



Understanding the origin of black carbon in the atmospheric brown cloud over the Indian Ocean

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[1] Atmospheric particulate matter samples were collected at two Maldives climate observatories from 30 August 2004 to 21 January 2005. This time period encompassed both wet and dry seasons, which correspond to low and high aerosol loadings. High aerosol loadings were observed in the northern sampling site in Hanimaadhoo, caused by long-range transport from south and Southeast Asia, whereas the southern sampling site, Gan, was not subject to as much continental inflow. The polluted period began in mid-November and lasted through the remainder of the sampling period. Fine particulate matter during this time was characterized by relatively high concentrations of aerosol mass and elemental carbon. Concentrations of water-soluble potassium, sulfate, levoglucosan, polyaromatic hydrocarbons, aliphatic diacids, aromatic diacids, and trace metals increased over the clean, transition, and polluted dry season. Organic speciation suggested that significant secondary organic aerosol formation occurred during the polluted dry season, meaning that traditional methods of source identification relying on fixed elemental and organic carbon ratios between source and receptors are not sufficient. Well-studied molecular markers for combustion sources were not adequate in fully attributing elemental carbon over the northern Indian Ocean to specific sources. Further source profiling of south and Southeast Asian biofuels and fossil fuels is recommended. A receptor-based positive matrix factorization model was applied to fine particulate matter trace metal measurements and showed that biofuel burning and fossil fuel combustion were equally important sources of elemental carbon during the polluted dry season.

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1. Introduction

[2] The Indian Ocean Experiment (INDOEX) field campaign identified high levels of black carbon (BC) aerosols over the Indian Ocean during the winter months of 1998–1999 [Ramanathan *et al.*, 2001]. This observation was notable because BC is believed to play an important role in climate forcing [Ramanathan *et al.*, 2001, 2002]. Evidence of localized climate forcing in the south Asian region consists of decreases in solar surface radiation, evaporation, and monsoon rainfall [Ramanathan *et al.*, 2005]. Potential long-term consequences include disturbances of the hydrological cycle, decreases in agricultural productivity, and adverse effects on human health [Centers for Cloud, Chemistry and Climate, 2002].

[3] Observations indicate that brown clouds, large aerosol masses containing visible amounts of black carbon, are present over the northern Indian Ocean annually, beginning in November and lasting until April [Ramanathan *et al.*, 2002; Jacobson, 2004; Hansen *et al.*, 2005]. The meteorology of this time period is characterized by low-level northeasterly winds and little precipitation to remove the aerosols from the atmosphere by wet deposition [Jayaraman *et al.*, 1998; Meywerk and Ramanathan, 1999; Chung and Ramanathan, 2004].

[4] The atmospheric brown cloud (ABC) observatories were established in order to investigate the long-term effects of these clouds. One component of understanding brown clouds is identifying the source of BC aerosols, which are not comprehensively understood. On the basis of INDOEX observations, it has been estimated that fossil fuel is the dominant source of BC (60–80%) and biofuel burning contributes to a lesser extent (20–40%) [Novakov *et al.*, 2000; Lelieveld *et al.*, 2001; Ramanathan *et al.*, 2001; Mayol-Bracero *et al.*, 2002]. These results are somewhat contrary to Indian emissions profiles that point to biofuel use as the major source of BC [Venkataraman *et al.*, 2005].

[5] The focus of this paper is to elucidate the relative contribution of anthropogenic aerosol sources to ambient

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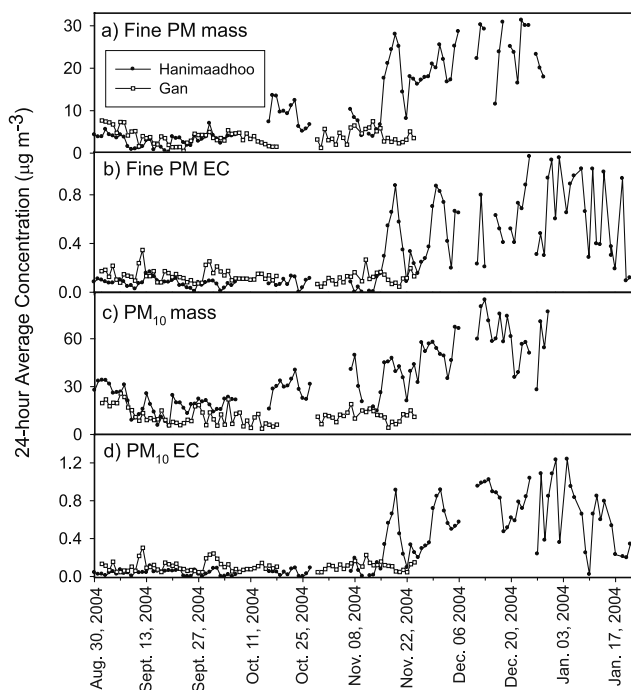


Figure 1. Daily mass and EC concentrations in fine particulate matter and PM_{10} in Hanimaadhoo and Gan from 30 August 2004 to 21 January 2005.

BC concentrations. State-of-the-art field techniques and experimental methods were applied to two ground-based aerosol sampling sites in the Maldives, located in the northern Indian Ocean. Clean sampling techniques were used to collect daily samples over the course of several months spanning both periods of clear and polluted atmospheres. Chemical analyses consisted of well-established bulk chemical measurements as well as specialized organic and trace metal speciation. The methods were specifically chosen to quantify molecular markers to aid in source reconciliation and provide improved understanding of the source origins of BC over the Arabian Sea.

2. Methods

[6] Particulate matter discussed in this paper was collected at the Maldives climate observatories in Hanimaadhoo and Gan, sampling sites in the ABC monitoring network [Ramanathan *et al.*, 2007]. The former is $6^{\circ}87'$ north of the equator at the northern tip of the island chain and the latter is located $0^{\circ}25'$ south of the equator. The Hanimaadhoo sampling site is located at the northern tip of the island of Hanimaadhoo in northern Haa Dhaalu Atoll. The site is approximately 50 m from the ocean on the north, west, and east, and is approximately 1.5 km north of the town. Samples were collected on a tower approximately 15 m high. The Gan sampling site was located on the southern edge of southern Addu Atoll. Samples were collected at ground level approximately 100 m from the ocean on the southern side.

[7] Particulate matter samples were collected between 30 August 2004 and 21 January 2005. Filter-based samples began at approximately 8AM each day and continued for

23 hours. The Hanimaadhoo sampling site was operational throughout this period, except for four separate week-long intervals corresponding to sampling problems. The Gan site was in operation from 1 September 2004 to 24 November 2004 with a week-long break in sampling from 19–28 October. Data points in Figure 1 correspond to days when filter samples were collected.

[8] Fine particulate matter and PM_{10} fractions were collected daily using a medium-volume $PM_{2.5}$ and PM_{10} sampler (URG Corporation, Chapel Hill, North Carolina, United States, URG-3000ABC). Aerosol inlets and filter holders were made of Teflon-coated aluminum. Fine particulates were separated on the basis of aerodynamic diameters using cyclones at a flow rate of 16 liters per minute. The PM_{10} fraction was collected through a PM_{10} inlet at a flow rate of 32 liters per minute. Air flow was driven by a vacuum pump, controlled by critical orifices, and monitored before and after sample collection using a calibrated rotameter.

[9] Particulate matter samples were collected on quartz fiber filters (47 mm, Tissuquartz, Pall Life Sciences) and Teflon filters (47 mm, 2.0 μm pore size, Teflo Membrane, Pall Life Sciences). Filters were managed using clean handling techniques. All substrates were prepared in the laboratory prior to sampling. Quartz fiber filters (QFF) were prebaked at 550°C for a minimum of 16 hours and stored in prebaked aluminum foil. All filters were stored in plastic Petri dishes and wrapped with Teflon tape prior to sampling and postsampling.

[10] Gravimetric mass was determined with a high-precision scale (Mettler Toledo 5) using a robot (Bohdan Automation). The instrument was calibrated using certified weights (Rice Lake Weighing Systems). Before assessment, the filters were allowed to equilibrate in a temperature and humidity controlled environment for a minimum of 24 hours ($21^{\circ} \pm 2^{\circ}\text{C}$, RH $35 \pm 3\%$). Each filter was weighed twice before and after sample collection; respective tare weights were averaged. The difference of the two measurements corresponded to total particle mass. Uncertainty of particulate matter mass concentrations was estimated to be 10% of the total measurement.

[11] Inorganic, water-soluble ions—chloride, nitrate, phosphate, sulfate, sodium, potassium, and ammonium—were determined by ion chromatography (1000, Dionex, Sunnyvale, California). Sampled Teflon filters were wetted with 0.2 mL isopropyl alcohol and extracted with 20 mL ultra pure water by agitation in precleaned centrifuge tubes for three hours [Lough *et al.*, 2005].

[12] Elemental and organic carbon (EC and OC) were analyzed using a thermal optical analyzer (Sunset Laboratory, Forest Grove, Oregon) following the ACE-Asia method [Schauer *et al.*, 2003]. Organic speciation was determined by Soxhlet extraction and gas chromatography mass spectrometry (GCMS). QFF were composited chronologically on the basis of time periods with similar concentrations of OC. Filters were spiked with isotopically labeled internal recovery standards used in quantification [Sheesley *et al.*, 2004]. Composites were extracted by methylene chloride and methanol using Soxhlets. Aliquots of filter extracts were derivatized using diazomethane to quantify polar compounds [Schauer *et al.*, 2002] and N, O-bis(trimethylsilyl)trifluoroacetamide with 1% trimethylchlorosilane (Fluka, Buchs,

Switzerland) to quantify levoglucosan and cholesterol [Nolte *et al.*, 2002].

[13] BC mass concentrations were determined by an aethalometer (Magee Scientific Company, Berkeley, California, United States) which measured light absorption of aerosol particles collected on a filter [Corrigan *et al.*, 2006]. To avoid absorption interferences from chemical bonds in organic material, data for black carbon concentrations were taken at a wavelength of 880 nm. The absorption coefficient at 880 nm was derived from reported methods [Arnott *et al.*, 2005] and converted to BC mass concentration by applying an absorption cross section (ACS) value to the absorption coefficient. The ACS for ambient BC has been estimated to cover a wide range of values ($5\text{--}20\text{ m}^2\text{ g}^{-1}$) depending upon location and sources of BC [Lioussé *et al.*, 1993]. For this study a value of $10\text{ m}^2\text{ g}^{-1}$ was employed [Corrigan *et al.*, 2006].

[14] Metal species were measured using inductively coupled plasma mass spectrometry (ICP-MS) (PQ Excell, ThermoElemental) techniques developed to analyze low-level trace elements in aerosol samples [Lough *et al.*, 2005]. Teflon filters were digested in a solution of nitric, hydrochloric, and hydrofluoric acid inside Teflon bombs with the assistance of microwave radiation. Digestates were analyzed for 48 trace metal species using two different data acquisition methods, a standard ICPMS and a cool plasma/shielded torch operation.

[15] Positive matrix factorization (EPA PMF 1.1) is a receptor-based model used to analyze the covariation of select chemical species over time and to identify a number of factors contributing to ambient measurements based on a constrained weighted least squares matrix [Paatero and Tapper, 1994; Paatero, 1997; Lee *et al.*, 1999]. The model used a nonnegative constraint to assure that all factors contributed positively to receptor-based observations. The PMF model has previously been used in source apportionment of ambient aerosol [Lee *et al.*, 1999; Ramadan *et al.*, 2000; Kim *et al.*, 2003, 2005a, 2005b; Begum *et al.*, 2004, 2005; Han *et al.*, 2006; Yuan *et al.*, 2006]. Trace elements and metals, along with EC, were measured every other day in Hanimaadhoo between 1 October and 5 December 2004 and input into the model. The elements included in the model were sodium (Na), magnesium (Mg), aluminum (Al), phosphorus (P), potassium (K), calcium (Ca), iron (Fe), titanium (Ti), vanadium (V), chromium (Cr), copper (Cu), zinc (Zn), rubidium (Rb), strontium (Sr), cadmium (Cd), antimony (Sb), barium (Ba), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), and lead (Pb), along with EC. Signal-to-noise ratios, calculated for each element, were divided into three classes of strong, medium, and weak as defined by the PMF model. Elements falling into the first two categories were included in the model whereas elements with weak signal to noise were excluded from the model.

3. Results and Discussion

[16] Mass concentrations of fine particulate matter and PM_{10} from 30 August 2004 to 29 December 2004 for Hanimaadhoo and from 1 September 2004 to 24 November 2004 for Gan are presented in Figures 1a and 1c. EC concentration data are presented in Figures 1b and 1d for

Gan over the same time period whereas EC data for Hanimaadhoo extend to 21 January 2005. Fine particulate matter is defined in this paper as particles of aerodynamic diameter (D_a) less than $2.5\text{ }\mu\text{m}$ and PM_{10} as particles of D_a less than $10\text{ }\mu\text{m}$. Mass of particulate matter in the smaller size fraction is dominated by accumulation mode particles which are formed by the accumulation of or condensation of gases on particles formed by nucleation of atmospheric species or combustion-related condensation [Seinfeld and Pandis, 1998]. PM_{10} includes fine particulate matter, but also coarse mode aerosols ($\text{PM}_{10-2.5}$) with D_a $2.5\text{--}10\text{ }\mu\text{m}$. Coarse mode aerosols are generally formed by mechanical processes [Seinfeld and Pandis, 1998] such as sea spray and wind-blown dust. Elemental carbon is formed only through the combustion of fossil fuels and biomasses [Neusüß *et al.*, 2002] and signifies anthropogenic activity. It has been historically used as a tracer for diesel fuel in certain locations where residual fuel combustion is not significant [Friedlan, 1973] but is emitted in significant quantities from biofuel [Venkataraman *et al.*, 2005], fuel oil, and coal combustion [Schauer, 2003].

[17] During the INDOEX study, aerosol measurements were taken at the Kaashidhoo Climate Observatory located on Kaashidhoo Island in the Maldives from 11 to 26 February 1999. This time period was characterized by a brown cloud and average fine particle mass ($D_a < 1.8\text{ }\mu\text{m}$) of $17.7 \pm 0.22\text{ }\mu\text{g m}^{-3}$ [Chowdhury *et al.*, 2001].

[18] In contrast, ABC measurements taken in Gan during the fall of 2004 correspond to a much cleaner atmosphere. Fine aerosol mass ranged $0.5\text{--}7.7\text{ }\mu\text{g m}^{-3}$ (Figure 1a). This value is comparable to remote aerosol concentrations [Seinfeld and Pandis, 1998]. PM_{10} mass concentrations in Gan, $3.5\text{--}25.6\text{ }\mu\text{g m}^{-3}$, were significantly greater than in fine particulate matter which indicates the importance of coarse mode aerosols ($\text{PM}_{10-2.5}$), generated by mechanical processes. It is likely that sea spray was an important coarse mode source due to the coastal geography of Gan. Aerosol mass concentration in fine particulate matter and PM_{10} were relatively constant throughout the sampling period. EC concentrations varied between 0.045 ± 0.038 and $0.254 \pm 0.055\text{ }\mu\text{g m}^{-3}$ in fine particulate matter. PM_{10} EC concentrations were equal to fine particulate matter EC concentrations, making coarse-mode EC negligible (Figures 1b and 1d). The fine particulate matter value was similar to the background EC range of remote oceanic aerosols, $0\text{--}0.3\text{ }\mu\text{g m}^{-3}$ [Rau and Khalil, 1993], corresponding to a clear atmosphere. EC levels were relatively constant over the sampling period in Gan, although slight increases in EC, visible in both fine and coarse modes, were apparent in mid-September and late September. These increases may be due to Asian transport or local sources, but overall, the observed levels were very low.

[19] In Hanimaadhoo, observed aerosol concentrations were higher. Fine particulate matter concentrations increased from $0.2\text{ }\mu\text{g m}^{-3}$ in September to $30.8\text{ }\mu\text{g m}^{-3}$ in December 2004 (Figure 1a). PM_{10} concentrations in Hanimaadhoo increased from $5.1\text{ }\mu\text{g m}^{-3}$ to $84.2\text{ }\mu\text{g m}^{-3}$ (Figure 1c) over the same time period. The high-end measurement for fine particulate matter was comparable to the highest particle concentrations observed in Kaashidhoo in February 1999, which peaked at $24.7 \pm 0.21\text{ }\mu\text{g m}^{-3}$ [Chowdhury *et al.*, 2001]. Mass concentrations in fine

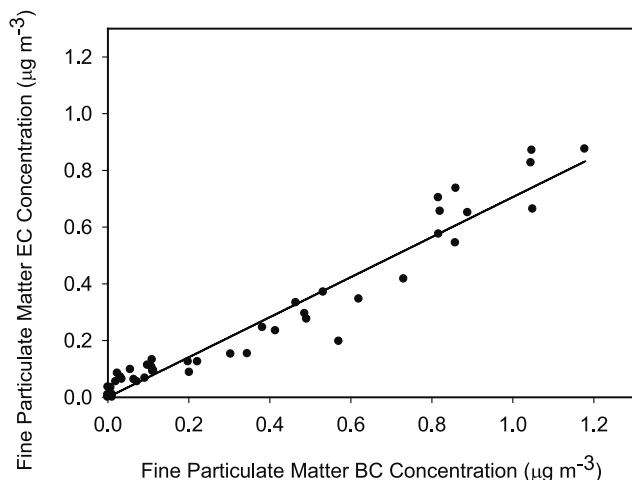


Figure 2. Comparison of fine particulate matter EC as determined chemically and BC as determined by an aethalometer ($R^2 = 0.968$).

particulate matter were relatively low from the beginning of the sampling period until late October, when fine particulate matter mass nearly doubled and transitioned to an elevated level. PM_{10} mass concentrations exhibited the same general trend, with less dramatic changes. The elevated mass concentrations persisted throughout the remainder of the sampling period, but were subject to fluctuation with changing meteorological conditions.

[20] EC concentrations in Hanimaadhoo reached $1.11 \pm 0.09 \mu\text{g m}^{-3}$ for fine particulate matter (Figure 1b) and $1.23 \pm 0.01 \mu\text{g m}^{-3}$ for PM_{10} (Figure 1d), which occurred in late December 2004 or early January 2005, respectively. These EC levels were much higher than those observed in Gan. Such levels of EC were observed in Kaashidhoo [Chowdhury *et al.*, 2001] and are comparable to those measured in submicron particles ($D_a < 1.0 \mu\text{m}$) on the Indian subcontinent ($1.67 \mu\text{g m}^{-3}$) and the Bay of Bengal ($0.74 \mu\text{g m}^{-3}$) during the INDOEX study in February and March 1999 [Neusüß *et al.*, 2002]. These levels of EC are well above the expected level for rural locations but are several times lower than EC concentrations observed in urban settings on the Asian continent [Lin and Tai, 2001; Feng *et al.*, 2006]. Temporal trends observed in EC concentrations mimic aerosol mass trends in Hanimaadhoo. Average EC concentrations in both the fine particulate matter and PM_{10} are relatively low (less than $0.10 \mu\text{g m}^{-3}$) until mid-November when they increase dramatically to $0.49 \mu\text{g m}^{-3}$ and $0.60 \mu\text{g m}^{-3}$, respectively. The simultaneous increases in aerosol mass and EC concentrations observed in mid-November are consistent with the development of a brown cloud, both chemically [Chowdhury *et al.*, 2001] and temporally [Chung and Ramanathan, 2004].

[21] Fine mode EC, as determined chemically by thermal-optical measurements, was compared to daily averages of BC measurements determined optically (Figure 2). The linear relationship between the two measurements exhibited a strong correlation ($R^2 = 0.968$) which demonstrates that EC measured chemically is a suitable surrogate for BC. The deviation of the slope from unity supports the well-documented hypothesis that fundamental differences between real-time and filter-based optical measurements

exist and suggests that the method of converting light absorption measurements into black carbon mass concentrations is not optimal [Lioussé *et al.*, 1993; Hitzenberger *et al.*, 1999; Sharma *et al.*, 2002; Borak *et al.*, 2003; Jeong *et al.*, 2004].

[22] Aerosol composition in Hanimaadhoo from 16 September to 25 December and in Gan from 16 September to 27 November is presented in Figure 3. Chemical species measured include elemental carbon, organic matter, and water soluble ions: chloride, nitrate, sulfate, sodium, ammonium, and potassium. Results are presented as weekly composites, defined as Sunday through Saturday. A ratio of 2.0 was used to convert OC to organic matter (OM), a reasonable estimate for nonurban aerosols [Turpin and Lim, 2001]. The chemical composition of fine particulate matter and PM_{10} in Gan was relatively constant during the sampling period (Figure 3b). On average, fine particulate matter in Gan was composed of 44.3% organic matter, 3.9% elemental carbon, 12.7% chloride, 1.5% nitrate, 18.2% sulfate, 10.2% sodium, 1.6% ammonium, 0.5% water-soluble potassium, and 7.2% other species.

[23] In contrast to Gan, aerosol composition in Hanimaadhoo varied throughout the duration of the study with a change in composition occurring during the week of 15 November. The observed increase in aerosol mass at this time corresponds to similar increases in OM and sulfate concentrations in ambient air (Figure 3a). Analogously, absolute EC and water-soluble potassium concentrations noticeably increased. These bulk chemical measurements provide important information about species contributing to the increasing aerosol mass in Hanimaadhoo, although they do little to elucidate specific aerosol sources.

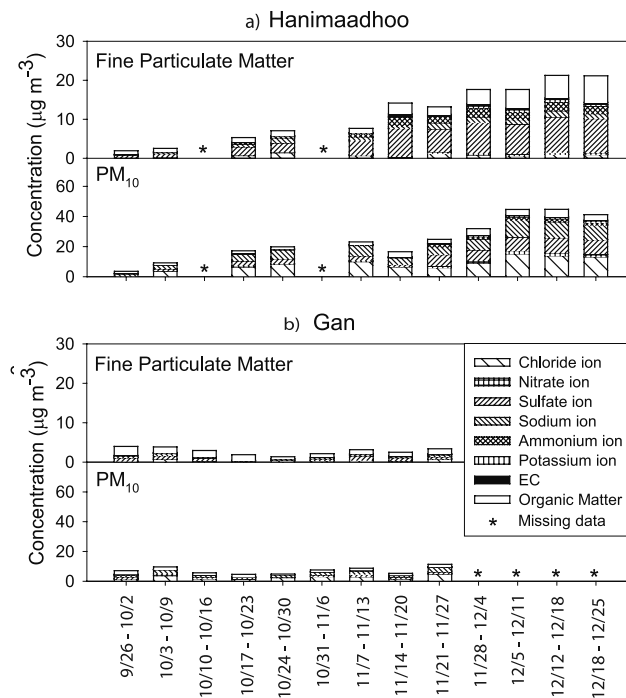


Figure 3. Chemical composition of fine particulate matter and PM_{10} measured in Hanimaadhoo and Gan. Data are presented as weekly (Sunday–Saturday) averages.

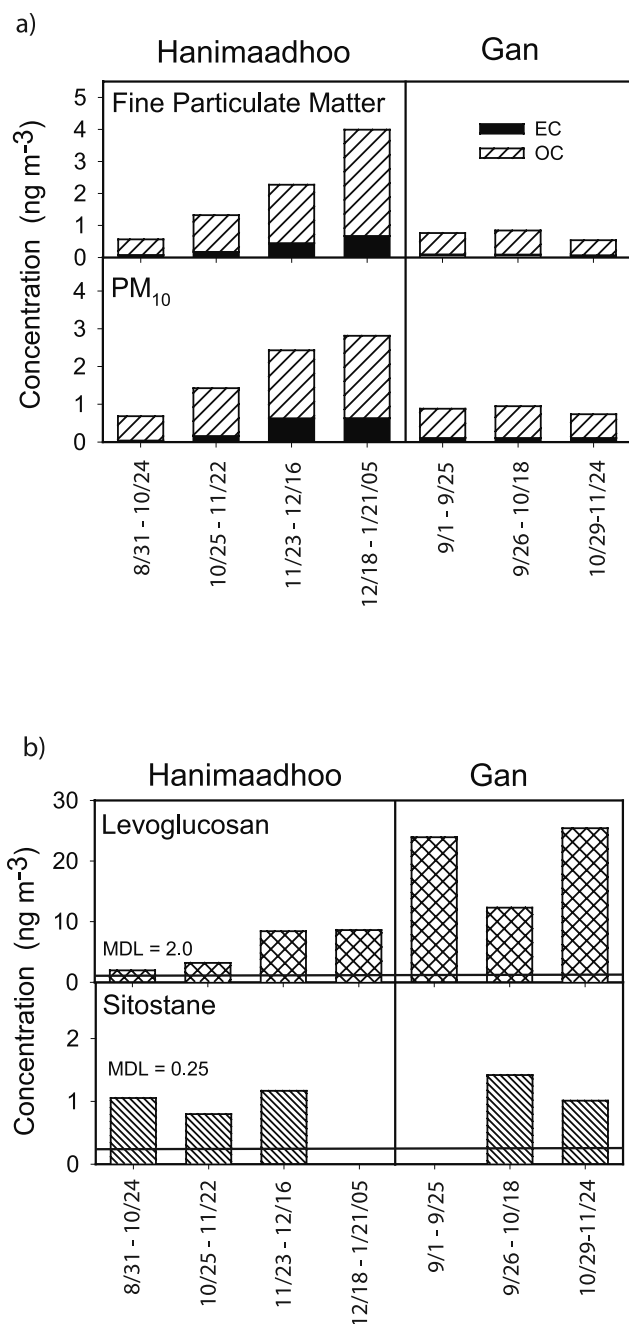


Figure 4. Concentrations of carbonaceous species for time periods corresponding to organic speciation of fine particulate matter for Hanimaadhoo and Gan. (a) Elemental and organic carbon concentrations in fine particulate matter and PM₁₀. (b) Levoglucosan and 20(R&S)5 α (H), 14 β (H), 17 β (H)-sitostane concentrations in fine particulate matter.

[24] Sea spray is a dominant source of coarse mode aerosol (PM_{10-2.5}) in both Hanimaadhoo and Gan. This is demonstrated by the high mass concentrations of sodium and chloride ions in PM₁₀ that is not observed in fine particulate matter. The absolute concentration of sodium and chloride ions is similar in Hanimaadhoo and Gan at the beginning of the study, from 16 September to 10 October (Figure 3). However, in Hanimaadhoo, during the transition

from the monsoon to polluted dry season, the absolute concentration of sodium and chloride concentrations increase analogously to mass. This augmentation in aerosol loading probably corresponds to meteorological changes from the wet to dry seasons, during which wet deposition of aerosols decreases and aerosol residence time is lengthened.

[25] The observed aerosol compositions of the polluted dry season in Hanimaadhoo are comparable with those observed during the INDOEX study at the Kaashidhoo during February 1999. At Kaashidhoo, mass was composed of 37% sulfate, 7% ammonium, 21% organic matter, 6% EC, 0% chloride, 1% nitrate, and 28% other species likely of crustal or sea spray origin [Chowdhury *et al.*, 2001]. Chloride was not a measurable component of aerosol in Kaashidhoo whereas chloride made up significant fractions of fine particulate matter in both Hanimaadhoo (6.2%) and Gan (12.7%). It is likely that the smaller particle definition for fine mode aerosols employed in the INDOEX ($D_a = 1.8 \mu\text{m}$) study eliminated the majority of sea spray aerosols whereas fine particulate matter defined in this study ($D_a = 2.5 \mu\text{m}$) did not. Similarly, the percentage of mass attributed to ammonium and EC in Hanimaadhoo and Gan is lower than in Kaashidhoo.

[26] Organic species in fine mode PM were investigated as chronological composites of filter samples with similar EC concentrations. These breakdowns and corresponding EC and OC concentrations for fine particulate matter and PM₁₀ are presented in Figure 4a. The first Hanimaadhoo composite (31 August to 24 October) and all three Gan composites (1–25 September, 26 September to 18 October, and 29 October to 24 November) are similar in that they have relatively low concentrations of EC ($<0.10 \mu\text{g m}^{-3}$) and OC ($<1.0 \mu\text{g m}^{-3}$). The second Hanimaadhoo composite (25 October to 22 November) is representative of the transitional period of increasing EC ($0.17 \mu\text{g m}^{-3}$) and OC concentrations ($1.15 \mu\text{g m}^{-3}$). The final two Hanimaadhoo composites (23 November to 16 December and 18 December to 21 January) represent polluted dry periods with highest the EC ($>0.45 \mu\text{g m}^{-3}$) and OC ($>1.80 \mu\text{g m}^{-3}$) concentrations.

[27] Levoglucosan, a product of cellulose degradation, is a well-studied tracer for wood smoke [Simoneit *et al.*, 1999; Schauer and Cass, 2000] and has been demonstrated as chemically stable under ambient temperature and light conditions [Locker, 1988]. Concentrations of levoglucosan vary up to 50% between different types of wood [Schauer *et al.*, 2001] and more between types of biofuel: 2.0% of cow dung versus 10% of synthetic log emissions [Sheesley *et al.*, 2003]. This organic tracer was detected in all samples from the Hanimaadhoo and Gan sampling sites (Figure 4b). The observed levels of levoglucosan are very low and correspond to less than $0.1 \mu\text{g m}^{-3}$ of traditional biomass aerosol.

[28] Levoglucosan concentrations in Gan range from 12.3–25.4 ng m⁻³ but do not follow a temporal trend. It is probable that the observed levoglucosan concentrations in Gan are caused by local activity. The four samples from Hanimaadhoo have increasing concentrations of levoglucosan with time, from 1.97–8.62 ng m⁻³ which follow the same temporal trends of EC concentrations. This result implies that biomass burning contributes to BC observed

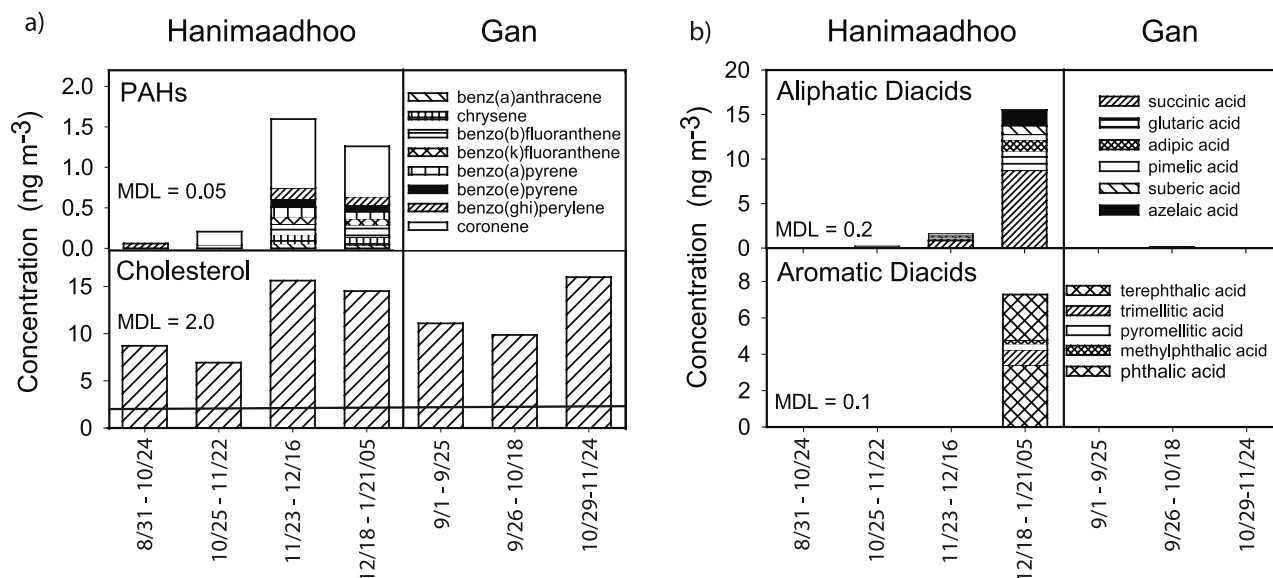


Figure 5. Concentrations of carbonaceous species for time periods corresponding to organic speciation of fine particulate matter for Hanimaadhoo and Gan. (a) Concentrations of eight measured PAHs, with molecular weights greater than 228 amu, and cholesterol. (b) Concentrations of aliphatic and aromatic diacids.

in the northern Indian Ocean but does not prove causality. The levels of levoglucosan detected are one to three orders of magnitude smaller than ambient measurements taken during haze events heavily influenced by wood smoke [bin Abas *et al.*, 2004]. The measured concentrations are on the same scale as those observed in ambient air in a wilderness area where wood smoke contributions to PM are minimal [Sheesley *et al.*, 2004]. EC to levoglucosan ratios reported in source profiles for Bangladeshi biomasses range from 0.11 for biomass briquettes to 0.60 for rice straw [Sheesley *et al.*, 2003]. Traditional biomass burning that emits significant amounts of levoglucosan account for only 5.5% of observed EC in Hanimaadhoo. This finding suggests that biofuel burning may be an important source of BC. Biofuel burning differs from traditional biomass burning in starting materials, temperature, and burn rate [Streets *et al.*, 2001; Venkataraman *et al.*, 2005]. Biofuel combustion is generally more efficient than traditional biomass burning, which results in higher production of EC and lower OC. To definitively determine the role of biofuel combustion in the northern Indian Ocean would require better source characterization of biofuel indigenous to south and Southeast Asia under various burn conditions.

[29] Hopanes and steranes are accepted tracers for fossil fuel combustion, in particular motor vehicle emissions, including gasoline and diesel vehicle exhaust [Schauer *et al.*, 1996, 1999b 2002; Schauer and Cass, 2000], fuel oil combustion [Rogge *et al.*, 1997], and coal combustion [Oros and Simoneit, 2000]. Of sixteen hopanes and steranes monitored, only 20(R&S), 5 α (H), 14 β (H), 17 β (H)-sitostane was quantified and, in all ambient samples, its concentration ranged from below detection limit ($<0.25 \text{ ng m}^{-3}$) to 1.16 ng m^{-3} in Hanimaadhoo and to 1.42 ng m^{-3} in Gan (Figure 4b). Measured concentrations of sitostane, in Los Angeles, an urban city heavily influenced by motor vehicle traffic, range from 0.52 to 1.67 ng m^{-3} . The measured

concentrations in Hanimaadhoo and Gan are relatively high for rural locations with little motor vehicle traffic. Therefore aerosol measured in the Maldives was likely transported from south or Southeast Asia where motor vehicles and fossil fuel combustion sources are important contributors to BC.

[30] Polyaromatic hydrocarbons (PAH) are formed during the incomplete combustion of carbonaceous material. Because PAH are emitted from nearly all combustion processes—including both fossil fuel combustion and biofuel burning—they are not sufficiently unique to be used as molecular markers for specific emissions [Simoneit, 2002]. The distribution of PAH in emissions from combustion is not well understood and is likely influenced by combustion temperature, aeration, and burn duration [Simoneit, 2002]. Furthermore, chamber studies have indicated that these compounds are not thermodynamically stable in the ambient atmosphere and undergo transformation [Li and Kamens, 1993]. The observed concentrations of eight PAH of molecular weight (MW) greater than 228 amu are presented in Figure 5a. These PAHs were below detection limit in all of the Gan samples, but were detected in all four Hanimaadhoo composites. The greatest concentration of PAH were observed in the third grouping, lasting from 23 November to 16 December 2004 with a sum total concentration of 1.48 ng m^{-3} . Coronene was the most abundant PAH observed in concentrations of 0.16–0.85 ng m^{-3} . Compared to ambient PAH concentrations observed in the Los Angeles [Schauer *et al.*, 1996], these values are relatively small. The concentration of high MW PAH in time series corresponds to a major increase in atmospheric EC concentrations which supports the hypothesis that combustion is the major source of BC in the development of the Maldivian brown cloud, although this result does not provide further insight into its source.

[31] Cholesterol has been widely used as an indicator of aerosol emissions generated by the cooking of meat [Nolte et al., 2002; Fine et al., 2004]. This sterol is found in the cell membranes in all animals, and can enter the atmosphere through a variety of pathways. Cholesterol was detected in all samples from both Hanimaadhoo and Gan (Figure 5a). Measured concentrations ranged from 6.93 to 16.00 ng m⁻³ and are relatively constant between the two sampling sites over the duration of this study. Reported ambient concentrations of cholesterol determined by silylation GCMS are in the range of 5 ng m⁻³ [Nolte et al., 1999], indicating that atmospheric cholesterol concentrations over the Arabian Sea are relatively high. It has been observed that cholesterol is secreted from marine organisms [Nichols and Espey, 1991] and can be associated with marine aerosols. This is consistent with cholesterol not being formed by combustion sources. High concentrations of cholesterol measured in ambient aerosol in the Los Angeles Basin have been attributed to this biogenic origin where sea spray is an important aerosol source [Fine et al., 2004]. It is likely that marine organisms are major contributors to cholesterol concentrations measured in the Arabian Sea.

[32] Aliphatic and aromatic diacids are accepted indicators of secondary organic aerosol (SOA) in remote locations where primary source contributions are minimal [Fine et al., 2004; Sheesley et al., 2004]. SOA is produced by the oxidation of organic compounds in the atmosphere. The concentrations of aliphatic and aromatic diacids observed in Hanimaadhoo and Gan are presented in Figure 5b. Aliphatic diacids are measurable only in the third and fourth Hanimaadhoo composites (2.81 and 15.50 ng m⁻³, respectively) and aromatic diacids only in the fourth (7.11 ng m⁻³). In Hanimaadhoo, the ratio of aliphatic diacids to OC was 0.46 ng μg⁻¹ in the third period and 4.46 ng μg⁻¹ in the fourth period. The significant increase in diacid concentrations relative to OC between these periods indicates SOA is more important in the polluted dry period and that aerosol precursors may be different. The measured diacid concentrations are greater than those observed in situations which facilitate SOA formation. During the summer months concentrations of individual aromatic diacids ranged from 0.5 to 1.0 ng m⁻³ in rural settings [Sheesley et al., 2004] and up to 3ng m⁻³ midday in urban settings [Fine et al., 2004]. Evidence of SOA formation was documented in the INDOEX study where organic acid concentrations were lowest during clean periods and highest when aerosol mass and OC loadings were elevated [Neusüß et al., 2002].

[33] The organic aerosol collected between 18 December and 21 January exhibited considerably higher concentrations of aliphatic and aromatic diacids, suggesting that SOA formation has contributed to the observed concentration of OC. If this is the case, traditional methods of comparing EC to OC in ambient atmospheres to source profiles will be biased because an excess of OC in ambient air will lessen the EC to OC ratio relative to its original value. Similarly, calculations involving particulate total carbon (TC) will be skewed. Traditionally, EC to OC or EC to TC ratios have been used to differentiate fossil fuel combustion (EC/OC > 1.0; 0.6 < EC/TC < 0.7) and biomass burning (EC/OC < 0.5; 0.1 < EC/TC < 0.2) [Novakov et al., 2000; Salam et al., 2003; Venkataraman et al., 2005]. It has been shown, however, that biofuel burning in India deviates from these

accepted values as EC to OC ratios reach 3.53 in biofuel aerosols [Venkataraman et al., 2005]. Consequently, biofuel aerosol may be misinterpreted as products of fossil fuel combustion. Or, the weakening of the EC to OC ratio of such biofuel by SOA formation may falsely cause this type of combustion to be interpreted as traditional biomass burning low in EC. To better understand the origins of EC, chemical profiling of biofuels and fossil fuels in terms of species not influenced by secondary formation or transformation in the south and Southeast Asian region should be explored.

[34] Organic speciation analysis of hopanes, steranes, and levoglucosan suggests that both biofuels and fossil fuels are important sources of EC over the Arabian Sea. However, advanced chemical approaches using levoglucosan as a molecular marker for biomass burning and hopanes and steranes for fossil fuel combustion are sufficient only where combustion sources are well characterized and comprehensively understood. The formation of SOA is significant in the Hanimaadhoo haze period, and further complicates specific source identification and apportionment.

[35] Specific inorganic elements may be useful molecular markers. Potassium, found in plants but not fossil fuels, can be used as a marker of biomass combustion [Watson et al., 2001; Mayol-Bracero et al., 2002; Fang et al., 2005; Zheng et al., 2005]. In the study of common Bangladeshi biofuels such as coconut leaves, rice straw, jackfruit branches, dried cow dung patties, and biomass briquettes, significant levels of water-soluble potassium were observed [Sheesley et al., 2004]. It has been documented that nonmineral potassium is also found in particles emitted from meat charbroiling [Hildemann et al., 1991; Schauer et al., 1999a Schauer and Cass, 2000], however this source is considered minimal for the samples discussed in this paper. Potassium can be associated with coal combustion, although its water-soluble fraction is minimal [Watson et al., 2001]. The water-soluble potassium concentration observed in Hanimaadhoo from 31 August to 21 January is presented in Figure 6a, in composites corresponding to those used in organic speciation. Water-soluble potassium concentrations were relatively high in the third and fourth periods reaching 0.39 and 0.60 μg m⁻³, respectively. These concentrations are slightly higher than the average water-soluble potassium concentrations observed during the INDOEX study (0.32 μg m⁻³) [Mayol-Bracero et al., 2002]. However, these concentrations are considerably elevated in comparison to fine particulate matter sampled in unpolluted areas and on par with measurements taken downstream of urban areas with high levels of biomass burning [Chow et al., 1996]. The observed temporal trend in water-soluble potassium correlates well with observed EC concentrations (R² = 0.933), demonstrating that biofuel burning is a likely contributor to BC. Because of the reduced levoglucosan concentrations and relatively elevated water-soluble potassium concentrations observed in the polluted dry season in Hanimaadhoo, it is likely that biofuel combustion, rather than traditional biomass burning, is an important source of BC in the northern Indian Ocean.

[36] Trace metals may also be useful molecular markers specific to aerosol sources. Measured concentrations of Si, Zn, Sb, Ni, V, Se, and Pb in fine particulate matter are presented in Figure 6 for Hanimaadhoo sampling periods corresponding to organics analysis. Si is largely associated

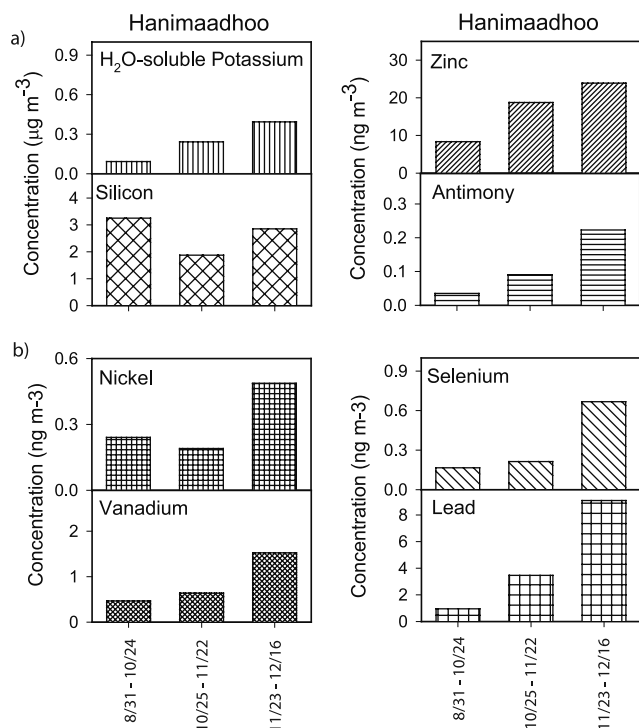


Figure 6. Concentrations of metal species measured in Hanimaadhoo, presented as averages over time periods corresponding to organic speciation. (a) Water-soluble potassium, silicon, zinc, and antimony. (b) Nickel, vanadium, selenium, and lead.

with aerosols deriving from soil sources or vegetative detritus [Hildemann *et al.*, 1991; Lough *et al.*, 2005]. Its temporal variability does not correspond to EC concentrations confirming that they are derived from different sources. Zn is a trace element associated with industrial sources and mobile sources [Chen *et al.*, 2001; Hien *et al.*, 2001; Chun and Yi, 2003; Lough *et al.*, 2005]. The observed Zn concentrations in Hanimaadhoo were after mid-November are five times larger than observed concentration in rural and wilderness settings [Fang *et al.*, 2005]. Sb in particulate matter is likely caused by industrial processing or burning of fossil fuels by motor vehicles [Hien *et al.*, 2001] and Ni and V are considered to be products of heavy fuel oil combustion [Pakkanen *et al.*, 2001]. The V measured in Hanimaadhoo was almost entirely in the fine fraction and eliminates road dust as a source of V [Fang *et al.*, 2005]. Se is a crustal trace element emitted by coal combustion [Hien *et al.*, 2001; Fang *et al.*, 2005], and concentrations more than quadruple between the clean and polluted sampling periods. Pb is predominantly associated with industrial processes [Hien *et al.*, 2001], fuel and motor oil combustion, and brake wear [Lough *et al.*, 2005]. The observed ambient concentrations in Hanimaadhoo are on par with concentrations observed in rural Asian settings [Fang *et al.*, 2005]. The select trace elements show visible temporal correlations with observed EC and point to anthropogenic combustion as sources of BC.

[37] Neither organic nor trace metal speciation point to a definitive source of BC, and thus PMF is employed to elucidate the relative source contributions of biofuel and fossil fuel combustion. Unlike source apportionment models

that require source profile inputs, PMF requires no a priori source information but does require a posteriori analysis of calculated factors to correctly interpret results. The PMF analysis identified five factors contributing to EC: Local 1, Local 2, Fossil Fuel, Biofuel, and Sea (Table 1). The two local sources are likely indicative of crustal materials, indigenous biomass, and/or local fuel use. The factor designated to fossil fuel burning was high in toxic metals, elemental carbon, and contained some potassium, consistent with trace metal molecular markers discussed previously. The biofuel factor was high in both EC and potassium and low in toxic metals. The aerosol factor linked with sea spray had high levels of sodium. A minimal amount of EC was associated with the sea spray factor which may be a result of aerosol mixing state. The relative contributions of these five factors to ambient EC concentrations are presented in Figure 7. The final category, labeled other, corresponds to unapportioned EC. Local sources contribute to 20% of EC prior to 15 November whereas they contribute merely 2% afterward, in accordance with observations of long-range transport (LRT) of aerosol mass high in EC. Some EC was associated with the sea spray factor, possibly a result of ships powered by fossil fuels. Meanwhile, EC from anthropogenic combustion sources was augmented during the period of high pollution: fossil fuel burning's contribution increased from 20 to almost 50% while EC related to biofuel burning jumped from 20 to nearly 40%. It is notable that both fossil fuel and biofuel burning contribute significantly to EC in Hanimaadhoo after the development of the brown cloud in mid-November.

4. Conclusion

[38] The development of a brown cloud was evidenced in Hanimaadhoo during the winter months of 2004 by increas-

Table 1. Fractional Composition of Each of the Five Factors Calculated by the PMF Model^a

	Local 1	Local 2	Sea Spray	Biofuel	Fossil Fuel
Na	0.4727	0.1001	0.7883	0.1205	0.0538
Mg	0.0313	0.0953	0.0643	0.0000	0.0000
Al	0.0019	0.2375	0.0051	0.0370	0.0000
P	0.0022	0.0055	0.0027	0.0019	<i>0.0061</i>
K	0.1022	0.0442	0.0514	0.3042	0.1123
Ca	0.2744	0.1592	0.0151	0.0000	0.0000
Mn	0.0005	0.0045	0.0009	0.0016	0.0081
Fe	0.0268	0.1925	0.0003	0.0351	0.0183
Ti	0.0046	<i>0.0165</i>	0.0004	0.0075	0.0010
V	0.0002	0.0022	0.0007	0.0008	0.0018
Cr	0.0003	0.0011	0.0002	0.0004	0.0005
Cu	0.0013	0.0006	0.0005	0.0011	0.0003
Zn	<i>0.0795</i>	0.0061	0.0000	0.0095	<i>0.0416</i>
Rb	0.0000	0.0005	0.0002	0.0001	0.0005
Sr	0.0008	0.0016	0.0005	0.0003	0.0001
Cd	0.0000	0.0000	0.0002	0.0000	0.0005
Sb	0.0001	0.0000	0.0001	0.0001	0.0003
Ba	0.0004	0.0017	0.0001	<i>0.0028</i>	0.0008
La	0.0000	0.0003	0.0000	0.0000	0.0000
Ce	0.0000	0.0006	0.0000	0.0001	0.0000
Pr	0.0000	0.0001	0.0000	0.0000	0.0000
Nd	0.0000	0.0002	0.0000	0.0000	0.0000
Pb	0.0007	0.0000	0.0034	0.0030	<i>0.0168</i>
EC	0.0000	0.1294	0.0656	0.4739	0.7371

^aProfile components shown in bold explain more than 60% of the variability observed in the atmospheric measurements by that source. Italicized components explain 40–60% of the variability.

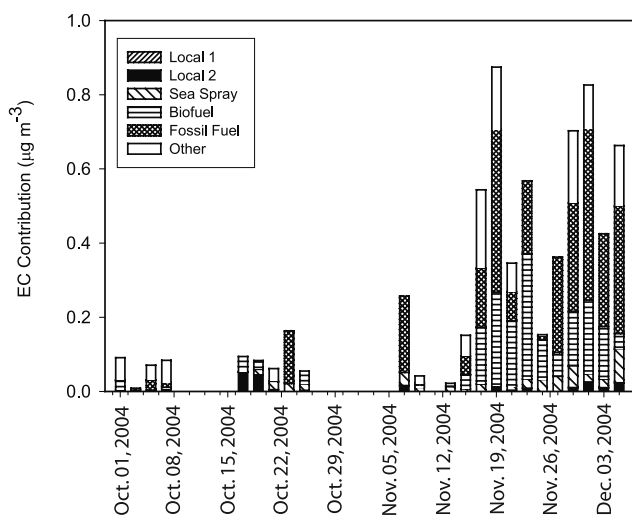


Figure 7. EC contribution of each of the five factors calculated by the PMF model. The difference between measured and calculated concentrations is attributed to other sources.

ing aerosol mass and EC concentrations. Meanwhile, ambient measurements in Gan were indicative of low levels, expected for the Maldives where few combustion sources are present. The polluted dry atmosphere in Hanimaadhoo was characterized by increasing concentrations of water-soluble potassium and levoglucosan, molecular markers for biomass burning. However, the relatively low concentration of levoglucosan compared to water-soluble potassium suggests that biofuel combustion rather than traditional biomass burning is the important source of BC. Similarly, toxic metals associated with fossil fuel combustion were present in increasing concentrations. Organic molecular markers suggested that both biofuel burning and fossil fuel combustion contributed to elevated EC concentrations but failed to reveal their relative contribution. To improve this situation, extensive source profiling for south and Southeast Asian biofuels is recommended. PMF modeling results based on trace metal speciation are consistent with trends observed in water-soluble ions and organic markers. This model predicted that biofuels accounted for 30–40% and fossil fuels accounted for 40–50% of EC observed during the period of high pollution in the winter months of 2004–2005. The significance of this result is that EC has two major sources that would need to be addressed in order to reduce EC concentrations in the northern Indian Ocean. More chemical measurements with better time resolution would improve the accuracy of this model and possibly provide further insight into specific biofuel and fossil fuel sources.

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