Exploratory Workshop Scheme

Scientific Review Group for Life, Earth and Environmental Sciences

ESF Strategic Workshop on

THE MOLECULAR IDENTIFICATION OF ORGANIC COMPOUNDS IN THE ATMOSPHERE

Cambridge (UK), March 24 – 28, 2013

Convened by:
Barbara Nozière[①], Magda Claeys[②] and Markus Kalberer[③]

SCIENTIFIC REPORT

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1. Executive summary

The workshop was held at Emmanuel College, University of Cambridge, UK, from March 24 to March 28, 2013. 23 out of the 25 confirmed participants were present (two had last-minute emergencies preventing them from attending). Each participant was equaly assigned to one oral presentation and 24 presentations were given over three days.

This workshop was the first one to be entirely dedicated to the topic of the identification of organic compounds in the atmosphere, including particulate and gaseous constituents. Although these compounds play central roles in many areas of atmospheric chemistry, air quality and the Earth's climate system, the development of techniques to identify them has been underestimated by the atmospheric community until now and those available today result mostly from isolated initiatives. The objectives of this workshop were thus:

1) to strengthen the sub-community focusing on atmospheric organic compounds by sharing its knowledge, planning concerted actions, and
2) to give it more visibility by preparing reference publications and international events (special sessions at international conferences).

The oral presentations focused each on one specific area, so that the 24 presentations gave a complete overview and state-of-the-art techniques and applications, thus answering objective 1) (sharing knowledge). These presentations were distributed into three main sessions, focusing each on an important field of atmospheric chemistry but also addressing important aspects beyond the inventory such as recommending best practice, determining strategic areas, and proposing future tools and investigation strategies. In addition, two discussion sessions of half a day each were held to prepare a review article and future events, thus answering objective 2).

Overall conclusions: All participants were very pleased with the initiative and objectives of this workshop. All agreed that the molecular identification of organic compounds is central to the understanding of fundamental atmospheric processes, but that both the unique value and challenges in developing reliable analyses are underestimated by the atmospheric community. The necessity of a workshop focusing on these questions was thus acknowledged, as well as the 30 min format for all talks/discussions (as opposed to a plenary/regular talks system) because these topics are rarely presented in invited talks at other events. The participants acknowledged the informative quality of these talks, and were enthousiastic about preparing a review article on this topic, which has been missing in the atmospheric chemical literature. This review is now in preparation. The talks were followed by lifely and sometimes controversial discussions.

All the participants were in favour of continuing to organise such focused events and the discussion sessions resulted in several plans for submitting special sessions on this topic at international conferences, such as the Annual Assemblies of the European and American Geophysical Unions. In addition, some community actions were spontaneously proposed, such as the sharing of standard compounds, to uniformise compound characterisation and limit the synthesis costs, and the development of community databases, for instance of electron ionisation mass spectra for atmospheric compounds, not available in commercial databases. As today analytical development work for atmospheric organic compounds is difficult to fund, rarely integrated to international projects, and somewhat neglected in high-ranking journals compared to real-time techniques, all the follow-up actions proposed at this workshop were regarded as important for the future of this sub-discipline to foster concerted efforts (collaborative projects), and obtain a better visibility and appreciation from the

atmospheric community, national and international sponsors, journals, and scientific societies.

2. Scientific content of the event

Session I: Current and future tools

This session was dedicated in presenting the state-of-the-art of the different techniques available for the identification of organic compounds in the atmosphere (gas and aerosols). The discussions where generally about recommending best practice when using these techniques, and identifying promising future developments and investigation strategies.

Presentation 1: "Best practice in the identification of organic compounds", Magda Claeys
The necessity for the molecular identification of organic compounds in the atmosphere was discussed and good practices for achieving such identification in complex mixtures such as atmospheric aerosols were presented. It was stressed that good practices generally involve sample workup, chromatographic separation of the individual compounds using gas or liquid chromatography, and a combination of various mass spectrometric approaches including accurate mass measurements.

Presentation 2: "The analysis of atmospheric organic volatile and semi-volatile organic compounds with GC/MS techniques", Euripides Stephanou
This presentation gave an overview of the GC/MS techniques currently available to analyse gas-phase organic compounds, which play essential roles in the chemistry of the lower atmosphere. Their advantages, limits, and ranges of application were discussed. Particular emphasis was made on applications (alkanes, PCBs...) where these "classical" techniques can not be replaced by newer, real-time techniques such as those presented in Presentation 3.

Presentation 3: "Analyzing atmospheric organic gases with PTR-MS", Armin Wisthaler
An overview of this on-line technique for the identification/monitoring of many organic gases in the atmosphere and its new developments was given. Novel ionisation techniques to broaden the range of accessible compound classes were discussed as well as innovative ideas to use this technique for particle-phase analysis.

Presentation 4: "Soft desorption techniques and on-line analysis of aerosol components", Jürgen Schnelle-Kreis
The wide range of recent developments in on-line MS instrumentation for the characterisation of organic particle components was presented, witnessing the "renaissance" of this field over the last decade. The emphasis was on mass spectrometric techniques avoiding fragmention (chemical ionisation) and providing a direct molecular information.

Presentation 5: **"On-line analysis of organic aerosol components with the Aerodyne AMS",** James Allan
The performance of this widely popular real-time instrument was presented and the challenges to obtain molecular information from it were discussed. A lifely discussion followed the presentation on how to integrate and combine the bulk/statistical information obtained with this instrument with more detailed compound-specific analysis techniques.

Presentation 6: "Field sampling of organic aerosols and artifacts" Willy Maenhaut (given by M. Claeys)
An overview was given of the different field samplers that can be deployed for the collection of ambient aerosols and sampler additions to avoid or assess sampling artifacts. Sampling artifacts in aerosol collection were addressed and discussed in more detail for dicarboxylic acids.

Presentation 7: "GC/MS techniques for the analysis of aerosol organic compounds", Mohammed Jaoui
This presentation gave an overview of gas chromatography/mass spectrometry techniques for the identification of organic compounds but, unlike Presentation 2, focused more specifically on the derivatisation techniques applicable to atmospheric aerosols.

Presentation 8: "LC/Q Tof techniques for the analysis of aerosol organic compounds", Yoshi Iinuma

A very thorough historical and technical overview on mass spectrometry and ionisation techniques used to characterise organic aerosol components was given. Recent developments of potential importance in the future were also presented, such as 2D-GC, a wide range of soft and direct ionisation techniques, and novel extraction techniques such as supercritical fluid extraction, which were compared with conventional methods.

Presentation 9: "High Resolution Mass Spectrometry for the analysis of atmospheric compounds", Ivan Kourtchev
This presentation introduced the advanced technique of high resolution MS and its first application to atmospheric studies. Both the advantages (high-resolution allowing for molecular formula identification) and challenging aspects of data analysis (large amount of data requiring statistical approaches) were presented. The discussion focused on how this advanced technique can help and complement existing mass spectrometric techniques to identify and quantify organic compounds in the atmosphere.

Presentation 10: "NMR for the analysis of atmospheric compounds", Stefano Decesari
Although NMR has long been the technique of reference for molecular identification and quantification in laboratory, its application to complex mixtures, such as atmospheric aerosols, is much more challenging. This presentation reviewed the studies where this technique successfully identified important organic markers. Differences and advantages of NMR compared, for example, to mass spectrometry were discussed.

Presentation 11: "**Ion chromatography, IR and UV spectroscopies for the analysis of atmospheric compounds",** Emanuela Finessi
This presentation reviewed the use of more conventional techniques (UV, IR, IC) to the identification of organic compounds in atmospheric aerosols and cloud/fog water. Not only a number of important tracers can be detected by these techniques but Ion Chromatography was reported to be the only technique able to detect Methyl Sulfonic Acid ("MSA"), an essential component of the marine atmosphere. New technical developments and coupling with other techniques were also presented.

Session II: Reactivity and Secondary Organic Aerosol formation
Sessions II and III focused on the roles and transformation processes of organic compounds in the atmosphere, the understanding of which requires the identification of the compounds involved. Session II focused on the transformation processes: chemical reactions, transfer to the particulate phase, secondary aerosol formation…

Presentation 12 "The detection of organic radicals and intermediate ions in the atmosphere", Barbara Nozière
Beside stable compounds, the identification of short-lived organic species such as radicals and reaction intermediates in the gas-phase atmosphere or in aerosols is important for the understanding of fundamental atmospheric processes, such as the oxidising capacity of the atmosphere or the aging of organic compounds in aerosols. The techniques available or under development to observe such short-lived species were summarised and discussed.

Presentation 13 "Organic compounds in clouds", Irena Grgic
This presentation addressed the (photo-)chemistry of organic compounds in cloud droplets, which is potentially a significant source of organic aerosols. Particular emphasis was given on the reactions of selected carbonyls (e.g. glyoxal, methylglyoxal, glycolaldehyde) and monoaromatic compounds (e.g. guaiacol), abundant in these aqueous media, and the suitable measurement techniques.

Presentation 14 "The analysis of organosulfates in atmospheric aerosols", Rafal Szmigielski
This presentation gave the current state of knowledge on organosulfates, one of the main class of compounds produced exclusively by atmospheric processes, including their formation mechanisms, characterisation and analysis methods (mostly mass spectrometric approaches). The discussion concerned the need to develop reliable quantitative and screening methods, as well as the synthesis of reference compounds.

Presentation 15 "Organic acids in atmospheric aerosols", Sanna Saarikoski

This presentation gave an overview of one class of compounds among the most studied in atmospheric chemistry, organic acids. Current knowledge of their roles was presented (tracers for oxidation mechanisms, cloud-forming compounds...) as well as their identification in atmospheric samples and the various techniques used for it.

Presentation 16 "Health-hasardous compounds in atmospheric aerosols", Markus Kalberer
This presentation focused on compounds present in aerosols that have health-effects and toxic properties ("reactive oxygen species" ...) and on the analytical techniques available to analyse and quantify them. Future research needs were presented. The discussion addressed the need to identify the most health-relevant, yet unknown, compounds in atmospheric particles.

Presentation 17 "The molecular composition of SOA: 30 years of investigation", Jacqui Hamilton
This presentation gave an overview of one of the main topic in atmospheric chemistry today, Secondary Organic Aerosols (SOA): their investigation, in laboratory, smog chamber, and the atmosphere over the last three decades, and the wide range of analytical techniques used. The many outstanding questions on these aerosols were also discussed.

Presentation 18 "An overview of isoprene chemistry and secondary aerosol formation", Jason Surratt
This presentation was complementary to Presentation 17, but focusing exclusively on SOA produced by isoprene, which is a vast area of investigation in itself. The various possible formation mechanisms for these SOA were presented (gas-phase oxidation under different NO_x regimes, particulate-phase reactions...), as well the different analytical techniques and reference standards employed to identify reaction tracers,.

Presentation 19 "Secondary tracer standards and synthesis", Christopher Kampf
An overview was given of the different atmospheric marker compounds that have been identified thanks to the synthesis of authentic standards or surrogate compounds. The urgent need for reference compounds was highlighted in the discussion.

Session III: The climate contributors
This session focused on the organic compounds playing a role in the climate budget: the climate-warming light- absorbing compounds present in the particulate phase (brown carbon, HULIS...) and the cloud-forming compounds, contributing to the main cooling factor (surfactants).

Presentation 21 "Brown carbon: properties and molecular identification", Jean-Luc Jaffrezo
This presentation summarized the current knowledge on the light-absorbing organic matter in atmospheric aerosols, also known as "brown carbon", which has a direct warming contribution to climate by absorbing sunlight. This material is still not well characterized. Its main properties and the techniques used to characterise it were presented.

Presentation 22 "Tracers for biomass burning, fossil fuel burning, and biogenic emissions", Ariane Kahnt
An overview about organic tracer compounds originating from different combustion sources and for primary organic aerosol was provided. The presentation summarised current state of knowledge and discussed the suitability of tracer compounds for the characterisation of atmospheric aerosol.

Presentation 23 "Properties and molecular identification of HULIS", Gyula Kiss
This presentation summarised the current knowledge of a macromolecular fraction found in aerosols, "Hunic-like substances or HULIS" which is similar to fractions found in other natural environments such as soil or seawater. The different characterisation of this material, the techniques used for it, and its properties – in particular the light-absorbing ones, were presented.

Presentation 24 "Surfactants in atmospheric aerosols", Marianne Glasius
This presentation dealt with several aspects of surface-active compounds in the atmosphere, which, according to Köhler theory, are the main class of organic compounds contributing to the

transformation of aerosol particles into cloud droplets, thus in cloud formation. The surfactants identified so far and the techniques used were presented. It was emphasised that more research is needed on this topic, in collaboration with the cloud scientists community and modellers.

3. Assessment of the results, contribution to the future direction of the field, outcome

The presentations and discussions at this workshop led to the conclusion that the chemical characterisation of organic compounds in the atmosphere is essential for the fundamental understanding of many atmospheric processes, such as the oxidising capacity of the atmosphere, aerosol formation and aging, climate, and for the development of mitigation strategies to decrease air pollution-related health impacts. Despite decades of efforts, there is therefore an urgent need for further research in the characterisation and identification of gas- and particulate organic compounds in the atmosphere.

It was also acknowledged at this workshop that, in spite of the unique value of such analytical development work, this type of work is often neglected by the atmospheric science community and needs urgently to gain a higher visibility and appreciation. For this, a list of future actions was made. These actions are:

- The preparation of a review article presenting the state-of-the-art in the topic, which has been missing in the atmospheric chemical literature and should serve as a reference,

- The organisation of special sessions on this topic at international conferences such as the Annual Assemblies of the European and American Geophysical Unions,

- The organisation of community actions such as the sharing of standards of reference compounds and of a database for Electron Ionisation mass spectra for the compounds analysed by gas chromatography/mass spectrometry. The lack of standards was identified as a critical shortcoming of the atmospheric chemistry community as only very few groups have the resources and expertise to perform a challenging synthesis. It was agreed to develop a website with information about research groups that have synthesised organic standards and are willing to share these compounds with other groups. This will allow advancing the urgently needed quantitative analyses of atmospherically relevant organic compounds.

4. Final programme

Sunday, March 24, 2013

Afternoon	*Arrival*
18.00	*Get-together and dinner*

Monday, March 25, 2013

08.30-09.00	**Coffee and welcome by Convenor** **Barbara Nozière** (Ircelyon-CNRS, Lyon, France)
09.20-09.40	**Presentation of the European Science Foundation (ESF)** **Wolfgang WEISSER** (Scientific Review Group for Life, Earth and Environmental Sciences)
09.30-12.20	**Session I: Current and future tools**
09.30-10.00	**Presentation 1 "Best practice in the identification of organic compounds"** **Magda Claeys** (University of Antwerp, Antwerp, Belgium)

10.00-10.30	**Presentation 2 "The analysis of atmospheric organic volatile and semi-volatile organic compounds with GC/MS techniques"** **Euripides Stephanou** (University of Crete, Heraklion, Greece)
10.30-11.00	*Coffee / Tea Break*
10.10-11.30	**Presentation 3 "Analyzing atmospheric organic gases with PTr-MS"** **Armin Wisthaler** (Norwegian Institute for Air Research, Kjeller, Norway)
11.30-12.00	**Presentation 4 "Soft desorption techniques and on-line analysis of aerosol components"** **Jürgen Schnelle-Kreis** (Helmholtz Zentrum München, Munich, Germany)
12.00-12.30	**Presentation 5 "On-line analysis of organic aerosol components with the Aerodyne AMS"** **James Allan** (University of Manchester, Manchester, United Kingdom)
12.30-14.00	*Lunch*
14.00-17.30	**Session I (continued)**
14.00-14.30	**Presentation 6 "Field sampling of organic aerosols and artifacts"** ***Willy Maenhaut*** (Ghent University, Gent, Belgium) ***Given by M. Claeys***
14.30-15.00	**Presentation 7 "GC/MS techniques for the analysis of aerosol organic compounds"** **Mohammed Jaoui** (Alion Science & Technology, Research Triangle park, USA)
15.00-15.30	**Presentation 8 "LC/Q Tof techniques for the analysis of aerosol organic compounds"** **Yoshi Iinuma** (Leibniz-Institut für Troposphärenforschung, Leipzig, Germany)
15.30-16.00	*Coffee / Tea break*
16.00-16.30	**Presentation 9 "High Resolution Mass Spectrometry for the analysis of atmospheric compounds"** **Ivan Kourtchev** (Univerty of Cambridge, Cambridge, United Kingdom)
16.30-17.00	**Presentation 10 "NMR for the analysis of atmospheric compounds"** **Stefano Decesari** (Istituto ISAC - C.N.R., Bologna, Italy)
17.00-17.30	**Presentation 11"Ion chromatography, IR and UV spectroscopies for the analysis of atmospheric compounds"** **Emanuela Finessi** (University of York, York, United Kingdom)
19.00	*Dinner*

Tuesday, March 26, 2013

09.00-12.30	**Session II: Reactivity and Secondary Organic Aerosol formation**
09.00-09.30	**Presentation 12 "The detection of organic radicals and intermediate ions in the atmosphere "** **Barbara Nozière** (Ircelyon-CNRS, Lyon, France)
09.30-10.00	**Presentation 13 "Organic compounds in clouds"** **Irena Grgic** (Laboratory for analytical chemistry, Ljubljana, Slovenia)
10.00-10.30	**Presentation 14 "The analysis of organosulfates in atmospheric aerosols"** **Rafal Szmigielski** (Polish Academy of Sciences, Warsaw, Poland)
10.30-11.00	*Coffee / Tea Break*
11.00-11.30	**Presentation 15 "Organic acids in atmospheric aerosols"** **Sanna Saarikoski** (Finnish Meteorological Institute, Helsinki, Finland)
11.30-12.00	**Presentation 16 "Health-hasardous compounds in atmospheric aerosols"** **Markus Kalberer** (University of Cambridge, Cambridge, United Kingdom)

12.30-14.00 *Lunch*

14.00-17.00 **Discussion Session 1: "Tools, guidelines and recommendations"**

Discussion summarizing the presentations and preparing a review article. *Coffee/Tea break at 15.30*

19.00 *Conference Dinner*

Wednesday, March 27, 2013

09.00-12.30 **Session II (continued)**

09.00-09.30 **Presentation 17 "The molecular composition of SOA: 30 years of investigation"**
Jacqui Hamilton (University of York, York, United Kingdom)

09.30-10.00 **Presentation 18 "An overview of isoprene chemistry and secondary aerosol formation"**
Jason Surratt (University of North Carolina at Chapel Hill, Chapel Hill, USA)

10.00-10.30 **Presentation 19 "Secondary tracer standards and synthesis"**
Christopher Kampf (Max Planck Institute for Chemistry, Mainz, Germany)

10.30-11.00 *Coffee / Tea Break*

11.00-11.30 **Presentation 22 "Tracers for biomass burning, fossil fuel burning, and biogenic emissions"**
Ariane Kahnt (University of Antwerp, Antwerp, Belgium)

11.30-12.00 **Presentation 21 "Brown carbon: properties and molecular identification"**
Jean-Luc Jaffrezo (Laboratoire de Glaciologie et Géophysique de l'Environnement/CNRS, Grenoble, France)

12.00-14.00 *Lunch*

14.00-15.30 **Session III: The climate contributors**

14.00-14.30 **Presentation 23 "Properties and molecular identification of HULIS"**
Gyula Kiss (University of Pannonia, Veszprém, Hungary)

14.30-15.00 **Presentation 24 "Surfactants in atmospheric aerosols"**
Marianne Glasius (University of Aarhus, Aarhus, Denmark)

15.00-15.30 *Coffee / Tea break*

19.00 *Dinner*

Thursday, March 28, 2013

09.00-12.30 **Discussion Session 2: Current challenges & Future perspectives**

*These **discussions** will have for objectives:*
- to prepare future collaborative projects to establish networks for the education of young scientists (for instance an EC Initial Training Network), investigate strategic topics or develop new techniques,
- to prepare wider workshops on this topic and/or special sessions at atmospheric or chemistry conferences,
- to discuss other community actions such as the preparation of special issues in scientific journals.

Coffee / Tea Break at 10.30

12.30-14.00 *Lunch*

14.00 End of Workshop and departure

5. Final list of participants

Convenor:

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6. Statistical information on participants

The 23 participants represented 12 countries: Belgium, Denmark, Finland, France, Germany, Greece, Hungary, Italy, Poland, Slovenia, UK, USA

The gender repartition was 61/39 %

The age range represented was 30 – 65, with a maximum of the participants between 40 and 45.