [2004] emphasized, PAHs emitted from Africa may be crucial to the global inventory. The elevated PAH concentrations in this study suggest an increase of PAH emissions in the areas adjacent to Africa and highlight the sources in Africa. In addition, the congener patterns in the particulate samples were inconsistent with those of the northeastern tropical and subtropical Atlantic Ocean [Del Vento and Dachs, 2007], possibly implying input of other sources different from previous studies.

3.2. Spatial Distributions

[19] In general, PAH concentrations were elevated in harbors, close to Asia, and to the equator (Figures S3 and S4). As Crimmins *et al.* [2004] and Jaward *et al.* [2004] noted, the concentrations of some PAHs, such as Acy, Flu,

Phe, BbF, were significantly higher in the Northern Hemisphere than in the Southern Hemisphere in this study (Detail can be found in Figures 2–5 and Figures S5–S11).

[20] The gas-phase total PAH concentrations were elevated on the approach to China and the Indian subcontinent, especially close to harbors such as Shanghai and Bangkok (Figure S3). As backward trajectories illustrates, the continental influence on the samples from the Indian and Atlantic Oceans was generally weak before the ship's arrival into port. Therefore, the drop in PAH concentrations, especially for aerosol samples, were seen after leaving the Indian subcontinent. Elevated values were also observed near the equator over the Indian and Atlantic Oceans. This is likely because of the downward movement of air masses containing pollutants near the Intertropical Convergence Zone (ITCZ) [Crimmins *et al.*, 2004] or other processes such as surface evaporation or biological emission. In terms of individual compounds, the spatial pattern was the same as that of the total PAHs in the gas phase. The enhancement of Ace and Acy near the ITCZ was less clear than other gaseous PAHs, possibly due to the faster degradation rate of the two compounds.

[21] Total particle-bound PAHs increased when the ship was close to continental sources, especially to the Indian subcontinent and Guinea in West Africa (Figure S4). The increased levels close to West Africa were found for all the particle-bound PAHs in this study, consistent with previous studies along the Atlantic East Coast region (gas plus particulate) [Jaward *et al.*, 2004; Nizzetto *et al.*, 2008]. With regard to other marine air samples, individual PAHs exhibited diverse spatial patterns. Low-molecular-weight PAHs

such as Ace, Acy, Flu, Ant and Phe were elevated close to Southeast Asia and near the ITCZ (Figures 3 and S8). High concentrations of Flu, Pyr and BaA occurred over the Bay of Bengal and ITCZ (Figures 4 and S9). The other PAHs with high molecular weights over the Bay of Bengal were several-fold greater than the average levels (Figures S10–S11). The spatial variations of individual PAHs could reflect the differences in emission factors and source-strength of adjacent areas as well as the environmental fate of PAH congeners [Lang *et al.*, 2008].

3.3. Potential Source Areas

[22] The PAH concentrations are generally influenced by long-range transport from continental sources, biogenic emission from water bodies and other physicochemical processes. Over some oceanic areas, such as the Indian Ocean, atmospheric transport and biogenic emission may lead to the high LMW PAHs in the particulate phase. In contrast, continental sources contributed more to those samples collected relatively close to the continents.

[23] China and India were identified as important sources of PAHs, contributing 30% and 23.6% of the total global emissions, respectively [Zhang and Tao, 2009]. Africa was another source region which contributed 18.8% of the global total [Zhang and Tao, 2009]. In this study, high PAH concentrations occurred in the vicinity of all three areas. The air concentrations over the adjacent oceans generally increased in the following order: Africa < India < China. This cruise data broadly supports that previous global emission inventories that the three areas could be sources of significance.

3.3.1. PAH Emissions From China and India

[24] It is difficult to compare the relative strength of Chinese and Indian sources in particulate samples due to the different distances from the ship and potential sources as well as absence of filter samples from January 16th to 24th. In the case of PAHs in the gas phase, the concentrations over the East and South China Seas were generally higher than those close to the Indian subcontinent (Figures 2 and S3). In particular, the high proportion of Flu (~25%) along the East and South China Seas (Figure 5) merits some attention. After moving away from China, the average concentration of Flu decreased from 8,100 to 1,800 pg m^{-3} and the relative abundance decreased to ~10% of the total PAHs. The atmospheric lifetime of Flu is relatively short [Brubaker and Hites, 1998], and it thus tends to be influenced by adjacent continental sources, namely, mainland China. Flu has been considered as a marker of the coke industry or coal combustion emission [Ma *et al.*, 2010; Simcik *et al.*, 1999]. These two factors ranked second and third among PAH emission sources in China, but accounted for <2% in India [Zhang and Tao, 2009]. As Figure 5 illustrates, China has the highest total coal consumption in the world. In addition, when the ship crossed the East China Sea, the air masses mainly originated from northeast China, where coal and coke related combustion is intensive. Consequently, a high proportion of Flu might be due to intensive coal and coke combustion in China.

[25] India is another potential source region for PAHs during this voyage. The reported ambient atmospheric concentration of PAHs in Indian cities range from 100 to 1000 ng m^{-3} , which is among the highest levels globally

[Mohanraj *et al.*, 2010; Sharma *et al.*, 2007]. Similarly, the highest total particulate PAH concentrations in this study were recorded at the harbor in Chennai, where heavy PAHs (molecular weight ≥ 252) contributed as much as 72% (SI). In this study, the resemblance of congener profiles between our samples and previous report in cities nearby also indicates that the influences of Indian sources.

3.3.2. Wildfire Emission

[26] Globally, wildfires in South America, South and Central Africa and Southeast Asia contribute ~17.0% of the total global PAH emissions [Zhang and Tao, 2009]. Figure 6 is the global fire map during this voyage (<http://firefly.geog.umd.edu/firemap/>) that shows that intensive biomass burning was taking place in Africa and Southeast Asia during the time of the voyage. Some events could have been captured as the ship passed through those regions.

[27] Particulate-associated PAH levels showed a marked rise on the approach to Guinea (Figures 4 and S4). Similar spatial trends of total PAHs in air (including gas and particulate phases) have been reported elsewhere [Jaward *et al.*, 2004; Nizzetto *et al.*, 2008]. Nizzetto *et al.* [2008] indicated that oil extraction in Senegal, ship exhaust, biomass burning and microbial activity in the tropics could contribute to the elevated PAHs close to West Africa. The total PAHs of 13D-Mar in the particulate phase was 2600 pg m^{-3} , which was the third-highest aerosol sample in this study. (The first and second highest concentrations of particle-bound PAHs were found at the port of Chennai.) The relative abundance of high molecular weight congeners was elevated in this sample. However, total gaseous PAHs of 13D-Mar (8700 pg m^{-3}) were lower than the average level (13000 pg m^{-3}) over the Atlantic Ocean. This result is different from the observed characteristics of PAH emission from oil extraction or microbial activity along West Africa from October to November, 2005 [Nizzetto *et al.*, 2008]. Biomass-burning plumes from Africa have resulted in higher values of other variables, such as elemental carbon, inorganic oxidized material and aerosol optical properties, on other cruises [Quinn and Bates, 2005]. During the voyage of the Scholar Ship a combined a Saharan dust incursion and smoke plume were observed on March 13th. The observed weather on the ship was cloudy and dusty accordingly. This is well represented on the NAAPS Total Optical Depth (Figure S12) and the samples collected on board the Scholar Ship on that day. These are marked by high PM_{10} and PM_1 levels of 120 and 30 $\mu\text{g m}^{-3}$ in contrast to ca 30 and 10 $\mu\text{g m}^{-3}$ respectively in the preceding days [Pérez *et al.*, 2010], with high levels of carbon, crustal major elements and trace metals [Moreno *et al.*, 2010]. The concentrations decreased later in the day [Pérez *et al.*, 2010]. Correspondingly, the aerosol-phase PAH concentrations increased significantly during the daytime on March 13th (Figure S4). Therefore, the elevation in particle-bound PAHs in 13D-Mar could be influenced by biomass burning and African dust intrusion rather than other factors such as oil evaporation.

[28] Similarly, the presence of biomass smoke might explain the rise, to a lesser degree, in high-molecular-weight PAHs of the particulate phase of 12N-Feb. Figure S13 depicts the NAAPS (Navy Aerosol Analysis and Prediction System) surface concentrations of dust and smoke in Southeast Asia at 18:00 on February 12th. While passing Sri

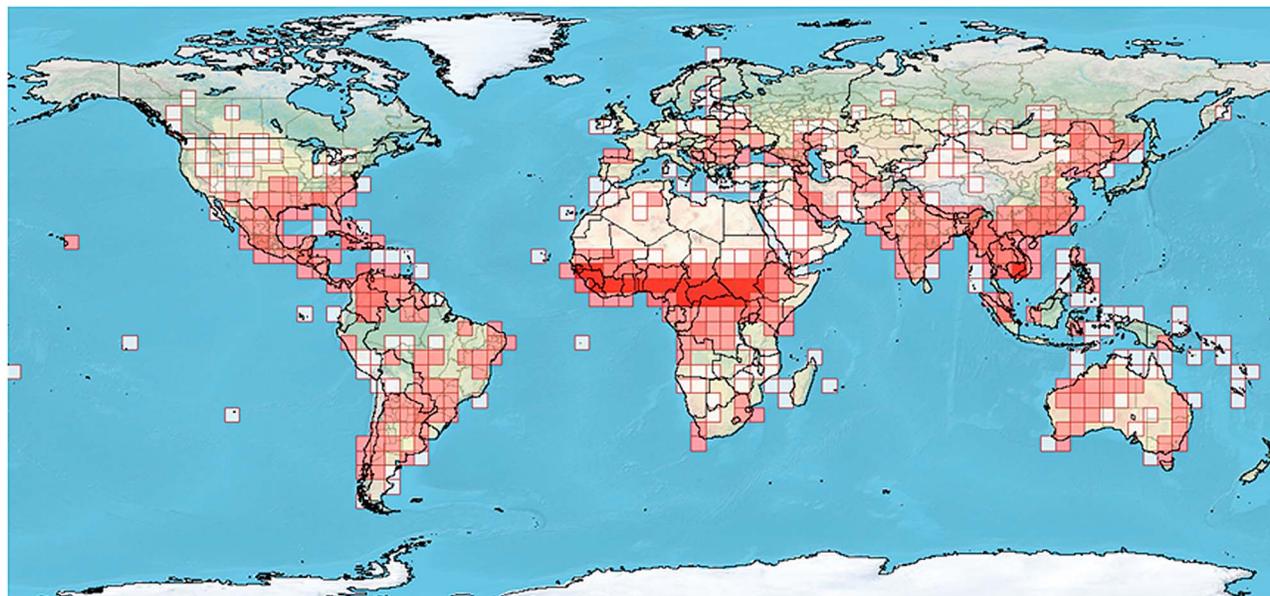


Figure 6. Fire map from January 16th to March 14th, 2008. (FIRMS Web Fire Mapper, <http://firefly.geog.umd.edu/firemap/>).

Lanka, the ship encountered a smoke plume originating from Southeast Asia. However, the total particulate PAH concentration was not as high as 13D-Mar because the ship was ~2000 km away from the emission center.

4. Conclusions

[29] This study reported the atmospheric concentrations of PAHs in gas and particulate phases over the marginal seas of Asia, the tropical and subtropical Indian Ocean and the Southern Hemisphere Atlantic Ocean. The concentration levels were lower than those of some adjacent land areas with intensive anthropogenic activities, but were of the same magnitude or higher than marine background concentrations. On the approach to a continent, the PAH congener profiles resemble those of the nearby terrestrial areas, suggesting the impact of land-based emissions. Spatially, high concentrations occurred close to areas with high estimated PAH emissions [Zhang and Tao, 2009]. Compared with oceanic atmospheric studies in the past, PAH concentrations were increased over the Atlantic Ocean and low-molecular-weight PAH concentrations in the particulate phase were increased over the Indian Ocean. Although the different voyage route and seasonal variations prevented us from giving a precise conclusion on long-term trends in oceanic PAHs in the atmosphere, the elevated PAH concentrations still indicate high emissions in some areas, especially Africa. Emission from China and India also exert significant influence on the atmosphere over adjacent seas. In contrast to the many reports associating urban PAHs emitted from industries and/or intense road traffic to environmental and human health impacts, this study also indicates that biomass burning in Africa and Southeast Asia could be important to the marine atmosphere on PAHs. This study may serve as a reference for further investigations on the impact of PAHs emitted by such sources on remote

oceans to facilitate a more detailed diagnosis of PAHs sources of global significance.

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