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Particulate polycyclic aromatic hydrocarbons in the Atlantic and Indian Ocean atmospheres during the Indian Ocean Experiment and Aerosols99: Continental sources to the marine atmosphere

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[1] Polycyclic aromatic hydrocarbons (PAHs), mutagenic compounds predominantly derived from combustion, have been used as markers of combustion sources to the atmosphere. Marine aerosol collected aboard the NOAA R/V *Ronald Brown* during the Aerosols99 and the Indian Ocean Experiment (INDOEX) projects was analyzed for PAHs to assess the continental impact of combustion-derived particulate matter on the Atlantic and Indian Ocean atmospheres. PAH concentrations in the Atlantic and southern Indian Ocean atmospheres were consistent and low, ranging from <0.45 pg/m^3 for coronene to 30 pg/m^3 for 9, 10-dimethylanthracene. PAH concentrations increased ten fold as the ship crossed the Intertropical Convergence Zone (ITCZ) into the northern Indian Ocean, indicating an increased anthropogenic influence. PAH concentrations over the northern Indian Ocean atmosphere were approximately an order of magnitude greater than those in the northern Atlantic Ocean atmosphere. PAH composition profiles over the northern Indian Ocean were specific to wind regimes and influenced by a combination of biomass and fossil fuel combustion. This was supported by significant correlations between select PAHs and organic carbon (OC), elemental carbon (EC), SO_4^{-2} and K^+ for particular wind regimes. Indeno[1,2,3-*cd*]pyrene/EC ratios used as a combustion source marker suggest that fossil fuel combustion, rather than biomass burning, is the predominant source of PAHs to the Northern Hemisphere Indian Ocean atmosphere. Interestingly, fossil fuel consumption in the Indian sub-continent is a fraction of that in Europe and the United States but the soot and PAH levels in the adjacent Northern Indian Ocean atmosphere are significantly greater than those in the Northern Atlantic atmosphere. *INDEX TERMS:* 0305 Atmospheric Composition and Structure: Aerosols and particles (0345, 4801); 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; *KEYWORDS:* INDOEX, PAHs, aerosol

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1. Introduction

[2] The atmospheric transport of high molecular weight organic contaminants to the marine environment has received little attention. *Duce and Gagosian* [1982] compiled estimates for the atmospheric input of *n*-C_{10} to *n*-C_{30} alkanes to the ocean from four data sources. This initial attempt to assess anthropogenic impacts on the marine coastal atmosphere did not include polycyclic aromatic hydrocarbons (PAHs). Elsewhere specific atmospheric PAHs (i.e., benzo[*a*]pyrene) have been studied extensively, especially in urban and rural continental areas. Over-water studies have been performed on the Great Lakes [*Baker and Eisenreich*, 1990; *Simcik et al.*, 1997; *McVeety and Hites*, 1988], the Chesapeake Bay [*Offenberg and Baker*, 1999; *Dickhut and Gustafson*, 1995], the Baltic Sea [*Halkiewicz et al.*, 1987], the Canadian Arctic [*Halsall et al.*, 1997], the Mediterranean Sea [*Stephanou*, 1992], the tropical Atlantic

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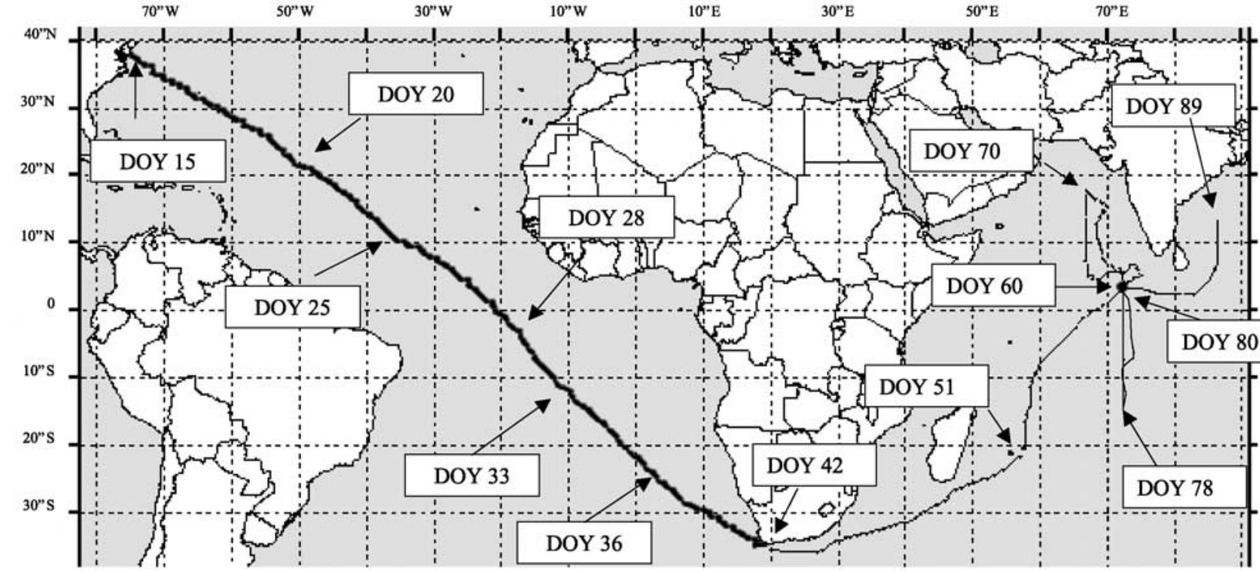

Figure 1. Cruise track of the R/V *Brown* during the Aerosols99 and INDOEX sampling campaigns. Selected sampling Julian dates (DOY) are identified to coincide with wind regimes outlined in Table 1.

[*Marty et al.*, 1984] and Pacific Ocean [*Fraser et al.*, 1998]. Recently, estimates for dry and wet deposition of alkanes and PAHs were made for rural and urban coastal atmospheres extending 0–3 km, 3–200 km and >200 km off the coast [*National Research Council* (*NRC*), 2003]. Owing to paucity of data, the particulate phase PAH concentrations had to be estimated from studies in remote regions of the United States.

[3] In 1999, two research cruises were performed as part of the Aerosols99 and INDOEX projects. The objective of the Aerosols99 project was to determine the chemical and optical properties of aerosols as well as the ozone, CO and peroxyradical chemistry in the marine boundary layer [*Bates et al.*, 2001; *Hernández et al.*, 2001; *Thompson et al.*, 2000]. Aerosols99 consisted of a cruise from Norfolk, VA, USA to Cape Town, South Africa (Figure 1) on the NOAA R/V *Ronald H Brown*. Seven wind regimes (Table 1) were determined from meteorological parameters, back trajectory analysis and trace gas and aerosol chemical composition [*Bates et al.*, 2001]. These meteorological regimes included aged marine (continental influence greater than three days prior to arriving at the ship in the Northern and Southern Hemispheres of the Atlantic Ocean), aged (2–4 days marine influenced) North American, influenced by biomass burning from Africa along the northern edge of the Intertropical Convergence Zone (ITCZ), and influenced by African dust. Elevated levels of K$^+$ and elemental carbon (EC) were found in the denoted biomass-burning influenced air masses. *Bates et al.* [2001] concluded that biomass burning-derived aerosols were transported by upper level air masses (750 mb) then mixed down near the ITCZ (8°N to 5°S). All of the air masses sampled in the Aerosols99 cruise had bimodal aerosol size distributions, with the exception of the biomass burning regime located along the Atlantic Ocean ITCZ. The biomass burning aerosol was unimodal, with a number distribution similar to the larger diameter (median ~200 nm) of the two modes found in other identified regimes in the Atlantic transect [*Bates et al.*, 2001]. During the Aerosols99 cruise, the particulate organic matter (POM) concentration was highest in the aged North American regime while EC was greatest in the biomass burning/African dust mixed regime [*Bates et al.*, 2001]. Sub-micron non-sea salt sulfate concentrations were greatest in the North American air masses, consistent with long-range transport of aerosols from anthropogenic sources [*Bates et al.*, 2001].

[4] The INDOEX project was developed to address the heavy aerosol burden observed over the northern Indian Ocean by *Rhoads et al.* [1997]. A primary objective of the INDOEX project was to elucidate aerosol properties such as chemical composition and microphysical properties and their effect on direct and indirect forcing to evaluate climate model estimates [*Ramanathan et al.*, 2001; *Lelieveld et al.*, 2001]. Similar to the Aerosols99 cruise, 10 wind regimes were defined based on meteorological parameters (Table 1). A distinct increase in the optical depth at 0.5 μm from the Southern to Northern Indian Ocean was found aboard the R/V *Sagar Kanya* using a multiwavelength Sun photometer, indicating heavily polluted air extending ~1000 km from the Indian subcontinent [*Ramanathan et al.*, 2001]. A thick haze layer extends over most of the Northern Indian Ocean, advected from the Indian sub-continent in a well-defined aerosol layer above the MBL [*Leon et al.*, 2001].

[5] The source of carbonaceous aerosols to the Northern Hemisphere Indian Ocean atmosphere is still in debate. *Mayol-Bracero et al.* [2002] measured SO$_2$, POM, black carbon and water-soluble ionic species using the National Center for Atmospheric Research's (NCAR) C-130 aircraft. The authors employed reported ratios of these species characteristic of biomass-burning and fossil fuel combustion, concluding that 60–80% of the aerosol was from fossil fuel combustion. Similarly, *Novakov et al.* [2000] sampled <1.3 μm aerosol for organic carbon (OC), EC, SO$_4^{-2}$ and K$^+$ determination using the NCAR C-130 over the Indian Ocean in February and March of 1999. Using source ratios of

Table 1. Meteorological Conditions During Aerosols99 and the Indian Ocean Experiment

Aerosols99[a]	Day of Year	Back Trajectory
North American	15–16	Back trajectories rapidly passed over North America 2–4 days back.
North Atlantic Marine	16–24	Trajectories over the North Atlantic, >6-day marine influence.
Mineral Dust	24–26	Air mass crossed north west Africa ~3 days back
Biomass Burning	27–29	Convective boundary layer, upper back trajectories from southwestern north Africa, ~2–3 days back.
South Atlantic Tropical Marine	31–35	Trajectories over Atlantic Ocean from SSE, most > 6 days from continental influence.
South Atlantic Temperate Marine	36–39	Trajectories became more elongated and to the west but remained over the Southern Atlantic Ocean, >6 days from continental influence.
INDOEX[b,c]		
SHmX	42–46	Elongated trajectories over the southern Indian and Atlantic Oceans, > 6 days marine influence, 34°S–30°S.
ShmE	47–58	Southeasterly trade winds from the Indian Ocean, >6 days marine influence, 30°S–1°N.
NHcT-Sri Lanka	58–59	Enter ITCZ, trajectories from the southeastern tip of India, 2–4 days prior continental influence.
NHcT-Bengal 1	63–65	Trajectories from north east coast of India over Bay of Bengal then over southern tip of India, continental influence 2–4 days back.
NHcT-w	65–67	Boundary layer air from the west coast of India to the Arabian Sea for 2–3 days prior continental influence.
NHcX	68–70	Trajectories from Persian Gulf area, 3–4 days continental influence.
NHc	71–75	Low-level trajectories from Persian Gulf mixed with upper level Indian continental subsidence influence, 2–4 days prior continental influence.
NHmE	76–80	Trajectories from mid eastern Indian Ocean, >6-day prior continental influence.
NHcT-Bengal 2	81, 85–86	Mixture of boundary layer Arabian Sea air mixed with mid-eastern Indian continental air 4–5 days back.
NHcT- Bengal 3	87–89	Trajectories from the mid-eastern shore of India to Bay of Bengal 2–3 days back.

[a] *Bates et al.* [2001].
[b] *Ball et al.* [2003].
[c] *Wisthaler et al.* [2002].

potential biomass and fossil fuel markers, they determined that the major source of carbonaceous aerosols was fossil fuel combustion. *Ramanathan et al.* [2001] note the size distribution of EC in the Northern Hemisphere is 3 to 5 fold larger than that reported for fresh engine exhaust and up to twice as large as the reported size distribution in the ambient Los Angeles air basin [*Kleeman et al.*, 2000, 1997]. *Leon et al.* [2001] measured columnar aerosol optical thickness at inland (Dharwar) and coastal sites (Goa University) in India. These measurements combined with the reported density of forest fires suggest that biomass burning contributes significant quantities of soot the Northern Indian Ocean Atmosphere. *De Gouw et al.* [2001] measured trace gas concentrations aboard the Citation aircraft and calculated emission factors that were consistent with biomass burning, suggesting this as the dominant source of gaseous pollutants. *Guazzotti et al.* [2003] employed a single particle mass spectrometer aboard the R/V *Ronald Brown* to measure various elements, including K, Li, S, and C moieties to decipher the source of carbonaceous particles over the Northern Indian Ocean. Using K^+ as a biomass-burning marker, the authors concluded that the dominant source of carbonaceous particles to the Northern Hemisphere Indian Ocean atmosphere was biomass burning. *Dickerson et al.* [2002] compiled an emission inventory for South Asia and concluded that biomass burning was the larger source, but that known emission factors could not account for the high concentrations of EC observed.

[6] Aerosols99 and INDOEX provide an opportunity to assess the anthropogenic impact of continentally derived PAHs on the marine atmosphere. The present study utilizes aerosol samples taken aboard the R/V *Ronald Brown* during the three-month cruise through the Atlantic and Indian Oceans. This study provides a current assessment of the spatial distribution of particulate phase PAHs in the marine atmosphere during the Northern Hemisphere winter of 1999. In addition, in the Northern Indian Ocean atmosphere the ancillary parameters EC, non-sea salt potassium ($nssK^+$) and non-sea salt sulfate ($nssSO_4^{-2}$) are used to provide further insight into the sources of particulate phase PAHs. This study provides additional organic speciation of marine aerosol in pristine and coastally impacted areas of the world and further probes the possible sources of carbonaceous aerosol in the Northern Indian Ocean atmosphere.

2. Experiment

[7] Sample collection has been described elsewhere [*Ball et al.*, 2003] and only briefly discussed here. Aerosol samples were collected using a high-volume Sierra Instruments bulk sampler located atop a 10 m tower ~15 m above the sea surface [*Ball et al.*, 2003]. The 20 by 25 cm Whatman 41 filters were removed from the filter head, placed in polypropylene bags and refrigerated. Sampling was stopped when wind speeds were below 3 m/s or when the wind arriving at the samplers was from the direction of the ship to avoid local contamination. Upon returning to the laboratory, filters were sub-sampled (~1/10) and sealed in individual polyethylene bags and placed in the freezer (approximately −20°C) until analysis. Field blanks (n = 4) were created by exposing the filter substrate to ambient air in the field, then sealing and storing the filters in a similar manner as the aerosol samples. Laboratory blanks (n = 4) were defined as filter substrate handled in a similar manner as the field samples without exposure to ambient air in the field. The analytical methods for the determination of OC, EC, $nssSO_4$ and $nssK^+$ have been previously published [*Ball et al.*, 2003].

[8] For PAH analysis each filter sub-sample (see below) was placed in a pre-rinsed (dichloromethane) 20 ml tube with 15 ml of dichloromethane, sealed with a Teflon lined lid and sonicated for 30 min. The samples were then stored in the dark at −20°C for 48 h. Prior to sonication 100 μl of surrogate solution containing ~1000 ng/ml of fluoranthene-

Table 2. Hemispheric Distribution of PAHs in the Atlantic and Indian Oceans

		Atlantic NH (n = 11)			Atlantic SH (n = 13)			Indian SH (n = 18)			Indian NH (n = 39)		
	DL[a] (n = 8)	Mean[b]	Std	% >DL[c]	Mean	Std	% >DL	Mean	Std	% >DL	Mean	Std	% >DL
Fluoranthene	2.3	3.0	1.5	17	2.8	1.9	8	2.5	0.75	6	25	19	85
Pyrene	1.4	2.3	1.6	25	1.5	0.4	8	1.5	0.37	6	22	18	95
9,10-Dimethylanthracene	18	22	9.6	17	30	34	23	19	4.7	6	18	0.44	3
Benzo[*a*]fluorene	0.53	0.59	0.21	8	0.6	0.24	8	0.67	0.46	11	2.0	1.6	62
Benzo[*b*]fluorene	0.33	0.40	0.18	17	<DL	–	–	0.63	0.83	17	1.0	0.81	54
Benz[*a*]anthracene	3.8	<DL[d]	–	–	8.7	16	15	<DL	–	–	5.1	3.1	18
Cyclopenta[*cd*]pyrene	3.3	<DL	–	–	7.9	11	15	<DL	–	–	5.8	7.7	26
Chrysene + Triphenylene	7.9	11	12	8	15	14	23	<DL	–	–	16	13	33
Naphthacene	1.0	<DL	–	–	1.3	0.87	15	<DL	–	–	1.7	3.5	10
Retene	5.0	<DL	–	–	5.1	0.00	0	<DL	–	–	6.9	4.3	18
Benzo[*b*]fluoranthene	0.70	4.0	3.1	67	2.4	5.5	10	7.4	8.0	67	24	27	64
Benzo[*k*]fluoranthene	0.58	1.6	2.2	25	0.91	1.0	10	2.3	2.6	40	15	16	64
Benzo[*e*]pyrene	1.0	3.7	2.7	50	2.5	1.9	46	3.6	4.8	33	17	14	92
Benzo[*a*]pyrene	1.6	3.3	1.9	50	2.0	1.7	8	4.2	6.2	17	24	20	87
Perylene	2.7	2.9	0.85	8	<DL	–	–	<DL	–	–	3.4	1.7	18
Dimethylbenz[*a*]anthracene	4.9	<DL	–	–	<DL	–	–	<DL	–	–	5.5	2.6	8
3-Methylcholanthrene	4.1	<DL	–	–	<DL	–	–	<DL	–	–	10	11	36
Indeno[1,2,3-*cd*]pyrene	0.64	1.1	1.1	17	<DL	–	–	<DL	–	–	18	17	95
Benzo[*ghi*]perylene	0.66	1.9	2.1	25	0.97	1.1	8	1.2	1.1	17	17	15	100
Anthanthrene	0.53	<DL	–	–	<DL	–	–	0.96	1.8	6	1.6	1.3	49
Dibenz[*ah* + *ac*]anthracene	1.0	<DL	–	–	<DL	–	–	<DL	–	–	1.3	0.70	13
Coronene	0.45	0.65	0.68	8	<DL	–	–	0.57	0.41	11	8.1	7.4	90

[a] Detection Limit see text.
[b] Arithmetic mean.
[c] Percent greater than reporting limit.
[d] Concentrations in pg/m^3.

d_{12} and perylene-d_{12} was added to each tube. The extracts were concentrated under dry N$_2$ to $\sim$100 μl. 100 μl of injection internal standard containing $\sim$1000 ng/ml of acenapthene-d_{10}, phenanthrene-d_{10}, benzo[*a*]anthracene-d_{12}, benzo[*a*]pyrene-d_{12} and benzo[*ghi*]perylene-d_{12} was then added to each extract just prior to injection.

[9] Samples were quantified using an Agilent Technologies 6890/5973 gas chromatograph/mass spectrometer in electron ionization mode equipped with a Programmable Temperature Vaporization (PTV) large volume injector and a 30m × 0.25 mm i.d. with a 0.25 μm film thickness DB-5 GC Column (J & W Scientific, Inc. Folson, CA). 25 μl of each extract was injected using the pulsed splitless mode with an injector temperature program of 50°C for 1 min, then ramped to 250°C at 600°C/min and held for the duration of the run. The oven temperature program was held at an initial temperature of 40°C for 1 min, then ramped to 280°C at 10°C/min followed by a 5°C/min ramp to a final temperature of 310°C and held for 10 min. Compounds were identified and quantified using authentic standards based on retention time and ion fragmentation in selective ion monitoring mode.

[10] A series of field and laboratory blanks consisting of identical filter substrate were stored, processed and analyzed in parallel with the particulate matter samples collected during the Aerosols99 and INDOEX cruises. Background contamination of the filters was defined as the mass detected/100 m^3, as the mean volume collected in the samples was 1000 m^3 and $\sim$1/10 of the total filter was analyzed. Using this method, the blank values for the filters ranged from not detected (ND) for benzo[*ghi*]perylene to 6 pg/m^3 for 9, 10-dimethylanthracene. Instrumental detection limits (IDL), using the methods described above, were $\sim$0.1 pg/m^3 for each of the PAHs quantified. Table 2 displays the reporting limits (DL) for the PAHs analyzed in this study. We define the reporting limits as the greater of 3 times the instrumental limit or mean blank value. The mean surrogate recoveries ranged 70–98% and 91–117% for fluoranthene-d_{12} and perylene-d_{12} with mean (arithmetic mean ± 1 standard deviation) recoveries of 84 ± 4.0% and 108 ± 4.5%, respectively.

3. Results and Discussion

3.1. Hemispheric Marine Polycyclic Aromatic Hydrocarbons (PAH) Distribution

[11] PAH concentrations for the air regimes identified in Table 1 are compiled into Southern and Northern Atlantic and Indian Oceans categories in Table 2. PAH concentrations were infrequently above reporting limits for samples from the Northern and Southern Atlantic Ocean and the Southern Indian Ocean atmospheres. Mean values (Table 2) were calculated using the measured values, if above reporting limits, or the reporting limit value (DL in Table 1) if below. Particulate phase PAH concentrations are similar between the Northern and Southern Atlantic and Southern Indian Oceans' atmospheres.

[12] In the Northern Hemisphere Atlantic Ocean, benzo[*b*]fluoranthene concentrations were the most frequently above reporting limits (4.0 ± 3.1 pg/m^3, 67% of the samples collected), while benz[*a*]anthracene, cyclopenta[*cd*]pyrene, chrysene+triphenylene, naphthacene, retene, dimethylbenz[*a*]anthracene, 3-methylcholanthrene, anthanthrene and dibenz[*ah*+*ac*]anthracene were below reporting limits in all samples collected. Benzo[*a*]pyrene and benzo[*e*]pyrene concentrations were above reporting limits in 50% of the samples collected for this region. In the Southern Hemisphere of the Atlantic Ocean benzo[*e*]pyrene concentrations were above reporting limits in the greatest number of

samples (46%). Benzo[*b*]fluorene, perylene, dimethylbenz[*a*]anthracene, 3-methylcholanthene, indeno[1,2,3-*cd*]pyrene, anthanthrene, dibenz[*ah*+*ac*]anthracene and coronene concentrations were not above reporting limits in any of the samples collected in this region.

[13] The lowest number of PAHs above reporting limits was found in the Southern Hemisphere Indian Ocean atmosphere. Twelve of the 22 PAHs analyzed were below reporting limits. Conversely, in the Northern Hemisphere Indian Ocean atmosphere all PAHs analyzed were above reporting limits for at least one of the samples. Concentrations for 5 PAHs (pyrene, benzo[*e*]pyrene, indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and coronene) were above reporting limits in 90+% of the samples. PAH concentrations in the Atlantic Ocean and southern Indian Ocean atmospheres were above detection limits a similar percentage of time and the concentrations were not statistically different. Therefore these three regions appear to represent a consistent marine background particulate phase PAH concentration.

[14] Indeno[*cd*-1,2,3]pyrene and benzo[*ghi*]perylene concentrations in the Atlantic and Southern Indian Ocean atmospheres are consistent with levels found in the Canadian Arctic during the summer of 1993 when Pacific marine air dominated the sampling period (<1.8 and 3 pg m^{-3}, respectively) [*Halsall et al.*, 1997]. They were lower than continental remote levels measured at Siskiwit Lake ~200 km from urban influence (6 and 4 pg m^{-3}, respectively) [*McVeety and Hites*, 1988] and estimated marine background levels (2.5 and 4.1 pg m^{-3}, respectively) [*NRC*, 2003]. Although PAH analysis of the remote marine atmosphere (Atlantic Ocean and Southern Indian Ocean) were close to the reporting limits of this study, we propose that these results are the most recent 'conservative' estimate of marine particulate PAH concentrations extending our knowledge of the remote marine atmosphere PAH burden.

[15] In contrast, PAH concentrations in the Northern Hemisphere Indian Ocean were an order of magnitude greater than the other three regimes (Table 2). The concentrations of benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene were five fold greater in the Northern Hemisphere Indian Ocean atmosphere than air masses influenced 2–4 days back by North America (4.5 and 4.4 pg/m^3, respectively, data not shown). This is consistent with a five fold greater concentration of EC in the northern Indian Ocean atmosphere compared to the Northern Atlantic [*Bates et al.*, 2001]. Fluoranthene and pyrene concentrations for the tropical Atlantic Ocean (23 and 11 pg/m^3, respectively) [*Marty et al.*, 1984] were four times greater than values reported here for the Northern Hemisphere Indian Ocean. Baltic Sea aerosols collected in 1983 contained 3 orders of magnitude more benzo[*ghi*]perylene (5.0–48 ng/m^3) [*Halkiewicz et al.*, 1987] than those in the Northern Indian Ocean atmosphere. These elevated values may be due to the large quantities of lignite used in Eastern Europe. In contrast, particulate phase PAH concentrations 85 km northeast of Stockholm in the Swedish Baltic coast atmosphere were approximately five times higher than those in the Northern Indian Ocean atmosphere (110 and 70 pg/m^3 for indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene, respectively) [*Broman et al.*, 1991]. Concentrations of coronene, benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene near Lakes Superior and Erie averaged 10 ± 84, 13 ± 77, and 15 ± 82 pg/m^3, respectively [*Cortes et al.*, 2000], which are similar to the mean values for the Northern Hemisphere Indian Ocean atmosphere. In the Russian Arctic, *Halsall et al.* [1997] found concentrations of benzo[*ghi*]perylene and indeno[1,2,3-*cd*]pyrene (61 ± 42 and 48 ± 34 pg/m^3, respectively) consistent with the northern Indian Ocean atmosphere. The Arctic wind regimes were influenced by industrial areas in the northern and western regions of Siberia (3000 km upwind) that contained large industrial areas impacted by severe combustion-derived pollution [*Halsall et al.*, 1997].

[16] Lake Michigan aerosol particles, collected 20 km northeast of Chicago contained ~20-fold higher benzo[*ghi*]perylene than the Northern Indian Ocean atmosphere [*Simcik et al.*, 1999]. Background levels of particulate phase chrysene (56 pg/m^3, assuming 40% total concentration on the particle) [see *Fraser et al.*, 1998, Figure 2] measured on San Nicolas Island, ~100 km off the coast of Southern California, USA in 1993 were 3 fold above the northern Indian Ocean atmosphere values. PAH concentrations in Chesapeake Bay aerosol collected ~40 km from Baltimore, MD (~10 pg/m^3 for indeno[1,2,3-*cd*]pyrene and benzo[*ghi*]perylene) [*Offenberg and Baker*, 1999] were approximately one half levels in the Northern Hemisphere of the Indian Ocean atmosphere. *Baker and Eisenreich* [1990] found levels of these two PAHs (13 and 16 pg/m^3, respectively) over Lake Superior similar to the Indian Ocean Northern Hemisphere.

[17] There are a limited number of particulate phase PAH concentrations reported for the Indian sub-continent. *Rao et al.* [1982] found levels of benzo[*a*]pyrene in an urban (Matunga) and a suburban (Deonar) region of Bombay (14.7–2.6 and 0.3–1.3 ng/m^3, respectively) that were several orders of magnitude above the Northern Indian Ocean atmosphere concentrations (Table 2). *Kulkarni and Venkataraman* [2000] measured the size distribution of PAHs at two locations in Mumbai (formerly Bombay), India. Again, benzo[*a*]pyrene and indeno[1,2,3-*cd*]pyrene were orders of magnitude greater than values reported here for the Northern Indian Ocean atmosphere (~2 ng/m^3 each). The highest benzo[*ghi*]perylene concentration (58 ng/m^3) in India (Calcutta) was reported by *Chakraborti et al.* [1988]. Particulate phase PAH concentrations in rural Lahore, Pakistan (indeno[1,2,3-*cd*]pyrene >11 ng/m^3) [*Smith and Harrison*, 1996] were similar to Bombay values and 2 orders of magnitude above concentrations found in the Northern Indian Ocean atmosphere.

3.2. Sources of Particulate Phase PAHs to the Northern Indian Ocean

[18] The elevated particulate phase PAH concentration in the northern Indian Ocean atmosphere allows for further analysis of possible PAH sources using concurrent measurements of SO_4^{2-}, organic carbon (OC), black carbon (EC) and K^+ [*Ball et al.*, 2003]. K^+ has been used as a source marker for biomass burning [*Cachier and Ducret*, 1991]. Non-sea salt SO_4^{2-} is formed from the oxidation of SO_2 and has been used extensively as a marker for coal combustion [*Huang et al.*, 2001] but care must be taken when using this marker for India-derived aerosols as significant quantities of SO_2 are emitted from biomass and biofuel combustion [*Reddy and

Table 3. Wind Regime Particulate PAHs and Ancillary Measurements in the Northern Indian Ocean Atmosphere[a]

	NHcT-Sri Lanka (n = 2)	NHcT-Bengal 1 (n = 5)	NHcT-w (n = 6)	NHcX (n = 7)	NHc (n = 8)	NHcT-Bengal 2 (n = 4)	NHcT-Bengal 3 (n = 4)
Fluoranthene[b]	45 ± 12[c]	50 ± 22	45 ± 25	15 ± 4.5	24 ± 8.6	26 ± 13	34 ± 20
Pyrene	38 ± 8.1	48 ± 20	41 ± 25	12 ± 3.9	22 ± 7.4	18 ± 11	29 ± 18
9,10-Dimethylanthracene	–[d]	–	–	–	18 ± 1.0	–	–
Benzo[*a*]fluorene	3.8 ± 0.7	4.3 ± 1.3	3.2 ± 1.8	1.1 ± 0.5	1.8 ± 1.0	1.9 ± 1.1	2.3 ± 2.2
Benzo[*b*]fluorene	2.0 ± 0.4	2.2 ± 0.7	1.8 ± 0.9	0.45 ± 0.24	0.93 ± 0.66	1.1 ± 0.6	1.1 ± 0.9
Benz[*a*]anthracene	6.0 ± 3.1	11 ± 4.8	7.5 ± 5.8	–	4.3 ± 1.4	5.2 ± 2.8	–
Cyclopenta[*cd*]pyrene	5.6 ± 3.3	9.9 ± 4.7	6.8 ± 5.7	–	5.3 ± 3.1	15 ± 23	–
Chrysene + Triphenylene	30 ± 5.5	39 ± 14	26 ± 21	–	9.4 ± 4.4	14 ± 8.2	22 ± 18
Naphthacene	1.5 ± 0.7	–	–	1.5 ± 1.4	–	6.5 ± 11	–
Retene	–	6.4 ± 3.1	6.2 ± 2.8	–	6.8 ± 4.9	10 ± 1.0	12 ± 7.6
Benzo[*b*]fluoranthene	55 ± 3.6	42 ± 40	37 ± 31	8.2 ± 14	16 ± 14	22 ± 22	39 ± 39
Benzo[*k*]fluoranthene	35 ± 3.7	28 ± 26	22 ± 20	3.9 ± 5.0	13 ± 14	13 ± 14	18 ± 15
Benzo[*e*]pyrene	29 ± 5.7	39 ± 14	31 ± 19	6.9 ± 4.1	16 ± 5.3	16 ± 12	23 ± 11
Benzo[*a*]pyrene	36 ± 2.2	50 ± 18	38 ± 26	4.3 ± 5.0	21 ± 8	41 ± 22	28 ± 21
Perylene	–	4.6 ± 1.8	3.8 ± 1.8	–	3.9 ± 2.4	4.4 ± 3.4	–
Dimethylbenz[*a*]anthracene	–	–	6.6 ± 4.3	6.4 ± 4.0	6.4 ± 4.5	–	–
3-Methylcholanthrene	–	12 ± 11	8.0 ± 6.4	13 ± 12	14 ± 13	6.2 ± 4.3	15 ± 22
Indeno[1,2,3-*cd*]pyrene	34 ± 0.9	46 ± 16	36 ± 22	6.6 ± 4.2	16 ± 5.2	16 ± 12	23 ± 15
Benzo[*ghi*]perylene	28 ± 2.1	41 ± 16	35 ± 21	6.5 ± 4.5	15 ± 4.9	16 ± 12	22 ± 13
Anthanthrene	2.6 ± 0.2	3.2 ± 1.2	3.1 ± 1.8	0.69 ± 0.42	1.4 ± 0.7	1.4 ± 1.2	1.7 ± 1.6
Dibenz[*ah*+*ac*]anthracene	1.7 ± 1.0	2.7 ± 1.1	1.8 ± 1.2	–	–	–	–
Coronene	12 ± 0.3	20 ± 7.3	17 ± 9.8	3.2 ± 2.2	7.1 ± 2.5	7.2 ± 5.1	11 ± 6.4
OC[e]	1.0 ± 1.0	1.4 ± 0.25	1.3 ± 0.81	0.65 ± 0.18	1.3 ± 0.92	0.57 ± 0.28	0.54 ± 0.11
EC[e]	0.26 ± 0.07	1.8 ± 0.32	0.98 ± 0.49	0.21 ± 0.09	0.71 ± 0.4	0.41 ± 0.16	0.50 ± 0.18
K^{+}[e]	0.06 ± 0.06	0.35 ± 0.17	0.23 ± 0.14	0.01 ± 0.01	0.20 ± 0.06	0.13 ± 0.12	0.16 ± 0.04
SO_4^{-2}[e]	3.2 ± 1.7	8.0 ± 0.33	6.3 ± 2.7	1.3 ± 0.25	3.2 ± 0.94	2.10 ± 1.74	1.4 ± 1.3

[a] See Table 1 for nomenclature.

[b] Concentrations in pg/m^3.

[c] 1 Standard deviation.

[d] Below reporting limits in all samples.

[e] Concentrations in μg/m^3 *Ball et al.* [2003].

Venkataraman, 2002]. Elevated OC/EC ratios have been used as a marker for the production of secondary organic carbon [*Turpin and Huntzicker*, 1995]. In contrast, long-range transport may include the selective depletion/deposition of OC with respect to EC noted by *Lim et al.* [2003] in bulk particulate matter. The ratio of EC/OC also appears to change dramatically with the size and conditions of biofuel cooking fires (C. Venkataraman, personal communication 2003), making this ratio less useful in distinguishing fossil fuel from biomass/biofuel combustion.

[19] Various wind regimes were identified along the cruise transect (Figure 1). The origins and labels for the Northern Hemisphere Indian Ocean (Table 1) were determined using meteorological parameters and 6-day back trajectories at various altitudes using HYSPLIT from the ship's position for 0000, 0600, 1200 and 1800 UTC [*Bates et al.*, 2001; *Ball et al.*, 2003; *Wisthaler et al.*, 2002]. The elevated levels of PAHs in the Northern Hemisphere Indian Ocean allow for a comparison of the various wind regimes with respect to air mass origins identified in Table 3.

[20] The total PAH (tPAH) concentration in the particulate phase for the continentally impacted (<6 days prior continental influence) northern Indian Ocean regimes, described above, was significantly correlated (Figure 2) with EC ($R^2 = 0.42$, $p < 0.01$), SO_4^{2-} ($R^2 = 0.62$, $p < 0.01$) and K^+ ($R^2 = 0.34$, $p < 0.01$). tPAH was less correlated with organic carbon ($R^2 = 0.15$, $p = 0.052$), indicating an alternative OC source or reaction pathway such as secondary organic aerosol production. Although OC is also emitted in combustion and was strongly correlated with EC [*Ball et al.*, 2003], the lower correlation between t-PAH and OC suggests that either the OC content is not solely indicative of the PAH sources or that the production of PAHs and OC do not co-vary with respect to EC, suggesting changing combustion sources during the sampling campaign in the northern Indian Ocean atmosphere.

[21] The particulate phase PAH samples from the Northern Indian Ocean atmosphere were categorized according to previously defined meteorological regimes (Table 1). The samples will be identified either by wind regime and/or the Julian day of the year (DOY) they were collected. For the first portion of the Northern Indian Ocean sampling, the NHcT-Sri Lanka, NHcT-Bengal, NHcT-w (DOY 58–59, 63–65 and 65–67, respectively) and NHcT-Bengal 2 and 3 (DOY 81, 85–86 and 87–89, respectively) were combined based similar PAH profiles. Selected PAHs (indeno [1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and coronene) were then correlated with the aforementioned ancillary parameters. These PAHs were chosen based their low volatility (>95% on the particle phase) and stability relative to the 2 to 6 day transport time from the continent to the ship. As the vessel crossed the Indian Ocean ITCZ, the particulate phase samples from the first set of continentally impacted meteorological regimes (DOY 58–67) exhibited poor correlations ($p > 0.1$) between the selected PAHs and EC, OC, K^+ and SO_4^{-2}. Similarly, as the vessel entered the NHcX meteorological regime (DOY 68A - 70) indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and coronene were not significantly correlated with K^+ and SO_4^{-2}. Only two OC and EC values were reported for this regime,

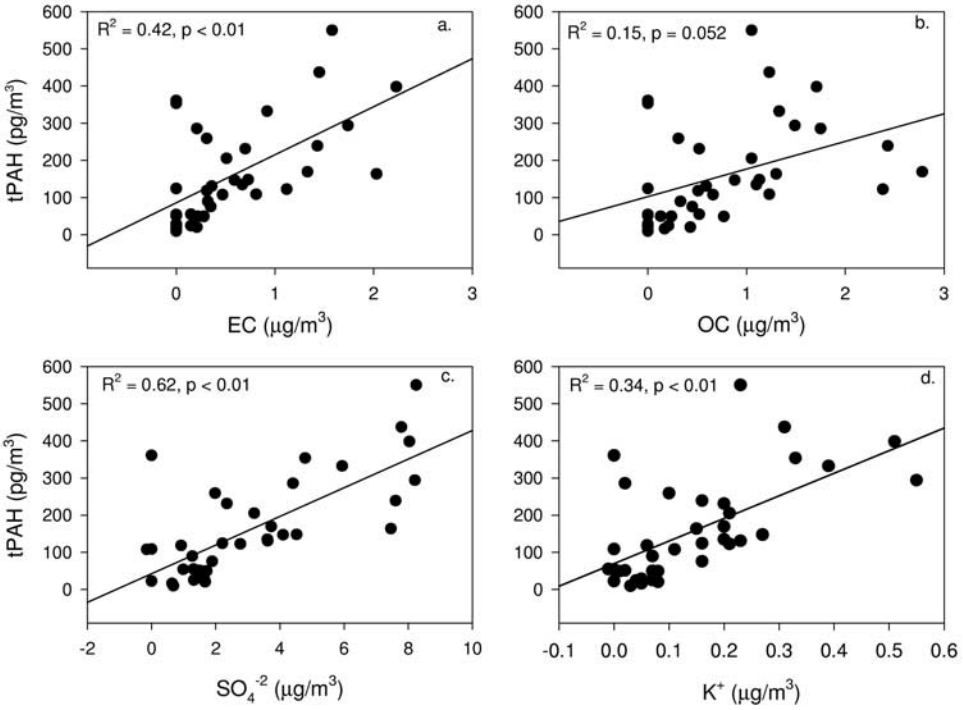

Figure 2. Sum of all PAHs detected in the Northern Hemisphere Indian Ocean aerosols continentally influenced <6 days sampling versus (a) EC, (b) OC, (c) SO_4^{-2} and (d) K^+. Specifically, NHcT-Sri Lanka, NHcT-Bengal 1, 2 and 3, NHcX and NHcT-w meteorological regimes (See Table 1 for description of regimes).

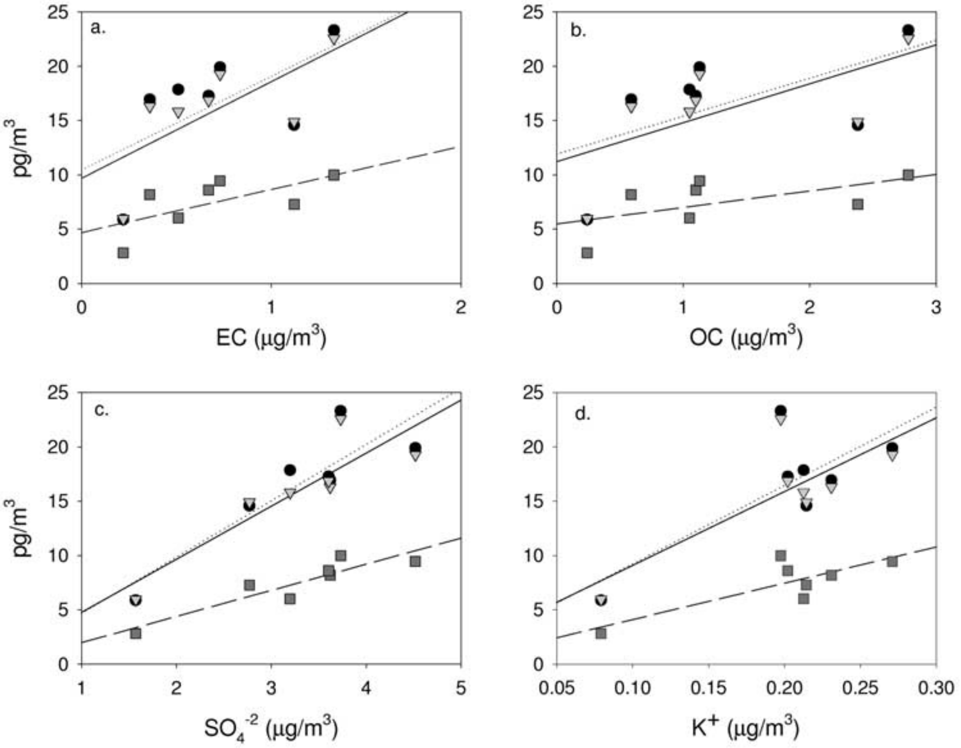

Figure 3. NHc meteorological regime plots of indeno[1,2,3-*cd*]pyrene (solid circles), benzo[*ghi*]perylene (triangles) and coronene (squares) versus (a) EC, (b) OC, (c) SO_4^{-2} and (d) K^+. The selected PAHs were highly correlated with SO_4^{-2} (R^2 = 0.77, 0.77 and 0.83, respectively, $p < 0.01$) and to a lesser extent K^+ (R^2 = 0.61, 0.61 and 0.66, respectively, $p < 0.05$). The selected PAHs were not significantly correlated with EC (R^2 = 0.40, 0.48 and 0.42, respectively) or OC (0.35, 0.41 and 0.32, respectively).

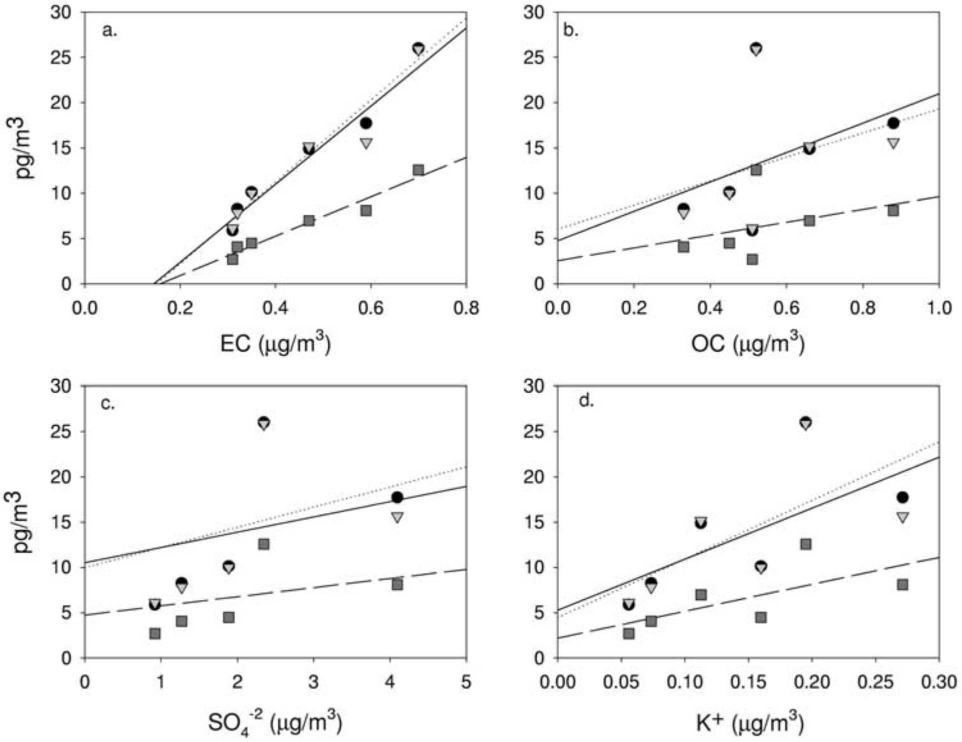

Figure 4. Plots of NHcT Bengal 2 and 3 meteorological regime indeno[1,2,3-*cd*]pyrene (solid circles), benzo[*ghi*]perylene (triangles) and coronene (squares) versus (a) EC, (b) OC, (c) SO_4^{-2} and (d) K^+. All PAHs were highly correlated with EC (R^2 = 0.96, 0.92, 0.94, respectively, $p < 0.01$). The selected PAHs were not correlated with K^+ (R^2 = 0.50, 0.40, and 0.45, respectively), SO_4^{-2} (R^2 = 0.18, 0.12 and 0.17, respectively) or OC (R^2 = 0.18, 0.13, and 0.15, respectively).

therefore using these combustion markers is not informative. Trace gas measurements [*Wisthaler et al.*, 2002] and back trajectories suggest that PAHs in this regime mainly originate from fossil fuel combustion in the Arabian Peninsula. The poor correlation between these PAHs and the biomass and industrial markers is consistent with combustion of low sulfur content fossil fuel such as petroleum.

[22] The next regime (NHc-mixed regime, DOY 71 – 75P) exhibited a strong correlation (Figure 3) between indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, coronene and K^+ (R^2 = 0.61, 0.61 and 0.66, respectively where $p < 0.05$) and SO_4^{2-} (R^2 = 0.77, 0.77 and 0.83, respectively where $p < 0.01$). This supports a mixed biomass/fossil fuel component to these non-volatile, stable PAHs similar to the trace gas measurements by *Wisthaler et al.* [2002].

[23] As the vessel entered the last continentally impacted regions, (DOY 81–89) an increase in the concentration of retene (Table 3) was observed, a suggested marker for softwood combustion [*Fine et al.*, 2001]. Indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene and coronene were strongly correlated (Figure 4) to EC (R^2 = 0.96, 0.92, 0.94, respectively, where $p < 0.01$). Indeno[1,2,3-*cd*]pyrene, benzo[*ghi*]perylene, coronene were not correlated with K^+ (R^2 = 0.50 p = 0.12, R^2 = 0.40 p = 0.12, R^2 = 0.45 p = 0.14, respectively) or SO_4^{2-} (R^2 = 0.18 p = 0.39, R^2 = 0.12 p = 0.51, R^2 = 0.17 p = 0.42, respectively). Also of note is the elevated correlation between EC and K^+ in this regime (R^2 = 0.59, p = 0.07), which supports an increased influence of biomass combustion on the EC and particle PAH burden in this regime.

3.3. Indeno[1,2,3-cd]pyrene/EC Ratio as a Source Marker

[24] The use of PAHs as source markers for aerosol particles has its limitations, especially when the organic matrix of the particle population ages during long-range transport. Because of the varying degrees of chemical degradation among the PAHs, caution must be taken when inferring PAH profiles from previous source studies. As mentioned above, the OC fraction was less significantly correlated with t-PAHs than was EC for the continentally influenced Northern Indian Ocean atmosphere. *Venkataraman and Freidlander* [1994a] employed reactivity normalized PAHs and EC in conjunction with a chemical mass balance approach to apportion particulate phase PAHs to automobile emissions and meat cooking in Los Angeles CA. Gas and particulate phase PAHs have been used in multivariate source apportionment models by *Simcik et al.* [1999] and *Larsen and Baker* [2003] in urban areas close to PAH emission sources. *Harrison et al.* [1996] used a combination of PAHs and metals to allocate the sources of PAH burden on ambient aerosol. This study is quite different in that the aerosol transport time (2–5 days) allows photochemical reactions to alter the organic composition and alters the PAH profile with respect to the reactivity and volatility of the PAHs studied.

Table 4. Elemental Carbon Normalized Indeno[1,2,3-*cd*]Pyrene Concentrations in the Northern Hemisphere Indian Ocean Atmosphere, Calculated Values from Source Studies and Ambient Measurements

Source	IND/EC, μg/g	References
	Vehicles	
Catalytic converter	590	*Schauer et al.* [2002]
Non-catalytic converter	11,000	*Schauer et al.* [2002]
Diesel 1	2.9	*Rogge et al.* [1993]
Diesel 2	12	SRM 1650
Diesel 3	2.0	SRM 2975
	Biomass/Biofuel Combustion	
Southern U.S. trees	2,000	*Fine et al.* [2001]
Mixed wood	30,000	*Hays et al.* [2002]
Coconut leaves	1,200	*Sheesley et al.* [2003]
Cow dung patties	2400	
Rice Straw	320	*Sheesley et al.* [2003]
Biomass Briquette	17,000	*Sheesley et al.* [2003]
Jackfruit	1,000	*Sheesley et al.* [2003]
	Fossil Fuels Stationary Sources	
Coal	700–16,000	*Oros and Simoneit* [2000] and *Reddy and Venkataraman* [2002]
Distillate Oil No. 2	0.3–0.7	*Rogge et al.*, [1997]
	Ambient	
Caldecott Tunnel, Berkley, CA	60	*Venkataraman and Friedlander* [1994a, 1994b]
Sepulveda Tunnel, Los Angeles, CA	480	*Venkataraman and Friedlander* [1994a, 1994b]
Chicago	600 ± 330	*Simcik et al.* [1999]
Lake Michigan	1100 ± 1000	*Simcik et al.* [1999]
Lahore, Pakistan	600–700	*Smith et al.* [1996]
	This Study	
DOY 58–59	140 ± 38	
DOY 63–89	27 ± 10	

[25] To minimize the effect of photo-degradation of the more reactive, semi-volatile PAHs (i.e., cyclopenta[*cd*]pyrene and benzo[*a*]pyrene) one of the least reactive PAHs, indeno[1,2,3-*cd*]pyrene (half-life >800 days) [*Nielsen*, 1984; *Finlayson-Pitts and Pitts*, 2000, and references therein] was chosen as a representative marker for combustion. Secondly, a recent study has found the selective depletion of OC with respect to EC in aerosol over the Pacific Ocean [*Lim et al.*, 2003]. Owing to the stability and co-emission of both indeno[1,2,3-*cd*]pyrene and black carbon, this ratio may give further insight into the sources of particulate PAHs in the Northern Hemisphere of the Indian Ocean. Therefore we have calculated indeno[1,2,3-*cd*] pyrene/EC ratios from various literature source studies (Table 4) including biomass/biofuel combustion, vehicular emissions (diesel and gasoline), and stationary fossil fuel sources to elucidate the potential sources of PAHs and EC to the northern Indian Ocean atmosphere.

3.3.1. Vehicular Emissions

[26] *Schauer et al.* [2002] measured the PAH profiles of emissions from automobiles with and without catalytic converters. Catalyst-equipped vehicles emitted 7.5 mg/km of particulate matter (PM) and 10% of the PM mass was EC. The indeno[1,2,3-*cd*]pyrene emission rate was 0.44 μg/km, resulting in an indeno[1,2,3-*cd*]pyrene/EC ratio of 590 μg/g EC (Table 4). Comparable data from non-catalytic converter equipped vehicles (590 mg/km of PM, 1.4% EC and 92 μg/km of indeno[1,2,3-*cd*]pyrene [*Schauer et al.*, 2002]) result in an indeno[1,2,3-*cd*]pyrene/EC ratio of 11,000 μg/g (EC). Indeno[1,2,3-*cd*]pyrene was not present in diesel exhaust above detection limits using similar sampling and analytical techniques. However, a maximum ratio can be calculated by normalizing the lowest reported value for indeno[1,2,3-*cd*]pyrene for the gasoline exhaust source test (0.47 μg/km; *Rogge et al.* [1993]) to the reported 160 mg/kg EC emission rate (40% of 410 mg/km PM reported). A maximum indeno[1,2,3-*cd*]pyrene/EC ratio in diesel exhaust is, therefore, 2.9 μg/g EC. A second diesel exhaust ratio can be determined using published indeno[1,2,3-*cd*]pyrene concentrations for the diesel exhaust Standard Reference Materials (SRM) distributed by the National Institutes of Standards and Technology, Gaithersburg, MD. For SRM 1650 the certified concentration of indeno[1,2,3-*cd*]pyrene is 5.62 mg/kg. *Gustafsson et al.* [2001] reported an EC content of 480 g/kg resulting in diesel concentration of 12 μg/g EC. Similarly SRM 2975 has an inden[*cd*]pyrene concentration of 1.4 mg/kg and an EC content of 680 g/kg [*Gustafsson et al.*, 2001] resulting in a ratio of 2.0 μg/g EC. These estimated concentrations are similar to the 27 ± 10 μg/g (EC) found in samples collected during days 63–89 and somewhat lower than DOY 58–59 (140 ± 38 μg/g EC).

3.3.2. Biomass/Biofuel Emissions

[27] Reported wood combustion emissions of PM (3g/kg), EC (10%) and indeno[1,2,3-*cd*]pyrene (2 mg/g) by *Fine et al.* [2001] for 5 species of southern United States trees result in an indeno[1,2,3-*cd*]pyrene ratio of ∼2000 μg/g, ∼1 to 2 orders of magnitude above the results presented here for continentally derived Indian aerosols. A calculation for mixed wood fuels from using data from *Hays et al.* [2002] (PM = 20 g/kg fuel, indeno[1,2,3-*cd*]pyrene = 0.0006% PM2.5, EC = 0.4 g/kg fuel) results in an indeno[1,2,3-*cd*]pyrene/EC ratio of 30,000 μg/g (EC). *Sheesley et al.* [2003] provide the best estimates of the indeno[1,2,3-*cd*] pyrene/EC ratios for South Asia biomass combustion sources. The authors performed controlled combustion experiments similar to *Hays et al.* [2002] using coconut leaves (1,200 μg/g), rice straw (320 μg/g), cowdung patties (2400 μg/g), biomass briquettes (17,000 μg/g) and jackfruit branches (1,000 μg/g) collected from various markets in Dhaka. Interestingly the rice straw indeno[1,2,3-*cd*]pyrene/EC ratio is only three times greater than that observed in the DOY 58–59 samples (140 μg/g EC).

3.3.3. Fossil Fuels Stationary Source Emissions

[28] *Rogge et al.* [1997] did not report indeno[1,2,3-*cd*]pyrene for the source characterization of industrial boiler distillate fuel No. 2 combustion. If we assume that a maximum value for the concentration of indeno[1,2,3-*cd*]pyrene is equal to the lowest PAH reported (1 pg/kJ), using the reported EC emission (5–13 μg/kJ PM where 29% is EC) the indeno[1,2,3-*cd*]pyrene/EC ratio is 0.3–0.7 μg/g EC. This concentration is on the lower edge of the calculated diesel values presented above.

[29] *Oros and Simoneit* [2000] were not able to detect indeno[1,2,3-*cd*]pyrene in the combustion of lignite, one of the major coals used in the northern portion of India [*Reddy and Venkataraman*, 2002]. Therefore the calculation was performed using indeno[1,2,3-*cd*]pyrene emissions from bituminous coal (158 mg/kg smoke) [*Oros and Simoneit*,

Table 5. Particulate Matter Chemical Speciation on the R/V *Anderson* During INDOEX

Sampling Apparatus	Analytes	Conclusions	Reference
ATOFMS[a] ($0.2 < Dp^b < 1.0$)	K, Li, sulfates, carbon	Using K containing particles as a marker, biomass/biofuel combustion accounts for ~74% of the carbonaceous aerosol observed in the northern Indian Ocean atmosphere	*Guazzotti et al.* [2003]
3 stage Berner Impactors, PSAP[c] ($0.18 < Dp < 10$ μm)	OC, EC, alkanes, PAHs, organic acids, particle absorption	Carboxylic acids from biomass/biofuel and secondary sources, alkanes exhibit anthropogenic signature, EC maximum $0.3 < Dp < 0.54$ μm, an important part of the OC is of secondary origin	*Neusüß et al.* [2002]
Anderson bulk aerosol sampler	PAHs, OC, EC, K, sulfate	A mixed biomass/biofuel/fossil fuel sources of PAHs observed, EC normalized indeno[1,2,3-*cd*]pyrene concentrations suggest fossil fuels (diesel) is the major source of EC	this study

[a] Aerosol time-of-flight mass spectrometer.
[b] Particle size range collected.
[c] Particle Soot Absorption Photometer.

2000] and assuming the smoke is essentially PM 2.5. From coal emissions estimates of PM (8.1 g/kg) and EC (0.08 g/kg and 1.83 g/kg for utilities and brick kilns respectively), the indeno[1,2,3-*cd*]pyrene concentration due to coal combustion is 16,000 and 700 μg/g EC for utilities and brick kilns, respectively.

3.3.4. Northern Indian Ocean Atmosphere

[30] The EC normalized indeno[1,2,3-*cd*]pyrene concentrations in the northern Indian Ocean atmosphere (22–140 μg/g EC, Table 4) suggest that the particulate matter measured in the NHcT regimes is more similar to vehicle emissions, specifically diesel or other combustion sources that have significantly lower indeno[1,2,3-*cd*]pyrene/EC ratios. Biomass/biofuel combustion is significantly enriched in indeno[1,2,3-*cd*]pyrene with respect to EC and does not resemble the ratios reported in this study (Table 4).

[31] In support of the calculated coal indeno[1,2,3-*cd*]pyrene/EC ratio, *Simcik et al.* [1999] found that the source contributions to PAHs in the Chicago atmosphere were coal, natural gas, coke and vehicles at 48%, 26%, 14% and 9%, respectively. The indeno[1,2,3-*cd*]pyrene/EC concentration was 600 ± 330 μg/g EC in the city and 1100 ± 1000 μg/g EC over Lake Michigan 20 km off the coast of Chicago (Table 4). An elevated indeno[1,2,3-*cd*]pyrene/EC ratio in the Chicago and Lake Michigan atmosphere may be due to the elevated contribution of coal combustion to the particulate PAH and EC in this area. *Venkataraman et al.* [1994] and *Venkataraman and Friedlander* [1994b] performed EC and PAH measurements in two California tunnels and found an EC normalized indeno[1,2,3-*cd*]pyrene ratio of 60 μg/g (EC) and 480 μg/g (EC) for Caldecott and Sepulveda Tunnels in Berkley and Los Angeles, California, respectively (Table 4). The greater abundance of diesel vehicles in the Caldecott compared to the Sepulveda Tunnel during this study is consistent with the lower measured indeno[1,2,3-*cd*]pyrene/EC ratio calculated above for diesel and results from the northern Indian Ocean atmosphere.

[32] The above calculations assume that the EC and indeno[1,2,3-*cd*]pyrene emission profiles from North America can be extrapolated to the Indian sub-continent. *Smith et al.* [1996] found indeno[1,2,3-*cd*]pyrene/EC ratios for Lahore, Pakistan of 600–700 μg/g EC. Urban, industrial and rural areas were sampled, where the rural area was ~20 km from the city. The authors cite a previous source apportionment study on the area using Principal Component Analysis [*Smith*, 1995] that indicated vehicular emissions were the dominant source of the higher molecular weight PAHs. Vehicular emissions in the city and industrial region would appear to be representative of the Indian sub-continent [*Dickerson et al.*, 2002, and references therein]. The Lahore vehicle fleet resembles the Indian fleet in the high number of two-stoke vehicles, and poor maintenance of roads and vehicles, but the indeno[1,2,3-*cd*]pyrene/EC ratio for this area is 5–30 fold above results presented here for the Northern Indian Ocean atmosphere. The authors note brick kilns heavily impact the rural area in this study. The indeno[1,2,3-*cd*]pyrene/EC concentration more resemble the coal values presented above and are orders of magnitude lower than the non-catalyst equipped values calculated in Table 4. The fact that the indeno[1,2,3-*cd*]pyrene/EC value is consistent among the rural, city and industrial cites in this study suggests that a regional signature (possibly coal) may dominant the indeno[1,2,3-*cd*]pyrene/EC ratio.

[33] Other authors have attempted to assign source strengths to the aerosol sampled during northern Indian Ocean cruise using different sampling techniques and source markers (Table 5). *Guazzotti et al.* [2003] reported that ~75% percent of carbon-containing particles from the Indian sub-continent were from biomass/biofuel combustion using a single particle mass spectrometer (SPMS). This instrument was calibrated to collect particles between 0.2 μm to 1.0 μm employing K^+ as a source marker for biomass combustion. Recently, *Kleeman et al.* [2000] measured the composition of particles emitted from non-catalyst equipped gasoline engines and found a trace bimodal (maximums at ~0.1 and 1.0 μm) K^+ component. The mass median aerodynamic diameter (MMAD) of indeno[1,2,3-*cd*]pyrene for biomass combustion is 0.4 μm accompanied by a MMAD for the PM emissions of 0.5–0.8 μm [*Venkataraman et al.*, 2002]. This is significantly larger than vehicular emission MMADs of 0.13 and 0.07 μm for indeno[1,2,3-*cd*]pyrene and 0.11 and 0.15 μm for EC measured at the Caldecott and Sepulveda Tunnels, respectively [*Venkataraman et al.*, 1994; *Venkataraman and Friedlander*, 1994b]. In this tunnel study, 80% of the PAH mass was on particles less than 0.12 μm. Interestingly, the EC size distribution for vehicle emissions of PAHs and EC for the two California tunnels is approximately one half the smallest particles collected using the SPMS mentioned above. Non-catalyst equipped car emissions also exhibit the largest EC concentration in particle sizes <0.25 μm [*Kleeman et al.*, 2000].

[34] During INDOEX, the maximum EC concentration was in the $0.3 < Dp < 0.54$ μm size range (Table 5), which is consistent with the emission profile of biomass/biofuel combustion. But, the cutoff points of the Berner impactor employed in that study were not calibrated to collect particles smaller than 0.18 μm, suggesting again that a vehicular emission source size particle population may not have been efficiently collected. Therefore we suggest that the maximum EC concentration observed by *Neusüß et al.* [2002] may be skewed to larger size distributions than would be expected for direct vehicle emissions. This is consistent with the elevated EC concentrations found using the Anderson hi-vol (1.0–1.3 μg/m^3, Table 3, NHcT-Sri Lanka, Bengal-1 and NHcT-w regimes) in this study compared to the Northern Indian Ocean values (0.12 μg/m^3) reported by *Neusüß et al.* [2002]. Interestingly, EC concentrations reported by *Neusüß et al.* [2002] for the Bay of Bengal (0.74 μg/m^3) are similar to the concentrations found here for the NHcT-Bengal 2 and 3 (Table 3) where biomass combustion appeared to have a greater impact on the PAH profiles. This is consistent with the difference in emission size distribution discussed above for biomass and vehicular combustion. Therefore we conclude that the majority of the elemental carbon found in the northern Indian Ocean originates from fossil fuel combustion, specifically diesel emissions, with biomass combustion relatively more important in the NHcT-Bengal 2 and 3 regimes (DOY 81–89).

4. Conclusions

[35] Marine aerosol was analyzed for PAHs, providing current estimates of marine background PAH concentrations for the Atlantic and Indian Oceans. A consistent and low level of particulate phase PAHs was found for the Atlantic and Southern Indian Ocean, representing the background marine aerosol PAH burden. A dramatic increase in PAH concentrations north of the ITCZ in the Indian Ocean was consistent with the enhanced anthropogenic emissions from the Indian sub-continent. These levels are greater than rural concentrations detected in the North American Great Lakes. The sources of particulate PAHs in this region were of a mixture of biomass and fossil fuel combustion. Our analysis of indeno[1,2,3-*cd*]pyrene/EC ratios for the various wind regimes suggests the dominant source of the particulate phase PAHs to the Northern Indian Ocean atmosphere is fossil fuel combustion. Biomass combustion was relatively more important in air masses that originated from the mid-eastern portion of the India (DOY 81–89). Although recent work has been performed on the biomass PAH distribution and emission in India, vehicles have received little attention. *Dickerson et al.* [2002] suggest that the fuel adulteration (kerosene addition to gasoline) impacts the EC emissions from the Indian sub-continent. The PAH/EC ratios suggest that biomass/biofuel combustion is not dominant source EC associated PAHs. Therefore we point toward the need for extensive characterization of the fossil fuel emissions in India to truly quantify the impact of India's fossil fuel emissions on the region.

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References

Baker, J. E., and S. J. Eisenreich (1990), Concentrations and fluxes of polycyclic aromatic hydrocarbons and polychlorinated biphenyls across the air-water interface of Lake Superior, *Environ. Sci. Technol.*, *24*, 342–352.

Ball, W., R. R. Dickerson, B. G. Doddridge, B. G. Stehr, T. L. Miller, D. Savoie, and T. P. Carsey (2003), Bulk and size segregated aerosol composition observed during INDOEX 1999: Overview of meteorology and continental impacts, *J. Geophys. Res.*, *108*(D10), 8001, doi:10.1029/2002JD002467.

Bates, T. M., P. K. Quinn, D. J. Coffman, J. E. Johnson, T. L. Miller, D. S. Covert, A. Wiedensohler, S. Leinnert, A. Nowak, and C. Neususs (2001), Regional physical and chemical properties of the marine boundary layer aerosol across the Atlantic during Aerosols99: An overview, *J. Geophys. Res.*, *106*, 20,767–20,782.

Broman, D., C. Näf, and Y. Zebühr (1991), Long-term high- and low-volume air sampling of polychlorinated dibenzo-p-dioxins and dibenzofurans and polycyclic aromatic hydrocarbons along a transect from urban to remote areas on the Swedish Baltic Coast, *Environ. Sci. Technol.*, *25*, 1841–1850.

Cachier, H., and Ducret (1991), Influence of biomass burning on the equatorial African rains, *Nature*, *352*, 228–230.

Chakraborti, D., L. van Vaeck, and P. van Espen (1988), Calcutta pollutants: Part 2. Polynuclear aromatic hydrocarbons and some metal concentrations on air particulates during winter 1984, *Int. J. Environ. Anal. Chem.*, *32*, 109–120.

Cortes, D. R., I. Basu, C. W. Sweet, and R. A. Hites (2000), Temporal trends in and influence of wind on PAH concentrations measured near the Great Lakes, *Environ. Sci. Technol.*, *34*, 356–360.

de Gouw, J. A., et al. (2001), Overview of trace gas measurements on board the citation aircraft during the intensive field phase of INDOEX, *J. Geophys. Res.*, *106*, 28,453–28,467.

Dickerson, R. R., M. O. Andreae, T. Campos, O. L. Mayol-Bracero, C. Neusuess, and D. G. Streets (2002), Analysis of black carbon and carbon monoxide observed over the Indian Ocean: Implications for emissions and photochemistry, *J. Geophys. Res.*, *107*(D19), 8017, doi:10.1029/2001JD00501.

Dickhut, R. M., and K. E. Gustafson (1995), Atmospheric washout of polycyclic aromatic hydrocarbons in the southern Chesapeake Bay Region, *Environ. Sci. Technol.*, *29*, 1518–1525.

Duce, R. A., and R. B. Gagosian (1982), The input of atmospheric *n*-C10 to *n*-C30 alkanes to the Ocean, *J. Geophys. Res.*, *87*, 7192–7200.

Fine, P. M., G. R. Cass, and B. R. T. Simoneit (2001), Chemical characterization of fine particle emissions from fireplace combustion of woods grown in the southern United States, *Environ. Sci. Technol.*, *35*, 2665–2675.

Finlayson-Pitts, B., and J. N. Pitts Jr. (2000), *Chemistry of the Upper and Lower Atmosphere, Theory, Experiments and Applications*, pp. 504–527, Academic, San Diego, Calif.

Fraser, M. P., G. R. Cass, B. R. T. Simoneit, and R. A. Rasmussen (1998), Air quality model evaluation data for organics. 5. C6–C22 nonpolar and semipolar aromatic compounds, *Environ. Sci. Technol.*, *32*, 1760–1770.

Guazzotti, S. A., et al. (2003), Characterization of carbonaceous aerosols outflow from India and Arabia: Biomass burning and fossil fuel combustion, *J. Geophys. Res.*, *108*(D15), 4485, doi:10.1029/2002JD003277.

Gustafsson, O., T. D. Bucheli, Z. Kukulska, M. Andersson, C. Largeau, J. N. Rouzaud, C. M. Reddy, and T. I. Eglinton (2001), Evaluation of a protocol for the quantification of black carbon in sediments, *Global Biogeochem. Cycles*, *15*, 881–890.

Halkiewcz, J., H. Lamparczyk, J. Grzybowski, and A. Radecki (1987), On the aliphatic and polycyclic aromatic hydrocarbon levels in the southern Baltic Sea Atmosphere, *Atmos. Environ.*, *21*.

Halsall, C. J., L. A. Barrie, P. Fellin, D. C. G. Muir, B. N. Billeck, L. Lockhart, F. Rovinsky, E. Kononov, and B. Pastukov (1997), Spatial and temporal variation of polycyclic aromatic hydrocarbons in the Arctic atmosphere, *Environ. Sci. Technol.*, *31*, 3593–3599.

Harrison, J. M., D. J. T. Smith, and L. Luhana (1996), Source apportionment of polycyclic aromatic hydrocarbons collected from an urban location in Birmingham, U.K., *Environ. Sci. Technol.*, *30*, 825–832.

Hays, M. D., C. D. Geron, K. J. Linna, N. D. Smith, and J. J. Schauer (2002), Speciation of gas phase and fine particle emissions from burning foliar fuels, *Environ. Sci. Technol.*, *36*, 2281–2295.

Hernández, M. D. A., J. Burkert, L. Reichert, D. Stöbener, J. Meyer-Arnek, and J. Burrows (2001), Marine boundary layer peroxy-radical chemistry during the Aerosols99 campaign: Measurements and analysis, *J. Geophys. Res.*, *106*, 20,833–20,846.

Huang, S., R. Arimotot, and K. A. Rahn (2001), Sources and source variations for aerosol at Mace Head, Ireland, *Atmos. Environ.*, *35*, 1421–1437.

Kleeman, M. J., G. R. Cass, and A. Eldering (1997), Modeling the airborne particle complex as a source-oriented external mixture, *J. Geophys. Res.*, *102*, 21,355–21,372.

Kleeman, M. J., J. J. Schauer, and G. R. Cass (2000), Size and composition distribution of fine particulate matter emitted from motor vehicles, *Environ. Sci. Technol.*, *34*, 1132–1142.

Kulkarni, P., and C. Venkataraman (2000), Atmospheric polycyclic aromatic hydrocarbons in Mumbai, India, *Atmos. Environ.*, *34*, 2785–2790.

Larsen, R., and J. Baker (2003), Source apportionment of polycylic aromatic hydrocarbons in the urban atmosphere: A comparison of three methods, *Environ. Sci. Technol.*, *37*, 1873–1881.

Leliveld, J., et al. (2001), The Indian Ocean Experiment: Widespread air pollution from South and Southeast Asia, *Science*, *291*, 1031–1036.

Leon, J.-F., et al. (2001), Large-scale advection of continental aerosols during INDOEX, *J. Geophys. Res.*, *106*, 28,427–28,439.

Lim, H. J., B. J. Turpin, L. M. Russell, and T. S. Bates (2003), Organic and elemental carbon measurements during ACE-Asia suggest a longer atmospheric lifetime for elemental carbon, *Environ. Sci. Technol.*, *37*, 3055–3061.

Marty, J. C., M. J. Tissier, and A. Saliot (1984), Gaseous and particulate polycyclic aromatic hydrocarbons (PAH) from the marine atmosphere, *Atmos. Environ.*, *18*, 2183–2190.

Mayol-Bracero, O. L., R. Gabriel, M. O. Andreae, T. W. Kirchstetter, T. Novakov, J. Ogren, P. Sheridan, and D. G. Streets (2002), Carbonaceous aerosols over the Indian Ocean during the Indian Ocean Experiment (INDOEX): Chemical characterization, optical properties, and probable sources, *J. Geophys. Res.*, *107*(D19), 8030, doi:10.1029/2000JD000039.

McVeety, B. D., and R. Hites (1988), Atmospheric deposition of polycylic aromatic hydrocarbons to surface waters: A mass balance approach, *Atmos. Environ.*, *22*, 511–536.

National Research Council (2003), *Oil in the Sea*, vol. 3, *Inputs, Fates and Effects*, pp. 223–232, Natl. Acad. of Sci., Washington, D. C.

Neusüß, C., T. Gnauk, A. Plewka, H. Herrman, and P. K. Quinn (2002), Carbonaceous aerosol over the Indian Ocean: OC/EC fractions and selected specifications from size-segregated onboard samples, *J. Geophys. Res.*, *107*(D19), 8031, doi:10.1029/2001JD000327.

Nielsen, T. (1984), Reactivity of Polycyclic aromatic hydrocarbons toward nitrating species, *Environ. Sci. Technol.*, *18*, 157–163.

Novakov, T., M. O. Andreae, R. Gabriel, T. W. Kirschstetter, O. L. Mayol-Bracero, and V. Ramanathan (2000), Origin of carbonaceous aerosols over the tropical Indian Ocean: Biomass burning or fossil fuels?, *Geophys. Res. Lett.*, *27*, 4061–4064.

Offenberg, J. H., and J. E. Baker (1999), Influence of Baltimore's urban atmosphere on organic contaminants over the northern Chesapeake Bay, *J. Air Waste Manage. Assoc.*, *49*, 959–965.

Oros, D. R., and B. R. T. Simoneit (2000), Identification and emission rates of molecular tracers in coal smoke particulate matter, *Fuel*, *79*, 515–536.

Ramanathan, V., et al. (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.

Rao, A. M. M., R. Rajagopalan, M. H. Doshi, and K. G. Vohra (1982), Measurements of benzo[*a*]pyrene in the city of Bombay for the evaluation of carcinogenic risk, *Sci. Total Environ.*, *22*, 105–113.

Reddy, M. S., and C. Venkatarman (2002), Inventory of aerosol and sulphur dioxide emissions from India: I-Fossil fuel combustion, *Atmos. Environ.*, *36*, 677–697.

Rhoads, K. P., P. Kelley, R. R. Dickerson, T. P. Carsey, M. Farmer, D. Savoie, and J. Prospero (1997), The composition of the troposphere over the Indian Ocean during the monsoonal transition, *J. Geophys. Res.*, *102*, 18,981–18,995.

Rogge, W. F., L. M. Hildemann, M. M. Mazurek, G. R. Cass, and B. R. T. Simoneit (1993), Sources of fine organic aerosol. 2. Noncatalyst and catalyst equipped automobiles and heavy-duty diesel trucks, *Environ. Sci. Technol.*, *27*, 636–651.

Rogge, W. F., L. M. Hildemann, M. M. Mazurek, G. R. Cass, and B. R. T. Simoneit (1997), Sources of organic aerosol. 8. Boilers No. 2 distillate fuel oil, *Environ. Sci. Technol.*, *31*, 2731–2737.

Schauer, J. J., M. J. Kleeman, G. R. Cass, and B. R. T. Cass (2002), Measurement of emissions from air pollution sources. 5. C1–C32 Organic compounds from gasoline powered motor vehicles, *Environ. Sci. Technol.*, *36*, 1169–1180.

Sheesley, R. J., J. J. Schauer, Z. Chowdhury, G. R. Cass, and B. R. T. Simoneit (2003), Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia, *J. Geophys. Res.*, *108*(D9), 4285, doi:10.1029/2002JD002981.

Simcik, M. F., H. Zhang, S. J. Eisenreich, and T. P. Franz (1997), Urban contamination of the Chicago/Coastal Lake Michigan atmosphere by PCBs and PAHs during AEOLOS, *Environ. Sci. Technol.*, *31*, 2141–2147.

Simcik, M. F., S. J. Eisenreich, and P. J. Lioy (1999), Source apportionment and source/sink relationships of PAHs in the coastal atmosphere of Chicago and Lake Michigan, *Atmos. Environ.*, *33*, 5071–5079.

Smith, D. J. T. (1995), Source apportionment of atmospheric particles in the U.K., Portugal and Pakistan, Ph.D. thesis, Univ. of Birmingham, Birmingham, UK.

Smith, D. J. T., and R. H. Harrison (1996), Concentrations, trends and vehicle source profile of polynuclear aromatic hydrocarbons in the U.K. atmosphere, *Atmos. Environ.*, *30*, 2513–2525.

Smith, D. J. T., R. H. Harrison, L. Luhana, C. A. Pio, L. M. Castro, M. N. Tariq, S. Hayat, and T. Quaishi (1996), Concentrations of particulate airborne polycyclic aromatic hydrocarbons and metals collected in Lahore, Pakistan, *Atmos. Environ.*, *30*, 4031–4040.

Stephanou, E. G. (1992), Biogenic and anthropogenic organic compounds in aeolian particulates in the East Mediterranean region-I. Occurrence and origin, *Atmos. Environ.*, *Part A*, *26*, 2821–2829.

Thompson, A. M., B. G. Doddridge, J. C. Witte, R. D. Hudson, W. T. Luke, J. E. Johnson, B. J. Johnson, S. J. Oltmans, and R. Weller (2000), A Tropical Atlantic Paradox: Shipboard and satellite views of tropospheric ozone maximum and wave-one in January–February 1999, *Geophys. Res. Lett.*, *27*, 3317–3320.

Turpin, B. J., and J. J. Huntzicker (1995), Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS, *Atmos. Environ.*, *29*, 3527–3544.

Venkataraman, C., and S. K. Friedlander (1994a), Source of fine particulate polycyclic aromatic hydrocarbons using a receptor model modified for reactivity, *J. Air Waste Manage. Assoc.*, *44*, 1103–1108.

Venkataraman, C., and S. K. Friedlander (1994b), Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 2. Ambient measurements and effects of atmospheric processes, *Environ. Sci. Technol.*, *28*, 563–572.

Venkataraman, C., J. M. Lyons, and S. K. Friedlander (1994), Size distributions of polycyclic aromatic hydrocarbons and elemental carbon. 1. Sampling, measurement methods, and source characterization, *Environ. Sci. Technol.*, *28*, 555–562.

Venkataraman, C., G. Negi, S. B. Sardar, and R. Rastogi (2002), Size distributions of polycyclic aromatic hydrocarbons in aerosol emissions from biofuel combustion, *J. Aerosol Sci.*, *33*, 503–518.

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.

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