Evidence of organonitrate formation at a high altitude site, Mahabaleshwar during pre-monsoon season

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Abstract

The presence of organonitrate and organosulfate was identified at a high altitude site, Mahabaleshwar during the pre-monsoon of 2016. The Time of Flight Aerosol Chemical Speciation Monitor (ToF-ACSM) was used to measure the organic and inorganic components of non-refractory particulate matter (NR-PM$_1$) aerosol. Positive Matrix Factorization (PMF) was performed on the (i) organics mass spectra of aerosol (PMF$_{OA}$) (ii) organics mass spectra merged with inorganics (PMF$_{OA+IOA}$) and (iii) integrated mass spectra of organics with NO$^+$ and NO$_2$$^+$ ions (PMF$_{OA+NOx}$) to derive the chemical information on organonitrate and organosulfate. The results of PMF$_{OA}$ were used as a reference for validating the factors obtained through PMF$_{OA+IOA}$ and PMF$_{OA+NOx}$ results. The analysis of PMF$_{OA}$ resolved four PMF factors - hydrocarbon like OA (HOA), biomass burning like OA (BBOA), oxygenated OA -1 (OOA-1) and OOA-2. The analysis of PMF$_{OA+IOA}$ identified two additional inorganic factors - sulfate organic aerosol (OA) and nitrate OA. The factors-sulfate OA and nitrate OA contributed 36% and 6% respectively to the total aerosol mass. Although secondarily originated, the sulfate OA and nitrate OA displayed different diurnal profiles. The results of PMF$_{OA+NOx}$ were used for the quantification and apportionment of nitrate aerosol into two forms - organic nitrate and inorganic nitrate. Organic nitrate and inorganic nitrate contributed 38% and 62% respectively to the total nitrate aerosol mass. The diurnal variation of organic...
nitrate highlights photochemical oxidation as well as nocturnal oxidation by nitrate radical as
the two major sources. This source apportionment study with combined (organic and
inorganic) dataset provides new source factors and improves understanding about the sources
and chemical nature of submicron aerosols in atmosphere. However, the quantification of
organosulfate remains a limitation in this study.

Key words: Tof-ACSM, PMF, organonitrate, organosulfate, NIA

Introduction

Organic aerosols (OA) makes up a substantial fraction of tropospheric fine (submicron)
particulate matter, accounting for 20-90 % of the total aerosol mass. This important
component of submicron aerosol is originated from a wide variety of natural (wildfires) and
anthropogenic sources (fossil fuel combustion and biomass burning). A significant fraction of
OA is also formed as a secondary organic aerosol (SOA) either by the oxidation of volatile
organic compounds or aqueous-phase oxidation (Kroll and Seinfeld, 2008; Lukacs et al.,
2009; Lim et al., 2010; Hallquist et al., 2009). Of the known SOA precursors, isoprene and
monoterpenes contributes significantly to the global SOA budget, owing to their large global
emission rates (Guenther et al., 1995) and high reactivity with atmospheric oxidants -
hydroxyl radical (OH), ozone (O3), and nitrate radical (NO3). Several studies have tracked
down the nature of origin and processes of OA through fast acquisition of OA mass spectrum
using Aerosol Mass Spectrometers and/or Aerosol Chemical Speciation Monitors and
analysing them with positive matrix factorization (PMF) (Paatero and Tapper, 1994; Zhang et
al., 2005; Mohr et al., 2012; Xu et al., 2015; Sun et al., 2016,Carbone et al., 2013, Aurela et
al., 2015, Iwamoto et al., 2016). However, most of the previous studies have performed PMF
on the OA spectra only, leaving behind the inorganic species (sulfate, nitrate, chloride and
ammonium). Recently, a study by Sun et al., (2012) performed PMF analysis on the merged spectra of organic (OA) and inorganic aerosol (IOA) i.e. PMF_{OA+IOA} and identified two additional factors - sulfate-OA (organosulfate) and nitrate-OA (organonitrate). Since the organic and inorganic species undergo different formation mechanisms in the atmosphere, it is believed that the OA factors associated with inorganics may provide insights into the intrinsic relationship between organic and inorganic species.

Both laboratory-generated and air sampling studies have provided the evidence of presence of organosulfate (Surratt et al., 2007; Inuma et al., 2007; Liggio et al., 2007; Surratt et al., 2008) and organonitrate (Nielsen et al., 1998; Lim et al., 2016; Reemtsma et al., 2006; Ng et al., 2007; Stone et al., 2009; Day et al., 2010; Bruns et al., 2010; Fry et al., 2009) as an important component of SOA. Due to the lack of measurement approaches, the formation mechanisms and aging of organonitrate (ON) and organosulfate (OS) remains unexplored and is largely ignored in models. Organonitrates have been identified as significant component of NO_y in the gas phase (Nielsen et al., 1998; Day et al., 2003; Perring et al., 2009) and is likely to affect the nitrogen cycle and ozone production (Rosen et al., 2004; Mao et al., 2012; Perring et al., 2013). ON are formed in the atmosphere either through photochemical (OH-initiated) or nocturnal (NO_3-initiated) oxidation reactions of biogenic and anthropogenic VOCs in the presence of NOx (Hallquist et al., 1999; Pitts and Pitts, 1999). NO_3 oxidation of isoprene and monoterpenes have been identified as a significant source for ON (Ng et al., 2008; Fry et al., 2009) whereas photochemical oxidation of VOC produces minor ON (Atkinson and Arey 2003). The smaller molecular weight ON product tends to remain in the gas phase while larger, multifunctional ON having lower vapor pressure undergoes partitioning and forms SOA. Despite lower ON yields during the daytime, model studies including ON production
have reported that photochemically produced ON accounts for the significant fraction of SOA functionalization (Camredon et al., 2007).

Several studies (Surratt et al., 2008; Liggio et al., 2006, Romero and Oehme, 2005; Reemtsma et al., 2006) have reported the enhanced formation of organosulfates through oxidation of several biogenic VOCs including isoprene, limonene, α-pinene, β-pinene, in the presence of sulfate seed aerosol. Thus, the formation of organosulfates is influenced by both biogenic (BVOCs) and anthropogenic (which provides an acidic medium) emissions and it is identified as a secondary (or aged) product. Studies have also indicated the significant contribution of OS to SOA (Altieri et al., 2009; Gao et al., 2006; Gilardoni et al., 2007). Considering the aged nature, organosulfate may play an important role in aerosol microphysics.

So far, the studies on PMF analysis of OA mass spectrum have been performed either at an urban or a rural site, dominated either by anthropogenic or biogenic emissions (Ng et al., 2010, Carbone et al., 2013, Aurela et al., 2015). Aurela et al., 2015 performed PMF on the organic mass spectra for residential area, highway, curbside and described OOA as the major fraction of submicron aerosol. A study by Hao et al., (2014) performed PMF analysis in the mixed environment i.e. at a semi-urban site, which is influenced by both biogenic and anthropogenic sources. Weber et al., 2007 have also observed the significant impact of anthropogenic activities on biogenic emissions. In the present study, an attempt has been made to comprehend the likely interactions of organic species with inorganic species of the aerosol. The study was carried out in the pre-monsoon of 2016 at High Altitude Cloud Physics Laboratory (HACPL), Mahabaleshwar. Mahabaleshwar is a rural tourist town in the Western Ghats of India, where ~80% of the land is covered with forest. Being a tourist
place and forest covered site, HACPL observes both fresh anthropogenic emissions (vehicular, fossil fuel combustion, etc.) and biogenic emissions. This study mainly focuses on the identification of organic sulphate and organic nitrate in the ambient air at HACPL during the pre-monsoon season. The quantification of organic and inorganic nitrate has been performed using state of the art PMF methodology. This study is expected to not only strengthen our understanding about the sources, processes and associated chemical characteristics of OA in the ambient air but also improve the chemical composition derived hygroscopicity value ($\kappa$) of aerosols using the knowledge of two forms of sulphate and nitrate. The hygroscopicity parameter is generally calculated by considering the measured sulphate and nitrate as purely inorganic in origin (hence overestimation) and thus assigns a high hygroscopicity value ($\sim 0.6$ to $0.7$). This uncertainty in chemically derived hygroscopicity value can be reduced by considering the actual concentration of inorganic species.

### 2 Method

#### 2.1 Measurement Site

The observatory, HACPL at Mahabaleshwar ($17.92^\circ$ N, $73.65^\circ$ E) is situated at a height of 1378 m above mean sea level (a.m.s.l.). The map in figure 1 gives a picturesque description of the sampling site. Mahabaleshwar serves as a tourist destination during the pre-monsoon season. The site is surrounded with dense vegetation, residential houses, hotels and a rural market. During the study period (March to May 2016), the site experiences high solar radiation (mean $\sim 471.4 \pm 297.9$ Wm$^{-2}$), high surface temperature (mean $\sim 26.3 \pm 5.5$ $^\circ$C), moderate relative humidity (mean $\sim 46.4 \pm 8.2$ %) and moderate wind speed (mean $\sim 2.5 \pm 1.6$ ms$^{-1}$). These meteorological parameters were measured using Automatic Weather Station (AWS) at an interval of one minute.
2.2 Time of Flight - Aerosol Chemical Speciation Monitor

Time of Flight - Aerosol Chemical Speciation Monitor (ToF-ACSM) was used for measuring the submicron NR-PM$_1$ data at an interval of 10 minutes. This high resolution was averaged to 1 hour for the analysis. The chemical information of the mass spectra was extracted by following the protocol of Allan et al., (2004). The calibration and operation of ToF-ACSM is discussed elsewhere in detail (Nget al., 2011; Fröhlich et al., 2013). In brief, the particle beam impacts on a resistively heated porous tungsten surface ($T \approx 600^\circ$C), flash vaporized into the non-refractory constituents that are ionized by electron impact ($E_{\text{kin}} = 70$ eV) and detection by ToF analyser on the basis of respective mass-to-charge ratios. The mass spectral matrices of organic and inorganic species were extracted for subsequent PMF analysis. The details on QA/QC of ToF-ACSM are given in Mukherjee et al., 2018.

2.3 Positive Matrix Factorization

PMF was used to deconvolve the mass spectral matrix into source related factors (Paatero and Tapper, 1994). In this study, Unit Mass Resolution (UMR) matrix ($m/z$ 12- 220) and error matrix was generated for both organic and organic + inorganic species, by using ToFware (Igor Pro Wavemetrics, Inc. Oregon USA), following the protocol of Ulbrich et al., 2009. The ions ($m/z$) were chosen up to 110 only for PMF analysis due to lower signal to noise ratio (S/N) at larger $m/z$ (>110). Ions with S/N ratio less than 0.2 were removed while the ions with $0.2 < S/N < 2$ were downweighted by a factor of 2. Further, the particulate ions, H$_2$O$^+$, O$^+$, HO$^+$ and CO$^+$ were also downweighted to avoid the additional weighting by CO$_2^+$. The rotational ambiguity in both the runs was tested by varying the forcing parameter, $F_{\text{peak}}$ between -1 and 1 with an increment of 0.2 and PMF solutions were tested up to 9 factors.
The merged mass spectrum was prepared by integrating the inorganic fragment ions (nitrate, sulfate, ammonium and chloride) with OA matrix. The major fragment ions included for inorganic species are - NO\(^+\) (m/z 30) and NO\(_2^+\) (m/z 46) for nitrate, SO\(^+\) (m/z 48), SO\(_2^+\) (m/z 64), SO\(_3^+\) (m/z 80), HSO\(_3^+\) (m/z 81) and H\(_2\)SO\(_4^+\) (m/z 98) for sulfate, Cl\(^+\) (m/z 35) and HCl\(^+\) (m/z 36) for chloride, NH\(^+\) (m/z 15), NH\(_2^+\) (m/z 16) and NH\(_3^+\) (m/z 17) for ammonium. The sum of chosen ions represents a major fraction of nitrate (95.3 %), sulfate (62.5 %), chloride (75.6%) and ammonium (99.9%) respectively. These fragment ions correlated strongly (r\(^2\) ~ 0.99; p-value = 0.005) with the mass concentration of respective inorganic species (Figure S1). After PMF run, the 4-factor and 6-factor solution was selected as an optimum solution for OA mass spectra and merged mass spectra respectively. The optimal solution for PMF\(_{OA}\) and PMF\(_{OA+IOA}\) was determined by examining the scaled residuals of PMF fits, the change in Q/Q\(_{exp}\) with increasing number of factors, factor correlations with external tracer, EC and comparing the component mass spectra with reference mass spectra available in AMS spectral database (Ulbrich et al., 2009; Huang et al., 2010; He et al., 2011). The change in Q/Q\(_{exp}\), time series of change in Q/Q\(_{exp}\), scaled residual, factor correlations with external tracers and correlation of the resolved mass spectral profiles with reference mass spectra are provided in the supplementary material (figures S2 to S4 and table S1). An optimum f\(_{peak}\) value of 0 was used for PMF analysis in both the cases. The PMF analysis of merged mass spectra yielded two additional factors - SO\(_4^-\)-OA (organosulfate) and NO\(_3^-\)-OA (organonitrate).

### 2.4 Quantification of Organic Nitrate

In general, the nitrate measured by ToF-ACSM accounts for total nitrate functionality (-ONO\(_2\)), which could arise from both organic and inorganic nitrates. So far, the direct measurements of organic nitrates are not available. However, few studies (Bruns et al., 2010; Sato et al., 2010 and Farmer et al., 2010) have suggested some indirect methods for
quantifying organic nitrate in the atmosphere. Of the reported indirect methods, PMF method
was used in this study to apportion the measured total nitrates. This method could
unequivocally determine the relative contributions of organic and inorganic nitrates (Sun et
al., 2012; Hao et al., 2014; Xu et al., 2015a & b). The PMF analysis of merged (NO$_3$+org)
mass spectra deconvolved a nitrate inorganic aerosol (NIA) factor along with other organic
aerosol factors. The optimal solution for PMF analysis on the merged mass spectra was
selected in a similar way as done with the PMF analysis of organic mass spectra. The selected
factors were further validated by comparing the mass spectrum and mass concentration
(figure 5) with the PMF$_{org}$ results (figure 3). The total nitrate functionality was apportioned
into organic and inorganic signals with the following set of equations:

\[
[\text{NO}_3^{+}_{\text{org}}] = \sum ([\text{OA factor}]_i \times f_{\text{NO}_i}) \quad \ldots \text{iv})
\]

\[
[\text{NO}_2^{+}_{\text{org}}] = \sum ([\text{OA factor}]_i \times f_{\text{NO}_2i}) \quad \ldots \text{v})
\]

\[
\text{NO}_3^{\text{org}} = \frac{([\text{NO}_3^{+}_{\text{org}}] + [\text{NO}_2^{+}_{\text{org}}])}{0.95} \quad \ldots \text{vi})
\]

where [OA factor]$_i$ is the mass concentration of $i^{th}$ OA factor and $f_{\text{NO}_i}$ and $f_{\text{NO}_2i}$ are the mass
fraction of NO$^+$ and NO$_2^+$ respectively in the $i^{th}$ OA factor. Since the mass spectrum of nitrate
(measured by ACSM) was dominated with signals of NOx ions and the sum of which
accounts for 95% to total nitrate mass, a factor of 0.95 was applied in equation vi). Finally the
nitrate functionality from inorganic nitrate was calculated by subtracting NO$_3^{\text{org}}$ from the
total nitrate, measured by ACSM.

3 Results and Discussion

3.1 Mass concentration and Diurnal variation of NR-PM$_1$ species
With the mean mass concentration of \(6.3 \pm 5.1 \mu g m^{-3}\), organics contributed ~61% to the total NR-PM\(_1\) mass (10.3 \pm 8.2 \mu g m^{-3}\). This was followed by sulfate, an inorganic constituent of NR-PM\(_1\) with ~23% contribution and an average concentration of 2.4 \pm 1.7 \mu g m^{-3}\.

Subsequently, ammonium, nitrate and chloride followed with percentage contribution of ~10%, ~5% and ~1% respectively. The mean mass concentration was measured as 1.0 \pm 0.7 \mu g m^{-3}\) for ammonium, 0.6 \pm 0.6 \mu g m^{-3}\) for nitrate and 0.1 \pm 0.1 \mu g m^{-3}\) for chloride. Each aerosol specie exhibited different mean diurnal pattern. Organics, sulfate and nitrate displayed a daytime build-up and evening high whereas, chloride showed a morning and evening high (Figure 2). Since the diurnal pattern of organics is governed both by primary emissions (anthropogenic activities) and secondary formation (gas to particle partitioning) (Xu et al., 2015b; Almeida et al., 2014; Sun et al., 2016), the sources of organics were identified by performing PMF. The daytime build-up of sulfate and nitrate was attributed to their photochemical formation from precursor gases -SO\(_x\) and NO\(_x\) respectively. Sulfate also displayed high background concentration throughout the day. This concentration was likely attributed to the regional transport. Nitrate high during the evening hours was attributed to gas-particle partitioning under high relative humidity and low surface temperature conditions (Figure 2f). The high concentration of chloride during morning and evening hours was ascribed to local anthropogenic activities (biomass and fossil fuel burning). It is important to note that all NR-PM\(_1\) species reflected a significant peak during evening hours. This peak was attributed the combined effect of source (or source processes) and low PBL height (Figure S7). The diurnal pattern of ammonium represents the combined result of ammonium chloride, ammonium sulfate and ammonium nitrate. The amount of ammonium (NH\(_4^+\)) required to achieve a charge balance with measured inorganic anions - SO\(_4^{2-}\), NO\(_3^-\) and Cl\(^-\) was calculated and observed to be higher than measured NH\(_4^+\) (Figure 2e). Few outliers deviating from one-to-one line of calculated vs measured NH\(_4^+\) were observed with the slope.
value of 1.12. The slope value greater than 1 is indicative of possible presence of organic
associated nitrate, sulfate and chloride. This over-prediction of NH$_4^+$ was correlated with
each inorganic anion. The satisfactory correlation of over-predicted NH$_4^+$ with nitrate ($r^2 = 0.51$; p-value = 0.001), sulfate ($r^2 = 0.43$; p-value = 0.001) and chloride ($r^2 = 0.40$; p-value = 0.001) suggested relative presence of organo-nitrate, organo-sulfate and organo-chloride in
the ambient air.

To study the possible influence of regional transport on the measured mass concentrations,
the Potential Source Contribution Function (PSCF) analysis was performed (Figure S5). PSCF plot shows that the site is influenced by the possible contribution from Mumbai during the study period. This regional influence was also reflected by the diurnal variation in mass concentration of organics and sulfate. Further, the hourly time series of NR-PM$_1$ species was studied (Figure S6). The time series indicate different mass loading of NR-PM$_1$ species during the study period. To foresee the effect of air-mass origin on observed mass concentrations, 3 time windows (window 1, 2 and 3) were selected randomly. Windows 1 and 3 exhibited comparatively low concentrations while window 2 showed significantly high concentrations. The hourly backward trajectory analysis during the selected time windows revealed that the air-mass originated from the Arabian sea (clean air mass) during window 1 and 3. On the other hand, air-mass originated mostly from the continent and carried pollutants along the trajectory pathway during window 2.

### 3.2 Positive Matrix Factorization (PMF)

#### 3.2.1 PMF: Organic mass spectra (PMF$_{OA}$)

PMF analysis of the organic mass spectra yielded four source related factors (Figure 3). The mass spectrum of source factor 1 was dominated with marker ions at $m/z$ 41 (C$_3$H$_5^+$), 55
(C₄H₇⁻) and 57 (C₃H₅O⁺). Based on the close resemblance of mass spectrum of factor 1 with previously reported HOA (hydrocarbon-like OA) spectra by Zhang et al., 2005, factor 1 was assigned as HOA. The morning and evening peak of HOA were related to vehicular emissions. The afternoon peak of HOA was related to cooking activities based on the fraction of mass sticks at m/z 55 and 57. Since the mass spectrum of cooking OA (COA) is identical to HOA (Mohr et al., 2012; Sun et al., 2012) and they cannot be separated with UMR (unit mass resolution) data, some contribution from cooking emissions may be anticipated. The second factor showed morning and evening high with dominant marker ions at m/z 60 (C₂H₄O₂⁻) and 73 (C₃H₅O₂⁻). This factor was identified as BBOA - biomass-burning OA. The morning & evening peaks of BBOA were attributed to fresh anthropogenic activities (wood burning). Further, the evening peaks of HOA and BBOA were also attributed to low PBL height. The two factors- HOA and BBOA were validated with EC (an external tracer for anthropogenic activities, r²=0.61, p-value = 0.003 with HOA and 0.71, p-value = 0.002 with BBOA).

The factors 3 & 4 were identified as- OOA-1 (oxygenated OA-1) and OOA-2 (oxygenated OA-2), based on the fractional contribution of mass stick at m/z 44 and O:C ratio. The mass spectrum of OOA-1 was identified with higher contribution from m/z 44 (~0.31) and higher O:C ratio (~1.27) while OOA-2 was identified with lower contribution at m/z 44 (~0.15) and low O:C ratio (~0.66). The O:C ratios were calculated by following the methodology of Bougiatioti et al., 2014. Based on the respective O:C ratios, OOA-1 was defined as an aged and processed aerosol and OOA-2 as freshly formed aerosol. The diurnal variation of OOA-1 showed daytime (12:00 - 16:00 h) maxima and evening high (18:00 - 21:00 h). The daytime high was likely due to secondary formation of aerosols under high solar radiation and temperature. The evening high was attributed to rapid oxidation of freshly emitted gas phase
species to SOA under high relative humidity (~65-70%) and low temperature and low PBL conditions. Moreover high background (1.3 - 1.8 µgm⁻³) of OOA-1 was also observed throughout the day. This background was probably due to the regional transport of processed/aged aerosols. OOA-1 showed good agreement with sulfate ($r^2 = 0.92$; p-value = 0.003) and therefore, OOA-1 was assumed to be mixed aerosol (both secondarily formed and regionally transported).

OOA-2 was identified as IEPOX-OA based on fractional contribution of mass stick at m/z 82 (C₅H₆O⁺). This mass stick is related with isoprene degradation to SOA. The time series of m/z 82 ion ($r^2=0.72$; p-value = 0.05) and OOA-2 ($r^2=0.78$; p-value = 0.05) correlated strongly with literature reported IEPOX-OA (Isoprene Epoxydiol-OA) factor (available in the AMS Spectral Database at http://cires.colorado.edu/jimenez-group/AMSsd/). On a diurnal scale, IEPOX-OA displayed daytime maxima, consistent with the isoprene chemistry and solar radiation cycle. IEPOX-OA also exhibited evening high due to low boundary layer height and high relative humidity conditions. The evening high may be attributed to gas particle partitioning under favourable meteorological conditions. In terms of relative contribution, OOA-1 contributed ~ 33% to the total OA mass followed by HOA (~32%), BBOA (~18%) and OOA-2 (~17%).

3.2.2 PMF: Organic mass spectra integrated with inorganics (PMF<sub>OA+IOA</sub>)

PMF analysis on the integrated mass spectra (organic and inorganic) yields 6 PMF factors. Figure 4 gives the mass spectral profile and corresponding diurnal variation of these factors. Based on the mass sticks identified at m/z 15 (NH⁺), 16 (NH₂⁺), 17 (NH₃⁺), 30 (NO⁺), 46 (NO₂⁺), 48 (SO⁻), 64 (SO₂⁻), 80 (SO₃⁻), 81 (HSO₃⁻) and 98 (H₂SO₄⁻), two factors were identified as sulfate OA (SO₄-OA) and nitrate OA (NO₃-OA). However a factor related to
ammonium chloride was not identified. This may be due to the lower concentration of inorganic chloride in the atmosphere and thus was difficult to be retrieved by PMF. However, some fraction of chloride (m/z 35 and 36) was apportioned with BBOA, suggestive of common emission source (biomass burning). The results of PMF<sub>OA</sub> were compared with PMF<sub>OA+IOA</sub>. The time series and spectral profile of HOA and BBOA exhibited similar pattern (Figures 3 and 4), thereby indicative of minor influence of merged PMF analysis over these factors. However, slight differences were observed in the time series of OOA-1 and OOA-2. This may be probably due to the apportionment of some fraction of OOA-1 and OOA-2 to SO<sub>4</sub>-OA and NO<sub>3</sub>-OA. Since the chosen fragment ions of sulfate constitutes 63% of the total sulfate mass (measured by ACSM), we are reporting only the presence of ammonium sulfate and quantification of organic and inorganic constituents of sulphate remains a limitation in this study. Besides this, 95% contribution of NOx ions to the total nitrate mass enabled quantification of two forms (organic and inorganic) of nitrate. This was achieved by following the protocol outlined in Xu et al., 2015 (see section 2.4) and will be discussed in section 3.3.

The fraction of mass sticks related to NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>+</sup> accounted for 70% of the total mass of SO<sub>4</sub><sup>-</sup>-OA factor. This indicated that SO<sub>4</sub><sup>-</sup>-OA factor is primarily composed of ammonium sulfate. With high degree of oxidation (O:C ratio ~ 0.7), SO<sub>4</sub><sup>-</sup>-OA factor displayed a relatively flat pattern along the day. This observation indicated the aged and processed nature of SO<sub>4</sub><sup>-</sup>-OA, likely contributed by the regional transport. Based on the (i) close resemblance with sulfate diurnal (ii) high correlation with sulfate mass (r<sup>2</sup> = 0.98; p-value = 0.004) and CO<sub>2</sub><sup>+</sup> ion (r<sup>2</sup> = 0.82; p-value = 0.004), this factor may be characterized as the feature of transported aerosol. Nevertheless, remaining 30% of sulfate related ions were found to form association with organics, as evident from the mass spectral profile of OOA-1 and OOA-2. It
was inferred that the significant noontime peak of OOA factors may account for the photochemical formation of organosulfate, in agreement with the higher rate of sulphuric acid production. The apportionment of $SO_4^{2-}$ related ions in different factors indicated the sources of sulfate aerosol as- (i) long-range transport and (ii) photochemical formation.

Another factor, nitrate OA was dominantly composed of $NH_4^+$ and $NO_3^+$ related ions. With percentage contribution of 69% to the total nitrate mass, this factor was primarily identified as ammonium nitrate. The diurnal pattern of nitrate OA displayed increase in concentration during the evening hours (19:00 to 21:00 h) under enhanced relative humidity and low temperature conditions (Figure 2f). This diurnal profile of nitrate OA synchronized well with the diurnal profile of equilibrium constant between particle phase nitrate and gas phase nitric acid, indicative of the formation of particulate nitrate (DallÓsto et al., 2009; Petetin et al., 2016). However, lower concentrations were observed during other hours of the day. An appreciable fraction of $NO^+$ related ions were found to be associated with OOA factors. These OOA factors displayed a significant noon peak which suggests photochemically produced OOA factors as probable source of organic nitrate (Mather et al., 2004). With the percentage fraction of 36%, $SO_4^{-}$-OA contributed majorly to the total aerosol mass. This was followed by OOA-1 (21%), HOA (17%), BBOA (10%), OOA-2 (10%) and nitrate OA (6%).

### 3.3 Quantification of Organic and Inorganic Nitrate

PMF analysis of OA mass spectra integrated with $NO^+$ and $NO_2^+$ ions (PMF$_{OA+NOx}$) was performed to quantify the organic and inorganic components of nitrate. An additional factor - nitrate inorganic aerosol (NIA) was resolved while retaining the previously resolved PMF factors - HOA, BBOA, OOA-1 and OOA-2 (Figure 5). The mass spectra and diurnal variation of PMF factors are given in Figure 5 and Table S2 gives the correlation between
mass spectra and time series of PMF factors resolved through PMF\textsubscript{OA} and PMF\textsubscript{OA+NOx}. A good correlation (r = 0.96 to 0.98) among different factors validated the individual PMF methodology. In terms of percentage contribution, OOA-1 (32\%) contributed maximum to the total aerosol mass followed by HOA (29\%), BBOA (17\%), OOA-2 (16\%) and NIA (6\%). The NIA factor was characterized by the signals of NO\textsuperscript{+} and NO\textsubscript{2}\textsuperscript{+} at m/z 30 and 46 respectively. On mass basis, these two ions formed 65\% of this factor, with remaining species from organic fragments. The ratio of NO\textsuperscript{+}/NO\textsubscript{2}\textsuperscript{+} for NIA factor was observed as 1.28, which is very much close to 1.11 - a value for NH\textsubscript{4}NO\textsubscript{3} determined while calibration of ACSM. Moreover, the mass concentration of NIA factor correlated strongly (r\textsuperscript{2} = 0.96; p-value = 0.004) with the mass concentration of nitrate (as measured with ACSM), thus referring this factor as NH\textsubscript{4}NO\textsubscript{3} factor. Based on different physicochemical properties of organic and inorganic components of nitrate, NO\textsubscript{x} ions tend to form association with other organic factors as well. Consequently, 62\% of NO\textsubscript{x}-ions were apportioned to NIA factor, 19\% to OOA-2, 13\% to OOA-1, with minor contributions to BBOA (4\%) and HOA (2\%)(Figure 6). Based on this distribution of NO\textsubscript{x} ions with organic and inorganic factors, an estimation of nitrate in organic and inorganic form was made, referred to as organic nitrate and inorganic nitrate respectively. Considering only the OA factors, approximately 86\% of the organic nitrate was found to be associated with OOA factors.

Figure 7 gives the diurnal variation of organic nitrate (ON) and inorganic nitrate (ION). The mean mass concentration of ON and ION was found to be 0.17 ± 0.1 µgm\textsuperscript{-3} and 0.29 ± 0.2 µgm\textsuperscript{-3} respectively. The two forms contributed 38\% (organic) and 62\% (inorganic) to the total nitrate mass. The diurnal variation of ION closely resembled the variation of nitrate aerosol with higher mass concentration than ON throughout the day. Lower ION concentration observed during the daytime with significant enhancement in the evening
This evening high may be due to gas-particle partitioning of HNO₃ under high relative humidity and low temperature conditions (Figure 2f). This feature was evident from Figure S8 as well where production of ION follows synchronous variation with Kp, an equilibrium constant of partitioning of ammonium nitrate. Kp was calculated using equation:

\[ k(T) = k(298) \exp \left\{ a \left( \frac{298}{T} - 1 \right) + b \left[ 1 + \ln \left( \frac{298}{T} \right) - \frac{298}{T} \right] \right\} \]

Where, T is the ambient temperature in Kelvin. \( K(298) = 3.35 \times 10^{16} \, \text{atm}^{-2} \), \( a = 75.11 \) and \( b = -13.5 \).

However, Kp and ION displayed different variation during the morning hours. This variation may be due to (a) less or no availability of precursor gases (sources were mostly inactive) and (b) comparatively high wind speed. Further ON aerosol observed a relatively flat pattern with higher concentration during daytime (14:00 to 16:00 h) and evening hours (20:00 to 22:00 h). Since formation of ON did not follow the Kp path, it is believed that the daytime high was due to photochemical production of ON from the oxidation of biogenic VOCs in the presence of NOx, while nocturnal oxidation of VOCs by nitrate radical led to night-time concentration of ON. The sampling site, being a high-altitude forested site observes high solar intensity and moderate surface temperature, thereby making conditions favourable for the enhanced biogenic VOC emissions and hence a significant source for ON aerosol. Beside this, the \( \text{NO}^+/\text{NO}_2^+ \) ratio for nitrate associated with OOA-2 was observed as ~6.1, much higher than ratio of NH₄NO₃. The higher contribution of organic nitrate (38%) to total nitrate explains the statistically different values for NOₓ ratio. The value of ~6.1 lies close to value of organic nitrate produced from isoprene oxidation (~5; Fry et al., 2009; Bruns et al., 2010) and thus indicative of photochemical oxidation of isoprene as a probable source of organic nitrate at this site. On an average, organic nitrate makes up to 2% of the total NR-PM₁ aerosol with dominance of inorganic nitrate over organic nitrate. To validate the source apportionment result, we have calculated the organic nitrate concentration with conventional NOₓ ratio
method assuming the ratio of $\text{NO}^+/\text{NO}_2^+$ ($R_{\text{ON}}$) first as 5 (formed from isoprene) and second as 10 (formed from monoterpene). The mean concentration of organo nitrate ($0.17 \pm 0.1 \mu \text{gm}^{-3}$) obtained from PMF apportionment methodology lies in between the mean organonitrate concentration obtained from $\text{NO}_x$ ratio method ($0.19 \pm 0.1$ at $R_{\text{ON}}$ 5 and $0.15 \pm 0.1$ at $R_{\text{ON}}$ 10). Figure S9 shows the correlation of calculated organo nitrate by the two methods - PMF method and $\text{NO}_x$ ratio method.

The results are indicative of the presence of organonitrate and organosulfate in the ambient air. However, while dealing with UMR data of ACSM, some interference (~4%) by organic components were observed at $m/z$ 30 in this study. Therefore this may lead to uncertainty in the quantification of organic nitrate and thus the mass concentrations of organic nitrate may be read as an upper limit. Since these aerosol components are the product of atmospheric processing (gas to particle conversion through subsequent adsorption), are believed to be highly oxidized and aged in nature. These species are hence expected to act as cloud condensation nuclei after attaining optimum size under favourable meteorological conditions. However, the quantification of organosulfate warrants further study.

Conclusion

ToF-ACSM was used to measure NR-PM$_1$ aerosol at Mahabaleshwar during the pre-monsoon of 2016. The PMF analysis of organic and inorganic mass spectra was performed to obtain the intrinsic information on interactions between organic and inorganic components of aerosol. For this, PMF was applied on the organic mass spectra merged with inorganics (PMF$_{\text{OA+IOA}}$) and integrated mass spectra of organic with $\text{NO}^+$ and $\text{NO}_2^+$ ions (PMF$_{\text{OA+NO}_x}$). Results of PMF$_{\text{OA+IOA}}$ provided the evidence of presence of organosulfate and organonitrate based on two additional inorganic factors - sulfate OA and nitrate OA. The diurnal variation
of sulfate OA accounted for regional transport and photochemical formation as the major sources while gas-particle partitioning of nitric acid and photochemically formed OOA served as the probable sources for nitrate OA. On an average, sulfate OA and nitrate OA contributed 36% and 6% respectively to the total aerosol mass. The PMF_{OA+NOx} analysis enabled the quantification of organic nitrate aerosol. The total nitrate functionality was contributed with ~38% by organic form and ~62% by inorganic form. The photochemical oxidation of VOCs by hydroxyl and nocturnal oxidation by nitrate radical were recognized as the major sources of organic nitrate during the daytime and late evening hours respectively. The results suggested the relative importance of both biogenic and anthropogenic emissions as the probable sources for organosulfate and organonitrate formation at this site during the study period.

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References


Figure 1: Map showing the Google Earth view of HACPL at Mahabaleshwar

Figure 2: Mean diurnal variation of (a) Organics (b) Sulphate (c) Nitrate (d) Chloride and (f) Temperature and Relative Humidity. The vertical bar represents standard deviation. Figure (e) shows the correlation between predicted NH$_4$$^+$ and measured NH$_4$$^+$. The dotted line represents one to one line.

Figure 3: Mass spectral profile and diurnal variation by PMF analysis of OA mass spectrum (PMFOA) at four-factor solution with $f_{peak}$ =0. HOA, hydrocarbon-like organic aerosol; BBOA, biomass burning-like organic aerosol; OOA-1 and OOA-2, Oxygenated organic aerosol 1 and 2.

Figure 4: Mass spectral profile and diurnal variation by PMF analysis of OA mass spectrum merged with inorganics (PMFOA+IOA) at six-factor solution with $f_{peak}$ =0. HOA, hydrocarbon-
like organic aerosol; BBOA, biomass burning-like organic aerosol; OOA-1 and OOA-2, oxygenated organic aerosol 1 and 2; Nitrate OA, nitrate organic aerosol, Sulphate OA, sulphate organic aerosol.

Figure 5: Mass spectral profile and diurnal variation by PMF analysis of OA mass spectrum merged with NO$^+$ and NO$_2^+$ ions (PMF$_{OA+NOx}$) at five-factor solution with f$_{peak}$ = 0. HOA, hydrocarbon-like organic aerosol; BBOA, biomass burning-like organic aerosol; OOA-1 and OOA-2, Oxygenated organic aerosol 1 and 2; NIA, nitrate inorganic aerosol.

Figure 6: Mass fraction of NOx ions: Apportionment NOx ions among PMF factors

Figure 7: Source apportionment of nitrate - diurnal variation of organic and inorganic forms

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