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ON THE ORIGIN OF AMS "COOKING ORGANIC AEROSOL" AT A RURAL SITE

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Abstract

A number of field observations employing aerosol mass spectrometers (AMS) have demonstrated that organic matter rich in monocarboxylic acids and aliphatic carbonyls originating from cooking activities (the COA factor) contributes significantly to ambient Organic Matter (OM) in urban environments. Little is known about the contribution and nature of COA in rural localities. We studied the correlation of COA with chemical tracers at a rural site in the Po Valley, Italy. Our statistical approach, based on Positive Matrix Factorization (PMF) shows that the COA factor was clearly linked to local emissions of chloride and methane sulphonic acid (MSA), chemical tracers not associated with cooking emissions, or with combustion sources. While the association with Cl is not understood at this stage, the emission of reduced sulphur compounds, aliphatic carbonyls and monocarboxylic acids is consistent with several agricultural practices (e.g., manure storage) and waste disposal systems (e.g., landfills) which characterize the sub-urban and rural areas of the Po Valley and of other many populated environments. It is concluded that the nature and origins of the AMS COA factor measured at a rural site are complex and include far more than the emissions from food cooking.

KEY WORDS: Aerosol mass spectrometer; cooking organic aerosol; COA; ATOFMS

1. INTRODUCTION

Urban air quality provides one of the main drivers for the study of atmospheric science, especially due to growing urbanization. Although considerable progress in improving air quality has been made, it is imperative to better understand the source attribution of particles and health effects in the urban atmosphere[1]. Among the constituents, organic aerosol (OA) accounts for a large fraction of urban particulate matter[2]. Primary OA (POA) is directly emitted from fossil fuel combustion, biomass burning, and other sources, but the atmospheric evolution of POA after emission remains poorly characterized[3-5]. Whilst road traffic is often a major contributor to aerosol in urban areas next to major roads, OA in urban background areas is not easily associated with a specific source. Few studies have sought to characterise the sources of OA in rural areas, remote from major sources.

In recent years Mass Spectrometry of Atmospheric Aerosol (MSAA) has become one of the fastest growing area of aerosol research[6]. Such techniques have greatly enhanced our capacity of observing the atmospheric processes responsible for the formation and evolution of airborne particles. In this regard, the Aerodyne Aerosol Mass Spectrometer (AMS) is able not only to measure the OA concentration and size distribution but also to provide its mass spectrum[7]. Analysis of AMS data collected at a large number of sites has revealed that the oxidised OA component (OOA) tends to dominate everywhere, including some heavily urbanized regions[2,8].

Many AMS studies have focused on the application of factor analysis to the organic mass fraction in an attempt to deconvolve it into descriptive sub-components, namely a hydrocarbon-like organic aerosol (HOA) factor, an oxygenated organic aerosol (OOA) factor, and a semi-volatile factor (SV-OOA)[4,9]. Such assignments are based primarily upon the main mass spectral components and the diurnal profile. In some cases, supporting evidence from chamber experiments is available. Recently, a previously reported AMS spectrum[10,11] has been firmly associated with primary emissions from cooking activities. Such emissions have been claimed to account for up to half of the total primary urban OA at sites in Europe[12-14], Asia[15] and America[16] . However, there is a possibility for a factor to include a combination of factors associated with different sources[11,17], and some recent studies report a COA factor lacking the diurnal profile expected from cooking activities, although possible explanations have been given[13,18]. Other studies have also expressed the view that it is most reasonable to characterize the COA component as "cooking influenced” but not purely from cooking sources[19]. In a comparison of source apportionment by AMS-PMF with a Chemical Mass Balance model, the AMS estimate of COA for a site in London exceeded the CMB-derived concentration of cooking aerosol by a factor of ca 1.6[20].

Taken together, evidence for source attribution of the AMS COA factor is currently incomplete and most importantly not well supported by other measurement techniques. This lack of knowledge needs to be filled, and the goal of this paper is to use results of a source apportionment study using six state-of-the-art spectrometric techniques deployed at a rural site in the Po Valley (Italy) in 2009 to investigate the nature of the AMS COA factor. Previous work[21] provides a comprehensive picture of the nature of organic and inorganic aerosols and aerosol precursors at a European rural site with an unprecedented level of detail. Figure S1 shows an example of the high time resolution particle mass spectrometry instruments deployed. In this study Positive Matrix Factorization (PMF) has been applied to all the high time resolution data in order to better elucidate aerosol sources not clearly identified when analyzing results from individual aerosol techniques on their own. Particular attention is given to the AMS COA factor, but a complete overview of the aerosol sources apportioned is also presented and discussed.

2. EXPERIMENTAL

2.1 Study Site

The Po Valley is located in Northern Italy between two mountain ranges, the Alps in the north and west and the Apennines in the south. The Po Valley has 20 million inhabitants spread over an area of 48,000 km^2 (Fig S2). In the present study we used the EMEP Station of San Pietro Capofiume (SPC, 44°23′N 11°22′E, 11 m a.s.l.), a rural background site (distance from major pollution sources: 10 – 50 km[22]). The measurements were conducted from 26 June to 15 July 2009.

2.2 Aerosol Mass Spectrometry Techniques

Four on-line aerosol spectrometers were used: the TSI Aerosol Time-Of-Flight Mass Spectrometer (ATOFMS), the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-TOF-AMS) and Soot Particle Aerosol Mass Spectrometer (SP-AMS), and finally a Thermal Desorption Aerosol Gas Chromatograph AMS (TAG-AMS). Twelve-hour resolution proton nuclear magnetic resonance (H-NMR) spectra were also obtained by off-line analysis. Finally, information on gas-phase precursors of secondary aerosols was acquired using Chemical Ionization Mass Spectrometry (CIMS). A set of other measurements are described in detail elsewhere[21]. Overall, the state-of-the-art instruments used for this analysis measure different species with different accuracy and precision, as discussed in great detail in other publications[23-25].

2.3 Factor Analysis

Factor analysis involves a wide set of multivariate statistical techniques that have been extensively used in atmospheric science. Its aim in this field is to apportion aerosol sources on the basis of the internal correlations of observational data collected at a measurement point, called the “receptor site”. Receptor modeling by factor analysis does not need any detailed a prior knowledge of source profiles and it is therefore very useful for determination of aerosol fractions of secondary origin. “Positive Matrix Factorization” (PMF)[26,27] has been used extensively for source apportionment of ambient particulate matter (PM), and in particular is so far the most widespread tool for AMS spectral data analysis[28] .In this study the EPA open-source software EPA-PMF v3.0 was used for PMF analysis. PMF was applied on the hourly data obtained by the analytical techniques described above and also by the previous PMF analysis on spectroscopic data reported elsewhere[21].

The criteria adopted in this study for input data treatment, including the uncertainty matrix, and for the evaluation of the PMF solutions are discussed extensively in the supplementary material.

3. RESULTS

PMF analysis was performed for one to ten factors, and it was found that the solutions with factor numbers greater than five provided no new meaningful information for both datasets. Rotational constraint was explored with Fpeak. The solutions ultimately selected was based on an Fpeak value of zero. Additional factors resulted in a splitting of the existing factors (mainly splitting of secondary organic and inorganic components (Figures S5 and S6; Table S2 and S3). Table S4 shows there is no clear improvement with the six factor solutions from either of the two datasets. A full list of variables is found in Table S1. The figures in brackets after the PMF input variable represent the percent contribution of that atmospheric variable within the whole five factor solution (% of species). A description of the strong agreement between the solutions from the two datasets is presented at the end of this section. More details on the PMF diagnostics are presented in supplementary material.

3.1 Dataset 1 : Results from the Full Campaign (“ALL”)

Five factors were found very well describing the long time series dataset (16 days). This dataset included the first week of the study when the anticyclonic conditions favoured transport of aerosol at the regional scale and the recirculation of pollutants in the Po basin[21]. Figure 1 and table 1 show all the PMF factor profiles of this solution, whereas the temporal trends and the diurnal profiles can be seen in Figures 2 and S9a, respectively. The individual factors are as follows:

- Oxidised Organic Aerosol from photooxidation processes "Photox OOA" (30% of the total, Figure 1a). It represents oxidised organic aerosols (accounting for a substantial percentage of AMS_ LV-OOA MO 48% and AMS_LV-OOA LO 49%), AMS_sulphate (48%), Ozone (83%) and CIMS_MA (84%). This is associated with photochemically aged secondary aerosols, and the temporal trends (Figure 2, S9a) show this aerosol component occurring mainly during daytime and during the first week of the study.
- Nitrate "NIT-Regional" (18%, Figure 1b). This factor is strongly associated with AMS_Nitrate (79%) and ATOFMS_NIT-Regional (32%). There is an important component of AMS_Cl (38%) and AMS_SV-OOA (27%) associated with it. This factor is associated with nitrate containing aerosol of regional origin[29] , and related to high RH (Figure 2), with time trends modulated by the diurnal variations of temperature and relative humidity which regulate the concentration of semivolatile compounds in the aerosol (ammonium nitrate and chloride, SV-OOA).
- Sulphate "SUL-Regional" (23%, Figure 1c). This aerosol source is mainly composed of sulphate (ATOFMS_SUL-Reg 90%), ATOFMS_EC-Reg (72%), and AMS_OOA-MO

(32%). This aerosol source accounted for 35% of explained variation during the first week of the study (stagnant air), but only 3% during the second week (Figure S9a). Part of this component is thought to be the aerosol core from the evaporating regional nitrate during daytime[21,29]. This factor seems to be linked to the transport of sulphate and BC during the days of anticyclonic conditions.

- "NO" (12%, Figure 1d). This represents the smallest aerosol source contribution as expected given the rural location of San Pietro Capofiume. The factor is well described primarily by NO (90%), followed by minor contributions from AMS_HOA (23%) and NO_2 (25%). BC is only partially described by this factor (6%). Although the diurnal profile (Figure 2) shows a main morning spike during the urban rush hour (7am), processes other than traffic and certainly including photolysis of NO_2 and of HONO most probably contributed to NO at the site. Other studies[21,30,31] have already demonstrated the presence of a traffic-influenced component at SPC station with contributions ranging between 14-24% of total OA. This non-negligible contribution and its diurnal trend could be explained both by the proximity of main transportation routes and by the accumulation of the primary emissions overnight because of the reduced atmospheric mixing and dispersion. However the NO apportioned in this study could be also formed from photochemical activity (photolysis of NO_2 in the first hours after the sunrise) and so we prefer to label this factor simply as “NO”, the most represented species, without assigning a specific source.
- "Cooking" Organic Aerosol "COA" (17%, Figure 1e). This factor accounts for a high proportion of AMS COA (77%) and ATOFMS OC-SUL-NIT (77%). Other interesting variables describing this factor includes CIMS MSA (41% of the total), AMS Cl (35%) and NO_2 (31%). The temporal trends show a major occurrence during the second week (24%) rather than the first regional pollution week (14%). The diurnal profile shows a minor spike during evening time (7-9pm), followed by sustained

concentrations overnight. There is a lack of the midday peak seen associated with COA factors in many studies[13,18].

The analysis of the correlation of the five factor concentrations with local wind direction (Figure S10a) shows that the first three factors are associated with sustained winds from either east (OOA), west (NIT-regional) or south-west (SUL-regional) directions, while the COA factor is most concentrated in calm conditions. Therefore, the COA is more influenced by local sources compared to the first three factors which are mainly transported to the site. The NO factor shows an intermediate behaviour, with a component from the west (possibly NO_x transport) and another local (possibly soil emissions[32]).

3.2 Dataset 2: Three Measurement Days Including SP-AMS Data ("HIGH" Resolution)

The factors of the dataset_2 (HIGH) PMF solution can be seen in Table 1 and Figure 3. In the last days of the campaign, which were covered by the measurements described in this section, the weather conditions were unfavourable for pollutant recirculation and the aerosol concentrations were fairly low in day-time when the planetary boundary layer was fully developed. Conversely, the concentrations at night-time and in the early morning continued to be sustained by local sources in the Po Valley[21]. The analysis of this campaign period is therefore particularly useful for the source apportionment of the aerosol components originating from emissions in the Po Valley, such as cooking aerosols, because the interference from the background particles is smaller with respect to the first part of the campaign[21]. The diurnal profiles can be seen in Figure 2 and the temporal trends in Figure S9b. Three of the five factors presented previously (Section 3.1, ALL) were also found in this second solution, including:

- Oxygenated Organic Aerosol "Photox OOA" (38%, Figure 3a). This described Secondary Organic aged aerosols accounting for a high percentage of AMS LV-OOA MO (81%), SP-AMS “SV-OOA Day” (89%), ozone (83%) and sulphate from both HR-AMS (68%) and SP-AMS (67%) instruments.
- Nitrate regional "NIT-Regional" (17%). A strong nitrate signal from all the on-line spectrometers including HR-AMS (72%), SP-AMS (45%) and ATOFMS (NIT-Reg 71%) can be seen (Figures S9b and 2). Additionally, an hydrocarbon like contribution of HOA (21%) and BC (20%) is notable.
- ”NO” (17%). This shows a strong NO signature (93%) followed by HOA (22%) and BC (11%) (Figure 3c). The diurnal profile seen in Figures 2 and S9b shows a morning peak likely to be associated with traffic and/or photolysis.

Unlike the “ALL” solution, in this 3-day dataset_2 (AMS, ATOFMS, SP, CIMS, gas, 33 variables, last 3 days of the field study, dataset_2, HIGH) a factor related to sulphate of regional origin was not identified. This is very likely due to the fact that during the second week of the field study there was little contribution of regional pollution, so the solution was not able to extract the SUL-Reg factor, mainly seen during the first week (Figure S9a). By contrast, during nighttime the relatively higher concentration of nitrate allowed identification of the NIT-Reg. factor. During daytime the SUL-Reg., if present, is likely to be incorporated in the regional OOA factor.

However, the second solution with more variables (33 in total) was able to provide a better description of the COA factor, because the statistical correlations of AMS COA concentrations with the other variables are much more clear in the HIGH dataset than in the ALL one (Table S6). The factor analysis of the HIGH set of variables actually provided two different aerosol sources associated with the AMS “cooking aerosols” and specifically:

- "Cooking" organic aerosol "COA-MSA-Cl" (seen in Figure 3d). This factor presents a strong AMS COA signal (54%), with CIMS_MSA (36%) and a strong inorganic AMS Cl signature (70%). A strong semi-volatile component is also present (AMS SV-OOA and SP-AMS “SV-OOA Night”, both 58%). Additionally, the factor ATOFMS OC-SUL-NIT is also associated with this factor (32%). In summary, this COA factor is associated with MSA, chloride and semi-volatile OA components.
- "Cooking" organic aerosol "COA-MSA-HOA" (seen in Figure 3e). This factor shares the part of the AMS_COA signal (46%) not identified by the previous factor (54%) and a strong association with CIMS MSA (37%). However, this factor is more associated with AMS HOA (38%) SP-AMS HOA (42%) and contains almost no semi-volatile component. Interestingly, this factor is associated with nitrate of local origin (ATOFMS NIT-Local, 42%). In support of this, it accounts for the highest percentage of NO_2 (33%) of all factors. In summary, this second "COA" factor is associated with anthropogenic HOA and somehow related to nitrate locally formed, organic nitrate and nitrogenous gaseous[29]. This fingerprint could be characteristic of urban sources near to the site.

3.3 Comparison Among the two PMF Solutions and External Correlations Support

The two PMF solution (ALL and HIGH) provided three common factors (OOA, NIT-Reg and Traffic). When correlation of the overlapping temporal trends of the last three days are examined, Table S4 shows a very good agreement between the two PMF solutions: OOA (34-38%, R^2=0.95), Nitrate regional (14-17%, R^2=0.94) and NO (14-17%, R^2=0.85). Sulphate Regional cannot be temporally compared, although the apportionment contributions is similar for both solutions (0-3%). The "Cooking" factor solution for the dataset_ALL is found to contribute less (25%) than the sum of the two "cooking" aerosol factors of the dataset _HIGH (38%). However, it is important to note that the temporal correlation between "COA" from dataset_ALL and the sum of COAs from dataset_HIGH ("COA-MSA-Cl" and "COA-MSA-HOA" together) is very high (R^2=0.85).

The factors presented are strongly supported by correlations with external measurements presented elsewhere[21] .Table S5 shows that factor Photox. OOA correlates very well with NMR_PMF_F4 (Aged humic-like substances, R^2=0.90), whereas factor SUL-Reg. correlates well with NMR_PMF_F3 (organic sulphate and less aged humic-like substances, R^2=0.57). Furthermore, whilst COA-MSA-Cl correlates only with NMR_PMF_F1 (aliphatic amines and unspeciated aliphatic compounds, R^2=0.77), factor COA-MSA-HOA correlates only with NMR_PMF_F2 (aliphatic alkanoic acids and oxo-acids, R^2=0.95). These are robust external correlations which strongly support our PMF solutions. Correlations reported in Table S4 are much stronger (R^2=0.7-1.0) than those previously reported (R^2=0.3-0.6)[21] because the chemical profiles of the PMF solutions herein presented are less dependent upon specific markers, but rather show a combination of markers that better describe an organic aerosol source.

4. DISCUSSION

4.1 Major Constituents

The analysis of the correlations between the “regional” aerosol components (i.e., the components expected to exhibit an extended source footprint) suggests that the OOA atmospheric evolution over north Italy is completely distinct from that of nitrate of regional origin. Factor “Photox. OOA” was found mainly associated with oxidised organic aerosols (48-88%) and sulphate (48-68%). This is in line with previous studies[33] who reported aged

OOA detected above the Po Valley column to be secondary in nature and highly oxidized in the regional aerosol, with much higher amounts of sulphate and organics relative to nitrate. By contrast, NIT-Reg. is found to account for the majority of nitrate aerosol detected (AMS_Nit 72-79%), of regional nature (ATOFMS NIT-Reg 32-71%). The organic component in this factor is found to be of primary origin: AMS_HOA (21-45%). The association of NIT-Reg. with HOA may suggest a larger size mode of nitrate during the night acting as a coagulation sink for fresher finer local aerosols. Alternatively, the HOA may in part be subjected to transport across the Po Valley basin together with nitrate. This factor is associated with a specific mass spectrum and a characteristic temporal dynamic already reported in London[29], Wales[34] and Barcelona[35]. The LRT-NIT particle type is volatile, going into the gas phase during the day and leaving a non-volatile internally mixed core mostly composed of sulphate, elemental and organic carbon. The SUL-Reg is mainly composed of EC-Sulphate (90%), BC (42%) and sulphate (27%). During this study we find local, less aged nitrate of finer size mode of local origin (ATOFMS_NIT-local) associated with COA-MSA-HOA.

HOA and BC are usually related to fresh traffic emissions in many AMS studies. This work shows that traffic makes only a small contribution to BC (11%) and a modest one to HOA (23%). By contrast, the majority of BC is related to the core of the regional nitrate, being internally mixed with sulphate and BC (42% of total BC). As a result, it is important to stress that the HOA and BC is mainly seen during nighttime and mainly associated with nitrate.

4.2 The "Cooking" Aerosol Factor(s)

The mass spectrum of the AMS COA factor obtained from San Pietro Capofiume was converted in m/z unit mass resolution and compared with other factors in the literature. All factors were compared at unit mass resolution. The COA factor did not correlate (R^2<0.1) with any of the HOA, SV-OOA or LV-OOA in the literature. A good correlation (R^2) was found with AMS COA reported in seven previous studies: 0.84 (laboratory studies[11]); 0.74 and 0.83 (London[12]); 0.75 (Manchester[12]); 0.80 (Paris[14,36)]; 0.75 (Zurich[10]); 0.85 (Cork[18]). Therefore, the same name "COA" was kept for this study.

The composition of the aerosol and of the air masses associated with the AMS COA factors are key indicators of its origins. A first, unexpected finding is that the PMF analyses from both datasets (ALL and HIGH) show the association of AMS COA with secondary organic aerosol components (CIMS MSA and ATOFMS OC-SUL-NIT) rather than with markers of primary combustion (or thermal) processes. More specifically, the analysis of the HIGH dataset decomposes the “COA” factor into two, with one (COA-MSA-HOA) retaining a partial fingerprint for primary sources (HOA, BC, NOx) together with that of secondary components (nitrate, MSA) while the other factor (COA-MSA-Cl) shows very small correlations with the primary tracers. Fig. S11 shows the main differences among the two COA PMF factors. The low correlation of COA with tracers of urban pollution in this last factor was unexpected because cooking aerosols should be transported in urban plumes to the countryside along with the products of traffic emissions (BC, NO_x, HOA). It is important to stress that very little is known on the transformation of COA in the atmosphere[37]. Preliminary findings of meat cooking aerosol ageing show an increase of the AMS O:C ratio from 0.1 up to 0.3[38]. By looking at the prevalent wind directions associated with the two COA factors in the HIGH datasets, the COA-MSA-HOA shows a transport component from the west, while the COA-MSA-Cl has a more local footprint. Therefore, it is very unlikely that the COA-MSA-Cl originated from cooking activities in urban areas. The local sources to be indicated could be cooking in rural houses and small towns in the vicinity of SPC, but this does not explain the low correlation with the traffic markers (as people who live there still use cars). Most importantly, the source profile emerging from COA-MSA-Cl is inconsistent with the known composition of cooking aerosol, in which particles are mainly organic in nature with inorganic ions being present only in trace amounts[37], while here the aerosol mass AMS Cl/ AMS COA ratio is 1.63. These findings indicate that either the published emission composition for cooking emissions does not apply to this environment, or cooking is not a major source for the organic aerosol included in the COA-MSA-Cl factor.

Explaining the correlation between COA and aerosol chloride is challenging. Aerosol chloride in this study is mainly non-sea salt chloride, which may originate from various anthropogenic sources including industry, combustion and incinerators(39,45). There are no industrial plants around SPC. Incinerators emit hydrochloric acid which comes from the combustion of plastic material(39,45). However, the single particle mass spectra associated with this factor (ATOFMS_OC-NIT-SUL) does not have metals previously identified with Cl-containing aerosols emitted by waste incinerators[39]. Also the SP-AMS did not observe any mass fragments from metals such as lead which typically characterize the emissions of incinerators (Dr. J. Allan, personal communication).

Finally, the source profile of COA-MSA-Cl indicates that the same source is responsible for the emission of reduced sulfur species (precursors of gas-phase MSA measured by CIMS) which is inconsistent with the hypothesis of a high-temperature combustion process such as in an incinerator. This is because in thermal oxidizers such as industrial incinerators chemically reduced pollutants are generally destroyed via combustion forming more oxidised species such as CO_2, SO_2 and H_2O. On the contrary, the production of reduced sulfur species points to thermal processes occurring at low temperature (including some cooking practices) or to emissions at ambient temperature[40]. Dimethylsulfide emissions from marine biota are believed to be largely responsible for global MSA production[41]; however, in this study gas-phase MSA was not associated with marine air masses. On the contrary the MSA concentrations reach a maximum at nighttime when the circulation is mainly from the inland to the sea[21]. A recent review on cooking aerosol tracers actually does not mention sulphur compounds as cooking tracers[37]. However, it is worth mentioning that roasting of coffee beans may be a source of reduced sulphur compounds[42] and also meat cooking can produce several thioethers[43]. However, cooking is only one of the possible anthropogenic sources of sulfur compounds. Urban sources of DMS include aerobic composting of food wastes[40,44-47]. More generally, volatile organic sulphur compounds can readily form from the aerobic and anaerobic degradation of organic matter, including solid wastes, wastewater, manure and livestock excreta and feed[44-48]. If we quantify such sources using co-emitted compounds such as ammonia, then emissions in the Po Valley are dominated by the agricultural practices and animal husbandry activities. A prevalent source of MSA precursors in rural areas, with emissions from manure management, livestock and agricultural land is consistent with the appearance of the COA-MSA-Cl factor as a local source at SPC unrelated to urban sources. The origin of organic particulate matter associated with the aerobic/anaerobic organic matter decomposition in agricultural land is poorly documented. Broadly, air pollutants emitted from the agricultural sector are mainly methane (CH_4) and other VOCs, nitrous oxide (N_2O) and ammonia (NH_3). Agriculture is also a main source of PM, both primary and secondary in origin originating from livestock production, application of fertilizers and pesticides, land preparation, harvesting and field burning of agricultural waste[46-48]. It is know that some husbandry activities (poultry) are strong point sources of PM_{10} and $PM_{2.5}$, but this aerosol source has never been related to the AMS COA prior to this study. By contrast, the emissions of VOCs from livestock and manure management have been characterized in some detail and often associated with the production of reduced sulfur species[50-51]. Such VOCs comprise low-molecular weight organic acids, but also C_6-C_{10} aliphatic aldehydes and monocarboxylic acids. These chemical compounds are analogous to the organic compounds believed to contribute to the AMS COA but exhibit too low a molecular weight to exist in the particulate phase. Therefore, the production of COA from these VOCs is possible only via a gas-phase oxidation step. $C_{>8}$ n-alkanals in particular can form SOA under low NO_x conditions[52], while unsaturated alkanals[53] are good SOA precursors also in NO_x-rich environments[49]. According to this hypothesis, the COA in the rural Po Valley may be contributed from secondary organic compounds in the same manner that MSA is produced by the oxidation of reduced sulfur species. It is worthy of note that MSA and COA concentrations peak at nighttime, when OH concentrations are near zero while the nitrate radical NO_3 becomes the major oxidant[52-54]. Unlike OH, the concentrations of NO_3 depend on the availability of NO_x, which can explain why the COA-MSA factors show a component of westerly transport, i.e., from the more polluted sector of the valley. It can also explain the correlation of COA with urban tracers (including NOx) in the factor COA-MSA-HOA. The correlation of COA with aerosol chloride cannot be fully explained by this hypothesis. Possible point sources for hydrochloric acid, reduced sulfur species and VOCs from organic matter degradation are landfills, and there are actually two at ten-twenty km west of SPC.

In conclusion, the origin of factor COA-MSA-Cl (21% of total aerosol, 54% of AMS COA) can be explained by hypothesizing emissions from agricultural/husbandry activities with a potential additional contribution from waste disposal at urban sites. A second AMS COA source (COA-MSA-HOA, 17% of the total aerosol, 46% of the remaining AMS COA) was also linked with secondary components (nitrate, MSA), although retaining a partial fingerprint for primary traffic sources (HOA, BC, NOx).

Quantification of such sources is challenging and calls for more research. However, the results of this study suggests that the current estimates of OA sources from organic matter degradation processes in agricultural and waste systems in populated areas may be substantially underestimated. The COA factor as determined by the AMS includes far more sources and processes than solely primary emissions from cooking activities.

Associated content

Supporting Information

A description and details of the field campaign discussed in the manuscript; PMF analysis, temporal trends of the PMF solutions, external correlation between this PMF study and previous ones are discussed. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Biogenic vs. Anthropogenic emissions on Clouds and Climate: towards a Holistic UnderStanding” (BACCHUS), project no. 603445. Programme Ramon y Cajal (RYC-2012-11922) also provided financial support. Dr. James Allan (NCAS, University of Manchester, England) is particularly acknowledge for very fruitful discussion which much improved the manuscript.

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TABLE LEGEND

Table 1. Percentages of factors over the same time interval (9-12/07/2009) for the dataset_1 (all field study) and dataset_2 (high, only second part).

FIGURE LEGENDS

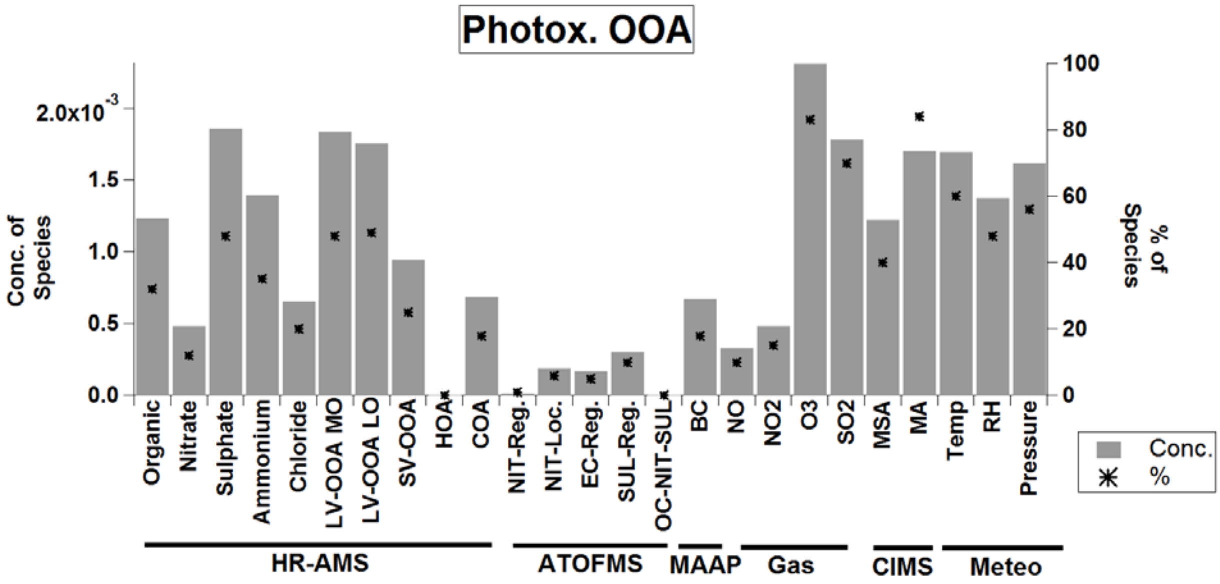
Figure 1. PMF factors of the dataset 1 (ALL field study).

Figure 2. Diurnal profiles of dataset_1 (ALL field study) and dataset_2 (second part, HIGH). Figure 3 (1-2) shows again the COA factors coming from dataset_1 (COA) and dataset_2 (COA-MSA-Cl and COA-MSA-HOA).

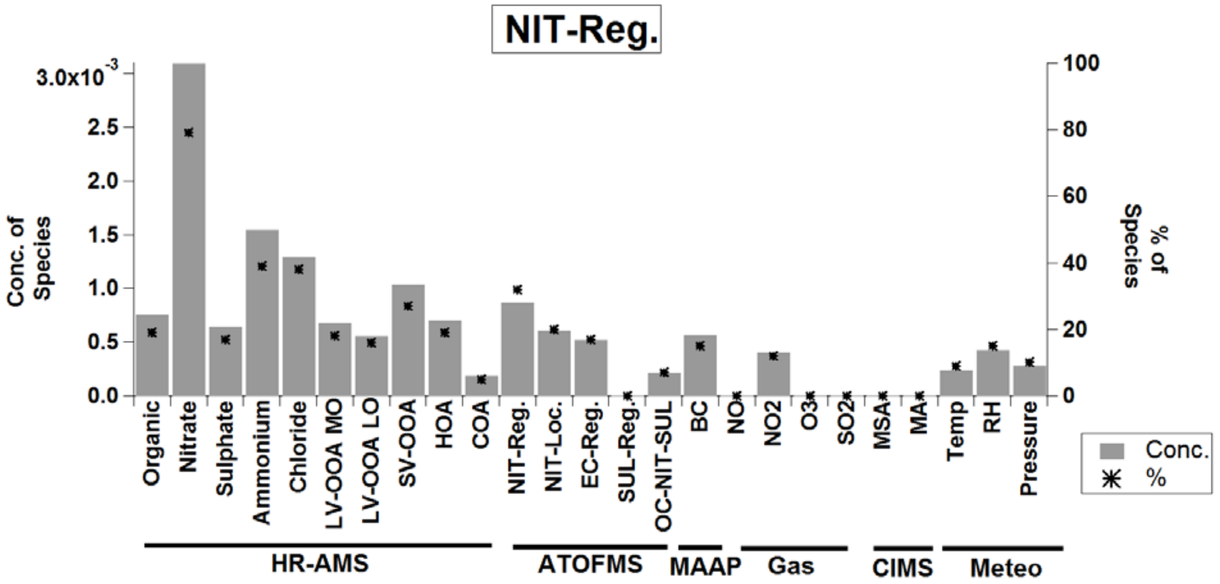
Figure 3. PMF factors of the dataset_2 for the second part of the field study (HIGH).

Table 1. Percentages of factors over the same time interval (9-12/07/2009) for the dataset_1 (all field study) and dataset_2 (high, only second part)

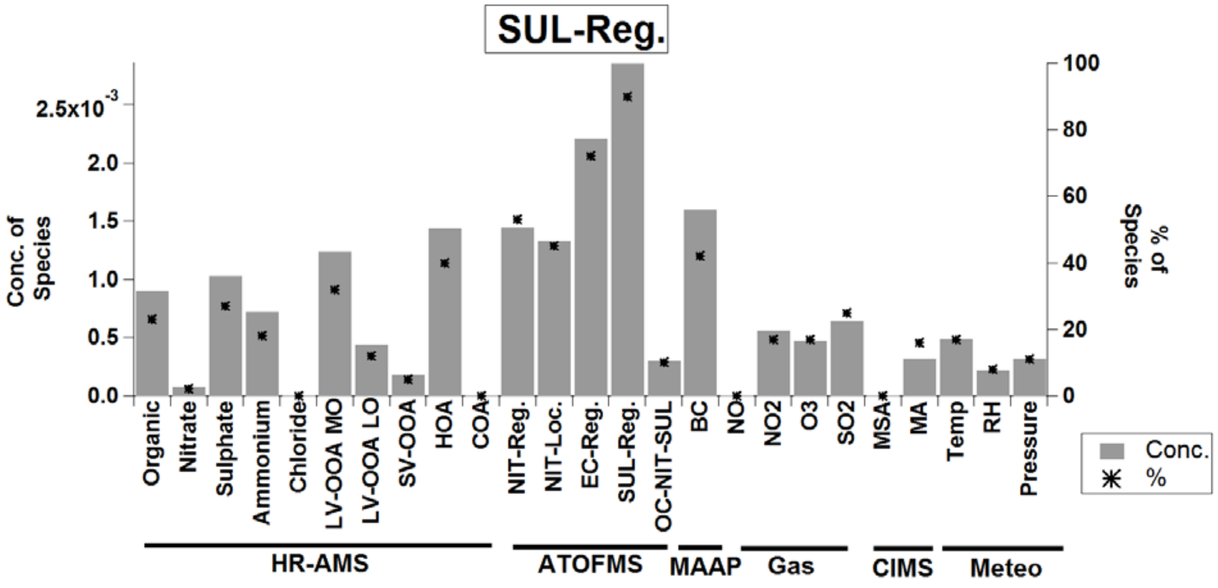
Time period	**dataset type**	**OOA-Reg.**	**NIT-Reg.**	**SUL-Reg.**	**NO**	**COA-MSA-Cl (from ALL)**	**COA-MSA-Cl (from HIGH)**	**COA-MSA-HOA (from HIGH)**
Whole study	ALL	30	18	23	12	17		
Only 9-12/07/2009	ALL	38	17	3	17	25		
Only 9-12/07/2009	HIGH	34	14	0	14		21	17


Photox. OOA
Conc. of Species
% of Species
2.0x10^{-3}
1.5
1.0
0.5
0.0
100
80
60
40
20
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-Reg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
O3
SO2
MSA
MA
Temp
RH
Pressure
Conc.
%
HR-AMS
ATOFMS
MAAP
Gas
CIMS
Meteo

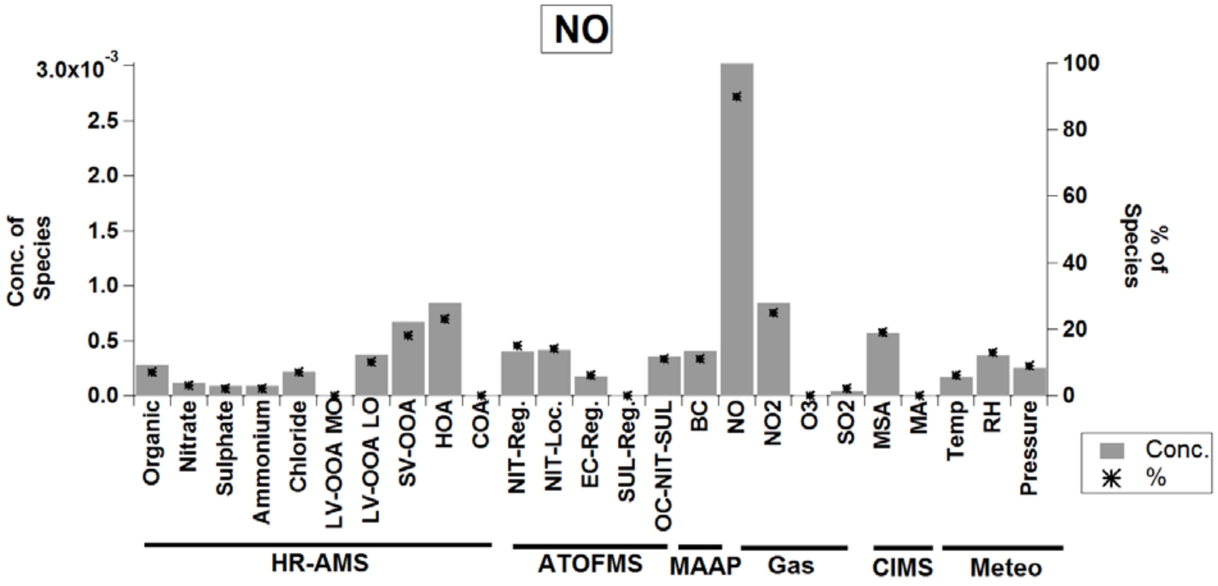
(a)


NIT-Reg.
Conc. of Species
% of Species
3.0x10^{-3}
2.5
2.0
1.5
1.0
0.5
0.0
100
80
60
40
20
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-Reg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
O3
SO2
MSA
MA
Temp
RH
Pressure
Conc.
%
HR-AMS
ATOFMS
MAAP
Gas
CIMS
Meteo

(b)


SUL-Reg.
Conc. of Species
% of Species
2.5x10-3
2.0
1.5
1.0
0.5
0.0
100
80
60
40
20
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-Reg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
O3
SO2
MSA
MA
Temp
RH
Pressure
Conc.
%
HR-AMS
ATOFMS
MAAP
Gas
CIMS
Meteo

(c)


NO
Conc. of Species
% of Species
3.0x10-3
2.5
2.0
1.5
1.0
0.5
0.0
100
80
60
40
20
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-Reg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
O3
SO2
MSA
MA
Temp
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%
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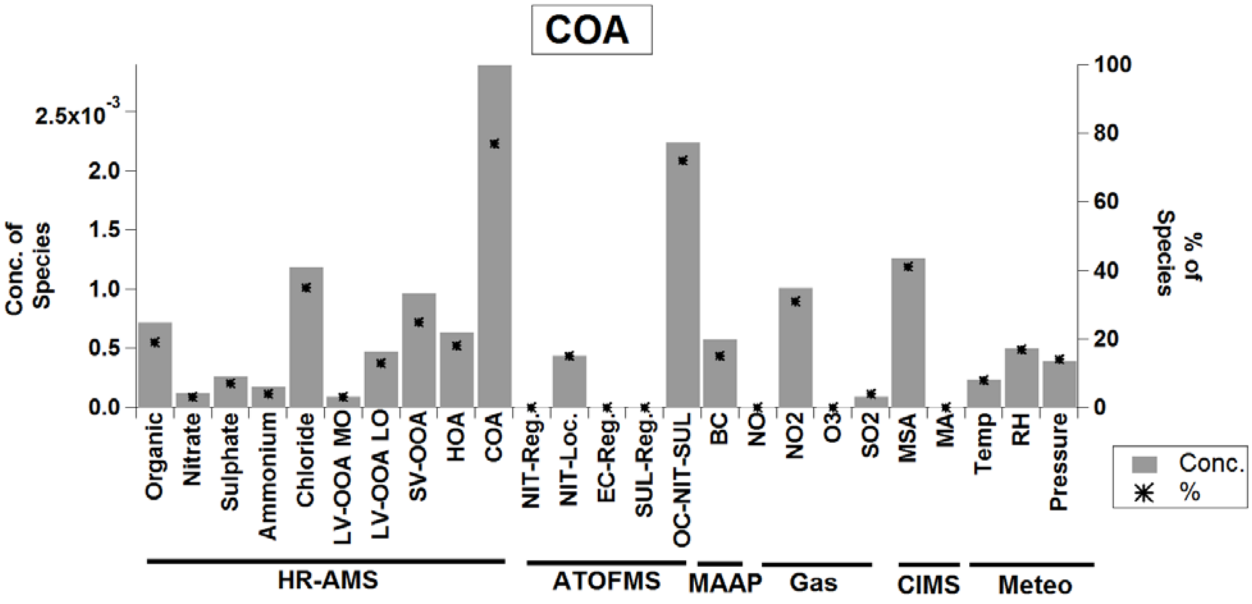
ATOFMS
MAAP
Gas
CIMS
Meteo

(d)



(e)

Figure 1. PMF factors of the dataset 1 (ALL field study)

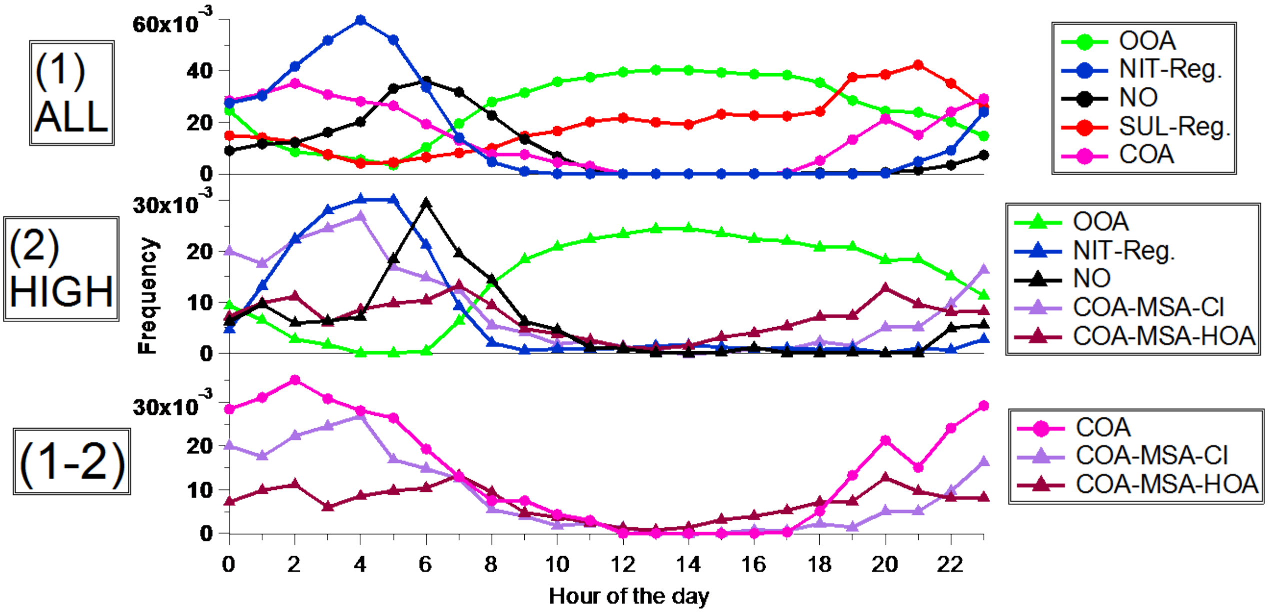
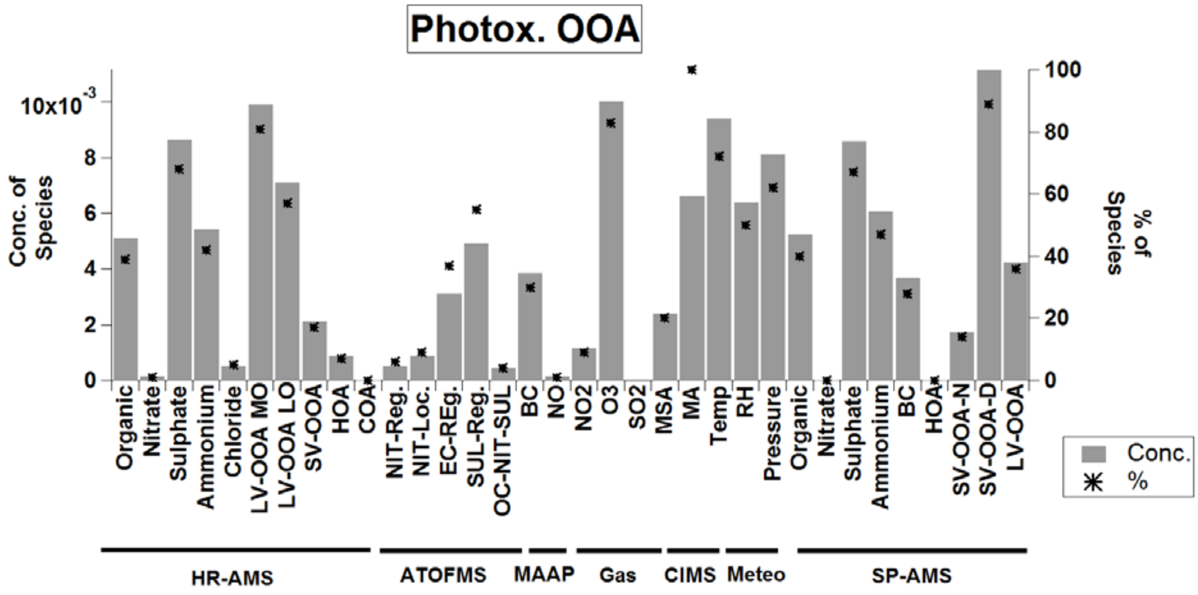
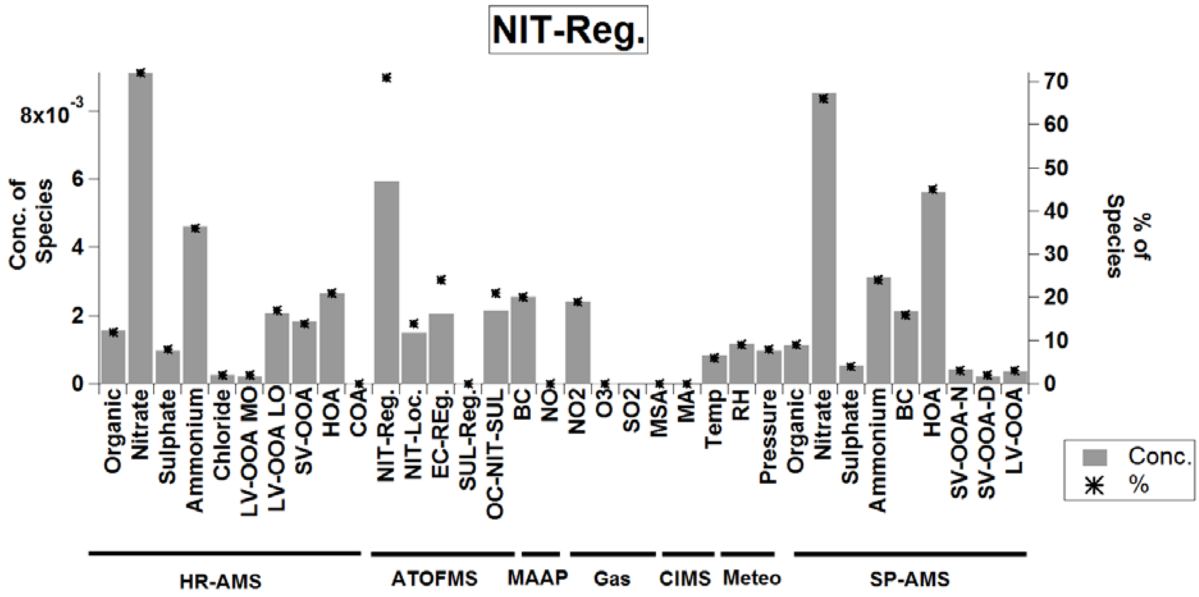


Figure 2. Diurnal profiles of dataset_1 (ALL field study) and dataset_2 (second part, HIGH). Figure (1-2) shows again the COA factors coming from dataset_1 (COA) and dataset_2 (COA-MSA-Cl and COA-MSA-HOA)


Photox. OOA
Conc. of Species
% of Species
10x10-3
8
6
4
2
0
100
80
60
40
20
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-REg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
O3
SO2
MSA
MA
Temp
RH
Pressure
Organic
Nitrate
Sulphate
Ammonium
BC
HOA
SV-OOA-N
SV-OOA-D
LV-OOA
Conc.
%
HR-AMS
ATOFMS
MAAP
Gas
CIMS
Meteo
SP-AMS

(a)


NIT-Reg.
Conc. of Species
% of Species
8x10-3
6
4
2
0
70
60
50
40
30
20
10
0
Organic
Nitrate
Sulphate
Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
EC-REg.
SUL-Reg.
OC-NIT-SUL
BC
NO
NO2
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SO2
MSA
MA
Temp
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Pressure
Organic
Nitrate
Sulphate
Ammonium
BC
HOA
SV-OOA-N
SV-OOA-D
LV-OOA
Conc.
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HR-AMS
ATOFMS
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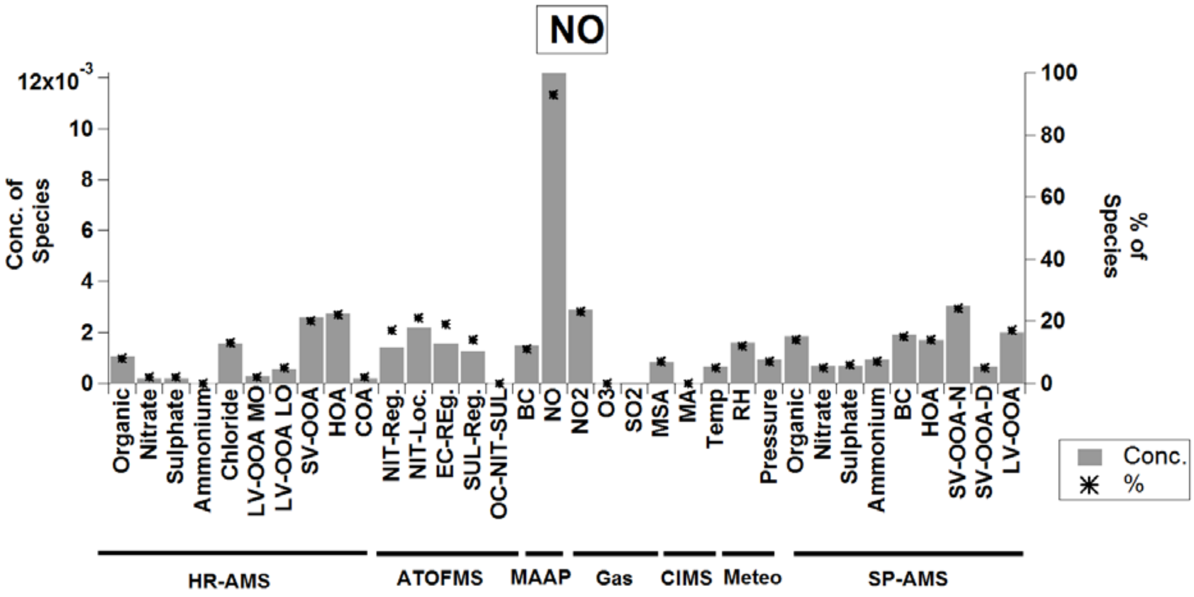
Gas
CIMS
Meteo
SP-AMS

(b)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Conc. of Species
% of Species
100
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Organic
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Ammonium
Chloride
LV-OOA MO
LV-OOA LO
SV-OOA
HOA
COA
NIT-Reg.
NIT-Loc.
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SUL-Reg.
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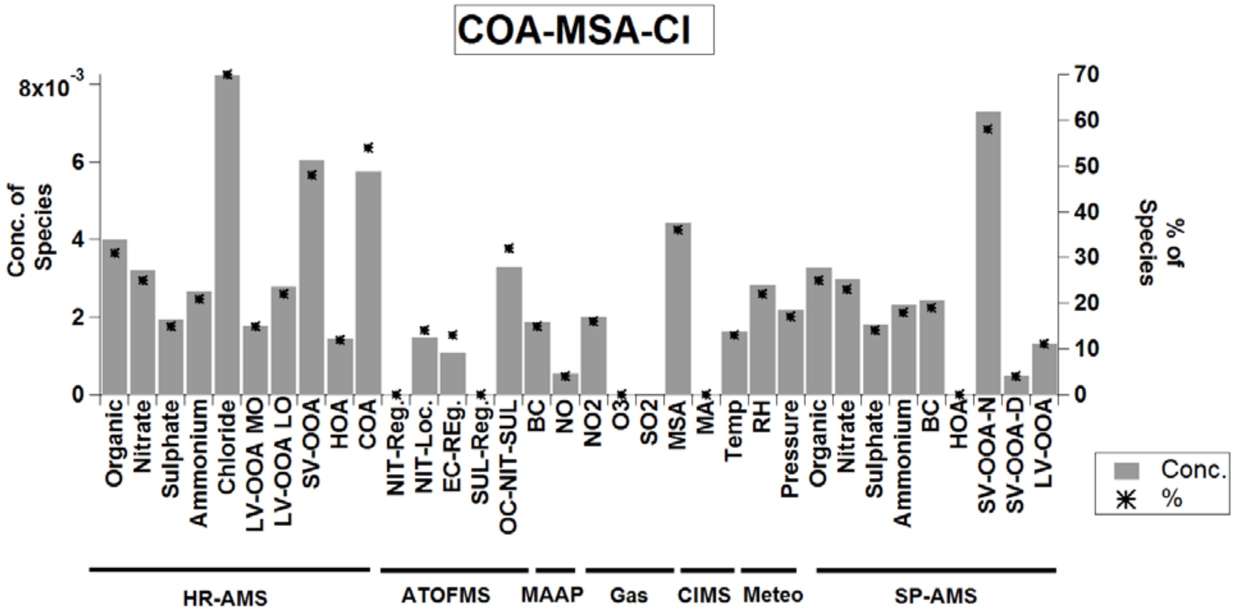
(c)


COA-MSA-Cl
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Conc. of Species
% of Species
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LV-OOA LO
SV-OOA
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COA
NIT-Reg.
NIT-Loc.
EC-REg.
SUL-Reg.
OC-NIT-SUL
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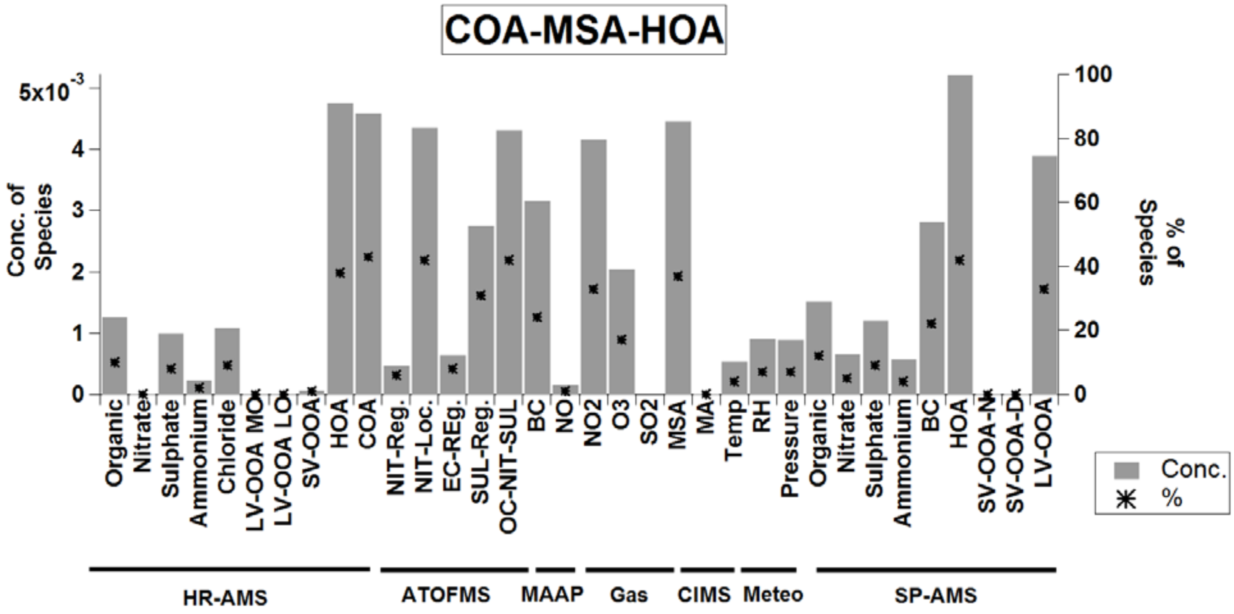
Nitrate
Sulphate
Ammonium
BC
HOA
SV-OOA-N
SV-OOA-D
LV-OOA
Conc.
%
HR-AMS
ATOFMS
MAAP
Gas
CIMS
Meteo
SP-AMS

(d)



(e)

Figure 3. PMF factors of the dataset_2 for the second part of the field study (HIGH)