Characteristics of Aerosols over Suburban and Urban Site of Semiarid Region in India: Seasonal and Spatial Variations

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Abstract

This paper deals with atmospheric concentrations of SPM (Suspended Particulate Matter) and its water soluble components, their size distribution, and seasonal and spatial variations. Ambient aerosol samples were collected over tropical India at an urban and suburban site in the Agra region. All samples were collected on Whatman-41 filters using a CPS-105 size-segregated impactor. The mean concentration of SPM was 154 $\mu g/m^3$ with approximately 55% in coarse mode at Dayalbagh and 228.9 $\mu g/m^3$ at St. John's with approximately 41% in coarse mode. The concentration of NH_4^+ was highest at both sites, followed by $Mg^{2+} > Ca^{2+} > SO_4^{2-} > Cl^- > K^+ > NO_3^- > Na^+ > F^-$ at Dayalbagh, and $Mg^{2+} > Cl^- > Ca^{2+} > SO_4^{2-} > NO_3^- > F^- > Na^+ > K^+$ at St. John's. The difference between the sums of cations and anions in fine mode was 181.5 and 77.06 neq/m^3 at Dayalbagh and St. John's, respectively; and in coarse mode, 172.76 and 82.49 neq/m^3 respectively. The mass size distribution of particulate showed bimodal distribution at both the sites with one peak in the fine mode and another peak in the coarse mode. Unimodal distribution was observed for F^-, NO_3^- and Na^+ and bimodal for K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, and SO_4^{2-} at both sites. The mean load of SPM was highest in monsoon followed by summer and winter, probably due to high wind speed, unstable atmospheric conditions and minimum rainfall during the study period.

Key words: Particulate matter; Concentration; Fine; Coarse; Size distribution; Seasonal variation.

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INTRODUCTION

One of the most basic and useful indicators for judging the degree of air pollution is the level of total suspended particulates (TSP) (Momin *et al.,* 1999). Atmospheric particulates play an important role in radiative forcing and climate change. In addition, they are responsible for visibility impairment and have significant implications for human health. Particulates are also associated with acid deposition and, therefore, effects on terrestrial and aquatic ecosystems. There are a number of properties of particles which are important to their role in atmospheric processes. These include, in addition to their number concentration, their mass, size, chemical composition and aerodynamic and optical properties. Of these, size is the most important; it not only reflects the nature of the source of the particles, but also relates to their health effects (Bates *et al.,* 1966) and to their aesthetic and climatic effects via their light scattering properties. Some means of expressing the size of such particles is essential since many important properties of the particles, such as volume, mass and settling velocity depend on the size. The effective diameter is particularly useful because it can determine residence time in the air, it reflects the various regions of the respiratory system in which different sized particles are deposited. Atmospheric particles may have diameters anywhere within the range of 0.002-100 µm. Because the size of atmospheric particles plays such an important role in both their chemistry and physics in the atmosphere, as well as in their effects, it is important to know the distribution of sizes.

Airborne particulates may be caused by a variety of sources; e.g., natural sea spray or wind blown dust, or anthropogenic activities such as stationary fuel combustion, industrial processes, transportation and solid waste disposal (Momin *et al.,* 1999). Chemical composition of these emissions varies widely. In order to trace down the pollution sources and determine the extent of the anthropogenic contribution, a fundamental study of the chemical composition and mass size distribution of atmospheric particulates is required.

Cities act as sources of aerosol and are likely to be important on a regional scale. Despite this, no direct measurements have been made of the rate of aerosol production and transport above cities. Urban aerosol is a topic of current interest (Micallef and Cols, 1998; Fenger, 1999; Mayer, 1999; Harrison and Yin, 2000; Colvile *et al.,* 2001) because of the climate forcing caused by aerosol, and because of rapidly increasing global urban populations. It is thought that around half of the world's population currently lives in cities, with global population still rising rapidly, especially in the developing world (Fenger, 1999). Much of the current work is devoted to the measurement of PM_{10} and $PM_{2.5}$ concentrations within cities, but making inferences from these measurements about the amount and character of aerosol leaving cities may be a cause of error in assessments of the effect of cities on a regional scale (Dorsey *et al.,* 2002).

The effects of urban aerosols outside their city of origin are many and varied. Aerosol deposits on land downwind of cities and on agricultural and potentially sensitive ecosystems modify the

chemical and radiative (Jacovides *et al.,* 1999) properties of the downwind atmosphere and alter regional cloud precipitation (Hitzenberg *et al.,* 1999), depending upon their number, composition and size distribution. In order to make a proper assessment of the effect of the urban plume on atmospheric chemistry and microphysics, information is required on the number and size distribution of the aerosol, rather than the more commonly measured mass loading. Additionally, particle size distribution data is essential to assess inhalation health hazards (Trijoins, 1983).

Several investigators have studied the chemical composition and mass size distribution of atmospheric aerosols both in India (Khemani *et al.,* 1985; Mahadevan, 1986; Safai *et al.,* 1993; Tripathi *et al.,* 1996; Kulshrestha *et al.,* 1998; Parmar *et al.,* 2001; Kumar *et al.,* 2003, 2006) and abroad (Whitbey, 1978; Hubert and Lazrus, 1980; Shrestha *et al.,* 2000). A bimodal distribution of ambient aerosol has been reported for many urban sites (Lioy and Daisey, 1987; Aceves and Grimalt, 1993; Lin *et al.,* 1999). The coarse fraction is mainly due to crustal material, paved road dust, non-catalyst equipped gasoline engines and background sea salts. The fine fraction is a mixture of primary and secondary aerosol emitted from anthropogenic, rather than natural, sources, or formed by vapor nucleation/condensation mechanisms (Hildemann *et al.,* 1991; Kleeman and Cass, 1998;). In Agra a few sporadic measurements have been made (Kulshrestha *et al.,* 1998; Parmar *et al.,* 2001) in which chemical compositions of particulate matter has been reported. The systematic study of aerosol particles concentration in any air shed, their characteristic diameter, distribution in fine and coarse mode, as well as their seasonal variations is needed. In this paper we discuss the chemical composition of aerosols, their mass size distribution and seasonal variations at St. John's, an urban area, and Dayalbagh, a suburban site in the Agra region of tropical India.

MATERIALS AND METHODS

Sampling site

The study conducted at suburban Dayalbagh and urban St John's in Agra (27°10'N, 78°05'E) is in North Central India, which is about 200 km southeast of Delhi. Two thirds of its peripheral boundaries (SE, W and NW) are bounded by the Thar Desert of Rajasthan and is therefore a semi arid area (Fig. 1). Study sites fall in the Indo-Gangetic plain where agriculture is the major activity. The soil type is a mixture of sand and loam, containing an excess of salts. It has high exchangeable sodium percentage (ESP) values and moderate water retaining capacity. The major industrial activities are ferrous and non-ferrous metal casting, rubber processing, tanneries, lime oxidation and pulverization, engineering works, chemicals and brick kilns. Apart from the local sources, Mathura refinery and Ferozabad glass industries are both situated 40 km from Agra. Agra's climate is tropical and strongly influenced by the Aeolian dust blown from the Asian subcontinent and Thar Desert of Rajasthan. Agra, which is about 169 m above the mean sea level

(msl), has a semiarid climate with atmospheric temperature ranges of 11-48°C (max) and 0.7-30°C (min), relative humidity 25-95%, light intensity 0.7-5.6 oktas (cloudiness), and an annual rainfall 650 mm. Unexpectedly for the year 2000 and 2001 total rainfall values fell to 377 and 385 mm, respectively. Agra's climate has been broadly classified into three seasons: winter (November to February), summer (March to June) and monsoon (July to October). The atmospheric calm condition at Agra in summer, monsoon, and winter seasons are 47%, 35%, and 76%, respectively. Calm conditions are represented by a wind velocity of < 1 m/s. The wind speed in the Agra is mostly in the range of 1-2 m/s. The prevailing directions follow two distinct patterns: during monsoon winds are from W, NW, SW and NE sector while during other seasons they are from the W and NW sector. Details of climatic conditions for Agra can be found elsewhere (Kumar *et al.,* 2006).

Fig. 1. Map showing sampling sites.

All Dayalbagh samples were collected at 8 m above the ground on the roof of the Science faculty building on the Dayalbagh Educational Institute's campus. Suburban Dayalbagh is 10 km away from the industrial sector of the city where, due to agricultural practices, vegetation predominates. Agriculture is the major activity and fields around the sampling site are covered with a variety of crops in the winter. In the summer, uncultivated fields lie barren and dry. The soil is sandy and calcareous by nature. The population around the sampling site is about 15,000. A stockyard of about 800 cattle is situated at a distance of 400 m west of the sampling site. The sampling site lies by the side of the road that carries mixed vehicular traffic on the order of 10^3

vehicles in a day. National highway NH-II, 2 km to the south, has dense vehicular traffic (10^5 vehicles in a day). The city's industrial areas some distance away from Dayalbagh in the NE, SE, E and SW sectors; giving Dayalbagh characteristics representative of suburban Agra (Fig. 2).
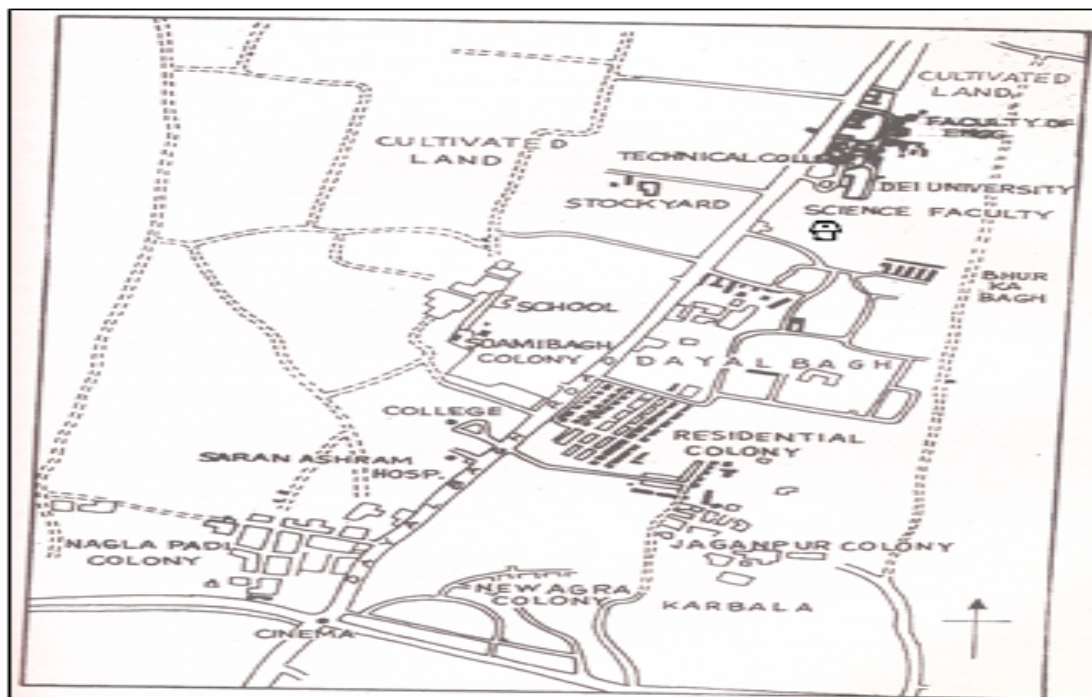

Fig. 2. Map showing Dayalbagh site and its surroundings.

St John's, the urban site, lies in the heart of Agra city. The sampling site is located 20 m away from a road to the west side of a busy traffic junction. All samples were collected 8 m above ground on the roof of the Chemistry Department building located on the St. John's College campus. There are two major traffic junctions and a railway station at about 200 m on the either side of the sampling site. Residential colonies and commercial complexes lie in the area immediately surrounding the site. The major industries (ferrous and non ferrous foundries) are located 4 km to the E, NE and SW. Most "Petha" units that use coal are situated in this area, and about 25% of the population uses biomass fuels (coal and cokes) for domestic purposes. About 30,000 vehicles move on this road in a day and are usually poorly maintained. As St. John's site lies in the heart of Agra city, this site is a true representative of an urban site in the Agra region.

Sample collection

Prior to collection, all the plastic wares used in collection and storage were cleaned by soaking in detergent for a few hours, followed by rinsing with deionized water several times. Particulate samples were collected with KIMOTO (Model: CPS-105) four-stage, size-segregated impactor using a high-volume sampler (HVS) equipped with automatic flow rate controller at a flow rate

of 1000 L/min. The first stage collects particles in the range of 0.7-1.6 µm, second stage 1.6-5.4 µm, third stage 5.4-10.9 µm, and fourth stage 10.9-20 µm with characteristic mean diameters of 0.9 µm, 3.6 µm, 8.2 µm and 15.5 µm, respectively. In this study, particles less than 3.6 µm were considered as fine particles, and those more than 3.6 µm as coarse particles; as it was not possible with this impactor to take around 2 µm as cut point for fine and coarse particles. The impactor separates particles in air according to their aerodynamic diameter. The particles are separated from a moving gas stream according to their mass by inertial impaction (Pitts and Pitts, 1986). There are four perforated steel plates in the impactor in which the perforations get smaller with each successive plate.

This impactor measures the number of particles in specific size ranges. A 50% cutoff point was selected to characterize size intervals for each stage, where the cutoff point is defined as the diameter of spheres of unit density, 50% of which are collected by that stage of the impactor. Roughly speaking, each stage captures particles ranging from a diameter corresponding to midway between its cut point to that of the next higher and lower stage (Pitts and Pitts, 1986). Using these assumptions, the ranges of particle diameters captured by each stage for a typical impactor are given in Table 1. Also given are the diameter intervals ΔD and Δlog D for each stage.

Table 1. 50% cutoff points and approximate representative range of particle diameters captured by each stage in a five-stage impactor.

Stage	50% Cutoff point (µm)	Size range of particle diameters captured by that stage (µm)	Representative diameter (D)	ΔD	Δ log D	Log D
1	12	20-10.9	15.45	9.1	0.263	1.189
2	6	10.9-5.4	8.15	5.5	0.305	0.911
3	3	5.4-1.6	3.5	3.8	0.53	0.544
4	0.8	1.6-0.7	1.15	0.9	0.359	0.061
After filter	0.4	0.7-0.1	0.4	0.4	0.85	-0.071

Sample preparation and storage

Predesiccated and preweighed Whatman-41 filters were used as collecting surfaces. After a 24 h collection period, filters were withdrawn and kept in desiccators, since airborne particulates and filters used in the impactor have hygroscopic characteristics. The mass of particles collected during each stage was determined gravimetrically. The sum of difference in mass of the filter of each stage before and after collection gave the value of SPM. Each filter was extracted in 100 mL deionized water for two hours and was kept on ultrasonic bath for half an hour and then filtered through Whatman-41 paper into polyethylene bottles. Samples were treated in the similar manner as dry deposition samples and stored under refrigeration until analysis. A total number of 40

(summer = 15, monsoon = 15, winter = 10) samples were collected at Dayalbagh and 35 (summer = 13, monsoon = 12, winter = 10) samples were collected at each site.

Chemical analysis

Samples were analyzed for major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}), NH_4^+ and major anions (F^-, Cl^-, NO_3^-, SO_4^{2-}). Major anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) were analyzed by a Dionex DX-500 Ion chromatograph system equipped with guard column (AS 11A), separator column (AS 11ASC), self-regenerating suppressor (SRS) and conductivity detector (CD-20), using 5.5 mM NaOH as eluant at flow rate of 1 mL/m. The major cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were analyzed by double beam Atomic Absorption Spectrophotometer (Perkin Elmer-2380) with an air acetylene flame. Na^+ and K^+ were measured in the emission mode, while Ca^{2+} and Mg^{2+} were measured in the absorption mode. NH_4^+ was analyzed by UV-Visible Spectrophotometer (Shimadzu Model-1601) using Indo-phenol blue method at 620 nm (Harrison and Perry, 1986).

Uncertainty

Uncertainties can be of two kinds: analytical and experimental. Analytical uncertainties arise from the non-ideal chemical or physical behavior of analytical systems. The instrument Dionex DX-500 Ion Chromatograph was calibrated daily with a fresh working standard solution of 2 ppm, prepared daily from 1000 ppm stock standard solutions of F^-, Cl^-, NO_3^-, and SO_4^{2-} solution. Although the standard peak heights never changed by more than a few percent throughout the day and the variation in peak area was found to be less than 5%, the instrument was recalibrated after every five samples.

The term *precision* is used to describe the reproducibility of results. In order to calculate the precision, a standard of 1 ppm was run nine times, then the precision reported as a deviation from the mean in terms of percentage. The term *accuracy* denotes the nearness of a measurement to its accepted value and is expressed in terms of error. The accuracy was calculated by the difference between observed value X_o and the accepted value X_a.

$$A = X_o - X_a \tag{1}$$

In this expression, the accepted value may itself be subjected to considerable uncertainty, so the more realistic term is relative error, which is error in terms of percentage. The accuracy has been calculated in terms of relative errors (%). Analytical precision, accuracy and detection limits of instruments are given in Table 2.

Table 2. Analytical protocol.

Parameters	Technique	Instrument	Precision (%)	Accuracy (%)	Analytical detection limit (µg/mL)
Na^+	Atomic emission, Air/C_2H_2 589.0 nm	AAS, Perkin Elmer Model 2380	5.0	2.0	0.02
K^+	Atomic emission, Air/C_2H_2 766.5 nm	AAS, Perkin Elmer Model 2380	2.0	1.0	0.02
Ca^{2+}	Atomic absorption, Air/C_2H_2 422.7 nm	AAS, Perkin Elmer Model 2380	13.0	7.0	0.02
Mg^{2+}	Atomic absorption, Air/C_2H_2 285.2 nm	AAS, Perkin Elmer Model 2380	15.0	5.0	0.01
NH_4^+	Colorimetric as Indophenols blue method 620 nm	Shimadzu-1601 UV-Visible Spectrophotometer	10.0	5.0	0.25
F^-	Chromatography, Eluant-5.5 mM NaOH, Flow rate 1 mL/min	Dionex Dx-500 Ion Chromatograph	1.2	3.3	0.04
Cl^-	Chromatography, Eluant-5.5 mM NaOH, Flow rate 1 mL/min	Dionex Dx-500 Ion Chromatograph	0.76	4.3	0.05
NO_3^-	Chromatography, Eluant-5.5 mM NaOH, Flow rate 1 mL/min	Dionex Dx-500 Ion Chromatograph	1.2	4.2	0.08
SO_4^{2-}	Chromatography, Eluant-5.5 mM NaOH, Flow rate 1 mL/min	Dionex Dx-500 Ion Chromatograph	1.21	6.3	0.08

By determining the field blank, experimental uncertainties can be checked. Field blanks for particulate samples were collected by mounting the Whatman filter paper in the sampler and putting the system on just for one minute. The concentration of average analytes was found to be below the detection limits. Details can be found elsewhere (Kumar *et al.,* 2006).

RESULTS AND DISCUSSIONS

Atmospheric concentration of particulate matter

The annual arithmetic mean of suspended particulate matter (SPM) and its water-soluble major ions at Dayalbagh and St. John's sites are presented in Table 3. The table also shows mass median diameter (MMD) of each ion and SPM, and also percentage distribution in fine and coarse mode. The mean value of SPM at Dayalbagh was 154 µg/m^3 and at St. John's 228.9 µg/m^3. These values of SPM are comparable to values reported earlier for the Dayalbagh site by cascade impactor (Kulshrestha *et al.,* 1998), but lower than that of a high-volume sampler located in this region. This difference may be because dust particles of diameters greater than 20 µm are not collected by a cascade impactor (Parmar *et al.,* 2001). The atmospheric load of SPM at St. John's was found to be higher than at Dayalbagh, probably due to the proximity to the large number of industries, high vehicular density, and a large number of diesel engine electrical generators, in addition to the use of biomass as domestic fuel.

Chemical constituents of SPM

Although SPM was higher at St. John's than at Dayalbagh, the sum concentration of water-soluble major ions was higher at Dayalbagh (14.43 µg/m^3) than at St. John's (12.24 µg/m^3). This may be because of unmeasured organic and carbon soot, which come out in significant amounts from vehicles and diesel generators, and which are present in great numbers at St. John's. It was also observed that collection filters turned completely black at the St. John's site.

The percentage contribution of coarse fraction was around 55% at Dayalbagh and about 41% at St. John's. The concentration of NH_4^+ was highest at both sites, followed by $Mg^{2+} > Ca^{2+} > SO_4^{2-} > Cl^- > K^+ > NO_3^- > Na^+ > F^-$ at Dayalbagh, and $Mg^{2+} > Cl^- > Ca^{2+} > SO_4^{2-} > NO_3^- > F^- > Na^+ > K^+$ at St. John's. The difference in order of distribution could be attributed to differences in site characteristics. On comparing the two sites, the concentration of NH_4^+, Mg^{2+}, Ca^{2+}, K^+ was high at Dayalbagh, while Cl$^-$ was highly concentrated at St. John's. The high concentration of NH_4^+ at Dayalbagh may be due to a stockyard 400 m away, and emissions from vegetation and soil. The high concentration of Ca^{2+} and Mg^{2+}, which are terrigeneous tracers at Dayalbagh, might be due to soil contribution. This finds further support from the higher percentage contribution of coarse fractions to the total suspended particulate matter at Dayalbagh than at St. John's. Well-known sources of K^+ are biomass burning, vegetative emissions and soil. High values of K^+ at Dayalbagh may be attributed to vegetative emissions since agriculture is the main activity at this site. Soil may also have contributed to high values of K^+, as well.

Cl$^-$ was highest at St. John's and around 52% was contributed by fine fraction, while only 48% of the total at Dayalbagh exists in the fine fraction. No anthropogenic sources are known to contribute Cl$^-$ to the atmosphere. HCl is formed in the atmosphere by the reaction of HNO_3 and

H_2SO_4 with chloride salts, which combines with NH_3 to form NH_4Cl, but at low RH and high temperature it dissociates back to NH_3 and HCl (Seinfeld and Pandis, 1998).

Table 3. Annual arithmetic mean of atmospheric concentration (neq/m^3) of particulate and their species at Dayalbagh and St. John's site.

	SPM*	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Dayalbagh										
Total mass concentration	154	16.6	43.94	20.0	56.66	19.56	23.33	103.5	146.66	198.33
Concentration in fine mode	69	7.8	21.14	13.22	35.41	8.94	14.1	43.0	67.5	125.54
Concentration in coarse mode	85	8.8	22.8	6.78	21.25	10.62	9.23	60.5	79.16	72.79
% Concentration in fine mode	44.8	46.7	48.1	66.1	62.3	45.7	60.4	41.5	46	63.3
% Concentration in coarse mode	55.2	53.3	51.9	33.9	37.7	54.3	39.6	58.5	54	36.7
MMD (µm)	5.3	5.3	5.0	3.6	3.9	5.2	3.8	5.7	5.2	3.5
St. John's										
Total mass concentration	228.9	20.0	64.22	21.12	57.08	19.13	15.12	60.5	100.0	127.22
Concentration in fine mode	135.6	9.7	33.52	15.0	33.54	8.7	9.23	29.0	42.5	79.39
Concentration in coarse mode	93.3	10.3	30.7	6.12	23.54	10.43	5.89	31.5	57.5	47.83
% Concentration in fine mode	59.25	48.3	52.2	71	58.8	45.5	61	47.9	42.5	62.4
% Concentration in coarse mode	40.75	51.7	47.8	39	41.2	54.5	39	52.1	57.5	37.6
MMD (µm)	4.1	4.9	4.8	3.44	4.4	5.45	3.78	5.0	5.6	3.8

*in $\mu g/m^3$

Table 4 shows ionic balance between total cations and total anions (TC-TA) in fine and coarse fraction of SPM at both sites. Difference between the sum of cations (Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) and the sum of anions (F^-, Cl^-, NO_3^- and SO_4^{2-}) in fine mode was 181.51 and 77.06 neq/m^3 at Dayalbagh and St. John's, respectively; while in coarse mode, 172.76 and 82.49 neq/m^3 at

Dayalbagh and St. John's, respectively. This anion deficit may be due to unanalyzed HCO_3^- and CO_3^{2-} ions, which are major soil constituents in this region. This indicates an alkaline nature of atmospheric particulate matter at both sites. The percentage contribution of cations was around 78.2% at Dayalbagh and 66.5% at St. John's.

Table 4. Ionic balance (neq/m^3) in particulate matter.

Sites	Mode	TC	TA	TC-TA	$(SO_4^{2-}+NO_3^-)/NH_4^+$
Dayalbagh	Total	491.38	137.2	354.18	0.39
	Fine	259.08	77.57	181.51	0.39
	Coarse	232.39	59.63	172.76	0.39
St. John's	Total	321.97	162.42	159.55	0.61
	Fine	168.82	91.76	77.06	0.61
	Coarse	153.15	70.66	82.49	0.62

Table 5 shows a correlation matrix of chemical components of aerosol. It reveals good correlation between Ca^{2+} and Mg^{2+} ($r = 0.70$), indicating that their origins are from similar sources. Significant correlation of F^- with NO_3^- ($r = 0.48$), with SO_4^{2-} ($r = 0.37$) and with K^+ ($r = 0.35$) indicates their contribution from similar sources, as well; however, the extent of their correlation are different. Cl^- shows significant correlation with Na^+ ($r = 0.55$) and K^+ ($r = 50$), which implies that their origins are from similar sources almost similar in strength. NO_3^- had good correlation with SO_4^{2-} ($r = 0.52$), probably due to their similar anthropogenic origins. Ca^{2+} had correlation with NO_3^- ($r = 0.32$) and SO_4^{2-} ($r = 0.39$). This shows their contribution from similar sources.

Table 5. Correlation matrix of major ions of aerosols during study period.

Species	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
F^-	1								
Cl^-	0.12	1							
NO_3^-	0.48**	-0.14	1						
SO_4^{2-}	0.37*	0.16	0.52**	1					
Na^+	0.33	0.55**	-0.28	-0.08	1				
K^+	0.35*	0.50**	-0.35	-0.11	0.69**	1			
Ca^{2+}	0.13	0.34	0.32	0.39	0.26	0.23	1		
Mg^{2+}	0.09	0.06	0.29	0.33	0.05	0.09	0.70**	1	
NH_4^+	0.19	0.26	0.38	0.42	0.06	0.22	0.59**	0.57*	1

* - Signif. p= 0.05   ** - Signif. p= 0.01

Mass size distribution of particulate matter

Particle size distribution of each component was normalized to obtain the fractional amount of species collected on each stage. Log normal mass size distribution of particulate matter and its chemical constituents (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) at Dayalbagh and St. John's site are shown in Fig. 3. The figures show that mass size distribution for particulates was bimodal at both the sites, with one peak in the fine mode and another peak in the coarse mode. Fine mode dominates at St. John's, while coarse mode dominates at Dayalbagh. The particles in the fine size range are produced by gas-to-particle conversion processes and are contributed by anthropogenic sources; whereas, particles in the coarse size range are contributed by natural sources, such as soil, etc. (Momin *et al.,* 1999).

Figures show unimodal distribution for F^-, NO_3^- and Na^+, and bimodal for K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, and SO_4^{2-} at Dayalbagh and St. John's. Generally the components with high MMD (> 2.0 µm) are produced by natural sources whereas those with low MMDs (< 2.0 µm) are produced from man made sources (Khemani *et al.,* 1985). However, certain natural sources (vegetation) could also be contributing towards SO_4^{2-}, NH_4^+, NO_3^- and K^+ along with man-made (biomass burning) sources (Momin *et al.,* 1999).

(a)   (b)
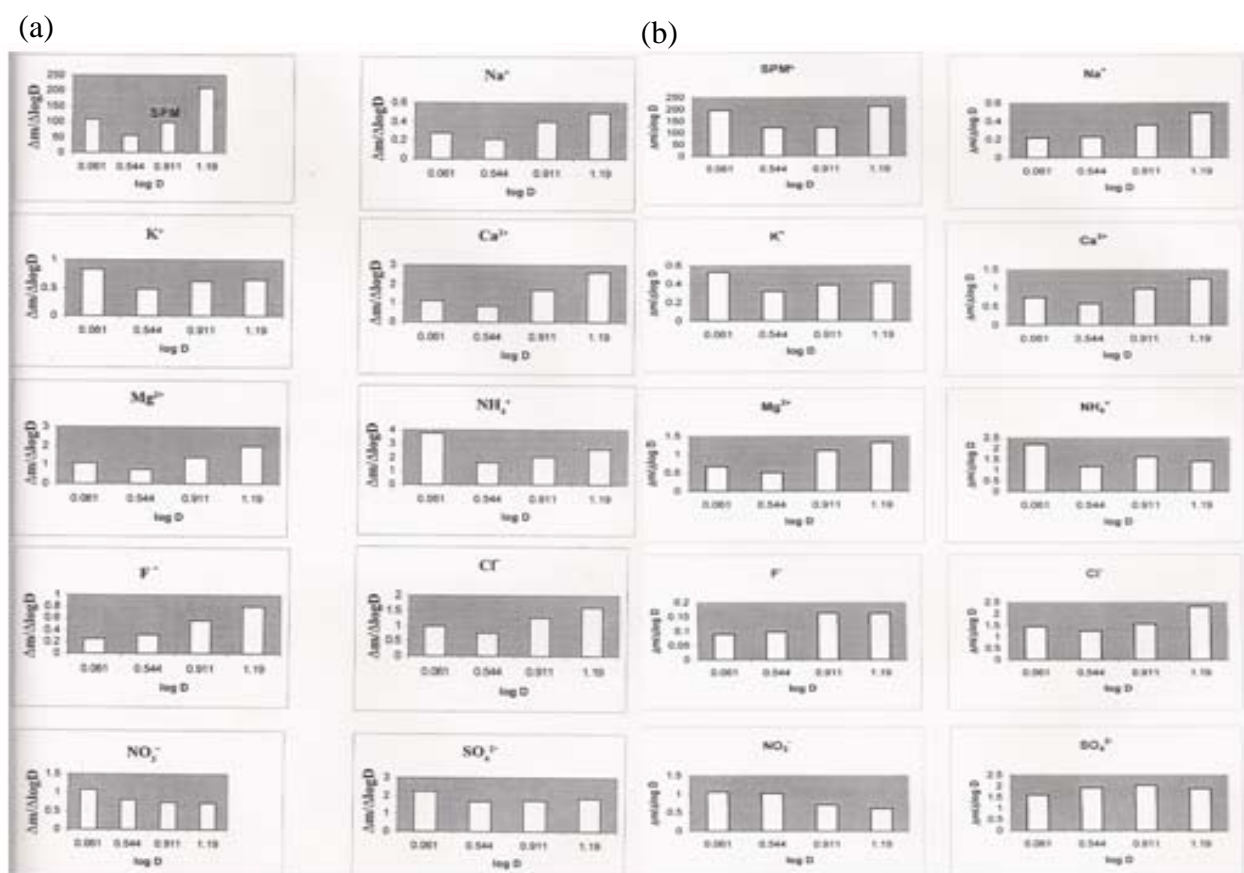

Fig. 3. Log normal mass size distribution of SPM and their water soluble components at (a) Dayalbagh and (b) St. John's.

F^- showed unimodal mass size distribution at both sites with one peak in coarse size range at MMD 5.3 µm and 4.9 µm at Dayalbagh and St. John's, respectively, indicating the main source of F^- to be the soil. Chloride showed bimodal distribution at both sites with a one peak in coarse range (> 10.9 µm) and another in fine range (1.7µm). The fine fraction was 48% at Dayalbagh and 52% at St John's. Fine mode Cl^- could be a result of surface reaction of HCl with preexisting aerosol, possibly Na^+, K^+, Ca^{2+} in fine mode.

The MMD of SO_4^{2-} was 3.9 µm at Dayalbagh and 4.4 µm at St. John's. An examination of mass size distribution showed that SO_4^{2-} had bimodal distribution with one peak in coarse range (5.4-10.9 µm) and another in fine range (0.7-1.6 µm). However, the percentage contribution of fine range particles were higher (62% at Dayalbagh and 59% at St. John's) (Kumar *et al.,* 2003, 2006). Sub-micrometer sulfate had usually been ascribed to homogeneous gas phase reactions of SO_2 and its reaction with pre-existing accumulation-mode particles (Calvert *et al.,* 1985). Under the prevailing meteorological conditions (RH $\geq$ 85%), heterogeneous oxidation of SO_2 with alkaline particles of Ca^{2+} and Mg^{2+} takes place. This is corroborated by the fact that a small fraction of Ca^{2+} and Mg^{2+} appeared in the same size range (0.7-1.6 µm). In Agra, numerous ferrous and non-ferrous foundries operate cupola furnaces, which emit both gaseous and particulate pollutants. In addition, SO_3 vapors are directly emitted from foundries.

NO_3^- had unimodal distribution with a prominent peak in the 0.7–1.6 µm range and had MMD of 3.6 µm at Dayalbagh and 3.4 µm at St. John's. At Dayalbagh, 66% of NO_3^- was present in fine mode, while at St. John's 71% of NO_3^- was present in fine mode. Fine mode nitrate may be formed by the homogeneous gas phase oxidation of NO to NO_2, and subsequently to HNO_3 vapor by gas phase reactions (Pitts and Pitts, 1986) with the OH radical, most of which occurs in the troposphere in the presence of photooxidants and with sufficiently warm temperature, which reacts with atmospheric NH_3 and forms ammonium nitrate.

Na^+ had unimodal distribution at both the sites with maximum peak in the coarse size range. The MMD for Na^+ was 5.4 µm at both the sites. K^+ was present in smaller particles with MMD of 3.8 µm at both sites. It showed bimodal distribution with a prominent peak in fine mode (0.7-1.6 µm). About 61% of the total mass of particulate K^+ was contributed by fine particles at both sites. Dayalbagh site is surrounded by vegetation; hence, vegetation may be one of the major contributors for a high percentage of fine size K^+ in the particulate, as vegetation emits K^+ through its respiration (Clairac *et al.,* 1988). Guttation may be the cause of this emission, which occurs by the transport of K^+ from the roots to the leaves and is released through the stomata (Momin *et al.,* 1999). At St. John's, high contributions of fine fraction may be due to biomass burning. K^+ is usually volatile, and elevated concentrations in the fine mode have been observed in the presence of burning plant material (Cooper, 1980). Ca^{2+} and Mg^{2+} were present predominantly as large particles with MMDs of 5.7 µm and 5.2 µm at Dayalbagh, and 5.0 µm and 5.6 µm at St. John's site, respectively. The figure demonstrates that Ca^{2+} and Mg^{2+} had

bimodal distribution with a large peak in the coarse rage (10.9-20 µm) and small peak in the fine size range (0.7-1.6 µm). NH_4^+ had unimodal distribution at both sites with a large peak in the fine size range. Fine mode particulate contributed about 63% of the total NH_4^+ particulate at both sites. The MMD for NH_4^+ was 3.5 µm at Dayalbagh site and 3.7 µm at St. John's.

Seasonal variation

Tables 6 and 7 present mean seasonal concentrations of SPM and its water-soluble components for Dayalbagh and St. John's (only winter and summer values are given). The table shows that SPM was higher in monsoon, followed by summer and winter. The loading of SPM in monsoon may be due to high wind speed and atmospheric instability. As a result, aerosols from the nearby Thar Desert are lifted up and a high concentration is maintained in the lower troposphere. The low loading of SPM in winter may be due to calm conditions. As a result of this, dispersion of local emissions and lifting up of soil particles was suppressed and loading of SPM was minimum. This is in contrast to earlier reported studies where high loading of SPM has been seen in summer and lower in monsoon. This may be due to very low rain in these last two years. Furthermore, abundances of all water soluble constituents of aerosols show large seasonal variations at both sites. These variations arise due to variation in meteorological parameters, source strength of aerosols and physico-chemical transformation processes occurring in the atmosphere (Rastogi and Sarin, 2005). At Dayalbagh, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+ were highest in monsoon and lowest in winter, except Na^+ which was lowest in summer. Cl^- was highest in summer and lowest in winter, probably due to the shutting down of brick-kiln industries in the monsoon. At St. John's, all the species were higher in summer and lower in winter. This may be due to unstable atmospheric conditions in summer.

CONCLUSION

The presented study was performed at Dayalbagh, a suburban area, and at St. John's, an urban site, located in semiarid India during the period of July 1999 to June 2001. The annual mean concentration of total suspended particulate matter (SPM) was 154 µg/m^3 with approximately 55% in coarse mode at Dayalbagh and 228.9 µg/m^3, with approximately 41% in coarse mode at St. John's. The comparatively higher atmospheric load of SPM at St. John's compared to Dayalbagh is akin to site characteristics. Although SPM was higher at St. John's than at Dayalbagh, the sum concentration of water-soluble major ions was higher at Dayalbagh (14.43 µg/m^3) than at St. John's (12.24 µg/m^3); which may be because of unmeasured organic and carbon soot. The concentration of NH_4^+ was highest at both sites, followed by $Mg^{2+} > Ca^{2+} > SO_4^{2-} > Cl^- > K^+ > NO_3^- > Na^+ > F^-$ at Dayalbagh, and $Mg^{2+} > Cl^- > Ca^{2+} > SO_4^{2-} > NO_3^- > F^- > Na^+ > K^+$ at St. John's. The chemical composition of total suspended particulate matter showed that the cations

dominated the anions at both sites. The contribution of sum of major cations was higher than the sum of major anions.

Table 6. Seasonal arithmetic mean of the atmospheric Concentration of SPM and their water-soluble components ($\mu g/m^3$) at Dayalbagh.

	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Summer									
Total Mass Concentration	21.44	63.38	21.9	52.29	16.95	23.07	96.0	143.3	203.88
Concentration in fine mode	11.44	32.95	15.32	29.37	7.39	13.84	44.5	70.0	125.0
Concentration in coarse mode	10.0	33.23	6.61	22.91	9.56	9.23	51.5	73.33	78.88
% Concentration in fine mode	53.4	52	69.9	56.2	43.6	60	46.4	48.8	61.3
% Concentration in coarse mode	56.6	58	30.1	43.8	56.4	40	53.6	51.2	38.7
MMD (μm)	4.7	5.2	3.58	4.4	5.4	3.77	5.2	4.78	3.6
Winter									
Total Mass Concentration	10.55	32.39	12.9	35.2	20.0	21.5	60.0	108.38	163.33
Concentration in fine mode	5.11	14.64	8.87	22.08	9.56	12.8	26.5	49.16	95.0
Concentration in coarse mode	5.44	17.74	4.03	13.12	10.43	8.7	33.5	59.16	60.33
% Concentration in fine mode	48.4	45.2	68.8	62.7	47.8	59.5	44.2	45.4	58.2
% Concentration in coarse mode	51.6	54.8	31.2	37.3	52.2	40.5	55.8	54.6	41.8
MMD (μm)	5.1	7.15	5.35	5.8	4.9	6.9	6.9	6.85	4.1
Monsoon									
Total Mass Concentration	17.7	33.23	25.0	82.7	23.9	24.87	156.0	195.8	227.77
Concentration in fine mode	6.8	15.49	15.64	55.0	11.3	15.12	58.5	81.6	146.66
Concentration in coarse mode	10.88	17.74	9.35	27.70	12.6	9.74	97.5	114.16	81.11
% Concentration in fine mode	38.8	46.6	62.6	66.5	47.3	60.8	37.5	41.7	64.4
% Concentration in coarse mode	61.2	53.4	37.4	33.5	52.7	39.2	62.5	58.3	35.6
MMD (μm)	6.2	5.3	5.51	5.37	5.1	5.7	6.2	5.67	3.1

This indicates the alkaline nature of aerosol in this region, further indicating that the aerosols are alkaline in nature. Lognormal mass size distribution of major ions (F^-, Cl^-, NO_3^-, SO_4^{2-}, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+) in particulate shows bimodal distribution at both the sites with one peak in the fine mode and another peak in the coarse mode. Unimodal distribution was seen for F^-, NO_3^- and Na^+, and bimodal for K^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl^-, and SO_4^{2-} at both sites. Seasonally, concentrations of SPM were highest in monsoon. The high loading of SPM in monsoon may be due to high wind speed and atmospheric instability.

Table 7. Seasonal arithmetic mean of the atmospheric concentration of SPM and their water soluble components ($\mu g/m^3$) at St. John's.

	F^-	Cl^-	NO_3^-	SO_4^{2-}	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Summer									
Total Mass Concentration	26.6	81.12	31.93	85.83	19.13	20.25	67.0	105.0	135.0
Concentration in fine mode	14.44	50.14	22.74	53.12	8.26	12.82	32.5	45.8	75.0
Concentration in coarse mode	12.22	30.98	9.19	32.7	10.86	7.43	34.5	59.16	60.0
% Concentration in fine mode	54.2	61.8	71.2	61.9	43.2	63.3	48.5	43.7	55.6
% Concentration in coarse mode	55.8	38.2	28.8	58.1	56.8	36.7	51.5	56.3	54.4
MMD (μm)	4.3	4.18	4.1	4.15	7.9	3.7	4.86	5.5	4.2
Winter									
Total Mass Concentration	13.33	47.04	10.0	27.9	18.69	9.80	52.0	91.66	96.1
Concentration in fine mode	4.4	16.61	7.09	4.16	8.69	5.64	24.5	37.5	56.11
Concentration in coarse mode	8.8	30.4	2.9	4.79	10.0	3.58	27.5	54.16	40.0
% Concentration in fine mode	33.3	35.3	71.0	46.5	46.5	57.0	47.1	40.9	58.4
% Concentration in coarse mode	62.7	64.7	29.0	53.5	53.5	43.0	52.9	58.1	41.6
MMD (μm)	6.9	6.2	2.87	5.27	5.73	4.04	5.3	4.99	4.1

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