Results of the IES–ENEA Implementation of the JRC–ENEA Memorandum of Understanding

Edited by: Patrizia Pistochni, Annette Borowiak, Luisella Ciancarella

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Results of the IES-ENEA implementation of the JRC-ENEA Memorandum of Understanding (MoU)

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Foreword

This report describes the status and the results achieved under the Collaboration Agreement signed within the MoU between JRC and ENEA in the framework of “Environment” on the Technical Annex “AEROSOURCES”.

The annex was based on a common interest in establishing reliable studies from both institutes and improvement of inter-institute collaboration. A common scientific paper, contributions to international conferences and attendance to workshops were the key performance indicators.

As Liaison Officer for ENEA and JRC, I would like to thank both Coordinators and Projects Leaders for their close collaboration in the definition and execution of this Agreement that has achieved the established goals at mutual benefit.

Patrizia Pistochini
Introduction
This annual collaboration report describes the progress, results and impact of the common project, achieved until November 2015.

Since the inception of the Memorandum of Understanding in March 2010, a number of collaborative projects have been undertaken, particularly in the field of Energy, as reported in the Technical Report ‘Results of the IET – ENEA implementation of the JRC – ENEA Memorandum of Understanding’ dated 2014. All projects have been based on a “Technical Annex”, describing the objectives, expected deliverables and content of each project.

On 17 March 2010, a general Memorandum of Understanding JRC-ENEA was signed by Mr. Giovanni Lelli, Commissioner ENEA and Mr. Roland Schenkel, Director General for JRC; Mr. Massimo Busuoli and Mrs. Marina Leonardi for ENEA and Mr. Giancarlo Caratti di Lanzacco and Mr. David Wilkinson for JRC were appointed as coordinators.

The MoU includes the following topics:
1. Energy.
2. Environment.
4. High-performance scientific computing (HPC), in particular GRID computing.
5. Nuclear, in particular security.

For Environment, the first Collaboration Agreement was signed in 2014 with the view of focusing on “Aerosources” where the JRC and ENEA expertise would be complementary, and which are of priority for both institutions.

The above-mentioned MoU expired in March 2015. The content of the new MoU is under revision by both the partners.

Collaboration status

The detailed descriptions in this document are based on input from the research groups involved on both sides.
The collaboration team of the Technical Annex Aerosources

Programme Management

Giancarlo Caratti di Lanzacco | JRC – Coordinator of the Memorandum of Understanding JRC-ENEA
Massimo Busuoli | ENEA – Coordinator of the Memorandum of Understanding JRC-ENEA

Governance

Maria Betti | JRC – IES | Director of the Institute for Environment and Sustainability
Gabriele Zanini | ENEA – SSPT MET ex UTVALAMB | Head of the Division “Models and Technologies for Anthropogenic and Natural Risks Reduction” of Department of Sustainability

Actual governance

David Wilkinson | JRC - IES | Director of the Institute for Environment and Sustainability
Roberto Morabito | ENEA – SSPT | Head of Sustainable Territorial and Production Systems Department

Liaison officer JRC / ENEA

Patrizia Pistochni | ENEA – Energy Technologies Department | Smart Energy Division | Smart Cities and Communities Laboratory

Coordinators of Collaboration Agreement No. 33493

Annette Borowiak for JRC - IES
Luisella Ciancarella for ENEA - SSPT

Scientist Leaders

- Claudio Belis | JRC – IES – ACU
- Massimo Berico | ENEA – SSPT-MET-INAT
- Fabrizia Cavalli | JRC – IES – ACU
- Antonella Malaguti | ENEA – SSPT-MET-INAT

Scientist Collaborators

- Michael Bressi | JRC – IES - ACU
- Ettore Petralia | ENEA – SSPT-MET-INAT
- Milena Stracquadanio | ENEA – SSPT-MET-INAT
The “Aerosources” Collaboration Agreement JRC-ENEA

The contacts between the JRC and ENEA scientists involved in this Collaboration Agreement (CA) started in 2010 and were focused on instruments and methods for the measurements of airborne elemental, organic and carbonaceous carbon.

At the end of 2012, during an Italian Aerosol Society (IAS) meeting in Bergamo (Italy), a joint interest on the new Aerosol Chemical Speciation Monitor (ACSM) acquired by ENEA, has been discussed. Collaboration objectives, program activities, and JRC and ENEA staff involved were then discussed in phone calls, video-conferences and during a JRC-ENEA meeting in Ispra (June 2013).

At the end of 2013 a new Collaboration Agreement (CA No 33493) between JRC and ENEA was signed, with reference to the art.1, point 1.4, of the general Memorandum of Understanding. This Collaboration Agreement was focused on scientific issues in the field of air quality and in particular the following objectives were set:

a) To improve the co-ordination and effectiveness of co-operation efforts between ENEA and the JRC in the field of air quality and, in particular, of particulate matter chemical composition and sources.
b) To obtain the scientific data needed to investigate the annual variability of the particulate matter chemical composition at urban and at regional scale and to understand the most relevant atmospheric processes and emission sources.
c) To assess the suitability of innovative analytical tools for the determination of particulate matter chemical components regulated by Air Quality Directives.
d) To accomplish pollution source identification on the basis of the factor analysis of high time resolution data and validate the output by comparison with external information (e.g. other pollutants, meteorological data, other source apportionment techniques).

A Technical Annex was attached to the CA as AEROSOURCES - Aerosol chemical composition and sources identification from online measurements with the Aerodyne Aerosol Chemical Speciation Monitor. The duration of the project was scheduled from June 2013 to June 2015.
Conclusions

In general, the collaboration has been very rewarding. Despite the short duration of the Collaboration Agreement, the Technical Annex “Aerosources” produced a common scientific paper accepted for publication and team members have attended workshops and seminars and made contributions to international conferences.

Three factors must be highlighted as fundamental to the success of the collaboration:

1. Good organisation in terms of setting objectives, describing the project deliverables and following up.

2. Contact between the scientists involved and the continuous exchange of views, data and results in many meetings, phone calls and video-conferences.

3. The positive influence of temporary JRC and ENEA staff who worked together creating strong links and a common training on experimental and data analyses procedures.

The way forward

In this phase a general review of the Memorandum of Understanding between JRC and ENEA is in place. Environmental and sustainability issues will still be some of the central themes of the new Agreement.

A future development of Collaboration Agreement on air quality issues is advocated by the scientific teams, aiming:

- to include further campaigns at urban sites for covering different aerosol composition and different atmospheric conditions;
- to compare ACSM measurements with off-line analysis and with data from other collocated on-line analysers;
- to validate pollution source identification based on the factor analysis of ACSM data with other source apportionment techniques applied at the same monitoring sites.

Annette Borowiak  Luisella Ciancarella
The Technical Annex “Aerosources”

A thorough understanding of the chemical composition and the sources of aerosol and of its organic fraction is essential to address aerosol-related environmental issues, e.g. source emissions control strategies and to improve the predictive capability of air quality models. Recently, the combination of highly time resolved chemical composition data and factor analysis has been shown as a powerful approach for elucidation of aerosol sources and lifecycle processes.

The Aerodyne Aerosol Chemical Speciation Monitor (ACSM) is a new instrument which allows on-line measurement of the total mass and chemical composition of non-refractory submicron ambient aerosol. It provides particulate ammonium, nitrate, sulphate, chloride, and organic mass concentration. It also reports the temporal variation of the composition and concentration of the organic aerosol in the form of an array of measured mass spectra compiled over sampling time steps. The data matrix is subsequently deconvolved into unique factors using multivariate factor analysis. This is usually accomplished by solving a two-dimensional bilinear model that expresses mass conservation.

The ACSM is built upon the same technology as the widely used Aerodyne Aerosol Mass Spectrometer (AMS). Modifications in the design, however, allow it to be smaller, less expensive, and simpler to operate than the AMS and still capable of delivering data with a time resolution of half an hour. All these features make the ACSM instrument ideal for long-term monitoring.

| Project Leaders: | for JRC: Fabrizia Cavalli/Claudio Belis  
for ENEA: Antonella Malaguti/Massimo Berico |
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Project Title</td>
<td>AeroSources - Aerosol chemical composition and sources identification from online measurements with the Aerodyne Aerosol Chemical Speciation Monitor</td>
</tr>
</tbody>
</table>
| Objectives       | 1. To investigate the annual variability of aerosol chemical composition at an urban site and at a rural background site aiming at understanding the most relevant atmospheric processes and sources influencing each site  
2. To assess the suitability of ACSM for the determination of particulate matter chemical components regulated by Air Quality Directive by comparing its performance, in sites with different characteristics, with that one of the multiple off-line chemical analyses currently used for that purpose. To assess precision, accuracy and instrumental problems by participation in intercomparison studies.  
3. To accomplish pollution source identification on the basis of the factor analysis of ACSM data and validate the output by comparison with other source apportionment techniques applied at the same monitoring sites. |
In terms of human resources, both JRC and ENEA committed about 16 person-months for each year.

<table>
<thead>
<tr>
<th>Annex</th>
<th>JRC person-months</th>
<th>ENEA person-months</th>
</tr>
</thead>
<tbody>
<tr>
<td>AEROSOURCES</td>
<td>32</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 1: Staff involved in the Technical Annex June 2013 - June 2015

The Kick-off meeting on 18th June 2013

People present at the meeting (in order of intervention): Patrizia Pistochni (PP), Fabrizia Cavalli (FC), Michael Bressi (MH), Claudio Belis (CB), Sebastiao Dos Santos (SDS), Massimo Berico (MB), Antonella Malaguti (AM), Ettore Petralia (EP), Milena Stracquadanio (MS).

The meeting was introduced by PP, who gave an overview of the MoU between JRC and ENEA. She explained that the first agreement signed in 2008 was related to energy and all technical annexes were completed. Last year the MoU for Energy was updated and new technical annexes were agreed including a collaboration between ENEA – Environment and JRC.

The general MoU was signed in 2010 and, in addition to energy, it included environment, security, high performance scientific computing/grid computing, and nuclear/security.

On 3rd June 2013 Mr. Ristori and Mr Lelli met together in order to review progress in the collaboration between JRC and ENEA and to promote future cooperation focused on topics of strategic importance for both organisations. They noted with satisfaction that the MoU has significantly increased collaboration in several important areas, and therefore it must be pursued. In particular, during 2012, a collaboration agreement was signed for the benchmarking of EMAS to JRC with the support of ENEA Bologna and Trisaia and the present annex “Aerosol chemical composition and sources identification from online measurements with the Aerodyne Aerosol Chemical Speciation Monitor” finalized.

PP has been charged on behalf of Massimo Busuoli, the coordinator of the General MOU JRC- ENEA, to promote and coordinate the relative activities. PP clarified also that a governance has to be appointed and an annual technical report describing the results is expected.

FC: Introduces the JRC-IIES team and highlights the interest of the institute to collaborate with the ENEA for integrating measurements, instrument intercomparison and practical applications;

MH: Presents some data and setting parameters about the PSI’s ACSM performance for measures of NO$_3$, NH$_4$, Cl, SO$_4$ and Organics at Ispra site, and some preliminary results on
the comparison of ACSM data with airborne particulate matter data from other instruments at Ispra site as well;

CB: Intervenes about the importance to insert within the source apportionment analysis, together with chemical parameters (Carbon, Anions and Cations, Organics compounds, Metals, etc.) measured by on-line and off-line instruments, other typology of parameters e.g. particulate size distribution and meteorology to have a better identification of certain incident sources and their behaviour in space and time;

SS: Intervenes about the ACSM calibration operations and the equipment utilised; in particular he defines the characteristics of the aerosol generator device and the neutralizer device with a Kr-85 radioactive source.

MB: Intervenes about the mathematical-statistical method of Positive Matrix Factorization (PMF) for source apportionment analysis, outlining the strengths and weaknesses of this method, and presenting the approach with which the laboratory LECOP-MIA is currently using this statistical tool; he also presented some preliminary data on the correlation between Organic Carbon measured by Sunset and non-refractory Organics measured by ACSM, both from Bologna site.

AM: Intervenes about the fact that the ACSM is capable of measuring only part of the organic carbon and not the elemental carbon, therefore she underlines the importance of combining ACSM measures also with the measures of OC/EC made by Sunset device;

EP: Intervenes about the Multilinear Engine-2 (ME-2) methodology, evolution of the PMF, for the source apportionment where is possible to constrain known profile factors or to fix parameters from literature for an advanced source identification; he also revealed that the group had already executed PMF and ME-2 with preliminary identification of factors for ACSM spring data in Bologna.

MS: Intervenes about the possibility to utilize organic compounds as the Levoglucosan or other anhydrosugar to increase the components pool for the source apportionments analysis.

The Board plans the project objectives and the schedule for the following days:

1. assessment of the suitability of ACSM for the determination of particulate matter chemical components regulated by Air Quality Directives, by comparing its performance, in sites with different characteristics, with that of the multiple off-line chemical analyses currently used for that purpose;
2. investigating the annual variability of aerosol chemical composition at an urban site (Bologna) and at a rural background site (Ispra) aiming at understanding the most relevant atmospheric processes and sources influencing each site;

3. opportunity and importance to activate and/or participate at intercomparison activity to assess precision, accuracy and instrumental problems and also to create a measures network;

4. ENEA’s ACSM starting operational procedures (connection to the inlet sampling flow-line system, lens alignment, calibration and ionization efficiency settings);

5. synchronization with PSI’s ACSM for measuring comparison;

6. contributing to accomplish pollution source identification on the basis of the factor analysis of ACSM data and validate the output by comparison with other source apportionment techniques applied at the same monitoring sites.

The expected outcomes are:

1. Database with chemical composition of aerosol.
2. Report on the comparison between ACSM and other chemical composition measurement measurements.
Results

Aerosol chemical composition and sources identification from online measurements with ACSM - EXPERIMENTAL ACTIVITY REPORT

ACSM’s operating principles

The ACSM is a mass spectrometer capable of analysing in real-time, with a temporal resolution of 30 minutes, the non-refractory at 600°C component of the fine (<1 µm) particulate (NR-PM1). The instrument performs the mass spectrum for 100 different macromolecules that constitute the NR-PM1, providing the measurement of the main organic and inorganic chemical components (organic carbon, ammonium, sulphate, nitrate and chloride). For these technical features the ACSM allows, with respect to conventional measurement systems, to have more information on the activity of the emission sources (variations within the daily cycle), to perform measurement campaigns also for limited periods, to have a sufficient amount of data for application of multivariate statistical techniques that can contribute to the identification and quantification of the emission sources.

This instrument ACSM has aroused great interest among government agencies (EPA, CE, etc.) for its possible involvement in monitoring networks.

The instrument works by sampling air along an intake system that goes to an aerodynamics lens. The sub-micron fraction (~ 40-800 nm in aerodynamic diameter) of the aerosol selected from the lens is focused, inside a vacuum chamber, into a beam directed to a vaporizer at 600°C mounted within an electronic impact ionizer; the particles simultaneously vaporized and ionized are then drawn along a quadrupole mass spectrometer and time-selected depending their molecular mass (amu). The set of amu provides the mass spectra of the aerosol used for speciation and quantification of the main components of particulate air pollution; the combinations of the time series of spectra so obtained can give information, after processing with multivariate analysis (Positive Matrix Factorization, Cluster Analysis, etc.), to identify eventual chemically distinct groups of pollutants. A PMF analysis on the data of the organics permit the pre-identification, depending on the site in question, of a number of factors (emission profiles); of these, according with literature, in general those defined with greater assurance are Traffic factor, Biomass Combustion factor and the family of Secondary oxygenated organics.

Experimental monitoring campaigns: generalities

For the presentation of the results in this report, as representative of the methodological approach followed during the entire study, we selected the three periods indicated below:
1. JRC-Ispra, 24 January - 4 March 2014
2. ENEA-Bologna, 30 March - 14 July 2014
3. Veggiano (Padua), ORION s.r.l. site, 9 January - 19 February 2015

Fundamental premises about sampling features and data analysis for the entire study period:
- JRC-Ispra: background site;
- ENEA-Bologna: urban area;
Veggiano (Padoa): regional background suburban area;
measuring in real-time, with a temporal resolution of 30 minutes;
measurement of organic matter, ammonium, sulphate, nitrate and chloride;
data analysis with descriptive and basic statistics (correlation, regression, percentage, etc.) to perform comparison between ACSM results and other chemical composition measurements;
data analysis with advanced multivariate statistics (PMF, ME2) to perform sources identification: the organic fraction was apportioned using the Positive Matrix Factorization receptor model (PMF, Paatero and Tapper, 1994; Ulbrich et al., 2009; Zhang et al., 2011) applying the Multilinear Engine 2 approach (ME2, Norris et al., 2009; Paatero, 2000) within the SoFi tool (Canonaco et al., 2013; Crippa et al., 2014).

Measurements obtained by ACSM as monitor, during the different campaigns in the background site (JRC-Ispra), urban area (ENEA-Bologna) and industrial area (ORION-Veggiano), have provided important information on trends in the short and medium-time of the main chemical components, organic and inorganic. Hereinafter more details and results for the three selected periods will be shown.

**JRC-Ispra, 24 January – 4 March 2014**
The period counts 40 sampling days and a time resolution of 30 min for the ACSM, with about 48 samples per day, for a total amount of 1778 records.

**Trends of Organics, Ammonium, Sulphate, Nitrate, Chloride and comparison between ACSM and other chemical composition conventional measurements**
Together with ACSM Parameters, several so called reference External Parameters were simultaneously sampled with standard filter method (24h) or non-conventional methods (1h), to perform comparison and assess similarity to verify and validate ACSM measurements. Table 1 summarizes all the measured parameters with relative acquisition resolution time. In the case of comparison with 24h filters data, ACSM data were averaged and expressed as 24h mean data.

<table>
<thead>
<tr>
<th>ACSM Parameters:</th>
<th>External Parameters for comparison:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org (30 min)</td>
<td>BC (1 h)</td>
</tr>
<tr>
<td>NO₃⁻ (30 min)</td>
<td>NO₃⁻ (NO, NO₂) (1 h)</td>
</tr>
<tr>
<td>SO₂⁻ (30 min)</td>
<td>EC (24 h)</td>
</tr>
<tr>
<td>NH₄⁺ (30 min)</td>
<td>OM (24 h)</td>
</tr>
<tr>
<td>Cl⁻ (30 min)</td>
<td>NO₂⁻ (24 h)</td>
</tr>
<tr>
<td>n.73 amu organic species (30 min)</td>
<td>SO₄²⁻ (24 h)</td>
</tr>
<tr>
<td></td>
<td>NH₄⁺ (24 h)</td>
</tr>
<tr>
<td></td>
<td>Cl⁻ (24 h)</td>
</tr>
<tr>
<td></td>
<td>K⁺ (24 h)</td>
</tr>
<tr>
<td></td>
<td>Meteo parameters (1 h)</td>
</tr>
</tbody>
</table>

Table 2 – Measured parameters (and time resolution)

Figure 1 shows an overview of the time series of Organics (green), Ammonium (orange), Sulphate (red), Nitrate (blu) and Chloride (pink), with almost regular variation and not really...
evident events except for 27 – 30 January; figure 2 presents the percentage contribution relative to NR-PM1 of the five measured classes: it appears clearly that the most abundant component is Organics with 62%, corresponding to almost twice the sum of the other four.

Figure 1 – ACSM Parameters’ Time series

Figure 2 – ACSM Parameters’ Percentage contribution

The comparison of ACSM 24h time resolution with 24h standard filters data (Fig. 3), has shown a very good accordance between all the couple of similar components (ACSM Organics vs Filter Organic Matter; ACSM rough HOA vs Filter EC; ACSM Nitrate vs Filter Nitrate; ACSM Sulphate vs Filter Sulphate; ACSM Ammonium vs Filter Ammonium; ACSM Chloride vs Filter Chloride. Blue lines: ACSM data; red lines: Filters data).
The high correlation between similar components is revealed also by the Coefficient of determination ($R^2$) from linear regression analysis. Results are summarized in Table 2.

<table>
<thead>
<tr>
<th>Components</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org vs OM</td>
<td>0.99</td>
</tr>
<tr>
<td>Rough HOA vs EC</td>
<td>0.71</td>
</tr>
<tr>
<td>$NO^+_A$ vs $NO^+_F$</td>
<td>0.89</td>
</tr>
<tr>
<td>$SO^+_A$ vs $SO^+_F$</td>
<td>0.95</td>
</tr>
<tr>
<td>$NH^+_A$ vs $NH^+_F$</td>
<td>0.96</td>
</tr>
<tr>
<td>$Cl^-_A$ vs $Cl^-_F$</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Table 3 – 24h ACSM Parameters vs 24h Standard filters Data ($R^2$)

Sources identification
A first PMF analysis conducted to the separation of the organic contribution between organic hydrogenated (HOA), linked to primary emissions, and organic oxygenated (OOA), related to secondary pollution.
A complete PMF-ME2 analysis on the data of the organics has led to the individuation and pre-identification of 5 factors (emission profiles). After comparison with literature, those factors were defined as: Traffic (HOA), Biomass combustion (BBOA), Cooking activity (COA),
Semi-volatile organic oxygenated (SV-OOA), Low-volatile organic oxygenated (LV-OOA). Spectra profiles and Time series of these 5 factors are presented in Figure 4 and Figure 5.

Figure 4 – Factors’ profiles

Figure 5 – Factors’ time series

Figure 6 shows the percentage contribution of each factor: the primary organics (HOA+COA+BBOA) counts for the 48% of the total, with a clear predominance of Biomass combustion (BBOA); the secondary organics (SV-OOA+LV-OOA) amounts to 52% with a balance of the two components. In Table 3 is expressed, per factor, the mean contribution in $\mu$/m$^3$. 
Each Factor presents its own characteristic diurnal cycle, as shown in Figure 7: the bimodal trend of HOA traffic (green) is clearly determined by people moving and cars utilization, with two peaks at 6-11 and 16-19; the trend of COA (red) is determined by people cooking activity (mainly restaurants, fast-foods, fry-shops, canteens), with two peaks at 6-12 and 16-20; the trend of BBOA (brown) presents an increase during evening and night, most likely linked to the crepuscular-nocturnal house-heating activity; the trend of SV-OOA (blue) presents an increase during evening-night, and could be associated to activity of surrounding villages (local secondary aerosol); the trend of LV-OOA (pink) presents an increase during day-time, and it’s reasonable to consider LV-OOA as the classic pure SOA with mostly regional origin.
ENEA-Bologna, 30 March – 14 July 2014

The ENEA period counts 107 sampling days and a time resolution of 30 min for the ACSM, with about 48 samples per day, for a total amount of 3405 records.

Trends of Organics, Ammonium, Sulphate, Nitrate, Chloride and comparison between ACSM and other chemical composition non-conventional measurements

Together with ACSM Parameters, several so called reference External Parameters were simultaneously sampled by other non-conventional monitors, to perform comparison with ACSM measurements. Table 4 summarizes all the measured parameters with relative acquisition resolution time.

<table>
<thead>
<tr>
<th>ACSM Parameters:</th>
<th>External Parameters for comparison:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org (30 min)</td>
<td>BC (5 min)</td>
</tr>
<tr>
<td>NO$_3$ (30 min)</td>
<td>OC (2 h)</td>
</tr>
<tr>
<td>SO$_4$ (30 min)</td>
<td>PAH (5 min)</td>
</tr>
<tr>
<td>NH$_4$ (30 min)</td>
<td>PSA (particulate-matter surface area) (2 min)</td>
</tr>
<tr>
<td>Cl (30 min)</td>
<td>Particle number (#/L) PM0.25 (5 min)</td>
</tr>
<tr>
<td>n.73 amu organic species (30 min)</td>
<td>Particle number (#/L) PM0.25-0.40 (5 min)</td>
</tr>
<tr>
<td></td>
<td>Particle number (#/L) PM0.40-0.65 (5 min)</td>
</tr>
<tr>
<td></td>
<td>Particle number (#/L) PM0.65-0.80 (5 min)</td>
</tr>
<tr>
<td></td>
<td>Meteo parameters (1 h)</td>
</tr>
</tbody>
</table>

Table 5 – Measured parameters (and time resolution)

Figure 8 shows an overview of the Time series of Organics (green), Ammonium (orange), Sulphate (red), Nitrate (blue) and Chloride (pink), with a relatively increase, mainly for organics, during 6 – 14 June; Figure 9 presents the percentage contribution relative to NR-PM1 of the five measured classes: it appears clearly that about 50% is represented by Organics.
The comparison, in 1h time resolution, of ACSM parameters with data from other instruments involved along the campaign (e.g. Fig. 10 - 13), has shown a quite good accordance (at different degree) between Org, NH$_4$, SO$_4$, NO$_3$ and PM0.25-0.40, 0.40-0.65, and accordance for Org with OC and PSA.
The various correlation values between components (Coefficient of determination, $R^2$) are summarized in Table 6.

<table>
<thead>
<tr>
<th></th>
<th>ACSM</th>
<th>PM0.25</th>
<th>PM0.25-0.40</th>
<th>PM0.40-0.65</th>
<th>PM0.65-0.80</th>
<th>BC</th>
<th>OC</th>
<th>PSA</th>
<th>PAH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Org</td>
<td>0.0004</td>
<td>0.83</td>
<td>0.61</td>
<td>0.40</td>
<td>0.08</td>
<td>0.72</td>
<td>0.53</td>
<td>0.04</td>
<td></td>
</tr>
<tr>
<td>NH₄</td>
<td>0.0009</td>
<td>0.70</td>
<td>0.75</td>
<td>0.44</td>
<td>0.01</td>
<td>0.16</td>
<td>0.29</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>SO₄</td>
<td>0.008</td>
<td>0.76</td>
<td>0.47</td>
<td>0.34</td>
<td>0.005</td>
<td>0.35</td>
<td>0.31</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>NO₃</td>
<td>0.02</td>
<td>0.52</td>
<td>0.77</td>
<td>0.38</td>
<td>0.04</td>
<td>0.01</td>
<td>0.22</td>
<td>0.03</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.12</td>
<td>0.20</td>
<td>0.28</td>
<td>0.15</td>
<td>0.03</td>
<td>0.0004</td>
<td>0.05</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6** – ACSM Parameters vs External parameters ($R^2$)

**Sources identification**

A first PMF analysis has been conducted to the separation of the organic contribution between organic hydrogenated (HOA), linked to primary emissions, and organic oxygenated (OOA), related to pollution secondary.

A complete PMF-ME2 analysis on the data of the organics has led to the individuation and pre-identification of 4 factors (emission profiles). After comparison with literature, those factors were defined as: Traffic (HOA), Cooking activity (COA), Semi-volatile organic oxygenated (SV-OOA), Low-volatile organic oxygenated (LV-OOA). Spectra profiles and Time series of these 4 factors are presented in Figure 14 and Figure 15.
Figure 16 shows the percentage contribution of each factor: the primary organics (HOA+COA) counts just for the 13% of the total, while the secondary organics (SV-OOA+LV-OOA) is almost equally divided for the two components. In Table 6 is expressed, per factor, the mean contribution in $\mu$/m$^3$. 
Table 7 – Factors contribution µ/m³

<table>
<thead>
<tr>
<th>Factor</th>
<th>Contribution µ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOA</td>
<td>0.17</td>
</tr>
<tr>
<td>COA</td>
<td>0.28</td>
</tr>
<tr>
<td>SV-OOA</td>
<td>1.45</td>
</tr>
<tr>
<td>LV-OOA</td>
<td>1.56</td>
</tr>
</tbody>
</table>

Each Factor presents its own characteristic diurnal cycle, as shown in Figure 17: the bimodal trend of HOA traffic (green) is clearly determined by people moving and cars utilization, with two peaks at 6-8 and 20-23 (it’s important to underline that the site refers to an urban area nearby the highway); the trend of COA (red) is determined by people cooking activity (mainly restaurants, fast-foods, fry-shops, canteens), with two peaks at 7-13 and 20-23; the trend of SV-OOA (blue) presents an increase during early-morning; the trend of LV-OOA (pink) presents an increase during day-time, and it’s reasonable to consider LV-OOA as the classic pure SOA even produced by photochemical reactions.
Veggiano (Padua), 9 January – 19 February 2015

The period counts 42 sampling days and a time resolution of 30 min for the ACSM, with about 48 samples per day, for a total amount of 1954 records. Preliminary ACSM results are reported below.

**Trends of Organics, Ammonium, Sulphate, Nitrate, Chloride**

Figure 18 shows an overview of the Time series of Organics (green), Ammonium (purple), Sulphate (blue), Nitrate (pink) and Chloride (orange); figure 19 presents the percentage contribution relative to NR-PM1 of the five measured classes: it appears clearly that more than 50% is represented by Organics.

![ACSM Parameters' Time series](image1.png)

![ACSM Parameters' Percentage contribution](image2.png)
Sources identification
A first PMF analysis was conducted to the separation of the organic contribution between organic hydrogenated (HOA), linked to primary emissions, and organic oxygenated (OOA), related to pollution secondary.
A more advanced PMF-ME2 analysis on the data of the organics has led to the individuation and pre-identification of 3 factors (emission profiles). After comparison with literature, those factors were defined as: Traffic (HOA), Biomass combustion (BBOA) and Secondary oxygenated (OOA). Spectra profiles of these 3 factors are presented in Figure 20.

Figure 20 – Factors’ profiles

Figure 21 shows the percentage contribution of each factor; apparently the measured organic fraction is equally divided into the two main clusters: primary organics (HOA+BBOA, 51%) and secondary organics (OOA, 49%).
Each Factor presents its own characteristic diurnal cycle, as shown in Figure 22: the bimodal trend of HOA traffic (black) is clearly determined by people moving and cars utilization, with two peaks at 6-9 and 17-22; the trend of BBOA (brown) is increasing during late evening possibly due to house-heating.
Overall conclusions

Based on the results obtained for both background and urban sites with different characteristic, the present study confirms ACSM as suitable for the determination and trend individuation of particulate matter chemical components regulated by Air Quality Directive (2008/50/CE Ann. IV) such as NH4+, SO42-, NO3- and Cl-; besides it can even follow with reasonably proximity the Organic Carbon. This was assessed especially through the very good accordance of ACSM data and standard filter data. However the precision and accuracy of the instrument is definitively linked to its correct and periodic calibration, necessary to evaluate proper collection efficiency, ionization efficiency, response factor and ion transmission.

Regarding the campaigns in Ispra and Bologna, about factor analysis and source apportionment accomplished starting from Organics’ m/z data, we consider satisfactory the individuation of 5 and 4 factors respectively in Ispra and Bologna. The factors in common to both sites are Traffic, Cooking activity and the two Secondary oxygenated organics; every factor can be of course influenced by fixed and changeable peculiarity of the site (topography, meteorology, sources distribution), but they resulted presenting intrinsic features, as delineated in the text before, common to all the sites (for instance Traffic, with its two noticeable peaks). In our case the difference in number of factors (5 for Ispra and 4 for Bologna) may depend on the season: the 5th factor for Ispra was Biomass combustion linked mainly to house-heating activity; there it can be expected considering that the reference seasonal period was winter. In Bologna the reference period was spring-summer and the Biomass combustion factor did not appeared.

Regarding the Padua campaign, as already said, data are still under processing; the very preliminary results showed consistent data.

Figure 23 – The JRC Ispra Campaign
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