Aerosol Source Assessment Based on Organic Chemical Markers

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The aim of this paper is to identify the potential sources of fine aerosols in Magurele, Romania, during an intensive campaign of 2 weeks performed in August-September 2014, based on mass concentration, species proportions and specific chemical markers.Major contributors to submicronic non-refractory aerosols are organic species, ammonium and sulphate. The inorganic species have been present as salts of ammonium nitrate and ammonium sulphate, while strong influence of traffic related source has been identified during the entire measurements period from organic species analysis. Other contributions besides those mentioned above are biomass burning and two different oxidized organic aerosols.

Keywords: organic species, oxidized organic aerosols, mass spectrometry

Aerosols represent the airborne particulate matter (PM), an important component of the atmosphere. High loadings of aerosol have a negative effect on human health, being related with respiratory[1-3] and cardiovascular diseases [4] and have also an impact on visibility[5], resulting in a transportation safety issue. The radiative effect of aerosols has been intensively mentioned and deliberated in the latest ICCP report [6] due to the challenge to establish their positive or negative effect. For example, the potential of black carbon is primarily to absorb radiation and the opposite in the case of organics. Beside the direct effect, aerosols have an indirect radiative effect, acting as cloud condensation nuclei. Therefore in order to improve the aerosols characterization and understanding, it is important to evaluate their concentrations, chemical composition and possible sources.

The primary aerosols (PA) are particles emitted directly into atmosphere from natural (mineral dust, sea salt) or anthropogenic (formaldehydes from vehicle combustion, biomass aerosol from wood combustion) sources. PA are directly involved in chemical reactions and physical transformations during daytime or night time processes, becoming secondary aerosols (SA), with different chemical composition [5] and optical properties.

In the past 20 years, mass spectrometry has proved to be a proper tool to evaluate the composition of aerosols. Although the mass spectra represent: superposition of multiple different particles; the base for deconvolutions of different chemical species and markers for evaluating the type of the aerosol sampled. Because more than 50% of total submicronic aerosol represents organic aerosol (OA)[8], the best way to analyze the submicronic aerosols is to evaluate the specific markers presented in the organic mass spectra. Taking into account the degree of oxidation of organics, which is an indicator for aging, aerosols can be divided into aerosols related to primary aerosols, freshly emitted with a short time of residence in the atmosphere and more oxidized aerosols: semi-volatile (SV-OOA) and low-volatile OA (LV-OOA) as secondary aerosols. In Europe, OA is composed mostly (70%) by secondary aerosol (SV-OOA and LV-OOA) as Crippa et al. [9] pin pointed in the study of 25 AMS measurements placed all over Europe, in sites with different influences from rural, urban or locations at high altitude.

Secondary Organic Aerosols (SOA) are formed by changing the volatility through chemical reactions in the particulate and gas phase [10] and heterogeneous acid catalyzed carbonyl reactions in the particulate phase such as polymerization, hydration, aldol condensation[11]. Secondary inorganic aerosol formation is well described by Seinfield et al. [13]. Ammonia neutralizes the acidic species and forms ammonium nitrate and ammonium sulphate, when atmospheric conditions like temperature or humidity favour their formations.

This paper focuses on aerosol composition assessment for a period of almost two weeks in August-September 2014 at our measurement site placed in a peri-urban area, Magurele-Ilfov, with influences from the agricultural zones, power plants and traffic [11]. Estimation of aerosols' oxidation degree is made using the ions 44, 43, 57, while assessment of biomass burning presence is made using ions 60 and 73. Only several studies have been conducted in this part of Europe regarding the aerosols chemical composition and their sources. Up to now aerosol size and composition at this site have been investigated, depicting high concentration of NO_3 during the winter[14] and important organic species during the summer [15].

Experimental part
Methodology

Submicronic non-refractory particles have been sampled with a Compact Time Of Flight Aerosol Mass Spectrometer (C-TOF AMS) in order to retrieve information about the composition and the aerosols size[16].

The system is composed of three main chambers: sampling, sizing and detection and chemical analysis. Aerosols are collected through a particle inlet with a constant flow rate of 6 L/m and focused into a 1 mm diameter beam, the gas being removed by 6 aerodynamic lens with differential pumping (up to 10^{-3}Torr).The second chamber consists of a 395 mm tube, held at a pressure of 10^{-5}Torr [17]. The size of particles is retrieved with the time of flight technique using a beam chopper mechanism. The gas expansion between the two chambers create a distribution of velocities: particles with a smaller diameter are accelerated faster than the aerosols with a larger diameter. The size depending velocity is calculated as the ratio between the length of the tube and the time required for a particle to travel through the tube, and to reach the detector. The time travelled between the end of the tube to the detector is three order of magnitude smaller the time travelled by a particle in the tube, so that the time in flight

in the tube is approximated with the time measured from the chopper slit to the detector. In order to derive the vacuum aerodynamic diameter from the velocity, size calibration is required, the entire procedure being described in detail by Drewnick et al. [16].

The particle beam is focused on a tungsten vaporizer heated at 600ºC. Electrons emitted by a heated filament ionize the plasma formatted by the non-refractory particles. The resulting positive ions are analyzed by mass spectrometry in the time of flight geometry where ions are separated according to their mass number to charge number ratio (m/z). The equipment is sensitive just only for non-refractory particles, defined as particles that evaporate quickly under vacuum at temperatures higher than 500ºC. Refractory aerosols like dust, black carbon, sea salt cannot be measured by C-TOF AMS, due to lack of volatility at this temperature. Mass concentrations ($\mu g/m^3$)[18] for 5 chemical species (s): organics, nitrate, ammonium, sulphate and chloride are retrieved using the formula:

$$C_S = 10^{12} \frac{MW_{NO3}}{CE_S RIE_S IE_{NO3} Q N_A} \sum_i I_{s,i}$$

where:

MW_{NO3} is the molecular weight of NO_3, CE is the collection efficiency;

RIE is the relative ionization efficiency;

IE_{NO3} – ionization efficiency for NO_3, Q volumetric flow rate;

N_A –Avogadro's number, $I_{s,i}$ number of ions per second.

The subscript i is an index for ions corresponding to the same species.

The standard fragmentation table [19] and collection efficiency of 0.5 [18] are used in our study for all the species. Both modes of operation of the instrument have been used, measuring both the size distribution for vacuum aerodynamic diameter and mass spectrum of the chemical species.

Assessment of aerosol sources can be made based on two different approaches: source oriented (e.g. dispersion models) or receptor oriented analyses (positive matrix factorization -PMF, Multilinear Engine 2- ME2 etc.). This study is based on receptor oriented analyses ME2, some of the profile sources being known. The receptor oriented analyses or source apportionment is the usual practice of deriving information about pollution sources and the amount they contribute to ambient air pollution levels.These tools have the advantage of providing information derived from real-world measurements. This model was first developed by Paatero et al. [20, 21] and integrated later in other tools like Source Finder [22].

The ME2 model is a bilinear model considering a matrix X formed by n number of observations (time series) and m chemical species that for our case represent the mass to charge ratio concentrations. This matrix of data recorded at receptor site can be influenced by p sources.

The deconvolution of sources can be represented mathematical like:

$$X = G * F + E$$

where:

G = p*n,F=p*m;

E - represent the errors associated to the model (n*m).

The source apportionment was applied for two weeks of measurements made at 2 minute time resolution, collecting sufficient data necessary for the model to run properly.

The analyses of chemical markers from organic spectra retrieved from C-TOF AMS is used in present study to pre-process the data and to assess the factors that can influence the aerosols formation at our site, in order to obtain a better deconvolution of profiles.

Types of organic aerosols have been evaluated using also the delta pattern-Δ analysis, following the protocol described by McGuire, et al. [23]:

$$\Delta = \frac{m}{z} - 14n + 1$$

where n is the number of CH_2 groups in the functional group.

Markers used for this study was characteristic for alkans and alkenes: m/z 57 particlefreshand non-oxygenated; m/z 43organic particles fresh, non-acidic oxygenates; m/z 44characteristics for aged, oxygenated organic aerosol and for sugar fragments resulted from cellulose pyrolysis like m/z 60 or m/z 73. Some values widely described in the literature of $f44$and $f60$ (ratio of m/z to total signal in the component mass spectrum) are used for description of low volatility oxidized component and biomass burning organic aerosols(BBOA) respectively. For $f60$ the existing limit value, established by Cubisonet al. [24] is used to underline the presence of BBOA over the background level $0.3\pm0.06\%$. Also similarly the corresponding fractions of m/z $44, 43, 55, 57$ are used to indicate the oxidation state and aerosols age.

Results and discussions

For the period studied, the aerosol mass loadings mean measured where characteristic for rural sites [9], with a slightly higher proportion of organic aerosol. The main species at Magurele have been, organic species (54%), ammonium (17%) and sulphate (22%), with low amounts of nitrate and chloride. Even if the organics loadings dominated the AMS time series (fig. 1) for the entire period, several episodes of important peaks were present, as in the case of September7th, when their concentration reached15 $\mu g/m^3$due to local sources.

The size distribution of aerosol highlights the accumulation mode (fig. 2), the peaks for organics and sulphate, nitrate and ammonium being centred at 350 nm, and 380 nm respectively. The unimodal shape, as well as central diameter of size distribution, indicates a possible internal mixture of those species and same source (fig. 2). The formation of two aerosols: ammonium sulphate and ammonium nitrate depends on the ammonia concentration as well as the atmospheric conditions. In the measurement period, the atmosphere has been ammonia rich, the measured ammonia exceeding the predicted ammonia to neutralize the acidic sulphate aerosol (the slope between NH_4 measured and NH_4 predicted was1.3).

The calculated delta pattern, which gives information about the length of the molecule's backbone, pin pointed that the measurement periods have beendominated by series with $\Delta< -2$ specific for aromatics; $\Delta=0..2$ specific for alkanes and alkenes and $\Delta=3$ for oxidized species[25].
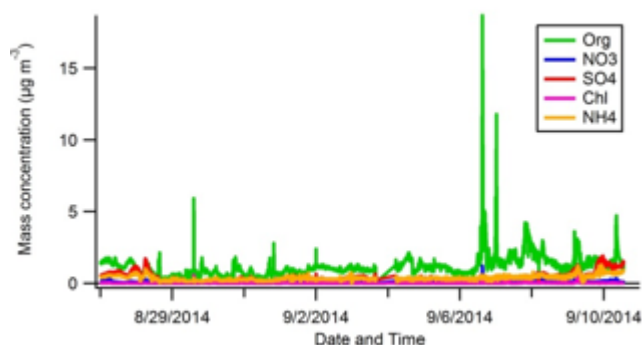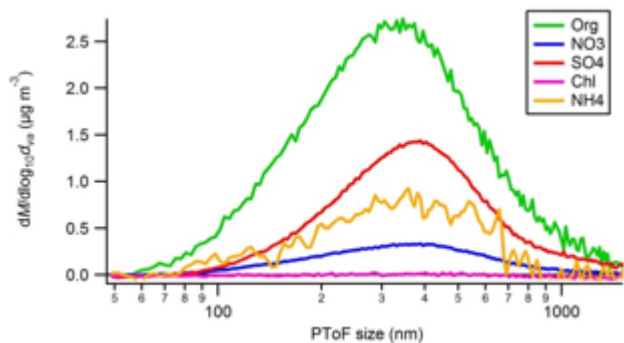

Fig. 1. Mass concentration time series

Fig. 2.Mass size distribution of submicronic non-refractory aerosols

Fig. 4. *f44* versus *f43*

The marker analyses underline the dominance of SOA on entire period of measurements, *f44* having values up to 0.3 and emphasising the presence of oxidized organic aerosols.The degree of aerosol oxidation is evidenced by *f44* increases and *f43* decreases[26], values between 0.05-0.1 of *f44,* being representative for semi-volatile since values above 0.1 are linked to oxidized aerosol. About 94% from the total measurements are dominated by *f44* values that exceed the 0.1 threshold. More semi-volatile aerosol is generated in the last part of the measurements, from 6 to 10th September (fig. 4).

Even the SOA are dominated fractions, the presence of POA as BBOA aerosol, estimated using the *f60* factor [24], underlines that in 79% of cases, the measured values are higher than the background level of 0.003 (fig. 3).
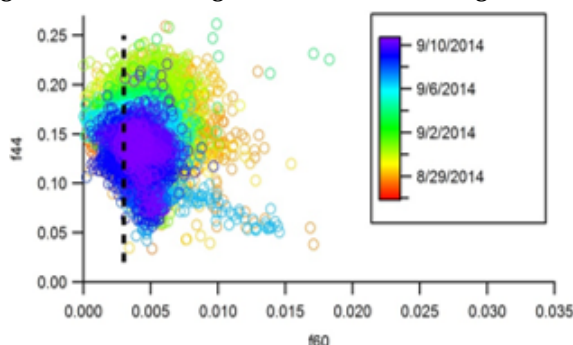

Fig. 3. *f44* versus *f60*

He et al.[28] attributed values to $m/z 57$ ion abundance between 0.02 and 0.06 for cooking or biomass burning aerosol, and much higher values for aerosol resulted from vehicle exhaust and plastic burning. Adler et al. [27] calculated a slope of $m/z 57$ to total organics of 0.02 for aged BBOA and 0.04 for fresh BBOA.The presence of BBOAin our data is also confirmed by slope value between $m/z 57$ and organics, of 0.014 that is in a good agreement with Ä, *f44, f43* and *f60* analyses, the aerosols not being freshly emitted.
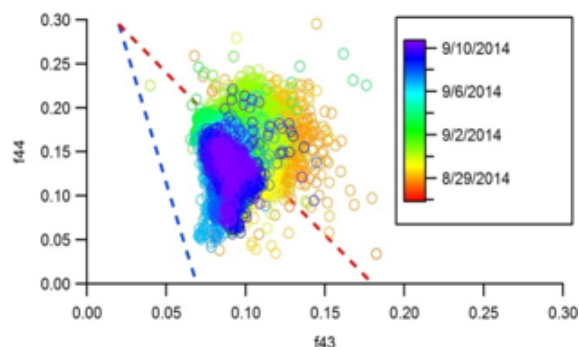
Another primary aerosol that is present in the data is HOA assimilated with values around 0.05 for *f44* and with the signal at m/z 57 corresponds to saturated hydrocarbons $(C_4H_9^+)$ or long alkyl chains $(C_3H_5O^+)$[27].

The investigation of organic markers underlines the presence of some clear influences like BBOA and oxidized aerosols. To evaluate the proportion of main submicronic organic sources the ME2 was set-up after several runs and sensitivity tests. The sensitivity tests included settings related with degrees of freedom for two factors, HOA and BBOA. The tests on the model start from totally unconstrained runs that emphasize the presence of four main factors. The most suitable deconvolution of the factors was obtained after we implement the main advantage of the method, the option to use as input the known pattern of m/z. Previous studies [9] confirm that the m/z pattern for BBOA and HOA are almost constant for different sites since oxidized organics had different patterns specific to particular locations. For sensitivity tests the constrained approach was made varying the value that allow degree of freedom from 0.1 to total unconstrained with 0.1 steps. The resulted profiles are in accordance with previous study and marker analyses made above.

The oxidized organic aerosol profile has an important signal at $m/z 44$ dominated by CO^+_2ion, that is a result of thermal decomposition of oxidized long alkyl chains. The signal in $m/z 44$ is related with volatility of chemical species, so high signal is related with low volatility of organics. The separation between factors is analysed from the point of specific chemical markers that must be attributed by the model to a certain source. Therefore the high presence of $m/z 60$ in HOA spectra is a clear indicator for the mixture of these factors. The sensitivity tests for this particular case show that the best separation between factors was obtained using a constrained by 0.5 for BBOA and 0.4 for HOA. The last two factors were totally free (unconstrained), the solution given by the model showing the presence of two oxidized factors (fig. 5,6). The difference between these two factors is related with their
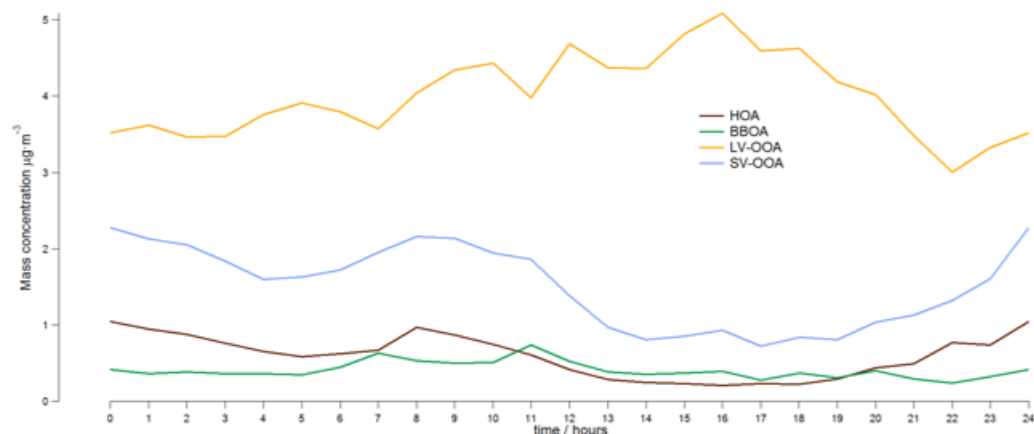

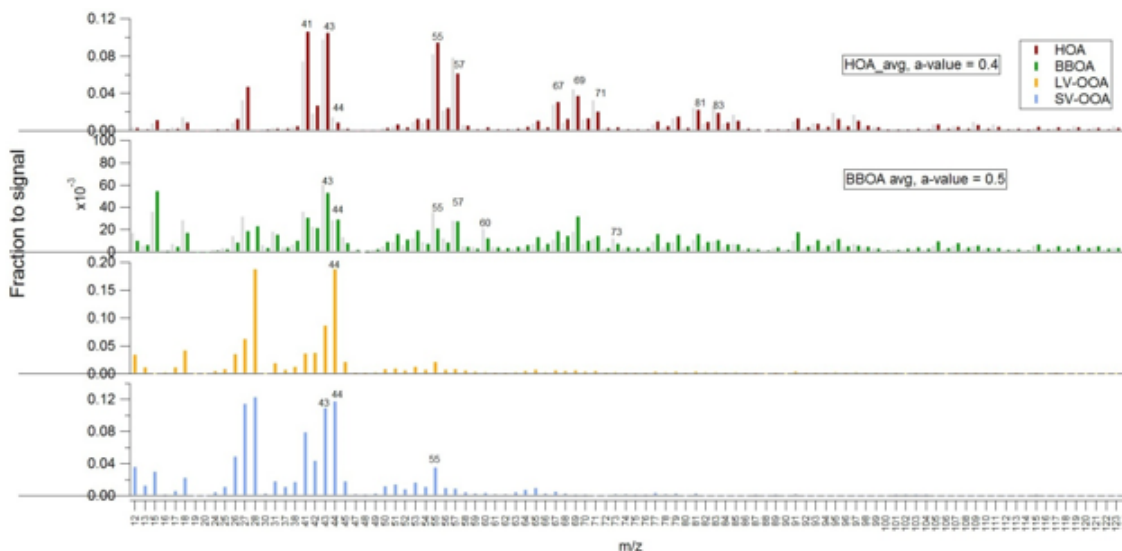Fig.5.Diurnal pattern of submicronic organic factor identified during work days

Fig.6.Mass spectra of the factor organic components

degree of oxidation, marked by report between *m/z 43* and *m/z 44*. The highly oxidized factor identified by the model has a higher peak in *m/z 44* and lower degree of volatility. The low volatility organic oxidized aerosol (LV-OOA) is less correlated with POA (primary organic aerosols), the main source being related with long-range transport (fig. 5). The second oxidized factor profile the semi volatile oxidized organic aerosol (SV-OOA) show a diurnal trend and is correlated with HOA (Fig.5), this factor being mainly a secondary product resulted from oxidation of traffic related organic aerosols.

The most important POA is traffic related and is dominated by *m/z* characteristics for long alkyl chains hydrocarbons, such as *m/z 41* ($C_3H_7^+$), *m/z 43* ($C_3H_7^+$), *m/z 55* ($C_4H_7^+$), *m/z 57* ($C_4H_9^+$), *m/z 67* ($C_5H_7^+$), *m/z 69* ($C_5H_9^+$), *m/z 71* ($C_5H_{11}^+$), *m/z 79* ($C_6H_7^+$), *m/z 81* ($C_6H_9^+$) and *m/z 83* ($C_6H_{11}^+$) [9] (fig. 6). The HOA diurnal pattern highlights the increase of traffic activity starting with 7 AM local time, decreasing at noon and increasing together with the rush hours in the evening (6 PM). The most important contribution from *m/z 60* ($C_2H_4O_2^+$) and *73* ($C_3H_5O_2^+$) (fig. 6) is attributed to BBOA factor that has a less pronounced diurnal pattern (fig.5), and probably is influenced by vegetation fires and agricultural practices.

The model solutions demonstrate a clear dominance of SOA against POA, the dominant factor being LV-OOA with a percent of 62%, followed by SV-OOA with 23%, since HOA represent 9% and BBOA 6% from the total organic submicronic particles.

Conclusions

This study presents time-resolved measurements of submicron non-refractory aerosol chemical composition using a CTOF Aerosol Mass Spectrometer in Magurele, Romania. The main species of fine particles have been organic species (54%), ammonium (17%) and sulphate (22%). The specific chemical markers found during the intensive campaign in August-September 2014 indicate several sources of aerosols, fresher like HOA or BBOA and aged organic aerosols with different levels of oxidation.

Running the ME2 model for distinct factors were evidenced: HOA- traffic related; BBOA- influenced by vegetation fires from agriculture most probably; SV-OOA correlated with traffic activity and LV-OOA linked more with long-range transport.

A unimodal aerosols size distribution has been characteristic within accumulation mode centered in the range of 350-400nm for organics, sulphate, nitrate and ammonium. The same shape and peaks indicated a possible internal mixture of those species and therefore the same source.

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