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Source apportionment of carbonaceous fine particulate matter ($PM_{2.5}$) in two contrasting cities across the Indo–Gangetic Plain

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ABSTRACT

Agra and Kanpur are heavily polluted Indian cities and are the fourth and second largest cities in Uttar Pradesh State, respectively. $PM_{2.5}$ was collected from December 2011 to May 2012 in Agra and from December 2011 to October 2012 in Kanpur every 6th day. The samples were chemically analyzed to determine organic carbon (OC), water soluble organic carbon (WSOC), elemental carbon (EC), secondary inorganic ions, and particle–phase organic compounds. A chemical mass balance (CMB) receptor model using organic tracers was used to estimate source contributions to $PM_{2.5}$. Concentrations of carbonaceous aerosols were on average 23±16 $\mu g/m^3$ in Agra and 33±21 $\mu g/m^3$ in Kanpur during the winter and summer periods, and had a strong seasonal trend with highest levels in winter (December–February) and then decreasing to summer (March–May). Five primary sources were identified. In Agra, biomass burning was the major source of OC in the winter months with decreasing relative and absolute concentrations in summer. In Kanpur, biomass burning was also the most important primary source of OC, but was about half the concentration found in Agra. Mobile source contributions to OC were on average 25±9% and 25±22% in Agra and Kanpur, respectively, with similar absolute concentrations of 2.5±1.9 $\mu g/m^3$ in most months. Secondary organic aerosol (SOA) was estimated from non–biomass burning WSOC and the unapportioned OC, with each method indicating SOA as a major source of OC in the winter in both cities, apportioning 25% of OC in Agra and 65% in Kanpur. SOA in Kanpur in December was four times higher than in Agra. Overall, results suggest differences in aerosol chemical composition and sources at these two sites across the Indo–Gangetic plain with biomass burning making up a larger fraction of the particulate OC in Agra, and SOA being a more important contributor to OC mass in Kanpur.

Keywords: *Source apportionment, CMB, organic compounds, WSOC, SOA*

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1. Introduction

The composition of atmospheric particulate matter (PM) and the PM sources vary considerably across space and time but in most urban locations PM is largely comprised of organic carbon (OC), elemental carbon (EC), ions, resuspended dust and trace metals. Organic material is made up of a mixture of hundreds of organic compounds, which are difficult to quantify (Saxena and Hildemann, 1996). They usually account for 20 to 50% of $PM_{2.5}$ mass (Saxena and Hildemann, 1996; Putaud et al., 2004). In most urbanized locations both primary and secondary sources are important contributors to particulate matter in the context of human health and climate forcing. Numerous studies have demonstrated the adverse effect of exposure to particulate matter on human health, including asthma, bronchitis, and premature death (Pope et al., 2004; Analitis et al., 2006; Pope and Dockery, 2006). Many large cities in India suffer from high levels of particulate matter pollution, which have been reported in several studies (Karar and Gupta, 2006; Ram and Sarin, 2011; Kumar et al., 2012); however, most of the studies are focused on the analysis of PM_{10}. As many regions of the world are focusing on controlling $PM_{2.5}$ to better protect human health, there is a need to better quantify the composition and sources of fine particulate matter in highly populated cities in India.

Studies conducted in Asian countries have determined that typical $PM_{2.5}$ sources are gasoline exhaust, diesel engine emission, coal combustion, biomass burning, and soil dust. The relative contributions of the sources vary according to the zone and the season of the year. In Bangladesh, a study at semi–residential and urban areas, which used the elemental composition of the samples in a Positive Matrix Factorization (PMF) model, calculated that motor vehicle contributed about 48% of $PM_{2.5}$ in the residential area and biomass burning contributed about 50% of fine particles in the urban area (Begum et al., 2004). In contrast, a study in a traffic corridor in Hyderabad, India, determined through a chemical mass balance (CMB) model using 12 metals that the predominant sources of $PM_{2.5}$ were vehicular pollution (31%) and resuspended dust (26%) (Gummeneni et al., 2011). Another study in a campus area in Lahore, Pakistan, which used organic tracer species in a CMB model, determined that the major source of $PM_{2.5}$ OC was non–catalyzed motor vehicles (53%), and the second largest source was biomass burning (10%) (Stone et al., 2010).

Agra and Kanpur, two large Indian cities in Uttar Pradesh State, have high $PM_{2.5}$ concentrations. Previous studies of air quality in Agra have reported concentrations of 116 $\mu g/m^3$ in winter, and 80 $\mu g/m^3$ as the annual average (Pachauri et al., 2013b). Studies in Kanpur have documented $PM_{2.5}$ concentrations of 163 $\mu g/m^3$ in wintertime (Ram and Sarin, 2011). Although organic particulate matter was shown to be an important fraction of particulate matter in these cities, the knowledge and understanding of the sources and composition of organic particulate matter in these cities is still for the most part unknown. Most published particulate matter studies conducted in these cities only cover short periods of time, mainly winter months. In general, these current studies are focused on gravimetric, OC, EC, ions, and metals analysis (Behera and Sharma, 2010; Ram and Sarin, 2011; Pachauri et al., 2013a). These studies have employed ratios such as OC/EC or K^+/EC to estimate the source of combustion (biomass or fossil fuel) and secondary organic aerosols (SOA). However, individual organic compound concentrations of $PM_{2.5}$ particles have not been previously reported for fine particulate matter in these cities. Concentrations of particle–phase organic compounds have been used to understand the sources of particulate matter in many regions of the world (Chowdhury et al., 2007; Stone et al., 2008; Stone et al., 2010; Daher et al., 2012; Heo et al., 2013). These measurements have been used in CMB models to estimate the sources of $PM_{2.5}$, but these methods have had limited application to India to date.

The objective of this study is to identify the sources of $PM_{2.5}$ in Agra and Kanpur and to quantify their contribution to fine particulate matter concentrations. To achieve this goal, a chemical characterization of particles was done, and organic compound concentrations were used in the CMB model to estimate the source apportionment to $PM_{2.5}$. The results of this research are expected to help develop appropriate policies and design strategies to control air pollution in Agra and Kanpur.

2. Methodology

2.1. Sampling sites description

Fine particulate matter was collected in Agra and Kanpur, two Indian cities located in the Uttar Pradesh State in the north of India. Agra is located in the northwestern part of the state (27°10′ N latitude and 78°1′ E longitude) at 171 m above sea level. Situated on the banks of the River Yamuna, this city is a world famous tourist destination for Taj Mahal. The climate is semiarid; it has mild winters (October–February), hot summers (March–June), and heavy rainfall in monsoon season (July–September). Agra is one of the most populated cities in Uttar Pradesh (population about 1.6 million). Agriculture and tourism are the base of the economy in Agra. Samples were collected inside the Taj Mahal complex (27°10′30″N, 78°02′31″E), which is located next to the Yamuna river. Kanpur is located on the banks of the River Ganges (26°47′ N latitude and 80°35′ E longitude) at 126 meters above sea level, and is a typical urban area in India. It is the most populous city in the state (population about 2.7 million) and one of the major industrial cities in the country. The city is surrounded by several point sources of pollution, including thermal power plants, fertilizer plants, and refineries (Mehta et al., 2009). In Kanpur, sampling was carried out in the Indian Institute of Technology Kanpur (IITK), which is located in an institutional and residential area. Both sampling sites are located in complexes that are not directly impacted by any specific source; they are away from major roadways, industrial sites and emissions from typical high density residential neighborhoods.

2.2. Sampling method and schedule

The duration of sampling was from December 2011 to May 2012 in Agra, and from December 2011 to October 2012 in Kanpur. Sampling methods were the same in both cities. Samples were collected every sixth day. In Agra and Kanpur, 30 and 52 samples were collected respectively. Sampling began at 9:00 local time and continued for 8 hours. $PM_{2.5}$ particles were collected on 47 mm quartz fiber filters (Tissuquartz™ Filters, 2500 QAT–UP, Pall Corporation) and Teflon filters (PTFE filters, Pall Corporation). Before sampling, quartz filters were baked at 500 C for at least 15 hours to remove organic compounds. In each sampler, a cyclone was used to remove particles with aerodynamic diameters bigger than 2.5 μm. Samplers were operated at a flow rate of 23 liters per minute (Lpm), which was controlled by critical orifice. After sampling, filters were placed in petri dishes, sealed, and stored in a freezer until analysis to prevent vaporization of compounds.

2.3. Chemical analysis

Elemental and organic carbon (EC and OC) were measured with a thermal–optical carbon analyzer (Sunset Laboratory, USA) using a thermal–optical transmittance (TOT) method according to the ACE–Asia base case protocol (Schauer et al., 2003). A portion of each quartz filter (1.5 cm^2) was placed in the instrument for analysis. In the first stage of the analysis, OC and EC produced by pyrolysis were thermally removed in a non–oxidant atmosphere, and afterwards in a second stage, EC was removed in an oxidant atmosphere at high temperatures. Laser transmittance was monitored throughout the process and was used to establish the split point which separates OC and EC, and to correct for the EC produced by pyrolysis. Water soluble organic carbon (WSOC) concentrations were measured using a TOC–V SCH Shimadzu total organic carbon analyzer. A portion of each quartz filter (1.5 cm^2) was water extracted using Milli–Q water (MQW) (resistivity 18.2 MΩ). Samples placed in tubes with MQW were shaken for 6 hours and filtered using 0.45 μm syringe filters before the analysis. More details of the method can be found elsewhere (Yang et al., 2003). Water–insoluble organic carbon (WIOC) was calculated as the difference between OC and WSOC and the uncertainty for WIOC was calculated by propagation of the uncertainties. Water soluble inorganic ions (SO_4^{2-} and NO_3^-) were measured using Ion Chromatography (Metrohm compact, IC 761) (Wang and Shooter, 2001). Organic speciation was conducted in monthly composites. Each composite had approximately 500 μg of OC to ensure detection of organic species by Gas Chromatography/ Mass Spectrometry (GC/MS). Sample composites were spiked with isotopically–labeled standard solutions before the extraction. Samples were extracted using 50/50 dichloromethane and acetone in a sonicator, followed by evaporation in a rotary evaporator, and blowing down using ultrapure nitrogen. Two aliquots of the extracts were analyzed by GC/MS. One aliquot was derivatized with diazomethane and the other aliquot was silylated. Additional details are described elsewhere (Stone et al., 2008). The average of all field blanks was used to correct the measurements.

2.4. Source apportionment

Given the study design focused on advanced chemical analysis of a limited number of sample composites, a molecular marker CMB model was used to calculate source contributions. Although it would have been desirable to compare apportionment results from the CMB model to a multivariate model such as PMF (Paatero and Tapper, 1994; Paatero, 1997) as was done by Heo et al. (2013), the use of a multivariate model requires the analysis of hundreds of independent measurements that was not possible for the subject study.

Primary source contributions to OC were calculated using the CMB model software available from the United States Environmental Protection Agency (EPA–CMB version 8.2). The software solves the effective variance least square solution of a set of linear equations of source profiles and receptor concentrations to calculate the source contribution to ambient concentrations (Watson et al., 1984). Molecular markers selected as tracers are stable during transport from source to receptor; they do not undergo chemical reactions and do not volatilize (Schauer et al., 1996). Seven source profiles were selected from literature based in previous studies in the United States, and profiles from Asia were used when possible. There is some potential bias that is introduced by the use of source profiles from the USA, but a number of studies have examined the sensitivity of the molecular marker CMB models to source profiles (Lough and Schauer, 2007; Sheesley et al., 2007; Stone et al., 2009). These studies have shown that although emission rates vary considerably across different regions of the world for specific sources, the profiles are reasonably stable in the context of apportioning organic aerosols to source categories. Source profiles included residential coal briquette combustion soot (Zhang et al., 2008), vegetative detritus (Rogge et al., 1993), diesel (Lough et al., 2007), smoking vehicle (Lough et al., 2007), gasoline emission (Lough et al., 2007), cow dung (Sheesley et al., 2003), and wood (Sheesley et al., 2007) (see the Supporting Material, SM, Table S1). Twenty one molecular markers were selected, including EC, benzo[*b*]fluoranthene, benzo[*k*]-fluoranthene, benzo[*e*]pyrene, indeno[1,2,3–*cd*]pyrene, benzo-[*ghi*]perylene, picene, 17α(H)–22,29,30–trisnorhopane, 17α(H)–21β(H)–30–norhopane, 17α(H)–21β (H)–hopane, ABB–20R–C27–cholestane, ABB–20R–C29–sitostane, ABB–20S–C29–sitostane, n–alkanes, and levoglucosan. CMB results are considered acceptable if R^2>0.8, X^2<8, and concentration of calculated species agree within 25% of measured concentrations. If some source profiles showed co–linearity or the CMB results did not converge, a sensitivity analysis was done to combine sources of OC. When organic molecular markers of a source were not detected, the source was not included in the model.

3. Results and Discussion

3.1. Composition

In both cities, OC, EC, WSOC, and WIOC followed the same pattern; the highest concentrations were registered in winter, especially in December as shown in Figure S1 (see the SM). Organic carbon had significantly different concentrations. In contrast, EC concentrations in December were only slightly higher than for the rest of the period. It could be as a result of more emissions from biogenic sources and formation of SOA in winter.

In both cities, monthly OC concentrations were higher during December and decreased continuously into the summer and monsoon months. In Agra, values ranged from a high of 24.1 μg/m^3 during December to a low of 4.7 μg/m^3 in April, with an average of 10.2±7.2 μg/m^3. WIOC and WSOC average concentrations were 6.8±3.9 μg/m^3 and 3.4±3.3 μg/m^3 respectively. WSOC/OC decreased from 40% during December to 13% in April, with an average of 28.5±11.7%. EC concentrations had an average of 1.3±0.8 μg/m^3, with no apparent seasonal trend. Monthly concentrations of OC, divided into WSOC and WIOC, and EC for all months analyzed are given in Figure 1. The OC/EC average of winter and summer seasons was 8.1±1.2. A previous study in Agra reported average concentrations of winter and summer months (October–June) of OC, EC and OC/EC of 28.2 μg/m^3, 4.0 μg/m^3, and 6.9 respectively (Pachauri et al., 2013b). These previously reported OC and EC concentrations were about 3 times higher than concentrations measured in this study; however, OC/EC ratios are similar. These relatively high OC/EC ratios indicate presence of SOA and biogenic emissions. Another study in Agra reported a OC/EC ratio of 8.1 in winter in a campus area (Pachauri et al., 2013), which is a similar area to the Taj Mahal location. Similarly, in the present study, the OC/EC ratio for winter was 7.8. In Kanpur, OC ranged from 30.13 μg/m^3 in December to 2.55 μg/m^3 in September, averaging 9.3±7.9 μg/m^3. WIOC and WSOC average concentrations were 5.5±4.4 μg/m^3 and 3.8±3.8 μg/m^3, respectively. WSOC/OC did not follow any trend and it constituted an average of 41±12%. Average EC concentration was 1.11±0.88 μg/m^3, and the OC/EC average was 11.0±8.6. Considering only the period between December to May in Kanpur, average OC and EC concentrations, and OC/EC were 13.5±8.8 μg/m^3, 1.7±0.8 μg/m^3, and 7.6±1.7 respectively. The average OC/EC ratio is slightly lower than a previously reported ratio around 11 (Kaul et al., 2011). OC and EC concentrations in Agra and Kanpur were lower than concentrations reported in other major Indian cities like Delhi, where OC and EC concentrations (winter 2010 and 2011) were 54±39 μg/m^3 and 10±5 μg/m^3 respectively (Tiwari et al., 2013). Average concentrations reported for Mumbai (2007–2008) of OC and EC were higher than 20 μg/m^3 and 5 μg/m^3, respectively (Abba et al., 2012).

Concentrations of secondary inorganic aerosols (SIA), ammonium sulfate [$(NH_4)_2SO_4$] and ammonium nitrate (NH_4NO_3), were estimated using concentrations of sulfate (SO_4^{2-}) and nitrate (NO_3^-) ions. SIA concentrations were calculated assuming that sulfate and nitrate were present as ammonium sulfate and ammonium nitrate respectively. It is possible that this is an overestimate of ammonium if calcium nitrate or ammonium bisulfate is present as well.

3.2. Organic species

Molecular markers concentrations account for a small fraction of organic compounds; however, they provide valuable information about the sources of aerosols. Monthly concentrations of the main molecular markers; levoglucosan, hopanes, and polycyclic aromatic hydrocarbons (PAHs), in Agra and Kanpur, from December to May, are shown in Figure 2. Concentrations of biomarkers in Kanpur from December to October are presented in Figure S2 (see the SM).

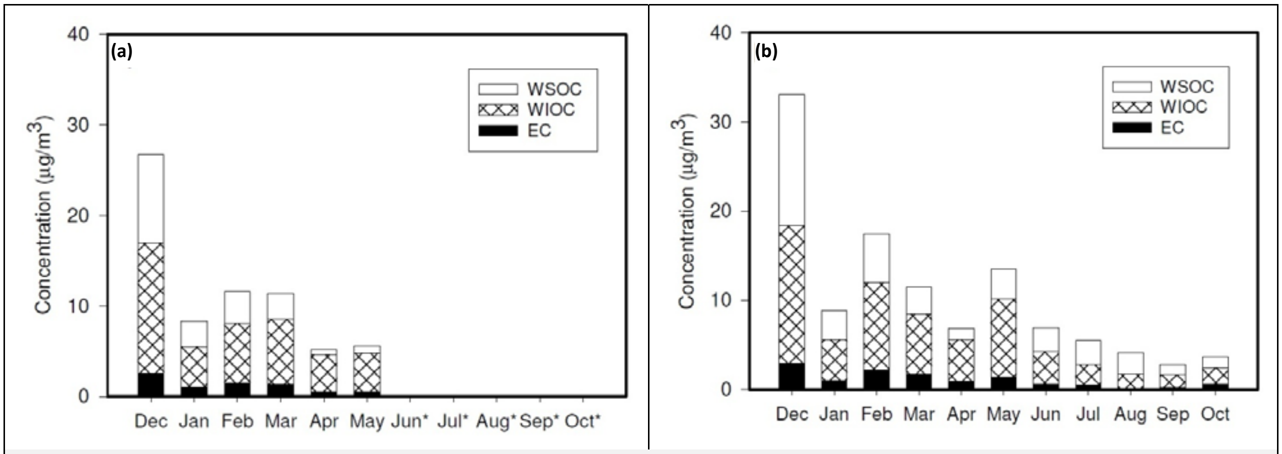

Figure 1. *Monthly EC, WIOC, and WSOC concentrations in **(a)** Agra and **(b)** Kanpur from December to October. *Samples were not collected.*

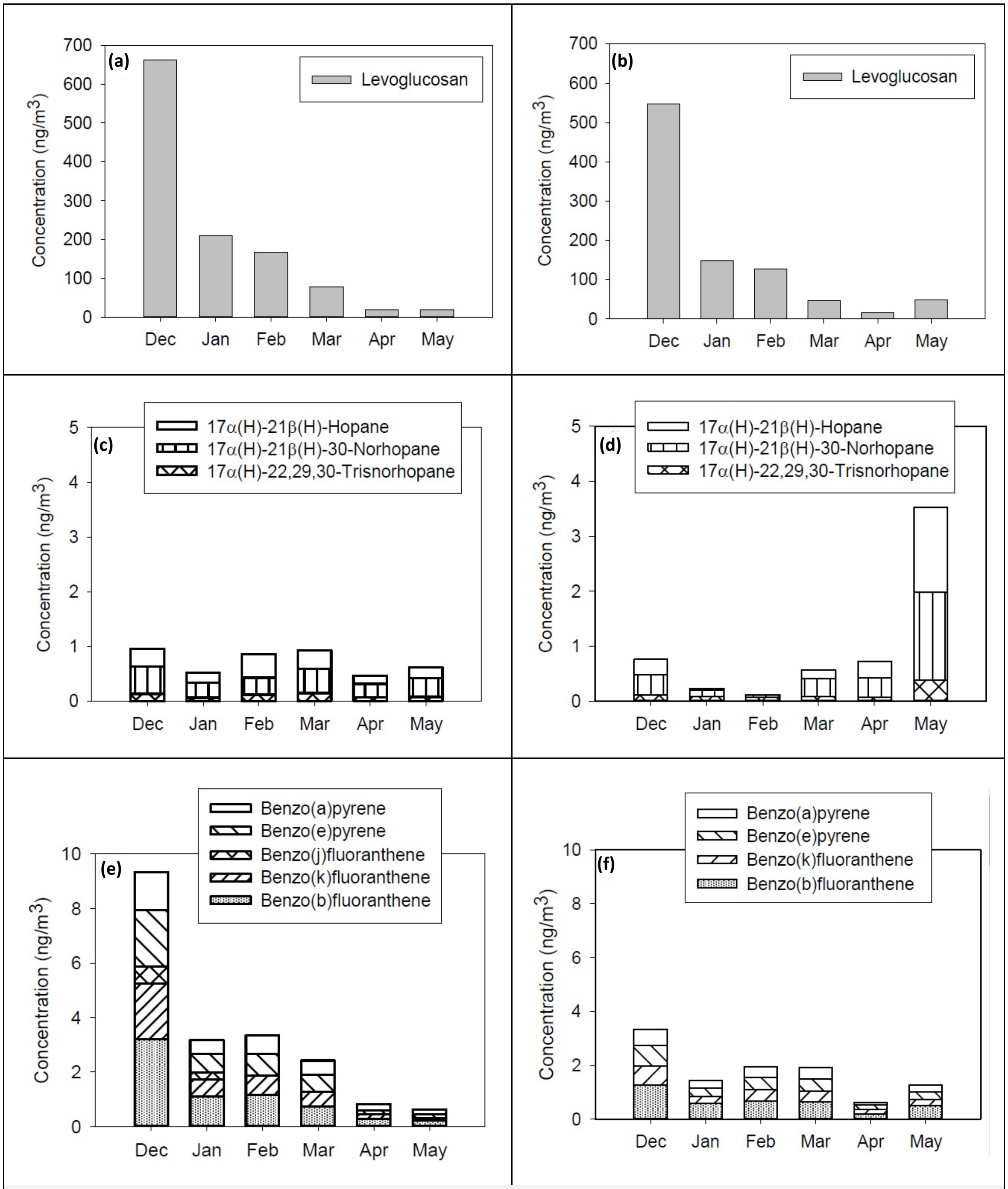

Figure 2. *Monthly concentrations of* ***(a)*** *levoglucosan in Agra,* ***(b)*** *levoglucosan in Kanpur,* ***(c)*** *hopanes in Agra,* ***(d)*** *hopanes in Kanpur,* ***(e)*** *PAHs in Agra, and* ***(f)*** *PAHs in Kanpur from December to May.*

Levoglucosan, a well–recognized tracer for biomass burning (Simoneit et al., 1999), shows a clearly seasonal pattern in Agra and Kanpur. In both cities the highest concentrations were in winter and decreased continuously to summer. In Agra, it ranged from 663 ng/m^3 (December) to 19 ng/m^3 (April). Similarly, in Kanpur, levoglucosan ranged from 546 ng/m^3 (December) to 15 ng/m^3 (April). The higher concentrations in December are explained by the cold temperatures in winter that increases the use of biomass for domestic heating. A previous study in another Asian city (Lahore, Pakistan) reported higher levoglucosan concentrations in winter; reaching about 1 800 ng/m^3 during December (Stone et al., 2010). The main kinds of biomass used in Asia are wood, cow dung, and crop residues (Sheesley et al., 2003). The large demand for biomass is because of the great availability and low price, in contrast with fossil fuels. In India, cow dung is more available than crop residues and it is more used in urban and rural areas among all social classes (Leach, 1987).

Hopanes are biomarkers of fuel oil combustion (Rogge et al., 1997), mobile sources including diesel and gasoline vehicle engine (Shrivastava et al., 2007), and coal combustion (Oros and Simoneit, 2000). Figures 2c and 2d show concentrations of 17α(H)–22,29,30–trisnorhopane, 17α(H)–21β(H)–30–norhopane, and 17α(H)–21β(H)–hopane. They did not follow a clear pattern in Agra or

Kanpur. In Agra, average concentration of the sum of the hopanes was 0.73±0.21 ng/m^3, and similarly, it was 1.0±1.3 ng/m^3 in Kanpur. Agra showed a higher concentration in May that could have been produced by a strong increase in emissions from a localized source.

PAHs are produced as a result of incomplete combustion of fossil fuels at high temperatures (Ravindra et al., 2008). PAHs are biomarkers of gasoline spark ignition, wood combustion, and diesel engine emissions. In the United States, gasoline and wood are the main sources of PAHs (Li and Kamens, 1993). Some of these compounds are carcinogenic, like benzo[*b*]fluoranthene, benzo[*k*]-fluoranthene, and benzo[*a*]pyrene, which are included in the 16 US Environmental Protection Agency (EPA) priority PAHs (Ravindra et al., 2008). Concentrations of PAHs shown in Figures 2e and 2f follow a clear trend. The highest concentrations were in December and decreased into summer. In Agra, total PAH concentration ranged from 9.3±0.95 ng/m^3 during December to 0.6±0.1 ng/m^3 in May. In Kanpur, concentrations were slightly lower. Values ranged from 3.3±0.3 ng/m^3 in December to 0.6±0.1 ng/m^3 in April. PAH concentrations in Kanpur were under detection limit during monsoon season (see the SM, Figure S2). PAH concentrations were much lower than a previous study in Lahore, Pakistan, which reported concentrations between 10 and 55 ng/m^3 (Stone et al., 2010); however, levels were comparable to Milan, which registered concentrations from about 0.3 ng/m^3 to 7.5 ng/m^3 (Daher et al., 2012).

Picene is a polycyclic aromatic hydrocarbon which is a specific molecular biomarker of coal combustion (Oros and Simoneit, 2000). It was detected only in winter in both cities. In Agra, the picene concentration was 0.41±0.12 ng/m^3 and in Kanpur (only detected in December) it was 0.38 ng/m^3. These concentrations were lower than previously reported in Lahore (0.6–2.4 ng/m^3) (Stone et al., 2010). Because picene was detected only in winter, it appears that coal emissions are dominated by residential heating, or could be produced by brick kilns during the winter.

In Agra, C_{27-33} n–alkanes had the highest concentration in December and it decreased into May. n–Alkanes concentrations ranged from 171.1±8.6 ng/m^3 to 8.9±2.0 ng/m^3. In contrast, in Kanpur n–alkanes did not follow any pattern. Their concentrations ranged from 79.2±6.4 ng/m^3 (May) to 16.1±2.9 ng/m^3 (April). In both cities CPI (carbon preference index), which is the ratio of odd n–alkanes to even n–alkanes and is used to determine the origin of n–alkanes, was calculated. Origin of n–alkanes could be vegetative detritus (plant wax, microbes) and anthropogenic emissions (oil, soot) (Simoneit, 1986). CPI values from 0.85 to 1.15 indicate that n–alkanes come from crude oil, if CPI is higher (up to 10) it suggests that leaf waxes are the origin of the n–alkanes (Wils et al., 1982). Average CPI in Agra is 1.7, and in Kanpur it is 2.1, which clearly indicates that the origin of n–alkanes is not fossil fuels.

3.3. Chemical mass balance results

Source apportionment of $PM_{2.5}$ OC. Results of the CMB model including the seven primary sources preselected were not satisfactory because the three mobile source profiles included in the model led to co–linearity problems in both cities. Consequently, the model was re–run using only diesel and smoking vehicle profiles as mobile sources. Sensitivity analyses in both cities determined that mobile source contributions were not significantly different when three (diesel, smoking vehicle, and gasoline) or two (diesel and smoking vehicle) source profiles were included in the model (see the SM, Figure S3). Therefore, only diesel and smoking vehicle were selected as mobile sources in both cities.

Monthly primary contributions to OC were estimated using the CMB model. Results are presented in Figure 3 and summarized in Table S2 (see the SM). Percentage contributions to OC are shown in the SM, Figure S4. Primary sources selected are vegetative detritus, biomass burning, diesel emission, smoking vehicle, and coal combustion. "Others" represents SOA and unknown primary sources. It is calculated as the difference between the OC concentration measured and the sum of the contribution of primary sources.

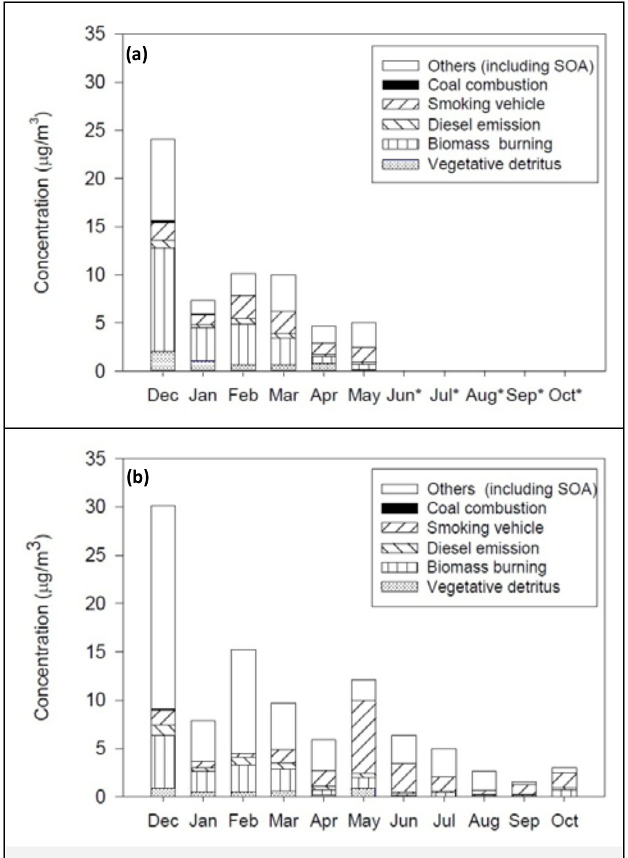

Figure 3. *Monthly source apportionment of $PM_{2.5}$ OC from December to October estimated by CMB model in **(a)** Agra and **(b)** Kanpur. *Samples were not collected.*

In Agra, biomass burning concentration was highest during December decreasing continuously to May. Biomass burning was the major source of OC in winter (December–February) accounting for 44±3%. In the summer season (March–May) it accounted for 18±8% of OC. Concentrations ranged from 10.8±2.1 μg/m^3 (average±standard error) in December to 0.6±0.3 μg/m^3 in May, averaging 3.74±3.72 μg/m^3. Contribution in December was more than twice that in other months, suggesting that biomass is used for domestic heating and cooking. Smoking vehicle was the second most important source of OC in Agra. Contributions did not significantly change during the months analyzed and they did not have any pattern. The average contribution to OC was 1.7±0.6 μg/m^3, which accounted for 15±8% in winter and 26±4% in summer of OC. Diesel contributions did not follow any trend. Its average concentration was 0.4±0.2 μg/m^3. This source contributes to 4% of OC in winter and summer. Coal contributed the least to OC. This source was identified only in December and January contributing 0.24±0.12 μg/m^3 and 0.12±0.03 μg/m^3 respectively. The average estimated contribution to OC was only 0.9%. Coal emissions could be produced by brick kilns, or residential heating considering that it was detected only in winter. However, it is consumed in a proportion much lower than biomass. Vegetative detritus contributed an average of 0.92±0.64 μg/m^3 to OC. Its contribution decreased from 2.06±0.25 μg/m^3 in December to 0.15±0.07 μg/m^3 in May, apportioning 10±4% and 9±5% in winter and summer respectively. "Others" contributed the highest in

December, 8.43±2.52 μg/m^3, and its average concentration was 3.3±2.6 μg/m^3 during the entire period. The contribution to OC represented 25±9% in winter and 42±8% in summer.

In Kanpur, biomass burning also was the most important primary source in winter, especially in December, and its concentration decreased in warmer months. It contributed from 5.51±1.13 μg/m^3 in December to 0.18±0.04 μg/m^3 in September. Although biomass burning contribution followed the same trend as in Agra, in Kanpur the concentration was about half that of Agra in the winter season. Smoking vehicles followed a different pattern; the contribution to OC was higher in summer (March–June). Smoking vehicle concentrations ranged from 7.55±0.92 μg/m^3 in May to 0.43±0.35 μg/m^3 in August. The average contribution from December to May was 2.19±2.68 μg/m^3. In winter, it contributed to only 5±3% of OC; however, in summer and monsoon seasons, it contributed 35±21% and 40±22% to OC respectively. Diesel contribution was higher in December (1.06±0.18 μg/m^3) and decreased continuously to August (0.03±0.01 μg/m^3). Its contribution to OC was relatively low: 5±1% in winter, 4±2% in monsoon season, and 6±2% in summer. Relative contribution was similar to Agra. In the same way as Agra, coal contributed the least to OC. This source was identified only in December, contributing 0.11±0.07 μg/m^3. It represented only 0.4% of the contribution to OC in December. This result suggests that coal in Kanpur could have the same use as in Agra–brick kilns or residential heating. Vegetative detritus contributions to OC did not have any pattern. Its contribution ranged from a low of 0.13±0.07 μg/m^3 in June to a high of 0.92±0.13 μg/m^3 in May. It contributed 4±2% in winter and 5±3% in summer. This source did not contribute to OC in monsoon season because their molecular markers were not detected between July and October. "Others" had highest contributions in December and decreased into October. It contributed from 21.03±1.79 μg/m^3 in December to 0.33±0.97 μg/m^3 in September. It was the most important contributor to OC in winter, apportioning 65±10%. In summer and monsoon season, contributions were also relevant, 40±20% and 43±28% respectively, averaging 52±18% from December to May. The higher concentrations in winter, especially in December, could be explained by the high VOC emissions from industrial processes.

Source apportionment of $PM_{2.5}$. To estimate the apportionment to $PM_{2.5}$, specific OC/$PM_{2.5}$ factors were applied to the OC results of the CMB model for each source: residential coal briquette soot (Zhang et al., 2008), vegetative detritus (Rogge et al., 1993), diesel (Lough et al., 2007), smoking vehicle (Lough et al., 2007), cow dung (Sheesley et al., 2003), wood (Sheesley et al., 2007), SOA and other sources (Turpin and Lim, 2001) (see the SM, Table S3). Figure 4 shows a summary of the contributions to $PM_{2.5}$ in Agra and Kanpur, and Table S4 shows all the contributions to $PM_{2.5}$.

In Agra, SIA were an important source of $PM_{2.5}$. Their contributions to $PM_{2.5}$ generally decreased from December to May. Contribution ranged from 26.4 μg/m^3 in December to 6.3 μg/m^3 in May. Biomass burning had a high contribution in December, 20.16 μg/m^3, which decreased to 1.30 μg/m^3 in May. Its contribution ranged from 27% in December to 7% in April. SOA also was an important source of $PM_{2.5}$, especially in December.

In Kanpur, SOA was the most important source of $PM_{2.5}$. Its contribution decreased from 42 μg/m^3 in December to 0.67 μg/m^3 in September. It apportioned from a high 68% of $PM_{2.5}$ in December to a low 20% in May. SOA contributed to $PM_{2.5}$ 24±17.0 μg/m^3 in winter, 6.7±2.7 μg/m^3 in summer, and 3.4±2.4 μg/m^3 in monsoon, representing 58±13%, 33±12%, and 46±23% respectively. Inorganic aerosol contribution was much lower than in Agra, accounting for only 11% of apportioned mass. Their concentrations did not follow any trend, but in monsoon season they are lower than in the rest of the year. Contribution ranged from 4.83 μg/m^3 in March to 0.02 μg/m^3 in August. The annual average contribution to $PM_{2.5}$ was 2.17±1.8 μg/m^3.

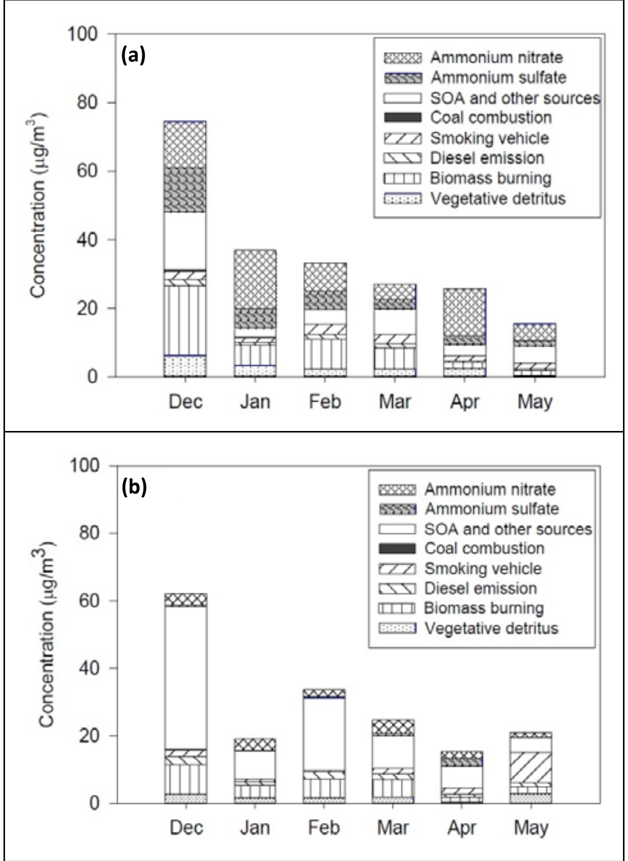

Figure 4. *Monthly source apportionment of $PM_{2.5}$ mass in **(a)** Agra and **(b)** Kanpur from December to May.*

In consideration of the characteristics of the sampling sites in Agra and Kanpur, the source contributions calculated in this study are reasonably comparable but not representative of all sites in these cities.

4. Summary and Conclusions

Average ambient concentrations of $PM_{2.5}$ in Agra and Kanpur are higher than the $PM_{2.5}$ standard recommended by World Health Organization, especially in winter; although levels measured during this field study are generally lower than what has been reported for other Indian megacities. CMB modeling was used to estimate source contributions to OC. In Agra, biomass burning contribution was the major source of OC. The highest contribution was during December and decreased to May. Concentrations ranged from 10.8±2 μg/m^3 to 0.6±0.3 μg/m^3. These results could indicate that biomass is used for residential heating in winter, and in warmer seasons it is used only for cooking. Smoking vehicle was the second important primary source of OC in Agra, which is constant during all months. The average concentration was 1.7±0.6 μg/m^3. SOA contribution was similar in all months (averaging 2.3±0.9 μg/m^3 from January to May) except during December when it was 8.4±2.5 μg/m^3. SOA contributed 25±9% in winter and 42±8% in summer months. Coal combustion contributed only in winter, which suggests that coal could be used for residential heating or in brick kilns. Coal combustion contributed only 0.9±0.8% of OC in this season. In Kanpur, biomass burning was the most important primary source of OC. It contributed from 5.5±1.1 μg/m^3 in December to 0.2±0.0 μg/m^3 in September. Biomass burning apportionment to OC in Kanpur was about half of that in Agra. Smoking vehicle had higher contributions in summer than in winter and monsoon season. Apportionment ranged from 7.6±0.9 μg/m^3 in May to 0.4±0.4 μg/m^3 in August. It contributed to 35±21% and

40±22% of OC in summer and monsoon respectively. SOA contribution was higher during December and decreased continuously to October. Contribution ranged from 21.0±1.8 μg/m^3 to 0.33±1.0 μg/m^3. SOA was the major source in winter, apportioning 65±10% of OC; in summer and monsoon it contributed 40±20% and 43±28% respectively. In Agra, SIA were an important source of PM$_{2.5}$, especially in winter period. Biomass burning and SOA were the other important sources of PM$_{2.5}$. In Kanpur, SOA were the most important source of PM$_{2.5}$, especially in winter season. The contribution ranged from 42 μg/m^3 in December to 0.67 μg/m^3 in September.

Acknowledgments

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Supporting Material Available

Source profiles used for CMB model (Table S1), Source apportionment to OC estimated by CMB in Agra and Kanpur (Table S2), OC/PM$_{2.5}$ factors (Table S3), Source contributions to PM$_{2.5}$ in Agra and Kanpur (Table S4), Concentrations of a) organic carbon, (b) elemental carbon, (c) water soluble organic carbon, and (d) water–insoluble organic carbon in Agra and Kanpur (Figure S1), Monthly concentrations of (a) levoglucosan, (b) hopanes, and (c) PAHs in Kanpur from December to October (Figure S2), Sensitivity analysis of mobile sources in Agra and Kanpur (Figure S3), Percentage contribution to PM$_{2.5}$ OC in Agra and Kanpur (Figure S4). This information is available free of charge via the internet at http://www.atmospolres.com.

References

Abba, E.J., Unnikrishnan, S., Kumar, R., Yeole, B., Chowdhury, Z., 2012. Fine aerosol and PAH carcinogenicity estimation in outdoor environment of Mumbai City, India. *International Journal of Environmental Health Research* 22, 134–149.

Analitis, A., Katsouyanni, K., Dimakopoulou, K., Samoli, E., Nikoloulopoulos, A.K., Petasakis, Y., Touloumi, G., Schwartz, J., Anderson, H.R., Cambra, K., Forastiere, F., Zmirou, D., Vonk, J.M., Clancy, L., Kriz, B., Bobvos, J., Pekkanen, J., 2006. Short–term effects of ambient particles on cardiovascular and respiratory mortality. *Epidemiology* 17, 230–233.

Begum, B.A., Kim, E., Biswas, S.K., Hopke, P.K., 2004. Investigation of sources of atmospheric aerosol at urban and semi–urban areas in Bangladesh. *Atmospheric Environment* 38, 3025–3038.

Behera, S.N., Sharma, M., 2010. Reconstructing primary and secondary components of PM$_{2.5}$ composition for an urban atmosphere. *Aerosol Science and Technology* 44, 983–992.

Chowdhury, Z., Zheng, M., Schauer, J.J., Sheesley, R.J., Salmon, L.G., Cass, G.R., Russell, A.G., 2007. Speciation of ambient fine organic carbon particles and source apportionment of PM$_{2.5}$ in Indian cities. *Journal of Geophysical Research–Atmospheres* 112, art. no. D15303.

Daher, N., Ruprecht, A., Invernizzi, G., De Marco, C., Miller–Schulze, J., Heo, J.B., Shafer, M.M., Shelton, B.R., Schauer, J.J., Sioutas, C., 2012. Characterization, sources and redox activity of fine and coarse particulate matter in Milan, Italy. *Atmospheric Environment* 49, 130–141.

Gummeneni, S., Bin Yusup, Y., Chavali, M., Samadi, S.Z., 2011. Source apportionment of particulate matter in the ambient air of Hyderabad City, India. *Atmospheric Research* 101, 752–764.

Heo, J.B., Dulger, M., Olson, M.R., McGinnis, J.E., Shelton, B.R., Matsunaga, A., Sioutas, C., Schauer, J.J., 2013. Source apportionments of PM$_{2.5}$ organic carbon using molecular marker Positive Matrix Factorization and comparison of results from different receptor models. *Atmospheric Environment* 73, 51–61.

Karar, K., Gupta, A.K., 2006. Seasonal variations and chemical characterization of ambient PM$_{10}$ at residential and industrial sites of an urban region of Kolkata (Calcutta), India. *Atmospheric Research* 81, 36–53.

Kaul, D.S., Gupta, T., Tripathi, S.N., Tare, V., Collett, J.L., 2011. Secondary organic aerosol: A comparison between foggy and nonfoggy days. *Environmental Science & Technology* 45, 7307–7313.

Kumar, A., Sudheer, A.K., Goswami, V., Bhushan, R., 2012. Influence of continental outflow on aerosol chemical characteristics over the Arabian Sea during winter. *Atmospheric Environment* 50, 182–191.

Leach, G., 1987. Household energy in South–Asia. *Biomass* 12, 155–184.

Li, C.K., Kamens, R.M., 1993. The use of polycyclic aromatic–hydrocarbons as source signatures in receptor modeling. *Atmospheric Environment Part A–General Topics* 27, 523–532.

Lough, G.C., Schauer, J.J., 2007. Sensitivity of source apportionment of urban particulate matter to uncertainty in motor vehicle emissions profiles. *Journal of the Air & Waste Management Association* 57, 1200–1213.

Lough, G.C., Christensen, C.G., Schauer, J.J., Tortorelli, J., Mani, E., Lawson, D.R., Clark, N.N., Gabele, P.A., 2007. Development of molecular marker source profiles for emissions from on–road gasoline and diesel vehicle fleets. *Journal of the Air & Waste Management Association* 57, 1190–1199.

Mehta, B., Venkataraman, C., Bhushan, M., Tripathi, S.N., 2009. Identification of sources affecting fog formation using receptor modeling approaches and inventory estimates of sectoral emissions. *Atmospheric Environment* 43, 1288–1295.

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

Paatero, P., 1997. Least squares formulation of robust non–negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23–35.

Paatero, P., Tapper, U., 1994. Positive matrix factorization: A nonnegative factor model with optimal utilization of error estimates of data values. *Environmetrics* 5, 111–126.

Pachauri, T., Satsangi, A., Singla, V., Lakhani, A., Kumari, K.M., 2013. Characteristics and sources of carbonaceous aerosols in PM$_{2.5}$ during wintertime in Agra, India. *Aerosol and Air Quality Research* 13, 977–991.

Pachauri, T., Singla, V., Satsangi, A., Lakhani, A., Kumari, K.M., 2013. Characterization of carbonaceous aerosols with special reference to episodic events at Agra, India. *Atmospheric Research* 128, 98–110.

Pope, C.A., Dockery, D.W., 2006. Health effects of fine particulate air pollution: Lines that connect. *Journal of the Air & Waste Management Association* 56, 709–742.

Pope, C.A., Burnett, R.T., Thurston, G.D., Thun, M.J., Calle, E.E., Krewski, D., Godleski, J.J., 2004. Cardiovascular mortality and long–term exposure to particulate air pollution – Epidemiological evidence of general pathophysiological pathways of disease. *Circulation* 109, 71–77.

Putaud, J.P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Muller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., Brink, H.T., Torseth, K., Wiedensohler, A., 2004. A European aerosol phenomenology—2: Chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmospheric Environment* 38, 2579–2595.

Ram, K., Sarin, M.M., 2011. Day–night variability of EC, OC, WSOC and inorganic ions in urban environment of Indo–Gangetic Plain: Implications to secondary aerosol formation. *Atmospheric Environment* 45, 460–468.

Ravindra, K., Sokhi, R., Van Grieken, R., 2008. Atmospheric polycyclic aromatic hydrocarbons: Source attribution, emission factors and regulation. *Atmospheric Environment* 42, 2895–2921.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1997. Sources of fine organic aerosol. 8. Boilers burning No. 2 distillate fuel oil. *Environmental Science & Technology* 31, 2731–2737.

Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1993. Sources of fine organic aerosol. 4. Particulate abrasion products from leaf surfaces of urban plants. *Environmental Science & Technology* 27, 2700–2711.

Saxena, P., Hildemann, L.M., 1996. Water–soluble organics in atmospheric particles: A critical review of the literature and application of thermodynamics to identify candidate compounds. *Journal of Atmospheric Chemistry* 24, 57–109.

Schauer, J.J., Mader, B.T., Deminter, J.T., Heidemann, G., Bae, M.S., Seinfeld, J.H., Flagan, R.C., Cary, R.A., Smith, D., Huebert, B.J., Bertram, T., Howell, S., Kline, J.T., Quinn, P., Bates, T., Turpin, B., Lim, H.J., Yu, J.Z., Yang, H., Keywood, M.D., 2003. ACE–Asia intercomparison of a thermal–optical method for the determination of particle–phase organic and elemental carbon. *Environmental Science & Technology* 37, 993–1001.

Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R., Simoneit, B.R.T., 1996. Source apportionment of airborne particulate matter using organic compounds as tracers. *Atmospheric Environment* 30, 3837–3855.

Sheesley, R.J., Schauer, J.J., Zheng, M., Wang, B., 2007. Sensitivity of molecular marker–based CBM models to biomass burning source profiles. *Atmospheric Environment* 41, 9050–9063.

Sheesley, R.J., Schauer, J.J., Chowdhury, Z., Cass, G.R., Simoneit, B.R.T., 2003. Characterization of organic aerosols emitted from the combustion of biomass indigenous to South Asia. *Journal of Geophysical Research–Atmospheres* 108, art. no. 4285.

Shrivastava, M.K., Subramanian, R., Rogge, W.F., Robinson, A.L., 2007. Sources of organic aerosol: Positive Matrix Factorization of molecular marker data and comparison of results from different source apportionment models. *Atmospheric Environment* 41, 9353–9369.

Simoneit, B.R.T., 1986. Characterization of organic–constituents in aerosols in relation to their origin and transport – A review. *International Journal of Environmental Analytical Chemistry* 23, 207–237.

Simoneit, B.R.T., Schauer, J.J., Nolte, C.G., Oros, D.R., Elias, V.O., Fraser, M.P., Rogge, W.F., Cass, G.R., 1999. Levoglucosan, a tracer for cellulose in biomass burning and atmospheric particles. *Atmospheric Environment* 33, 173–182.

Stone, E., Schauer, J., Quraishi, T.A., Mahmood, A., 2010. Chemical characterization and source apportionment of fine and coarse particulate matter in Lahore, Pakistan. *Atmospheric Environment* 44, 1062–1070.

Stone, E.A., Zhou, J.B., Snyder, D.C., Rutter, A.P., Mieritz, M., Schauer, J.J., 2009. A comparison of summertime secondary organic aerosol source contributions at contrasting urban locations. *Environmental Science & Technology* 43, 3448–3454.

Stone, E.A., Snyder, D.C., Sheesley, R.J., Sullivan, A.P., Weber, R.J., Schauer, J.J., 2008. Source apportionment of fine organic aerosol in Mexico City during the MILAGRO experiment 2006. *Atmospheric Chemistry and Physics* 8, 1249–1259.

Tiwari, S., Srivastava, A.K., Bisht, D.S., Safai, P.D., Parmita, P., 2013. Assessment of carbonaceous aerosol over Delhi in the Indo–Gangetic Basin: Characterization, sources and temporal variability. *Natural Hazards* 65, 1745–1764.

Turpin, B.J., Lim, H.J., 2001. Species contributions to $PM_{2.5}$ mass concentrations: Revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602–610.

Wang, H.B., Shooter, D., 2001. Water soluble ions of atmospheric aerosols in three New Zealand cities: Seasonal changes and sources. *Atmospheric Environment* 35, 6031–6040.

Watson, J.G., Cooper, J.A., Huntzicker, J.J., 1984. The effective variance weighting for least–squares calculations applied to the mass balance receptor model. *Atmospheric Environment* 18, 1347–1355.

Wils, E.R.J., Hulst, A.G., Denhartog, J.C., 1982. The occurrence of plant wax constituents in airborne particulate matter in an urbanized area. *Chemosphere* 11, 1087–1096.

Yang, H., Li, Q.F., Yu, J.Z., 2003. Comparison of two methods for the determination of water–soluble organic carbon in atmospheric particles. *Atmospheric Environment* 37, 865–870.

Zhang, Y.X., Schauer, J.J., Zhang, Y.H., Zeng, L.M., Wei, Y.J., Liu, Y., Shao, M., 2008. Characteristics of particulate carbon emissions from real–world Chinese coal combustion. *Environmental Science & Technology* 42, 5068–5073.

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SUPPORTING MATERIAL

Source apportionment of carbonaceous fine particulate matter ($PM_{2.5}$) in two contrasting cities across the Indo-Gangetic Plain

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Content

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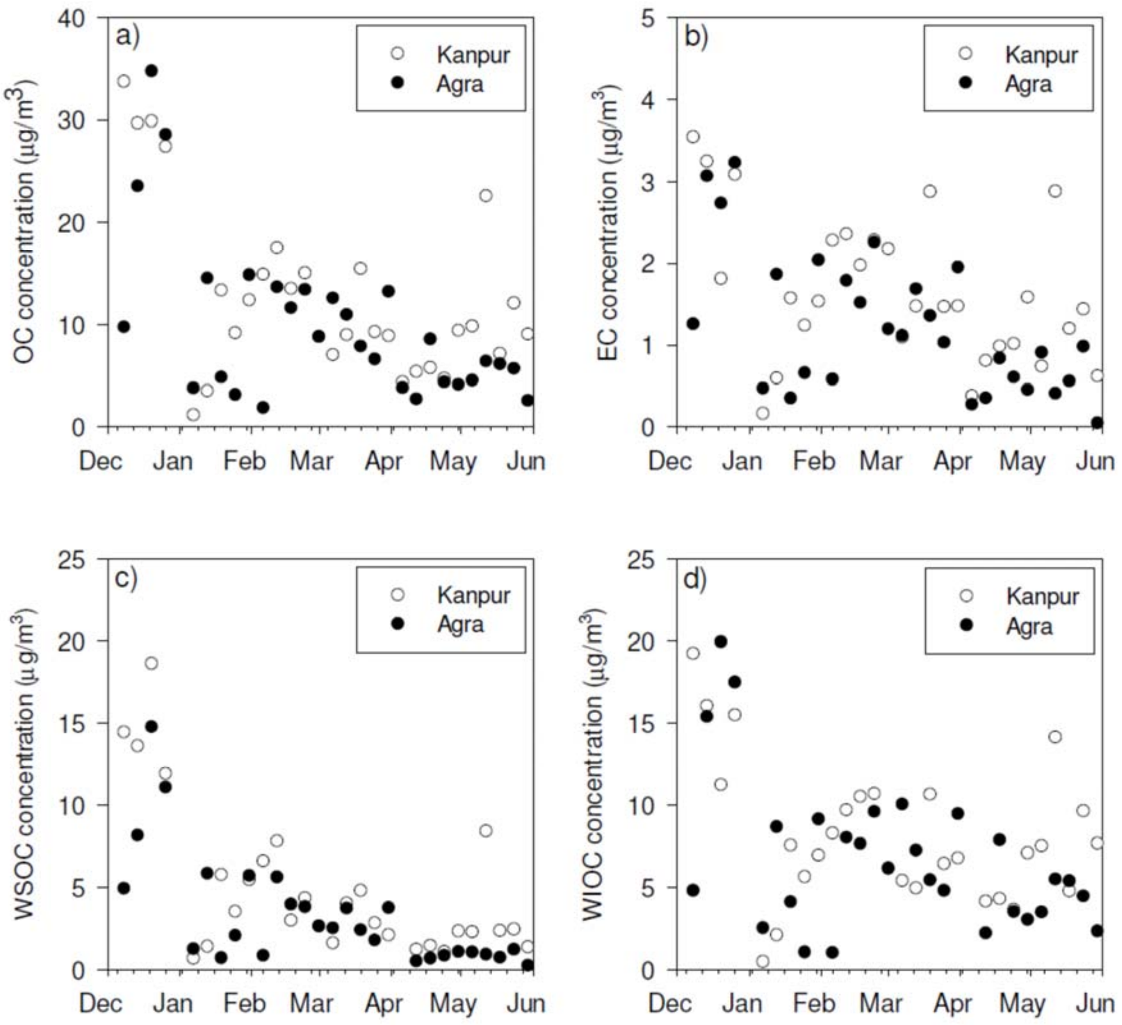


Figure S1. Concentrations of **(a)** Organic carbon, **(b)** Elemental carbon, **(c)** Water soluble organic carbon, and **(d)** Water-insoluble organic carbon in Agra and Kanpur.

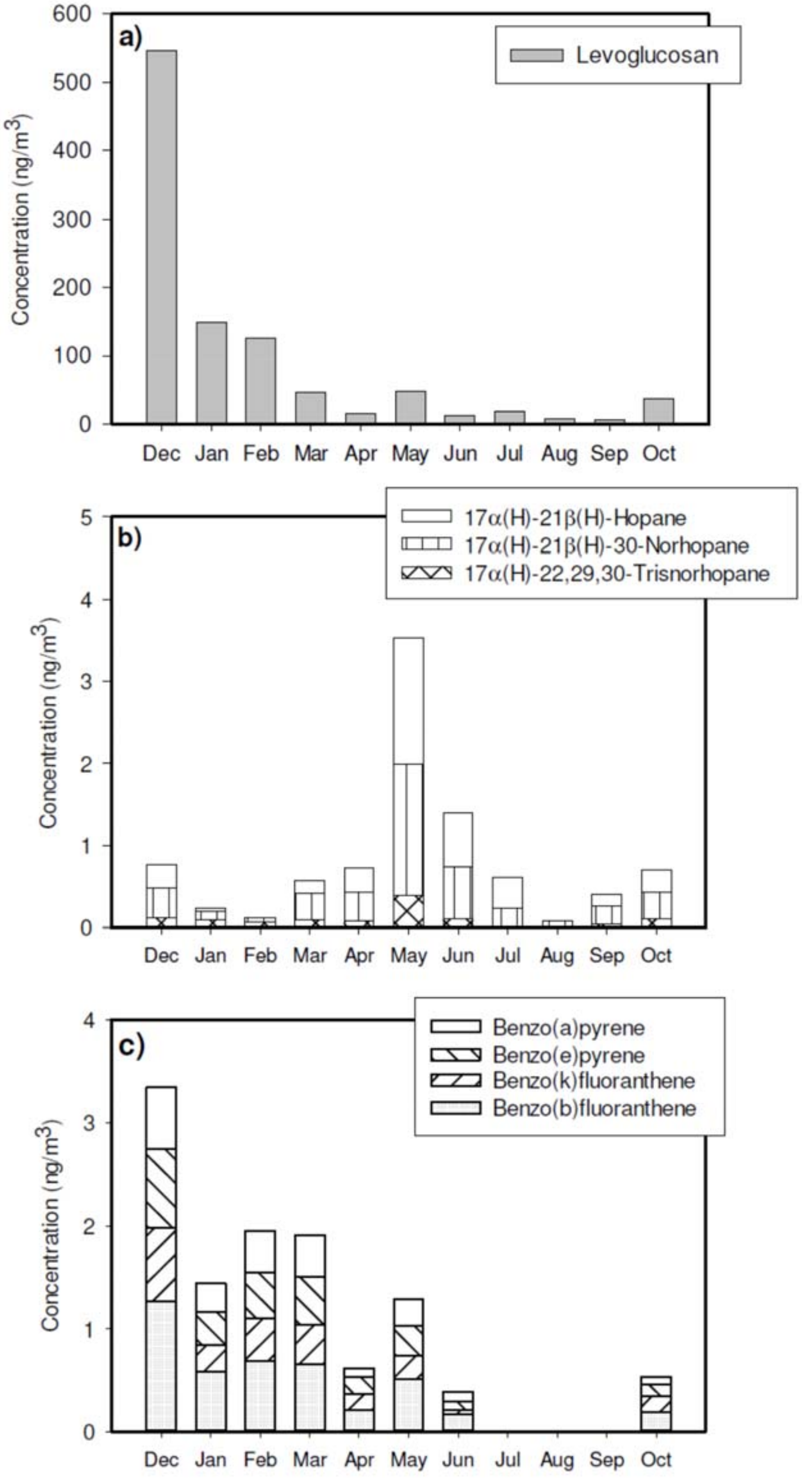


Figure S2. Monthly concentrations of **(a)** levoglucosan, **(b)** hopanes, and **(c)** PAHs in Kanpur from December to October.

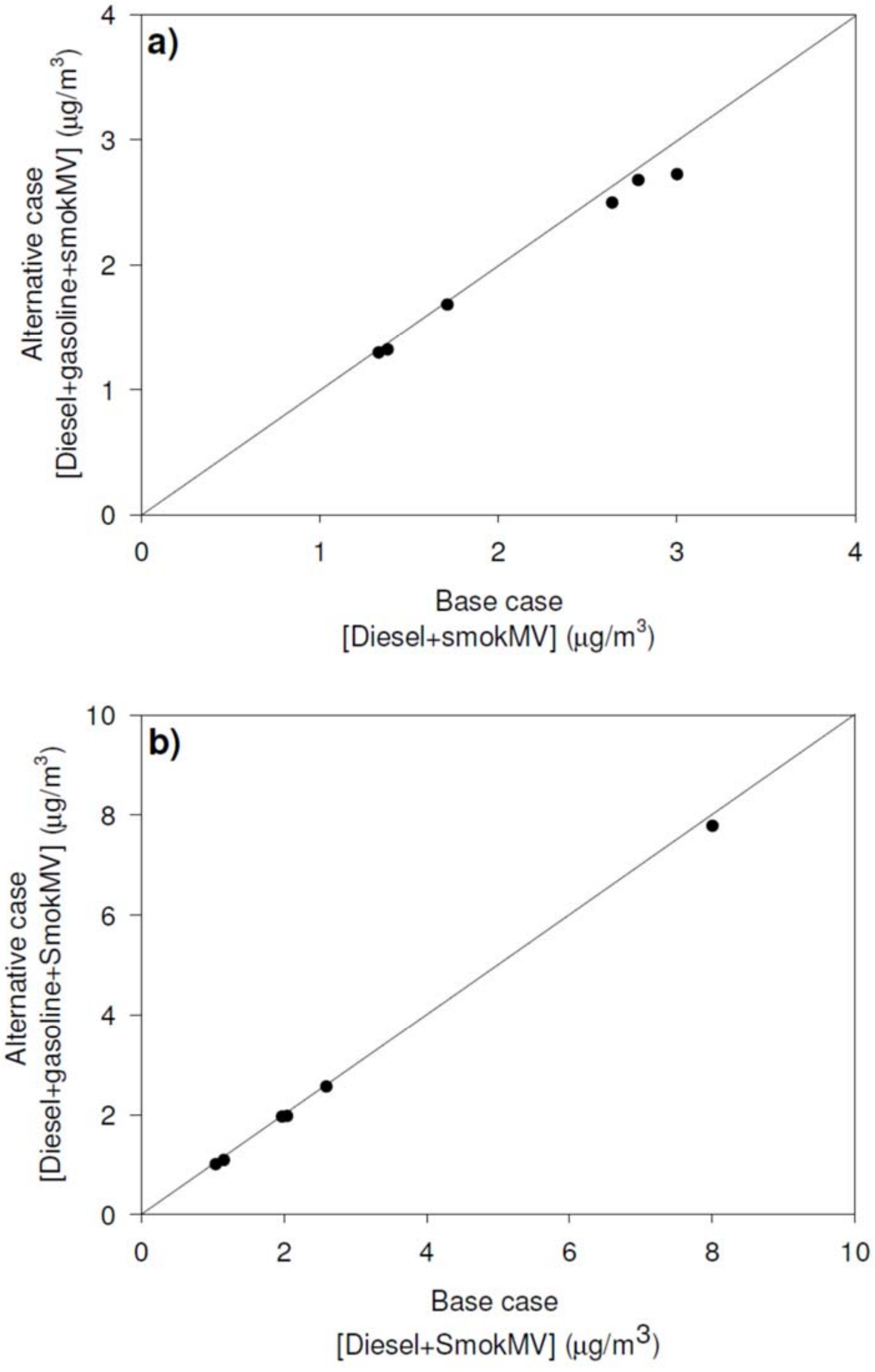


Figure S3. Sensitivity analysis of mobile sources in **(a)** Agra and **(b)** Kanpur.

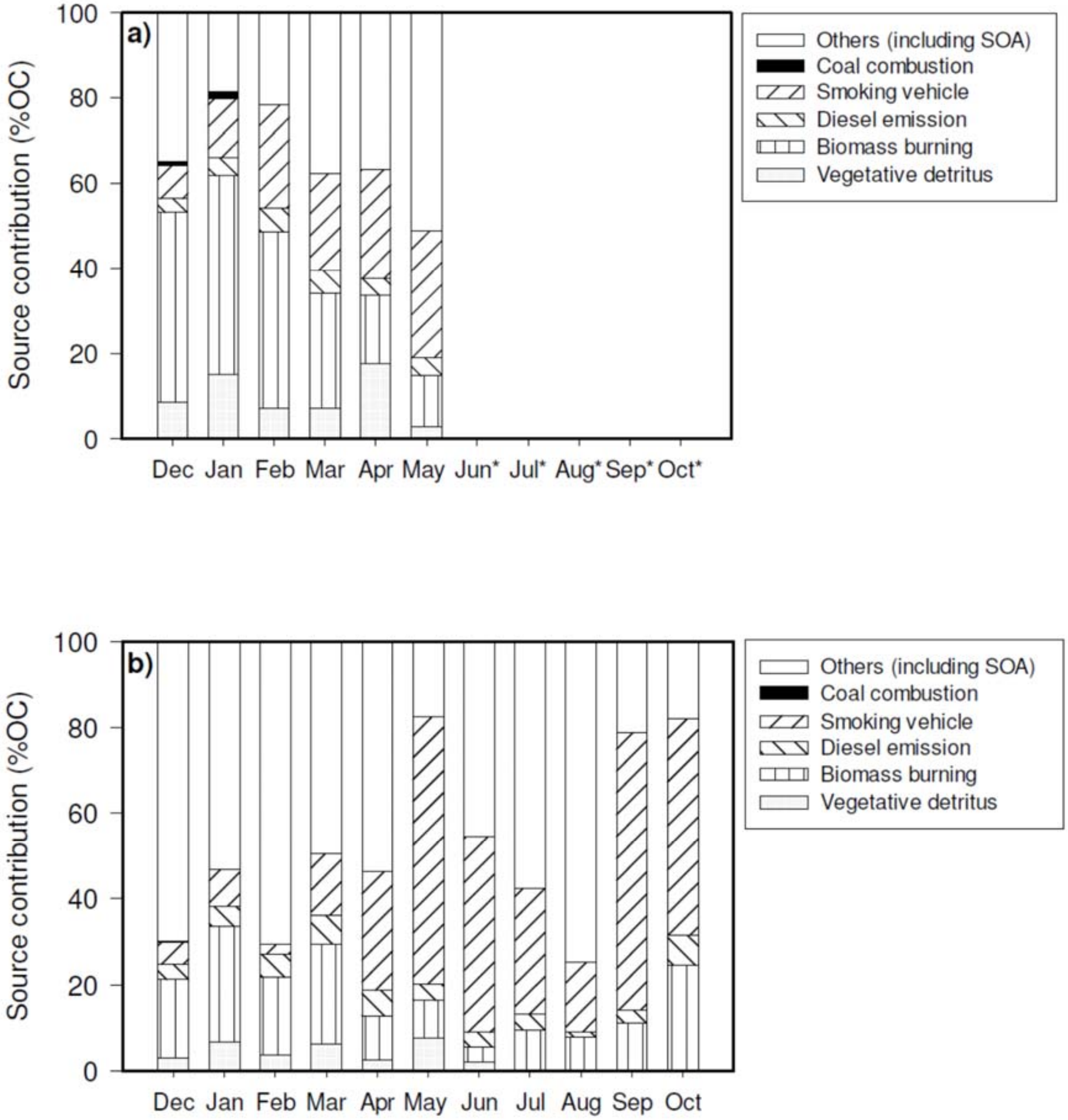


Figure S4. Percentage contribution to $PM_{2.5}$ OC in **(a)** Agra and **(b)** Kanpur.

Table S1. Source profiles used for CMB model

Compound ID	Vegetative detritus µg/µg OC	Unc	Wood burning µg/µg OC	Unc	Cow dung µg/µg OC	Unc	Diesel emission µg/µg OC	Unc	Gasoline emission µg/µg OC	Unc	Smoking vehicle µg/µg OC	Unc	Coal combustion µg/µg OC	Unc
EC	2.90E-02	5.80E-03	8.15E-02	3.26E-02	1.26E-02	0.001594	2.56E+00	2.34E-01	2.88E-01	1.59E-02	1.94E-02	3.57E-03	4.19E-02	2.10E-03
A27	2.54E-03	5.07E-04	5.11E-06	1.02E-06	0.00E+00	0.00E+00	1.13E-04	2.26E-05	0.00E+00	1.00E-08	0.00E+00	1.00E-08	4.96E-04	9.92E-05
A28	7.24E-04	1.45E-04	1.35E-06	2.71E-07	0.00E+00	0.00E+00	9.52E-05	1.90E-05	1.06E-05	2.99E-06	0.00E+00	1.00E-08	1.44E-04	2.88E-05
A29	1.84E-02	3.68E-03	3.54E-06	7.09E-07	0.00E+00	0.00E+00	6.52E-05	1.31E-05	1.79E-04	5.06E-05	0.00E+00	1.00E-08	1.49E-04	2.98E-05
A30	1.34E-03	2.68E-04	0.00E+00	1.00E-05	0.00E+00	0.00E+00	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	1.00E-08	5.28E-05	1.06E-05
A31	2.93E-02	5.86E-03	0.00E+00	1.00E-05	0.00E+00	0.00E+00	1.52E-04	3.04E-05	3.56E-06	1.01E-06	0.00E+00	1.00E-08	1.90E-05	3.80E-06
A32	2.34E-03	4.68E-04	0.00E+00	1.00E-05	0.00E+00	0.00E+00	3.97E-05	7.94E-06	7.15E-06	2.02E-06	0.00E+00	1.00E-08	2.13E-05	4.26E-06
A33	1.43E-02	2.86E-03	0.00E+00	1.00E-05	0.00E+00	0.00E+00	8.27E-06	1.66E-06	2.29E-06	6.49E-07	0.00E+00	1.00E-08	0.00E+00	1.00E-08
A34	2.79E-04	5.57E-05	0.00E+00	1.00E-05	0.00E+00	0.00E+00	0.00E+00	1.00E-08	2.25E-06	6.38E-07	0.00E+00	1.00E-08	0.00E+00	1.00E-08
LEVOG	0.00E+00	1.00E-08	9.31E-02	1.86E-02	4.00E-02	7.79E-03	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	1.00E-08	1.30E-02	2.60E-03
ABBCHL	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	7.43E-06	1.49E-06	6.71E-05	1.34E-05	8.06E-05	1.61E-05	0.00E+00	1.00E-08
SITO	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	6.37E-06	1.27E-06	1.25E-04	2.49E-05	9.53E-05	1.91E-05	0.00E+00	1.00E-08
TNOHO	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	6.28E-06	1.26E-06	5.68E-05	1.14E-05	7.41E-05	1.48E-05	1.77E-04	3.54E-05
B17NHO	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	3.62E-05	7.24E-06	1.80E-04	3.64E-05	1.69E-04	3.38E-05	2.66E-04	5.32E-05
A17HOP	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	1.65E-05	3.30E-06	2.02E-04	4.11E-05	1.40E-04	2.81E-05	1.50E-04	3.00E-05
PICENE	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	0.00E+00	0.00E+00	1.00E-08	0.00E+00	1.00E-08	0.00E+00	1.00E-08	9.89E-04	1.98E-04
BZBFLU	0.00E+00	1.00E-08	7.81E-05	1.56E-05	2.51E-04	4.37E-05	2.07E-05	4.14E-06	2.29E-04	4.65E-05	2.27E-05	4.54E-06	3.78E-03	7.56E-04
BZKFLU	0.00E+00	1.00E-08	7.26E-05	1.45E-05	2.09E-04	4.31E-05	2.90E-05	5.80E-06	1.72E-04	3.49E-05	1.26E-05	2.53E-06	4.67E-04	9.34E-05
BZEPYR	0.00E+00	1.00E-08	4.79E-05	9.57E-06	1.88E-04	2.30E-05	3.40E-05	6.79E-06	3.15E-04	6.46E-05	1.76E-05	3.51E-06	3.89E-03	7.78E-04
INDPYR	0.00E+00	1.00E-08	7.84E-05	1.57E-05	2.51E-04	2.44E-05	1.15E-07	2.93E-08	1.83E-04	3.79E-05	0.00E+00	1.00E-08	1.13E-03	2.26E-04
BZGHPL	0.00E+00	1.00E-08	4.07E-05	8.15E-06	1.88E-04	4.29E-05	6.22E-06	1.25E-06	6.62E-04	1.33E-04	2.76E-05	5.52E-06	1.96E-03	3.92E-04

Compound codes:

EC	Elemental carbon
A27	Heptacosane
A28	Octacosane
A29	Nonacosane
A30	Triacontane
A31	Hentriacontane
A32	Dotriacontane
A33	Tritriacontane
A34	Tetratriacontane
LEVOG	levoglucosan
ABBCHL	ABB-20R-C27-Cholestane
SITO	ABB-20R-C29-Sitostane / ABB-20S-C29-Sitostane
TNOHO	17A(H)-22,29,30-Trisnorhopane
B17NHO	17B(H)-21A(H)-30-Norhopane
A17HOP	17A(H)-21B(H)-Hopane
PICENE	Picene
BZBFLU	Benzo(b)fluoranthene
BZKFLU	Benzo(k)fluoranthene
BZEPYR	Benzo(e)pyrene
INDPYR	Indeno(1,2,3-cd)pyrene
BZGHPL	Benzo(GHI)perylene

Table S2. Source apportionment to ambient $PM_{2.5}$ OC estimated by CMB model in **(a)** Agra from December to May and **(b)** Kanpur from December to October

a)

	Vegetative Detritus		Biomass Burning		Diesel Emission		Smoking Vehicle		Coal Combustion		Others (including SOA)		R^2	x^2
Month	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc		
Dec	2.06	0.25	10.75	2.14	0.79	0.16	1.85	0.45	0.24	0.12	8.43	2.52	0.80	6.82
Jan	1.11	0.14	3.43	0.73	0.31	0.05	1.02	0.26	0.12	0.03	1.36	1.13	0.80	7.63
Feb	0.72	0.12	4.19	0.49	0.55	0.08	2.45	0.37	nd		2.18	1.19	0.91	2.25
Mar	0.70	0.10	2.71	0.54	0.52	0.06	2.27	0.37	nd		3.76	1.06	0.91	2.32
Apr	0.82	0.12	0.76	0.21	0.18	0.02	1.20	0.28	nd		1.72	0.93	0.81	3.89
May	0.15	0.07	0.59	0.30	0.21	0.03	1.51	0.29	nd		2.57	0.95	0.96	0.59

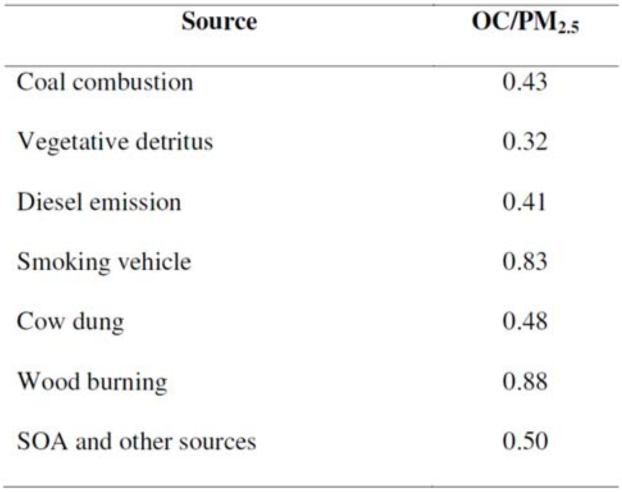
b)

	Vegetative Detritus		Biomass Burning		Diesel Emission		Smoking Vehicle		Coal Combustion		Others (including SOA)		R^2	x^2
Month	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc	µg/m^3	unc		
Dec	0.88	0.14	5.51	1.13	1.06	0.18	1.54	0.39	0.11	0.07	21.03	1.79	0.91	1.93
Jan	0.53	0.09	2.11	0.38	0.37	0.05	0.68	0.25	nd		4.18	1.00	0.89	1.69
Feb	0.54	0.11	2.75	0.50	0.84	0.11	0.33	0.29	nd		10.74	1.22	0.91	1.36
Mar	0.59	0.09	2.26	0.44	0.66	0.07	1.39	0.27	nd		4.79	0.97	0.82	4.05
Apr	0.14	0.07	0.60	0.26	0.35	0.04	1.63	0.33	nd		3.16	0.96	0.90	1.69
May	0.92	0.13	1.05	0.31	0.46	0.06	7.55	0.92	nd		2.11	1.35	0.87	2.81
Jun	0.13	0.07	0.22	0.24	0.21	0.03	2.89	0.43	nd		2.89	0.98	0.90	1.98
Jul	nd		0.47	0.10	0.18	0.02	1.45	0.48	nd		2.86	1.05	1.00	0.29
Aug	nd		0.21	0.05	0.03	0.01	0.43	0.35	nd		1.97	0.90	1.00	0.00
Sep	nd		0.18	0.04	0.05	0.02	1.02	0.31	nd		0.33	0.97	0.98	0.32
Oct	nd		0.75	0.29	0.22	0.03	1.54	0.28	nd		0.55	0.92	0.98	0.38

nd: not detected

R^2 and x^2 are fitting parameters of the CMB model.

Table S3. OC/$PM_{2.5}$ factors for each source



Source	OC/$PM_{2.5}$
Coal combustion	0.43
Vegetative detritus	0.32
Diesel emission	0.41
Smoking vehicle	0.83
Cow dung	0.48
Wood burning	0.88
SOA and other sources	0.50

Table S4. Source contributions to $PM_{2.5}$ mass estimated by CMB model in **(a)** Agra from December to May and **(b)** Kanpur from December to October

a)

Month	Vegetative detritus µg/m^3	Biomass burning µg/m^3	Diesel emission µg/m^3	Smoking vehicle µg/m^3	Coal combustion µg/m^3	SOA (and other sources) µg/m^3	Ammonium sulfate µg/m^3	Ammonium nitrate µg/m^3
Dec	6.34	20.16	1.95	2.22	0.56	16.9	12.96	13.43
Jan	3.43	5.89	0.77	1.23	0.27	2.7	5.62	17.03
Feb	2.21	8.85	1.35	2.95	nd	4.4	5.27	8.13
Mar	2.15	6.26	1.27	2.73	nd	7.5	2.67	4.45
Apr	2.53	1.80	0.44	1.45	nd	3.4	2.39	13.72
May	0.46	1.30	0.52	1.81	nd	5.1	1.39	4.91

b)

Month	Vegetative detritus µg/m^3	Biomass burning µg/m^3	Diesel emission µg/m^3	Smoking vehicle µg/m^3	Coal combustion µg/m^3	SOA (and other sources) µg/m^3	Ammonium sulfate µg/m^3	Ammonium nitrate µg/m^3
Dec	2.70	8.61	2.60	1.86	0.25	42.06	0.72	3.25
Jan	1.63	3.85	0.90	0.82	nd	8.37	0.20	3.41
Feb	1.66	5.62	2.06	0.39	nd	21.47	0.28	2.11
Mar	1.83	5.12	1.63	1.67	nd	9.58	0.94	3.89
Apr	0.44	1.34	0.87	1.95	nd	6.33	2.41	1.99
May	2.85	2.13	1.13	9.08	nd	4.22	0.00	1.49
Jun	0.41	0.42	0.51	3.47	nd	5.78	1.23	0.60
Jul	nd	0.98	0.44	1.74	nd	5.71	0.59	0.56
Aug	nd	0.43	0.08	0.52	nd	3.94	0.02	0.00
Sep	nd	0.37	0.12	1.22	nd	0.67	0.02	0.14
Oct	nd	1.44	0.53	1.85	nd	1.09	0.00	0.00

nd: not detected