Chemical characterization of atmospheric PM in Delhi, India, during different periods of the year including Diwali festival

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ABSTRACT

A study of the chemical composition of atmospheric particulate matter has been carried out in the city of Delhi. During two 6–day special observation periods, in November 2009 and in March 2010, we have determined atmospheric concentration of element, ions, elemental carbon, organic carbon and levoglucosan, obtaining a satisfactory mass closure (better than 94%). The results show that during these periods, pollutants produced by combustion sources constituted 6 –7 % of the total mass, and that the rest of it, in the absence of desert storms, was evenly divided among species coming from the soil, inorganic secondary compounds formed in the atmosphere and organic species. The results of the analysis of levoglucosan concentration showed that during the cold season in the atmosphere of Delhi about one fifth of the organics was directly produced by biomass burning.

Elemental content of PM_{10} has also been determined once a week during the year 2008. It has been found that PM_{10} composition varies according to the season: soil components increase during the summer while secondary pollutants and organics increase during the post–monsoon and the winter.

Elemental and ionic content of PM_{10} and $PM_{2.5}$ have been determined every day during the week of Diwali festivals in 2008 and 2009. PM_{10} concentration has reached the value of 767 µg m^{-3} in 2008 and 620 µg m^{-3} in 2009; a remarkable increase of elements produced by firework combustion (Sr, Ba, Ti, Mg, Cu, K, S, V, Cl, Bi, Ga) has been detected. The analysis of the extractable and residual fraction of elements has shown that most of the elements were predominantly in the residual fraction and that changes in the size and solubility distribution occurred as a consequence of fireworks.

1. Introduction

Atmospheric pollution and the associated risk to human health are of particular concern in Delhi, one of the most polluted urban areas in the world. The city has a population of about 14 million, with an annual average growth rate of 3.85% (Srivastava et al., 2008), a rapidly increasing number of vehicles (more than 5 million, with an annual average growth rate of 5.85%, as reported by the Economic Survey of Delhi, 2005–2006), three coal–fired power plants and an increasing number of industrial units. These manifold sources of atmospheric pollutants have led to a serious deterioration of air quality in the Delhi area, which has been declared by the National Cancer Registry Program as the most cancer prone area in India (ICMR, 2005).

Atmospheric particulate matter (PM) is a very complex matrix as it contains a huge variety of solid and liquid particles of different sizes, coming from many sources and differing in terms of physical and chemical characteristics, effects on human health and ecosystem, persistence in the atmosphere and ability to react with each other. PM is one of the most harmful pollutants in Delhi: it has been reported that here the incidence of chronic bronchitis is 6 –14 times more than in other Indian areas (Saksena and Dayal, 2000) and that one out of every ten school children in the city suffers from asthma (Goyal and Sidharta, 2003).

PM can be classified according to many different criteria: organic and inorganic, natural (e.g., marine aerosol, crustal material) and anthropogenic (e.g., produced by combustion processes and industrial emissions), primary (emitted directly from the source) and secondary (produced in the atmosphere), fine (aerodynamic diameter below 2.5 µm) and coarse. This variety of sources, chemical nature and production pathways make the identification of the source contributions to PM a very difficult task. Understanding the sources of PM in the urban area of Delhi is particularly complex, since, in addition to transportation (emission from gasoline–, compressed natural gas– and diesel–powered vehicles), significant contributions to PM pollution in the city come from its three coal–based thermal power plants (for a total energy production of about 1 100 MW), its 130 000 small– and medium–scale industries (mainly electroplating, plastic and metal alloy), road dust re–suspension, also due to the very frequent street sweeping (Tandon et al., 2008), dust transport from the Thar desert, pollutants released from solid waste and emissions from the widespread domestic burning of biofuels, e.g. wood, briquette, dung cakes (Monkkonen et al., 2004).

A fundamental step towards the identification of the sources of atmospheric particles is constituted by the chemical characterisation of PM. In the scientific literature there are only a few papers dealing with the chemical characterization of atmospheric particles in Delhi, most of them addressed to elemental composition only (Balachandran et al., 2000; Srivastava

and Jain, 2007; Srivastava and Jain, 2008; Srivastava et al., 2008; Srivastava et al., 2009a; Tiwari et al., 2009). As far as we know, the mass closure, that is the measurement of as many chemical components as possible up to reach the gravimetric mass, has never been attempted in this area. In this paper, we report the results of five studies carried out in Delhi during the period 2008 – 2010. Two of them (2009 and 2010) are short studies when all PM_{10} macro–components have been determined and the mass closure has been obtained. The information gained from these short studies allowed us to interpret the results of two further short studies carried out during the periods of the Diwali festivals 2008 and 2009, which are characterised by extensive firework activity, and of a longer study carried out in 2008, when PM_{10} elemental composition has been determined one day a week.

2. Experimental

2.1. Area description and sampling site

Delhi, the capital city of India, is situated in North India (28°12'–28°63' N, 75°50'–77°23' E) at an altitude between 213 and 305 m above sea level. It is surrounded by the Thar Desert of Rajasthan to the west and the hot plains of Central India to the south. The distance from the nearest ocean exceeds one thousand kilometres. The climate of Delhi is semi–arid and is mainly influenced by its inland position and prevalence of continental air during most of the year. According to the classification given by Indian Meteorological Department (NAAQMS, 2001), Delhi has four distinct seasons: winter (December–March), pre–monsoon or summer (April–June), monsoon (July–September) and post–monsoon (October–November). Summer is long and extremely hot, with maximum temperatures of 45–48 °C and the maximum frequency of dust storms. Humidity is high only during the monsoon season, characterised by heavy rainfalls, while the air is dry during the rest of the year. Normal annual rainfall is between 600 and 800 mm, with more than 80% during the monsoon season. The winter season is moderately cold, with minimum temperatures around 1–4 °C. During this part of the year, conditions of atmospheric stability (low wind speed and temperature inversion) lead to the frequent accumulation of atmospheric pollutants in the lower atmospheric layer and morning hours are often thickly foggy. Wind speeds are typically higher in the summer and the monsoon periods; they are predominantly westerly and north–westerly and tend to be more northerly in the afternoons, except during the monsoon season, when they are easterly and north–easterly. Yearly mean wind speed is in the range 0.9 – 2.0 m s^{-1} (Srivastava et al., 2009a).

Sampling location was the campus of the Indian Institute of Tropical Meteorology (New Delhi Branch), Pune, located in the central urbanized part of Delhi (28° 35' N; 77° 12' E). The location of the site is shown in Figure 1. No major industrial sources are located within 5 km around the site. Sampling of PM_{10} and $PM_{2.5}$ was conducted on the rooftop of the building (~15 m above ground level).

2.2. Sampling

PM_{10} and $PM_{2.5}$ samplings were carried out by means of two single–stage aerosol samplers operating at the flow rate of 1 m^3 h^{-1} (APM 541 and APM 550, respectively, Envirotech Pvt. Ltd, India) and equipped with USEPA standardised impactors. Sampling time was 24 h. Teflon filters were Whatman Teflon Microfibre filter papers (47 mm diameter, 2 µm pore size); quartz filters were Whatman Quartz fibre filter (47 mm diameter, 2.5 µm pore size).

Sampling periods were as follows: during 2008, PM_{10} samplings were conducted once a week (on Monday) on Teflon filters. PM_{10} was also sampled daily between October 27th and 31st 2008, and between 15th and 21st 2009, in correspondence with the Diwali festivals (October 28th and October 17th, respectively). During the two Diwali periods we collected and analysed also $PM_{2.5}$.

Two Special Observation Periods (SOP) were scheduled on November 23rd–29th 2009 (samplings were performed every day) and March 2nd–12th, 2010 (samplings were performed every second day). During the two SOPs, PM_{10} was sampled on both Teflon and quartz fibre filters, in order to measure all PM macro–components and perform the mass closure. Meteorological conditions during both SOPs were characterised by very low wind intensity; prevalent wind direction was from West during the first period and from North–West during the second one; haze and fog occurred very often during both periods, particularly during the night and the morning hours; mean temperature was 18 °C (minimum 8 °C, maximum 28 °C) during the first SOP and 23 °C (minimum 14 °C, maximum 32 °C) during the second one.
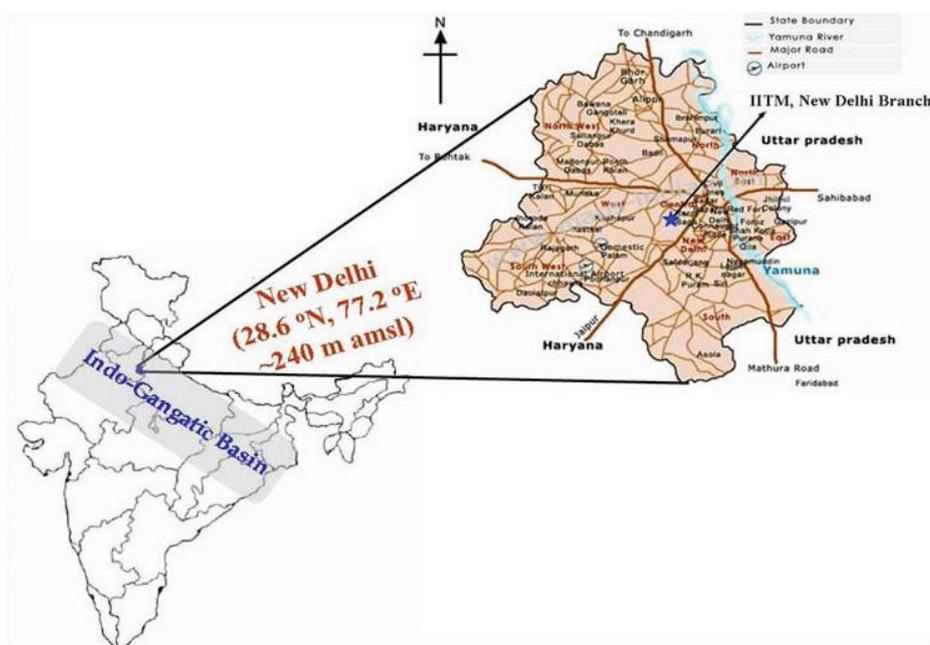

Figure 1. *Map of the sampling area.*

2.3. Analytical procedure

Before and after the sampling, Teflon filters were kept at relative humidity of 50% and temperature of 25 °C for 24 hours to remove the moisture content. Gravimetric determination of the collected mass was carried out using an electronic microbalance with 0.01 mg resolution (Model GR202, A&D Company Ltd., Japan).

Particulate matter collected on Teflon filters was analysed by ED–XRF (energy dispersion X–ray fluorescence), a non–destructive method for the determination of major elements (Na, Mg, Al, Si, P, S, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Br, Sr, Ba, Pb), by using a ED–XRF spectrometer mod. X–Lab 2000 (Spectro, Italy). Cd, Sn and Sb were in principle detectable, but their atmospheric concentrations were generally below the instrumental detection limits (0.006, 0.052, 0.068 µg m^{-3}, respectively). The detection limits for the other elements are reported in Table 1 (second column).

The calibration of the XRF spectrometer was carried out by using real atmospheric dust collected on the same filter material used for PM sampling (Teflon filters), following the procedure described in Astolfi et al. (2006). Briefly, 20 loaded filters were analysed by XRF and then re–analysed by ICP–OES, performing direct dissolution of the samples by HF acid digestion in microwave oven. ICP results were used for XRF calibration; in the course of time, the procedure was repeated by adding further data points to the calibration, up to reach around 30 data points per species.

We report in Table 1 (third column) the percent recovery of elements (R, %) from the XRF analysis of the Standard Reference Material NIST 2783 (air particulate sample reduced in particle size to simulate PM$_{2.5}$ and deposited on a polycarbonate filter membrane). R (%) was calculated as the average of ten readings, carried out by removing the filter and returning it to the sample holder after each trial. For the 18 certified or reference elements we obtained recoveries from 78% (Al) to 138% (Na); five elements (Mg, K, Ti, Mn and Zn) were in the range 90 – 110%. The difference in the filter material used for preparing NIST 2783 (polycarbonate) and for XRF calibration and real PM samplings (Teflon) is the main reason for the defective percent recoveries that were in some cases obtained on NIST. The different response of the instrument to different filter media, particularly when determining light elements, is the reason why we preferred to perform the calibration by using ICP results instead of the results obtained by analysing NIST reference material.

Table 1. *Detection limit (L.O.D. µg m^{-3}), recovery percentage from NIST 2783 (R%±σ, N=10), average, minimum and maximum concentration (µg m^{-3}) of individual elements in PM$_{10}$ during the two SOPs, the Diwali festivals of 2008 and 2009 and the 2008 study*

	L.O.D.	Recovery from NIST	FIRST SOP (2009) No. of samples: 7		SECOND SOP (2010) No. of samples: 6		DIWALI 2008 (October 28th) No. of samples: 1-1-3			DIWALI 2009 (October 17th) No. of samples: 1-1-3			2008 N. of samples: 53	
			AVG	Range	AVG	Range	pre-Diwali	Diwali	post-Diwali (AVG)	pre-Diwali	Diwali	post-Diwali (AVG)	AVG	Range
Na	0.053	138 ± 8	8.2	1.9–13	9.7	5.2–16	1.0	4.2	1.6	2.8	5.3	2.3	3.2	0.58-13
Mg	0.063	105 ± 3	0.47	0.27–0.71	0.42	0.10–0.88	1.2	6.3	1.6	0.31	5.5	0.69	0.65	0.14-1.2
Al	0.047	78 ± 3	2.2	0.79–3.3	3.1	1.9–4.6	4.0	18	5.4	7.4	22.6	6.0	2.5	0.53-4.6
Si	0.035	116 ± 2	9.9	3.1–15	14	8.4–19	15	11	18	22	12	17	11	2.2-20
P	0.041	-	0.17	0.070–0.24	0.21	0.16–0.26	0.25	0.32	0.26	0.35	0.34	0.25	0.17	0.048-0.34
S	0.022	126 ± 4	3.8	1.4–5.6	3.5	2.4–5.2	5.9	35	6.1	8.2	44	5.8	3.7	0.75-10
K	0.030	99 ± 2	3.8	1.4–5.8	3.1	2.2–4.1	8.9	68	11	12	81	9.8	3.0	0.68-10
Ca	0.025	133 ± 2	6.2	2.0–9.6	7.5	4.6–10	9.6	8.4	11	15	7.1	9.8	6.4	0.91-14
Ti	0.012	92 ± 3	0.29	0.079–0.48	0.35	0.21–0.54	0.12	1.8	0.18	0.29	1.7	0.18	0.33	0.046-0.67
V	0.005	125 ± 4	0.025	0.005–0.043	0.021	0.011–0.038	0.064	0.37	0.049	0.089	0.33	0.050	0.019	<LOD-0.044
Cr	0.005	135 ± 6	0.048	0.012–0.075	0.041	0.021–0.071	0.044	0.088	0.052	0.096	0.10	0.053	0.039	0.008-0.12
Mn	0.002	91 ± 3	0.094	0.025–0.14	0.079	0.042–0.12	0.055	0.19	0.065	0.10	0.17	0.061	0.080	0.014-0.17
Fe	0.018	81 ± 3	2.5	0.56-4.1	2.8	1.6–4.2	3.9	4.6	4.2	5.6	3.9	3.8	2.5	0.30-5.4
Ni	0.006	126 ± 4	0.014	<LOD—0.021	0.013	0.006–0.021	0.010	0.012	0.010	0.014	0.013	0.009	0.012	<LOD--0.025
Cu	0.023	124 ± 6	0.082	0.025–0.12	0.066	0.041–0.11	<LOD	0.11	<LOD	0.050	0.10	<LOD	0.074	0.022-0.23
Zn	0.012	101 ± 3	0.92	0.19–1.5	0.63	0.24–1.2	0.50	1.6	0.38	1.1	1.6	0.62	0.58	0.064-1.6
As	0.005	131 ± 3	0.086	0.020–0.15	0.061	0.037–0.11	0.030	0.069	0.026	0.034	0.047	0.026	0.048	0.005-0.16
Br	0.007	-	0.13	0.042–0.20	0.12	0.060–0.21	0.060	0.093	0.080	0.10	0.074	0.075	0.044	<LOD-0.18
Sr	0.022	-	0.047	0.022–0.067	0.057	0.040–0.071	0.094	1.8	0.14	0.23	1.6	0.14	0.046	0.023-0.097
Ba	0.038	135 ± 8	0.34	0.26–0.39	0.42	0.31–0.62	0.59	11	1.0	1.5	12	1.1	0.32	0.22-0.52
Pb	0.014	123 ± 2	0.79	0.10–1.7	0.38	0.18–0.56	0.79	1.4	0.66	0.63	0.94	0.56	0.43	<LOD -1.7

The repeatability of XRF determinations, calculated on 20 pairs of equivalent re–loaded filters is in the range of 2 – 10% (Canepari et al., 2009).

After XRF analysis, the Teflon filters were extracted in deionised water and analysed by ion chromatography (IC mod. DX–100, Dionex, Italy) for Cl^-, NO_3^-, $SO_4^=$, Na^+, NH_4^+, K^+, Mg^{++} and Ca^{++}.

In the case of Diwali festival, Teflon filters were also analysed by ICP–MS for the evaluation of the solubility distribution and for the determination of minor and trace elements (Li, Co, Ga, Rb, Cd, Sn, Sb, Cs, Ce, W, Tl and Bi), following the procedure reported in Canepari et al. (2006a; 2006b; 2008) and Perrino et al., (2007; 2009). In brief, after XRF analyses Teflon filters were extracted in acetate buffer solution (pH 4.5) by using an ultrasonic bath and the solutions divided into two portions. The first portion was regularly analysed by IC, the second one was analysed by ICP–MS (ICP–MS 810, cross–flow nebulizer MicroMist Varian, U.S.A.) for determining the extractable fraction of elements. The filters were then transferred into a PTFE vessel and a 4:2 HNO_3/H_2O_2 mixture was added; after microwave–assisted acid digestion, this solution was analysed by ICP–MS for the mineralised residual fraction. Rationale for the use of this digestion mixture, which is also suggested by CEN for the determination of Pb, As, Ni and Cd in PM samples (Bruno et al., 2000; CEN, UNI EN 14902:2005), and performance of the method, which assure a better analytical repeatability and lower quantification limits than the traditional HF digestion, are described in details in Canepari et al., (2009). For the elements that can be determined by both ICP–MS and XRF (Na, Mg, V, Mn, Fe, Ni, Cu, As, Sr, Ba and Pb) we obtained a very good correlation between the sum of the extractable and residual fractions determined by ICP and XRF values (Pearson's coefficient in the range 0.88 – 0.97 and slopes in the range 0.9–1.1).

Particulate matter collected on quartz filters during the SOPs was analysed by thermo–optical analysis (Sunset Laboratory, Forest Grove, OR–USA) for elemental carbon and organic carbon content (EC/OC). The instrument operates in two phases: in the first phase the filter is heated in He atmosphere up to 870 °C (evolution of organic carbon compounds); in the second phase it is heated again up to 900 °C in He + O_2 atmosphere (evolution of elemental carbon compounds). Carbon compounds are then converted from CO_2 to CH_4 and determined by a flame ionisation detector. Pyrolytic conversion is taken into account through laser monitoring. Calibration is carried out by analysing a known amount of sucrose standard deposited on a quartz membrane.

Quartz filters were also analysed for levoglucosan, a reliable tracer of biomass burning, by high–performance anion–exchange chromatography coupled to pulsed amperometric detection (HPAEC–PAD). The highly sensitive method, requires no complex sample pre–treatment procedures and shows good agreements with derivatization GC/MS or GC/FID methods (Engling et al., 2006; Caseiro et al., 2007). We used an IC mod. DX–500 (Dionex Corporation, USA) consisting of a DC ICS–3000 Chromatography Oven, a GP40 Gradient Pump and a Dionex ED50 Electrochemical Detector utilizing disposable gold electrodes. Separation of the individual anhydrosugars was achieved using a Dionex CarboPac PA10 Analytical Column with an 18 mM aqueous sodium hydroxide (NaOH) eluent at a flow rate of 0.5 mL min^{-1}. The analytical limit of detection was estimated to be better than 0.002 ng ml^{-1}. The quantitative analysis was carried out by analysing a 1 ppm levoglucosan standard solution immediately before and after each sample.

The overall procedure consisting in the analysis of elements by XRF, ions by IC end EC/OC by thermo–optical analysis allows the determination of each individual component typically accounting for more than 1% of the PM_{10} mass (macro–components) and of the main inorganic micro–components; the whole of the analysed species, after applying appropriate corrections for oxygen in metal oxides and for non–carbon atoms in organic matter, generally allows the identification of $95 \pm 10\%$ of the total mass (mass closure) (Perrino et al., 2009; Perrino et al., 2010). The unaccounted fraction may be attributed to atmospheric water uptake: although the hydrophobic Teflon membranes minimize the retention of atmospheric water on the filter structure, some particles may themselves show a hygroscopic behaviour and be responsible of water absorption.

3. Results and Discussion

3.1. Special observation periods

There is only a small number of chemical species that typically constitutes a significant fraction of the PM mass. Taking 1% of the mass as a lower limit, the species of interest include a few elements (aluminum, silicon, iron, calcium, potassium and magnesium), the main anions and cations (chloride, nitrate, sulfate, carbonate, sodium and ammonium) and elemental carbon. Although organic substances altogether constitute a very high percentage of PM (20–60%), the number of individual organic species is extremely high (hundreds–thousands) and none of them individually constitutes more than 1% of the total mass; for this reason organic compounds are generally considered as a whole (organic matter).

In order to obtain the mass closure, we added all the results of the chemical determinations as follows (see also Perrino et al., 2009; Perrino et al., 2010):

• insoluble elements were considered as oxides: Al, Si, Fe and the insoluble fraction of Na, K, Mg and Ca, calculated as the difference between the XRF and the IC determinations;
• ions: Cl^-, NO_3^-, $SO_4^=$, Na^+, NH_4^+, K^+, Mg^{++}, Ca^{++} and $CO_3^=$; the latter was calculated as:
  $[CO_3^=] = 2.5 [Mg^{++}] + 1.5 [Ca^{++}]$
• elemental carbon
• organic matter (OM) calculated as the amount of organic carbon (OC) multiplied by a factor that takes into account non–carbon atoms; this factor depends on PM composition and, consequently, on the investigated environment (urban, rural, remote) (Viidanoja et al., 2002); for this study we applied a factor of 1.8, which is generally recommended for urban environments non directly exposed to traffic emissions (Turpin and Lim, 2001; Russell, 2003).

The comparison of PM_{10} mass concentration determined by gravimetry and by reconstruction from the results of chemical analyses is shown in Figure 2 (upper panel). During the two SOPs, chemical determinations accounted for 96% and 94% of the gravimetric PM mass, respectively, with an overall correlation having Pearson's coefficient better than 0.96. The ion balance, reported in the lower panel of Figure 2, was also adequate (Pearson's coefficient=0.895, slope=1.02).

Given the satisfactory results of the mass closure, we re–arranged the results of the chemical analyses considering the five groups of macro–components that are typically present in urban atmospheres, related to five different sources: soil, sea, atmosphere, combustion, and biosphere.

Main elements associated with soil (crustal fraction, CF, the first group) were calculated by adding the concentration of elements (as metal oxides) generally associated with mineral dust: Al, Si, Fe, insoluble fraction ($_{ins}$) of Na, K, Mg and Ca (Chan et al., 1997):

$CF = 1.89$ Al $+ 2.14$ Si $+ 1.42$ Fe $+ 1.35$ $Na_{ins} + 1.2$ $K_{ins} + 1.67$ $Mg_{ins} + 1.4$ Ca_{ins}
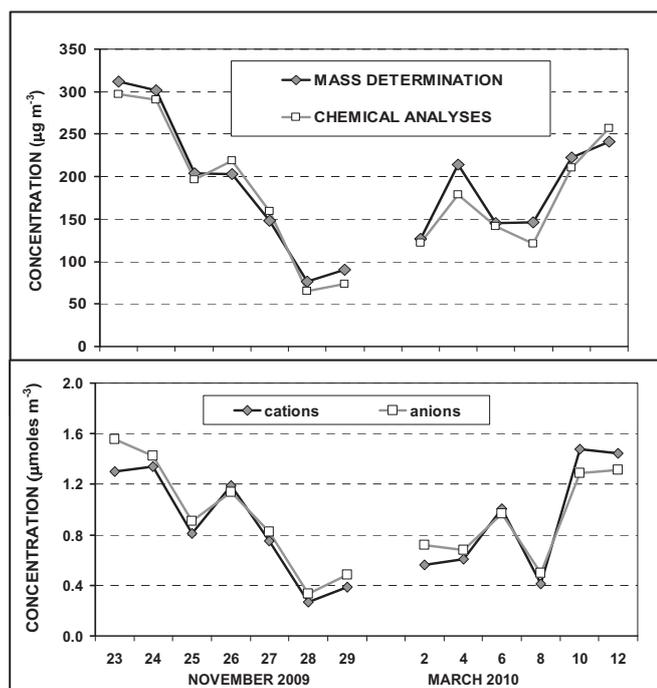
Figure 2. *Comparison of the PM$_{10}$ mass concentration determined by gravimetry and by reconstruction from the results of chemical analyses (upper panel); ion balance (lower panel).*

Given the distance of Delhi from the ocean, sea–spray (sodium chloride and minor sea–water components), the second group, was neglected. The data collected during the two SOPs shows, in fact, that the ratio Cl^-/Na^+ was very high (up to 30), while the typical value of fresh sea–spray, which is supposed to decrease with increasing distance from the coast, is 1.8. Similar very high values of the Cl^- to Na^+ ratio were also reported by Tiwari et al. (2009); particularly high wintertime chloride concentrations were also recorded by Srivastava et al. (2009b). In Delhi, production from coal combustion, biomass burning and waste incineration are the major anthropogenic sources of HCl, which in the atmosphere easily reacts with gaseous ammonia, producing particulate ammonium chloride. The production of ammonium chloride (as well as of all secondary species) is particularly enhanced in atmospheric stability conditions, when the aging of the air masses favour gas–to–gas and gas–to–particle interaction. It is worth noting that the meteorological conditions during the two SOPs, carried out at the very end of the post–monsoon season and during the winter, were characterised by shallow fog during both morning and evening hours and extremely low wind intensity during the whole day. In our data, the time patterns of chloride and ammonium were very similar, with a Pearson's coefficient better than 0.79; it is thus reasonable to assume that during the two SOPs ammonium chloride was the prevalent chlorine species in the atmosphere of Delhi. Being a secondary species, ammonium chloride was included in the third group.

Inorganic species formed by reaction in the atmosphere (ammonium nitrate, ammonium chloride, ammonium sulphate), the third group, were calculated by adding the concentration of nitrate, sulphate, chloride and ammonium.

The fourth group, combustion products, includes elemental carbon and an equal amount of organic carbon, which is supposed to condense from the exhaust gases and coat the surface of elemental carbon particles (Viidanoja et al., 2002).

The remaining organic carbon amount, multiplied by the OM/OC conversion factor, was attributed to the fifth group (organics), which includes the bio–aerosol (airborne particles consisting of, or originating from, micro–organisms) and the

particulate species produced in the atmosphere from anthropogenic and plant–emitted VOCs.

Figure 3 shows the daily variation of PM$_{10}$ composition during the two SOPs, together with the average composition of each period. The results indicate that combustion pollutants constitute a minor, but appreciable, fraction of PM$_{10}$ during both periods (average: 7% and 6%, respectively; range: 5–9% and 5–7% respectively); during November SOP the rest of the PM$_{10}$ mass was almost equally divided among organics (average: 33%; range: 28–37%), crustal species (average: 31%; range: 24–35%) and secondary inorganic species (average: 29%; range: 24–34%); during March SOP, instead, soil components prevailed (average: 43%; range: 32–53%) secondary inorganic species were at the same level (average: 31%; range: 21–40%) and organics were lower (average: 20%; range: 16–28%).

To estimate the fraction of organic PM that was due to biomass burning, quite frequent in the area of Delhi for both heating and cooking purposes, we measured the air concentrations of levoglucosan, emitted during the burning of wood as a product of cellulose thermal degradation. Figure 4 reports the concentrations of levoglucosan measured in Delhi during the two SOPs. The concentration of this tracer was evidently much higher during the first period, when the ambient temperature was lower (0.5 – 3.0 μg m^{-3} and 0.1 – 0.6 μg m^{-3}, respectively). It is worth noting that during the first SOP the time patterns of levoglucosan and PM$_{10}$ mass concentration were very similar (Pearson's coefficient = 0.96) and that the weight–to–weight ratio was always comprised between 0.6 and 1.0. This observation indicates that during the seven days of the November SOP the emission rate from biomass burning was fairly constant and that the wide concentration variations of both levoglucosan and PM$_{10}$ mass were mostly determined by variations in the dilution properties of the lower atmospheric layer (Perrino et al., 2008).

The average emission factor of levoglucosan in organic matter from biomass burning is estimated to be 11–17% of the total emitted organic matter (Fine at al., 2001; Jordan et al., 2006; Leithead et al., 2006). Taking the value of 14% as an indicative percentage, we can assume that during the first SOP the emission from biomass burning constituted 18.4 ± 2.1 % of the total organic matter and 5.9 ± 1.2 % of the total mass of PM$_{10}$ (on average, 3.2 μg m^{-3}). During March, instead, biomass burning constituted 9.1 ± 3.2 % of organic matter and 1.6 ± 0.5 % of PM$_{10}$ mass (on average, 0.8 μg m^{-3}). Given the difference in the atmospheric temperature during the two SOPs, from these data we may roughly estimate that in the area of Delhi about 10% of the atmospheric organic matter is produced by biomass burning from domestic heating (only during cold months), while another 10% comes from biomass burning from cooking activities (all year round).

The average, minimum and maximum concentration of individual elements during the two SOPs are summarized in Table 1 while the average, minimum and maximum concentration of individual ions, elemental carbon, organic carbon and levoglucosan are summarized in Table 2.

3.2. Diwali periods

Diwali, the Indian festival of lights, is characterised by large firework displays and by the use of oil lamps and candles to decorate the houses. The atmospheric emission of fireworks has a specific signature: Na and K are used as metal oxidisers, Al (white, silver), Mg (white, silver), Cu (blue), Ba (white as carbonates and nitrates, green as chlorates), Sr (red), Na (yellow) and Ti (silver) are colour and sparkle emitters, S is used as propellant, Zn is used to create smoke effects, chloride, nitrate and sulphate are components of metal salts producing colours, potassium nitrate, sulphur and potassium chlorate or perchlorate are component of the black powder, the combustible material. The reliability of

strontium, magnesium, barium, potassium and copper as firework tracers has been also reported by Vecchi et al. (2008) and Tandon et al. (2008).

PM concentrations in Delhi show a dramatic increase during the festival. In 2008 the average daily concentration of PM_{10} during Diwali (October 28th) was 767 μg m^{-3}, compared to 276 μg m^{-3} measured the day before; during Diwali 2009 (October 17th) it was 620 μg m^{-3} compared to 394 μg m^{-3}. The concentration of individual elements during Diwali, the day before (pre–Diwali) and the average concentration during the three following days (post–Diwali) are reported in Table 1 for the years 2008 and 2009. The concentrations of ionic species and of minor and trace elements during the same days are reported in Table 2 and 3, respectively.

From the data of Tables 1–3 it appears that the concentration of a number of species showed a marked increase during both festivals. Major increases, calculated as the concentration ratio between Diwali and the day before, were recorded for Sr, Ba, Ti and Bi (ratio higher than 10) and for Mg, Cu, K, S, V, Ga and chloride (ratio higher than 5), but a clear increase was observed also for Na, Al, Mn, Zn, As, Cr, Cd, Sn, Sb and nitrate. It is worth noting that a very high ratio (about 50) was observed for bismuth that is used instead of lead as bismuth trioxide or subcarbonate to produce an effect called "Dragon eggs"; to our knowledge, the ability of this element to trace fireworks has never been reported in the scientific literature. Negligible or no increase was observed for P, Fe, Ni, Br, Pb, Li, Co, Rb, Cs, Ce, W, Tl and ammonium, while Si and Ca showed a negative ratio. The decrease in the concentration of these two elements, which are soil components but are not contained in fireworks, is probably due to a lower impact of dust re–suspension. During Diwali, in fact, most people stay at home (the day is a National Holiday) and road traffic is reduced also because of the frequent burning of crackers in the streets.
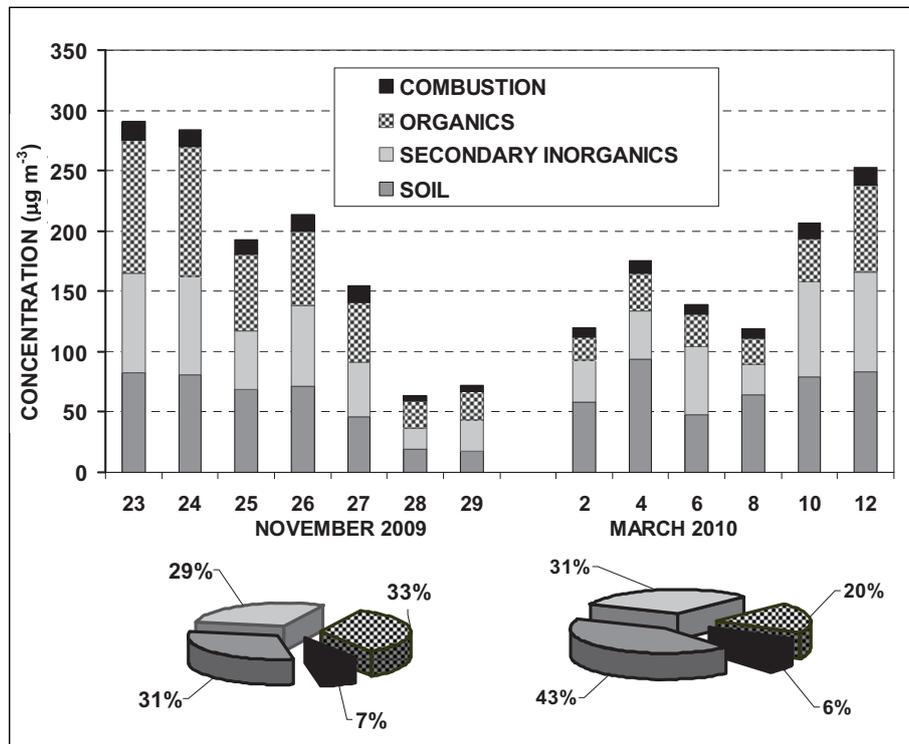

Figure 3. *Daily variation of PM_{10} composition during the two SOPs and average composition of each period.*
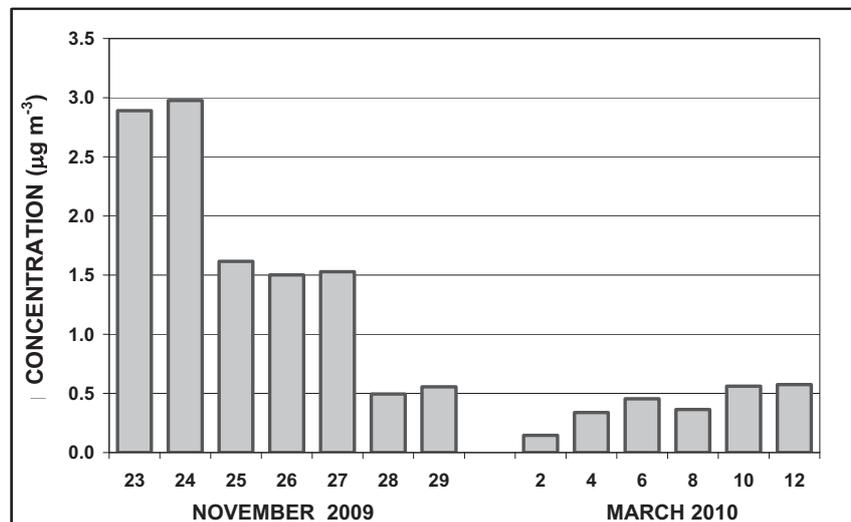

Figure 4. *Air concentration of levoglucosan during the two SOPs.*

Table 2. *Average, minimum and maximum concentration (in μg m⁻³) of PM mass, individual ions, elemental carbon, organic carbon and levoglucosan during the two SOPs; PM mass and concentration of individual ions during the Diwali festivals of 2008 and 2009*

	FIRST SOP (2009) No. of samples: 7		SECOND SOP (2010) No. of samples: 6		DIWALI 2008 (October 28th) No. of samples: 1-1-3			DIWALI 2009 (October 17th) No. of samples: 1-1-3		
	AVG	Range	AVG	Range	pre-Diwali	Diwali	post-Diwali (AVG)	pre-Diwali	Diwali	post-Diwali (AVG)
PM_{10}	191	76–312	183	127-241	276	767	282	394	620	278
$PM_{2.5}$					94	448	110	148	365	135
Cl^-	21	5.4-33	25	9.5–45	1.5	14	3.9	7.2	16	6.3
NO_3^-	14	5.6–26	6.2	3.9–9.0	5.1	20	7.6	14	11	11
$SO_4^=$	6.3	2.6–11	11	7.2– 5.6	7.3	49	6.8	5.1	44	5.7
Na^+	0.68	0.23–1.0	0.71	0.50–0.97	0.94	1.8	1.1	0.77	1.6	0.79
NH_4^+	13	4.6–19	12	4.6–18	0.51	1.3	1.0	1.2	0.64	2.3
K^+	2.9	0.99–4.7	1.9	1.1–2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Mg^{++}	0.26	0.09–0.49	0.28	0.19–0.46	0.46	5.7	0.60	1.0	5.1	0.59
Ca^{++}	4.6	1.7–9.2	6.6	4.3–8.3	7.8	7.9	8.9	13	6.2	8.4
EC	4.8	3.6-6.9	5.1	2.3-6.8						
OC	39	14-66	22	13-44						
LVGSN	1.7	0.50-3.0	0.41	0.15-0.57						

Table 3. *Detection limit (L.O.D. ng m⁻³), recovery percentage from NIST 1649a (R%±σ, N=10) and concentrations of minor and trace elements (in ng m⁻³) during the Diwali festivals of 2008 and 2009*

	L.O.D.	Recovery from NIST	DIWALI 2008 (October 28th) No. of samples: 1-1-3			DIWALI 2009 (October 17th) No. of samples: 1-1-3		
			pre-Diwali	Diwali	post-Diwali (AVG)	pre-Diwali	Diwali	post-Diwali (AVG)
Li	0.01		3.3	2.4	2.4	2.6	2.9	2.7
Co	0.01	91 ± 4	2.0	1.4	1.4	1.4	1.6	1.5
Ga	0.4		2.8	11	1.9	1.4	11	1.7
Rb	0.2	94 ± 5	11	7.3	7.3	8.3	9.1	8.8
Cd	0.02	101 ± 6	2.7	7.5	2.3	1.4	4.3	1.4
Sn	0.04	93 ± 3	7.3	21	13	8.5	22	9.7
Sb	0.02	91 ± 7	10	27	8.8	10	33	5.4
Cs	0.001	87 ± 9	0.91	0.63	0.64	0.75	0.78	0.71
Ce	0.03	89 ± 7	8.7	5.4	5.7	6.0	6.8	6.0
W	0.001	90 ± 8	0.80	0.56	0.61	0.74	0.65	0.69
Tl	0.001		0.31	0.22	0.18	0.27	0.32	0.21
Bi	0.009		4.4	187	7.0	2.1	130	7.8

From the data on Tables 1 and 2 we can roughly estimate that about half of the PM mass increase recorded during Diwali was due to element, chloride and sulphate directly produced by fireworks explosion. It is also reasonable that a remarkable increase of elemental carbon (non–metallic fuels used in fireworks contain charcoal) and organic matter (burning illumination are widely used during the festival) occur during Diwali. The time pattern of the main fireworks tracer during the festivals, as well as of PM_{10} and $PM_{2.5}$ mass concentration, is reported in Figure 5. It is worth noting that during the three days following Diwali the concentrations of most elements related to fireworks show a clear decreasing pattern. This indicates that, in spite of the short duration of the fireworks activity, a fraction of the produced aerosol is resuspended in the atmosphere during the following days as an action of both the wind and the street sweeping after the festival.

Some additional information about the firework aerosol may be obtained from the study of the size and solubility distributions of elements. We report in Table 4 the percentages of PM mass and of the main fireworks tracers in the fine fraction ($PM_{2.5}$) with respect to PM_{10} during the festival of 2008. A general increase of the fine fraction occurred on Diwali, which indicates that the contribution of the fireworks to PM is mostly in this size fraction.

This increase is particularly manifest for elements showing low percentages in $PM_{2.5}$ in pre– and post–Diwali samples, as Mg, Al, Ti, V, Cr, Mn and Ga. Similar results were obtained for Diwali 2009.

As far as the distribution between extractable and residual fractions are concerned, the extractable fraction was generally low for all the analysed elements, and much lower than the values recorded in other geographical areas (Canepari et al., 2008; Canepari et al., 2009). Extractable fraction in PM_{10} is below 5% for Li, V, Fe, Cu, Ga, Sn, Cs, Ba, Ce, W, Pb and Bi; it is between 5 and 20% for Mg, Mn, Co, Ni, As, Rb, Sr and Sb; it is between 20 and 40% only for Na, Cd and Tl. For some elements an interesting variation of the extractable fraction is observed during the festival (Figure 6). Mn, As, Ba and Pb show a minimum of the extractable fraction during Diwali, while Cu and Mg show the opposite behaviour. These variations are due to the prevalence of different chemical forms in the fireworks emission, more soluble in the case of Cu and Mg, less soluble in the case Mn, As, Ba and Pb. It is worth noting that the decrease solubility of Ba and Pb might be due to the precipitation of sulphates.
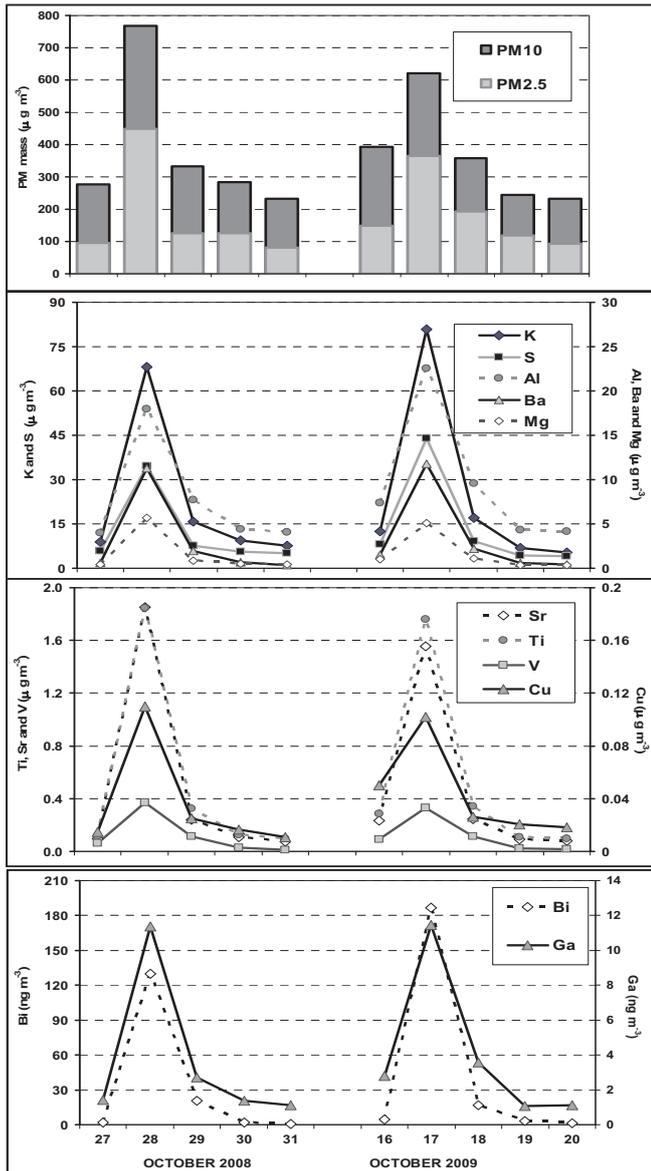
Figure 5. *Time pattern of the mass concentration of PM$_{10}$ and PM$_{2.5}$ and of the main firework tracers during Diwali festival 2008 and 2009.*

3.3. Weekly samplings during 2008

Daily PM$_{10}$ Teflon filters sampled once a week during 2008 were analysed for mass concentration and elements. Average PM$_{10}$ mass concentration during the year was 165 µg m^{-3} and exhibited a marked seasonal variation: it was 203 µg m^{-3} during the winter, 133 µg m^{-3} during the summer, 94 µg m^{-3} during the monsoon and 249 µg m^{-3} during the post–monsoon. The higher concentrations recorded during the winter are related to the intense atmospheric stability that is experienced during this season in the Delhi region, usually dominated by a high pressure centred over Western China; in addition, the lack of precipitation reduces the potential for wet deposition. During this period, the contribution of the increased domestic biomass burning to aerosol production must also be considered. During the summer atmospheric mixing height is at its maximum, but the frequent severe dust storms covering the area of Delhi may increase the crustal contribution to PM. During the monsoon, intense and frequent precipitation, high wind velocities and changes in the wind direction favour the decrease of atmospheric pollution and take PM concentration at a minimum value. During post–monsoon season PM increases again, as this season includes the period of severe atmospheric pollution of the

Diwali festival and is also generally characterised by strong atmospheric stability and low wind intensity.

Table 4. *Variation of the size distribution of PM and elements during Diwali festival 2008: concentration in PM$_{2.5}$ with respect to PM$_{10}$ (%)*

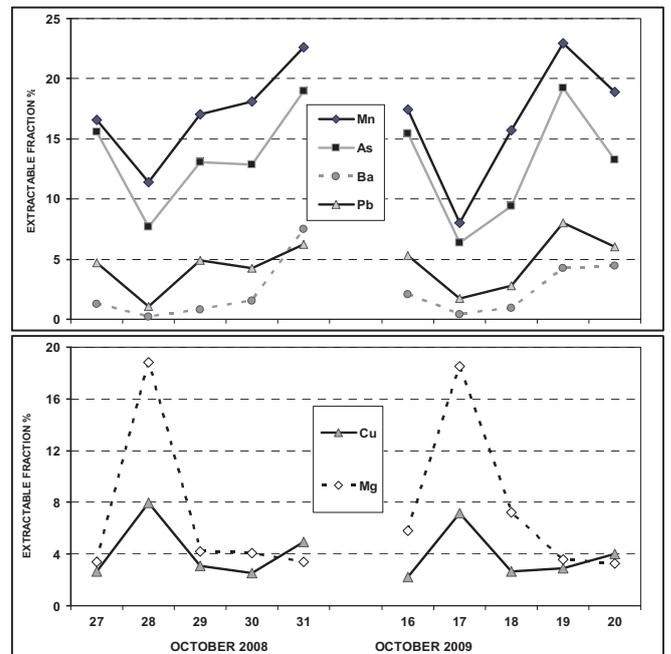|	October 27	October 28 (Diwali)	October 29	October 30	October 31
	% in PM$_{2.5}$	% in PM$_{2.5}$	% in PM$_{2.5}$	% in PM$_{2.5}$	% in PM$_{2.5}$
PM mass	34	58	38	44	35
Na	41	70	65	60	43
Mg	8	47	14	10	8
Al	22	98	56	29	10
S	56	99	71	72	65
K	50	81	65	61	52
Ti	21	65	41	29	9
V	18	99	55	61	35
Cr	21	83	32	32	17
Mn	15	60	27	25	15
Cu	32	75	60	58	34
Zn	36	68	49	54	49
Ga	15	76	50	29	8
As	47	71	64	63	41
Sr	35	66	51	47	23
Cd	45	69	49	51	54
Sn	53	82	72	69	56
Sb	75	92	90	84	57
Ba	67	71	73	78	63
Bi	55	72	72	75	53

Figure 6. *Solubility distribution of some elements during Diwali festival 2008 and 2009.*

Mean values of elemental concentrations during 2008 are reported in Table 1. In general, elemental concentrations were comparable to those reported by Srivastava and Jain (2007) for residential sites in Delhi. For every species, the range of

concentrations recorded in 2008 includes the individual concentrations recorded during the SOPs of 2009 and 2010. For many elements, instead, the concentrations measured during Diwali were widely outside of the range. Figure 7 reports the percent elemental composition of PM_{10} during 2008 (excluding Diwali) and during Diwali 2008. For the sake of clarity, only the ten elements at highest concentration were included. In the first case the elemental composition was dominated by silicon and calcium, and the Si/Al ratio was 4.4; in the second case, potassium and sulphur dominated, and the Si/Al ratio was only 0.6.
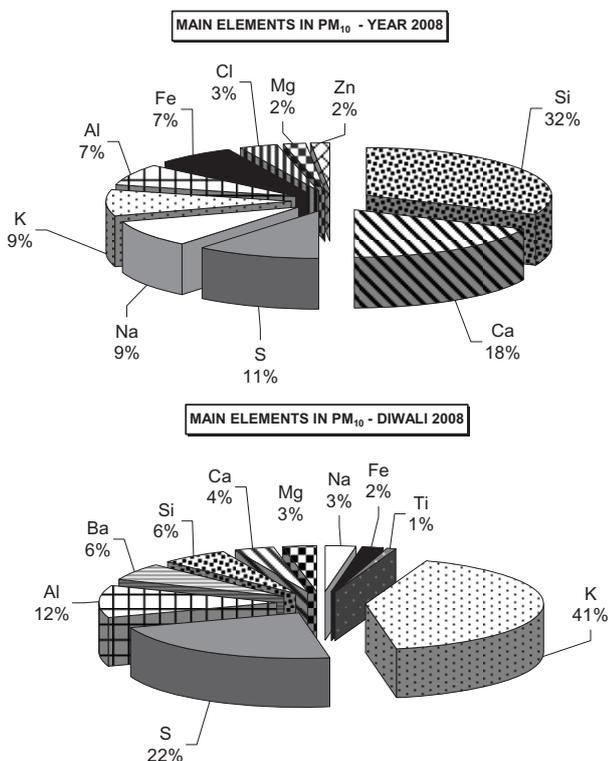
Figure 7. *Percent elemental composition of PM_{10} (ten elements at higher concentration) during 2008 (weekly samplings) and during Diwali 2008.*

The availability of samples regularly collected during the year allowed us to evaluate the main differences in PM elemental composition during the four seasons. A general decrease of the concentration of all elements, as well as of PM mass, was observed during the monsoon and, at a less extent, also during the summer. However, the decrease during the monsoon period was shown by all elements, with a monsoon–to–year ratio between 0.3 (Br) and 0.9 (Ba and Ni), while the decrease during the summer showed individual variability. During the summer, in particular, the most relevant decrease was shown by elements of anthropogenic origin (S, K, As, Br, Pb), while species of natural origin show negligible decrease or slight increase. This behaviour may be attributed to the more easily production and re–suspension of soil dust during the arid summer season and to the most frequent dust storms that are experienced during this period. The general decrease of PM and its components during the monsoon is, instead, mainly due to global wash–out and rain–out of particles during the frequent heavy rainfalls.

All elements showed a clear increase during the period from October to March (post–monsoon and winter), which is characterised by poor atmospheric dispersion and by the increase of biomass burning emissions. However, also in this case a group of elements including Cu, Zn, As, Br, Pb, of mainly anthropogenic origin, show a somewhat different behaviour and reach the highest concentration level during the winter period, while all other

elements reach their maximum levels during the post–monsoon period.

Finally, the results of the regression analysis, carried out on the 52 daily PM_{10} samples, show a very good co–variation of a group of elements related to soil (Al, Si, Fe, Mg, P, Ca, Ti, Sr, Mn), all characterized by Pearson's coefficient $R^2 > 0.8$. Pearson's coefficient better than 0.8 are also shown by As and Pb, of industrial origin, and by Ni and V, mainly produced by heavy oil combustion.

4. Conclusions

The analysis of all PM_{10} macro–components in the atmosphere of Delhi during two short periods in the winter seasons of 2009 and 2010 allowed us to obtain the mass closure and to estimate the strength of the main sources of PM: soil, secondary reactions, combustion processes and organic matter. During the winter secondary reactions are enhanced and the direct contribution of domestic biomass burning to PM emission, non negligible during the whole year, is particularly significant.

Remarkably high concentrations were measured during the Diwali festivals of 2008 and 2009, with a considerable increase of the concentrations of specific firework tracers and a change in the size distribution and solubility of many elements.

Element concentrations, determined all over 2008, showed a decrease during the monsoon and a marked increase during the cold seasons; crustal components also increased during the summer.

Acknowledgements

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