Source apportionment and aging of aerosol particles in the outflow of Paris during summer and winter time

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Aerosol particles are characterized by different chemical composition and physical properties which are often related to different emission sources and atmospheric physical-chemical reactions. The analysis of the chemical composition of atmospheric aerosols allows the investigation of the contribution of local emission sources, particle aging and secondary organic aerosol (SOA) formation mechanisms. Source apportionment techniques have been applied to identify the importance of primary emission sources and secondary formation.

Two measurements field campaigns have been performed during summer 2009 and winter 2010 (MEGAPOLI Project) at a sub-urban background site located in the South-West of Paris (SIRTA – Ecole Polytechnique). Stationary measurements allow the characterization of atmospheric aerosols, their gaseous precursors and the assessment of local sources and background contributions. In order to document the aerosol composition and properties close to sources, mass and chemical measurements based on high resolution data have been performed. Several instruments were deployed at the SIRTA fixed site to describe the chemical composition and physical properties of aerosol particles (HR-ToF-AMS, HV-TDMA, CCNC, SP2, particle counters, SMPS, Thermodenuder, Aethalometer, Nephelometer). HR-ToF-AMS (High Resolution Time of Flight Aerosol Mass Spectrometer) provides quantitative real-time size and chemical mass loading information for non-refractory sub-micron aerosol particles. Seasonal comparisons of mass concentration, chemical composition and particle size distribution have been performed. On average summer PM_1 mass concentration is mainly characterized by organics (46.9%) with smaller contributions from nitrate, sulfate and ammonium (4.8%, 23.5% and 8.1% respectively). During wintertime the organic fraction of the total mass was 29.7%, the nitrate fraction 25.2%, the sulfate contribution 14.4% and the ammonium one 12.1%. In both season the black carbon contribution is around 16-17%.

The combination of statistical models with high time resolution measurements allowed a more detailed source apportionment, with discrimination of many sources. Positive matrix Factorization (PMF) is a bilinear unmixing, receptor only, model used to describe the observed organics mass concentration with a combination of constant source profiles which have a different contribution during the time (Ulbrich et al., 2009).The model does not require a priori values of F and G, besides they are iteratively calculated applying a least square method. PMF has been applied to the summer and winter datasets to identify the main sources which contribute to the organic aerosol concentration. Preliminary results are presented in this poster. Positive Matrix Factorization (PMF) have been used to characterize organic aerosol in terms of HOA (Hydrocarbon-like Organic Aerosol, usually mostly from traffic), OOA (Oxygenated Organic Aerosol, usually mostly secondary organic aerosol) and WB (Wood Burning) (Lanz et al., 2007).

During summertime four factors have been identified: the oxygenated fraction of the organics aerosol (OOA), factors 1 and 2, is splitted between LV-OOA which correlates

with less volatile compounds (such as SO_4) and SV-OOA which is the volatile part (correlations with NO_3 and Chl). The total OOA represents the 67% of the organic mass, the hydrocarbon-like OA (HOA) contributes 24% to the organic mass besides the last factor is still associated to unknown sources (9%). Considering the winter dataset it was not possible to separate the oxidized fraction of organic aerosols (factor 1) into LV-OOA and SV-OOA, but further investigations need. Factor 2 is the hydrocarbon component (HOA) and it correlates with org57, black carbon and CO measurements, since it is related to traffic emissions. Factor 3 is particular of wintertime and it is associated with wood burning. OOA peaks in the night and in the afternoon (probably due to combustion and processed air), besides HOA and WB peak in the morning and in the evening due to traffic and domestic heating. Preliminary analyses suggest that primary organic wood burning emissions represent 20% of the organic mass concentration in winter at the suburban site in Paris, as confirmed by concurrent mobile measurements. Moreover the wood burning and traffic factors seem to be correlated during winter time as it has already been seen in previous studies (DeCarlo et al, 2010).
Although oxidized organic aerosols represent the main fraction of the total organic mass in both seasons (more than 50%), different photochemical and oxidation processes are involved, depending on the meteorological conditions and on the role of different primary emissions sources in winter and summer time. A big contribution from traffic (larger than e.g. in Switzerland) was observed in both seasons (HOA factor around 25%)
Concurrent mobile measurements were performed by the PSI mobile van to investigate the spatial distribution and the chemical evolution of the megacity plume. The use of combined mobile and ground based measurements of the chemical composition of organic aerosol allowed the evaluation of the secondary organic aerosol formation from aerosol precursors compared to background concentration levels during different stages of the plume development.

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Acknowledgements

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The MEGAPOLI Project

Two measurements field campaigns have been performed during summer 2009 and winter 2010 (MEGAPOLI Project) at a sub-urban background site located in the South-West of Paris (SIRTA – Ecole Polytechnique), shown in Figure 1.

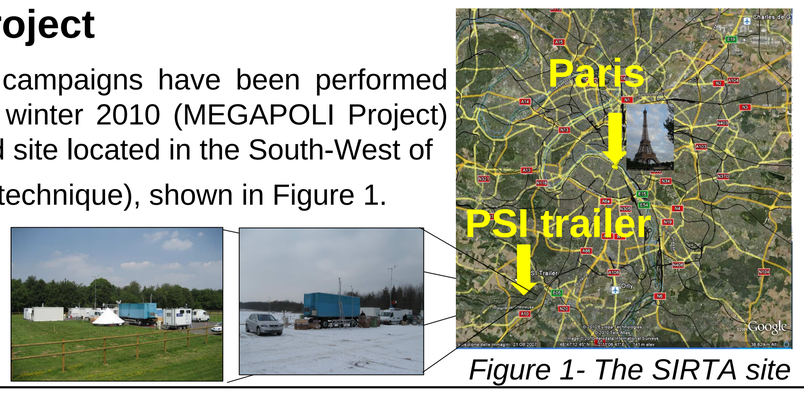


Figure 1- The SIRTA site

Goals

- Chemical characterization of aerosols particles
- Seasonal comparison of mass concentrations and chemical composition
- Source attribution in the Paris region

Instruments

Several instruments have been deployed by PSI at the stationary site (such as HR-ToF-AMS, HV-TDMA, CCNC, SP2, particle counters, SMPS, Thermodenuder, Aethalometer, Nephelometer) but this poster is focused mainly on AMS data.

Summer campaign: 1st- 31st July 2009

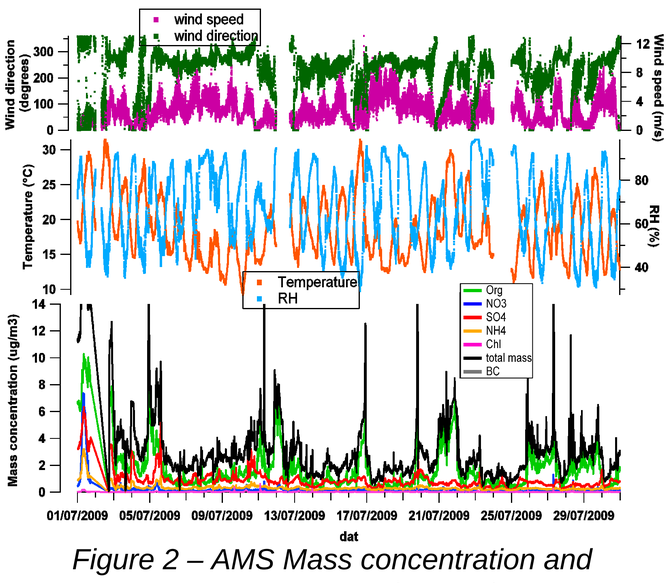
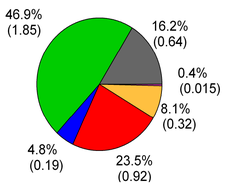


Figure 2 – AMS Mass concentration and meteo parameters time series

Unstable meteo conditions caused quite low concentrations during summertime. Figure 2 shows the AMS species time series and the meteo parameters (wind, temperature and RH). The average chemical composition of the particles is represented in the pie chart (average mass concentration values in brackets). A Collection Efficiency (CE) of 0.5 was assumed.



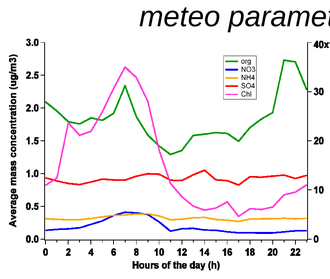


Figure 3 – Diurnal pattern of AMS species

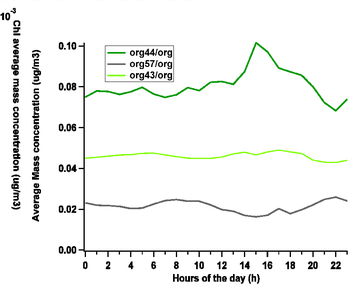


Figure 4 – Diurnals of some organics fragments

The diurnal pattern of the AMS species and of some organics fragments are shown in Figures 3 and 4. Organics reach maximum concentrations in the morning and in the evening (due to the traffic contribution) but also in the afternoon due to the photochemical production. Nitrate and cloride present a partitioning behaviour.

Winter campaign: 15th Jan - 15 Feb 2010

The total mass concentration was ranging between few ug/m^3 up to 40 ug/m^3 (CE=1) (Figure 5) and the monthly average chemical composition is represented in the following pie chart (average mass concentrations in brackets). Two high pollution periods were identified.

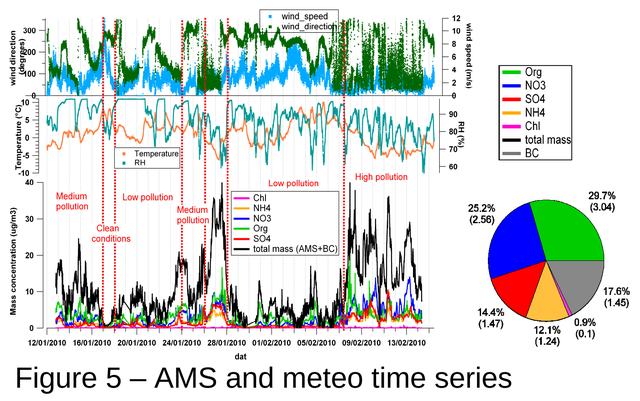


Figure 5 – AMS and meteo time series

Figure 6 shows that high pollution events were related to the air coming from 50 degrees (red spot) or to local sources associated with low wind speed.

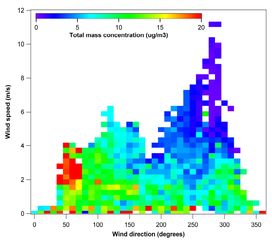


Figure 6 - Total mass concentration vs wind parameters

Figures 7 and 8 show the diurnal pattern of the AMS species and of some organics fragments.

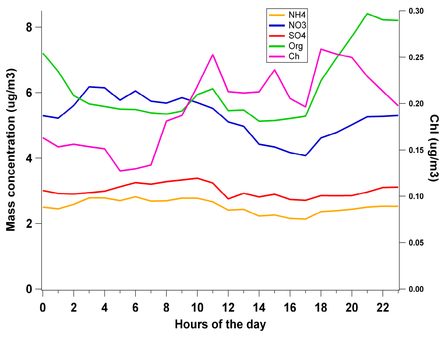


Figure 7 – Diurnal pattern of AMS species

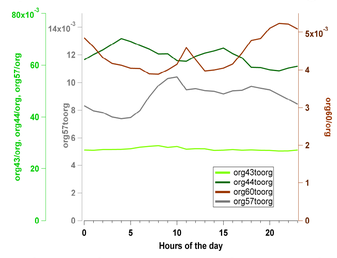
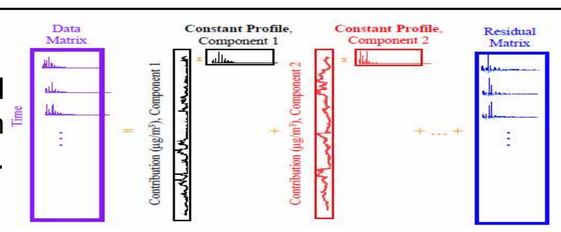


Figure 8 - Diurnal pattern of organics fragments

Organics peak in the morning (traffic contribution) and in the evening (role of wood buring and traffic); nitrates are higher in the night due to the lower temperatures which favor their condensation. NH_4 is mainly neutralized by SO_4 and they have a similar daily pattern.

Source apportionment: PMF

Positive matrix Factorization (PMF) is a bilinear unmixing receptor only model used to describe the observed organics mass concentration with a combination of constant source profiles which have a different contribution during the time. PMF can be represented with the following scheme (Ulbrich et al., 2009).



The model does not require a priori values of F and G, besides they are iteratively calculated applying a least square method.

PMF has been applied to the summer and winter datasets to identify the main sources which contribute to the organic aerosol concentration. Preliminary results are presented in this poster.

Summer apportionment

Four factors have been identified (Figure 9). The oxygenated fraction of the organics aerosol (OOA), interpreted to be mostly secondary organic aerosol, is splitted between LV-OOA (factor1) which correlates with less volatile compounds (such as SO_4) and SV-OOA (factor 2) which is the volatile part (correlations with NO_3 and Chl). OOA represents the 67% of the total organic mass. The hydrocarbon-like OA (HOA) contributes 24% to the organic mass. The last factor is associated to unknown sources (9%). The daily pattern of the 4 factors is represented in Figure 10 and a mass spectra comparison is shown in Figure 11.

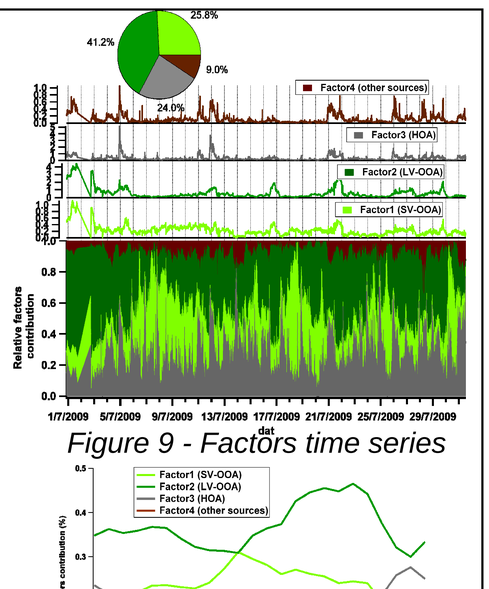


Figure 9 - Factors time series

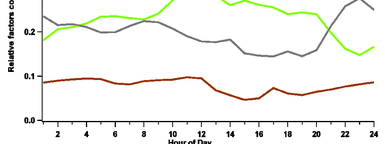


Figure 10 - Factors diurnals

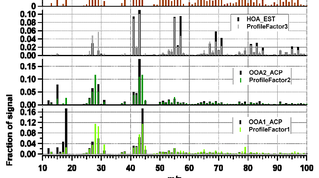


Figure 11- Mass spectra comparison

Winter apportionment

In Figure 11 the time series of the identified factors and their relative contribution are presented. The first factor is OOA and correlates well with SO_4 and org44 time series. Factor 2 is the hydrocarbon component (HOA) and it correlates with org57, black carbon and CO measurements, since it is related to traffic emissions. Factor 3 is particular for wintertime and it is associated with wood burning (WB).

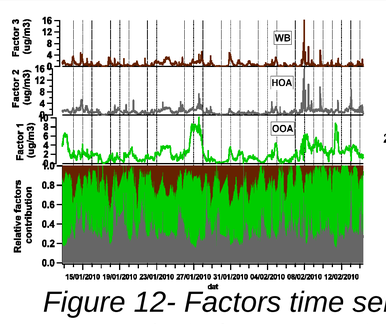


Figure 12- Factors time series

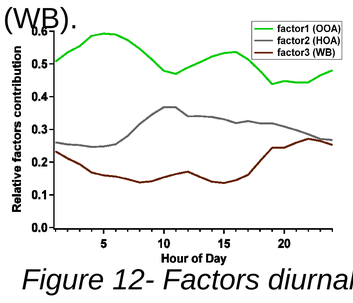


Figure 12- Factors diurnals

OOA peaks in the night and in the afternoon besides HOA peaks in the morning and WB in the evening due to traffic and domestic heating contributions (Figure12).

A comparison of the mass spectra is shown in Figure 13.

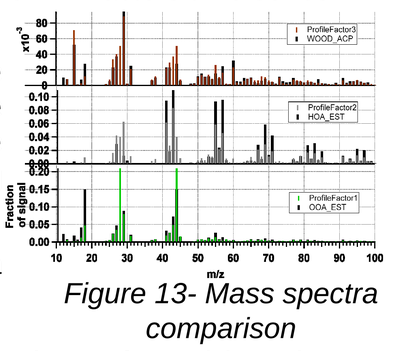


Figure 13- Mass spectra comparison

A 3 factors solution was chosen but further investigations need to be performed in order to eventually separate the less volatile and more volatile fractions of OOA.

Conclusions

- AMS measurements have been performed to describe the aerosol chemical composition in the Paris region and the plume transport from a megacity
- Preliminary source apportionment results have been obtained using PMF
- During summer and winter time, different sources and processes have been identified in the Paris region. Even if the oxydized fraction of organic aerosol is always the major part (more than 50%), a big contribution from traffic (larger than e.g. in Switzerland) was observed in both seasons (HOA factor around 25%)
- Wood burning represents a significant organic source during wintertime (20%)
- During summertime, fresh and more processed oxydized organic aerosols were identified.

References

Ulbrich, I.M., M.R. Canagaratna, Q. Zhang, D.R. Worsnop & J.L. Jimenez (2009), Atmos. Chem. Phys., 9, 2891-2918.

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