

Daily Variations in Sources of Carbonaceous Aerosol in Lahore, Pakistan during a High Pollution Spring Episode

Yuanxun Zhang¹, Tauseef Quraishi², James Jay Schauer^{1*}

¹ *Environmental Chemistry and Technology Program, University of Wisconsin – Madison, 660 N Park Street, Madison, Wisconsin 53706, USA*

² *Institute of Environmental Engineering and Research, University of Engineering and Technology, Lahore, 54890, Pakistan*

Abstract

Inhalable particles (PM₁₀) in Lahore, Pakistan, during a high polluting spring episode in 2006 were collected and analyzed for the ambient concentrations of organic and element carbon (OC, EC) and more than one hundred organic species. High PM₁₀ mass concentrations, averaging 459 µg/m³, were characterized by extremely high concentrations of mobile source related organic compounds including hopanes and PAHs. Source apportionment of PM₁₀ OC, EC and mass was performed using molecular marker based CMB receptor model. Results showed that traffic pollution, including exhaust from gasoline or diesel powered vehicles, was the predominate source of carbonaceous aerosols. Gasoline powered vehicles plus diesel exhausts contribute 47.5%, 88.3% and 15.4% of measured inhalable particulate OC, EC and mass, respectively. Though the contribution is not quantitatively calculated in this study, dust was estimated as another important source of PM₁₀, which is a significant contributor to coarse phase pollutions. Even compared to other mega-cities like Beijing, Mexico City, and Los Angeles, the motor vehicle associated pollution in Lahore was found to be very large. Other sources of carbonaceous aerosols were quantified including wood smoke, vegetative detritus, natural gas combustions and have relative small contributions compared with the traffic pollutions.

Keywords: Aerosol; Source attribution; Receptor model.

INTRODUCTION

Environmental pollution is a serious problem in many developing countries especially for those in the process of rapid industrialization, urbanization with increasing populations. As the second largest city of Pakistan, Lahore (Lat: 31°35'N, Long: 74°20'E) is plagued with high concentrations of atmospheric pollutants

*Corresponding author. Tel: 1-608-262-4495; Fax: 1-608-262-0454

E-mail address: jjschauer@wisc.edu

including lead, calcium, zinc, carbon monoxide, ozone, as well as many other hazardous pollutants that impact human health and welfare (Smith *et al.*, 1996; Younas *et al.*, 1998; Rattigan *et al.*, 2002; Waheed *et al.*, 2006; Ghauri *et al.*, 2007). Consequently, according to the World Bank (WorldBank, 2006), environmental degradation costs Pakistan at least 6 percent of GDP, in which illness and premature mortality caused by air pollution (indoor and outdoor) occupied almost half of the total damage cost.

In the previous research, inorganic matters such as ions and metal elements in total suspended particulates (TSP) have been measured in Lahore (Smith *et al.*, 1996; Harrison *et al.*, 1997; Rattigan *et al.*, 2002). Their ambient concentrations, sources and impacts have been studied in the 1990s (Smith *et al.*, 1996; Harrison *et al.*, 1997). Metals, ions, black carbon and organic carbon, etc., were measured and used for source tracking. Results showed that almost all particulate matters pollutants of concern have extremely high yearly concentrations, including lead ($3.92 \pm 4.46 \mu\text{g}/\text{m}^3$), OC ($76.9 \pm 39.1 \mu\text{g}/\text{m}^3$) and TSP ($607 \pm 403 \mu\text{g}/\text{m}^3$) measured in 1992-1993 (Smith *et al.*, 1996). Soil dust, coal combustions, vehicular exhausts and metallurgical processes were regarded as the main sources of the inorganic species (Harrison *et al.*, 1997; Younas *et al.*, 1998; Ghauri *et al.*, 2007). Limited organic compounds, mostly particle-associated polycyclic aromatic hydrocarbons (PAHs) were also measured at high concentrations around one order of magnitude higher than that in some European

cities (e.g., Birmingham, UK) (Smith *et al.*, 1995; Smith *et al.*, 1996). However, to our knowledge, pollution levels of many other speciated organic compounds have never been reported in Pakistan, nor has their sources been assessed. Carbonaceous particulate matters are usually large contributors to particulate mass and play important roles in human health, air quality and climate processes (Jacobson, 2002; Quinn *et al.*, 2005; Tabazadeh, 2005). Speciated organic compounds data can provide more source information than inorganic species (Schauer *et al.*, 1996; Cass, 1998). In the present study, daily urban inhalable particulate matters was collected and analyzed during a high pollution spring episode in 2006. Although little has been reported about the seasonality of particulate matter concentrations and sources in Lahore, the spring season was chosen to represent a typical period of pollution avoiding the extreme periods of winter, summer and the monsoons. Speciated organic compounds were quantified and their source contributions were evaluated using organic compounds as tracers in a chemical mass balance (CMB) receptor model. The results provide insight into PM₁₀ air quality pollutants of Lahore, Pakistan and can be used as a foundation to design future air quality mitigation strategies relating to management of the air pollution in Lahore, Pakistan. This goal of this manuscript is to demonstrate the feasibility and utility of molecular marker source apportionment studies in developing nations with significant atmospheric particulate matter pollution and very limited measurement based information on the sources of the particulate matter pollution.

As demonstrated in the current study, routine sampling efforts with a well designed chemical analysis strategy can provide significant insight into understanding the source of particulate matter, which can be used to design future monitoring, modelling and control strategy studies. Future projects of this nature should be pursued as collaborations between researchers in developing nations and international research groups to address sources of PM in developing nations with significant particulate matter pollution.

METHODS

Sampling

Daily atmospheric samples of PM₁₀ were collected with a High Volume PM₁₀ sampler (Thermo Scientific, Waltham, MA) in Lahore from March 13th to April 16th in the spring of 2006. The sampler was located on a 10 meter high building at the University of Engineering and Technology in the urban centre of Lahore. Samples were collected on quartz fibre filters, which were baked at a temperature of 550°C before samplings, and delivered to the sampling sites individually wrapped in baked aluminium foil and double packed in zip-lock bags. After sampling, the filters were re-wrapped in baked aluminium foil, double packed in zip-lock bags and stored in a low temperature (< 0°C) thermal-isolated box. For the purposes of QA/QC, blank samples were obtained by placing the filter in the sample with no air passing across the filter.

Chemical analysis

All of the samples were analyzed for water soluble metals, ions, organic carbon, as well as thermal-optical analyzed organic and element carbon. Results of water soluble ions and metal elements are not presented in the present paper. Eight daily samples from April 2nd through 10th were analyzed for speciated organic compounds by GC-MS method.

Water soluble organic carbon (WSOC) was quantified based on the modified method introduced in the previous studies (Wangersky, 1993). Particles on quartz filters were extracted by high purity MQ water in capped vials on a shaker table for 6 hours, then the solution were filtered through 0.2 µm polypropylene filters. Excess HCl was then added into the solution and purged to remove inorganic carbon. Finally, non-purgeable organic carbon was catalytically combusted to carbon dioxide and determined by NDIR detector thus the quantity of WSOC was obtained.

The detailed analysis process of organic compounds quantification by GC-MS could be found in many previous publications (Sheesley *et al.*, 2004; Zheng *et al.*, 2005; Zhang *et al.*, 2007b). Briefly, before extraction, filters were spiked with known quantities of labelled internal standards then extracted twice with methanol and three times with dichloromethane in thick wall bottles using a mild ultrasonic bath maintained at room temperature. The combined extracts were filtered and concentrated with vacuum evaporation and blow-down using ultra purified nitrogen. The final extract was split into several fractions and analyzed by GC-MS after methylation and silylation. Multipoint

Table 1. Source profiles used in CMB Analysis (Source profiles are presented in mass fraction normalized to organic carbon; UNC = Estimated Uncertainty.)

Species	Vegetative Detritus	Biomass Burning	Natural Gas Combustion	Diesel	High Emitted Non- catalyst Gasoline Vehicles	Coal Combustions
EC	2.90E-2	1.40E-1	7.89E-2	1.56E+0	1.67E-2	2.44E-1
EC UNC	5.80E-3	4.20E-2	1.58E-2	3.13E-1	3.34E-3	1.22E-2
n-Nonacosane	1.84E-2	0.00E+0	1.29E-3	1.67E-4	1.91E-4	2.65E-4
n-Nonacosane UNC	3.68E-3	1.00E-8	2.58E-4	3.35E-5	3.82E-5	5.30E-5
n-Triacotane	1.34E-3	0.00E+0	1.70E-4	0.00E+0	0.00E+0	1.43E-4
n-Triacotane UNC	2.68E-4	1.00E-8	3.40E-5	1.00E-8	1.00E-8	2.86E-5
n-Hentriacotane	2.93E-2	0.00E+0	4.27E-4	0.00E+0	0.00E+0	1.03E-4
n-Hentriacotane UNC	5.86E-3	1.00E-8	8.54E-5	1.00E-8	1.00E-8	2.07E-5
n-Dotriacotane	2.34E-3	0.00E+0	2.83E-5	0.00E+0	0.00E+0	3.55E-5
n-Dotriacotane UNC	4.68E-4	1.00E-8	5.66E-6	1.00E-8	1.00E-8	7.11E-6
n-Tritriacotane	1.43E-2	0.00E+0	1.80E-5	0.00E+0	0.00E+0	2.89E-5
n-Tritriacotane UNC	2.86E-3	1.00E-8	3.60E-6	1.00E-8	1.00E-8	5.77E-6
Levoglucosan	0.00E+0	1.35E-1	0.00E+0	0.00E+0	0.00E+0	8.77E-3
Levoglucosan UNC	1.00E-8	3.37E-2	1.00E-8	1.00E-8	1.00E-8	1.75E-3
17 α (H)-22,29,30-Trinorhopane	0.00E+0	0.00E+0	0.00E+0	2.72E-5	1.39E-4	4.92E-4
17 α (H)-22,29,30-Trinorhopane UNC	1.00E-8	1.00E-8	1.00E-8	5.43E-6	2.77E-5	9.84E-5
17 β (H),21 α (H)-Norhopane	0.00E+0	0.00E+0	0.00E+0	3.10E-4	5.67E-4	6.41E-4
17 β (H),21 α (H)-Norhopane UNC	1.00E-8	1.00E-8	1.00E-8	6.20E-5	1.13E-4	1.28E-4
17 α (H),21 β (H)-Hopane	0.00E+0	0.00E+0	0.00E+0	3.13E-4	6.45E-4	3.09E-4
17 α (H),21 β (H)-Hopane UNC	1.00E-8	1.00E-8	1.00E-8	6.26E-5	1.29E-4	6.18E-5
Benzo[b]fluoranthene	0.00E+0	7.90E-5	7.31E-3	0.00E+0	7.50E-5	4.57E-3
Benzo[b]fluoranthene UNC	1.00E-8	1.61E-5	1.46E-3	1.00E-8	1.50E-5	9.15E-4
Benzo[k]fluoranthene	0.00E+0	8.53E-5	1.01E-2	0.00E+0	6.57E-5	8.97E-4
Benzo[k]fluoranthene UNC	1.00E-8	1.75E-5	2.03E-3	1.00E-8	1.32E-5	1.79E-4
Benzo[e]pyrene	0.00E+0	4.60E-5	2.98E-3	0.00E+0	7.68E-5	2.98E-3
Benzo[e]pyrene UNC	1.00E-8	9.28E-6	5.97E-4	1.00E-8	1.54E-5	5.96E-4
Indeno[1,2,3-cd]pyrene	0.00E+0	6.88E-5	0.00E+0	0.00E+0	1.85E-4	1.68E-3
Indeno[1,2,3-cd]pyrene UNC	1.00E-8	1.39E-5	1.00E-8	1.00E-8	3.70E-5	3.36E-4
Dibenzo[a,h]anthracene	0.00E+0	5.50E-6	0.00E+0	0.00E+0	0.00E+0	8.03E-4
Dibenzo[a,h]anthracene UNC	1.00E-8	1.14E-6	1.00E-8	1.00E-8	1.00E-8	1.61E-4
Benzo[ghi]perylene	0.00E+0	4.18E-5	0.00E+0	0.00E+0	0.00E+0	1.63E-3
Benzo[ghi]perylene UNC	1.00E-8	8.45E-6	1.00E-8	1.00E-8	1.00E-8	3.26E-4
20R&S-5 α (H),14 α (H),17 α (H)-Cholestane	0.00E+0	0.00E+0	0.00E+0	2.14E-5	3.42E-4	9.00E-7
20R&S-5 α (H),14 α (H),17 α (H)-Cholestane UNC	1.00E-8	1.00E-8	1.00E-8	4.28E-6	6.84E-5	1.80E-7
20R&S-5 α (H),14 β (H),17 β (H)-Sitostane	0.00E+0	0.00E+0	0.00E+0	7.16E-5	2.73E-4	2.90E-5
20R&S-5 α (H),14 β (H),17 β (H)-Sitostane UNC	1.00E-8	1.00E-8	1.00E-8	1.43E-5	5.46E-5	5.80E-6
22R&S-17 α (H),21 β (H)-Homohopane	0.00E+0	0.00E+0	0.00E+0	0.00E+0	5.21E-4	1.33E-4
22R&S-17 α (H),21 β (H)-Homohopane UNC	1.00E-8	1.00E-8	1.00E-8	1.00E-8	1.04E-4	2.66E-5
Picene	0.00E+0	0.00E+0	0.00E+0	0.00E+0	0.00E+0	5.70E-4
Picene UNC	1.00E-8	1.00E-8	1.00E-8	1.00E-8	1.00E-8	1.14E-4

calibration was employed using authentic standards spiked with the same final concentrations of internal standards as used in the samples. The authentic quantification standards included more than 150 organic compounds such as alkanes, alkanolic and aromatic acids, PAH, anhydrosaccharides, steranes and steroids, etc. Compounds without authentic standards were quantified based on the calibration curves of the similar species (Sheesley *et al.*, 2004; Zheng *et al.*, 2005; Zhang *et al.*, 2007b). In this study, the uncertainty of organic compound quantification was estimated to be 20% of the reported values.

Source apportionment model

Source apportionment was conducted by the USEPA chemical mass balance software (CMB8.2) using organic compounds as tracers which was developed by Schauer *et al.* and refined by Schauer and Cass (Schauer *et al.*, 1996; Schauer and Cass, 2000) from the middle of 1990s. The molecular marker based CMB model has been successfully used in many regions including Los Angeles, Houston, south eastern United States, Hong Kong and Beijing, etc. (Schauer *et al.*, 1996; Zheng *et al.*, 2000; Zheng *et al.*, 2002; Fraser *et al.*, 2003). Principle of CMB model was based on the assumption that the airborne particle concentrations were physically determined by the linear combination of different sources. Diagnostics of the CMB model include explained percent mass (target $100 \pm 20\%$), R^2 (target 0.8-1.0), χ^2 (target 0-4.0), T-STAT (Target > 2.0), degree of freedom (DF, target > 5), no co-linearity clusters, and calculated-to-

measured ratio (C/M ratio for fitting species, target 0.5-2.0) (Zheng *et al.*, 2002). Selections of the source profiles and fitting species in this study were based on the previous studies (Schauer *et al.*, 1996; Cass, 1998; Schauer *et al.*, 2002a; Zheng *et al.*, 2002). The source profiles applied in this study, which are listed in Table 1, are based on previously estimates of the main sources of carbonaceous aerosol in South Asia urban locations and were obtained from the literatures including vegetative detritus (Rogge *et al.*, 1993b), wood smoke (Fine *et al.*, 2004), natural gas combustion (Rogge *et al.*, 1993c), diesel exhaust (Schauer *et al.*, 1999), gasoline powered vehicle exhaust (Schauer *et al.*, 2002b) and coal combustion emissions (Zhang *et al.*, 2007a). It should be noted that the applied source profiles used in the analysis were not specific to Lahore but previous work has shown that the composition source profiles do not change greatly in different regions of the world (Sheesley *et al.*, 2007; Zhang *et al.*, 2007a). The source profile used for gasoline-powered vehicles was a non-catalyst emission profile, since the vehicles plying in Lahore are predominantly non-catalytic, including high emitting 2 stroke motorcycles and 3 wheelers. Most of the source profiles were measured in the US except the coal combustions tested in China. In addition, all of the source profiles were fine particulate matter emissions profiles, which are effectively PM_{10} profiles due to the fact that the organic compounds of the carbonaceous emissions of combustion sources were dominated by fine particulate fraction especially for combustion sources (Kleeman and Cass, 1998; Kleeman *et al.*, 1999, 2000).

The fitting species, including n-alkanes, PAH, hopanes and steranes, levoglucosan and EC, were selected based on prior experience with the use of these tracers in source apportionment calculations (Cass, 1998; Simoneit *et al.*, 1999).

RESULTS AND DISCUSSION

Bulk compositions of PM₁₀

Concentrations of PM₁₀ during the sampling period were showed in Fig. 1 including EC, organic mass (OM), and water soluble ions. Organic mass is estimated from the measurement of organic carbon (OC) and assuming that the sum of hydrogen, oxygen and nitrogen in organic compounds are 80 percent of the organic carbon mass (Turpin and Lim, 2001; Bae *et al.*, 2006). The largest fraction of PM₁₀ was organic mass, which is often

dominated by emissions from combustion processes such as vehicle exhausts, fossil fuel combustions and biomass burnings (Schauer *et al.*, 1996; Zheng *et al.*, 2002) and secondary organic aerosol (SOA). OM was split into two parts: water soluble and insoluble. The mass concentration of PM₁₀ ranged from 158 to 733 $\mu\text{g}/\text{m}^3$ with the average concentration of 361 $\mu\text{g}/\text{m}^3$. Comparatively, the pollution level of this study was much higher than the WHO 24-h mean air quality guideline of 50 $\mu\text{g}/\text{m}^3$, even higher than the previous measurement in Lahore by Ghauri *et al.* (2007), averagely 200 $\mu\text{g}/\text{m}^3$ during 2003 to 2004, showing the tendency toward increased PM₁₀ pollution during the past 2 or 3 years. WSOC in atmospheric particulate matter is largely from polar organic compounds with small molecular weights such as acids, alkanols,

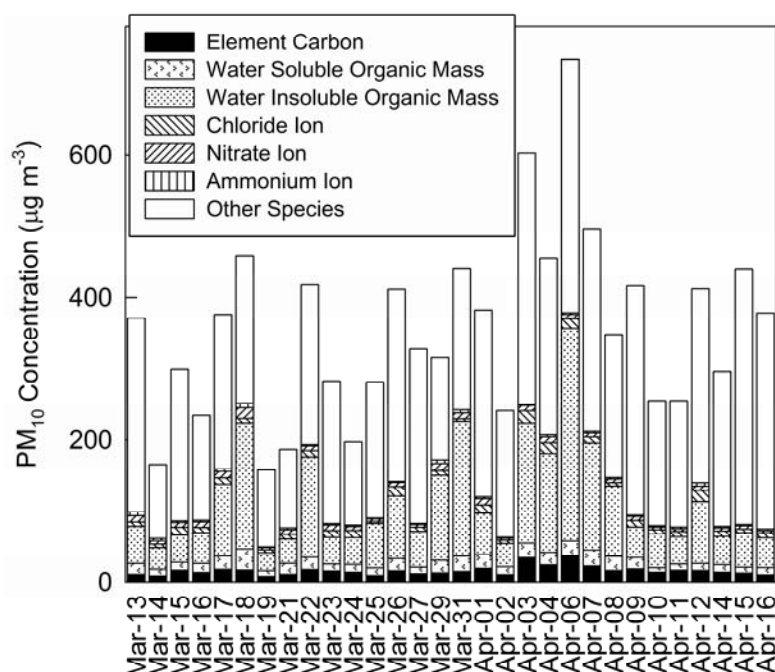


Fig. 1. Contributions of secondary inorganic species and carbon pools to 24-hour average PM₁₀ concentrations for a one month periods in Lahore, Pakistan in spring 2006.

levoglucosan and some sterols. The two dominant sources of WSOC in most locations are secondary organic aerosols (SOA) or biomass burnings. In this study, concentrations of WSOC averaged $8.46 \mu\text{g}/\text{m}^3$, approximately 18% of total organic carbon. Though the concentration of WSOC in Lahore is higher than some other cities such as Hong Kong (Ho

et al., 2006), the WSOC/OC ratios in this study are relatively lower than some other cities with WSOC/OC of about 30% (Grosjean *et al.*, 1978; Rogge *et al.*, 1993d; Stone *et al.*, 2007). Ratio of EC/OC in this study is averagely 0.28, similar to that of a previous measurement in Lahore, which averaged 0.22 (Smith *et al.*, 1996).

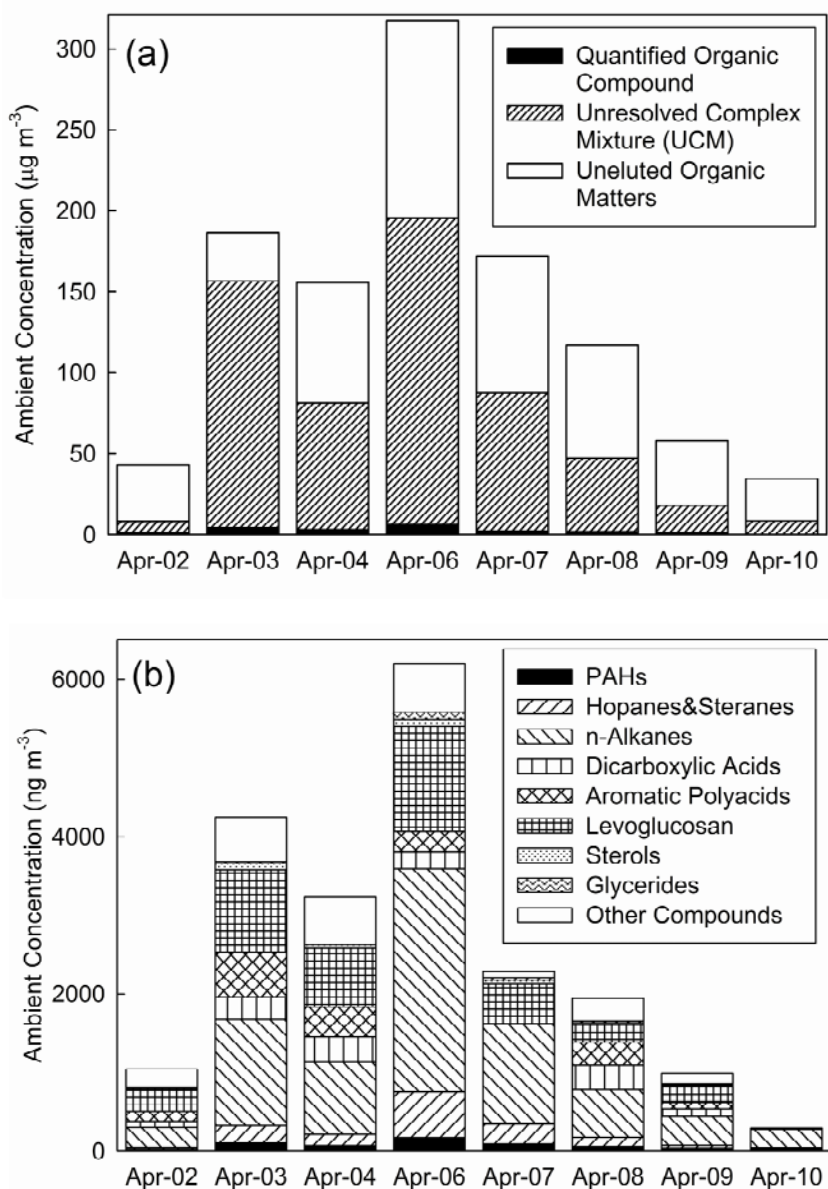


Fig. 2. Contributions of resolvable, elutable, and non-elutable organics compounds to 24-hour PM₁₀ organic compound mass for a one week period in Lahore, Pakistan in spring 2006

Quantified organic matter

More than one hundred organic compounds were quantitatively analyzed including n-alkanes, PAH, sterols, hopanes and steranes, etc. During the study period, concentrations of the total quantified organic compounds had large variability spanning from 300-6200 ng/m³. Large fractions of unresolved complex mixture (UCM) were detected and showed in Fig. 2(a). UCM was a hump in the GC generated by complex mixed branched and cyclic hydrocarbons which are typically associated with contribution from fossil fuel residue (Simoneit, 1986; Rogge *et al.*, 1993d). In this study, the UCM concentrations ranged from 7.3-190 ng/m³, occupied 17-96% of the total organic matters, which provides evidence of large contributions from fossil fuel combustions.

Concentrations of the quantified organic compounds are shown in Fig. 2(b) by compound class. Fatty acids were not reported in this study due to analytical problems resulting in very high uncertainties. The largest fractions were n-alkanes and levoglucosan, which averaged about 27% and 9% of the total quantified organic mass, respectively. The other important contributors to organic mass were dicarboxylic acids and aromatic polyacids, hopanes and steranes, as well as some other species with relatively low concentrations such as glycerides, sterols and PAHs.

Compared to other reported concentrations of levoglucosan in urban locations, such as Beijing (473 ng/m³), Bakersfield (> 1000 ng/m³), Houston (5-98 ng/m³) and Gent Brazil (19-477 ng/m³) (Schauer and Cass, 2000; Fraser *et al.*, 2002; Nolte *et al.*, 2002; Zdrahal

et al., 2002; Zheng *et al.*, 2005), atmospheric concentrations of levoglucosan in Lahore were relatively moderate as seen in Fig. 2(b). The Lahore ambient concentrations of levoglucosan, which is a tracer for biomass burning (Simoneit *et al.*, 1999) indicates that biomass burning is not the predominate source in Lahore.

Hopanes and steranes in the atmosphere are from fossil fuel combustions, including vehicle exhaust and coal combustions, and their distribution can be used as an indicator for different fossil fuel sources (Rogge *et al.*, 1993a; Schauer *et al.*, 1999; Oros and Simoneit, 2000; Schauer *et al.*, 2002b). Concentrations of hopanes in Lahore showed dramatically high level reaching a total concentration of quantified hopanes on April 6th of 363 ng/m³. Even the lowest concentration during the study period on April 10th was 10 ng/m³, which is significantly higher than many very polluted cities including cities in the south eastern US (0.4-2.2 ng/m³), Houston (1.6-2.1 ng/m³) and Beijing (10.7 ng/m³) (Fraser *et al.*, 2002; Zheng *et al.*, 2002; Zheng *et al.*, 2005), which indicates a very large contribution from fossil fuel combustion in Lahore. The daily pattern in hopane concentrations are shown in Fig. 3(a).

PAH are present in refined fossil fuels and are the byproducts of incomplete combustions of carbon based fuels. Benzo[ghi]perylene (BgP) and coronene (COR) are reasonable specific source tracers for gasoline powered vehicles and picene (PIC) is unique tracer of coal burnings (Oros and Simoneit, 2000; Zhang *et al.*, 2008). Average concentrations of BgP (8.3 ng/m³) and COR (4.1 ng/m³) were present in very high levels in Lahore, which suggests

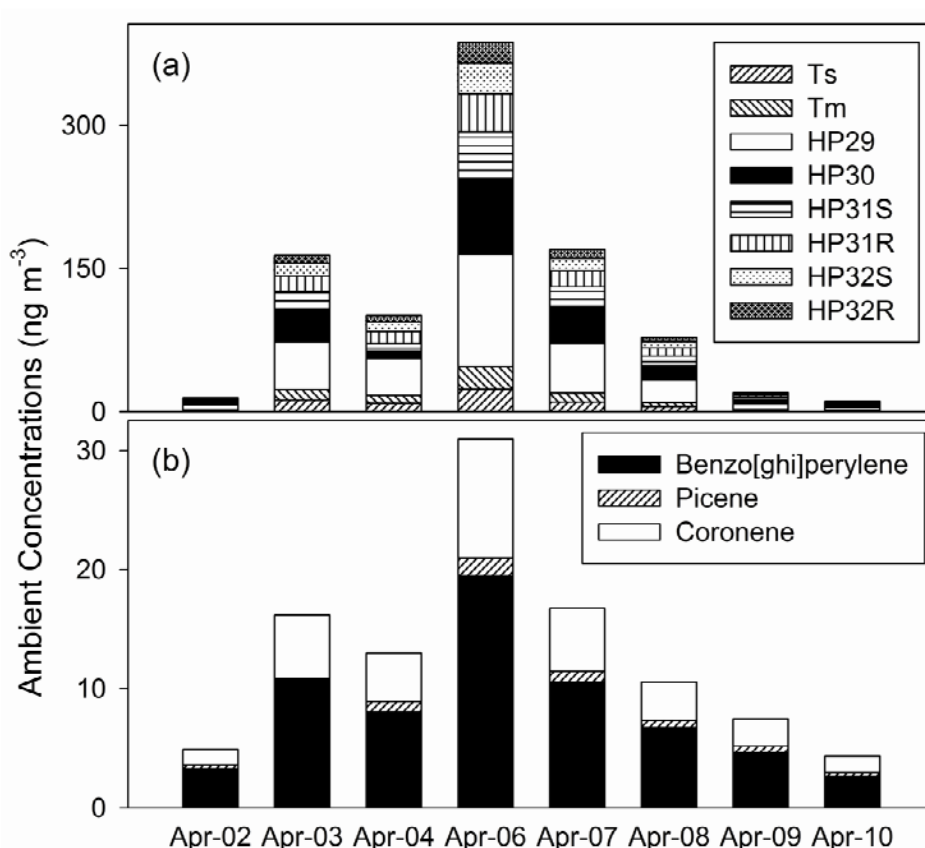


Fig. 3. 24-hour average PM₁₀ compositions of tracer organic compounds in Lahore, Pakistan in 2006. Abbreviated compounds: Ts - 18 α (H)-22,29,30-Trisnorheohopane; Tm - 17 α (H)-22,29,30-Trisnorhopane; HP29 - 17 β (H)-21 α (H)-30-Norhopane; HP30 - 17 α (H)-21 β (H)-Hopane; HP31S - 22(*S*)-Homohopane; HP31R - 22(*R*)-Homohopane; HP32S - 22(*S*)-Bishomohopane; HP32R - 22(*R*)-Bishomohopane.

that fossil fuel associated source contributions to particulate matter concentrations were dominated by vehicular exhaust during the study period. A previous study in Lahore measured a higher concentration of 14.64 and 5.40 ng/m³ for BgP and COR, respectively (Smith *et al.*, 1996). Concentrations of picene in this study averaged 0.7 ng/m³, which is in the range of concentrations measured in Beijing in spring, 0.47 ng/m³, and concentrations measured in Beijing in the winter, 1.34 ng/m³. Coal combustion is an important source of PAH

in Beijing in winter months (Zheng *et al.*, 2005), suggesting that coal combustion is a significant source of PAH in Lahore. Fig. 3(b) presents the daily trend in select PAH concentrations.

Source apportionment results of OC and EC

Source apportionment model results for OC and EC are presented in Fig. 4 and Table 2. Model diagnostic results yielded average R^2 and χ^2 , of 0.79 ± 0.07 and 4.89 ± 1.58 , respectively. The average C/M ratio of fitting species was 0.92 ± 0.44 (mean \pm stdev, $n = 159$).

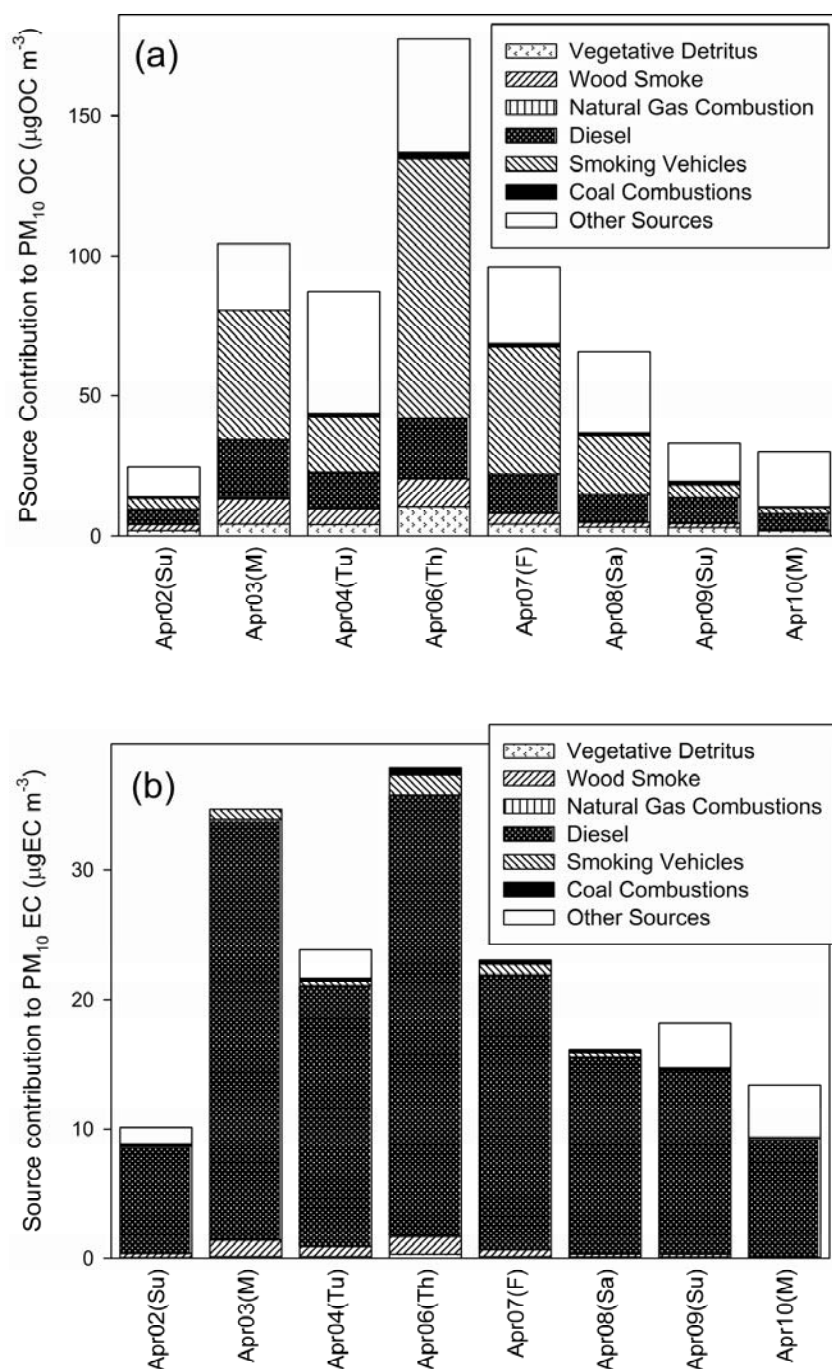


Fig. 4. Source contribution to daily PM₁₀ (a) organic, and (b) element carbon for a one week period in Lahore, Pakistan in spring 2006.

The explained OC percentage is $60.2 \pm 14.6\%$ (mean \pm stdev, $n = 8$) ranged from 34.6-77.2%, which is typical for a molecular marker CMB model that is used to apportion PM₁₀ and

does not include resuspended soil. Six sources were quantified in the molecular marker CMB model including vegetative detritus, wood smoke, natural gas combustion, diesel, gasoline

Table 2. Daily average PM₁₀ source contributions to organic carbon (mean \pm stdev, unit: $\mu\text{g}/\text{m}^3$)

Sampling date	Vegetative Detritus	Wood Smoke	Natural Gas Combustion	Diesel	Smoking Vehicles	Coal Combustions	Sum of identified sources	Measured organic carbon	R ²	χ^2
Apr02 (Su)	1.86 \pm 0.26	2.23 \pm 0.70	0.10 \pm 0.05	5.30 \pm 1.05	3.88 \pm 0.62	0.60 \pm 0.09	13.97 \pm 1.20	24.71 \pm 1.36	0.87	2.91
Apr03 (Mo)	4.24 \pm 0.69	8.90 \pm 2.69	0.48 \pm 0.16	20.82 \pm 4.30	46.01 \pm 5.33	0.00 \pm 0.00	80.45 \pm 6.65	104.42 \pm 5.32	0.66	7.82
Apr04 (Tu)	4.09 \pm 0.62	5.56 \pm 1.77	0.19 \pm 0.12	12.93 \pm 2.67	19.75 \pm 2.84	1.28 \pm 0.21	43.80 \pm 3.74	87.29 \pm 4.47	0.75	6.18
Apr06 (Th)	10.50 \pm 1.61	9.64 \pm 3.12	0.03 \pm 0.25	21.88 \pm 4.57	92.63 \pm 11.21	2.24 \pm 0.41	136.91 \pm 11.93	177.29 \pm 8.96	0.77	5.34
Apr07 (Fr)	4.25 \pm 0.67	3.67 \pm 1.19	0.12 \pm 0.15	13.64 \pm 2.84	45.80 \pm 5.50	1.48 \pm 0.26	68.96 \pm 5.94	96.25 \pm 4.91	0.79	4.87
Apr08 (Sa)	3.13 \pm 0.48	1.62 \pm 0.53	0.15 \pm 0.10	9.76 \pm 2.02	21.34 \pm 2.65	1.02 \pm 0.17	37.02 \pm 3.08	65.75 \pm 3.39	0.81	4.47
Apr09 (Su)	2.91 \pm 0.41	1.54 \pm 0.49	0.14 \pm 0.07	9.11 \pm 1.74	4.62 \pm 0.85	0.92 \pm 0.13	19.25 \pm 1.66	33.13 \pm 1.77	0.86	3.34
Apr10 (Mo)	1.80 \pm 0.25		0.16 \pm 0.05	5.91 \pm 1.09	2.12 \pm 0.46	0.47 \pm 0.06	10.46 \pm 0.95	30.22 \pm 1.96	0.82	4.18

vehicle exhaust and coal combustions. Among all the explained sources, gasoline powered vehicle exhaust was the largest contributor accounting for $29.5 \pm 16.0\%$ of the measured OC. Very high contributions from gasoline vehicles were observed as noted above, which is consistent with previous studies (Harrison *et al.*, 1997; Rattigan *et al.*, 2002; Ghauri *et al.*, 2007). The second largest source contribution was also associated with traffic and was diesel exhaust, with an average contribution of $18.1 \pm 5.0\%$ of the measured OC. The two combined traffic sources accounted for approximately half of the measured OC concentrations ($47.5 \pm 13.5\%$). This is a common characteristic for many mega-cities with large vehicular populations, such as Los Angeles, Beijing and Mexico City, where vehicular exhausts are also the largest OC sources, contributing about 50%, 20% and 50% of ambient OC, respectively (Schauer *et al.*, 1996; Zheng *et al.*, 2005; Stone *et al.*, 2007).

Comparatively, other sources contribute relatively small fractions of the organic carbonaceous concentration. Biomass burning and vegetative detritus have the largest contributions after traffic sources with contributions of $5.0 \pm 2.8\%$ and $5.8 \pm 1.5\%$ of the OC, respectively. In this study, biomass burning is expected to be due to the observed garbage combustions in Lahore including leaves, branches, mowed grass, as well as papers, plastic bags, etc. Coal and natural gas combustions were also quantified but have even small contributions to PM₁₀ OC concentrations. Natural gas combustion have smaller emission factors than coal stoves (Rogge *et al.*, 1993c,

1997; Oros and Simoneit, 2000), though residential fuel in Lahore is mostly natural gas, their contribution to OC was quite small. However, coal and natural gas combustions were important sources of PAHs and oxy-PAHs (Rogge *et al.*, 1993c). The large fractions of un-apportioned “Other sources” OC ranged from 23-65%, which is expected to be dominated sources excluded from the model including secondary organic aerosol (SOA), industrial point sources, and organic matters in resuspended dust. The measured WSOC can be used to better assess the likelihood of these different sources contributing the unapportioned OC concentrations. WSOC is largely from SOA and biomass smoke (Stone *et al.*, 2007). In this study, WSOC for the sample

is much lower than CMB un-apportioned OC, which means that the “Other sources” of organic cannot be explained by SOA, and is likely due to other sources not included in the model such as resuspended soil.

Source apportionment results of EC (Fig. 4b) were calculated according to the different source profile OC/EC ratios. The predominant source of the PM₁₀ EC was diesel exhaust, which occupy $86.4 \pm 9.8\%$ of the total measured EC. The present results are twice as large as a previous study in Lahore conducted more than ten years ago, which apportioned $7.6 \pm 2.5 \mu\text{g}/\text{m}^3$ TSP EC to vehicular sources (Harrison *et al.*, 1997). Other sources contributing EC include residential coal combustion, wood burning and natural gas

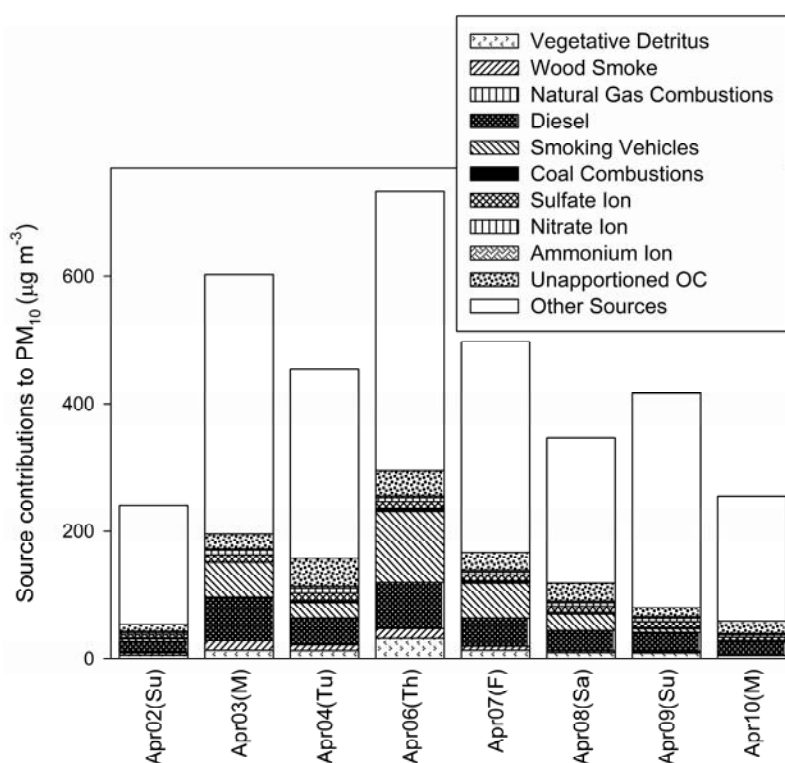


Fig. 5. Source contribution to daily PM₁₀ mass for a one week period in Lahore, Pakistan in spring 2006.

combustion. Harrison *et al.* (1997) reported a much higher impact of coal combustion on EC concentrations in Lahore more than ten years ago, which accounted for $32 \pm 16\%$ of total EC in TSP. The previous result is much larger than the current study, which may reflect changes in emissions over the past 10 years.

Source apportionment results of PM₁₀ mass

Source contributions of PM₁₀ mass (Fig. 5) were calculated according to the OC/PM₁₀ ratios of different sources. Secondary water soluble ions were also included in Fig. 5 to show their contribution to PM₁₀ concentration. The largest fraction is the unknown "Other sources" part ranged from 68-89% of total PM₁₀ mass, larger than that of the "Other sources" in OC apportionment. According to the previous measurement, soil occupy $62 \pm 3\%$ TSP (Harrison *et al.*, 1997), similar to the PM₁₀ mass "Other sources" percentages of the present result. Therefore, the large unknown PM₁₀ mass is expected to be from resuspended soil and/or dust.

CONCLUSIONS

Air pollution is a serious problem in Lahore, Pakistan, which is usually characterized with high ambient concentrations of particulate pollutants. Mass concentration of inhalable particles (PM₁₀) observed in a high polluting spring episode in 2006 also showed an extremely high level with the average concentration exceeds $450 \mu\text{g}/\text{m}^3$. Source apportionment by the CMB receptor model using speciated organic compounds as tracers

demonstrates the key sources for PM₁₀ organic carbon, element carbon and mass. Mobile sources, both gasoline and diesel powered vehicle emissions are the significant PM₁₀ sources which contribute 47.5% OC, 88.3% EC and 15.4% mass of inhalable particles, respectively. Besides, vehicle associated dust source was estimated as another important contributor of coarse phase PM₁₀ pollutants. Comparatively, other sources quantified during this polluting episode have relatively small contributions, including wood smoke, vegetative detritus, natural gas and coal combustions, etc.

ACKNOWLEDGMENTS

The authors are thankful to Dr. Rebecca J. Sheesley, Elizabeth A. Stone, Jeffrey T. DeMinter and Brandon R. Shelton for their helpful laboratorial assistance. This work was funded by the U.S. Agency for International Development and the Higher Education Commission, Government of Pakistan.

REFERENCES

- Bae, M.S., Schauer, J.J. and Turner, J.R. (2006). Estimation of the Monthly Average Ratios of Organic Mass to Organic Carbon for Fine Particulate Matter at an Urban Site. *Aerosol Sci. Technol.* 40: 1123-1139.
- Cass, G.R. (1998). Organic Molecular Tracers for Particulate Air Pollution Sources. *Trac, Trends Anal. Chem.* 17: 356-366.
- Fine, P.M., Chakrabarti, B., Krudysz, M., Schauer, J.J. and Sioutas, C. (2004). Diurnal

- Variations of Individual Organic Compound Constituents of Ultrafine and Accumulation Mode Particulate Matter in the Los Angeles Basin. *Environ. Sci. Technol.* 38: 1296-1304.
- Fraser, M.P., Yue, Z.W. and Buzcu, B. (2003). Source Apportionment of Fine Particulate Matter in Houston, TX, Using Organic Molecular Markers. *Atmos. Environ.* 37: 2117-2123.
- Fraser, M.P., Yue, Z.W., Tropp, R.J., Kohl, S.D. and Chow, J.C. (2002). Molecular Composition of Organic Fine Particulate Matter in Houston, TX. *Atmos. Environ.* 36: 5751-5758.
- Ghauri, B., Lodhi, A. and Mansha, M. (2007). Development of Baseline (Air Quality) Data in Pakistan. *Environ. Monit. Assess.* 127: 237-252.
- Grosjean, D., Vancauwenberghe, K., Schmid, J.P., Kelley, P.E. and Pitts, J.N. (1978). Identification of C3-C10 Aliphatic Dicarboxylic-Acids in Airborne Particulate Matter. *Environ. Sci. Technol.* 12: 313-317.
- Harrison, R.M., Smith, D.J.T., Pio, C.A. and Castro, L.M. (1997). Comparative Receptor Modelling Study of Airborne Particulate Pollutants in Birmingham (United Kingdom), Coimbra (Portugal) and Lahore (Pakistan). *Atmos. Environ.* 31: 3309-3321.
- Ho, K.F., Lee, S.C., Cao, J.J., Li, Y.S., Chow, J.C., Watson, J.G. and Fung, K. (2006). Variability of Organic and Elemental Carbon, Water Soluble Organic Carbon, and Isotopes in Hong Kong. *Atmos. Chem. Phys.* 6: 4569-4576.
- Jacobson, M.Z. (2002). Control of Fossil-Fuel Particulate Black Carbon and Organic Matter, Possibly the Most Effective Method of Slowing Global Warming. *J. Geophys. Res.-Atmos.* 107.
- Kleeman, M.J. and Cass, G.R. (1998). Source Contributions to the Size and Composition Distribution of Urban Particulate Air Pollution. *Atmos. Environ.* 32: 2803-2816.
- Kleeman, M.J., Schauer, J.J. and Cass, G.R. (1999). Size and Composition Distribution of Fine Particulate Matter Emitted From Wood Burning, Meat Charbroiling, and Cigarettes. *Environ. Sci. Technol.* 33: 3516-3523.
- Kleeman, M.J., Schauer, J.J. and Cass, G.R. (2000). Size and Composition Distribution of Fine Particulate Matter Emitted From Motor Vehicles. *Environ. Sci. Technol.* 34: 1132-1142.
- Nolte, C.G., Schauer, J.J., Cass, G.R. and Simoneit, B.R.T. (2002). Trimethylsilyl Derivatives of Organic Compounds in Source Samples and in Atmospheric Fine Particulate Matter. *Environ. Sci. Technol.* 36: 4273-4281.
- Oros, D.R. and Simoneit, B.R.T. (2000). Identification and Emission Rates of Molecular Tracers in Coal Smoke Particulate Matter. *Fuel* 79: 515-536.
- Quinn, P.K., Bates, T.S., Baynard, T., Clarke, A.D., Onasch, T.B., Wang, W., Rood, M.J., Andrews, E., Allan, J., Carrico, C.M., Coffman, D. and Worsnop, D. (2005). Impact of Particulate Organic Matter on the Relative Humidity Dependence of Light

- Scattering: A Simplified Parameterization. *Geophys. Res. Lett.* 32.
- Rattigan, O.V., Mirza, M.I., Ghauri, B.M., Khan, A.R., Swami, K., Yang, K. and Husain, L. (2002). Aerosol Sulfate and Trace Elements in Urban Fog. *Energy Fuels* 16: 640-646.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1993a). Sources Of Fine Organic Aerosol .2. Noncatalyst And Catalyst-Equipped Automobiles And Heavy-Duty Diesel Trucks. *Environ. Sci. Technol.* 27: 636-651.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1993b). Sources Of Fine Organic Aerosol .4. Particulate Abrasion Products From Leaf Surfaces Of Urban Plants. *Environ. Sci. Technol.* 27: 2700-2711.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1993c). Sources Of Fine Organic Aerosol .5. Natural-Gas Home Appliances. *Environ. Sci. Technol.* 27: 2736-2744.
- Rogge, W.F., Hildemann, L.M., Mazurek, M.A., Cass, G.R. and Simoneit, B.R.T. (1997). Sources of Fine Organic Aerosol .8. Boilers Burning No. 2 Distillate Fuel Oil. *Environ. Sci. Technol.* 31: 2731-2737.
- Rogge, W.F., Mazurek, M.A., Hildemann, L.M., Cass, G.R. and Simoneit, B.R.T. (1993d). Quantification Of Urban Organic Aerosols At A Molecular-Level - Identification, Abundance And Seasonal-Variation. *Atmo. Environ. Part A-General Topics* 27: 1309-1330.
- Schauer, J.J. and Cass, G.R. (2000). Source Apportionment of Wintertime Gas-phase and Particle-Phase Air Pollutants Using Organic Compounds as Tracers. *Environ. Sci. Technol.* 34: 1821-1832.
- Schauer, J.J., Fraser, M.P., Cass, G.R. and Simoneit, B.R.T. (2002a). Source Reconciliation of Atmospheric Gas-phase and Particle-phase Pollutants During a Severe Photochemical Smog episode. *Environ. Sci. Technol.* 36: 3806-3814.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (1999). Measurement of Emissions From Air Pollution Sources. 2. C-1 Through C-30 Organic Compounds From Medium Duty Diesel Trucks. *Environ. Sci. Technol.* 33: 1578-1587.
- Schauer, J.J., Kleeman, M.J., Cass, G.R. and Simoneit, B.R.T. (2002b). Measurement of Emissions From Air Pollution Sources. 5. C-1-C-32 Organic Compounds From Gasoline-Powered Motor Vehicles. *Environ. Sci. Technol.* 36: 1169-1180.
- Schauer, J.J., Rogge, W.F., Hildemann, L.M., Mazurek, M.A. and Cass, G.R. (1996). Source Apportionment of Airborne Particulate Matter Using Organic Compounds as Tracers. *Atmos. Environ.* 30: 3837-3855.
- Sheesley, R.J., Schauer, J.J., Bean, E. and Kenski, D. (2004). Trends in Secondary Organic Aerosol at a Remote Site in Michigan's Upper Peninsula. *Environ. Sci. Technol.* 38: 6491-6500.
- Sheesley, R.J., Schauer, J.J., Smith, T., Garshick, E., Laden, F., Marr, L. and Molina, L. (2007). Assessment of Diesel

- Particulate Matter Exposure in the Workplace: Freight Terminals. *J. Environ. Monit.* In review.
- Simoneit, B.R.T. (1986). Characterization of Organic-Constituents in Aerosols in Relation to Their Origin and Transport - a Review. *Int. J. Environ. Anal. Chem.* 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. and Cass, G.R. (1999). Levoglucosan, a Tracer for Cellulose in Biomass Burning and Atmospheric Particles. *Atmos. Environ.* 33: 173-182.
- Smith, D.J.T., Edelhauser, E.C. and Harrison, R.M. (1995). Polynuclear Aromatic Hydrocarbon Concentrations in Road Dust and Soil Samples Collected in the United-Kingdom and Pakistan. *Environ. Technol.* 16: 45-53.
- Smith, D.J.T., Harrison, R.M., Luhana, L., Pio, C.A., Castro, L.M., Tariq, M.N., Hayat, S. and Quraishi, T. (1996). Concentrations of Particulate Airborne Polycyclic Aromatic Hydrocarbons and Metals Collected in Lahore, Pakistan. *Atmos. Environ.* 30: 4031-4040.
- Stone, E.A., Snyder, D.C., Sheesley, R.J., Sullivan, A.P., Weber, R.J. and Schauer, J.J. (2007). Source Apportionment of Fine Organic Aerosol in Mexico City During the MILAGRO Experiment 2006. *Atmos. Chem. Phys.* 7: 9635-9661.
- Tabazadeh, A., (2005). Organic Aggregate Formation in Aerosols and its Impact on the Physicochemical Properties of Atmospheric Particles. *Atmos. Environ.* 39, 5472-5480.
- Turpin, B.J. and 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.
- Waheed, S., Rahman, A., Khalid, N. and Ahmad, S. (2006). Assessment of Air Quality of Two Metropolitan Cities in Pakistan: Elemental Analysis Using INAA and AAS. *Radiochim. Acta* 94: 161-166.
- Wangersky, P.J. (1993). Dissolved Organic-Carbon Methods - a Critical-Review. *Mar. Chem.* 41: 61-74.
- WorldBank, (2006). *Pakistan Strategic Country Environmental Assessment*. The World Bank.
- Younas, M., Shahzad, F., Afzal, S., Khan, M.I. and Ali, K. (1998). Assessment of Cd, Ni, Cu, and Pb pollution in Lahore, Pakistan. *Environ. Int.* 24: 761-766.
- Zdrahal, Z., Oliveira, J., Vermeylen, R., Claeys, M. and Maenhaut, W. (2002). Improved Method for Quantifying Levoglucosan and Related Monosaccharide Anhydrides in Atmospheric Aerosols and Application to Samples From Urban and Tropical Locations. *Environ. Sci. Technol.* 36: 747-753.
- Zhang, Y.X., Schauer, J.J., Zhang, Y.H., Zeng, L.M., Wei, Y.J., Liu, Y. and Shao, M. (2008). Characteristics of Particulate Carbon Emissions from Real-World Chinese Coal Combustion. *Environ. Sci. Technol.* Accepted and in press.
- Zhang, Y.X., Shao, M., Zhang, Y.H., Zeng, L.M., He, L.Y., Zhu, B., Wei, Y.J. and Zhu, X.L. (2007b). Source Profiles of Particulate

- Organic Matters Emitted From Cereal Straw Burnings. *Journal of Environ. Sci. China*, 19: 167-175.
- Zheng, M., Cass, G.R., Schauer, J.J. and Edgerton, E.S. (2002). Source Apportionment of PM_{2.5} in the Southeastern United States Using Solvent-Extractable Organic Compounds as Tracers. *Environ. Sci. Technol.* 36: 2361-2371.
- Zheng, M., Fang, M., Wang, F. and To, K.L. (2000). Characterization of the Solvent Extractable Organic Compounds in PM_{2.5} Aerosols in Hong Kong. *Atmos. Environ.* 34: 2691-2702.
- Zheng, M., Salmon, L.G., Schauer, J.J., Zeng, L.M., Kiang, C.S., Zhang, Y.H. and Cass, G.R. (2005). Seasonal Trends in PM_{2.5} Source Contributions in Beijing, China. *Atmos. Environ.* 39: 3967-3976.
- Received for review, September 27, 2007*
Accepted, March 15, 2008