Aerosol acidity and secondary organic aerosol formation during wintertime over urban environment in western India

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1. Introduction

Carbonaceous aerosols, consisting of elemental carbon (EC) and organic carbon (OC), constitute a major fraction of the fine-mode aerosol mass (PM$_{2.5}$) in an urban atmosphere and significantly influence the regional air quality and climate (Gelencsér, 2004). A substantial fraction of organic aerosols, emitted from both natural and anthropogenic sources, is secondary in nature produced by oxidation products of volatile organic compounds (VOC) (Seinfeld and Pankow, 2006; Carlton et al., 2009). Estimates of secondary organic aerosol (SOA) formation based on biogenic and anthropogenic VOC fluxes, suggest their dominance over the primary component (Kanakidou et al., 2005). Although several of the precursors originate from industrial and automobile emission sources, the dominant fraction of the global SOA budget is thought to originate from biogenic VOCs (Hallquist et al., 2009 and references therein). Recent studies suggest that SOA contribution from anthropogenic precursors, especially from urban environment, to the global SOA budget could be significantly higher than the earlier estimates (de Gouw et al., 2005; Volkamer et al., 2006). However, large discrepancies, as much as an order of magnitude, are associated with the estimated fluxes. These inconsistencies arise largely due to the poor understanding of the formation mechanism of SOA from the precursors (Hallquist et al., 2009).

Several laboratory experiments have demonstrated a close-link between formation of SOA from oxidation of VOC and particle phase acidity (Jang et al., 2002; Gao et al., 2004; Surratt et al., 2007; Linuma et al., 2009; Surratt et al., 2010; Offenberg et al., 2009). An increase up to several fold of SOA mass from terpenes (group of biogenic VOCs) has been observed when acidic seed particles were used in these chamber studies. Particle-phase reactions catalyzed by H$^+$ ions leading to the formation of high molecular weight compounds have been proposed to explain the observed enhancement (Dommen et al., 2006; Carlton et al., 2009). Mass spectrometry and FTIR spectrometric analysis of organic aerosols indicate that polymeric products are present in laboratory-generated aerosols (Hallquist et al., 2009 and references therein), which was present in ambient aerosol to a larger extent than what had been initially speculated (Jang and Kamens, 2001). Gao et al. (2004) have reported that an increase in aerosol acidity causes rapid polymerization of organic precursors resulting in higher SOA formation. Surratt et al. (2007) have shown that SOA yield increased with increasing acidity due to an acid hydrolysis mechanism for organosulphate formation of biogenic VOC oxidation products (epoxides). However, real-time measurements based on field studies are limited for the characterization and quantitative assessment of the influence of aerosol acidity on SOA formation from the precursors (Lewandowski et al., 2007; Hawkins et al., 2010). Also, some of the observations present results inconsistent with the laboratory studies, suggesting that there is no direct evidence for the relation between aerosol acidity and SOA formation during field measurements (Zhang et al., 2004; Gao et al., 2006; Peltier et al., 2007). Based on off-line field measurements, we present results on the chemical composition of aerosol documenting the co-variation between secondary organic
carbon (SOC) and particle phase acidity (expressed as hydrogen ion concentration, [H\(^+\)]\(_{\text{air}}\)) in urban environment during the wintertime.

2. Experiment

PM\(_{2.5}\) samples (particles with aerodynamic diameter <2.5 μm) were collected on Tissuquartz™ filters (Pall Life Sciences) using a high-volume air sampler (Tisch Inc., USA) during the wintertime (from 8th December, 2006 to 7th January, 2007) at an urban location (Ahmedabad, 23°2’N, 72°32’E), in a semi-arid region of western India. Samplers were operated daily for 8–10 h during day time. Aerosol samples were also collected in summer (May–June are the hottest months of the year for tropical India, followed by onset of southwest monsoon) once a week (March 21 – June 13, 2007). Relative humidity (RH) and ambient temperature varied between 30–60% and 16–28 °C respectively, during sampling period in winter. The corresponding parameters in summer varied as 35–65% and 30–42 °C, respectively. Concentrations of EC and OC were measured on EC-OC analyzer (Sunset Laboratory) using NIOSH protocol (Birch and Cary, 1996; Rengarajan et al., 2007). An aliquot of sample filter was also treated with Milli-Q water for extraction of water-soluble organic carbon (WSOC) measured on TOC analyzer (Shimadzu, TOC5000A), and for inorganic constituents (K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4\)^+) measured on Ion-chromatography system (DIONEX®) (Rengarajan et al., 2007). HCO\(_3\) in the water extract was measured on auto-titrator system using fixed pH (4.3) end point method (Rastogi and Sarin, 2005). All measured parameters were corrected for procedural filter blanks. The aerosol acidity, [H\(^+\)]\(_{\text{air}}\), was determined following the procedures of Surratt et al. (2007) and Offenberg et al. (2009). Briefly, pH of the water extract was measured immediately after the extraction using a glass electrode (Metrohm, 6.0256.100) with a precision of ±0.05 unit. The aqueous H\(^+\) ion concentration ([H\(^+\)\(_{\text{aq-extract}}\)]) is multiplied by the total volume of water used for the extraction after making appropriate blank corrections. The average concentration of hydrogen ion in the aerosol samples is calculated as

\[
[H^+]_{\text{air}} = \frac{(H^+_{\text{aq-extract}} \times \text{Vol}_{\text{H}_2\text{O}})}{\text{Vol}_{\text{air filtered}}}
\]

In this study we have used quartz filters unlike the use of teflon filters reported in earlier studies (Surratt et al., 2007; Offenberg et al., 2009). The H\(^+\)\(_{\text{aq-extract}}\) for blank filters are no more than 10\(^{-9}\) M and the necessary corrections were applied for samples. The measured inorganic species are also used in the thermodynamic equilibrium model for aerosols, ISSOROPIA-II (Fountoukis and Nenes, 2007, http://nenes.eas.gatech.edu/ISSOROPIA/), for calculating the [H\(^+\)]\(_{\text{air}}\) and for comparison with the experimental data. The model was run as ‘reverse problem’ in which particle-phase composition, ambient temperature and relative humidity are used as input. Also, positive or negative artifact in the measurement of NH\(_4\)\(^+\) ion is not addressed in this study; hence an upper limit of 20% correction is applied for the measured NH\(_4\)\(^+\) ion concentration, considering the over all acidic nature of the samples. Positive artifact on NO\(_3\) measurement is likely to be minimum because of the presence of high abundances of acidic SO\(_4\)\(^2-\) and hence not attempted to account for it. Also this is more pronounced for cellulose filters and glass fiber filters compared to quartz filter which was used for this study (Schaap et al., 2004). SOC is estimated by the EC-tracer method assuming minimum OC/EC as the primary ratio (Castro et al., 1999; Rengarajan et al., 2007). Using the following equation, OC\(_{\text{sec}}\) can be semi-quantitatively estimated for a specific region of interest:

\[
\text{OC}_{\text{pri}} = \text{EC}^* (\text{OC}/\text{EC})_{\text{pri}} \tag{1}
\]

\[
\text{OC}_{\text{sec}} = \text{OC}_{\text{meas}} - \text{OC}_{\text{pri}} \tag{2}
\]

where \(\text{OC}_{\text{meas}}\) is the measured OC in ambient aerosols, \(\text{OC}_{\text{pri}}\) the primary OC and \((\text{OC}/\text{EC})_{\text{pri}}\) the primary OC/EC ratio observed during the sampling period. In addition, WSOC measured in this study serves as a potential tracer for SOA formation (Sullivan et al., 2004; Miyazaki et al., 2006; Salma et al., 2007; Weber et al., 2007).

3. Results and discussion

3.1. Aerosol chemical composition: dominance of anthropogenic species

PM\(_{2.5}\) mass ranged from 32 to 106 μg m\(^{-3}\) (Average: 56 μg m\(^{-3}\)) during the 30-day sampling in wintertime. Average chemical composition is summarized in Fig. 1. Water-soluble inorganic species constitute 29% of PM\(_{2.5}\) mass whereas the contribution of organic matter (OC × 1.6, typical urban OM/OC ratio; Turpin and Lim, 2001) constitutes 29% of PM\(_{2.5}\) mass whereas the contribution of organic matter (OC × 1.6, typical urban OM/OC ratio; Turpin and Lim, 2001)
and EC are 53% and 5.4% respectively. OC varied from 11 to 39 μg m$^{-3}$ (organic mass: 17–62 μg m$^{-3}$) and exhibits a linear trend with EC indicating their major contribution from anthropogenic sources (Gelenčšér, 2004). The OC/EC ratio ranges between 4.0 and 8.1 (Average: 6.2). Among inorganic constituents, SO$_4^{2-}$ and NO$_3^-$ are the dominant acidic species derived from anthropogenic sources (SO$_4^{2-}$: 3.2–23 μg m$^{-3}$; NO$_3^-$: 0.7–2.1 μg m$^{-3}$) and are largely neutralized by NH$_4^+$ and K$^+$. The overall chemical composition of PM$_{2.5}$ (Fig. 1) reveals that almost 85% of the total mass is anthropogenic in origin (carbonaceous aerosol, SO$_4^{2-}$, NO$_3^-$, NH$_4^+$ and K$^+$). The unknown fraction is calculated by subtracting the measured mass of OC, EC and water-soluble ionic species from the total PM$_{2.5}$ mass. Ca$^{2+}$ measured can be considered as an index of dust contribution (Guinot et al., 2007) which shows significant correlation with the unknown fraction. Hence it is assigned as dust fraction and constitutes ~12%.

During the summer, PM$_{2.5}$ mass ranged between 20.0 and 51.9 μg m$^{-3}$ (Average: 39.2 μg m$^{-3}$). OC and EC concentrations ranged from 4.5 to 18.9 μg m$^{-3}$ (Average: 7.9 μg m$^{-3}$) and 0.51–3.1 μg m$^{-3}$ (Average: 0.99 μg m$^{-3}$); whereas the average SO$_4^{2-}$ and NO$_3^-$ concentrations were 5.9 and 0.6 μg m$^{-3}$, respectively. In contrast to the winter samples, the contribution of anthropogenic constituents to PM$_{2.5}$ during summer is ~57% and insoluble dust component is ~40%, indicating substantial increase in the dust contribution to the PM$_{2.5}$ mass.

### 3.2. SOA and water-soluble organic component

The concentration of SOC, estimated by EC-tracer method, ranged between 2 and 12.5 μg m$^{-3}$, on average it accounts for ~25% of the total OC during winter. Yuan et al. (2006) have reported that the estimated SOC based on EC-tracer method is consistently higher compared to Positive matrix factorization method. Also, it largely depends on the assumed primary OC/EC ratio. We have considered minimum ratio as primary OC/EC ratio, in which contribution from SOC cannot be completely ruled out. Hence, SOC reported in this study can be considered as the lower limit and temporal variability can be compared with other parameters. Water-soluble organic matter (WSOM = WSOC$\text{measured} \times 1.9$, typical value for urban environment; Fuzzi et al., 2001) ranged from 7.6 to 28 μg m$^{-3}$. WSOM consists of oxygenated organic compounds containing various functional groups such as alcohols, carboxyls, and dicarboxylic acids and considerable fraction of the SOC is expected to be water-soluble (Fuzzi et al., 2001; Kiss et al., 2002; Graham et al., 2002; Hallquist et al., 2009). Experimental studies investigating the water solubility of urban aerosols have indicated that anthropogenically influenced SOA component is almost exclusively water soluble (Weber et al., 2007; Miyazaki et al., 2006). SOC and WSOC exhibit a significant linear relation ($r = 0.80$, $p < 0.001$; Fig. 2) and their similar temporal variability in winter samples suggest major contribution of SOA to WSOC; and that WSOC can also be considered as a proxy for the SOA. WSOC/OC ratio varied from 0.26 to 0.52 and on an average, WSOC constitutes ~41% of the total OC during the winter period. The estimated SOC was 3.3 μg m$^{-3}$ during summer and average WSOC mass concentration was 3.8 μg m$^{-3}$. A similar trend between SOC and WSOC is observed during summer as well (Fig. 2) whereas values in summer are low compared with those in winter. Also WSOC was highly correlated with the derived SOC, with WSOC/SOC ratios of 1.75 and 1.27 for winter and summer respectively. These results suggest that SOC produced during winter and summer were different in their solubility characteristics.

### 3.3. Aerosol acidity and SOA

Jang et al. (2002) had suggested that the SOA formation is favoured by the acidic nature of pre-existing aerosols on which the heterogeneous uptake of reactive VOCs can occur. Laboratory studies have demonstrated that acid-catalyzed heterogeneous reactions lead to the formation of non-volatile oligomeric compounds from the volatile carbonyl containing species (Kroll et al., 2005). Surratt et al. (2007) have shown from a laboratory chamber study that the mass of SOA and measured acidity of laboratory-generated aerosol exhibit a linear relationship, the acid catalytic reactions responsible for such an observation is expected to be through reactive uptake of epoxydiols of precursor VOCs (Paulot et al., 2009; Surratt et al., 2010). In this study, SO$_4^{2-}$ and NO$_3^-$ are the dominant components of anthropogenic origin causing acidity of the ambient aerosols and the measured pH of the water extract (range: 4.3–6.5; Average: 4.9) represents an overall acidic character of the fine particulate matter during winter. In majority of the samples, HCO$_3^-$ concentration was not detectable.

In the summer season, a substantial increase in the fractional contribution of alkaline dust causes significant decrease in the acidity (Rastogi and Sarin, 2005). The pH of the water extract varied from 4.8 to 6.8 with an average value of 5.9. The measured [H$^+$]$\text{air}$ varied from 250 nmol m$^{-3}$–11 μmol m$^{-3}$ during winter. The modeled [H$^+$]$\text{air}$ determined from ISSOROPIA-II using the measured ionic composition of water extract of aerosol samples have been compared with the measured [H$^+$]$\text{air}$ (Fig. 3). Although the modeled [H$^+$]$\text{air}$ are lower by ~2 orders of magnitude than the measured data, similarity in their variability suggests that the two sets of data can be used as an index of aerosol acidity. Furthermore, difference in the two sets of [H$^+$]$\text{air}$ concentrations is due to the fact that measured [H$^+$]$\text{air}$ represents the extrapolation from H$_{aq\text{extract}}^+$ and the modeled [H$^+$]$\text{air}$ is the concentration derived based on measured ionic composition assuming a thermodynamically equilibrated gas-aerosol system. Daily variation of the modeled [H$^+$]$\text{air}$ determined from ISSOROPIA-II using the measured ionic species and computed SOC concentration of the aerosol samples at Ahmedabad during the study period is depicted in Fig. 4. The [H$^+$]$\text{air}$ shows an increasing trend and attains a maximum value (60 nmol m$^{-3}$), and then decreases. SOC mass concentration also increased from ~4.5–13 μg m$^{-3}$ during this period, suggesting that SOC abundance increases substantially at higher [H$^+$]$\text{air}$. 

Fig. 2. Scatter plot of WSOC and SOC concentrations in PM$_{2.5}$ during the winter and the summer.
We thus provide direct evidence for enhanced SOA formation under favourable conditions of higher acidity derived from nss-SO$_4^{2-}$, indicating that acid-catalyzed condensation reactions may contribute substantially to the formation of SOA during the winter-time. The modeled [H$^+$]$_{air}$ during summer was not found to be realistic because the water activity was insignificant as the average temperature was higher and the relative humidity was $\sim$50%. Takahama et al. (2006) studied aerosol acidity and OC in Pittsburgh, USA for evidence of acid-catalyzed heterogeneous chemistry leading to increased SOA concentrations and concluded that the effect of acidity on SOA was masked by the other atmospheric processes occurring simultaneously. Tanner et al. (2009) examined hourly-collected fine particle composition data from three sites in south eastern United States for the evidence of SOA formation catalyzed through aerosol acidity. Their result suggest that the acidity levels assessed from NH$_4$/$SO_4^{2-}$ ratios are too low to observe unequivocal evidence for the same. Peltier et al. (2007) had reported that the relationship between SOA formation and aerosol acidity is not meaningful during the airborne measurements conducted over coal-fired power plant plumes from Atlanta metropolitan region, USA. Their conclusion was based on indirect measurement of aerosol acidity by NH$_4$/$SO_4^{2-}$ ratios in the samples while our observation is based on measured H$^+$aq-extract and modeled [H$^+$]$_{air}$ which are more reasonable representations of acidity. Likewise, Gao et al. (2006) suggested that there is no evidence for oligomer formation and found no correlation between particle acidity and the detected polar organic species measured in the samples from southeastern United States; wherein the aerosol acidity was assessed by measured NH$_4$+, SO$_4^{2-}$ and NO$_3$. Lewandowski et al. (2007) have reported higher PM$_{2.5}$ and organic aerosol mass concentration under acidic condition in an urban location at North Carolina, USA where the acidity was assessed by difference in charge balance of measured water-soluble inorganic species. However, it is noteworthy that the NH$_4$+/SO$_4^{2-}$ equivalent ratio does not exhibit a consistent relationship with SOC or WSOC during our observation period (Fig. 4). In previous laboratory studies by Surratt et al. (2007) and Offenberg et al. (2009), the measured aerosol acidity was between 100 and 1000 nM m$^{-3}$ which clearly demonstrated enhancement of SOA from biogenic VOCs. In our field studies the [H$^+$]$_{air}$ observed are similar and hence the precursors could be similar biogenic VOCs, considering that agricultural and forest areas are located in the upwind region of the sampling location. However, there is no data available from the literature.

SOA is generally formed by the oxidation of VOCs which increases the polarity and hence large fraction of the resulting compounds is likely to be oxygenated making them soluble or partially soluble in water (Seinfeld and Pankow, 2003; Kondo et al., 2007). This is well reflected from the increase in the WSOC concentration with a parallel increase in [H$^+$]$_{air}$ (Fig. 4). The maximum value of the WSOC (14.7 µg m$^{-3}$) is observed on 26 December, with an increasing trend from 18 to 19 December onwards. Such comparison for the samples collected during summer is not possible because [H$^+$]$_{air}$ concentrations both measured as well as modeled are not realistic.

Linear regression analysis between [H$^+$]$_{air}$ and SOC for the winter samples suggest a significant correlation ($r = 0.82, p < 0.001$; Fig. 5) and the linear relation can be expressed as

$$\text{SOC} = 0.15 \times [\text{H}^+]_{\text{air}} + 2.5$$

This indicates that typically 0.15 mg of SOC is produced per nmol H$^+$. In the laboratory-based experiment by Offenberg et al. (2009), the observed SOC formation from $\alpha$-pinene on photo-oxidation was $\sim$0.015 µg per nmol H$^+$. The large difference between measurements and predictions based on known precursors reveals that...
there is a substantial amount of “missing SOA” especially in urban environments (Heald et al., 2005; de Gouw et al., 2005; Volkamer et al., 2006). Analysis of such empirical relationship between SOC mass and [H\(^+\)]\(_{air}\) in different environmental conditions is useful for regional and global scale models to decrease the discrepancy between the model prediction and observation of SOA. During summer, however, a combination of aerosol composition and low RH often induced solid-phase transitions in the aerosol (Khlystov et al., 2005), leading to lower concentrations of acidity.

High OC measured in these samples coincided with the peak SO\(_4^{2-}\) concentration. A plot of OC and SO\(_4^{2-}\) gives a positive correlation (r = 0.67, p < 0.001; Fig. 6). It is earlier observed that SOA yield increased with increasing acidity due to an acid hydrolysis mechanism for organosulphate formation of biogenic VOC oxidation products (epoxides) (Surratt et al., 2007; Minerath and Elrod, 2009; Hawkins et al., 2010). It should be noted that [H\(^+\)]\(_{air}\) is not only a function of the SO\(_4^{2-}\) concentration but also the amount of neutralizing base (predominantly NH\(_3\) in this area), the presence of other acidic species (e.g., NO\(_3^-\)), and also the water content of the aerosol. A detailed evaluation of the uptake of inorganic acid species and precursor VOCs by fine aerosols from urban environment to form organosulphate derivatives would be crucial to understand the influence on the budgets of reactive VOCs, as well as the radiative properties of the particles during the sampling period.

4. Conclusions

Aerosol acidity, [H\(^+\)]\(_{air}\) SOC mass concentration have been studied based on the aerosol chemical composition during winter from an urban location (Ahmedabad) in western India. Our assessment of secondary organic carbon (SOC) by the EC-tracer method and the measured [H\(^+\)]\(_{air}\) as well as that computed using an aerosol thermodynamic equilibrium model, ISSOROPIA-II, show significant positive correlation suggesting that acidity favours the formation of secondary organic aerosol (SOA) in the urban source region during winter. During summer, this relationship is not conspicuous because acidity is not significantly pronounced. Water-soluble organic carbon (WSOC) has also been used as an independent measure of SOA. Surratt et al. (2007, 2008, 2010) proposed that aerosol acidity arising due to high SO\(_4^{2-}\) concentration in an urban environment may lead to the formation of organosulphates. The role of aerosol acidity in SOA formation has been studied in laboratory experiments, by measuring the presence of organosulphates from natural VOCs (Surratt et al., 2008, 2010); however, the reaction pathways and feasibility for formation from anthropogenic VOCs in ambient atmosphere need further investigation.

Our observation based on ambient measurements of chemical parameters is significantly important for quantitative assessment of the factors controlling the chemical pathways for the SOA formation. In a rapidly growing scenario of anthropogenic activities and emissions from mega-cities, the increase in aerosol acidity leading to enhance formation of SOA has implications to poor air-quality and regional changes in atmospheric chemistry. Furthermore, formation of SOA with increase in aerosol acidity and its representation in the regional models is essential in order to link the compositional changes with key physical properties (e.g., volatility, hygroscopicity, light absorption) of the ambient aerosols in an urban environment.

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References


Fountoukis, C., Nenes, A., 2007. ISORROPIA II: a computationally efficient aerosol thermodynamic equilibrium model for K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), NH\(_4^+\), SO\(_4^{2-}\), NO\(_3^-\), Cl\(^-\), H\(_2\)O aerosols. Atmospheric Chemistry and Physics 7, 4639–4659.


