Key Points:
- PAHs in aerosols were studied over oceans from 8 January to 7 August 2007
- Wildfire emissions and petroleum combustion affected the South Indian Ocean
- PAHs emitted from China were associated with biomass/coal burning

The distribution and origin of PAHs over the Asian marginal seas, the Indian, and the Pacific Oceans: Implications for outflows from Asia and Africa

Junwen Liu[1,2], Yue Xu[1], Jun Li[1], Di Liu[1], Chongguo Tian[3], Chakra Chaemfa[1], and Gan Zhang[1]

[1]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China, [2]University of Chinese Academy of Sciences, Beijing, China, [3]Key Laboratory of Coastal Zone Environmental Processes and Ecological Remediation and Shandong Provincial Key Laboratory of Coastal Zone Environmental Processes, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, China

Abstract Aerosol samples were collected aboard the R/V *Dayang Yihao* from 8 January to 7 August 2007 to investigate the geographical distribution of polycyclic aromatic hydrocarbons (PAHs) over oceans and to assess their continental origins. The highest concentrations were found over the marginal seas in Asia, especially the East and South China Seas, indicating that China is a top source of emissions into the marine atmosphere in the areas monitored on this cruise. PAH concentrations over the west oceanic region in the South Indian Ocean were noticeably higher than in other areas of the Indian Ocean, most likely because air masses from Africa, the Arabian Sea, and the Bay of Bengal exert a negative impact on those regions through long-range atmospheric transport. The PAH isomer ratio values varied over the oceans that were impacted by continental sources but remained relatively uniform over most of the remote oceans. Using diagnostic ratio analysis, we found PAHs emitted from China were mainly associated with biomass/coal burning. The measurements of levoglucosan were consistent with the results mentioned above. The western part of the South Indian Ocean atmosphere was likely affected by wildfire emissions from Africa, while the northern part was by petroleum combustion, biofuel, and wildfire burning, because the winter monsoon most likely carries aerosol from the Arabian Peninsula and India across the equator. Using the monthly images of fire activity and aerosol optical depth, it can be confirmed biomass burning from Africa can significantly influence the aerosol over the Indian Ocean.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs), a group of organic compounds that have adverse effects on human health and the ecosystem, are predominantly derived from the incomplete combustion of carbonaceous materials, including fossil fuel and biomass. In 2004, it was estimated that the global total of PAH emissions was approximately 520 Gg, of which biomass burning made the largest contribution, approximately 73.7% of the global PAH inventory, followed by the consumption product (6.9%), traffic oil (4.8%), domestic coal (3.7%), and coke production (3.6%) [*Zhang and Tao*, 2009]. However, it should be noted that the relative contribution of atmospheric PAH emission sources differ regionally and seasonally due to differences in energy policies, vegetation, and degrees of industrialization and urbanization. For example, the proportions of PAHs generated from biomass burning in India, China, and the U.S. were 95.7%, 68.4%, and 12.4%, respectively [*Zhang and Tao*, 2009]. In China, the primary emission sources of atmospheric PAHs over the southern and northern regions were significantly different during the winter season: PAHs in North China are linked to coal and biofuel burning during this season [*Liu et al.*, 2007], while vehicle exhaust was the main source of atmospheric PAHs in South China. As markers of incomplete combustion, diagnostic ratios of PAHs are frequently used to identify emission sources. Through an analysis of PAH isomer ratios in the particulate phase, *Ding et al.* [2007] found that atmospheric aerosols collected in the North Pacific Ocean and Arctic regions predominantly came from biomass/coal burning.

The atmosphere over the open oceans can serve as the global atmospheric background level of PAHs due to a limitation of emission sources in the oceans. Generally, the transport of PAHs from the land to the atmosphere is considered the most important pathway controlling the levels of PAHs over the oceans [*Crimmins et al.*, 2004; *Ding et al.*, 2007; *Xu et al.*, 2012], and it is greater than a volatilization of PAHs from the
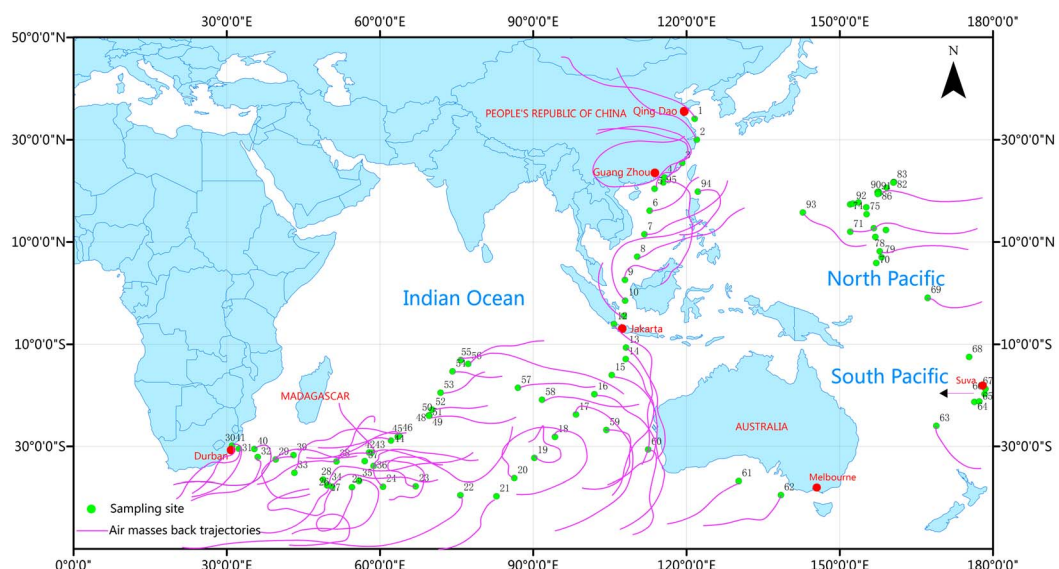
Figure 1. The sampling sites (green points noted by numbers), ship routes (in order from 1 to 95), and the air mass back trajectories. The arrow in the South Pacific Ocean denotes that the air masses were derived from the east for sample No. 64 to No. 68.

ocean itself [*Nizzetto et al.*, 2008]. Measurements of atmospheric PAH concentrations over the oceans not only provide a better understanding of the PAH levels in the global atmosphere, but provide information on how the continents impact PAH levels.

Currently, many studies on atmospheric PAHs over the oceans primarily focus on an individual oceanic region or single hemisphere. Although it is necessary and interesting to understand the global distribution of PAHs, studies on a global scale are still very limited. Studies examining global PAHs distribution would provide knowledge on the origins of the PAHs from different oceanic regions in both hemispheres. A research vessel (R/V) named "Dayang Yihao" was fitted out and cruised to collect atmospheric samples from Qingdao to Djakarta, Durban, Fiji Island, Ponape Island, and Guishan anchorage (Figure 1) during January to August 2007. The results of these samples will most likely provide a better understanding of the oceanic distribution characteristics of PAHs in aerosols over the marginal seas in Asia and the Indian and Pacific Oceans. Due to the long sampling period (January to August) and vast spatial sampling area (Asian marginal seas, the Indian Ocean, and the Pacific Ocean), the samples were not collected simultaneously. In addition, the aerosol characteristics from different areas were not only affected by the emission sources, but by atmospheric circulation, exotic sources, and seasonal variations. As a consequence, an overall trend of the global particulate PAHs was explored and evaluated. In this study, the PAHs in collected aerosol samples were determined to (1) map the PAH distribution in aerosols from the marine boundary layer and (2) identify the origin of PAHs using the combination of diagnostic ratios of PAHs, organic source tracer (levoglucosan), and remote sensing data, such as fire activity maps and aerosol optical depth (AOD) maps.

2. Materials and Methods

2.1. Sampling

During the cruise (from 8 January to 7 August 2007) a total of 95 total suspended particle samples were collected onboard the R/V *Dayang Yihao*. Air volumes of ~400–1200 m^3 were drawn through a quartz microfiber filter (QFF) (Grade GF/A, 20.3 × 25.4 cm, Whatman, Maidstone, England) using a high-volume sampler (Anderson type) at a flow rate of 300 L/min. The air sampler was placed at the front of the ship to avoid potential contamination from the ship exhaust. Prior to sampling, the QFFs were baked at 450°C for 12 h to remove any organic contaminants. After sampling, the QFFs were wrapped in prebaked aluminum foil, sealed with two layers of polyethylene bags, and stored at −20°C until analysis. Six clean QFFs were exposed to the air for a few seconds during the cruise and then stored in the freezer for use as field blank samples.

2.2. PAH Analysis

The filter samples were spiked with 1000 ng of deuterated PAHs. The filters were then Soxhlet-extracted using dichloromethane for 48 h. The extract was concentrated, underwent solvent-exchange, and then purified on an alumina/silica column. The purified fraction was eluted with a 15 ml mixture of dichloromethane and hexane (1:1 by volume) and was blown down under a gentle stream of nitrogen to a final volume of 25 μL. Prior to the analysis, 1000 ng of hexamethylbenzene (Aldrich Chemical, Gillingham, Dorset, USA) in dodecane was added as an internal standard. The PAHs were analyzed by 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 (Mass Selective Detector (MSD), Agilent 5975). The samples (1 μL) were injected under a splitless mode with a 10 min solvent delay time. High-purity helium was used as a carrier gas with a column flow rate of 1.83 mL/min. The temperature of the injector and transfer lines were 290°C and 300°C, respectively. The initial oven temperature was set at 60°C for 1 min and was raised to 290°C at a rate of 3°C/min and held for 20 min. Fifteen PAHs were quantified in this study: acenapthene (Ace), acenapthylene(Acy), fluorene (Flu), phenanthrene (Phe), anthracene (Ant), fluoranthene (Flua), 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). It should be noted that the gas adsorption artifact may overestimate the low molecular weight PAHs [*Mader and Pankow*, 2001], but their concentrations will be reported in the following discussion because other relevant studies [*Ding et al.*, 2007; *He and Balasubramanian*, 2009; *Xu et al.*, 2012] for comparison reported them.

2.3. Levoglucosan Analysis

The analysis of levoglucosan was conducted by a gas chromatography(GC)-MSD (Agilent 7890 GC and Agilent 5975 MS) with a capillary column (DB-5MS, 30 m, 0.25 mm, 0.25 μm) and is fully described by our previous study [*Liu et al.*, 2013]. Briefly, a section of the sample was put into a 25 mL Pyrex glass flask with a Teflon-lined stopper. Before extraction, 500 ng of the internal recovery standard (methyl-β-L-xylanopyranoside, m-XP) was added to the filter. Then the filter part was extracted with 10 mL methanol 10 min for 3 times using ultrasonic agitation. The volume of the combined extract was reduced to about 1 mL with a rotary evaporator and then filtered through a Teflon syringe filter (0.45 μm). Afterward, the filtrate was dried completely by a gentile nitrogen stream. Finally, a mixture of 40 μL containing N,O-Bis(trimethylsilyl)trifluoroacetamide (1% trimethylsilyl chloride) and pyridine (2:1 vol/vol) is added, and the reaction was conducted for 1 h at 70°C. Then 1 μL of the solution obtained is then immediately analyzed by GC-MSD. The recovery of spiked matrix is between 80 and 125% in this study.

2.4. Quality Control and Quality Assurance

A set of PAH standards was injected into the instrument daily to check its stability, and the deviation of the instrument was less than ± 10%. The deuterated PAH recoveries were 75% ± 12%, 90% ± 11%, 88% ± 15%, and 85% ± 10% for acenapthene-D10, phenanthrene-D10, chrysene-D12 and perylene-D12, respectively. Six field blanks were taken during the sampling period. The method detection limits (MDLs) were the average values of the blanks, plus or minus 3 times the standard deviations of the blanks. Three times of the instrumental detection limit (IDL) were used for calculating the MDLs. The IDL values were calculated using the lowest standards and extrapolating to the corresponding amount of analyte that generates a signal-to-noise ratio of 3:1. All target compounds detected in the samples and lab blanks were under the IDLs. The data reported in this study were not corrected by the recoveries.

The ship exhaust can potentially contaminate the air during sampling when the research involves combustion-derived compounds. In this study, the air sampler was placed at the uppermost front deck to minimize any contamination from discharged smoke from the ship's stack. *Cooper* [2001, 2003] and *Cooper et al.* [1996] found that low molecular PAHs were significantly dominant in the exhaust emitted from the ship, while the high molecular compounds (BbF, BkF, BaP, Ind, and BghiP) were usually undetectable. A similar phenomenon occurred in sediments polluted by ship activities [*Neşer et al.*, 2012]. The PAH profiles from those studies were quite different from the results found in this study. Moreover, as discussed later in detail, the PAH spatial distributions were similar to previous studies. Therefore, it is likely that the PAH measurements in this study were not affected by the ship's exhaust.

Table 1. Summary of the Concentrations of Particulate PAHs (pg/m³) and Levoglucosan (ng/m³) Measured in This Study

	MDL[a]	Asian Marginal Seas (n = 13)				South Indian Ocean (n = 50)				South Pacific Ocean (n = 7)				North Pacific Ocean (n = 25)			
		Arithmetic Mean[b]	Geometric Mean[b]	Median[b]	Range[b]	Arithmetic Mean	Geometric Mean	Median	Range	Arithmetic Mean	Geometric Mean	Median	Range	Arithmetic Mean	Geometric Mean	Median	Range
Acey	5.8	19	17	17	2.9–39	16	11	11.6	2.9–73	6.0	5.1	6.0	2.90–13	9.5	6.8	6.5	2.90–24
Ace	5.4	6.7	6.3	6.7	2.7–11	6.7	5.3	5.8	2.7–33	3.1	3.0	2.7	2.70–5.9	5.9	4.9	2.7	2.7–10
Flu	12	153	144	148	81–277	56	34	40	6.0–193	28	26	25	15–53	44	31	41	6–90
Phe	38	212	165	119	75–679	180	103	127	19–531	84	78	65	50–169	222	200	199	78–528
Ant	2.8	14	6.3	5.6	1.4–55	22	9.6	9.8	1.4–134	9.7	8.1	7.0	3.70–25	9.2	7.7	7.6	1.4–31
Flua	8	185	163	194	60–327	89	58	57	4.0–241	41	37	41	20–63	101	92	97	38–181
Pyr	12	145	124	94	59–310	58	38	50	6.0–197	28	22	25	6.00–55	81	68	72	22–261
BaA	4.6	49	31	41	2.3–116	14	8.5	9	2.3–54	12	6.3	7.7	2.3–53	5.3	4.3	2.3	2.3–11
Chr	2.8	152	129	127	38–378	35	26	26	5.7–144	70	21	14	6.1–408	28	26	28	10–58
BbF	1.2	399	203	164	5.3–976	43	17	12	2.2–338	55	17	10	5.0–316	46	33	39	3.0–101
BkF	0.82	92	46	65	1.2–236	12	4	3	0.41–72	11	2.6	1.8	0.41–69	10	7.2	8.4	0.41–35
BaP	0.56	131	45	29	9.5–531	13	3.1	2.2	0.28–123	9.5	1.6	0.88	0.28–60	11	3.4	2.3	0.28–106
Ind	0.76	603	346	374	44–1826	49	11	9	0.38–231	50	8.3	5.4	1.5–321	50	21	43	0.38–151
DahA	0.40	86	50	41	10–287	9.4	2.3	1.8	0.20–57	6.3	1.1	0.77	0.20–40	5.9	3.1	4.9	0.20–20
BghiP	1.2	532	342	314	50–1541	32	9	6.3	0.60–141	43	6.7	3.9	1.3–276	41	17	36	0.60–125
Total	104	2449	1531	1739	876–6974	636	341	370	66–1870	459	243	216	130–1799	670	525	589	194–1183
levoglucosan		40.8	19.8	17.8	3.00–149	1.72	0.78	0.72	0.10–22.4	4.47	0.53	0.38	0.11–29.5	0.30	0.19	0.17	0.01–0.99

[a]MDL, method detection limit.
[b]Half of the MDLs were used to calculate the arithmetic mean, geometric mean, median, and range when the measured values were less than M.

2.5. Air Mass Back Trajectory Analysis

During this sampling voyage, 5 day air mass back trajectories were derived in 6 h intervals using the Hybrid Single Particle Lagrangian Integrated Trajectory Model (4.8) developed by the National Oceanic and Atmospheric Administration Air Resource Laboratory (http://ready.arl.noaa.gov/HYSPLIT.php). Each back trajectory was determined at 100 m, 500 m, and 1000 m above the sea level.

3. Results and Discussions

3.1. Spatial Distribution

During the expedition, the total of particulate-bound PAHs (ΣPAHs) ranged from 66 to 6900 pg/m³ (Table 1). The PAH levels measured in this study were comparable to other marine atmospheric studies. For example, *Ding et al.* [2007] reported that the totals for the 15 particulate PAHs in the marine air of Far East Asia area to the Arctic region between July and September 2003 ranged from 23 to 4380 pg/m³. Figure 2 shows the regional and global variability of ΣPAH concentrations over the oceans crossed during the study period. As expected, the concentrations measured over oceans were lower than those detected in the adjacent coastal cities, such as Qingdao (2.2–240.5 ng/m³) [*Guo et al.*, 2003a], Guangzhou (4.7–98.7 ng/m³) [*Li et al.*, 2006], Djakarta (13.3–177 ng/m³) [*Panther et al.*, 1999], and Melbourne (1.68–21.53 ng/m³) [*Panther et al.*, 1999]. Generally, ΣPAH concentrations over the coastal seas were approximately 5 to 10 times higher than those found in the air far from the landmass, indicating that the land significantly impacts the atmospheric PAHs over the oceans.

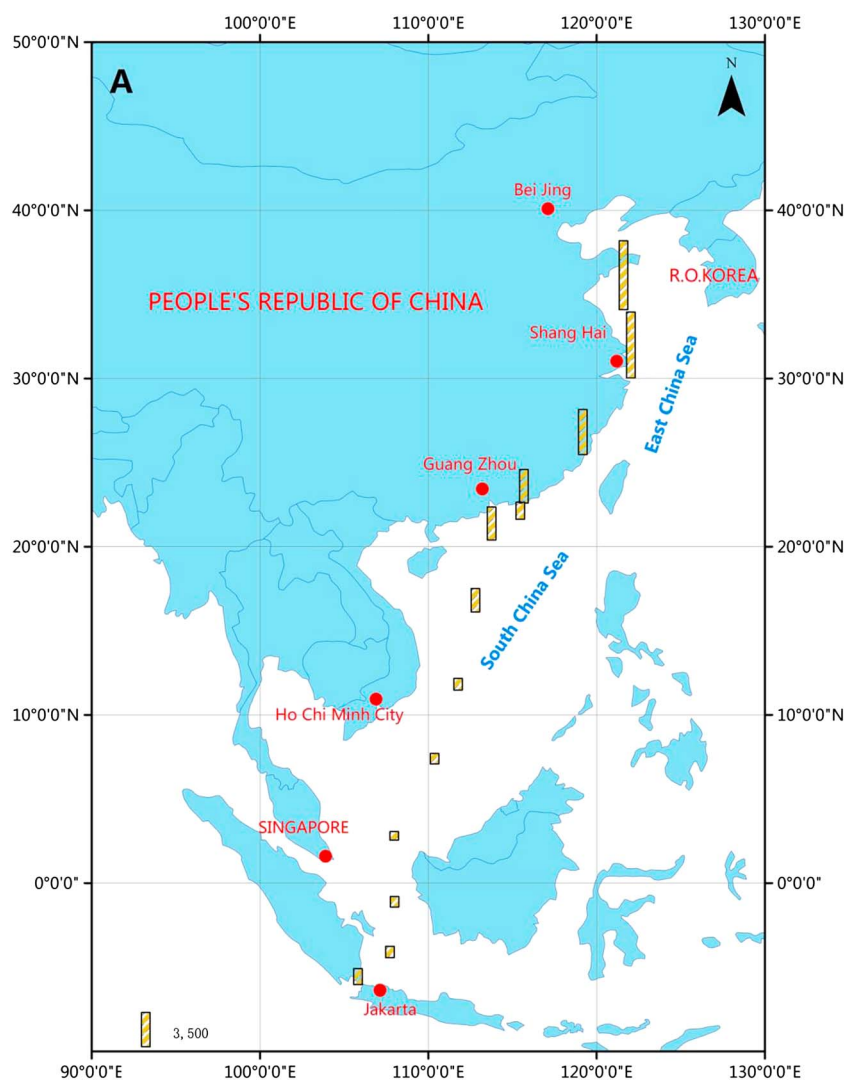The highest ΣPAH concentrations were observed over the Asian

Figure 2. Spatial distribution of total particulate PAHs in this study (pg/m^3). (a) Asian marginal seas, (b) South Indian Ocean, and (c) Pacific Ocean.

marginal seas (Table 1), especially in samples collected close to the Chinese mainland (Figure 2a, samples No. 1 to No. 5). The high level of PAHs over China's marginal seas was observed because China is the greatest contributor of PAHs to the global atmospheric emission inventory [*Zhang and Tao*, 2009] with 70% of PAHs produced by the Chinese mainland remaining in the offshore environment of the marginal seas [*Lang et al.*, 2008]. These contaminants from the continent can exert a negative influence on the marine atmosphere. In addition, less dilution of PAHs would happen during the atmospheric transportation due to the distance from sampling sites in Chinese marginal seas to land were much close to lands compared with other sampling sites (Figure 1). During the winter sampling period, the Chinese mainland atmosphere was influenced by the northern air masses (Figure 1) and coal and biofuel burning were very intensive in North China [*Liu et al.*, 2007]. In contrast, during the summer, the air masses were derived from the open ocean, influencing the atmosphere over the Chinese marginal seas (sample No. 95, collected on 5 to 7 August) and resulting in a dramatic decrease in PAH concentrations (Figures 1 and 2a).

Figure 2b displays the distribution patterns of ΣPAH concentrations over the southwest Indian Ocean, which ranged from 66 to 1870 pg/m^3 with a geometric mean of 341 pg/m^3. The distribution of PAH concentrations in this region was nonuniform. PAH levels over the west oceanic region were higher than those over the east and high-latitude maritime areas (>30°S). Lower PAH concentrations in the South Indian Ocean were observed over the high-latitude oceanic region, mainly because the air masses collected came from the
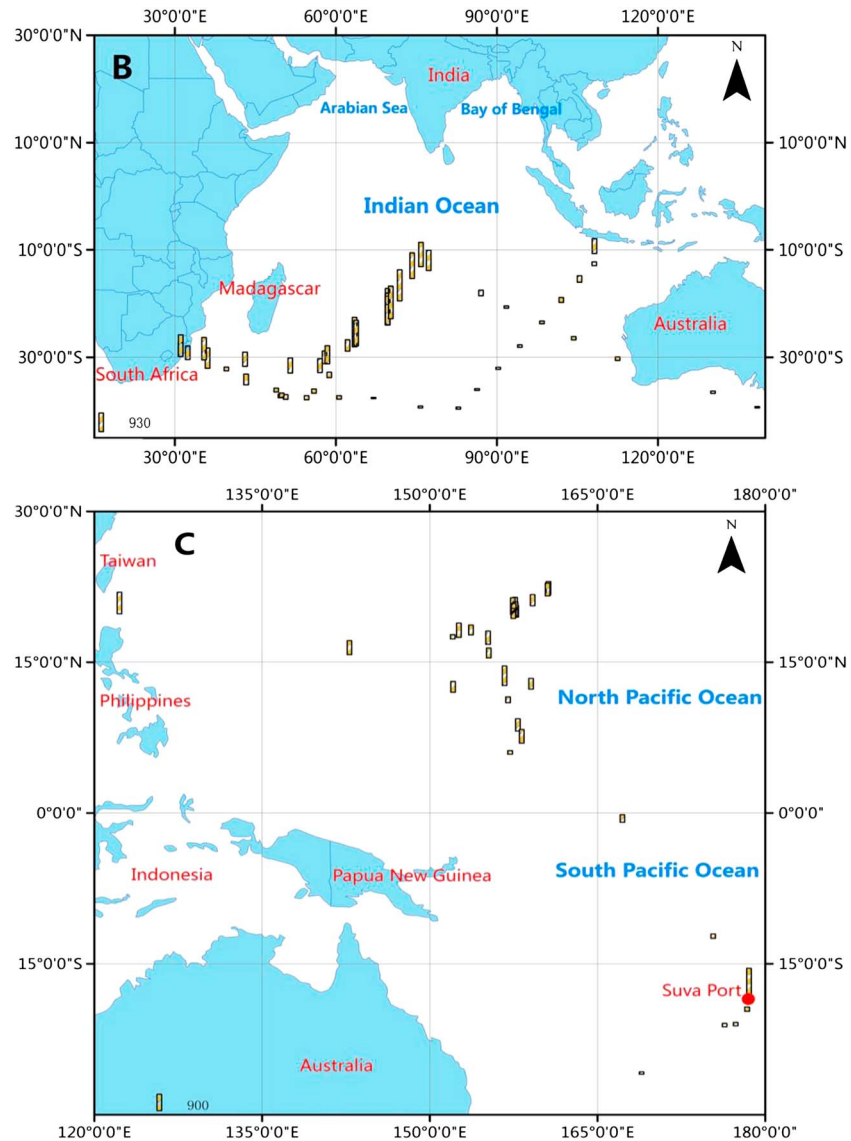
Figure 2. (continued)

remote and higher latitude regions during the sampling campaign (Figure 1). In addition, the impact from the land on the atmosphere of the South Indian Ocean was very significant. For example, in the samples close to South Africa (samples No. 30 and No. 32, No. 39 to No. 41), the PAH concentrations were relatively high compared to the others. A similar phenomenon was apparent in samples No. 13 to No. 17 and No. 57 to No. 59, where air masses have made contact with the land in West Australia before reaching the sampling sites (Figure 1). Although the air masses did not come from inland, the PAH concentrations for samples No. 42 to No. 56 were the highest from the South Indian Ocean. In the winter (December to April), the anthropogenic haze generally derived from the Arabian Sea and the Bay of Bengal can cross the equator with the movement of the monsoon [*Lelieveld et al.*, 2001; *Ramanathan et al.*, 2001]. *Dachs et al.* [1999] suggested that this monsoon plays a significant role on the global cycle of organic pollutants such as aliphatic hydrocarbons, PAHs, and polychlorinated biphenyls. Wind field showed that during the sampling campaign, the west oceanic region in the South Indian Ocean was most likely impacted by the air masses from the Arabian Sea, the Bay of Bengal, and Africa (Figure 3). The elevated PAH concentrations over these two former oceanic regions have been previously reported [*Crimmins et al.*, 2004; *Stone et al.*, 2007; *Xu et al.*, 2012]; however, few studies focused on the impact of the outflow of air from Africa to the Indian Ocean due to the relatively low industry and social development level in Africa. Nevertheless, studies have suggested that the open burning
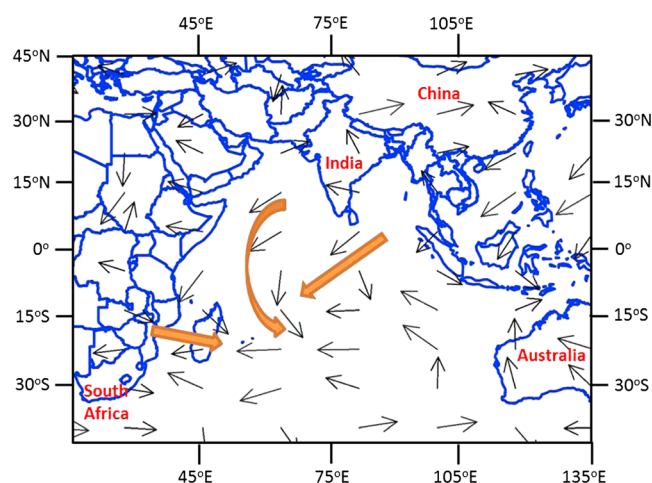
Figure 3. The wind field in the Indian Ocean during winter 2007.

in Africa can result in massive emission of PAHs [*Jaward et al.*, 2004; *Kakareka and Kukharchyk*, 2003]. Some studies reported that the Atlantic Ocean can be influenced by the outflow air from West Africa [*Jaward et al.*, 2004; *Xu et al.*, 2012]. Consequently, we believe that the atmosphere over the west oceanic region in the South Indian Ocean during this voyage was most likely polluted by South Asia and Africa, due to their extensive and consistent air current outflow throughout the winter. This conclusion agreed with the analysis of diagnostic ratios of PAH isomers and levoglucosan, which we will discuss in section 3.3.

The distribution of ∑PAH concentrations over the Pacific Ocean was considerably uniform, while the corresponding concentrations over the North Pacific Ocean were obviously higher than those over the South Pacific Ocean (Figure 2c), except for sample No. 67, which was collected at the Suva port. The samples collected over the Pacific Ocean were far away from continents; therefore, these PAH concentrations can serve as the background values for both the Northern and Southern Hemispheres. This result was consistent with the fact that anthropogenic activities in the Northern Hemisphere are much more intensive than those in the Southern Hemisphere [*Jaward et al.*, 2004].

3.2. Composition Profile

The PAH congener profiles were most likely influenced by the emission source [*Liu et al.*, 2007; *Xu et al.*, 2012] and the amount of photodegradation based on its lifetime in the atmosphere due to their different atmospheric reactivity [*Butler and Crossley*, 1981; *Ding et al.*, 2007]. Either associated with substrates containing low carbon content [*Behymer and Hites*, 1985, 1988] or high carbon content [*Butler and Crossley*, 1981], the half-lives of PAHs varied significantly. Agreement was made on that the atmospheric half-lives of Phe, Flua, Chr, and Pyr were obviously higher than BghiP, Ind, Ant, and BaP in most particle substrates [*Behymer and Hites*, 1985, 1988; *Butler and Crossley*, 1981; *Kamens et al.*, 1988], although controversies on the accurate values of half-lives is still ongoing. In addition, high molecular compounds with low vapor pressure (Ind, BghiP, and BbK) significantly dominated the PAH composition profile in atmospheric particles that was mainly impacted by the local emission [*Li et al.*, 2006; *Liu et al.*, 2007]. Therefore, the composition profile of PAH would be influenced by the atmospheric reaction to some extent.

Over the Asian marginal seas, samples were collected relatively close to the continents (Figure 1). The major contributors to the total PAHs were high molecular weight PAHs (Figure 4), with the following sequence: Ind (18.3%) > BghiP (17.8%) > BbF (12.6%) > Phe (9.8%). This profile pattern was consistent with the atmospheric aerosol samples collected from typical continental emission source sites, such as Tianjin (BghiP 15%, BbF 12%, Ind 8%, and Phe 5%) [*Wu et al.*, 2005], Guangzhou (BghiP 13%, Ind 12%, BbF 11%, and Phe 7%) [*Li et al.*, 2006], and Singapore (BghiP 19%, Ind 15%, BbF 14%, and Phe 6%) [*He and Balasubramanian*, 2009]. The consistent profile pattern indicates that the particulate PAHs over the Asian marginal seas came directly from the surrounding continents through short-range transport with less photodegradation.

Generally, the proportion of high molecular weight PAHs to ∑PAHs decreased significantly for samples near the open oceans (South Indian Ocean, South Pacific Ocean, and North Pacific Ocean), with the exception of some samples collected close to the land or harbors. The influence of the Oceans on the samples was characterized by a predominance of Phe, Flua, and Pyr (Figure 4), which accounted for 20–30%, 10–20%, and 10–15% of the ∑PAHs, respectively. A similar PAH congener profile was reported in other remote regions [*Xu et al.*, 2012]. The majority of high molecular weight PAHs was present in the particulate phase due to their low vapor pressures. As a result, high molecular weight PAHs scarcely reenter the atmosphere after scavenging by the intensive dry/wet deposition, which occurs frequently during long-range atmospheric
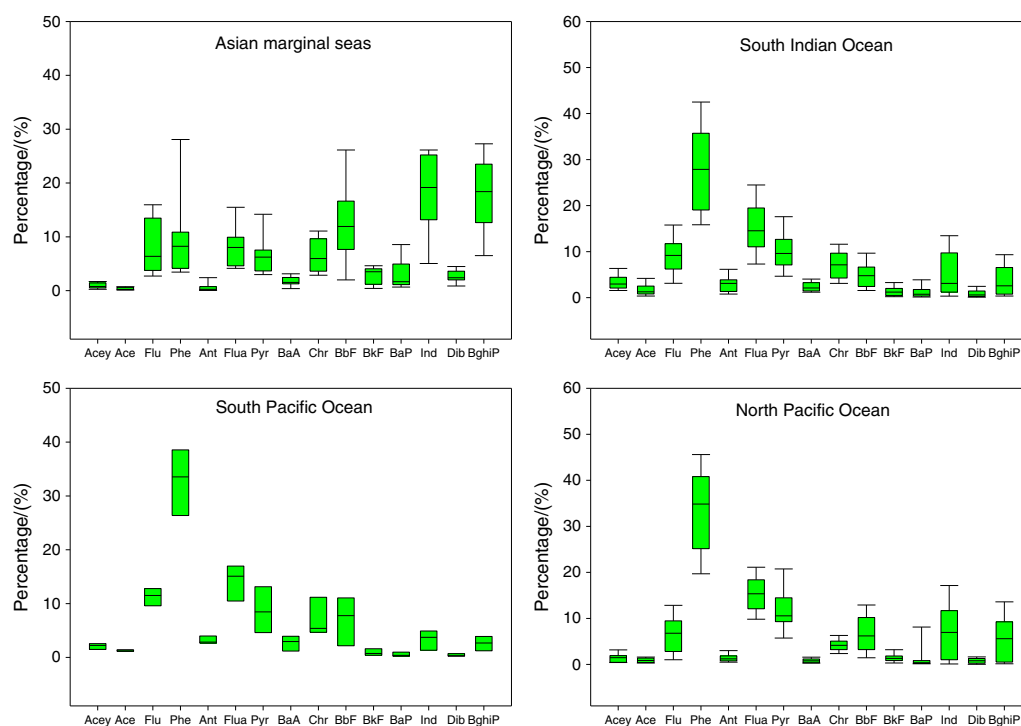
Figure 4. The box-whisker plot of PAHs congener profiles in the atmosphere over the Chinese marginal seas, the South Indian Ocean, the South Pacific Ocean, and the North Pacific Ocean.

transport. However, Phe, Flua, and Pyr can revolatilize from the oceanic surface into the atmosphere [*Jaward et al.*, 2004] and then repartition between two phases due to their appropriate vapor pressures, as well as their relative longer half-lives in particles as mentioned above, which would facilitate the increase of their relative contribution to PAH profile. This phenomenon is in agreement with the global fractionation theory, which suggests that high vapor pressure compounds tend to be transported to remote regions from the emission sources [*Simonich and Hites*, 1995; *Wania and MacKay*, 1996]. Consequently, the depletion of high molecular weight PAHs in the atmosphere occurred over the open oceans, which are isolated from both the land and emission sources.

3.3. Source Identification

Biomass, coal, and petroleum combustion are the three most important anthropogenic PAH emission sources [*Zhang et al.*, 2008]. Of the three, biomass burning is considered as the largest contributor globally [*Zhang and Tao*, 2009]. However, the relative contributions of numerous emission sources to ∑PAHs are significantly country dependent [*Zhang and Tao*, 2009] due to differences in energy utilization, area of forest/savanna cover, and the extent of development. Compared with the continents, the origins of atmospheric PAHs over the oceans are rather complicated to identify because of the complexity of physiochemical processes during transport and the difficulty in sampling. The PAH isomer ratios (Ant/Phe, BaA/Chr, Flua/Pyr, and Ind/BghiP) are frequently used as the indexes to differentiate emission sources qualitatively [*Ding et al.*, 2007; *Guo et al.*, 2003b; *Liu et al.*, 2007] based on the knowledge that some PAHs remain at constant ratios after they are emitted into the environment. Recently, studies found that only Ind/BghiP is robust enough to serve as source identification for PAHs both based on model evaluation [*Katsoyiannis*, 2014; *Zhang et al.*, 2005] and field observation [*Dvorská et al.*, 2011]. In general, A ratio of Ind/(Ind + BghiP) lower than 0.2 indicates nonburned petroleum as the primary input, a value between 0.2 to 0.5 indicates petroleum combustion, and values higher than 0.5 suggest that biomass and coal burning are the primary inputs [*Yunker et al.*, 2002]. However, the source apportionment values are not absolute boundaries [*Yunker et al.*, 2002]. The results of levoglucosan, an ideal molecular marker of biomass burning [*Simoneit et al.*, 1999] due to its exclusive emission source of biomass burning, were presented to better illustrate the potential sources of PAHs. Although the controversies with respect to the issue of the atmospheric degradation rate of levoglucosan
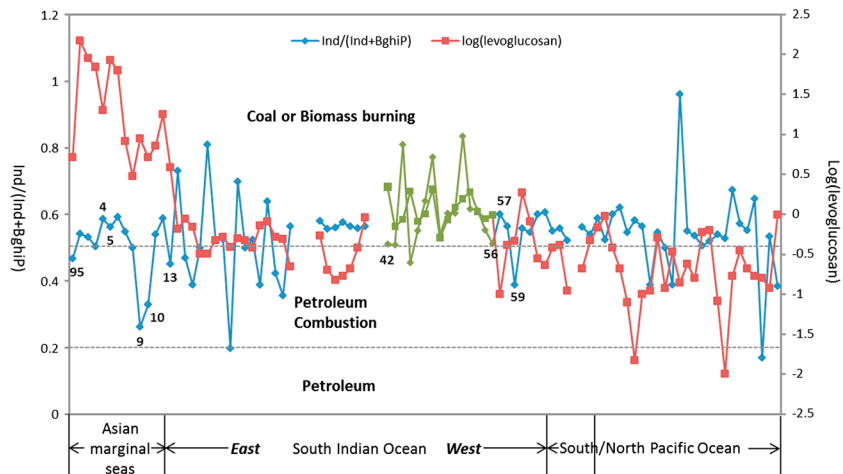
Figure 5. The variations in the values of Ind/(Ind + BghiP) and log(levoglucosan) over different oceanic regions along the cruise. The highlighted samples (green) with the relative high level of levoglucosan and diagnostic ratios were impacted by the biomass burning. Samples collected in harbors and neighboring area are excluded.

have never ended in laboratory experiments [*Fraser and Lakshmanan*, 2000; *Hennigan et al.*, 2010], in the field studies, levoglucosan, because of its large fraction in aerosols from biomass burning and relative atmospheric stability, was employed well as a molecular marker to evaluate the impact of the biomass burning on aerosols by numerous studies, including remote Arctic and Antarctic regions [*Ding et al.*, 2013; *Hu et al.*, 2013].

Figure 5 shows the variations of the Ind/(Ind + BghiP) ratios and levoglucosan concentrations during this study. The highest levoglucosan concentrations were observed off coast of the Asian marginal seas (Table 1), especially those samples close to the Chinese marginal seas (No. 1 to No. 6); except No. 95 collected in summertime when the area was covered by air masses came from the Pacific Ocean. Most of the Ind/(Ind + BghiP) ratios over this area indicate biomass and coal burning emissions, which was expected due to the fact that the air masses sampled came from North China where domestic coal and biofuel are used intensively for heating [*Liu et al.*, 2007]. The Ind/(Ind + BghiP) values for samples No. 9, No. 10, and No. 13 were relatively low, suggesting that petroleum combustion may exist. Sample No. 95 shows a signature of petroleum combustion as well. This sample was taken over the South China marginal sea, which was likely influenced by anthropogenic activities occurring in the coastal cities during that time period.

Over the South Indian Ocean, the highest levoglucosan concentrations occurred near harbors, which were excluded in Figure 5. The concentrations in the atmosphere of the east oceanic region and high-latitude ocean (>30°S) region were relatively lower than those collected in the atmosphere of west oceanic region (Figure 5). This result is consistent with the results based on the values of Ind/(Ind + BghiP). Most of the ratios from samples in the eastern area are lower than 0.5 or close to 0.5 suggesting less input from biomass/coal combustion. The east oceanic region is most likely influenced by the air masses coming from west Australia (Figure 1), where the prevailing wind can bring continental pollutants, possibly petroleum combustion related, to the open ocean [*Burt and Ebell*, 1995]. Over the high-latitude oceanic region (>30°S), the values of Ind/(Ind + BghiP) showed the similar characteristics of petroleum combustion. The air back trajectory model analysis suggests that there was no continental influence during sampling in the high-latitude oceanic region. In addition, in this latitude, the trade winds are from the remote open oceans. Therefore, the atmosphere over the high latitudes in the Southern Hemisphere might be polluted by anthropogenic activities, such as a holiday cruise, fishing, and scientific investigations. The more than 20 scientific stations in Antarctica have exerted a negative impact on the Antarctic region [*Caricchia et al.*, 1995; *Curtosi et al.*, 2007], as well as the exhaust emissions created during journeys to and from these scientific stations. When the ship entered the western area of the South Indian Ocean region, the concentration of levoglucosan became relatively high and the Ind/(Ind + BghiP) values were stable with a characteristic of predominately biomass/coal burning. As the ship traveled north, the values increased, suggesting a stronger influence from biomass/coal burning in this oceanic region. In samples No. 53 to No. 59, the Ind/(Ind + BghiP) value decreased significantly, indicating that the air masses originated from a nonbiomass burning location.

As mentioned in section 3.1, the oceanic region where samples (No. 53 to No. 56) were collected is most likely impacted by the air masses from the North Indian Ocean. It is well known that the atmosphere over the North Indian Ocean has been polluted by the combustion of biomass and fossil fuel [*Crimmins et al.*, 2004; *Lelieveld et al.*, 2001; *Wisthaler et al.*, 2002]; thus, this study demonstrates a similar condition over the South Indian Ocean.

Over the Pacific Ocean, the levoglucosan concentrations in the atmosphere of the North Pacific Ocean (0.3 ng/m^3) were at the same level as that in the atmosphere of the South Pacific Ocean (0.35 ng/m^3 on average except the sample of No. 67 collected at Suva harbor), which is largely different from the distributional pattern of PAHs over the Pacific Ocean in this study. It may relate to the similar emission inventory of biomass-based aerosols on the Northern and Southern Hemisphere [Intergovernmental Panel on Climate Change (*IPCC*), 2001]. The values of Ind/(Ind + BghiP) for the majority of the aerosol samples indicates biomass/coal burning emissions. The open ocean can serve as the background for global atmospheric levels, because it is far away from continental emission sources. Given that the coal combustion in the Southern Hemisphere is very limited [*Xu et al.*, 2012], we inferred that particulate PAHs over the South Pacific Ocean were due to biomass burning. However, it is worth pointing out that more lower values of Ind/(Ind + BghiP) appeared for the aerosol samples over the North Pacific Ocean suggesting that there is input of petroleum combustion besides biomass/coal combustion in the Northern Hemisphere. The global biomass burning-based aerosol were estimated as 28 and 26 Tg in the Northern Hemisphere and the Southern Hemisphere, respectively [*IPCC*, 2001], but the anthropogenic activity in the Northern Hemisphere is much greater than in the Southern Hemisphere. The levoglucosan measurements over the Pacific Ocean in this study also show that there is no difference for biomass burning between two hemispheres (Figure 5). Hence, it is reasonable to believe that the relatively high PAH concentrations over the North Pacific Ocean, as well as the low Ind/(Ind + BghiP) ratios, compared to the South Pacific Ocean were likely caused by the combination of emissions from different regions in the Northern Hemisphere.

3.4. Fire Activity and Aerosol Optical Depth

Wildfires, both natural and man-made, can produce large amounts of aerosols and reduce atmospheric visibility. *Zhang and Tao* [2009] reported that on a global basis, wildfire was the second highest contributor of PAHs, accounting for 17% of total PAHs. South America, Africa, and South/Southeast Asia are the three most important regions, where such fires are intense and occur regularly during the dry season each year. The aerosol optical depth (AOD), an indicator of the aerosol amounts based on optical properties, exhibits the same seasonal pattern. Figures S1–S4 (see supporting information) display the global map of active fire spots and AOD during our cruise of the Indian Ocean during the dry season (January 2007 to April 2007). The map shows that the high aerosol loads are discernibly linked to the fire activities (Figures S1–S4, each colored dot indicates a location where Moderate Resolution Imaging Spectroradiometer detected at least one fire during the compositing period. Color ranges from red where the fire count is low to yellow where number of fires is large, https://earthdata.nasa.gov/data/near-real-time-data/firms/active-fire). The severe fire activity and the high AOD were persistent throughout the dry season in Southeast Asia (Thailand, Cambodia, Laos, and Vietnam), especially in March and April. The high aerosol loads are discernibly linked to the fire activities. However, the aerosol amount can be elevated in the absence of significant fire activity. For example, there was no obvious fire activity in India during January and February, while the corresponding AOD was elevated, which was most likely a result from the large consumption of biofuel and fossil fuel in winter [*Lelieveld et al.*, 2001]. A similar phenomenon occurred in the East and South China. The AOD values in India were high in January and February and they kept rising from March to April, when significant fire activity appeared in the Indian subcontinent and elevated PAH concentrations were observed over the west oceanic region in the South Indian Ocean. It was well documented that northeasterly winds derived from the Arabian Sea and South Asia would exert a negative influence on the southern region of the Indian Ocean due to the southward movement of the Intertropical Convergence Zone during winter [*Crimmins et al.*, 2004; *Lelieveld et al.*, 2001; *Ramanathan et al.*, 2001; *Wisthaler et al.*, 2002]. *Lelieveld et al.* [2001] pointed out that fossil fuel combustion and burning of biomass caused high aerosol loading over the Indian Ocean, and that this pollution extensively degraded air quality. *Gustafsson et al.* [2009] further reported that the aerosol carbon over the Indian Ocean generated from biomass burning contributed 67% of the total carbon and 68% of the elemental carbon. These combined results from fire activities and AOD measurements demonstrated that except the wildfire burning in South/Southeast Asia, the combustion of the fossil fuel and biofuel was also an important contributor to the PAHs over Indian Ocean.
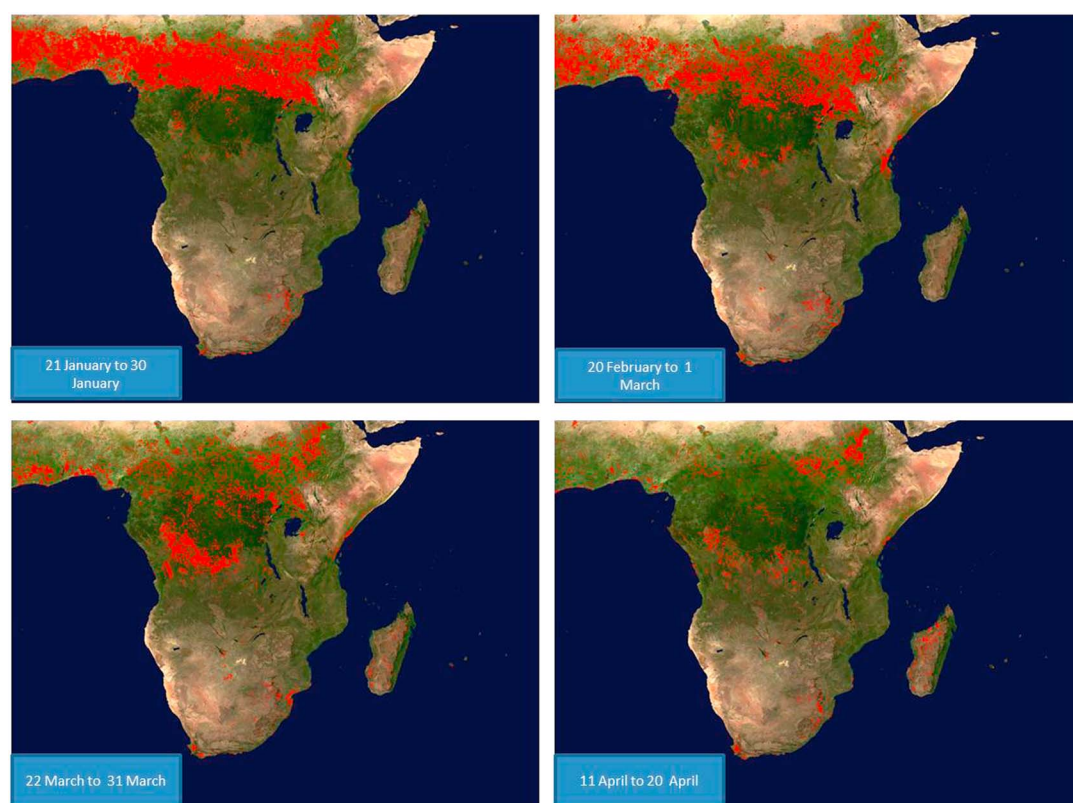
Figure 6. The temporal variations of fire activity in Africa (http://rapidfire.sci.gsfc.nasa.gov).

In the African continent, the fire activity shows a slight migratory trend from the north to the south in this study. Several obvious fire incidents had already occurred in Southern Africa (Democratic Republic of the Congo, Angola, Zambia, and Madagascar) in March and April (Figure 6). Investigation of the atmospheric PAHs in Africa is still very limited, although emissions from this region accounted for 18.8% of the global total [*Zhang and Tao*, 2009]. It was reported that numerous small fires, such as bush fires, emitted a high level of PAHs in Africa [*Jaward et al.*, 2004], which potentially resulted in the elevated particulate PAH concentrations and diagnostic isomer ratios found over the oceanic region in this study during 1–10 April, which was influenced by the wind from Southern Africa (Figure 3). Surprisingly, a study by *Klanova et al.* [2009] using passive samplers found that the PAH concentrations at a background site in Mauritius (latitude −20.23, longitude 57.49), located to the east of Madagascar, were significantly higher than those of samples from Zimbabwe and South Africa. Although the PAH concentrations based on the passive samplers only represent the gaseous PAHs, both gas and particle phase PAHs could change similarly with the change of the emission sources [*Akyüz and Çabuk*, 2010]. Therefore, these PAH data based on the passive samples could reflect well the seasonal change of the emission sources. Furthermore, the PAH levels in Mauritius between March and April were higher than in January and February, suggesting that biomass burning in East Africa is likely to cause elevated PAHs over the west oceanic area in the Southern Indian Ocean [*Klanova et al.*, 2009].

4. Conclusions

The concentrations of PAHs in the atmospheric aerosols over the Asian marginal seas, southern Indian Ocean, southern Pacific Ocean, and northern Pacific Ocean were reported in this study. The PAH levels over the marginal seas were significantly higher than those over the open oceans, which suggested that activities on the land had a significant impact on the oceans. Highest PAH concentrations appeared over the Chinese marginal seas. This result was consistent with the fact that China is the biggest contributor to global PAH emissions. The atmosphere of the Western Indian Ocean is most likely influenced by the outflow from South/Southeast Asia or Africa, which leads to higher PAH concentrations in this oceanic region than

in the surrounding oceanic area. Due to the intensive atmospheric physicochemical processes present during long-range atmospheric transport, different PAH congener profiles were found between the open oceans and marginal seas.

Similar to the previous study, this study confirmed that wildfires are a critical emission source for atmospheric PAHs in Africa. These wildfire-based PAHs can migrate to the atmosphere in the western oceanic region in the South Indian Ocean during the active wildfire seasons, resulting in the relatively high values of Ind/(Ind + BghiP) and levoglucosan. For the aerosol samples collected in the vicinity of 12°S, the Ind/(Ind + BghiP) decreased due to the input of nonbiomass burning sources. It is thought that this region is impacted by mixed air masses from the Arabian Peninsula and South Asia. Overall, the PAH concentrations in the marginal seas and open oceans of the Northern Hemisphere and the Southern Hemisphere reported in this study provide a reference for future investigation of global oceanic atmospheric boundary layer PAHs with respect to the emission sources, spatial variation, and controlling factors.

References

Akyüz, M., and H. Çabuk (2010), Gas–particle partitioning and seasonal variation of polycyclic aromatic hydrocarbons in the atmosphere of Zonguldak, Turkey, *Sci. Total Environ.*, *408*, 5550–5558, doi:10.1016/j.scitotenv.2010.07.063.

Behymer, T. D., and R. A. Hites (1985), Photolysis of polycyclic aromatic hydrocarbons adsorbed on simulated atmospheric particulates, *Environ. Sci. Technol.*, *19*(10), 1004–1006, doi:10.1021/es00140a020.

Behymer, T. D., and R. A. Hites (1988), Photolysis of polycyclic aromatic hydrocarbons adsorbed on fly ash, *Environ. Sci. Technol.*, *22*(11), 1311–1319, doi:10.1021/es00176a011.

Burt, J. S., and G. F. Ebell (1995), Organic pollutants in mussels and sediments of the coastal waters off Perth, Western Australia, *Mar. Pollut. Bull.*, *30*(11), 723–732, doi:10.1016/0025-326X(95)00063-S.

Butler, J. D., and P. Crossley (1981), Reactivity of polycyclic aromatic hydrocarbons adsorbed on soot particles, *Atmos. Environ.*, *15*(1), 91–94, doi:10.1016/0004-6981(81)90129-3.

Caricchia, A. M., S. Chiavarini, C. Cremisini, R. Morabito, A. Perini, and M. Pezza (1995), Determination of PAH in atmospheric particulates in the area of the Italian base in Antarctica: Report on monitoring activities during the last three scientific expeditions, *Environ. Pollut.*, *87*(3), 345–356, doi:10.1016/0269-7491(94)P4166-L.

Cooper, D. A. (2001), Exhaust emissions from high speed passenger ferries, *Atmos. Environ.*, *35*(24), 4189–4200, doi:10.1016/S1352-2310(01)00192-3.

Cooper, D. A. (2003), Exhaust emissions from ships at berth, *Atmos. Environ.*, *37*(27), 3817–3830, doi:10.1016/S1352-2310(03)00446-1.

Cooper, D. A., K. Peterson, and D. Simpson (1996), Hydrocarbon, PAH and PCB emissions from ferries: A case study in the Skagerrak-Kattegat-Øresund region, *Atmos. Environ.*, *30*(14), 2463–2473, doi:10.1016/1352-2310(95)00494-7.

Crimmins, B. S., R. R. Dickerson, B. G. Doddridge, and J. E. Baker (2004), Particulate polycyclic aromatic hydrocarbons in the Atlantic and Indian Ocean atmospheres during the Indian Ocean Experiment and Aerosols99: Continental sources to the marine atmosphere, *J. Geophys. Res.*, *109*, D05308, doi:10.1029/2003JD004192.

Curtosi, A., E. Pelletier, C. L. Vodopivez, and W. P. Mac Cormack (2007), Polycyclic aromatic hydrocarbons in soil and surface marine sediment near Jubany Station (Antarctica), Role of permafrost as a low-permeability barrier, *Sci. Total Environ.*, *383*, 193–204, doi:10.1016/j.scitotenv.2007.04.025.

Dachs, J., J. M. Bayona, V. Ittekkot, and J. Albaigés (1999), Monsoon-driven vertical fluxes of organic pollutants in the western Arabian Sea, *Environ. Sci. Technol.*, *33*(22), 3949–3956, doi:10.1021/es990200e.

Ding, X., X. M. Wang, Z. Q. Xie, C. H. Xiang, B. X. Mai, L. G. Sun, M. Zheng, G. Y. Sheng, J. M. Fu, and U. Pöschl (2007), Atmospheric polycyclic aromatic hydrocarbons observed over the North Pacific Ocean and the Arctic area: Spatial distribution and source identification, *Atmos. Environ.*, *41*, 2061–2072, doi:10.1016/j.atmosenv.2006.11.002.

Ding, X., X. Wang, Z. Xie, Z. Zhang, and L. Sun (2013), Impacts of Siberian biomass burning on organic aerosols over the North Pacific Ocean and the Arctic: Primary and secondary organic tracers, *Environ. Sci. Technol.*, *47*, 3149–3157, doi:10.1021/es3037093.

Dvorská, A., G. Lammel, and J. Klánová (2011), Use of diagnostic ratios for studying source apportionment and reactivity of ambient polycyclic aromatic hydrocarbons over Central Europe, *Atmos. Environ.*, *45*, 420–427, doi:10.1016/j.atmosenv.2010.09.063.

Fraser, M. P., and K. Lakshmanan (2000), Using levoglucosan as a molecular marker for the long-range transport of biomass combustion aerosols, *Environ. Sci. Technol.*, *34*(21), 4560–4564, doi:10.1021/es991229l.

Guo, H., S. C. Lee, K. F. Ho, X. M. Wang, and S. C. Zou (2003a), Particle-associated polycyclic aromatic hydrocarbons in urban air of Hong Kong, *Atmos. Environ.*, *37*(38), 5307–5317, doi:10.1016/j.atmosenv.2003.09.011.

Guo, L., L. F. Sheng, J. Feng, and M. Fang (2003b), Seasonal variation of solvent extractable organic compounds in the aerosols in Qingdao, China, *Atmos. Environ.*, *37*(13), 1825–1834, doi:10.1016/S1352-2310(03)00064-5.

Gustafsson, Ö., M. Kruså, Z. Zencak, R. J. Sheesley, L. Granat, E. Engström, P. Praveen, P. Rao, C. Leck, and H. Rodhe (2009), Brown clouds over South Asia: Biomass or fossil fuel combustion?, *Science*, *323*, 495–498, doi:10.1126/science.1164857.

He, J., and R. Balasubramanian (2009), A study of gas/particle partitioning of SVOCs in the tropical atmosphere of Southeast Asia, *Atmos. Environ.*, *43*, 4375–4383, doi:10.1016/j.atmosenv.2009.03.055.

Hennigan, C. J., A. P. Sullivan, J. L. Collett, and A. L. Robinson (2010), Levoglucosan stability in biomass burning particles exposed to hydroxyl radicals, *Geophys. Res. Lett.*, *37*, L09806, doi:10.1029/2010GL043088.

Hu, Q. H., Z. Q. Xie, X. M. Wang, H. Kang, and P. Zhang (2013), Levoglucosan indicates high levels of biomass burning aerosols over oceans from the Arctic to Antarctic, *Sci. Rep.*, *3*, 3119, doi:10.1038/srep03119.

IPCC (2001), *IPCC. Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change [M]*, Cambridge Univ. Press, Cambridge, U. K., and New York.

Jaward, F. M., J. L. Barber, K. Booij, and K. C. Jones (2004), Spatial distribution of atmospheric PAHs and PCNs along a north–south Atlantic transect, *Environ. Pollut.*, *132*, 173–181, doi:10.1016/j.envpol.2004.03.029.

Kakareka, S. V., and T. I. Kukharchyk (2003), PAH emission from the open burning of agricultural debris, *Sci. Total Environ.*, *308*(1–3), 257–261, doi:10.1016/S0048-9697(02)00650-2.

Kamens, R. M., Z. Guo, J. N. Fulcher, and D. A. Bell (1988), The influence of humidity, sunlight, and temperature on the daytime decay of polyaromatic hydrocarbons on atmospheric soot particles, *Environ. Sci. Technol.*, *22*(1), 103–108, doi:10.1021/es00166a012.

Katsoyiannis, A. (2014), Model-based evaluation of the use of PAH molecular diagnostic ratios as a source identification tool, *Environ. Pollut.*, *184*, 488–94, doi:10.1016/j.envpol.2013.09.028.

Klanova, J., P. Cupr, I. Holoubek, J. Boruvkova, P. Pribylova, R. Kares, T. Tomsej, and T. Ocelka (2009), Monitoring of persistent organic pollutants in Africa, Part 1: Passive air sampling across the continent in 2008, *J. Environ. Monit.*, *11*, 1952–1963, doi:10.1039/B913415H.

Lang, C., S. Tao, W. Liu, Y. Zhang, and S. Simonich (2008), Atmospheric transport and outflow of polycyclic aromatic hydrocarbons from China, *Environ. Sci. Technol.*, *42*, 5196–5201, doi:10.1021/es800453n.

Lelieveld, J., P. Crutzen, V. Ramanathan, M. Andreae, C. Brenninkmeijer, T. Campos, G. Cass, R. Dickerson, H. Fischer, and J. De Gouw (2001), The Indian Ocean experiment: Widespread air pollution from South and Southeast Asia, *Science*, *291*(5506), 1031–1036, doi:10.1126/science.1057103.

Li, J., G. Zhang, X. D. Li, S. H. Qi, G. Q. Liu, and X. Z. Peng (2006), Source seasonality of polycyclic aromatic hydrocarbons (PAHs) in a subtropical city, Guangzhou, South China, *Sci. Total Environ.*, *355*, 145–155, doi:10.1016/j.scitotenv.2005.02.042.

Liu, D., J. Li, Y. Zhang, Y. Xu, X. Liu, P. Ding, C. Shen, Y. Chen, C. Tian, and G. Zhang (2013), The use of levoglucosan and radiocarbon for source apportionment of PM2.5 carbonaceous aerosols at a background site in East China, *Environ. Sci. Technol.*, *47*, 10,454–10,461, doi:10.1021/es401250k.

Liu, S., S. Tao, W. Liu, Y. Liu, H. Dou, J. Zhao, L. Wang, J. Wang, Z. Tian, and Y. Gao (2007), Atmospheric polycyclic aromatic hydrocarbons in North China: A winter-time study, *Environ. Sci. Technol.*, *41*, 8256–8261, doi:10.1021/es0716249.

Mader, B. T., and J. F. Pankow (2001), Gas/solid partitioning of semivolatile organic compounds (SOCs) to air filters, 3. An analysis of gas adsorption artifacts in measurements of atmospheric SOCs and organic carbon (OC) when using Teflon membrane filters and quartz fiber filters, *Environ. Sci. Technol.*, *35*(17), 3422–3432, doi:10.1021/es0015951.

Neşer, G., A. Kontas, D. Ünsalan, O. Altay, E. Darılmaz, E. Uluturhan, F. Küçüksezgin, N. Tekoğul, and F. Yercan (2012), Polycyclic aromatic and aliphatic hydrocarbons pollution at the coast of Aliağa (Turkey) ship recycling zone, *Mar. Pollut. Bull.*, *64*, 1055–1059, doi:10.1016/j.marpolbul.2012.02.019.

Nizzetto, L., R. Lohmann, R. Gioia, A. Jahnke, C. Temme, J. Dachs, P. Herckes, A. D. Guardo, and K. C. Jones (2008), PAHs in air and seawater along a North–South Atlantic transect: Trends, processes and possible sources, *Environ. Sci. Technol.*, *42*, 1580–1585, doi:10.1021/es0717414.

Panther, B., M. Hooper, and N. Tapper (1999), A comparison of air particulate matter and associated polycyclic aromatic hydrocarbons in some tropical and temperate urban environments, *Atmos. Environ.*, *33*(24), 4087–4099, doi:10.1016/S1352-2310(99)00150-8.

Ramanathan, V., P. J. Crutzen, J. Lelieveld, A. Mitra, D. Althausen, J. Anderson, M. Andreae, W. Cantrell, G. Cass, and C. Chung (2001), Indian Ocean Experiment: An integrated analysis of the climate forcing and effects of the great Indo-Asian haze, *J. Geophys. Res.*, *106*, 28,371–28,398, doi:10.1029/2001JD900133.

Simoneit, B. R. T., J. J. Schauer, C. G. Nolte, D. R. Oros, V. O. Elias, M. P. Fraser, W. F. Rogge, and G. R. Cass (1999), Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles, *Atmos. Environ.*, *33*(2), 173–182, doi:10.1016/S1352-2310(98)00145-9.

Simonich, S., and R. Hites (1995), Global distribution of persistent organochlorine compounds, *Science*, *269*(5232), 1851–1854, doi:10.1126/science.7569923.

Stone, E. A., G. C. Lough, J. J. Schauer, P. S. Praveen, C. E. Corrigan, and V. Ramanathan (2007), Understanding the origin of black carbon in the atmospheric brown cloud over the Indian Ocean, *J. Geophys. Res.*, *112*, D22S23, doi:10.1029/2006JD008118.

Wania, F., and D. MacKay (1996), Peer reviewed: Tracking the distribution of persistent organic pollutants, *Environ. Sci. Technol.*, *30*, 390A–396A, doi:10.1021/es962399q.

Wisthaler, A., A. Hansel, R. R. Dickerson, and P. J. Crutzen (2002), Organic trace gas measurements by PTR-MS during INDOEX 1999, *J. Geophys. Res.*, *107*(D19), 8024, doi:10.1029/2001JD000576.

Wu, S. P., S. Tao, Z. H. Zhang, T. Lan, and Q. Zuo (2005), Distribution of particle-phase hydrocarbons, PAHs and OCPs in Tianjin, China, *Atmos. Environ.*, *39*, 7420–7432, doi:10.1016/j.atmosenv.2005.08.031.

Xu, Y., Y. L. Zhang, J. Li, R. Gioia, G. Zhang, X.-D. Li, B. Spiro, R. S. Bhatia, and K. C. Jones (2012), The spatial distribution and potential sources of polycyclic aromatic hydrocarbons (PAHs) over the Asian marginal seas and the Indian and Atlantic Oceans, *J. Geophys. Res.*, *117*, D07302, doi:10.1029/2011JD016585.

Yunker, M. B., R. W. Macdonald, R. Vingarzan, R. H. Mitchell, D. Goyette, and S. Sylvestre (2002), PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition, *Org. Geochem.*, *33*(4), 489–515, doi:10.1016/S0146-6380(02)00002-5.

Zhang, X. L., S. Tao, W. X. Liu, Y. Yang, Q. Zuo, and S. Z. Liu (2005), Source diagnostics of polycyclic aromatic hydrocarbons based on species ratios: A multimedia approach, *Environ. Sci. Technol.*, *39*, 9109–9114, doi:10.1021/es0513741.

Zhang, Y., and S. Tao (2009), Global atmospheric emission inventory of polycyclic aromatic hydrocarbons (PAHs) for 2004, *Atmos. Environ.*, *43*, 812–819, doi:10.1016/j.atmosenv.2008.10.050.

Zhang, Y., H. Dou, B. Chang, Z. Wei, W. Qiu, S. Liu, W. Liu, and S. Tao (2008), Emission of polycyclic aromatic hydrocarbons from indoor straw burning and emission inventory updating in China, *Ann. N. Y. Acad. Sci.*, *1140*, 218–227, doi:10.1196/annals.1454.006.