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THE MEGAPOLI PARIS CAMPAIGN FOR URBAN AEROSOL CHARACTERISATION – A COMPREHENSIVE DATA SET FOR AIR QUALITY MODEL EVALUATION

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Abstract: Within the FP7 MEGAPOLI project, two intensive field campaigns have been conducted in the Greater Paris region during July 2009 and January/February 2010. The major aim was to quantify sources of primary and secondary aerosol, and the interaction with gaseous precursors, in and around a large agglomeration in temperate latitudes. From this campaign, a comprehensive data set will be built which will be available for urban and regional scale air quality model evaluation. The paper will present campaign objectives and set-up, first results, and specific benchmarks, which should be most useful for model evaluation.

Key words: *organic aerosol, particulate matter, primary and secondary sources, benchmark for model evaluation.*

INTRODUCTION

Very dense pollutant emissions over megacities are strongly affecting air quality on an urban scale and chemical composition on a regional and even global scale. This ultimately affects both public health and regional to global climate. In order to assess the overall effects of megacity emissions, all links between emissions, transport, chemical transformation and deposition processes should be well understood, which is currently not yet achieved. In particular, despite its adverse effects on health and their potential effects on regional and global, primary and secondary sources of particulate matter in the urban atmosphere are not well qualified and quantified.

The FP7 and national French MEGAPOLI project aims at gaining an increasing comprehension of major processes affecting the abundance of particulate matter in a polluted atmosphere, in particular:

- to better assess primary sources of carbonaceous aerosols,
- to better assess secondary sources of organic aerosols through gas-to-particle conversion,
- using this knowledge, to evaluate and improve process and air quality models.

To reach these objectives, an experimental campaign in the Paris agglomeration, a major anthropogenic emission source surrounded by rural areas, has been conducted. A particular focus has been put on organic carbon, for which not only secondary formation, but also primary emissions are still not well quantified, despite the major contribution of organic carbon to urban and regional scale fine particulate matter levels. Greater Paris has been chosen for a large experimental air pollution campaign because it is a major and dense pollution source (more than 10 million inhabitants), surrounded by rural areas and relatively flat terrain.

Detailed aerosol measurements and gaseous precursor measurements have been conducted at an urban and two sub-urban sites, from five mobile platforms and from the French ATR-42 and Piper-Aztec research aircraft. State of the art instrumentation has allowed determination of aerosol chemical composition, either with very high frequency (several minutes to half an hour), or with large chemical detail (several dozens of organic compounds from filter samples). In addition, the size distribution, optical, hygroscopic and mixing properties have been determined in order to relate the aerosol chemical composition to its potential radiative and climate impact in the urban region and its plume. Gas phase measurements have focussed especially on detailed VOC measurements in order to relate SOA build-up to gaseous precursor species abundance. A network of backscatter lidars including urban, sub-urban and rural sites, in addition to mobile platforms gives access to the aerosol vertical distribution in the region and to variations of the boundary layer height at the urban / rural interface.

The results of this measurement campaign will constitute a comprehensive data set of aerosol composition and properties, for gaseous aerosol precursor species, for pollution tracers and for dynamical parameters. This data set will constitute an important benchmark for air quality model evaluation. In this paper, the campaign objectives will be presented, the experimental set-up will be described, first results will be presented and benchmarks for model evaluation will be identified

OBJECTIVES OF THE CAMPAIGN

The first major objective of the campaign deals with closing identified knowledge gaps and to provide experimental data for model improvement and evaluation. This concerns in particular formation processes of primary and secondary aerosol at regional scale, with a specific focus on organic matter. A number of specific objectives are pursued:

- to document the aerosol composition and properties, and gaseous precursor concentrations, within a large agglomeration and in its plume, with a focus on the chemical speciation of organic carbon;
- to provide source apportionment of elemental and organic carbon PM, in order to improve regional scale emission inventories,
- to document pathways of secondary organic aerosol build-up from gaseous precursors within the agglomeration and in its plume,
- finally, to use experimental data obtained through the project and already existing data bases in order to evaluate and to improve process (0D) and air quality (3D) models for a large range of conditions (effective emission strength, meteorological variables).

EXPERIMENTAL SET-UP

The intensive campaigns were active in both a summer and a winter period, from July 1 to 31, 2009, and January 15 to February 15, 2010. At the three primary sites, a very complete set-up of instruments was deployed (Figure 1) allowing for a detailed characterisation of aerosol properties, including their size distribution, volatility, hygroscopicity, optical properties, of aerosol chemical composition (from fast measurements with a time resolution of several minutes, by Aerosol Mass Spectrometry (AMS), including also single particle measurements) and chromatographic measurements (PILS)). This ensemble of instruments gives the mass concentration of inorganic ions, of primary and secondary organic carbon, respectively for PM1 and PM2.5 aerosol. Black carbon measurements were also performed with various methods. In addition, filter measurements were taken to allow for individual analysis of up to 100 individual organic compounds, which are tracers for specific emission sources and secondary formation mechanisms. Detailed gas phase measurements were performed, especially of VOC's as precursors of organic aerosol, including also secondary compounds, but also for compounds important for photoxydant pollution and the atmospheric oxidising capacity (ozone, nitrogen species, odd hydrogen radicals). Airborne and mobile measurements allowed in particular to assess the chemical evolution of the pollution plume, up to 200 km from the source region. Mobile platforms were deployed on the basis of chemical forecast provided by INERIS via the PREVAIR system. At one primary site (SIRTA), extensive dynamical measurements were performed, including especially wind profiles, and backscatter lidar measurements. At this site, and during the winter campaign, the cloud (fog) phase was also sampled. At two urban secondary sites (Jussieu in the center and Créteil in the south-east of the agglomeration), the spectroscopic column measurements and backscatter lidar measurements were carried out. During the winter campaign, an additional lidar network was set-up at an urban and at four suburban sites (red stars in Figure 1), using a homogeneous set of aerosol backscatter lidars produced by LEOSPHERE.

FIRST RESULTS

One of the interesting results from airborne primary pollutant measurements during the summer and winter campaigns was that the pollution plume was still well defined at more than 100 kilometres downwind from the agglomeration. This implies that a "safe" framework will be obtained for later studying secondary organic aerosol build-up in the plume from Paris agglomeration emissions. It also implies that one should be able to derive spatially average pollutant emission from tracer measurements (for example black carbon measurements shown in Figure 2) in the plume, provided that model transport is correct. Figure 2 also shows black carbon simulations with the CHIMERE model set-up (set-up for the MEGAPOLI campaign with a multiple nesting option over the Paris area (horizontal resolution 50 / 9 / 3 km). It appears that the plume position and extension are in general well simulated, with some deviations for particular days.

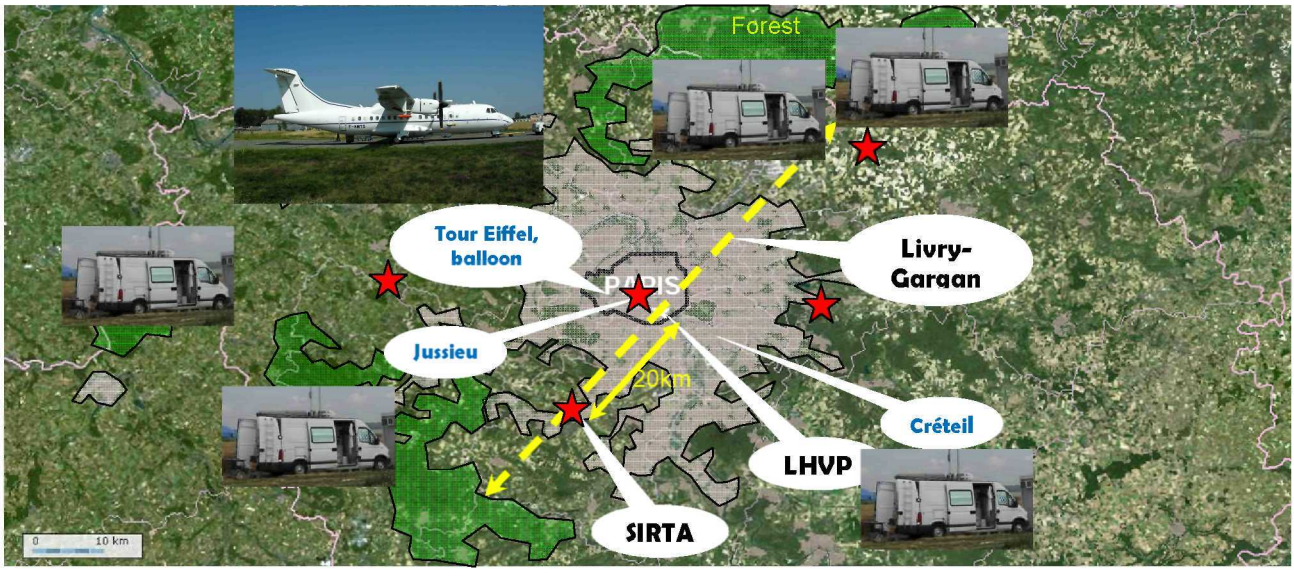

Figure 1: The campaign design included 3 primary (in black) and 3 secondary (in blue) fixed ground measurement sites, an aircraft and 5 mobile platforms. Primary sites are devoted to aerosols and gas phase chemistry, secondary sites to active and passive remote sensing. A specific lidar network was set-up at a central Paris site and at 4 cardinal points during the winter campaign (red stars).

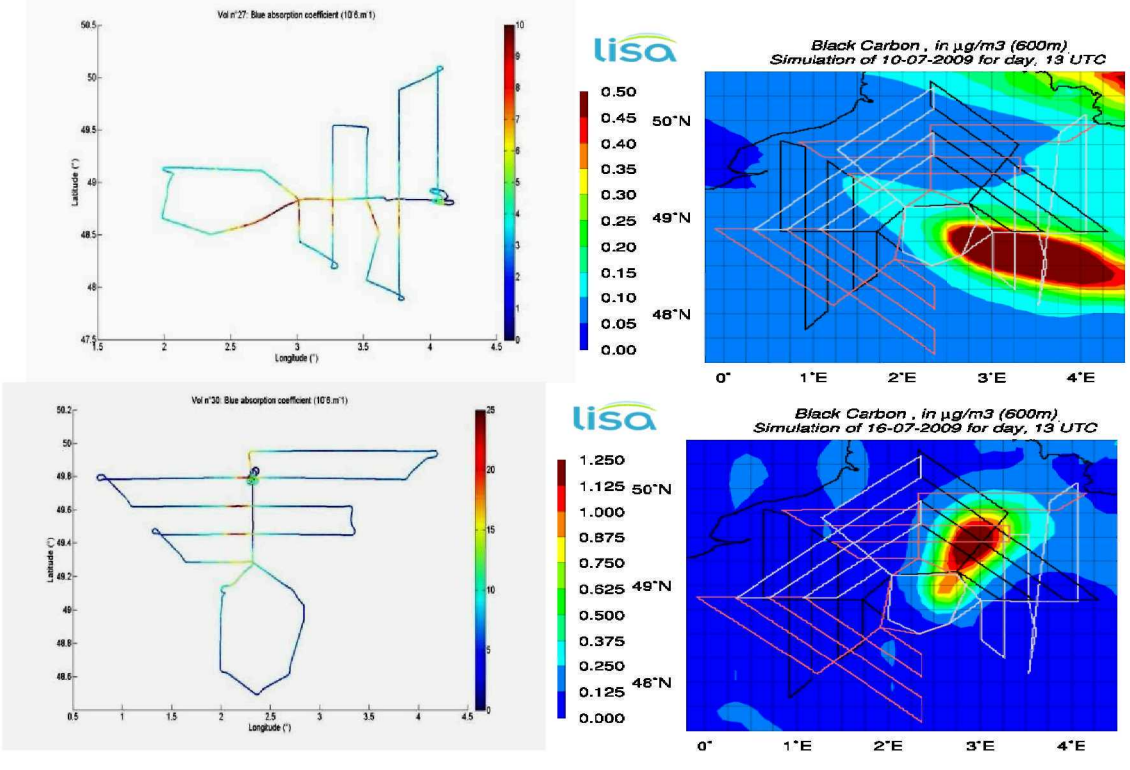

Figure 2: On the left, absorption coefficient, measured by a PSAP instrument from LaMP on the ATR-42. This instrument measures an absorption coefficient which can be related to black carbon content (courtesy, Alphons Schwarzenboeck, LaMP). On the right, CHIMERE simulations of black carbon (courtesy Q. Zhang) during the flight hours and at flight altitude (500 m). Top: flight on 10/7/2009, bottom flight on 16/09/2009. For the June 10, the direction of the plume is well simulated, while for June 16, a difference of about 45° is observed. These aircraft data are thus an important constraint for the simulated meteorology.

Significant new particle formation events were observed in the Paris area during the whole summer month of the campaign. These events were favoured by the relatively low particulate matter concentration levels and resulting low surface area during most of July 2009.

During both the summer and winter campaign, very preliminary attribution of organic aerosol (OA) from AMS mass spectrometer urban and peri-urban measurements , and also from ground-based mobile measurements in the plume show a large fraction of oxidised organic aerosol (OOA), comprising both chemically processed (oxidized) primary organic aerosol

and classical secondary organic aerosol (from aromatic and biogenic VOC precursors), and a smaller fraction of un-oxidised organic aerosol (HOA) of primary origin. Another aspect is water solubility of OA available from PILS-TOC measurements: At the urban LHVP site, about half of OA is water soluble (during the summer campaign), corresponding probably to classical secondary organic aerosol, another half is water insoluble, corresponding probably to primary and chemically processed primary OA. Obviously, these data will be valuable for constraining SOA formation in air quality models; models using SOA formation schemes built on results from older chamber measurements in general underpredict SOA formation from anthropogenic sources (e.g. Volkamer *et al.*, 2006). This data set also will allow to test new schemes, like the Volatility Basis Set (see for example Robinson *et al.* 2007) taking into account in a parameterised form a) the volatility of primary organic aerosol emissions and b) a decrease with time in volatility of semivolatile VOC species due to ongoing oxidation (see Zhang *et al.*, this issue, for using such a scheme within the CHIMERE model).

During the winter campaign, particulate matter levels were much larger than during summer, reaching more than 100 $\mu g/m^3$ PM2.5 at several occasions. Both local sources with a major OC fraction, and continental sources with a large nitrate fraction, contributed to these levels. A surprise was the major contribution of domestic wood burning to local OC. For this latter source, emission inventories are very uncertain, because emission factors strongly vary with the fire type. Thus campaign results will be very helpful to better constrain emission inventories.

Table 1: Experimental measurements performed during the MEGAPOLI campaign and constraint on model input data or processes

Measurement type performed	**Model parameter or process to be evaluated**
	Meteorology and transport
Lidar and sodar wind profiles	Synoptic wind speed
Radiosounding wind and T profiles	Synoptic wind speed and boundary layer height
Surface meteo network (temperature)	Urban heat island effect
Lidar derived boundary layer height	Urban heat island effect on BL height
Passive emission tracers (NOx at urban scale from AirParif network, urban + plume BC and NOy, including airborne)	Urban scale dispersion[1] (cumulated with uncertainty on emissions), regional scale advection
	Emissions
Airborne plume measurements of emission tracers (NOy, VOC, BC)	NOx, VOC, BC emissions (spatially integrated over Paris agglomeration) [1]
Urban scale VOC ratios	VOC emission ratios[1], source distribution [2]
PM chemical composition	PM and organic aerosol emission source distribution[2]
Airborne measurements of biogenic VOC and oxidation products	Biogenic VOC emissions over forested areas surrounding Paris agglomeration
	Gas phase chemistry (non exhaustive)
Oxidant (sum O3+NO2) content	Ozone formation efficiency
VOC ratios of different reactivity	Spatially averaged radical (OH) concentration
Odd hydrogen radical and source/ sink measurements	Odd hydrogen (OH, HO_2, RO_2) radical budget
	Aerosol properties
Aerosol size distribution, hygroscopicity	Correct representation of nucleation, coagulation, hygroscopic growth in models
Hygroscopicity and single particle measurements	Representation of mixing state
	Aerosol chemistry
Chemical PM1, PM2.5 mass closure (AMS, PILS, …)	Secondary and inorganic aerosol formation
Volatility, thermodenuder + AMS, O/C ratio	Specific volatility and oxidative properties of (secondary) OA, constraint on SOA schemes in models
C14 analysis (modern vs. old carbon)	Bulk evaluation of biogenic vs. anthropogenic SOA sources
OOA/ CO ratio versus –log(NOx/NOy)	Secondary aerosol build-up normalized by emission tracer and by integrated photochemical activity (time integrated OH); this is a very processes oriented benchmark

Notes (1) The conceptual idea is that for urban background sites, dispersion (vertical turbulence, horizontal advection) is more uncertain than emissions at least for NOx. For airborne maeasurements errors in the model transport can be partly corrected (e.g. boundary layer height) or normalised out (e.g. plume direction), allowing to derive spatially integrated emission estimates from plume measurements.

(2) Using statistical source apportionnement methods

CONCLUSION AND PERSPECTIVES

As a conclusion, the MEGAPOLI campaign allowed to gather a large data set of aerosol, gaseous species and dynamic measurements. First conclusions about the oxidised character of organic aerosol and about the importance of specific sources (wood burning in winter) have been drawn. As a concluding perspective, we show here a table, how different measurements will be used for model evaluation. It appears that different (combinations of) during the MEGAPOLI campaign will allow to evaluate specific modules (gas phase and aerosol chemistry, etc.) and input data (emissions, ...) within air quality models This data set will be first available for the MEGAPOLI consortium and later for the scientific community.

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REFERENCES

Robinson, A. L., Donahue, N. M., Shrivastava, M. K., Weitkamp, E. A., Sage, A. M., Grieshop, A. P., Lane, T. E., Pierce, J. R., Pandis, S. N., Rethinking organic aerosols: Semivolatile emissions and photochemical aging, Science, 315(5816), 1259-1262.

Volkamer, R., J.L. Jimenez, F. SanMartini, K. Dzepina, Q. Zhang, D. Salcedo, L. T. Molina, D. R. Worsnop, and M. J. Molina, 2006, Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected, Geophys. Res. Lett., 33, L17811, doi:10.1029/2006GL026899.