Chemical composition and characteristics of ambient aerosols and rainwater residues during Indian summer monsoon: Insight from aerosol mass spectrometry

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Abstract: Real time composition of non-refractory submicron aerosol (NR-PM_1) is measured via Aerosol mass spectrometer (AMS) for the first time during Indian summer monsoon at Kanpur, a polluted urban location located at the heart of Indo Gangetic Plain (IGP). Submicron aerosols are found to be dominated by organics followed by nitrate. Source apportionment of organic aerosols (OA) via positive matrix factorization (PMF) revealed several types of secondary/oxidized and primary organic aerosols. On average, OA are completely dominated by oxidized OA with a very little contribution from biomass burning OA. During rain events, PM_1 concentration is decreased almost by 60%, but its composition remains nearly the same. Oxidized OA showed slightly more decrease than primary OAs, probably due to their higher hygroscopicity. The presence of organo

nitrates (ON) is also detected in ambient aerosols. Apart from real-time sampling, collected fog and rainwater samples were also analyzed via AMS in offline mode and in the ICP-OES (Inductively coupled plasma – Optical emission spectrometry) for elements. The presence of sea salt, organo nitrates and sulfates has been observed. Rainwater residues are also dominated by organics but their O/C ratios are 15-20% lower than the observed values for ambient OA. Alkali metals such as Ca, Na, K are found to be most abundant in the rainwater followed by Zn. Rainwater residues are also found to be much less oxidized than the aerosols present inside the fog water, indicating presence of less oxidized organics. These findings indicate that rain can act as an effective scavenger of different types of pollutants even for submicron particle range. Rainwater residues also contain organo sulfates which indicate that some portion of the dissolved aerosols has undergone aqueous processing, possibly inside the cloud. Highly oxidized and possibly hygroscopic OA during monsoon period compared to other seasons (winter, post monsoon), indicates that they can act more efficiently as cloud condensation nuclei.

Keywords: Organic aerosols (OA), O/C ratio, rainwater, monsoon, elemental composition

1. Introduction:

Submicron aerosols constitute a large part of the ambient aerosols and can directly absorb/scatter incoming solar radiation depending upon their composition (Cahill et al., 2008; Carslaw et al., 2013) or indirectly reflect the solar radiation by forming cloud droplets while acting as cloud condensation nuclei (CCN). Due to their smaller sizes, they can also penetrate deep into the human respiratory system and cause several respiratory diseases (Dockery and Pope, 1994; Norris et al., 2000). However, depending upon location and season of the year, their properties can vary greatly; hence it is important to characterize submicron aerosols under different atmospheric conditions. Present study location of Kanpur is situated at the heart of Indo Gangetic

Plain (IGP) and is home to 4.5 million people (GOI, 2011). Kanpur is a major industrial hub of Northern India and considered to be one of the most polluted city in India and World (National ambient air quality standards, 2012). Mostly unregulated industrial emissions, biomass burning and vehicular emissions are the major sources of particulate pollution at this location (Behera and Sharma, 2010a, 2010b; Kaul et al., 2011).

Nearly 60% of the world population depends on the Asian summer monsoon to bring sufficient water for irrigation, drinking water supply and other essential purposes (Hyvarinen et al., 2011). In recent years, several studies have indicated possible effects of pollution on the Summer Monsoon. This may be especially important in Southern Asia since the area suffers from an intense and persistent particulate pollution called the "brown cloud" (Lelieveld et al., 2001; Nakajima et al., 2007; Ramanathan et al., 2007). Hyvärinen et al., (2011) reported 50-70% reduction in $PM_{2.5}$ and PM_{10} concentrations from pre monsoon to monsoon period at a site in the Northern India, however without any detail chemical characterization of $PM_{2.5}$ and PM_{10}. Yadav et al., (2013) characterized non-polar organic compounds of PM_{10} in Delhi during monsoon and reported highest fractional contributions from n-alkanes and BC to PM_{10} due to their hydrophobic nature, which prevented their washout by rain. Several online and offline based aerosol characterization studies have been carried out at this study location as well (Chakraborty and Gupta, 2010; Chakraborty et al., 2015; Kaul et al., 2011; Mishra et al., 2008; Misra et al., 2014), but mostly during winter or summer. Therefore, comprehensive chemical characterization of monsoon time submicron aerosols is yet to be carried out in India, especially types of organic aerosols (OA) present, their contributions and characteristics has never been reported. In this study, with the help of HR-ToF-AMS, we are reporting for the first time what is the composition of OA, what are the different types of OA dominated during monsoon period and how their

oxidation ratios (O/C) evolved apart from changes in different inorganic species like sulfate, nitrate, etc.

In addition to real time aerosol data, we have also collected and analyzed rainwater samples to understand its composition and what kind of species it is scavenging from the ambient air more efficiently. Several rainwater characterization studies have been carried out in India. Kulshrestha et al., (2005) in a review article on India's precipitation chemistry, compiled results from 100 sites with very different characteristics and found that majority of them only measured ions and elements present in the rainwater. Very few characterization study of rainwater organics has been carried out in India. Malik et al., (2007) showed the presence of chlorinated pesticides and PAHs in the rainwater samples collected from Lucknow. Salve et al., (2012) reported the presence of chromophoric organic compounds in rainwater samples collected at Rameswaram. A few studies have also reported the presence of organic acids and acetates in rainwater from India (Khare et al., 1998, 1997; Kulshreshta et al., 1993). However, bulk characteristics of rainwater organics or their overall oxidation levels have never been analyzed. It is interesting to analyze whether OA present inside rainwater are any different from ambient and/or fog water aerosols due to cloud processing and different scavenging efficiencies for different types of ambient OA as reported for fog (Chakraborty et al., 2015; Gilardoni et al., 2014). A real time study of aerosol composition along with OA source apportionment and offline analysis of rainwater in AMS has provided some new insights into the ambient aerosol characteristics during monsoon time.

2. Materials and methods:

Real time, non refractory ambient submicron aerosol sampling (will be referred to as **AA**, from now onwards) was carried out using HR-ToF-AMS from 24 May – 15 Aug 2015. Average

meteorological parameters are shown in Table 1. AMS was operated in V mode with 2 min resolution and regular IE calibration was performed using pure NH_4NO_3 solution.

Parameters	Monsoon
RH (%)	69
T (°C)	29.88
WS (m/s)	3.74
PBLH (m)	1024
Rainfall (mm)	466

Table 1: Average meteorological parameters during monsoon season. PBLH = Planetary boundary layer height.

Apart from NH_4NO_3, pure $(NH_4)_2SO_4$ and KNO_3 were also analyzed in AMS to determine ratios of different sulfate and nitrate fragments in the AMS like SO^+/SO_3^+, SO_2^+/SO_3^+, NO^+/NO_2^+ etc. to qualitatively identify any contributions from organic sulfates and/or metallic nitrates. A silica gel drier was placed in front of the AMS to prevent moisture from entering into the sampling lines. Periodical High efficiency particulate attainment (HEPA) filter measurements were taken to assess and rectify the gaseous interference on AMS mass spectra. Based on these measurements, some modifications are made at m/z 18, 28 & 44 of AMS fragmentation table. AMS data analysis is carried in Igor Pro using SQUIRREL 1.51H & PIKA 1.15H AMS data analysis software packages. HR Fitting in V mode is carried out till m/z 150 and accounts for 99% of the total AMS measured aerosol mass. A collection efficiency (CE) value of 0.5 is applied to AMS dataset to calculate accurately mass concentrations. This CE is chosen after

applying Middlebrook et al., (2012) equation which incorporates aerosol chemical composition, acidity, and RH of sampling line. This value of CE is previously found to be appropriate for most of the locations across the globe including for this location (Bhattu and Tripathi, 2015; Chakraborty et al., 2015) as well. A Vaisala RH & T sensor was operated until the end of July from which we have obtained RH & T values for the campaign. Wind speed and boundary layer height data are obtained from NOAA ARL dataset. A 3 day (72 h) back trajectory cluster analysis is carried out using HYSPLIT model with air masses arriving at every six hour interval at a height of 500 m. This enabled us to understand the major directions from which the wind is coming and possible impact of that.

Rainwater samples collector was placed on the rooftop (10 m above the ground and 1 m from the floor of the roof) of the laboratory building inside which other instruments were housed. Sampling was done manually on event basis using a wet collector, which was fitted with a 1-L borosilicate glass made collecting flask (at the bottom) and polyethylene funnel 26 cm in diameter. Before installation of collectors, the funnels and flasks were carefully cleaned (i.e. soaked in 10% HNO_3 for many hours and rinsed several times with deionized water). During a rain event, rainwater sample was collected after 30 min-1 h interval depending upon the rain intensity, and a minimum of 50 ml rainwater was collected per rain event to make sure that various kinds of analysis can be performed on these samples. Fog water samples were also collected via Caltech 3 stage fog water collector for 2012-2015 winter (December-February) period in 3 size fractions; coarse, medium and fine with 50% size cutoffs at 22, 16, 4 μm, respectively (Kaul et al., 2011; Raja et al., 2008). Immediately after collection, fog, and rainwater samples were filtered through 0.22 μm Whatman Nylon membrane filters to remove suspended insoluble particles. Filtered samples were stored in pre-cleaned polypropylene bottle

in dark at -20°C until further analysis, which was completed within three weeks of the last sample collection.

For analysis, filtered samples were then atomized using an atomizer (TSI Inc., USA) into the AMS after passing through to a silica gel drier (outlet RH < 20%) to prevent clogging of different instrument inlets and to avoid excessive moisture inside the AMS, which otherwise complicates the use of standard fragmentation table. So, essentially in AMS we have analyzed residues of fog and rain droplets, this may have resulted in loss of some small volatile organics like formic acid, formaldehyde etc. However, those species are unlikely to remain in particle phase under ambient conditions as well, so our inferences should still remain valid. This kind of offline analysis with the help of an atomizer has been previously carried out throughout the World (Joshi et al., 2012; Kaul et al., 2014; Lee et al., 2012) to understand different atmospheric processes associated with cloud/fog water, filter extracts. Rain and fog water samples were also analyzed for trace metals in Thermo Scientific ICP-OES (Inductively Coupled Plasma Optical Emission Spectrometer, ICAP 6300 Thermo Inc.). This instrument uses superheated Argon plasma of 7000–10000 K to break down and excite the atoms of the different elements and then identifies the elements from the characteristic wavelength emitted during the excitation process. It is a fairly rapid process and can identify up to 60 elements simultaneously. The instrument was calibrated using a multi-element standard, and samples were blank corrected. Ten rainwater samples were also analyzed in ion chromatography (Metrohm compact IC 761), for three anions (Cl^-, NO_3^-, SO_4^{2-}). Details of IC and ICP-OES detection limit and methods can be found in Chakraborty and Gupta, (2010).

3. Results and discussion:

3.1 Composition and characteristics of ambient aerosols:

AMS results reveal that monsoon time AA (Ambient aerosols) is dominated by organics as observed for other seasons as well (winter, post monsoon) at this location (Bhattu and Tripathi, 2015; Chakraborty et al., 2015; Kaul et al., 2011). Sulfate is the second most dominant species in AA followed by ammonium and nitrate (Fig. 1&2). Chloride is almost nonexistent during the sampling period. Diurnal variations of different aerosol species (Fig. 2) revealed that all species concentration peaked during the night, possibly due to lower boundary layer height, whereas observed decrease during the afternoon was caused by boundary layer expansion and enhanced mixing. Decrease in sulfate during the afternoon is relatively less pronounced, indicating that it is simultaneously being produced via photochemistry. Sulfate and nitrate are completely neutralized by ammonium which leads to non-acidic aerosols (Fig. 3) with ANR close to 1.

The aerosol neutralization ratio (ANR, equation 1) is defined in terms of the measured NH_4^+ (m)/NH_4^+ (p) ratio (Chakraborty et al., 2015) as follows:

ANR = NH_4^+measured (m)/NH_4^+predicted (p) ratio=

$$\frac{NH_4^+\,(m)}{18 \times \left(2 \times \frac{SO_4^{-2}\,(m)}{96} + \frac{NO_3^-(m)}{62} + \frac{Cl^-(m)}{35.5}\right)} \qquad (1)$$

where NH_4^+ (m), SO_4^{-2}(m), NO_3^-(m) and Cl^- (m) are the measured AMS mass concentrations of ammonium, sulfate, nitrate, and chloride, respectively, and NH_4^+ (p) is the predicted mass concentration of ammonium that was obtained by assuming that ammonium was the only cation that balanced these anions.

However, cation to anion ratio calculations in AMS can be misleading in case organo nitrates, organo sulfates and/or sea/mineral salts are present in the aerosols. We found that NO^+/NO_2^+

ratio of AA (= 9.89) is much higher than the value obtained from IE calibrations with pure NH_4NO_3 (= 3.5), indicating the presence of other forms of nitrate apart from NH_4NO_3. Mineral nitrate salts are usually associated with supermicron particles, and they have a very high NO^+/NO_2^+ ratio (around 40), sea salt particles are also associated with larger particles (Ovadnevaite et al., 2012) and have a very high NO^+/NO_2^+ ratio (Farmer et al., 2010). For the present AMS, NO^+/NO_2^+ ratio for pure KNO_3 is 50, way above the observed ambient NO^+/NO_2^+ ratio of 9.89, indicating negligible contributions of sea salt/mineral nitrates to submicron AA.

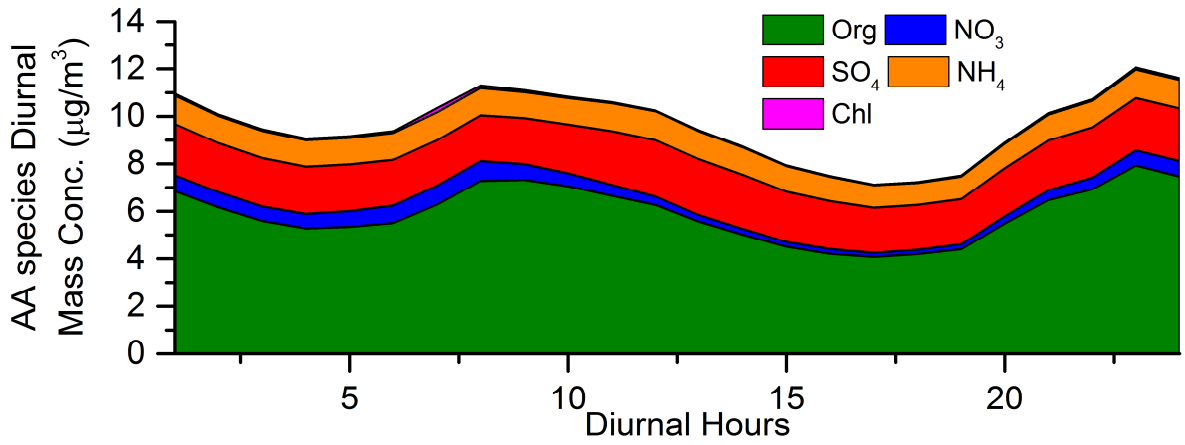


Fig. 1: Diurnal profile of different NR-PM_1 species.

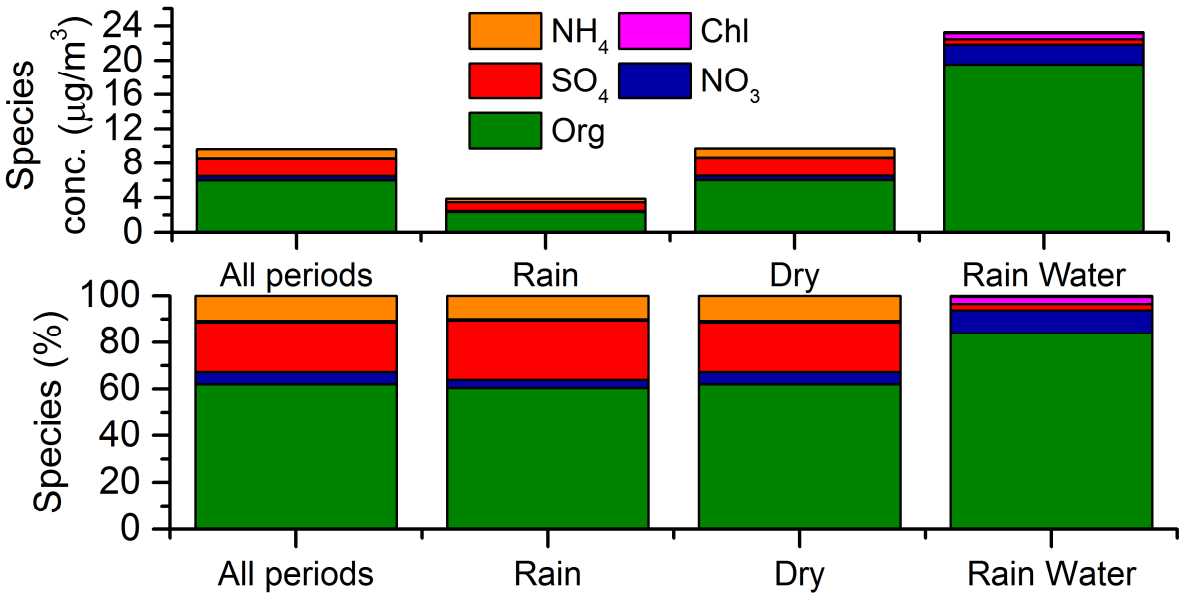
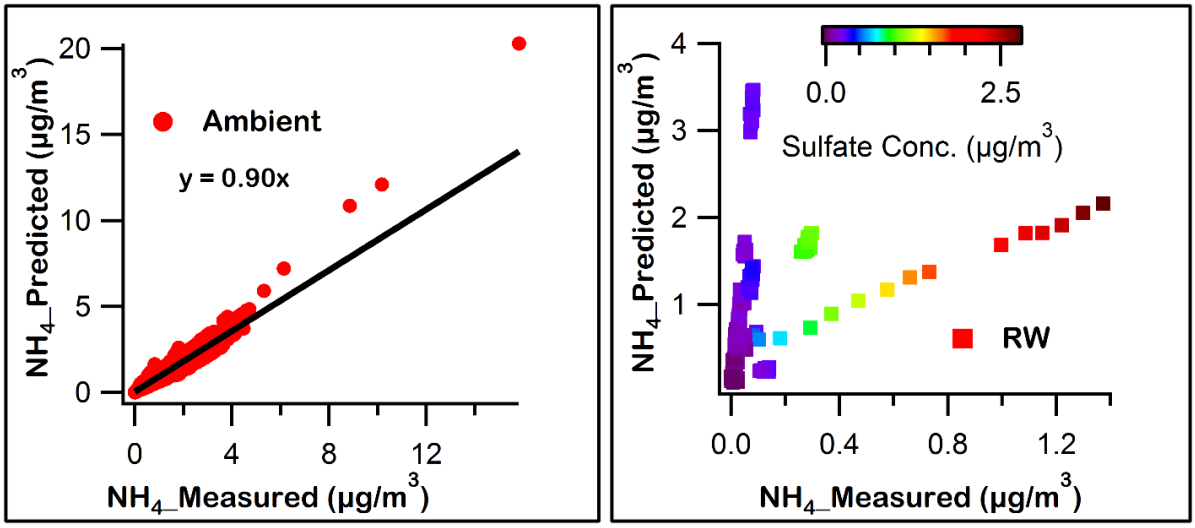


Fig. 2: Mass conc. and relative composition of NR-PM_1 aerosols present in ambient and rainwater (although rainwater concentrations may not be the representative of actual ambient concentrations as it is measured offline via atomization). "Rain" indicates PM_1 composition during rain events, while "dry" indicates PM_1 composition non rainy periods.

However, the observed NO^+/NO_2^+ ratio is very close to that reported for Organo nitrates (ON) in the literature (Farmer et al., 2010). Several organic nitrate fragments like; CH_4NO^+, $C_2H_5NO^+$, $C_3H_4NO^+$ have also been observed in AMS HR mass spectra of AA, this confirms the presence of ON in AA. This also indicates that AA was probably alkaline in nature as AMS fragmentation table assign all nitrate fragments (NO^+,NO_2^+) to inorganic nitrate while some part of those fragments was actually originated from organic nitrates. This means that AMS is overestimating the inorganic nitrate and in spite of that, an ANR value close to 1 (Fig. 3) indicates that excess amount of ammonium is present in the ambient aerosols. However, some of this excess ammonium may be associated with organic acids which are not included in acidity calculations. This hypothesis is also supported by the positive correlation of f44 (AMS marker for organic

196 acids) with ANR (Fig. S1) and also reported in a filter study from this location (Singh and Gupta,
197 2016). So, it's difficult to say conclusively whether AA was alkaline in nature or not, but higher
198 pH values (range: 6.75-7.82) of rain water samples indicates that AA was most likely alkaline in
199 nature. During rain events, overall composition changes only a little from dry time periods,
200 however, the mass concentration of AA reduced significantly during these rain events (9.76 to
201 3.88 µg/m^3, Fig. 2).



202

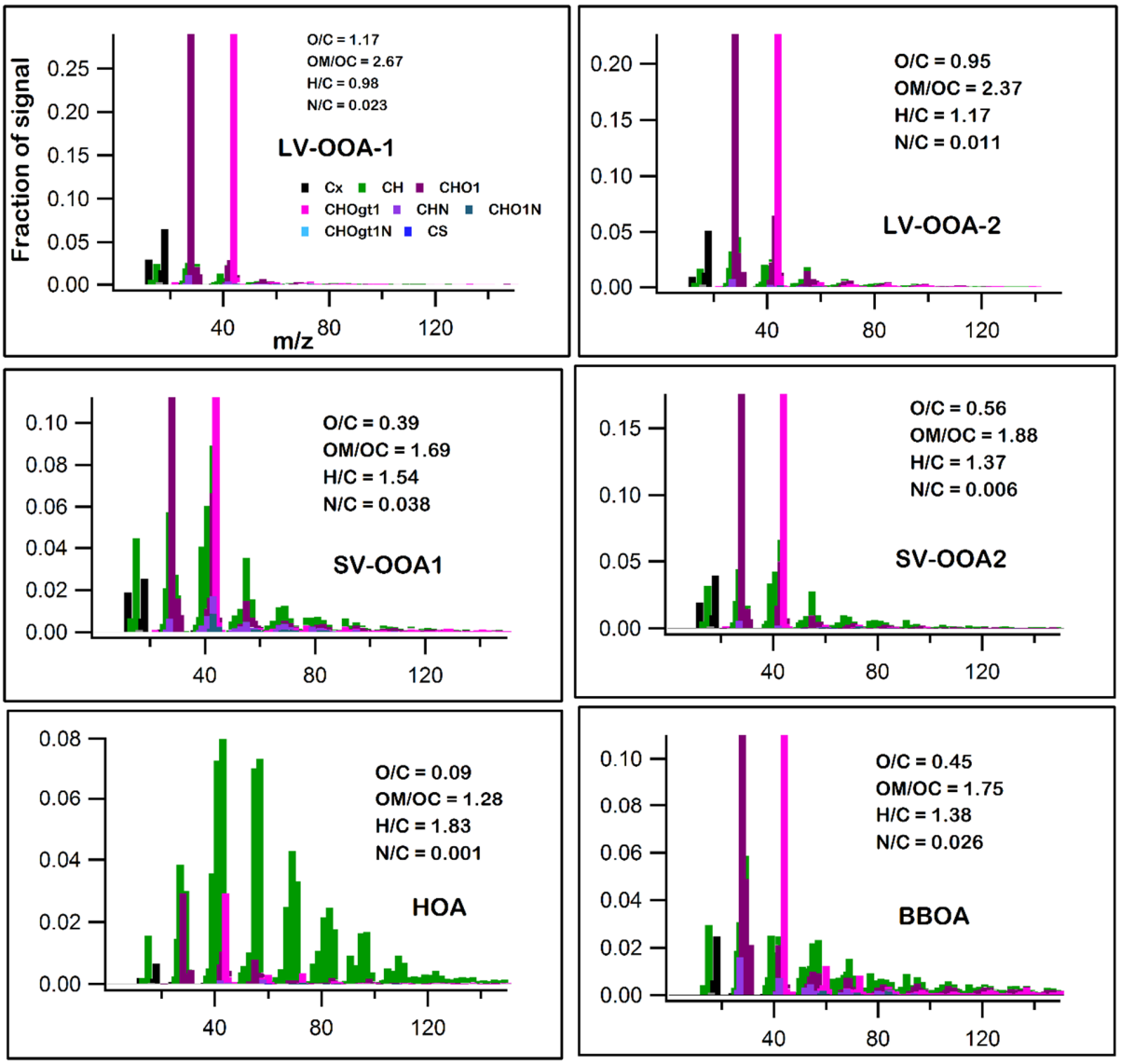
203 Fig. 3: Plot of AMS measured ammonium vs. required ammonium for neutralizing the anions.
204 RW measured ammonium is way below the required value for complete neutralization.

205 During rain events, AA (ANR = 0.87) are found to be slightly more acidic than dry periods
206 (ANR = 1.04), mostly because of increased contribution from sulfate. Cloud processing is an
207 important source of atmospheric sulfate (Moore et al., 2004; Raja et al., 2008), so it's possible
208 that additional sulfate was produced inside the cloud and then came down with the precipitation,
209 thus increasing its net concentration. No/little change in AA composition during rain events
210 indicates that rain can equally efficiently remove all aerosols species. Sulfate showed a slight
211 increase during the afternoon, indicating its photochemical production. Decrease in nitrate

concentration during daytime can be attributed to increased boundary layer height and higher temperature which drives most of the particulate nitrate into gas phase.

3.2 OA sources, composition, and characteristics:

To gain further insight into the ambient OA composition and characteristics, source apportionment via PMF (Paatero and Tapper, 1994; Ulbrich et al., 2009) is performed on the HR organic mass spectra of AMS. PMF analysis is carried out with fpeak range of +5 to -5 with 0.5 increments and up to 12 factors. PMF factors are chosen based on their interpretability, PMF diagnostics and factors correlation with external tracers (Fig. S2 & S3). The detailed rationale for selecting the factors can be found in the supplementary information (SI). Three major types of OA are identified, oxidized OA (OOA), Hydrocarbon like OA (HOA) and biomass burning OA (BBOA). Chosen PMF solution has six factors (Fig. 4) but for diurnal variations and mass concentrations, we have clubbed similar types of factors such as LV-OOA-1, 2 to LV-OOA and SV-OOA1, 2 to SV-OOA thus reducing the number to 4 (Fig. S4). Time series of factors with similar mass spectra and elemental ratios can be clubbed and presented as one factor, which can make data representation much easier and has been followed in several studies (Docherty et al., 2011; Timonen et al., 2013; Ulbrich et al., 2009). Detail description of these factors and their diurnal variations can be found in supplementary (Section 1.1 and fig. S4).



230

231 Fig. 4: Different types of OA, as identified by source apportionment of AMS ambient HR OA

232 mass spectra via PMF.

233 Higher contributions from primary OAs (HO+BBOA) during early morning rush hours and night

234 (Fig. S4) explains the significant diurnal variations in OA with peak concentration during those

235 two periods (Fig. 1) of the day. Lower boundary layer height during those two time periods of

236 the day may have also contributed to those observed peaks.

Elemental ratios of ambient OA also showed strong diurnal variations with O/C ratio peaking in the afternoon (Fig. 5) and dipping after sunset. Overall, daytime O/C ratio of 0.68 is much higher than night time O/C ratio of 0.58. Peaking of O/C ratio during afternoon coincides with the intense photochemistry and higher concentration of most oxidized LV-OOA (Fig. S4). Reduced O/C ratio during night time and early morning hours resulted from the absence of photochemistry with the higher concentration of primaty OAs (HOA+BBOA) from traffic emissions and burning activities (Fig. S4).

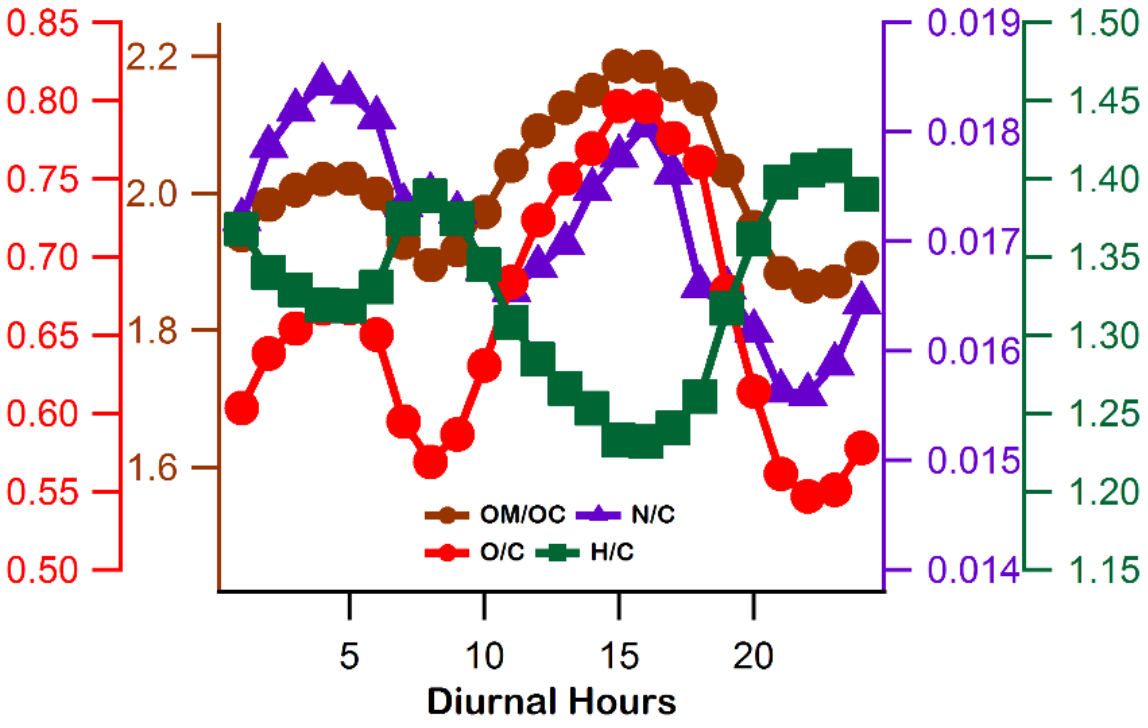


Fig. 5: Diurnal elemental ratios of ambient NR-PM_1. Daytime peak in O/C ratio clearly indicates production of oxidized OA via photochemistry.

OM/OC ratio followed the exactly similar trend as O/C ratio as expected while H/C ratio followed an opposite trend of O/C. Interestingly, during rain events, O/C of AA showed some reduction, from 0.67 during the dry period to 0.60 during rain events. This indicates that rain is

scavenging highly oxidized organics with a higher efficiency, possibly due to their higher polarity arising from higher oxygen content as reported for fog events from a previous study (Gilardoni et al., 2014). This is also evident from OA composition of monsoon time OA, which is completely dominated by oxidized OA (Fig. 6), with 85% mass of total ambient OA. Among oxidized OA, LV-OOA dominates over SV-OOA, indicating very high oxidation capacity of monsoon time ambient air and/or impact of long range transport as observed from the back trajectory analysis (Fig. S5). Among POAs, HOA dominates over BBOA, which is expected given that very low biomass burning activities are prevalent during monsoon time. During rain events, although OA mass decreased significantly by 60% (Fig. 6) overall OA composition remained the same (Fig. 6), indicating that rain droplets effectively scavenged all types OA. However, a slight enhancement in HOA contribution to ambient OA was observed during rain events (Fig. 6) which may indicate that efficiency of scavenging was slightly higher for other relatively more oxidized organics as compared to very less oxidized HOA.

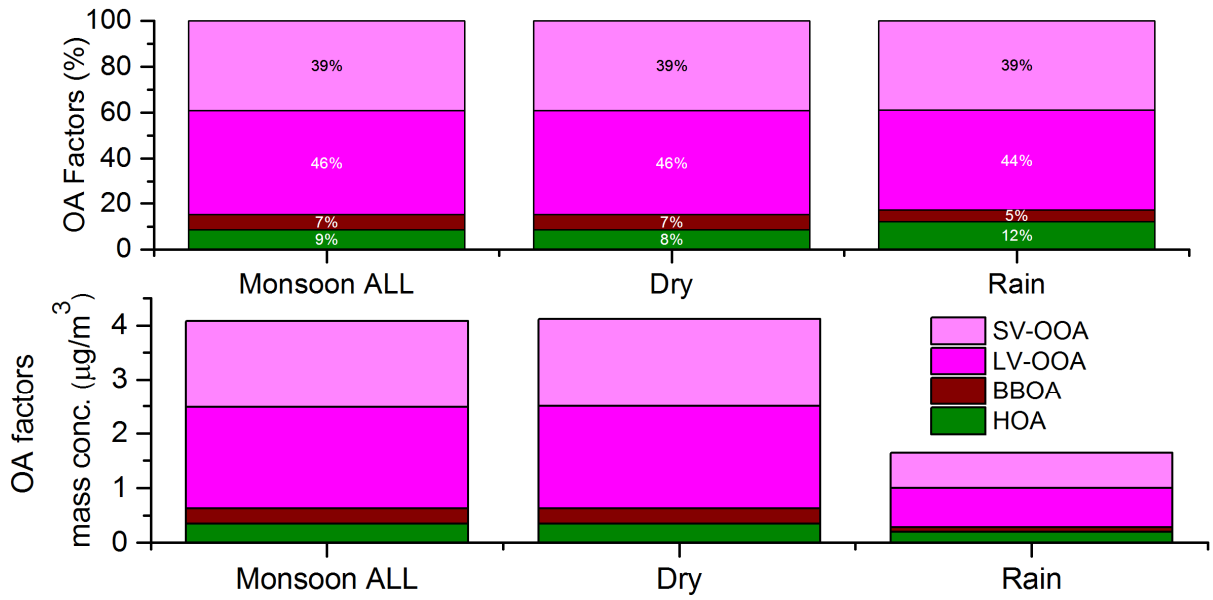
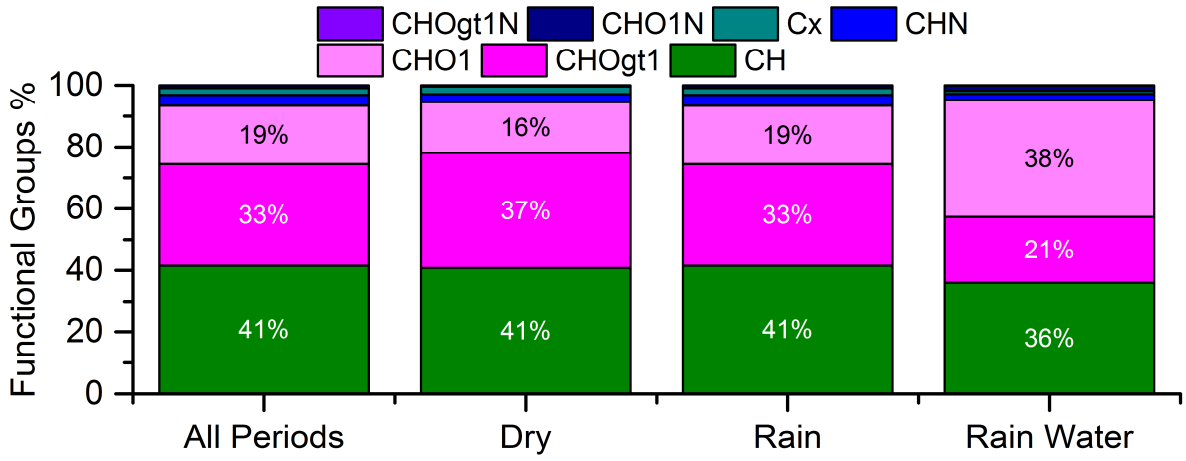


Fig. 6: Relative contributions of different types of OA to the total OA. Ambient OA is overwhelmingly dominated by oxidized OA. Dry = non rainy periods.

Changes in OA elemental characteristics is examined via Van Krevelen (VK) diagram (H/C vs. O/C plot), which shows that OA elemental ratios changes along a slope of – 0.72. Slopes of VK diagram can sometimes be used to gain insight into OA aging mechanism, a relatively shallow slope of -0.72 indicates the possible addition of –COOH/-OH functional groups to the carbon backbone (Heald et al., 2010; Ng et al., 2011). However, a particular slope or changes in slopes of VK diagram can also be caused by mixing of different types of OA from various sources, especially under ambient conditions. Thus, it's difficult to conclude whether the observed slope is due to the addition of some particular functional groups, a particular type of oxidation mechanism or due to mixing of different types of OA.

Ambient OA is dominated by oxidized organics fragments (aldehyde/acid/ketone etc.) as seen from OA functional group composition in the AMS (Fig. 7). CHO1, CHOgt1 fragments (organic fragments in AMS containing one and more than one oxygen, respectively) which are mostly generated from carbonyls and organic acid compounds (Ng et al., 2011; Takegawa et al., 2009; Zhang et al., 2007), contributes more than half of the ambient OA. CH fragments which mostly comes from less oxidized hydrocarbon like organics (Ng et al., 2011; Takegawa et al., 2009), contributes almost 40% to the total OA. However, OA functional group composition has changed little from dry to rainy periods while O/C ratio has decreased substantially (0.67 to 0.60) as mentioned earlier. These findings are at odds with each other; however, it is possible that higher oxygen containing fragments of the CHOgt1 group have been removed more preferentially during rain events thus leading to this substantial O/C ratio change but keeping overall functional groups composition almost the same. A slight increase of less oxidized HOA

287 contribution and subsequent decrease in most oxidized LV-OOA contribution to total OA (Fig.
288 6) during rain events can also explain this observed O/C decrease. During monsoon time,
289 biomass burning activities in northern India are usually not very frequent or intense, which is
290 also reflected in the PMF results with only 7% contribution from BBOA.



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292 Fig. 7: Contributions of different functional groups to total OA. Organics are dominated by
293 oxidized functional groups under all circumstances.

294 Marker for biomass burning in AMS is m/z 60 or $C_2H_4O_2^+$, originates from levoglucosan
295 fragmentation, its average relative contribution of 0.4% to total OA (m/z60/total ambient OA or
296 f60) during the campaign period (Fig. 8) is very close to the typical background level f60 of
297 0.3%, as mentioned in Cubison et al., (2011). This indicates that overall, a minor fraction of
298 ambient OA originated from biomass burning activities during the campaign period. However,
299 variations in f60 values are quite large, which means that some of the time periods were
300 influenced by biomass burning activities and/or some other sources like coal combustion, which
301 can also generate OA containing $C_2H_4O_2^+$ fragments (Wang et al., 2013). A strong anti-
302 correlation is also observed between f60 and f44 (m/z 44/total OA), which indicates that primary

biomass burning OA (BBOA) are being oxidized to organic acids (as represented by f44 (Ng et al., 2011; Takegawa et al., 2009)).

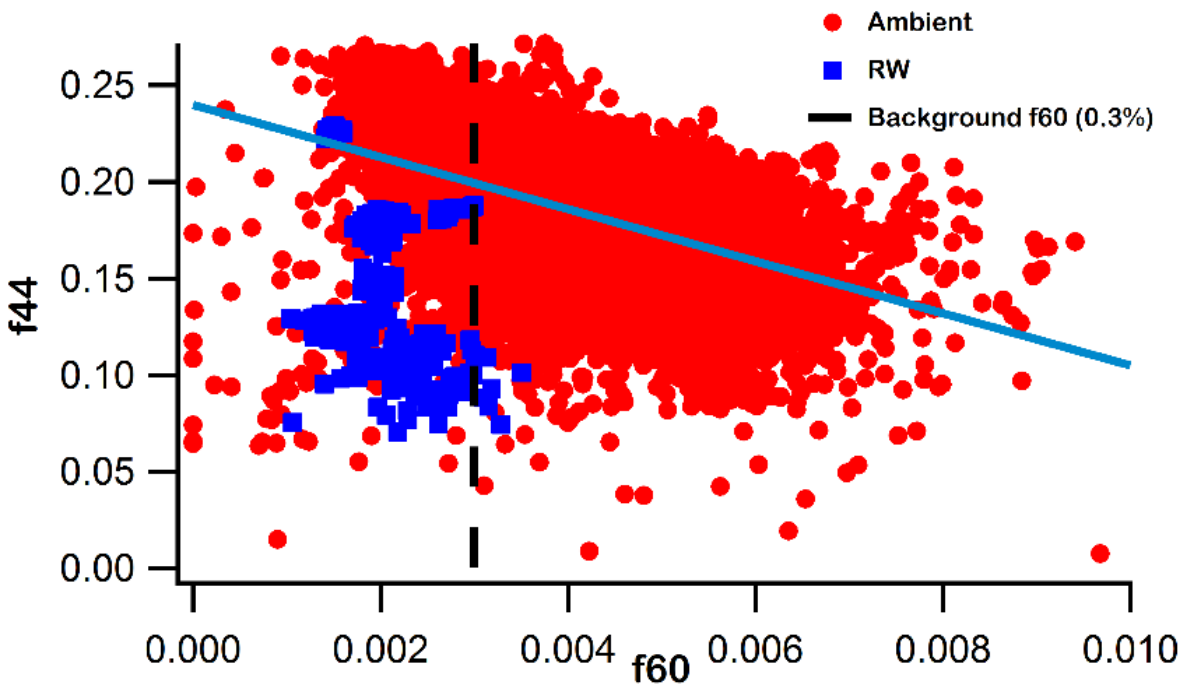

Fig. 8: Plot of f44 (a marker for carboxylic acids) vs. f60 (a marker for biomass burning). Strong anti-correlation is observed for ambient OA while none is there for rainwater organics. In rainwater f60 is below background level (0.3%), indicating that biomass burning OA may not be very water soluble. Similar observations were also made during an aircraft based study at Mexico City (Cubison et al., 2011).

3.3 Comparison of monsoon time ambient OA composition with other seasons:

Ambient OA loading and composition during monsoon time is very different from what was observed during post monsoon and winter time (Bhattu and Tripathi, 2015; Chakraborty et al., 2015) at this location. OA loading during monsoon (= 7.2 µg/m^3) is almost 10-15 times lower

316 than what was observed during post monsoon (= 72 µg/m^3, November 2012) and winter (= 110
317 µg/m^3, Dec 2012 – Jan 2013) (Chakraborty et al., 2015). Average O/C ratio during monsoon (=
318 0.65) is also higher than that observed for post monsoon and winter season (= 0.50 and 0.55,
319 respectively). This is not surprising as the dominance of oxidized OA in OA composition is
320 much more pronounced during monsoon than winter or post monsoon. During winter and post
321 monsoon oxidized OA contributed 57% and 69%, respectively to total OA, while during
322 monsoon that contribution is 85%, clearly indicating that during monsoon time OA was more
323 oxidized than other two seasons. However, during fog events O/C ratio of wintertime ambient
324 aerosols was increased by 15-20% while during rain events, O/C ratio of monsoon time AA was
325 decreased. This is possibly due to enhanced production of oxidized organics inside fog droplets
326 (Chakraborty et al., 2015; Ervens et al., 2011; Ge et al., 2012; Kaul et al., 2011) during fog
327 events which countered the removal of oxidized organics via fog scavenging and resulted in O/C
328 enhancement. Larger rain droplets can act more efficiently as a scavenger than smaller fog
329 droplets while due to their larger sizes, they have less residence time in ambient compared to
330 much smaller fog droplets. This possibly led to more scavenging and less aging/processing of
331 ambient aerosols. Apart from that, nature of aqueous processing and their end products may vary
332 significantly from more concentrated fog droplets to much diluted rain drops as reported for
333 cloud/fog droplets and aerosol water (Ervens et al., 2011).

334 Biomass burning contribution to OA was many times higher during the Nov-Jan period
335 compared to monsoon period. This is expected because of crop residue burning that takes place
336 every year during October – November (Bhattu and Tripathi, 2015) in Punjab and Haryana
337 (Northwestern part of India) and during winter, people in northern India burn several types of
338 biomass to get respite from cold (Behera and Sharma, 2010a; Kaul et al., 2011). So, huge

emissions of primary OA like BBOA, high OA loading and relatively weak solar radiation during winter than monsoon have possibly caused this lower O/C ratio in winter compared to monsoon. Also, unlike monsoon, no organo nitrates were identified in ambient aerosols during those two seasons, indicating atmospheric processes may have been different during the monsoon period.

3.4 Analysis of rainwater residues composition:

3.4.1 Inorganics:

Collected rainwater samples were analyzed in AMS. Each sample was atomized then passed through the silica gel drier and then put into AMS for 30 minutes, and a few samples were repeated twice to check reproducibility, which was excellent as every parameter was within 5% of the original values during the duplicate run. Like AA, rainwater residues (RS) are also dominated by organics and this dominance is even more pronounced in RS than AA (Fig. 2). Unlike AA, instead of sulfate, nitrate is the second most dominant species in RS, followed by sulfate and chloride. Ammonium concentration is almost negligible which led to ANR ratio of 0.11 for RS from AMS data, indicating that RS is extremely acidic. However, for the present case, this ratio is very misleading as pH measurements of rainwater revealed it's mildly acidic to alkaline nature with pH varying from 6.75-7.82. Apart from that concentration of alkali metals like Ca, Mg, K , Na detected via ICP-OES is found to be sufficient for complete neutralization of major anions (Cl^-, NO_3^-, SO_4^{2-}) detected via IC. Extremely low ANR for RS thus represents an artifact of AMS measurement due to the presence of organo nitrates, organo sulfates and/or sea salts like NaCl, KNO_3, and $NaNO_3$. The Very high average NO^+/NO_2^+ ratio of 14 (this value is almost 40% higher than the observed value of 9.81 for AA) for RS is also an indication of that. We have also detected very high concentrations of Na, K in RS from AMS data, much higher

than the values detected in AA, but part of these metals can also come from AMS vaporizer itself (Canagaratna et al., 2007; DeCarlo et al., 2006). Although this makes quantification of Na and K difficult in AMS, their relative trends can still be considered to gain insight into changes of K, Na concentration in ambient air (Slowik et al., 2010). AMS measured Na^+ and chloride concentrations in rainwater residues are highly correlated ($R^2 = 0.93$) while the correlation between NH_4^+ and Cl^- is moderate ($R^2 = 0.50$). Also, correlation between AMS measured real-time Na^+ and Cl^- is nonexistent ($R^2 = 0.02$) in AA, indicating that in RS, Na^+ is mostly in NaCl form originating from sea salts. Sea salts are usually associated with larger super micron particle sizes (Li et al., 2003; Murphy et al., 1998) and hence not detected during online sampling of AA via AMS.

K^+ and Na^+ concentrations in RS are 15 & 17 times higher than the concentrations of these elements found in AA. In RS, K^+ concentrations are on average ten times higher than K^+ in AA. Also, K^+ concentrations are much higher than that NH_4^+ in RS, while the opposite is true for AA. This suggests that a large part of the observed K^+ in RS originated from different sources as compared to that present in AA. Since biomass burning activities were minimal during summer monsoon and f60 levels are below background level in rainwater (Fig. 8), so another plausible source of K is sea /mineral salt in the form of KNO_3. Sea salt aerosols contain a high amount of KCl, which can be converted to KNO_3 and K_2SO_4 during transport from source to receptor location by interacting with nitrate & sulfate present in ambient air (Li et al., 2003; Song et al., 2005). Correlations between K^+, Na^+, and NO_3^- are also much better than that of NH_4^+ and NO_3^- (Fig. S6), indicating that in RS significant portion of nitrate may have come from KNO_3/$NaNO_3$. However, in AA, no correlation is observed between AMS measured K^+ and NO_3^- ($R^2 = 0.01$), indicating sources of nitrates were somewhat different for AA and RS. Also, with the inclusion

385 of AMS measured K^+ and Na^+ concentration as cations in rainwater ANR calculation, value
386 increased significantly to 0.72 from 0.11 (with NH_4^+ as the only cation), indicating that most of
387 the anions are accounted for by these three cations. We have also identified some of the ON
388 fragments in AMS mass spectra of RS, similar to that of ambient OA. This indicates that some
389 ON is also present in rainwater OA as well, so it seems a combination of metallic and organo
390 nitrates resulted in such high NO^+/NO_2^+ ratio (= 14) for RS. Interestingly, the correlation
391 between NH_4^+ and NO_3^- is slightly better for lower values of NH_4^+, while the correlation of NH_4^+
392 with SO_4^{-2}, in general, is much stronger than with NO_3^-. This indicates that higher values of
393 NH_4^+ were associated mostly with SO_4^{-2} (Fig. 3).

394 **3.4.2 Elemental and sea salt contribution to rainwater residues**

395 Rainwater residues also contain several elements including some trace metals like Cu, Zn as
396 detected by ICP-OES. Among elements, Ca, Na, and K are 3 of the most abundant ones followed
397 by Mg, Zn, Mn, Cu & Ni (Fig. S7, 9). This finding also confirms that the AMS is capturing the
398 trends of Na^+, K^+ well as it also detected very high Na^+ and K^+ values. Other elements of Fe, Cr,
399 V, Pb were found to be below the detection limit of ICP-OES. The presence of K in spite of low
400 biomass burning activities indicates that it may have originated from sea salt. The abundance of
401 Na also indicates sea salt presence in the rainwater as observed in some other studies conducted
402 in Northern India (Satsangi et al., 1998; Tiwari et al., 2008, 2006), its strong correlation with K
403 indicates that both are being originatedd from similar sources. Zn present in the rainwater
404 residues may have come from tire wear, from tail pipes of the vehicles. Cu can also emit from
405 similar sources as Zn (Aatmeeyata and Sharma, 2010; Aatmeeyata et al., 2009). Ca usually found
406 in soil but there are some anthropogenic sources for it as well. To get an idea about possible
407 sources of these metals we have calculated their enrichment factors (EF).

$EF = (X/X_{ref})_{rainwater}/(X/X_{ref})_{crustal}$,

Where X = Element in question, X_{ref} = Reference element of predominantly crust origin (Mn for this study)

EF are calculated using Ca as reference element as mentioned in several previous studies (Ghosh et al., 2014; Loska et al., 2005, 2004). EF ~ 1, usually indicates crustal, non-anthropogenic sources, while EF> 10 indicates a significant contribution from anthropogenic sources (Wang et al., 2009, 2006). Calculated EF is highest for Zn followed by Cu, K, Na, and Mg. Only for Zn, EF values are consistently above 10 in almost all the samples, indicating their anthropogenic origins, while EF for Mg is consistently below one across the samples, indicating its crustal origin (Fig. S7, 9). For K and Na, EF values are mostly below or slightly above 1 and matches well with the values reported for marine aerosols by Weller et al., (2008), which means that they mostly originated from natural sources (sea salt/crustal sources) with very low contributions from anthropogenic emissions. In general, elements in smaller aerosols size fractions (PM_1, $PM_{2.5}$) have much higher EF values compared to larger size fractions (PM_{10}, TSP) because of higher anthropogenic contributions in finer fractions of PM. Therefore, much lower EF values of different elements in rainwater residues support the hypothesis that rain droplets trapped mostly larger, super micron size particles.

3.4.3 Characteristics of rainwater organics:

Relative contributions of different functional groups to residual rainwater organics (will be referred to as residual OM from now onwards) are also different from that of ambient OA. Although residual OM is also dominated by oxidized functional groups (CHO1, CHOgt1) like ambient OA, this dominance is more pronounced in rainwater than ambient. Apart from that,

unlike ambient OA where CH functional group dominates, in rainwater organics, CHO1 group fragments are the most abundant ones (Fig. 7). However, in the case of ambient OA, more oxidized CHOgt1 fragments dominate over less oxidized CHO1 fragments, while the opposite is true for residual OM, this has led to higher O/C ratio of ambient OA (O/C = 0.66) compared to residual OM (O/C = 0.57). Observed O/C ratio of residual OM is also well within the range of values (0.4 ± 0.3) reported for rain/cloud water organics via FT-ICR-MS in other studies (Mead et al., 2013; Zhao et al., 2013). As in the case of ambient OA, residual OM also showed variation in O/C ratios from day to night time samples of rainwater, with daytime O/C ratio of 0.59 is found to be higher than the night time O/C ratio of 0.52. However, both day and night time O/C ratios of residual OM are lower than the values observed for ambient OA (= 0.68 & 0.58, respectively). Some of these differences between RS and AA can be explained by the fact that rainwater can also scavenge and dissolve constituents of much larger particles than PM_1 very efficiently (Croft et al., 2009; Henzing et al., 2006), which are mostly associated with mineral dust, soil resuspension and sea spray with low organics content (Whitby and Cantrell, 1976). However, in real time ambient sampling scenario AMS can only sample PM_1 dominated by organics.

One interesting finding is the presence of organic sulfates in AMS HR mass spectra of residual OM while none is found in ambient OA mass spectra. Organic sulfates can be present in the atmosphere as sulfur adducts like; HMS (Hydroxymethanesulfaonate), MSA (Methanesulfonic acid, CH_3SO_3H) or as separate organo sulfur (OS) compounds. Typical organic sulfur fragments which are detected from AMS HR spectra in previously reported studies (Farmer et al., 2010; Ge et al., 2012) includes; $CH_2SO_2^+$, $CH_3SO_2^+$, $CH_2SO_3^+$ and CHS, etc. Almost all of those fragments are observed in collected RW samples (Fig. S8) confirming the presence of organo sulfur

453 compounds. These mainly originate from sulfur adducts to organic compounds like HMS, MSA.
454 Actual OS compounds usually get fragmented to SO^+, SO_2^+ due to hard ionization of AMS.
455 However, if OS are present in sufficient quantity, then ratios like SO^+/SO_3^+, SO_2^+/SO_3^+ get
456 enhanced significantly as OS don't produce SO_3^+ fragments (Ge et al., 2012), so one can identify
457 qualitatively whether OS are present or not. For quantitative assessment, several OS standards
458 need to be run in the AMS, which unfortunately was not carried out in this study. Ge et al.,
459 (2012) developed an empirical method of calculating mass concentration of MSA from AMS
460 organo sulfur fragments like $CH_2SO_2^+$, $CH_3SO_2^+$ and $CH_4SO_3^+$, using that method we found that
461 MSA is contributing 9.5% of OOA (8% of total OA), which is much higher than 0.5% (of OOA)
462 reported by Ge et al., (2012) during foggy time, clearly indicating that here in RW, contributions
463 of organic sulfates are quite high. Hansen et al., (2015) recently shown from laboratory studies
464 that presence of organo sulfates can act as a very effective hygroscopic material and can reduce
465 the surface tension of a solution compared to pure water, especially in presence of inorganic salts
466 like ammonium sulfate. This indicates that organo sulfates can enhance the hygroscpocity of rain
467 water residues and they can more effectively work as condensation nuclei (CCN). In RS, almost
468 an order of magnitude enhancement in SO^+/SO_3^+, SO_2^+/SO_3^+ ratio (= 35 & 44, respectively) is
469 observed when compared to SO^+/SO_3^+, SO_2^+/SO_3^+ (= 6 & 7, respectively) ratio of pure
470 ammonium sulfate for the present AMS, which clearly indicates the presence of OS in rainwater.
471 Dissociation of dissolved metallic sulfates like K_2SO_4, $CaSO_4$ can also alter this sulfate
472 fragmentation ratios. However, dissociation of metallic sulfates usually occurs at much higher
473 temperatures (Stern, 1974) than 600°C, so chances of their flash vaporization (within a few
474 seconds) at 600°C in AMS are very low (Drewnick et al., 2015). Some metallic sulfates can also
475 produce SO_3 fragment during decomposition which can actually bring down those above

476 mentioned ratios. Apart from that SO^+/SO_2^+ ratio for RS and AA are close to each other (= 0.68
477 & 0.77, respectively). These findings indicate that enhancement in SO^+/SO_3^+, SO_2^+/SO_3^+ ratios
478 are mainly due to the presence of OS.

479 The presence of OS is interesting as it considered to be a marker of aqueous processing and also
480 found in fog water samples (Dall'Osto et al., 2009; Ge et al., 2012). It's possible that cloud
481 processing of organics and sulfur led to this formation of OS and sulfur adducts. However,
482 generally cloud processing led to the production of highly oxidized organics and enhancement of
483 O/C ratio (Ervens et al., 2011) but observed O/C ratio for residual OM is lower than ambient OA
484 as mentioned earlier. It is possible that larger, super micron particles, present in rainwater
485 contained less oxidized organics and given that 50-90% of the organics are found in submicron
486 particles (Hallquist et al., 2009; Ng et al., 2011) this finding is not surprising. The Larger
487 particles are also generally associated with mineral dust, soil resuspension and sea spray with
488 low organics content (Whitby and Cantrell, 1976). Another explanation could be underestimation
489 of oxygen content in OS and/or ON compounds by AMS, as their fragments like
490 NO^+,NO_2^+,SO^+,SO_2^+ are typically treated as inorganics by standard AMS fragmentation table
491 (Allan, 2003; Farmer et al., 2010). As mentioned the earlier significant presence of OS
492 compounds detected in residual OM, so this may have led to O/C underestimation. In residual
493 OM, no anti correlation between f60 and f44 is observed (Fig. 8), in fact, f60 values are below
494 back ground levels (< 0.3%) in residual OM, and this may indicate that organics from BB at this
495 location is not water soluble and/or it has been converted to some other oxidized form via
496 ambient oxidation processes (photochemistry/aqueous processing) (Cubison et al., 2011; Zhao et
497 al., 2014).

498 **3.4.4 Comparison of rain and fog water characteristics:**

Rain and fog both are natural cleansing agents but with very different characteristics like fog droplets forms at ground level while rain droplets forms at an elevated level inside clouds. Rain droplet sizes are usually much bigger and have much higher amount of LWC than fog droplets, so it can more efficiently remove ambient aerosols. So, by comparing we are trying to understand whether aerosol composition and chemistry are different within these two naturally occurring aqueous medium. We will be comparing rainwater samples with coarser fog droplets only as it has the largest droplet diameters (> 22 μm). Detailed analysis of size resolved fog water (FW) samples are already reported as part of a submitted manuscript, so we will only be discussing the major differences between coarse fog water and rainwater residues. Concentrations of different species like elements, organics, sulfate, nitrate, ammonium, and chloride are usually lower in rainwater residues than in fog water ones. This observation is expected as fog droplets are much lower in size than rain droplets with less LWC (Beiderwieden et al., 2005), so pollutants are more concentrated in them. Higher surface area of the smaller droplets may have allowed them to dissolve more pollutants from surroundings. Apart from that fog forms in the vicinity of the ground where pollutant concentrations are much higher than the elevated altitudes where clouds are generally formed and lastly aerosol loadings during winter were much higher than monsoon period. However, there are several differences in relative composition and chemistry inside these two aqueous mediums which can't be explained only by dilution or differences in aerosol loadings. For most of the anthropogenic elements, EF values are higher in FW than in RS (Fig. 9), indicating that sources and nature of aerosols dissolved in RS and FW may be very different.

Overall composition of both RS and FW are dominated by organics, but this domination is more pronounced in RS than in FW. OM composition of RS is dominated by CHO1 functional groups

while that of FW is dominated by CH group, however in FW contribution of CHOgt1 functional group to total OA is much higher than that of in RS (Fig. S9). Also, f44 and O/C ratio (= 0.68) of FW are much higher than that of RS (= 0.58); this clearly indicates that FW is more processed and oxidized than RS (Fig. 10). Apart from that O/C ratio of FW (= 0.68) is much higher than that of winter time ambient aerosols (= 0.55) (Chakraborty et al., 2015), on the contrary, O/C ratio of RS (= 0.58) is lower than that of monsoon time ambient aerosols (= 0.67). These differences can't be explained by simple dilution or aerosol loadings differences as O/C; f44 are normalized parameters.

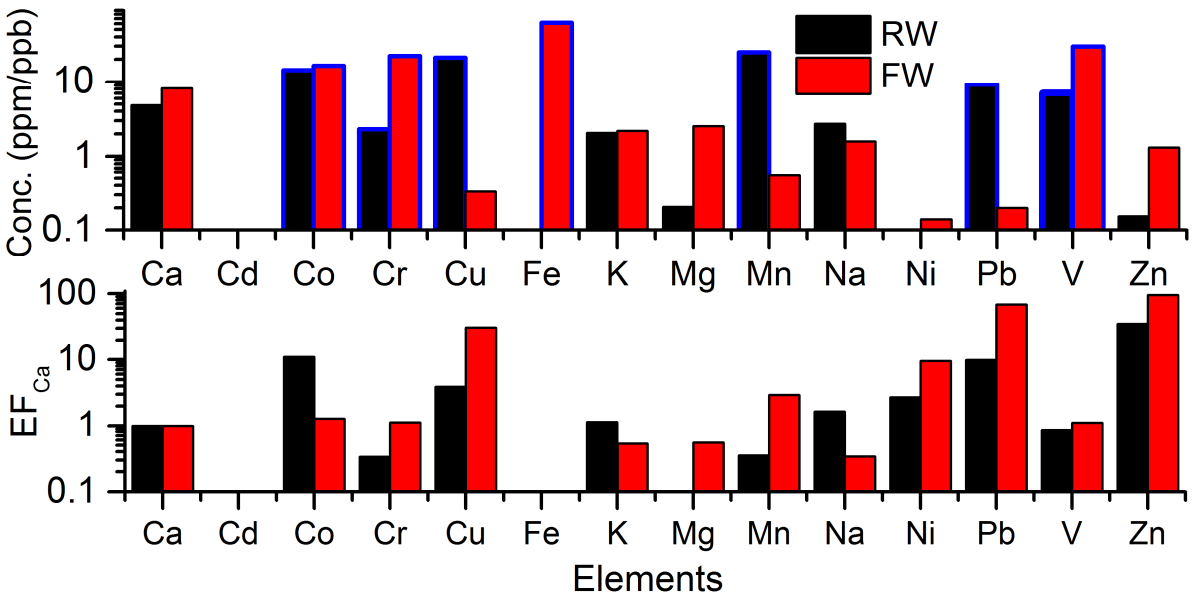

Fig. 9: Comparison of elemental concentrations and EF values between fog and rainwater samples. EF factor is calculated by taking Ca as a reference element. For blue bordered elements concentrations are in ppb while that of all others are in ppm.

However, several other factors can explain these differences; fog droplets being much smaller in size can remain in ambient for longer duration thus enhancing the processing time of dissolved aerosols. Due to smaller sizes, fog droplets can't capture much larger particles unlike rain

droplets, these larger particles may have been dominated by minerals and other species with very little soluble organics or having less oxidized organics leading to this outcome. Relatively lower EF values for dissolved elements in rainwater also suggests that aerosols trapped by rain droplets are mostly originating from crustal sources/natural values. Apart from these differences, there are some similarities like the dominance of organics and presence of organo sulfate in both RS and FW, indicating some amount of aqueous processing is taking place within both the medium.

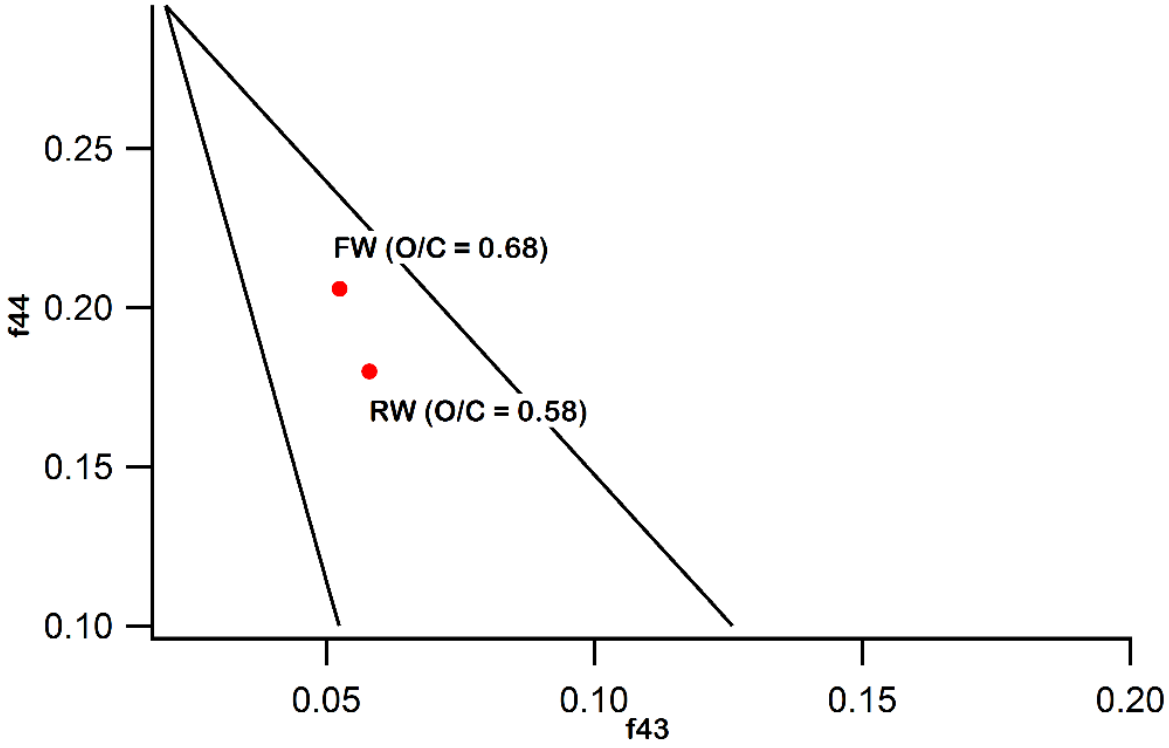

Fig. 10: Comparison of oxidation ratios and aging of organics present in fog (FW) and rainwater (RW).

4. Conclusions:

Ambient and rainwater residues were analyzed by AMS in online and offline modes, respectively. Both AA and RS are dominated by organics; this dominance is particularly

549 pronounced in RS. Inorganics are dominated by sulfate; however, enough ammonium is
550 available in the atmosphere to neutralize the anions completely. The presence of organic nitrate
551 is detected in AA via the elevated ratio of nitrate fragments (NO^+/ NO_2^+). Source apportionment
552 of ambient OA indicates that ambient OA is comprised mostly of oxidized OA followed by
553 primary OA like biomass burning and hydrocarbon like OA. Contributions of oxidized OA to
554 total OA during monsoon is far higher than the same during post-monsoon and winter season,
555 indicating the higher oxidative capacity of atmosphere during monsoon. Although overall AA
556 composition remains the same, slight differences are observed in ambient OA composition from
557 rain events to dry periods. During rain events, the contribution of primary OA to ambient OA is
558 slightly increased along with a slight decrease in O/C ratio compared to dry periods. In RS, anion
559 concentrations are much higher than NH_4^+ concentrations, however considering other cations
560 like Na^+ and K^+ reduces this gap significantly, indicating a strong presence of other metallic salts
561 in rainwater. O/C ratio of rainwater organics are slightly lower than that of ambient OA, possibly
562 due to entrapment of metallic salts rich larger particle sizes with less oxidized organics. The
563 presence of organic sulfate and nitrates are detected in rainwater from HR AMS mass spectra.
564 This finding indicates that some aqueous processing inside the cloud may have taken place to
565 produce these organo sulfates, which are absent in ambient OA HR mass spectra. Comparison
566 with fog water samples revealed that RS is less oxidized and less concentrated possibly due to
567 the longer residence time of fog droplets and larger sizes of rain droplets. These findings indicate
568 that rainwater can effectively trap all types of aerosols including both oxidized and non-oxidized
569 organics, despite low hygroscopicity of the later. Monsoon time ambient aerosols are enriched
570 with oxidized organics which may promote the growth of cloud droplets due to their
571 hygroscopicity and higher oxygen content.

Acknowledgements:

We would like to acknowledge IIT Kanpur for providing us HR-ToF-AMS. We would also like to NOAA ARL, for providing data of wind speed and boundary layer heights. We would also like to acknowledge funds received from Indian National Science Academy to partially support this study.

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