

# From Sea to Sky: Exploring Marine Atmospheric Chemistry Frontiers

Royal Met. Soc. Atmospheric Chemistry Special Interest Group (ACSG)

NCAS Building, Fairbairn House, 71-75 Clarendon Road, Leeds, LS2 9PH.

## Wednesday 7<sup>th</sup> Feb 2024, 10.00 am

The chemistry of the marine environment plays a crucial role in controlling trace gas concentration, greenhouse gas lifetimes, the tropospheric aerosol budget and radiative forcing. It is an exciting time for research in this field as new measurements provide insight into the fundamental processes at work and new model capability grows to understand their impact. The Atmospheric Chemistry Special Interest Group will host a one-day, in-person meeting at Fairbairn House, University of Leeds with a focus on the chemistry of marine regions and their impact on atmospheric composition. Focus will be on novel measurements of atmospheric composition, modelling of aerosol and gas phase processes across a range of scales, and use of models to understand and evaluate the global impact of these regions.

**Please bring posters on any atmospheric chemistry topic for discussion**

09.30	Arrival and tea/coffee	
10.00	Welcome and introduction	<b>ACSG co-Chairs</b>
10.10	Airborne observations over the North Atlantic Ocean reveal the first gas-phase measurements of urea in the atmosphere	<b>Emily Matthews</b> University of Manchester
10.40	The development of a dimethyl sulfide mechanism and evaluation through chamber studies	<b>Lorrie Jacob</b> University of Cambridge
11.10	Tea break	
11.30	Oceanic iodine and sulphur compounds as sources of cloud condensation nuclei	<b>Xu-Cheng He</b> University of Cambridge
12.00	What are the causes of unexpectedly high cloud droplet number concentrations of Southern Ocean liquid clouds?	<b>Eszter Kovacs</b> University of Leeds
12.30	Buffet lunch (provided) + posters	
13.30	TBC	<b>Matt Johnson</b> U. Copenhagen, Denmark
14.00	Scientific Highlights and Opportunities at the Cabo Verde Atmospheric Observatory (CVAO)	<b>Katie Read</b> U. York / NCAS
14.30	Tea break	
14.50	Isoprene in the Southern Ocean: source regions, emission schemes and atmospheric implications	<b>Valerio Ferracci</b> Cranfield University
15.20	Natural short-lived halogens exert an indirect cooling effect on climate	<b>Alfonso Saiz-Lopez</b> CSIC, Madrid, Spain
16.10	Refreshments + poster session	
17.00	Meeting closes	

**Please register by Fri 12 Jan 2024 at the [ACSG site](#)**

The registration fee is £26 to cover lunch and refreshments

Find the NCAS Building: <https://ncas.ac.uk/contact/>

Questions? Email one of the organising committee: Paul Griffiths ([paul.griffiths@ncas.ac.uk](mailto:paul.griffiths@ncas.ac.uk)), Ryan Hossaini ([r.hossaini@lancaster.ac.uk](mailto:r.hossaini@lancaster.ac.uk)) or Lorrie Jacob ([lj384@cam.ac.uk](mailto:lj384@cam.ac.uk))

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## Abstracts

### **Airborne observations over the North Atlantic Ocean reveal the first gas-phase measurements of urea in the atmosphere**

Emily Matthews, University of Manchester

Despite the reduced nitrogen (N) cycle being central to global biogeochemistry, there are large uncertainties surrounding its sources and rate of cycling. Here, we present the first observations of gas-phase urea ( $\text{CO}(\text{NH}_2)_2$ ) in the atmosphere from airborne high-resolution mass spectrometer measurements over the North Atlantic Ocean. We show that urea is ubiquitous in the marine lower troposphere during the Summer, Autumn and Winter flights but was found to be below the limit of detection during the Spring flights. The observations suggest the ocean is the primary emission source but further studies are required to understand the processes responsible for the air-sea exchange of urea. Urea is also frequently observed aloft due to long-range transport of biomass-burning plumes. These observations alongside global model simulations point to urea being an important, and as yet unaccounted for, component of reduced-N to the remote marine environment. Since we show it readily partitions between gas and particle phases, airborne transfer of urea between nutrient rich and poor parts of the ocean can occur readily and could impact ecosystems and oceanic uptake of  $\text{CO}_2$ , with potentially important atmospheric implications.

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### **The development of a dimethyl sulfide mechanism and evaluation through chamber studies**

Lorrie Jacob, University of Cambridge

Dimethyl sulfide (DMS), originating from phytoplankton, is the largest natural source of sulfur in the atmosphere. Some oxidation products of DMS have been found to contribute to cloud condensation nuclei; understanding the oxidation mechanism of DMS can help constrain its contribution to the Earth's radiative balance. The discovery of a new pathway of the DMS oxidation mechanism, forming hydroperoxymethyl thioformate, has led to chamber studies that further explore the OH-initiated oxidation of DMS, and the development of near-explicit DMS mechanisms. These mechanisms had yet to be evaluated through intercomparison studies. In this recently submitted work (Jacob et al., 2023), we conducted a thorough literature review to develop a gas-phase DMS oxidation mechanism based on the MCM v3.3.1, with 62 reactions added and 21 reactions adjusted. We evaluated this mechanism against other recently developed mechanisms by using them to simulate chamber studies. Our mechanism outperformed the other mechanisms, having the lowest average fractional gross error for 8 of the 14 measured DMS products. A box model of a marine boundary layer was run to assess how the mechanisms compare in more realistic conditions. We found that the deviations between the mechanisms were still prominent, indicating that the differences in the mechanisms are of atmospheric importance. Our work demonstrates the importance of the recent developments in the oxidation of DMS. It provides a new near-explicit mechanism, which has been evaluated against different mechanisms through chamber studies. This

mechanism can be used as a basis to compare the performance of reduced mechanisms used in global atmospheric models. <https://doi.org/10.5194/egusphere-2023-2223>

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## **Oceanic iodine and sulphur compounds as sources of cloud condensation nuclei**

Xu-Cheng He, University of Cambridge

Clouds in the marine and polar atmospheres play a crucial role in climate through cloud-radiation interactions. Secondary aerosols formed from gas precursors serve as potential cloud droplet nuclei, influencing cloud reflectivity and lifespan, and consequently impacting the climate indirectly. Understanding the processes involved in secondary aerosol and cloud formation in these regions is essential for predicting future changes, given the extensive coverage of marine and polar clouds and the observed rapid transformations in the Arctic. Despite their significance, marine and polar aerosol formation processes remain among the least investigated due to the challenges posed by experiments and logistics. In this presentation, compelling evidence derived from field observations and laboratory experiments will be showcased, highlighting the significance of iodine and sulfur species as crucial aerosol sources in polar and marine atmospheres.

The involvement of iodic acid and iodous acid in secondary aerosol formation processes has also been observed on a global scale. Traditionally, iodine aerosol formation has been predominantly associated with mid-latitude regions. However, our study has revealed the unequivocal presence of HIO<sub>3</sub> in a much broader range of environments, including polar regions, boreal forests, marine sites, and even polluted urban areas. Our experiments at the Cosmic Leaving Outdoor Droplets (CLOUD) facility further unveil a surprising synergistic particle formation resulting from iodine oxoacids and sulfuric acid. To comprehensively evaluate the worldwide implications of iodine and sulfur aerosol formation processes, a systematic analysis combining ambient observations, laboratory experiments, and global simulations is imperative.

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## **What are the causes of unexpectedly high cloud droplet number concentrations of Southern Ocean liquid clouds?**

Eszter Kovacs, University of Leeds

Aerosol-cloud interactions pose a large uncertainty in climate forcing predictions. Southern Ocean liquid clouds have a higher than expected cloud droplet number concentration (Nd), that global coupled models underpredict. This work investigates the source regions of natural cloud-relevant aerosol that influence summertime Nd of liquid clouds over the Southern Ocean. Satellite retrievals of Southern Ocean liquid clouds over the summer of 2018 were split into over 3000 0.5° × 0.5° cloud grid points. From each grid point, back-trajectories were simulated over 5 days in order to establish the sources of aerosol ending up in these clouds and influencing Nd, removing cloud grid points whose trajectories may be affected by anthropogenic emissions from continents other than Antarctica. The resulting dataset exhibits an increase in Nd towards higher latitudes as expected. The trajectories spending time at higher latitudes (south of 60°S) tend to lead to the highest Nd, reaching values over 200 cm<sup>-3</sup>. Exposure to sea ice or the Antarctic continent also seems to be a factor that increases Nd. Other factors influencing Nd include surface wind speed (related to sea spray aerosol generation), and the time air masses spent in the free troposphere as opposed to the marine boundary layer (increased new particle formation and nucleation). The surface seawater concentration of chlorophyll-a, which is widely used as a tracer of phytoplankton activity and a predictor of dimethyl sulphide (DMS) emission, showed a weak correlation with Nd, only on clouds also influenced by sea ice. This highlights the importance of sea ice algae and phytoplankton in the marginal ice zone in DMS production. This study has demonstrated

how aerosol source regions and location history influence Southern Ocean cloud droplet number concentrations.

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## Scientific Highlights and Opportunities at the Cabo Verde Atmospheric Observatory (CVAO)

Katie Read, National Centre for Atmospheric Science (NCAS) / University of York

The Global Atmosphere Watch (GAW) 'Global' Observatory at Cabo Verde, an international cooperation between the National Centre for Atmospheric Science (NCAS) UK, Leibniz Institute for Tropospheric Research (TROPOS), Germany, Max-Planck Institute for Biogeochemistry, Germany, and Instituto Nacional de Meteorologia e Geofísica (INMG), Cabo Verde; is ideally located to assess the chemistry of the marine boundary layer above the North Atlantic Ocean. 95% of the time air arrives at the CVAO from the northeast with FLEXPART trajectory analysis suggesting it has spent an average of 5 days over the open ocean prior to instrument detection. The site, established in 2006; is one of the most highly instrumented observatories in the world; measurements made there have contributed to many scientific findings, provided the scientific community with opportunities for focussed process-based studies to understand emission/loss processes, and supported model developments. This presentation will introduce the advantages of the site in terms of location and facilities, some research highlights and what the site and measurements continue to offer to our future scientific understanding in this region.

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## Isoprene in the Southern Ocean: source regions, emission schemes and atmospheric implications

Valerio Ferracci, Cranfield University

**Abstract:** Isoprene is a key trace component of the atmosphere emitted by vegetation and other organisms. It is highly reactive and can impact atmospheric composition and climate by affecting the greenhouse gases ozone and methane and secondary organic aerosol formation. Isoprene emissions from marine environments are poorly constrained due to the paucity of long-term measurements, which in turn limits our understanding of isoprene cycling in the ocean. The analysis of isoprene concentrations in the atmosphere measured across the Southern Ocean over 4 months in the summertime (Dec 2016-Mar 2017) indicated that the marginal ice zone (MIZ) was a significant source of isoprene at high latitudes. Using a global chemistry-climate model (UKESM1) we found that current estimates of sea-to-air isoprene fluxes are significantly low-biased, and a 20-fold increase in emissions is needed to reconcile the model with observations, along with a daytime source of isoprene. These increased isoprene emissions would lead to >8% decrease in the hydroxyl radical in regions of the Southern Ocean, with implications for our understanding of atmospheric oxidation and composition in remote environments, often used as proxies for the pre-industrial atmosphere.

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## Natural short-lived halogens exert an indirect cooling effect on climate

Alfonso Saiz-Lopez, CSIC, Madrid, Spain

**Abstract:** Natural short-lived halogens (SLH; chlorine, bromine and iodine) are emitted from the oceans, polar ice, and the biosphere. SLH influence the oxidative capacity of the atmosphere, and consequently the lifetime and abundance of short-lived climate forcers such as ozone, methane and aerosols. This communication presents results on the combined effect of SLH on the atmospheric radiative balance.

# Atmospheric Chemistry Special Interest Group

