

MEETING REPORT

COST Action: 735

Meeting title: Working Group Meeting Joint Workshop

Reference: COST-735-260410-06670

Meeting dates: 26-28/4/2010

Location: CNR Area della Ricerca di Bologna, via Gobetti 101, 40129, Bologna, Italy

Local organizer: Maria Cristina Facchini

The main aim of the workshop was to involve SOA experts in a discussion on secondary organic aerosol formation processes in the marine boundary layer (MBL).

A few SOA formation processes over the oceans are known since decades (e.g. methanesulfonic acid formation from dimethylsulfide), nevertheless the current knowledge on precursors, formation and transformation routes of SOA does not explain the relevant oxidized organic contribution to sub micron aerosol mass observed during high biological oceanic activity periods.

The workshop, therefore, was aimed at merging expertise in the field of biogenic SOA formation (terrestrial and marine) and expertise in MBL atmospheric chemistry (laboratory, field and modelling).

The meeting has been attended by 22 scientist, of which 20 supported by COST Action 735. Due to last minute changes in circumstance, two of the invited participants were unable to attend.

The meeting has been organized in 4 main sessions. At the conclusion of the meeting, the rapporteur of each session has summarized the main findings to address the final discussion.

The four sessions were:

- Chemical characterization of primary and secondary organic aerosols in the MBL, including organic nitrogen and halogens (rapporteur: Stefano Decesari);
- Newly identified processes of SOA formation, including halogen chemistry and nucleation of new particles (rapporteur: Rainer Volkamer);
- Effects of SOA on marine aerosol CCN activity and aerosol-cloud interaction (Rapporteur: Gordon Mc Figgans);
- Modelling and observations at the global scale (rapporteur: Dominick Spracklen).

The following presentations have been held during the meeting:

Session: "Effects of SOA on marine aerosol CCN activity and aerosol-cloud interaction"

- G. McFiggans: "Key uncertainties in SOA prediction and discrepancies in marine CCN prediction."
- M. Bilde: "Cloud droplet activation of mixed particles containing sodium chloride and fatty acid sodium salts".
- K. Bougiatioti: "Size-resolved CCN measurements in the Eastern Mediterranean".
- K. Sellegri: "Primary/secondary segregation of marine organic aerosol from physical characterization".

Session: "Newly identified processes of SOA formation, including halogen chemistry and nucleation of new particles"

- B. Danna: "Photoenhanced reaction of ozone with chlorophyll at the sea-water surface".
- Y. Iinuma: "Aliphatic amines in the marine environment \rightarrow origin and SOA formation".
- R. Volkamer: "Ocean sources of Glyoxal and Reactive Halogen Species over the Tropical Pacific Ocean Upwelling".
- D. Ceburnis (in substitution of C. O'Dowd): "Detection of open ocean nucleation and growth events".

- T. Hoffmann: “Characterization of the organic aerosol fraction in the marine and coastal atmosphere”.

Session: “Chemical characterization of primary and secondary organic aerosols in the MBL, including organic nitrogen and halogens”.

- S.R. Zorn: “Organic aerosol characterization in MBL of the Southern Atlantic Ocean”.
- S. Decesari: “New insight on marine SOA composition from MAP project”.
- Y. Iinuma (in substitution of M. Claeys): “Organosulfates of C9-C11 hydroxy fatty acids: tracers for a marine secondary organic aerosol formation process”.
- E. Stephanou: “Water soluble organic compounds over the eastern mediterranean: study of their occurrence and sources”.
- M. Rinaldi: “Biogenic source of oxalic acid in marine aerosol”.
- D. Ceburnis: “Chemical gradients, isotope analysis and origin of organic aerosol in MBL”.
- M. Martino: “Aerosol organic nitrogen and iodine”.

Session: “Modelling and observations at the global scale”.

- M. Kanakidou: “Organic aerosols in the marine atmosphere: What do we learn from TM4-ECPL global model results and comparison with observations”.
- D. Spracklen: “Estimating the global oceanic source of isoprene, monoterpenes and primary organic carbon”.
- J. Burrows: “Remote sensing of tropospheric aldehydes and IO from space”.

The key questions discussed in each session are summarized below:

Effects of SOA on marine aerosol CCN activity and aerosol-cloud interaction

Difficulties in reconciling HTDMA and CCN data in N. E. Atlantic and Tropical Atlantic (particles are easier to activate than HTDMA predicts) have been evidenced by the participants. To reconcile the discrepancy between the theory and observations, surface tension lowering effect, due to organic matter was suggested. Nevertheless, when including also organics surface-to-bulk partitioning, (partial) cancellation of the surface tension effect has been observed. Aerosol mixing state has been indicated as a possible key to solve the question: size and temporal averaging plus assumed internal mixing are unlikely to be tenable.

A better understanding of particles mixing state and the relations between primary and secondary marine particles could be reached by crossing the information obtained by size-resolved particle CCN measurements, hygroscopic and combined hygroscopicity-volatility properties, from data collected in remote and anthropogenic influenced marine regions.

Newly identified processes of SOA formation, including halogen chemistry and nucleation of new particles

During the discussion several question arose:

- Is there SOA observed in the marine environment?
- What is the source (aged primary, gas-particle conversion, transport, multiphase chemistry)?
- How relevant is SOA in the marine environment?
- Are there new (unidentified) processes in the MBL?
- How relevant are the unidentified processes?

The data available so far answer only partially to the above questions.

Laboratory studies showed the importance of biogenic organic matter degradation processes, at the air-sea interface, as VOCs sources (likely SOA precursors) in the MBL.

Field measurements and laboratory experiments confirmed the importance of amines as marine SOA components, showing that SOA formation routes beside that of MSA are active in the MBL.

Elevated concentrations of glyoxal have been observed inside the MBL, over the remote open ocean (3000km from land) and have been addressed as potentially important for marine SOA formation.

The first proofs, although indirect, of open ocean nucleation have been observed at Mace Head (Ireland), opening interesting scenarios as far as regards SOA role in particles formation and growth over the oceans.

Finally, the importance of iodine in the MBL chemistry has been highlighted evidencing an interesting potential route of I₂ recycling to the atmosphere inside aerosols, leading to the formation of aldehydes (I₂O₅ + alcohols → aldehydes + I₂).

Chemical characterization of primary and secondary organic aerosols in the MBL, including organic nitrogen and halogens

The entire discussion developed around the question: is the MBL a source or a receptor for particulate organic matter?

Evidence of the biogenic origin of particles collected in remote/unperturbed marine regions has been provided by several participants, through aerosol mass spectrometer measurements, proton nuclear magnetic resonance spectroscopy and combined ¹³C-¹⁴C isotopic analyses. Moreover, a marine source of oxalic acid have been proposed, based on measurements performed in both hemispheres.

The importance of heteroatoms (S, N, I) in marine aerosol chemistry has also been highlighted during the discussion.

In conclusion, from the discussion, the following key necessities for the future emerged:

- Extending the spatial and temporal coverage of in situ measurements.
- Adopting sophisticated analytical methods and isotopic measurements more systematically.
- Performing dedicated and well-focused intensive field campaigns, together with laboratory experiments designed to highlight “source fingerprints” for key processes of aerosol formation.
- Linking gas and aerosol chemistry in the MBL.

Modelling and observations at the global scale

The incomplete knowledge of marine organic aerosol causes large uncertainties in global scale modelling. The main issues discussed regarded SOA from isoprene and monoterpenes. While isoprene emission estimates have been reduced, justifying the limited evidence for isoprene SOA in marine aerosol, monoterpene- derived SOA can be a significant fraction of marine organic aerosol. Nevertheless, the high uncertainty of the precursor emissions makes this hypothesis anything but certain.

The recent advances in remote sensing techniques allow the observation of CHOCHO, HCHO, IO and BrO over remote oceans. Although the high uncertainties associated to this measurements, their importance for the future have been recognised during the discussion.

Many open questions, to be addressed in the future also through global scale modelling and remote sensing, emerged during the discussion:

- Is marine organic aerosol important for climate/air quality/...?
- What fraction of marine organics is from primary / secondary sources?
- What are the dominant marine SOA precursors?

The meeting proved to be highly successful, with the exchange of ideas and information between participants from different disciplines being particularly valuable. It was agreed that a manuscript would be prepared which would contain a synthesis of the key points discussed during the meeting. This manuscript would be submitted for publication in an appropriate journal so that the conclusions and recommendations of the group can be communicated to the wider community. Several ideas for new experimental work were also generated during the workshop.