Diurnal and Seasonal Characteristics of Aerosol Ionic Constituents over an Urban Location in Western India: Secondary Aerosol Formation and Meteorological Influence

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ABSTRACT

Water-soluble ionic constituents (Cl\(^{-}\), NO\(_3\)\(^{-}\), SO\(_4\)\(^{2-}\), Na\(^{+}\), NH\(_4\)\(^{+}\), K\(^{+}\), Mg\(^{2+}\) and Ca\(^{2+}\)) of PM\(_{2.5}\) were measured using Ambient Ion Monitor coupled-to Ion Chromatograph (AIM-IC) with a time resolution of one hour at Ahmedabad (an urban location in semi-arid region of western India) during summer and winter to study the diurnal and seasonal variations. Maximum abundances of most of the species were observed during after-noon hours in summer, whereas minimum concentrations were found during winter at the same local time. During summer, the concentration levels of most of the constituents in a diurnal cycle are largely influenced by ambient relative humidity variation. During winter, the emission strength and boundary layer dynamics impact the diurnal cycle. Secondary inorganic species like NH\(_4\)\(^{+}\), NO\(_3\)\(^{-}\) and SO\(_4\)\(^{2-}\) exhibit significant differences in their relative abundances during winter and summer. Four factors have been derived by Positive Matrix Factorization (PMF) analysis on water-soluble ionic constituents. These are secondary, sea-salt, mineral dust sources and the fourth factor is associated with K\(^{+}\), which is likely to be biomass burning emission.

Keywords: Aerosol chemistry; PM\(_{2.5}\); Secondary aerosol; GEOTRACES.

INTRODUCTION

One of the major uncertainties in quantitative assessment of climate change is the influence of atmospheric aerosol on global climate by direct and indirect effects (IPCC, 2007). Aerosol, mainly fine aerosol (PM\(_{2.5}\), particles < 2.5 \(\mu\)m aerodynamic diameter) are also responsible for reduction in visibility and have adverse health effects (Nel, 2005). Fine particles are formed from a variety of natural and anthropogenic sources and can be primary or secondary in nature. In urban areas, large fraction of fine particulate is water-soluble, where in inorganic ionic constituents comprise a major portion. Inorganic constituents are generally responsible for the hygroscopic nature of aerosol and influences CCN activation, thereby having profound impact on hydrological cycle on a regional scale. Major water-soluble ionic species such as SO\(_4\)\(^{2-}\), NO\(_3\)\(^{-}\) and NH\(_4\)\(^{+}\) are secondary in nature, produced from precursor gases, viz., SO\(_2\), NO\(_x\) and NH\(_3\). Formation of secondary aerosol, both organic and inorganic, has been recognized as a major factor for air pollution over mega-cities (Guo et al., 2010; Zhang et al., 2010).

Several studies addressing the chemical composition of atmospheric particulate matter over Indian sub-continent, a potential hot-spot region in terms of aerosol and pollutant emission, have been reported (Ram et al., 2008; Kulshrestha et al., 2009; Rengarajan et al., 2011; Ram et al., 2012). This region is characterized by high loading of both natural and anthropogenic aerosol during different seasons. In addition, this region is a potential source for variety of constituents transported to surrounding remote oceanic regions under favourable meteorological conditions (Kumar et al., 2008; Cherian et al., 2010; Kumar et al., 2012), which have significant impact on surface ocean biogeochemistry. Northwestern arid and semi-arid regions of India are known for high amount of mineral aerosol, especially during summer (Kumar and Sarin, 2009). During summer monsoon (June–September), most of the continental region is influenced by sea-salt aerosol transported by trade winds. During winter (December–January), anthropogenic emission from various sources is enhanced and surface meteorological condition is conducive for entrainment of pollutants in a shallow boundary layer, which is a regular phenomenon over Indo-Gangetic Plain (Tare et al., 2006). The observed seasonal
and inter-annual variability have been attributed to changes in meteorological conditions, emission source strength and changes in atmospheric processes. Significant day-night variability in aerosol ionic constituents has been reported indicating a prominent role of atmospheric processes on abundances of various aerosol constituents on shorter timescales (Ram and Sarin, 2011). Filter sampling technique employed in various studies integrating long period (12–24 hours or more) limits opportunity to understand variability in aerosol constituents at shorter timescales and relation of particle composition to emissions, transport pattern and meteorological conditions. It may also be noted that these techniques are having positive as well as negative artifacts which are difficult to quantify. Since emission, meteorological changes and atmospheric processes occur in timescales substantially shorter than 24 hours, highly time-resolved intensive measurements of aerosol constituents and related species are essential to study physical and chemical transformation processes as well as transport pattern of continental aerosol (Uematsu et al., 1992). In addition, diurnal trend in aerosol optical depth and single scattering albedo are considered largely due to relative humidity (RH) changes (Ramana et al., 2004). However, aerosol composition, number density and mass concentration also have significant impact. Over the past decade, several online measurement techniques were developed to overcome limitations of integrated sampling and study the chemical processes associated with aerosol particulate matter at shorter timescales (Jayne et al., 2000; Weber et al., 2001; Boring et al., 2002). Changes in aerosol chemistry which is not observed using conventional filter based techniques have been demonstrated by such studies (Weber et al., 2003).

So far, there are no studies reported from the Indian sub-continent and adjacent oceanic regions utilizing real-time measurement of aerosol chemical constituents. Time-resolved chemical composition has potential to provide insight into diversity of aerosol sources from natural and anthropogenic emissions as well as various chemical, physical and thermodynamic processes within diurnal cycle especially in the source region. In this paper, we present for the first time, results from a semi-continuous (near real-time) measurement of PM$_{2.5}$ ionic constituents at an urban location in semi-arid region of the western India, in order to elucidate factors influencing diurnal variation in aerosol major ionic constituents during summer and winter seasons.

**METHODOLOGY**

**Sampling Site and General Meteorology**

Measurements of PM$_{2.5}$ ionic composition was performed at Ahmedabad (22.0°N, 72.5°E), one of the largest cities in western India. The observations were carried out in the campus of Physical Research Laboratory located in western zone of Ahmedabad. Population of Ahmedabad is ~6 million with several small and large scale industrial establishments situated within ~200 km from sampling site, mostly located in south, south-west, east and north-east region of the city. Two thermal power plants are situated in north and north-east side within ~40 km distance of sampling location. Potential local aerosol sources mainly consist of road traffic with distinct diurnal variation, coal-based power plants and industrial emissions. During winter, surface wind direction over Ahmedabad is easterly or north-easterly and the sampled air masses are generally of continental origin. Whereas during summer, surface wind direction is westerly or south-westerly and the air masses are predominantly of marine origin. Local meteorological parameters (RH, temperature and wind direction) during the observation period are depicted in Fig. 1.

**Near-real Time Measurement of PM$_{2.5}$ Ionic Composition**

Ionic composition of PM$_{2.5}$ was measured with hourly time resolution using an ambient ion monitor (AIM, model URG 9000D, URG corporation, USA). AIM system was operated during summer from June 5 to July 4, 2012 and during winter from December 22, 2011 to January 16, 2012. This instrument mainly consists of two components: 1) Sample collection unit and 2) sample analysis unit and the entire set up is similar to that described by Markovic et al. (2012). PM$_{2.5}$ separation is achieved by a sharp cut off cyclone inlet (URG Inc. USA) operating at a flow rate of 3 L/min. Ambient air is taken using 1 m long inlet connected to a diffusion-based parallel plate wet denuder. Cellusep® membrane is used for the separation of gaseous components like SO$_2$, NO$_x$, NH$_3$, HNO$_3$, HCl in the parallel plate denuder. 5 mM hydrogen peroxide in de-ionized water is used as denuder solution. A steam jet aerosol collector, a modified design of Khlystov et al. (1995), is placed downstream of denuder for collection and extraction of aerosol particles. The water extract from the steam jet aerosol collector is subsequently filtered through an inline PTFE filter (Pall Life Sciences) and simultaneously analyzed for major cations and anions by two ion chromatographs (Model ICS-1100, DIONEX, USA). The denuder solution is also analyzed for cations and anions. All analysis is completed in one hour, thus, providing the aerosol ionic composition data with an hourly time resolution. For analysis of anions, Dionex AS-14A and AG-14A columns were used and for cations CS-12A and CG12A were used along with the appropriate electrolytic suppressors. The conductivity detectors used for detection and quantification of various analytes were calibrated with laboratory-made standard solutions and commercially available Merck® Ion chromatography standards. Standards solutions were periodically injected to check the consistency of sensitivity of the detectors. Air flow rate is frequently checked using a calibrated flow meter.

**Data Quality**

To verify the efficiency with which interfering gaseous species such as NH$_3$, SO$_2$, HCl, HNO$_3$ and NO$_x$ are removed by diffusion denuder, a quartz fiber filter (Tissuquartz, Pall Life Sciences, 0.3 µm, 99.9% retention; fixed in a 47 mm diameter filter cartridge) was connected at the inlet and the cation and anion concentrations were monitored in denuder solution and steam jet solution. Concentrations of Cl$^-$, SO$_4^{2-}$ and NO$_3^-$ measured in particle channel are below detection limits. Concentration of NH$_3$ is less than 5% of that observed.
in denuder solution confirming that more than 95% gaseous NH$_3$ is removed by denuder. Typical concentration levels of NH$_4^+$ in steam jet solution during sampling is about two order of magnitude higher than blank levels obtained with filter at the inlet. This confirms that gaseous components like NH$_3$, SO$_2$ and NO$_x$ are effectively removed by parallel plate wet denuder and their interference in the measured concentration of aerosol constituents is negligible. Ionic constituents measured in denuder solution provide concentration of gaseous species like NH$_3$ and SO$_2$, but independent validation with parallel measurement of these constituents was not performed. Hence, discussion on gaseous constituents is not presented in this paper.

Fifteen PM$_{2.5}$ samples were collected simultaneously with AIM data collection using high-volume (Thermo Scientific) sampler during the observation period in summer on Tissuquartz filters (Pall Life Sciences) integrating typically about 24 hours of sampling. The filters were sub-sampled and extracted with de-ionized water after 45 minutes ultrasonication. The water extract is analyzed on ion-chromatograph for anions and cations using suppressed conductivity detection method. Details of the procedure are discussed in earlier publications (Rengarajan et al., 2007; Kumar et al., 2012). Hourly data of AIM was averaged over sampling duration of high-volume samplers for comparison with filter-based measurements. Fig. S1 (Supplementary Materials) represents the comparison between filter-based measurements and average of online measurements for all measured ionic constituents. The measurement uncertainty was 10% as depicted by error bars for each data points. Na$^+$, K$^+$, Ca$^{2+}$ and SO$_4^{2-}$ exhibit on an average good agreement between both the measurements. The concentrations of NO$_3^-$ and Cl$^-$ exhibit large scatter and show overall lower values for filter-based measurements. This may be due to negative artifact of filter sampling arising from low stability of constituents like NH$_4$NO$_3$ at ambient temperatures during our observation (Schaap et al., 2004) and Cl$^-$ loss on particulate phase in presence of stronger acidic species such as SO$_4^{2-}$. NH$_4^+$ also exhibits deviation from the 1:1 line. Even though the high-volume samplers are not equipped with denuders for removing interfering trace gas constituents, the inter-comparison of SO$_4^{2-}$ measurements by both methods shows reasonably good agreement. The positive artifacts from gaseous components on measurements are negligible and negative artifact by volatilization is unlikely to occur during AIM.

Fig. 1. Temporal variation in meteorological parameters during a) winter and b) summer sampling period.
sampling. Hence, the data derived from AIM operation can be considered with minimum sampling bias and measurement artifacts with respect to these measured species.

Charge balance of anions and cations provides an estimate of completeness and accuracy of measured ionic constituents. Fig. S2 depicts the scatter plot between total anion and cations measured by AIM-IC system. The aerosol anions and cations show very good correlation ($r = 0.962$, $n = 692$ and $r = 0.988$, $n = 569$ for summer and winter data, respectively) with a slope of $\sim 1$ and negligible intercept suggesting that on an average fine particulate matter is neutral during our observation period. However, during summer the scatter is larger compared to that in winter. Cation excess may be due to the contribution of organic acid ions, bicarbonate and, on some occasion, NO$_2^-$ ions that were not quantified in this study. Anion excess is due to presence of significant amount of aerosol acidity since H$^+$ ions are not accounted in the charge balance.

RESULTS AND DISCUSSION

Temporal Variation of Ionic Constituents during Summer

Most of the constituents, especially those associated with mineral dust, like Ca$^{2+}$ and Mg$^{2+}$, exhibit large variability during initial few days of observation (Fig. 2). On June 13 and 16, light rain events were recorded at Ahmedabad. Ca$^{2+}$ and Mg$^{2+}$ concentrations show minimum levels on these days indicating their effective removal from ambient air and decreased emission of mineral aerosol. From June 17 onwards, these constituents show distinct diurnal pattern with minimum variability until July 2. On July 3 and 4, anthropogenic constituents like SO$_4^{2-}$, NO$_3^-$, K$^+$, NH$_4^+$ show sudden increase with a large diurnal amplitude. Light drizzles were recorded on these days also. Such temporal variations, in general, can arise from changes in source strengths of aerosol during the observational period, changes in meteorological conditions, or transport of pollutants from different source regions. There are three occasions when the wind direction drastically changed in a diurnal cycle; on June 12 and 16 as well as on July 3 (Fig. 1(a)). Rest of the period, sampling location witnessed mostly consistent local wind pattern and the observed variation in abundances of chemical constituents were not controlled by wind pattern and transport from local point sources. On June 12 night, south-westerly winds changed to almost northerly but there is no significant change in the concentration levels of various

![Fig. 2. Temporal variations in ionic constituents in PM$_{2.5}$ during summer season.](image-url)
constituents. However, long range transport may influence the observed concentrations, since the impact of sea-salt aerosol is conspicuous from June 16 onwards up to July 2. During these days, prevailing wind direction changed from south-westerly to westerly. This period is characterized by strong correlation between Na\(^+\) and Mg\(^{2+}\) indicating their common sources most likely to be sea-salt aerosol, whereas during initial days up to June 16, Ca\(^{2+}\) and Mg\(^{2+}\) were correlated indicating mineral dust as a major source. On July 3 and 4, the anthropogenic constituents like SO\(_4^{2-}\), NO\(_3^-\) and NH\(_4^+\) increased by more than factor of 5, whereas Na\(^+\), Mg\(^{2+}\), Ca\(^{2+}\) decreased significantly. This indicates that anthropogenic sources situated in eastern region of sampling location have influenced the aerosol composition during the reversal of wind direction on these days. Cl\(^-\) concentrations show a reverse trend compared to constituents like Mg\(^{2+}\), Na\(^+\) and Ca\(^{2+}\) and are closely associated with the anthropogenic components.

General wind direction changed from southerly to westerly from June 17 onwards, which is reflected in the Na\(^+\) and Mg\(^{2+}\) concentrations. These constituents typically originate from sea-salt emission and the sampling location is influenced by long-range transport of marine aerosols. Na\(^+\) and Mg\(^{2+}\) exhibit a good correlation (Fig. 3(a)) indicating their common sources, whereas Ca\(^{2+}\) and Na\(^+\) do not show such significant correlation (Fig. 3(b)). Ca\(^{2+}\) is considered typically originating from mineral dust and the contribution of Na\(^+\) from dust sources can be neglected. Since Mg\(^{2+}\) and Ca\(^{2+}\) also show a similar trend (Fig. 3(c)), some amount of Mg\(^{2+}\) is expected to be derived from dust as well. Thus, Na\(^+\) is the most suitable species to be used as sea-salt tracer. Even though the average Cl\(^-\)/Na\(^+\) ratio is ~1.7, close to seawater ratio (1.8), it shows a large variability (Keene et al., 1986). Especially during July 2 to July 4, it increased drastically to more than 10 and there was a corresponding change in wind direction during these days. During these days, the location was influenced largely by anthropogenically derived aerosol as evident from higher abundances of NO\(_3^-\), SO\(_4^{2-}\) and K\(^+\). Hence, it can be inferred that anthropogenic sources (like industrial emissions and/or waste incineration) are significantly affecting the observed Cl\(^-\) abundances when the winds are not near westerly or south-westerly. Mönkkönen et al. (2004) reported higher aerosol number concentration over Delhi, a polluted urban location in north India, during week days compared to weekends. Data collected at Ahmedabad during summer suggests that there is no significant difference between week days and weekends in concentrations levels or diurnal pattern of ionic constituents of PM\(_{2.5}\). This demonstrates that variation in traffic emission do not influence considerably on temporal changes in the observed concentration levels or diurnal pattern at the sampling site.

**Diurnal Variations in Summer**

In general, local wind direction did not influence the concentration levels or relative abundances of ionic constituents at Ahmedabad on a diurnal scale. This suggests that the local point emissions are not significant in influencing the observed aerosol composition and it can be considered as a representative site for urban background condition. NH\(_4^+\), SO\(_4^{2-}\) and NO\(_3^-\) concentrations are substantially higher during afternoon hours, showing an increase from 10:00 hours onwards and reached maximum at ~14:00–16:00 hours then decreased to background level by ~20:00 hours (Fig. 4). Similar patterns were observed with other constituents also, may be due to the combined result of many factors like aerosol sources, source strength, removal mechanisms and surface meteorology. Concentrations of SO\(_4^{2-}\) and NO\(_3^-\) are expected to be higher during periods conducive for more photochemical production and hence it is expected to be high during day time (Seinfeld and Pandis, 1998). However, day and night temperature differences can cause boundary layer changes and low concentration may be observed during the day due to dilution effect, which is in contrast to the observed pattern at Ahmedabad. The observed trend is possible, when contribution from
secondary formation to the variability in concentrations of \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) dominates over dilution effect due to dispersion. The constituents like \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) and \( \text{Na}^+ \) have distinctly different sources compared to that of secondary species. \( \text{Ca}^{2+} \) can be closely associated with mineral dust, whereas \( \text{Na}^+ \) and major fraction of \( \text{Mg}^{2+} \) are generally sea-salt derived, but their diurnal trend is similar to that of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \). From this observation, it may be inferred that the emission strength is not the only controlling factor for the observed trend.

Diurnal variations of \( \text{PM}_{2.5} \) and BC mass concentrations over Ahmedabad and southeastern Tibetan Plateau have been reported by earlier studies (Ramachandran and Rajesh, 2007; Engling et al., 2011). Minimum concentrations at about 14:00 hours and two peaks at ~8:00 hours and 22:00 hours has been observed and is attributed to the combination of emission as well as boundary layer dynamics. These reasons are very unlikely to cause different diurnal trends of \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \) and \( \text{Na}^+ \) during summer in our study. The observed pattern of ionic constituents at Ahmedabad is similar to that of BC reported from Manora Peak, a high altitude site in Himalayan region, northern India (Pant et al., 2006). The atmospheric processes causing this variability should be different, as similar boundary layer dynamics is not operative at both the sites. Inconsistent diurnal variation in \( \text{PM}_{2.5} \) mass and chemical constituents were reported by Lee et al. (2007) from Gosan supersite in Jeju Island. \( \text{PM}_{2.5} \) mass reaches maximum during afternoon while major constituents shows different diurnal pattern which is attributed to changes in transport of different air masses towards the sampling site. Such conspicuous changes in the wind pattern or air mass trajectory are not observed during our study and not a plausible reason for the observed diurnal trend.

Fig. 4. Diurnal variation in ionic constituents of \( \text{PM}_{2.5} \) during summer.
Hygroscopic nature of water-soluble ionic constituents can cause hygroscopic growth and preferential increase in deposition rate of these species under higher RH conditions compared to non-hygroscopic particles. Fig. 1(a) shows the typical diurnal variation in RH, which is opposite to the trend observed for ionic constituents. The average RH for the entire observation period is ~59%, ranging from 27 to 100%. Minimum RH observed in average diurnal cycle is at 16:00–17:00 hours, overlapping with maximum concentrations for inorganic constituents. Hence, the removal process by deposition can be lower at afternoon hours during summer and is likely to be a major controlling factor for the diurnal variations in concentrations of ionic constituents at this location. Constituents like NH$_4$$^+$, NO$_3$ and SO$_4^{2-}$ show ~100% or more increase during noon compared to constituents like Ca$^{2+}$, Mg$^{2+}$ and Na$^+$ showing an increase of 30–50%. This suggests that enhanced production also contribute significantly to the increase in NH$_4$$^+$, NO$_3$ and SO$_4^{2-}$ concentrations during afternoon hours. Major source of K$^+$ is biomass burning emissions and hence, major fraction of it may be associated with carbonaceous particles at this site. Freshly produced carbonaceous aerosol can be hydrophobic in nature which gets converted to hydrophilic with aging. Hence, removal process of K$^+$ bearing particles could be different compared to other ionic constituents. In 24-hour cycle, their removal efficiency may not be a dominant factor, leading to a different diurnal trend for K$^+$ with respect to other species.

Cl$^-$ concentration shows an inverse trend in diurnal cycle compared to NO$_3$ and SO$_4^{2-}$, because Cl$^-$ is preferentially degassed as HCl from sea-salt particles in presence of strong acidic species (Hsu et al., 2007; Sarin et al., 2010). During summer period, the sea-salt contribution to the ionic constituents is significant as the prevailing wind direction is westerly or southwesterly bringing marine air masses to the sampling site. These sea-salt particles can undergo aging processes under polluted environment resulting significant depletion of Cl$^-$. Cl$^-$ deficit (Cl$^-$ deficit) is calculated assuming Na$^+$ is exclusively of marine origin as follows:

$$\text{Cl}^- \text{deficit} = 1.8 \times [\text{Na}^+] - [\text{Cl}^-] \quad (1)$$

where [Na$^+$] and [Cl$^-$] are measured concentrations of Na$^+$ and Cl$^-$. Cl$^-$ deficit exhibits an excellent correlation with NO$_3$ ($r = 0.93$) indicating major role of nitric acid vapors in degassing HCl from sea-salt particles. The observed Cl$^-$ deficit ranges from 10% to 45% with an average value of 25% and the highest percentage depletion is observed during afternoon hours when the acidic species reached maximum value. The observed Cl$^-$ deficit ranges from 0.02 to 1.3 µg/m$^3$. Assuming steady state condition for total chlorine from sea-salt aerosol, degassed HCl concentrations equivalent to Cl$^-$ deficit is calculated, which will be lower limit from sea-salt origin. Estimated HCl mixing ratio ranges from ~0.02 ppbv to ~0.9 ppbv in the ambient air. This range is similar to the reported concentration levels of HCl in a typical urban atmosphere. Hence, HCl release from sea-salt particles is likely to be a major source to ambient HCl vapours in this region during summer. It has major implication on trace gas chemistry and secondary organic aerosol formation in a polluted atmosphere involving NO$_x$, O$_3$, VOCs and CO, because HCl can act as a potential source for Cl free radical through hydrogen abstraction reaction with OH radical (Lawler et al., 2009).

**Temporal Variation of Ionic Constituents during Winter**

Fig. 5 shows the temporal variations of PM$_{2.5}$ ionic constituents during winter. The measured concentration levels are conspicuously higher during this period compared to those during summer, presumably due to shallow boundary layer and enhanced emissions particularly from biomass burning sources. For example, average concentration of SO$_4^{2-}$ is 5.7 ± 2.5 and 4.7 ± 5.8 µg/m$^3$ during winter and summer, respectively. Corresponding average concentration of NO$_3$ is 5.0 ± 2.7 and 2.1 ± 5.8 µg/m$^3$, respectively. All the constituents show a large variability during the observation period with distinct diurnal pattern. Variation in ionic constituents in fine aerosol does not show dependence on local wind direction similar to the case observed during summer. Hence, during winter also, local emission from point sources does not seem to influence the measured concentrations of aerosol constituents. In general, winds were northerly and north-easterly, largely carrying polluted continental air-masses to the sampling site, whereas it is reversed during summer period. Hence, the concentration of marine aerosol is very low during this time period, which is evident from the concentration levels of Na$^+$. During summer, the concentration of Na$^+$ varied from near detection limit to ~3.5 µg/m$^3$, whereas during winter it was found to be < ~1 µg/m$^3$. Temporal trends of Mg$^{2+}$ and Na$^+$ are not similar unlike during summer, whereas similar temporal trend of Mg$^{2+}$ and Ca$^{2+}$ indicates that they can be largely from mineral aerosol. There is no systematic change in wind direction for extended duration during the sampling period and hence influence of long-range transport of air masses and associated variation in aerosol constituents is not observed during winter. During week days and weekends, observed concentrations of ionic constituents remain similar and the influence of change in traffic emission sources may not have significantly affected the temporal variation of these constituents. Throughout the study period, daily diurnal patterns of various constituents do not vary, suggesting that these observations are characteristic of a large spatial scale and not considerably impacted by local plume emissions. Hence, this data set can be considered as a typical representative of ionic concentration of fine particulates during winter in this region.

**Diurnal Variation in Winter**

Diurnal variation of ionic constituents during winter is presented in Fig. 6. The abundances of various constituents exhibit typically two maxima, one in the morning and another at night time. There is no general variation in wind direction, consistent with changes in the aerosol ionic concentrations. Similar trend has been reported for BC mass concentration from various locations during winter including Ahmedabad (Ganguly et al., 2006; Ramachandran...
and Rajesh, 2007). The reason for such a pattern is largely due to stable and shallow boundary layer during the night and dilution effect during the day. This indicates that the variability is largely controlled by the atmospheric boundary layer dynamics, causing nighttime peak due to lower boundary layer height and morning increase due to fumigation effect. Fig. 1 depicts the variation in the observed RH during the study period. In comparison to that observed during summer, the RH is relatively low, ranging from ~11% to ~95% with an average value of 50%. This causes lower hygroscopic growth and consequently deposition of hygroscopic particles from the ambient air is not likely to be a major factor in controlling the ambient concentration. Formation processes for secondary aerosol constituents like \( \text{NH}_4^+ \), \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \) are expected to be high during daytime, when photochemical activity is at its maximum, but the effect due to boundary layer dynamics dominates in deciding overall concentration of these species, which is evident from the noon time low concentrations of these species.

**Secondary Inorganic Aerosol: Seasonal Characteristics**

\( \text{NH}_4^+ \), \( \text{NO}_3^- \) and \( \text{SO}_4^{2-} \) constitute the major fraction of secondary inorganic aerosol produced by oxidation of \( \text{NO}_x \) and \( \text{SO}_2 \) and subsequent neutralization with ambient gaseous ammonia or scavenging by existing particles (Seinfeld and Pandis, 1998). In general, concentration levels of these species are relatively lower during summer than winter. The average concentration of \( \text{NH}_4^+ \) during summer is 1.2 \( \mu g/m^3 \) and average \( \text{NH}_4^+/\text{SO}_4^{2-} \) equivalent ratio is 0.63, indicative of ammonium-poor condition causing \( \text{NH}_4^+ \) and \( \text{SO}_4^{2-} \) could exist in the form of \( \text{NH}_4\text{HSO}_4 \). Fig. 7(a) depicts scatter plot between \( \text{NH}_4^+ \) and \( \text{SO}_4^{2-} \), exhibiting a good correlation for all data points with \( \text{NH}_4^+ \) concentration less than 200 neq/m^3. During July 3 and 4 (when RH was high and intermittent rain was recorded), the data exhibit a different trend with excess \( \text{NH}_4^+ \) with almost quantitative neutralization of \( \text{SO}_4^{2-} \).

During winter, the average \( \text{NH}_4^+ \) concentration is 4.6 \( \mu g/m^3 \) and \( \text{NH}_4^+/\text{SO}_4^{2-} \) ratio is 2.2, suggesting an ammonium-rich environment. Significant quantity of \( \text{NH}_3\text{NO}_3 \) is likely to be present in particulate form during this period. Plot between \( \text{NH}_4^+ \) and \( \text{SO}_4^{2-} \) is given in Fig. 7(b) indicating more scatter compared to summer period, probably due to significant fraction of total \( \text{NH}_4^+ \) is associated with \( \text{NO}_3^- \) during this period.
Fig. 6. Diurnal variation in ionic constituents of PM$_{2.5}$ during winter.

**Positive Matrix Factorization (PMF) Analysis**

PMF is a receptor model widely used in the source apportionment studies of atmospheric aerosol in the absence of source profile information (Lee et al., 2003; Jeong et al., 2008; Karanasiou et al., 2009; Sudheer and Rengarajan, 2012). EPA PMF 3.0.2.2 was used in this study in order to assess temporal variability of various source contributions to water-soluble inorganic constituents during the observation period. Details of the model have been described elsewhere (Kim et al., 2003; Norris et al., 2008; Sudheer and Rengarajan, 2012). Number of factors from 3 to 7 was examined using linearity of fit by the residual distributions along with interpretability of the resulting profiles (Kim et al., 2003). PMF analysis yielded four factors each for both summer and winter samples (Table 1). For the summer data, Factor 1 has dominant loading from NO$_3^-$, SO$_4^{2-}$ and NH$_4^+$ signifying the secondary sources. Factor 2 has 78% loading from Na$^+$ and 70% from Mg$^{2+}$, suggesting this factor corresponds to sea-salt emission. The third factor is characterized by 58% loading from Ca$^{2+}$, which can be considered as mineral dust sources. The fourth factor corresponding to 54% loading from K$^+$ and 40% loading from Cl$^-$. There is no significant loading from other species and K$^+$ is usually emitted from biomass burning, hence, this factor may correspond to biomass burning emission. Fig. 8(a) depicts the temporal variation of various factor contributions to PM$_{2.5}$ water-soluble constituents during our observation. On an average, secondary sources contribute 23% of total water-soluble inorganic constituents during the observation period in summer. Sea-salt and mineral dust fractions constitute 29 and 25% respectively. Temporal variation in sea-salt contribution is found in good agreement with Na$^+$ concentration.

The major three factors identified (factors 1, 2 and 3, Table 1) for winter are secondary sources, sea-salt, and
mineral dust for the measured ionic constituents. The secondary source factor is having loading from K⁺, hence it is not fully resolved from biomass burning sources as obtained for summer. The fourth source is associated with K⁺ (10% loading) and Cl⁻ (43%). Factor 4 for summer season is characterized by K⁺ and Cl⁻ loading. Cl⁻ also is associated with biological systems along with K⁺ and it is reasonable to consider this factor representing biomass burning emission. Temporal variation of various factors contribution to measured ionic constituents is depicted in Fig. 8(b). Percentage contribution of secondary sources during winter is substantially higher compared to summer. Meteorological conditions and ammonium-rich environment are conducive for secondary production of inorganic ionic constituents and could result in high abundance of these species in fine aerosol.

CONCLUSION

Temporal as well as diurnal variations of PM$_{2.5}$ water-soluble ionic constituents during summer and winter have been studied from Ahmedabad, an urban location situated in semi-arid region of western India, based on semi-continuous measurement for the first time. The results show distinctly different diurnal patterns of various constituents during summer and winter. During summer, the concentration levels of most of the constituents in a diurnal cycle are largely influenced by ambient relative humidity variation possibly due to hygroscopic growth and deposition processes. The secondary species like SO$_4^{2-}$, NO$_3^-$ and NH$_4^+$ are also influenced by photochemical production during day-time. Comparison with variability in other aerosol parameters and trace gases from earlier studies indicate that the diurnal variability observed during winter is mainly modulated by boundary layer dynamics. Secondary inorganic species, viz. NH$_4^+$, NO$_3^-$ and SO$_4^{2-}$ exhibit significant differences in their relative abundances during winter and summer. PMF analysis of the water-soluble ion data yielded four factors, identified as secondary, sea-salt, mineral dust sources and a source associated with K⁺, which is likely to be biomass burning emission. Since diurnal variation of aerosol constituents, number density and mass concentration may have significant impact on diurnal trend in aerosol optical depth and single scattering albedo, incorporation of such real-time measurements and delineation of controlling factors of the variability in radiative transfer calculations might result in more realistic aerosol forcing estimates.

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Fig. 8. Temporal variation of various factor contributions to PM$_{2.5}$ water-soluble ionic constituents during (a) summer and (b) winter sampling period.

SUPPLEMENTARY MATERIALS

Supplementary data associated with this article can be found in the online version at http://www.aaqr.org.

REFERENCES


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Fig. S1. Scatter plot of measured ionic constituents between the averaged concentration from AIM measurement and filter based measurement. Error bars indicate 10% uncertainty for AIM and filter measurements.
Fig. S2. Scatter plot between measured total anions and total cations showing the charge balance during winter and summer observation period.