



**British  
Antarctic Survey**

NATURAL ENVIRONMENT RESEARCH COUNCIL



## **Workshop on Chemical Atmosphere-Snow-Sea Ice Interactions: taking the next big step in the field, lab & modelling**

co-sponsored by



### **DATES & VENUE**

The British Antarctic Survey (BAS) is holding an International Workshop on Chemical Atmosphere-Snow-Sea Ice Interactions in 2014. The event will take place at Trinity Hall in **Cambridge, United Kingdom from 13 to 15 October 2014.**

### **SCOPE & AIMS**

The air-snow-sea ice system plays an important role in the global cycling of nitrogen, halogens, trace metals or carbon, including greenhouse gases (e.g. CO<sub>2</sub> air-sea flux), and therefore influences also climate. Its impact on atmospheric composition is illustrated for example by dramatic ozone and mercury depletion events which occur within or close to the sea ice zone (SIZ) mostly during polar spring and are catalysed by halogens released from SIZ ice, snow or aerosol. Recent field campaigns in the high Arctic (e.g. BROMEX, OASIS) and Antarctic (Weddell sea cruises) highlight the importance of snow on sea ice as a chemical reservoir and reactor, even during polar night. However, many processes, participating chemical species and their interactions are still poorly understood and/or lack any representation in current models. Furthermore, recent lab studies provide a lot of detail on the chemical environment and processes but need to be integrated much better to improve our understanding of a rapidly changing natural environment.

The aim of this three day workshop is to bring together experimental and theoretical scientists who work on the physics, chemistry or biology of the atmosphere-snow-sea ice system in order to discuss research status and challenges, which need to be addressed in the near future. An important objective is to foster new research collaborations and identify opportunities for international collaborative funding proposals. **An expected workshop outcome will be a publicly available white paper/conference report outlining research priorities and pathways how to address them.**

Enough time for discussion will be provided to identify imminent research priorities and how to address them through collaborative funding proposals.

## VENUE

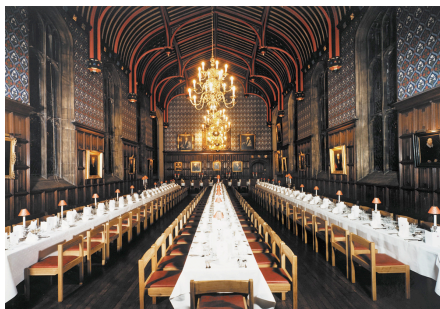
The conference will take place at one of the oldest Colleges of Cambridge University, Trinity Hall, founded in 1350 originally for the study of law. Today the beautiful riverside setting is home to a friendly community of undergraduate and graduate students studying a range of subjects.



How to get there: <https://www.trinhall.cam.ac.uk/contact/>

## CONFERENCE DINNER

The conference dinner will take place Corpus Christi College, only a 5 minute stroll away from Trinity Hall, on the evening of the second day. The Dining Hall, one of the most beautiful in Cambridge, is new gothic in style and the walls are lined with portraits of previous Masters. The upper walls are decorated in William Morris print, made from plates rediscovered in the 1960s and also found in the House of Commons.



How to get there: <https://www.corpus.cam.ac.uk/contact-us/how-to-find-us/>

## ACCOMMODATION

We have reserved rooms to accommodate everyone at the Arundel House Hotel (<http://www.arundelhousehotels.co.uk/cambridge/index.php>) in walking distance to the conference venue and the historic city center of Cambridge.

## TRAVELING TO CAMBRIDGE

[http://www.antarctica.ac.uk/about\\_bas/contact/travel\\_to\\_cambridge.php](http://www.antarctica.ac.uk/about_bas/contact/travel_to_cambridge.php)

## SCIENTIFIC PROGRAMME COMMITTEE

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## Oral presentations

Invited overview talks are 25 min (20 minutes + 5 min for questions), short talks are 15 min (12 min + 3 min for questions); exception is Session S5 with slightly different times, allow 3-5 minutes for questions.

## Posters

The format is A0 landscape (board size W x H 120cm x 86cm). Posters will be mounted in the Graham Storey Room on Monday morning 0800-0900 on the board with the matching presentation number. They will be on display during the entire workshop. **Short oral poster introductions are max 4 minutes (3 slides), no exceptions.**

Please provide all presentations in PDF format on a USB stick to upload before the session onto the PC computer or email over the weekend to [macy@bas.ac.uk](mailto:macy@bas.ac.uk)

CASSII WORKSHOP 13-15 OCT - ORAL PROGRAMME (Lecture Theater, Trinity Hall)		
Sunday, 12 October 2014 ICEBREAKER at the Castle Inn 1930 - 2200		
Monday, 13 October 2014		
08:00 - 09:00	Registration, Poster mounting & Coffee	
09:00 - 09:15	Welcome & Opening Remarks: David Vaughan (BAS Director of Science), Markus Frey (Organising Committee)	
S1: "Impacts of Chemical Atmosphere-Snow-Sea Ice interactions" (Chairs: von Glasow, Frey)		
9:15 - 9:40	P. A. Ariya	On the role of bio-organic compounds in atmospheric interfaces: Arctic case study (invited)
9:40 - 10:05	T. Lachlan-Cope	Clouds and Aerosols in the Arctic (invited)
10:05 - 10:20	R. Humphries	Evidence for a new source of Southern Ocean and Antarctic aerosol from tropospheric polar cell chemistry of sea ice emissions
10:20 - 10:35	U. Friess	On the abundance of iodine monoxide in the Antarctic boundary layer
10:35 - 11:05	COFFEE BREAK & DISCUSSION AT POSTERS	
11:05 - 11:20	A.-M. Blechschmidt	Transport of tropospheric BrO by polar cyclones observed from satellite
11:20 - 11:45	B. Alexander	Can isotopes of ice-core nitrate be used to quantify past variability in snow photochemistry? (invited)
11:45 - 12:00	W. Neff	Intermittent export of NO/NOx in katabatic flows from Antarctica and associated synoptic controls
12:00 - 13:00	S1 POSTER INTRODUCTION (posters 1-11)	
13:00 - 14:00	LUNCH	
14:00 - 14:20	S1 POSTER INTRODUCTION (posters 12-15)	
S2: "Biogeochemistry of the air-snow-sea ice-ocean system" (Chairs: Tison, Abrahamson)		
14:20 - 14:45	D. Nomura	CO <sub>2</sub> and Bromoform emissions over Antarctic Sea Ice (invited)
14:45 - 15:00	D. Bakker	Seasonal sea-ice coverage exerts strong controls on the Weddell Sea carbon cycle
15:00 - 15:25	W. Smith	Ecological impacts of changing ice concentrations in the coming century: the Ross Sea (invited)
15:25 - 15:55	COFFEE BREAK & DISCUSSION AT POSTERS	
15:55 - 16:10	C. Halsall	Enrichment of long-lived chemical contaminants in Arctic sea-ice: observations, processes & impact
16:10 - 16:35	S2 POSTER INTRODUCTION (posters 16-20)	
16:35 - 17:30	GENERAL DISCUSSION on S1 & S2	
17:30 - 18:30	POSTERS	
Tuesday, 14 October 2014		
S3: "Air-snow exchange processes – closing the gap between Field, Lab and Models" (Chairs: Dibb, King)		
9:00 - 9:25	T. Kahan	Laboratory perspectives on ice as a reaction medium (invited)
9:25 - 9:40	F. McNeill	Changes in the surface state of ice induced by trace gases
9:40 - 9:55	A. Jones	HO2NO2 and HNO3 in the coastal Antarctic winter night: A Lab-in-the-field Experiment
9:55 - 10:10	T. Bartels-Rausch	Can laboratory data explain field observations: The fluxes of HNO3 and HNO4 from snow in the lab and in Antarctica



10:10 - 10:35	C. Toubin	Molecular Modelling of the Air/ice interface: overview and connections with experiments (invited)
10:35 - 11:05	COFFEE BREAK & DISCUSSION AT POSTERS	
11:05 - 11:30	M. Frey	The OPALE project in East Antarctica - new insights into oxidant chemistry above polar snow (invited)
11:30 - 12:20	S3 POSTER INTRODUCTION (posters 21-30)	
12:20 - 13:00	GENERAL DISCUSSION on S3	
13:00 - 14:00	LUNCH	
S4: "New strategies – Developing optimal probes and systems for AICI lab, field & model studies" (Chairs: McNeill, Tang)		
14:00 - 14:25	H. Löwe	Controls of snow metamorphism and diffusion on chemical Air-Ice-Snow interactions (invited)
14:25 - 14:40	D. Heger	Impurities Location, Speciation and Spectroscopy in Artificial Snow and Frozen Aqueous Solutions
14:40 - 15:05	M. King	Calculating photochemical production rate in sea ice: sea ice tank studies at RHUL (invited)
15:05 - 15:30	R. v. Glasow	A novel sea-ice - snow chamber for polar research and linked modelling activities (invited)
15:30 - 16:00	COFFEE BREAK & DISCUSSION AT POSTERS	
16:00 - 16:15	M. Tang	Compilation and evaluation of gas-phase diffusion coefficients of inorganic reactive trace gases in the atmosphere
16:15 - 16:40	S4 POSTER INTRODUCTION (posters 31-35)	
16:40 - 17:00	J. P. Wilkinson	Successful large grant applications in the Arctic (invited)
17:00 - 17:45	GENERAL DISCUSSION on S3 & S4	
17:45 - 18:45	POSTERS	
19:30 - 22:30	CONFERENCE DINNER	
Wednesday, 15 October 2014		
S5: "Taking the next steps – challenges & opportunities" (Chairs: Thomas, Bartels-Rausch)		
9:00 - 9:10	K. Abrahamson	The Oden as a platform for a winter cruise into the SIZ in Antarctica
9:10 - 9:20	N. Brough	AICI-type opportunities at the CASLab, Halley, in coastal Antarctica
9:20 - 9:30	J.-L. Tison	Field research opportunities at Queen Elizabeth Station
9:30 - 9:40	S. Bauguitte	FAAM's aircraft Arctic capability: airborne measurements over the SIZ around Svalbard during the ACCACIA 2013 project
9:40 - 10:00	Dibb, Neff, Smith	US polar field platforms & science perspectives (GEO Summit, NOAA , NSF)
10:00 - 10:10	F. McNeill	AICI/OASIS/Future Earth
10:10 - 10:30	L. Gonzalez Pacheco	International funding opportunities for Earth Science research
10:30-11:00	COFFEE BREAK & DISCUSSION AT POSTERS	
S6: Discussion: the next steps – research priorities & strategy" (Chair: Frey, Panel: Neff, McNeill, King, Thomas)		
11:00 - 13:00	General discussion - What are research priorities & how do we get them funded? (I)	
13:00 - 14:00	LUNCH & removal of posters	
14:00 - 15:30	General discussion - What are research priorities & how do we get them funded? (II) - Wrap up & Close	

## Monday, 13 October 2014

**8:00**            **Registration, Poster mounting in the Graham Storey room & Coffee**

**9:00**            **Welcome by BAS and Opening Remarks**

**9:15**            **On the role of bio-organic compounds in atmospheric interfaces:  
Arctic case study**

Parisa A. Ariya<sup>1</sup>, R. Rangel-Alvarado<sup>1</sup>, R. Mortazaci<sup>1</sup>, G. Kos<sup>1</sup> and Y.  
Nazerenko<sup>1</sup>

<sup>1</sup>Department of Chemistry and Department of Atmospheric and Oceanic Sciences,  
McGill University, Montreal, Canada

Aerosols and their interactions with clouds “contribute the largest uncertainty to the total radiative forcing” driving climate change. The aerosol-cloud-induced uncertainty is as large as the effect of increasing atmospheric concentrations of well-mixed greenhouse gases. Ice and mixed-phase clouds form when water condenses on aerosol nucleation sites. In this talk, we provide an historic overview of the role of bio-aerosols in atmosphere and atmospheric interfaces, and open questions in the field. We also provide for the first time, snow and bio-aerosol measurement campaigns (2004-2014), along with their physical, chemical and biological analysis, in several Arctic and sub-Arctic sites in North America, as part of international campaigns and from permanent sites during the last decade and discuss their roles on our current understanding of nucleation microphysical processes at the snow-atmosphere interface.

**9:40**            **Clouds and Aerosols in the Arctic**

Tom Lachlan-Cope, British Antarctic Survey, UK

During 2013 a consortium of UK HEI and research institutes, including the British Antarctic Survey, carried out an extensive campaign in the Arctic to investigate clouds and aerosols at high latitudes and their interaction with the climate. At high latitudes atmospheric numerical models have problems representing clouds and this can cause large errors in the surface energy balance which in turn can lead to problems representing surface melt of sea and land ice. It is thought that one of the problems with the models representation of clouds lies with the aerosols that act as cloud condensation nuclei (CCN) (see Birch et al 2012). This campaign is intended to improve our knowledge of the source of CCN in the Arctic and the role they play in cloud formation.

### References:

Birch, C. E., Brooks, I. M., Tjernström, M., Shupe, M. D., Mauritsen, T., Sedlar, J., ...Leck, C. (2012). Modelling atmospheric structure, cloud and their response to CCN in the central Arctic: ASCOS case studies. *Atmospheric Chemistry and Physics*, 12(7), 3419, doi:10.5194/acp-12-3419-2012.

**10:05**            **Evidence for a new source of Southern Ocean and Antarctic aerosol from  
tropospheric polar cell chemistry of sea ice emissions**

Ruhi Humphries<sup>1</sup>, A. Klekociuk<sup>2</sup>, R. Schofield<sup>3</sup>, A. Robinson<sup>4</sup>, N. Harris<sup>4</sup>, M.  
Keywood<sup>5</sup>, J. Ward<sup>5</sup>, I. Galbally<sup>5</sup>, S. Molloy<sup>5</sup>, A. Thomas<sup>6</sup> and S. Wilson<sup>1</sup>

<sup>1</sup>University of Wollongong, Australia; <sup>2</sup>Australian Antarctic Division, Australia;

<sup>3</sup>University of Melbourne, Australia; <sup>4</sup>University of Cambridge, United Kingdom;

<sup>5</sup>CSIRO Marine and Atmospheric Research, Australia; <sup>6</sup>National Institute of Water and  
Atmospheric Research, New Zealand

Aerosol measurements in this pristine Antarctic environment allow the study of natural aerosols and polar atmospheric dynamics. Measurements in this region have been limited primarily to continental and coastal locations where permanent stations exist, with only one other measurement campaign passing through the sea ice region. The MAPS campaign (Measurements of Aerosols and Precursors during SIPEXII) occurred as part of SIPEX II (Sea Ice Physics and Ecosystems eXperiment II) voyage in Spring, 2012, and produced the first Antarctic pack-ice focused aerosol dataset aimed at characterizing new particle formation processes off the coast of East Antarctica (~65°S, 120°E). Numerous atmospheric parameters and species were measured, including the number of aerosol particles in the 3-10 nm size range, the range associated with nucleating particle formation. During the latitudinal transect through the sea ice, the Polar Front was identified from nucleating particle concentrations that exhibited an order of magnitude step change with latitude, with median concentrations of 45 cm<sup>-3</sup> north of the front in the Ferrel cell, and 530 cm<sup>-3</sup> south of the front in the Polar cell region. The Polar Front location was also confirmed by meteorological and back-trajectory data. Polar Cell background aerosol populations displayed no growth indicators, suggesting transport. Back-trajectories revealed that air parcels frequently descended from the free-troposphere within the previous 24-48 hrs. We propose a new model for particle formation in the Antarctic free troposphere from precursors uplifted in the Polar Front from the biologically active sea-ice region. After tropospheric formation, populations descending at the poles are transported northward and reach the sea ice surface, missing continental stations. Current measurements of Antarctic aerosol suggest very low loading which may be explained by these circulation patterns and may underestimate total regional loading and the contribution of Antarctic aerosol production to global loading. As climate change intensifies and the ozone hole recovers, the Antarctic polar front may shift latitudes, potentially changing Antarctic and regional aerosol loading, resulting in changes to tropospheric and stratospheric chemistry and radiative budgets.

#### **10:20 On the abundance of iodine monoxide in the Antarctic boundary layer**

Udo Friess<sup>1</sup>, J. Zielcke<sup>1</sup>, D. Pöhler<sup>1</sup>, T. Hay<sup>2</sup>, K. Kreher<sup>3</sup>, U. Platt<sup>1</sup>

<sup>1</sup>University of Heidelberg, Germany; <sup>2</sup>National Institute of Water and Atmospheric Research, New Zealand; <sup>3</sup>Bodeker Scientific, New Zealand

Iodine monoxide (IO) is thought to play an important role in the chemistry of the Antarctic marine boundary layer (MBL). Produced either by organic precursors or by inorganic processes, large areas of enhanced IO were detected by satellite not only around the coast of Antarctica, but also over the continent far from the coastal source regions. In the past, several active and passive remote sensing measurements at coastal stations confirmed the presence of IO, which is expected to have a significant impact on the oxidative capacity and the ozone budget in the MBL.

We present a summary of recent findings regarding IO in the Antarctic MBL, with a focus on two measurement campaigns conducted at the German Research Station Neumayer (70°S, 8°W), the New Zealand Station Scott Base (177°E, 78°S) and in the marginal sea ice zone of the Weddell Sea onboard the German research vessel Polarstern in austral summer 2011, spring 2012, and winter/spring 2013, respectively. During all three campaigns, IO was measured using a combination of active and passive DOAS remote sensing instruments, including a newly developed mobile open-path cavity-enhanced DOAS instrument.

Satellite measurements indicate that the area around Scott Base in the Ross Sea, but also the marginal sea ice zone, are subject to particularly high levels of IO. However, in contrast to previous ground-based and satellite borne observations, we find surprisingly low IO concentrations at Neumayer, Scott Base and in the marginal sea ice zone, with IO being below the detection limit (< 0.5 ppt) of the active DOAS instruments at all times. This raises the question to what extent IO is of importance for the chemistry of the Antarctic MBL.

#### **10:35 Coffee Break & Discussion at Posters**

**11:05      Transport of tropospheric BrO by polar cyclones observed from satellite**  
Anne-Marlene Blechschmidt<sup>1</sup>, A. Richter<sup>1</sup>, J.P. Burrows<sup>1</sup>, A. Schoenhardt<sup>1</sup>,  
L. Kaleschke<sup>2</sup> and X. Zhao<sup>3</sup>

<sup>1</sup>Institute of Environmental Physics, University of Bremen, Germany; <sup>2</sup>Institute of Oceanography, University of Hamburg, Germany; <sup>3</sup>Department of Physics, University of Toronto, Canada

GOME-2/MetOp-A and SCIAMACHY/Envisat provide observations of halogen oxides in the atmosphere over several years. These satellite observations demonstrate that intense, cyclone-like shaped plumes of tropospheric BrO regularly occur over sea ice during polar spring. Further investigation using model data indeed shows that the plumes are often transported by polar cyclones, sometimes over several days despite the short atmospheric lifetime of BrO.

Here, we investigate the role of high latitude cyclones for the development, duration and transport of bromine explosion events. The latter are caused by an autocatalytic chemical cycle associated with tropospheric ozone depletion, which requires the release of bromine from a condensed phase (e.g. young sea ice or salty blowing snow) to the atmosphere. Making combined use of satellite observations and numerical models, characteristics of BrO cyclone transport events such as their frequency and spatial distribution as well as favorable weather conditions are discussed. Our results show that BrO cyclone transport events are by far more common in the Antarctic than in the Arctic.

**Cancelled      Understanding winter Ozone pollution in regions of intense Oil and Gas production and the role of the snowpack**  
Pete Edwards, University of York, UK

In recent years the Uintah Basin in northeastern Utah has developed a problem with ground level ozone, and is now frequently in excess of the US National Ambient Air Quality Standards. This is unusual on several fronts as, counter to typical urban summertime ozone pollution, these events occur in a sparsely populated region during the wintertime. The basin is, however, home to some of the most intensive oil and gas production in the US, activities that have been accelerated by new technologies in that industry. High ozone episodes are coincident with the presence of snow, and stable “cold pool” conditions during which a stable shallow boundary layer persists for periods of a week to 10 days. Local emissions of NO<sub>x</sub> and VOCs build up under this layer, but the sources of radicals that initiate the photochemistry have been unclear since low photolysis rates and water vapor make the traditional channel, ozone photolysis, quite inefficient. Data from intensive studies over the past 3 years will be shown and the nature of the photochemistry driving these winter ozone events, including the role of the snowpack, will be discussed.

**11:20      Can isotopes of ice-core nitrate be used to quantify past variability in snow photochemistry?**

Becky Alexander<sup>1</sup>, M. Zatko<sup>1</sup> and L. Geng<sup>1</sup>  
<sup>1</sup>University of Washington, Seattle, WA, USA

Ice-core nitrate concentrations and isotopes have historically been measured with the goal of understanding the history of reactive nitrogen and oxidants in the atmosphere. The abundance of reactive nitrogen species in the troposphere strongly influences the oxidation capacity of the atmosphere, which determines the lifetime of most reduced trace gases in atmosphere. Interpretation of the ice-core nitrate record as such has been hampered by the lack of preservation of nitrate in snow and ice due to post-depositional processing. Recent studies have shown that photolysis is the dominant driver of post-depositional processing of nitrate. The photolysis of nitrate in the snowpack influences the oxidation capacity of snow covered regions directly via recycling of reactive nitrogen and indirectly via production of radicals in the snowpack that contribute to the generation of reactive halogens.

Recent studies have shown that the photolysis of snowpack nitrate leads to a large isotopic

fractionation, with the lighter isotope preferentially photolyzed, leaving the heavier isotopes in the snow. This renders the nitrogen isotopic composition of ice-core nitrate a potential indicator for past variability in snow photochemical reactions, with implications for our ability to reconstruct the past variability in the oxidation capacity of snow-covered regions and the intensity of ultraviolet radiation at the surface. Ice-core measurements of the nitrogen isotopic composition of nitrate may also aid the interpretation of other chemicals measured in ice cores such as halogens that are similarly influenced by photolytic processes. However, its interpretation as a proxy for past variability in snow photochemical reactions depends on our ability to understand and distinguish the importance of photolytic loss versus recycling of snowpack nitrate. I will present a modeling framework used to identify potential locations where observations of the nitrogen isotopic composition of ice-core nitrate can be useful to quantify the degree of snow photochemical processing in the past, and what we need from field and laboratory studies to improve confidence in the model results. I will also present new ice core measurements of the nitrogen isotopic composition of nitrate in light of interpreting such records as an indicator of past variability in snow photochemical reactions.

**11:45 Intermittent export of NO/NO<sub>x</sub> in katabatic flows from Antarctica and associated synoptic controls**

William Neff<sup>1</sup> and D. Davis<sup>2</sup>

<sup>1</sup>University of Colorado, USA; <sup>2</sup>Georgia Institute of Technology, USA

The Antarctic Tropospheric Chemistry Investigation (ANTCI) carried out two major field programs at the South Pole from late November through December. The first of these was in 2003 [Davis et al., 2008] and the second occurred in 2005 [Slusher et al., 2010]. Both studies included small-aircraft measurements of key chemical constituents in the boundary layer several hundred km from the Pole which revealed that the high NO concentrations seen at the Pole were also ubiquitous in its immediate vicinity. In particular, the 2005 ANTCI aircraft probing of the high plateau, as reported by [Slusher et al., 2010], found high concentrations of NO over a much larger portion of the plateau where sampling reached nearly to Vostok Station.

As part of both studies, a few of the flights probed portions of the katabatic outflow regions over Byrd and Reeves Glaciers, seeking evidence of export of NO<sub>x</sub> from the continent. On 11-27-2003, a flight was made in the drainage flow from Byrd Glacier during which very high concentrations of NO (~500 pptv) and NO<sub>y</sub> were observed. However, a second flight one day later did not reveal a similar plume of NO suggesting that the export due to katabatic flow was intermittent. On 11-21/22-2005, flights were also made over Reeves and David Glaciers and on 12-12-2005 over Byrd Glacier. These observations and those for O<sub>3</sub> showed smaller but still well-defined increases while traversing Reeves glacier at multiple heights. Similarly a single flight on 12-12-2005 above Byrd Glacier showed NO reaching 70 pptv over the center of the glacier with a well defined plume centered along the axis of the glacier. These results suggested a need for a closer examination of mechanisms controlling export of NO<sub>x</sub> and oxidants from the high plateau to coastal areas.

Katabatic outflow from the high plateau of East Antarctic has been well documented during the Austral winter [Breckenridge et al., 1993] where satellite imagery provides highly visual images of cold air surges across the Ross Ice Shelf [Bromwich, 1989]. In these cases, the cold surface of the ice sheet is disturbed by high surface winds, creating a warm signature that is revealed convincingly in satellite infrared imagery. However, similar analyses have been lacking in the summer season when photochemistry over the interior of the ice sheet is much more active. In this presentation we will examine potential controlling mechanisms for this intermittent transport during the summer season including:

1. Synoptic pressure gradients that inhibit downslope flow from the interior and allow, under clear sky and light to moderate wind conditions, the accumulation of NO<sub>x</sub>-rich air in the boundary layer.
2. A change in the synoptic conditions that allows a release of this cold air to flow down through the glacial valleys to the Ross Sea.
3. An examination of METOP high-resolution infrared satellite data for the summer seasons (late-November-December) available during 2012 and 2013 that show katabatic outflow signatures extending over 100 km over the Ross Sea (compared to as much as 500 km during



the winter season). Note, these events are typically preceded by light winds and colder temperatures over the interior as seen in AWS data from the high plateau.

4. Back-trajectory analysis that show many of these air streams near the exit of the Byrd Glacier originated on the plateau grid east of the South Pole.

Finally, we discuss future experiments that may better resolve the underlying mechanisms and the frequency of these events. This includes better placement of AWS stations in key glacial outflow areas, small UAS probing the glacial airflow, and small aircraft profiling across the outflow regions with real-time NO<sub>x</sub> and O<sub>3</sub> measurements. Also useful would be a determination of a concomitant signature in ozone as measured by a downward looking ozone lidar onboard a small aircraft.

**Acknowledgement:** J. Crawford, M. Buhr, and F. Eisele contributed significantly to the aircraft program in 2003 and 2005.

**References:**

Breckenridge, C. J., U. Radok, C. R. Stearns, and D. H. Bromwich (1993), Katabatic winds along the Transantarctic Mountains, Wiley Online Library.

Bromwich, D. H. (1989), Satellite Analysis of Antarctic Katabatic Wind Behavior Bulletin of the American Meteorological Society, 70(7), 738-749.

Davis, D. D., et al. (2008), A reassessment of Antarctic plateau reactive nitrogen based on ANTO 2003 airborne and ground based measurements, Atmospheric Environment, 42(12), 2831-2848.

Slusher, D. L., et al. (2010), Atmospheric chemistry results from the ANT-01 2005 Antarctic plateau airborne study, Journal of Geophysical Research-Atmospheres, 115.

**12:00 S1 Poster Introduction (Posters 1-11)**

**13:00 Lunch**

**14:00 S1 Poster Introduction (Posters 12-15)**

**14:20 CO<sub>2</sub> and Bromoform emissions over Antarctic sea-ice**

Daiki Nomura<sup>1</sup>, B. Delille<sup>2</sup>, A. Ooki<sup>1</sup>, G. S. Dieckmann<sup>3</sup>, J.-L. Tison<sup>4</sup>, K. M. Meiners<sup>5</sup>, M. A. Granskog<sup>6</sup>, and T. Tamura<sup>7</sup>

<sup>1</sup>Institute of Low Temperature Science, Hokkaido University, Japan; <sup>2</sup>Université de Liège, Belgium; <sup>3</sup>Alfred Wegener Institute for Polar and Marine Research, Germany; <sup>4</sup>Université Libre de Bruxelles, Belgium; <sup>5</sup>University of Tasmania and Australian Antarctic Division, Australia; <sup>6</sup>Norwegian Polar Institute, Norway; <sup>7</sup>National Institute of Polar Research, Japan

In order to understand the effects of sea-ice growth and decay processes on the biogeochemical cycles in the polar oceans, field observations in the Arctic, Antarctic, and Sea of Okhotsk as well as laboratory experiments were carried out. Sea ice has until now rarely been considered in estimates of global biogeochemical cycles, especially gas exchanges, because of the assumption that, in ice-covered seas, sea-ice acts as a barrier for atmosphere–ocean exchange. However, recent work has shown that sea ice and its snow cover play an active role in the exchange of gases between the ocean and atmosphere. In this presentation, we provide first evidence from two Antarctic Winter-Spring cruises (AWECS and SIPEX-2) that snow laden Antarctic sea ice can act as a source of atmospheric CO<sub>2</sub> and bromoform during the cold season.

**14:45 Seasonal sea-ice coverage exerts strong controls on the Weddell Sea carbon cycle**

Dorothee Bakker<sup>1</sup>, M. Hoppema<sup>2</sup>, M. Schröder<sup>2</sup>, W. Geibert<sup>3</sup>, and H. de Baar<sup>4</sup>

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Circumpolar Deep Water, locally known as Warm Deep Water (WDW), enters the Weddell Gyre in the southeast. Upward movement and entrainment of WDW into the winter mixed layer strongly increases dissolved inorganic carbon (DIC) and the fugacity of carbon dioxide (fCO<sub>2</sub>) below the wintertime sea ice, notably in the southern Weddell Gyre. Apparently, the ice cover largely prevents outgassing of CO<sub>2</sub> to the atmosphere. During and upon melting of the sea ice, biological activity rapidly reduces surface water fCO<sub>2</sub>, thus creating a sink for atmospheric CO<sub>2</sub>. Despite the tendency of the surfacing WDW to cause CO<sub>2</sub> supersaturation, the Weddell Gyre may well be a CO<sub>2</sub> sink on an annual basis due to this effective mechanism involving ice cover and ensuing biological fCO<sub>2</sub> reduction. Dissolution of ikaite, a hydrated calcium carbonate (CaCO<sub>3</sub>·6H<sub>2</sub>O), in melting sea ice may play a minor role in this rapid reduction of surface water fCO<sub>2</sub>. These findings have been published in Bakker et al. (2008).

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#### 15:00      **Ecological impacts of changing ice concentrations in the coming century: the Ross Sea**

Walker Smith<sup>1</sup> and M. Dinniman<sup>2</sup>

<sup>1</sup>Virginia Institute for Marine Sciences, USA; <sup>2</sup>Center for Physical Oceanography, Old Dominion University, USA

The Ross Sea is presently undergoing rapid change, with increasing ice cover, reduced duration of ice-free periods, and significant freshening. However, global climate models predict that these recent changes in ice cover will soon reverse due to the increased atmospheric temperatures that are expected to develop. We present results of simulations of the oceanography of the Ross Sea in future years that may occur as a result of changes in atmospheric forcing (temperatures and winds). We found that changes in the following occurred: altered date of opening and closing of the Ross Sea Polynya; increased ice-free duration; reduced ice cover in summer; shallower mixed layers in spring, summer and autumn; reduced, albeit only slightly, inputs of Modified Circumpolar Deep Water (MCDW); greatly reduced formation of dense High Salinity Shelf Water (HSSW); and slightly enhanced melting of the Ross Ice Shelf. Potential biological changes that result from these physical alterations, especially those that occur in ice, will be discussed.

#### 15:25      **Coffee Break & Discussion at Posters**

#### 15:55      **Enrichment of long-lived chemical contaminants in Arctic sea-ice: observations, processes & impact**

Crispin Halsall<sup>1</sup>, O.R. Bertrand<sup>1</sup>, D. Herzke<sup>2</sup>, S. Huber<sup>2</sup>, P. Carlsson<sup>3</sup>, R. Kallenborn<sup>4</sup>, S. Del Vento<sup>1</sup> and M. Hermanson<sup>3</sup>

<sup>1</sup>Lancaster University, UK; <sup>2</sup>Norwegian Air Research Institute (NILU), Norway; <sup>3</sup>The University Centre in Svalbard (UNIS), Norway; <sup>4</sup>Norwegian University of Life Sciences (UMB), Norway

Since the International Polar Year there have been a number of field campaigns in the Canadian and European Arctic that have examined the occurrence and fate of persistent organic pollutants. The driver behind this work is that these chemicals have a tendency to bio-accumulate, so that trace levels present in air and water eventually result in very high concentrations in Arctic marine fauna. The role of snow and ice in chemical transfer processes within the Arctic is poorly understood with sea-ice generally considered as a 'seasonal lid' preventing air-water exchange of gas-phase chemicals transported into the Arctic. Our work, however, challenges this view. Using perfluoroalkyl acids as an example (a homologous group (C4-C12) of highly persistent industrial chemicals), we observed concentrations of these compounds in sea ice (of varying age) that greatly exceed concentrations in surface seawater by >10-fold in some cases, resulting in levels in ice that are akin to concentrations observed in

European coastal waters (e.g. low nmolar). This enrichment process is not fully resolved, but is likely to include chemical entrapment in the ice during ice formation, retention during brine formation/expulsion and ingress into the ice with percolating melt water following snowpack melt. Chemical concentrations generally follow the order of multi-year ice  $\geq$  first-year ice  $>$  fresh ice, although this is uncertain given the low number of multi-year ice samples in our survey. The implications of this ice-enrichment phenomenon, especially in a warmer Arctic dominated by single-year ice, is that beneath ice seawater and ice-associated organisms (at the base of the marine food web) are exposed to markedly higher concentrations at specific times of the year and implies that sea ice is an important reservoir of atmospherically-derived pollutants of this type.

**16:10            S2 Poster Introduction (Posters 16-20)**

**16:35            General Discussion on S1 & S2**

**17:30            Posters**

**18:30            Close**

## **Tuesday, 14 October 2014**

**9:00            Laboratory perspectives on ice as a reaction medium**  
Tara Kahan, Syracuse University, USA

Ice is a complex reaction medium, and our understanding of its physical and chemical interactions with atmospheric species remains poor. Laboratory studies have been (and continue to be) used to interrogate the physicochemical properties of environmental ices and to investigate air-ice interactions at the molecular level. The resulting knowledge is helping to shape our understanding of the environment that ice presents to atmospheric species. I will provide an overview of some recent advances in laboratory investigations of air-ice interactions, and will discuss some challenges and opportunities to better link laboratory, field, and modelling studies.

**9:25            Changes in the surface state of ice induced by trace gases**  
V. Faye McNeill, Columbia University, USA

I will present our recent laboratory results demonstrating changes in the ice surface state (e.g., quasi-liquid layer formation, surface film formation) induced by trace gases including HCl, HNO<sub>3</sub>, formaldehyde and acetaldehyde under environmentally relevant conditions. I will discuss implications for these processes in the modeling of AICI in the polar boundary layer, and transport of water vapor from the upper troposphere to the stratosphere.

**9:40            HO<sub>2</sub>NO<sub>2</sub> and HNO<sub>3</sub> in the coastal Antarctic winter night: A “lab-in-the-field” experiment**  
Anna Jones<sup>1</sup>, N. Brough<sup>1</sup>, P. S. Anderson<sup>2</sup>, and E. W. Wolff  
<sup>1</sup>British Antarctic Survey, UK; <sup>2</sup>Scottish Association of Marine Science, UK; <sup>3</sup>Cambridge University, UK

Observations of peroxyxynitric acid (HO<sub>2</sub>NO<sub>2</sub>) and nitric acid (HNO<sub>3</sub>) were made during a 4 month period of Antarctic winter darkness at the coastal Antarctic research station, Halley. Mixing ratios of HNO<sub>3</sub> ranged from instrumental detection limits to ~8 parts per trillion by volume (pptv), and of HO<sub>2</sub>NO<sub>2</sub> from detection limits to ~5 pptv; the average ratio of HNO<sub>3</sub>:HO<sub>2</sub>NO<sub>2</sub> was 2.0(±0.6):1, with HNO<sub>3</sub> always present at greater mixing ratios than HO<sub>2</sub>NO<sub>2</sub> during the winter darkness. An extremely strong association existed for the entire measurement

period between mixing ratios of the respective trace gases and temperature: for  $\text{HO}_2\text{NO}_2$ ,  $R^2 = 0.72$ , and for  $\text{HNO}_3$ ,  $R^2 = 0.70$ . We focus on three cases with considerable variation in temperature, where wind speeds were low and constant, such that, with the lack of photochemistry, changes in mixing ratio were likely to be driven by adsorption/desorption mechanisms alone. We derived enthalpies of adsorption ( $\Delta H_{\text{ads}}$ ) for these three cases. The average  $\Delta H_{\text{ads}}$  for  $\text{HNO}_3$  was  $-42 \pm 7 \text{ kJ mol}^{-1}$  and for  $\text{HO}_2\text{NO}_2$  was  $-56 \pm 3 \text{ kJ mol}^{-1}$ ; these values are extremely close to laboratory-derived values. This exercise demonstrates i) that adsorption to/desorption from the snow pack should be taken into account when addressing budgets of boundary layer  $\text{HO}_2\text{NO}_2$  and  $\text{HNO}_3$  at any snow-covered site, and ii) that Antarctic winter can be used as a natural “laboratory in the field” for testing data on physical exchange mechanisms.

## 9:55 **Can laboratory data explain field observations? - The fluxes of $\text{HNO}_3$ and $\text{HNO}_4$ from snow in the lab and in Antarctica**

Thorsten Bartels-Rausch<sup>1</sup> and M. Ammann<sup>1</sup>

<sup>1</sup>Paul Scherrer Institut, Villigen, Switzerland

Fluxes of trace gases between Polar snow packs and the boundary layer air are of importance because they significantly impact the composition and reactivity of the lower atmosphere and of the snow pack. They thus need to be understood to predict the oxidative capacity of the atmosphere on a regional scale and to interpret ice core data for reconstruction of past environmental conditions. A full understanding of observed fluxes is however complicated by the variety of underlying, elemental processes that may drive the fluxes synchronously: chemical reactions; diffusion in the gas, solid, or liquid phase; adsorption or desorption; or by uptake to the bulk ice.

In recent decades, some of these processes have been carefully investigated in laboratory-based experiments. Here, I will present our recent results on the partitioning of  $\text{HNO}_4$  between snow and air. These results are the first acquired at relevant low concentrations and show a significant lower tendency of  $\text{HNO}_4$  to stick to snow than previously thought. Fluxes of  $\text{HNO}_4$  in polar environments are not only of importance because  $\text{HNO}_4$  is a reservoir for  $\text{HO}_x$  and  $\text{NO}_x$ ; but also suspected to lead to interferences in HONO measurements.

A key question with this -and similar laboratory measurements- is, how well the description of physical processes derived under the idealized laboratory conditions can be applied to complex environmental settings. A data set published this summer on gas phase concentrations of  $\text{HNO}_4$  and of  $\text{HNO}_3$  in coastal Antarctica during winter gives the first and unique opportunity to show how well the agreement between laboratory and field investigation is. The authors of the field study have carefully selected specific days from their data set where photochemistry and ventilation by wind is absent. They hypothesise and show that only ad- and desorption from the snow can explain the observed gas-phase concentrations.

Here, I go a significant step further and support the author's conclusion by discussing the equilibrium partitioning of  $\text{HNO}_3$  and  $\text{HNO}_4$  that one would expect based on selected laboratory data. Both, adsorption to the surface of the snow and uptake to the bulk forming a solid solution are discussed ( $\text{HNO}_3$  only). Further, I address the question, if the snow holds enough  $\text{HNO}_3$  and  $\text{HNO}_4$  at its surface or in its bulk ( $\text{HNO}_3$  only) to fuel the observed emissions. Thus both equilibrium conditions and molecular flux budgets are discussed.

These calculations show that adsorption/desorption can indeed explain the observed mixing ratio in the Antarctic boundary layer. Release from a solid solution seems to be too slow.

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Interactive comment on “ $\text{HO}_2\text{NO}_2$  and  $\text{HNO}_3$  in the coastal Antarctic winter night: a “lab-in-the-field” experiment” by A. E. Jones et al. , T. Bartels-Rausch thorsten.bartels-rausch@psi.ch Received and published: 11 July 2014  
Legrand, M., Preunkert, S., Frey, M., Bartels-Rausch, T., Kukui, A., King, M. D., et al. (2014). Large

mixing ratios of atmospheric nitrous acid (HONO) at Concordia (East Antarctic plateau) in summer: a strong source from surface snow? *Atmospheric Chemistry and Physics Discussions*, 14(8), 11749, doi:10.5194/acpd-14-11749-2014

Ulrich, T., Ammann, M., Leutwyler, S., & Bartels-Rausch, T. (2012). The adsorption of peroxyntic acid on ice between 230 K and 253 K. *Atmospheric Chemistry and Physics*, 12(4), 1833, doi:10.5194/acp-12-1833-2012

## 10:10      **Molecular Modeling of the Air/Ice interface: overview and connections with experiments**

Céline Toubin, PhLAM Laboratory, UMR CNRS 8523, Université Lille, France

Ice and snow substrates, while long considered to be spectators in environmental chemistry, are now known to play important roles in a variety of atmospheric and interstellar chemical phenomena. Research related to ice chemistry in the Arctic and Antarctic boundary layers has accelerated in recent decades, motivated by observations of ozone depletion events.

Theoreticians have also followed this trend within the scope of bringing insights, at the molecular level, of the fundamental interactions governing the physics and chemistry of the interfacial processes.

For instance, one of the major issues limiting our understanding of snowpack chemistry is the lack of knowledge of the location within snow crystals/grains where reactants reside. This knowledge is fundamental to theoretical studies of snow and ice photochemistry as well as of reactions of trace compounds in snow and ice with atmospheric oxidants. Reactants can be adsorbed on the surface of an ice crystal, incorporated in the ice crystal lattice, trapped in/on deposited aerosol particles, at grain boundaries in the polycrystalline ice or in the snowpack interstitial air. In connection with this issue, numerous molecular studies have investigated the adsorption of various species, ranging from small molecules such as HF, HCl and CH<sub>2</sub>O, through e.g. acetone, acetaldehyde and alcohols to polycyclic aromatic hydrocarbons on ice surface.

One major challenge of molecular modeling studies is to compare with laboratory experiments and field measurements and thus, to provide physically justified input for the atmospheric models to advance our understanding of air quality issues and global climate change.

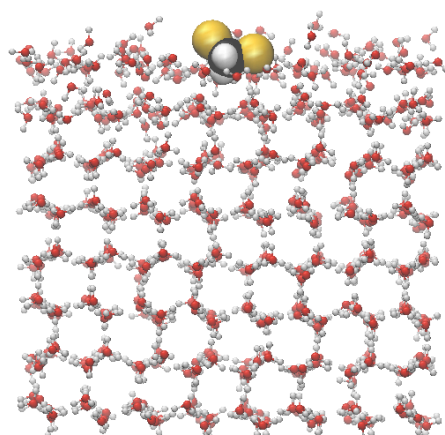


Figure 1. Snapshot issued from MD simulations of the adsorption of CH<sub>2</sub>Cl<sub>2</sub> on a hexagonal ice surface at T=235 K.

### References

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## 10:35      **Coffee Break & Discussion at Posters**



## The OPALE project in East Antarctica – new insights into oxidant chemistry above polar snow

Markus Frey<sup>1</sup>, M. Legrand<sup>2</sup>, S. Preunkert<sup>2</sup>, A. Kukui<sup>3</sup>, W. Vicars<sup>2</sup>, J. Savarino<sup>2</sup>, H. Gallée<sup>2</sup>, S. Bekki<sup>3</sup>, G. Ancellet<sup>3</sup>, J. Gil Roca<sup>3</sup>, J. Thomas<sup>4</sup>, B. Jourdain<sup>2</sup>, M. Kerbrat<sup>2</sup>, R. Loisil<sup>5</sup>, T. Bartels-Rausch<sup>6</sup>, J. France<sup>7</sup>, and M. King<sup>7</sup>

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The OPALE (Oxidant Production over Antarctic Land and its Export) project was launched in order to characterize the oxidative capacity of the atmosphere over East Antarctica and included measurement campaigns on the high plateau at Dome C (DC, 75.1°S 123.3°E) and on the coast at Dumont d'Urville (DDU, 66.7°S 140.0°E). The East Antarctic plateau is a region where processes are suspected to differ from those already identified at the South Pole, in particular those related to the recycling of reactive nitrogen between air and surface snow. A major difference is that Plateau regions North of South Pole experience strong diurnal variability in solar irradiance and temperature. Coastal sites such as DDU exposed to frequent katabatic outflow from the Plateau regions will also have a different atmospheric oxidative capacity than elsewhere, important for the interpretation of year-round observations in a region where large oceanic DMS emissions take place. OPALE measurements included OH, RO<sub>2</sub>, NO<sub>x</sub> (not at DDU), HONO, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, CH<sub>3</sub>OOH, and CH<sub>2</sub>O. Here I will present an overview of some of the main results

A major finding of the first OPALE season at DDU in January 2011 were the highest hydroxyl radical concentrations ever seen on the Antarctic coast with 24 h means of  $2 \times 10^6$  and  $3 \times 10^8$  molecule cm<sup>-3</sup> for OH and RO<sub>2</sub>, respectively. The large radical concentrations observed cannot be simply explained by the relatively high ozone mixing ratios occurring at this site due to efficient transport of air masses from the Antarctic Plateau. Steady state calculations suggest a RO<sub>2</sub> to OH conversion mechanism equivalent to 30 pptv of NO to explain observed HO<sub>x</sub> concentrations. Such rather high NO levels were confirmed by NO<sub>2</sub> measurements made in January 2012.

The second OPALE season took place at Dome C during December 2011- January 2012, and also included extensive observations of boundary layer physics to better understand the mixing behaviour of the chemical species measured. Median OH and RO<sub>2</sub> radicals were  $3 \times 10^6$  and  $9.9 \times 10^7$  molecule cm<sup>-3</sup>, respectively. These values are comparable to those observed previously at South Pole, showing that the elevated oxidative capacity of the atmospheric boundary layer is not restricted to South Pole but common on the Antarctic Plateau. The primary source of OH and RO<sub>2</sub> radicals at Dome C was found to be the photolysis of HONO (75%), followed CH<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. Other factors leading to large radical concentrations were elevated NO mixing ratios and fast recycling of RO<sub>2</sub> to OH.

HONO mixing ratios measured for the first time in Antarctica by using the long path absorption photometer (LOPAP) technique were on average 30 pptv, suggesting that in addition to weak production by NO + OH a local source must exist. Lab experiments using snow samples from Dome C demonstrate production of gas phase HONO about half that of NO<sub>x</sub> at Dome C temperatures. However, the snow emission flux of HONO based on the lab and field data can only account for about a third of the HONO mixing ratios observed at Dome C. Further tests were done both in the field and in the lab to explore the possibility that the presence of HNO<sub>4</sub> had biased the measurements.

Concentration profiles of NO<sub>x</sub> of the lower 100 m of the atmosphere confirm that, in contrast to South Pole, air chemistry at Dome C or sites at similar latitude on the Antarctic Plateau is dominated by strong diurnal cycles, both in down-welling solar radiation and atmospheric stability. Unusually large mixing ratios of NO<sub>x</sub> and significant variability in December 2011 are attributed to a combination of changes in mixing height and a significant increase in the snow emission flux of NO<sub>x</sub>. The latter is primarily driven by large concentrations of nitrate present in surface snow, and only to a secondary order by changes in column ozone and associated increase in nitrate photolysis rates. First time observations of BrO at Dom C suggest 2-3 pptv

near the ground, with higher levels in the free troposphere similar to Halley. The large NO<sub>2</sub>:NO ratios observed in ambient air are not consistent with measurements of peroxy and halogen radicals assuming steady state. The possibility of an interference by the presence of HNO<sub>4</sub> is explored.

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## 11:30 S3 Poster Introduction (Posters 21-30)

## 12:20 General Discussion on S3

## 13:00 Lunch

## 14:00 Controls of snow metamorphism and diffusion on chemical air-ice-snow interactions

Henning Löwe, WSL Institute for Snow and Avalanche Research SLF, Davos, Switzerland

In macroscopic transport models for chemical species, snow is often assumed to be a porous material with an invariant microstructure. From a naive snow physics perspective this is indeed a wrong assumption. In particular near the surface, where the gas exchange with the atmosphere occurs, prevailing temperature gradients give rise to a highly dynamic morphology with a rapidly evolving ice surface, leading to a reconstruction of the entire ice matrix. These morphological changes are commonly subsumed under the label snow metamorphism. Snow metamorphism is mediated by vapor transport, which principally contains all the relevant ingredients for the transport and uptake of any chemical species: i) desorption of molecules driven by local non-equilibrium conditions, ii) diffusion through the pore space along concentration gradients iii) advection under the influence of near-surface wind pumping iv) adsorption on remote parts of the ice matrix. The upscaling of these microscopic processes eventually leads to measurable macroscopic transport quantities, either for vapor or for other chemical species. We review the recent progress in snow metamorphism from the view point of vapor transport and related morphological changes which can be monitored by X-ray tomography. We present recent examples of laboratory-based, in-situ experiments in view of relevant time scales and speculate about the impact on the transport of other chemical species, which occurs concurrently with snow metamorphism.

## 14:25 Impurities Location, Speciation and Spectroscopy in Artificial Snow and Frozen Aqueous Solutions

Dominik Heger<sup>1</sup>, J. Krausko<sup>1</sup>, L. Krausková<sup>1</sup>, P. Klán<sup>1</sup> and J. Runštuk<sup>2</sup>

<sup>1</sup>RECETOX / Department of Chemistry, Faculty of Science, Masaryk University, Kamenice 5, 62500 Brno, Czech Republic; <sup>2</sup>Vilém Neděla / Institute of Scientific Instruments of the ASCR, Czech Republic

In our laboratory studies, we have utilized various model molecular probes for speciation, location and spectroscopic analyses in artificial snow and frozen aqueous solutions. [1] The location of the chemical impurities, such as uranyl cation, was assessed by environmental

scanning electron microscope at the temperatures above 250 K and pressures below 700 Pa, that is at nearly environmentally relevant conditions never reported before. Our study thus allowed us to obtain micrographs of a brine layer on ice for the first time. Regardless of the preparation method (slow freezing or nebulization into liquid nitrogen to produce artificial snow), the impurities were found in the brine layer wetting the ice grains. Slow freezing (at 267 K) resulted in a substantial increase in acidity of the brine, whereas flash freezing (at 77 K) lead to a smaller pH increase. [2] An inhomogeneous distribution of the probe molecules within the ice sample was revealed by the fluorescence lifetime measurement. The sign and amplitude of the measured freezing potential [3], created by freezing of aqueous ionic solutions (NaCl, KCl, sea water), were correlated with a resultant pH change determined spectrophotometrically. [2] The spectroscopy of benzene and (methyl)naphthalene in/on ice will also be discussed. [4, 5]

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#### **14:40            Calculating photochemical production rate in sea ice: sea ice tank studies at RHUL**

Martin King, Royal Holloway University of London, UK

The optical properties of snow packs and sea ice effect the rate of photochemical reactions within the snow and sea ice (they also effect the reflectivity which is important for modern climate change and the remote sensing of snow and sea ice from space). Photochemical reactions within snow can produce radicals and fluxes of gases from these snowpacks. The production of radicals within sea ice is also facile and the sea ice matrix is predisposed to halogen chemistry owing to the concentration of brine within the sea ice matrix. The optical properties and photolysis of chemicals within snowpacks can be predicted, however the optical properties of sea ice are less well known and much more complex. The new sea ice simulator at RHUL is two, 2 tonne, tanks of sea water that can be frozen to generate 30-80cm of realistic pack ice. The nadir reflectivity and the Bidirectional reflectance of the sea ice has been measured and reproduced with radiative transfer modelling, validating the radiative transfer calculations and allowing the production rate of photochemical reactions in sea ice to be calculated. Experiments have also been performed where the optical properties of the sea ice have been altered with the addition of black carbon and humic materials.

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#### **15:05            A novel sea-ice - snow chamber for polar research and linked modeling Activities**

Roland von Glasow, University of East Anglia, UK

A new sea ice/snow chamber is currently being developed at the University of East Anglia. This chamber is part of a project recently funded by the European Research Council with the

overriding aim of improving our quantitative understanding of the links between the Arctic atmosphere, snow, sea ice and the Arctic ocean. This chamber will be located in an environmental chamber with a minimum temperature of -40 °C, possible even -55 °C. The initial focus will be on investigating the physical and chemical properties of sea ice in various stages (freezing, melting, with and without wave action) with a focus on gas exchange through sea ice and emissions of reactive compounds from the sea ice to the atmosphere. In a next step snow photochemistry will be studied. The chamber will be constructed such that it can be used as a so-called smog chamber with tight control of its physical and chemical composition. The chamber work will be closely linked with numerical modeling on the scale of the chamber to the globe using a hierarchy of a 1D model, a regional 3D model and a global 3D model to investigate sea ice-snow-atmosphere-climate links on all relevant scales but with varying complexity. External partners are welcome to participate in experiments in this chamber. This presentation will outline the current progress and future plans and ways to get engaged in this project.

**15:30            Coffee Break & Discussion at Posters**

**16:00            Compilation and evaluation of gas-phase diffusion coefficients of inorganic reactive trace gases in the atmosphere**

Mingjin Tang, University of Cambridge, UK

Diffusion of gas molecules to the surface is the first step for all gas-surface reactions. Gas phase diffusion can influence and sometimes even limit the overall rates of these reactions; however, there is no database of the gas phase diffusion coefficients of atmospheric reactive trace gases. We have compiled and evaluated, for the first time, the diffusivities (pressure-independent diffusion coefficients) of atmospheric inorganic reactive trace gases reported in the literature (Tang et al., 2014). The measured diffusivities are then compared with estimated values using a semi-empirical method developed by Fuller et al. (1966). The diffusivities estimated using Fuller's method are typically found to be in good agreement with the measured values within  $\pm 30\%$ , and therefore Fuller's method can be used to estimate the diffusivities of trace gases for which experimental data are not available. The two experimental methods used in the atmospheric chemistry community to measure the gas phase diffusion coefficients are also discussed.

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**16:15            S4 Poster Introduction (Posters 31-35)**

**16:40            Successful large grant applications in the Arctic**

Jeremy Wilkinson, British Antarctic Survey, UK

The Arctic system is in a state of accelerated flux, and it has been clearly shown that Arctic change impacts the local, regional and global climate through complex coupling mechanisms within the Earth system. However these are not the only changes the Arctic is going through. It is predicted that commercial investment in the Arctic could reach \$100bn or more in the coming decade, with oil and gas, mining and the shipping industries being the biggest drivers. The environmental, socio-economic and geopolitical consequences of Arctic change will be considerable.

However the issues associated with Arctic change transcend national boundaries, only a few nations have Arctic sovereignty and all nations lack the combination of expertise, knowledge, logistical capability and budget to independently tackle these challenges; a truly international and integrated effort is needed. We present the benefits of an international, multi-sectorial approach to Arctic science through the example of three recent programmes: ACCESS, ICE-

**17:00            General Discussion on S3 & S4**

**17:45            Posters**

**18:45            Close**

## **Wednesday, 15 October 2014**

**9:00            The Oden as a platform for a winter cruise into the Sea Ice Zone in Antarctica**

Katarina Abrahamson, University of Gothenborg, Sweden

**9:10            AICI-type opportunities at the CASLab, Halley, in coastal Antarctica**

Neil Brough, British Antarctic Survey, UK

The Clean Air Sector Laboratory (CASLab) at Halley station is a specialist facility designed for studies of the clean, background atmosphere, and processes affecting polar atmospheric composition. With its location in coastal Antarctica, the CASLab is exposed to air masses with a variety of origins, including from the sea ice zone, the Southern Ocean, and from over the snowpack. Atmospheric composition at Halley is a strong function of wind direction, and thus air mass history. Solar irradiance varies considerably at Halley throughout the year, with 3 months of continual daylight during the summer months, and 3 months of continual darkness during the winter. These extremes offer opportunities to study AICI processes driven by physical mechanisms alone, or dominated by photochemistry. Halley is a GAW Global station, and measurements at the CASLab contribute both to long-term composition assessments as well as process studies. Here we introduce the CASLab, together with examples of measurements from previous campaigns, in order to demonstrate AICI-type opportunities presented by the CASLab.



### **References:**

[http://www.antarctica.ac.uk/bas\\_research/support/labs/caslab/index.php](http://www.antarctica.ac.uk/bas_research/support/labs/caslab/index.php)

<http://www.atmos-chem-phys.net/8/3789/2008/acp-8-3789-2008.pdf>

**9:20            Field Research opportunities at the Belgian Princess Elisabeth Station, Sør Rondane Mountains-Princess Ragnhild Coast, East Antarctica**

Jean-Louis Tison, Université Libre de Bruxelles, Belgium

Built in the framework of the International Polar year (IPY, 2008-2009), the new Belgian station “Princess Elisabeth” was inaugurated on February 15th 2009, some 40 years after the abandon of the former Belgian Antarctic station “Base Roi Baudouin”, located on an ice shelf near Breid Bay, less than 200 km North of the new station. Princess Elisabeth Station is a unique project in the Antarctic landscape, since it was built in a collaborative effort between the private world and the Federal State of Belgium, with a deliberate ambition to build a Base 100% fuelled on



recyclable energy (solar and wind turbines). The whole concept came to life under the pro-active leadership of Mr. Alain Hubert, a well-known Belgian polar explorer. The activity at the base is supervised by the “Secrétariat Polaire”, which is a balanced mixed Federal State-Private entity. The International Polar Foundation (IPF) founded by Alain Hubert, has led the construction of the base and is now hired by the federal State of Belgium as the logistic entity responsible for the running of the Base. BELSPO, the Belgian Science Policy Office, is responsible for the scientific programs run at the Princess Elisabeth Station. The structure is still in its “infancy”, so that official recurrent “Calls for projects”, involving international collaborations, are not yet finalized. There are however already opportunities for collaborative work with the Belgian teams involved in the first scientific programs initiated at the base.

This short presentation will introduce the audience to Princess Elisabeth Station, its “modus operandi”, and the science opportunities it provides. It will also briefly summarize the scientific projects already active at the Base and their first evaluation.

**9:30 FAAM's aircraft Arctic capability: airborne measurements over the SIZ around Svalbard during the ACCACIA 2013 project**

Stephane Bauguitte<sup>1</sup>, A. Wellpott<sup>1</sup>, J.D. Lee<sup>2</sup>, and I.M. Brooks<sup>3</sup>

<sup>1</sup>Facility for Airborne Atmospheric Measurements (FAAM), UK; <sup>2</sup>University of York, York, UK; <sup>3</sup>University of Leeds, Leeds, UK

The UK Natural Environment Research Council (NERC) recently upgraded the high latitude navigational capability of its flagship BAe146 large atmospheric research aircraft. This short talk will introduce the Facility for Airborne Atmospheric Measurements (FAAM) scientific payload, focussing on aerosol and gas-phase instrumentation relevant to the air-snow-sea ice system. We illustrate measurement opportunities during marine boundary layer trace gas sampling over the sea ice zone around Svalbard, when the FAAM aircraft operated from Longyearbyen during the ACCACIA (Aerosol-Cloud Coupling And Climate Interactions in the Arctic) 2013 project. Near-zero ozone mixing ratios were encountered during several missions, corroborating other ozone depletion events sampled onboard the Norwegian Polar Institute's RV Lance over the nearby Greenland Sea.

**9:40 US polar field platforms & science perspectives (GEO Summit, NOAA, NSF)**

Jack Dibb, William Neff, Walker Smith

**10:00 AICI/OASIS/Future Earth**

Faye McNeill

**10:10 European funding opportunities for Climate Change research**

Lucy Gonzalez Pacheco Sosa, British Antarctic Survey, UK

Horizon 2020 is the biggest EU Research and Innovation program ever, with 79 billion euros of funding available over 7 years (2014 to 2020). Almost 30% of the budget is directed at issues related to Climate Change, and there are numerous opportunities for individuals and organizations of all sizes. In this talk you will hear about the salient aspects of the program, learn about where and how to find relevant calls for you and your research, and have a chance to work through a call to get a taste of what writing a proposal is like. Questions and discussion are encouraged.

**10:30 Coffee Break & Discussion at Posters**

**11:00 General Discussion – What are our research priorities & how do we get**

**them funded? (I)**

**13:00 Lunch & Removal of posters**

**14:00 General Discussion – What are our research priorities & how do we get them funded? (II) – Wrap up**

**15:30 Close**

**Notes**

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## CASSII WORKSHOP 13-15 OCT - POSTER PROGRAMME (Graham Storey Rm, Trinity Hall)

ID S1: Impacts of Chemical Atmosphere-Snow-Sea Ice interactions		
1	X. Zhao	<i>A Transported Bromine Explosion Event in the Canadian High Arctic</i>
2	A. Saiz-Lopez	<i>Polar sea-ice emissions and sea-salt aerosol recycling of bromine in a global chemistry-climate model</i>
3	P. Griffiths	<i>Sources of reactive bromine in polar regions and its implications for ozone in the troposphere</i>
4	M. Frey	<i>On the significance of blowing snow above sea ice as a source of polar sea salt aerosol</i>
5	X. Yang	<i>Refining the parameterisation of sea salt aerosol production from blowing snow on sea ice based on data collected in the Weddell Sea</i>
6	N. Maffezzoli	<i>Halogens in ice cores as sea ice proxies</i>
7	H. Hartman Jenkins	<i>Drivers of sea salt variability measured in ice cores: a model study</i>
8	H. A. Kjaer	<i>What can be learnt about past Sea Ice extent from the Roosevelt Island Ice core?</i>
9	K. Pratt	<i>Arctic Atmospheric Particle Chemistry and Influences on Snow Chemistry</i>
10	J. Thomas	<i>Local pollution influences in the Arctic - perspectives from the ACCESS aircraft campaign and opportunities for future research</i>
11	J. Dibb	<i>The preservation of long-range transported nitrate in snow at Summit, Greenland</i>
12	M. Zatzko	<i>Snow Nitrate Photochemistry in the Uintah Basin, Utah</i>
13	C. Halsall	<i>The deposition and fate of perfluoroalkyl substances (PFAS) in the seasonal snowpack: implications for spring runoff</i>
14	H. A. Kjaer	<i>The Ice2Ice project: Does Arctic and sub-Arctic sea ice cover exert important controls on past and future Greenland temperature and ice sheet variations?</i>
15	G. Lloyd	<i>The Origin of Ice in Arctic Boundary Layer Clouds</i>
S2: Biogeochemistry of the air-snow-sea ice-ocean system		
16	E. Jones	<i>Rapid Changes in Surface Water CO<sub>2</sub> and Carbonate Chemistry During Antarctic Sea Ice Melt</i>
17	O. Legge	<i>The seasonal cycle of inorganic carbon in the seasonally sea-ice covered water of Ryder Bay, West Antarctic Peninsula</i>

18	B. DeLille	<i>How snow affects air-sea ice CO<sub>2</sub> fluxes ?</i>
19	G. Krysztofiak	<i>Bromoform and inorganic bromine in a global chemistry climate model</i>
20	R. Humphries	<i>Model examination of new Antarctic sea-ice, DMS derived, aerosol to the Southern Ocean region</i>
<b>S3: Air-snow exchange processes – closing the gap between Field, Lab and Models</b>		
21	W. Neff	<i>Boundary Layer and Temperature Effects on NO Concentrations at the South Pole</i>
22	S. Rohekar	<i>Estimating NO<sub>x</sub> fluxes from snow-packs at Halley, Antarctica</i>
23	M. Björkman	<i>Nitrate post-depositional processes in Svalbard coastal surface snow</i>
24	H. G. Chan	<i>The impact of parameterising light penetration into snowpack on the photochemical production of nitrogen oxide and OH radicals</i>
25	M. Zatko	<i>Incorporation of snow nitrate photochemistry into a global chemical transport model: Impact on boundary layer chemistry and ice core records in Antarctica</i>
26	K. Kim	<i>The enhanced iodide oxidation in frozen environment and the following release of gaseous iodine molecules (I<sub>2</sub>) to the atmosphere</i>
27	K. Kim	<i>Accelerated dissolution of iron oxides in ice media and its environmental effects</i>
28	T. Roberts	<i>Re-evaluating the reactive uptake of HOBr in the troposphere</i>
29	M. Roeselova	<i>Haloalkanes at the air - water and air - ice interfaces: A molecular picture</i>
30	A. Yadghar	<i>Air snow exchange modeling in elevated watersheds</i>
<b>S4: New strategies – Developing optimal probes and systems for AICI lab, field &amp; model studies</b>		
31	T. Häusler	<i>Investigation of Microcrystalline Cellulose as Ice Nucleus in Immersion Freezing Processes</i>
32	A. Waldner	<i>Acidic trace gas adsorption on ice: XPS and NEXAFS analysis with the new NAPP solid chamber at SLS</i>
33	R. Zellner	<i>Model simulations for gas adsorption on ice surfaces with combined ice bulk diffusion around 200 K</i>
34	A. Benton	<i>Multi-component Continuous Flow Analysis of ice cores: a tool for understanding changes to the chemical composition of the atmosphere</i>
35	X. Kong	<i>Development of a New Generation of Environmental Molecular Beam method</i>

# Poster Programme

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**P01      A Transported Bromine Explosion Event in the Canadian High Arctic**  
Xiaoyi Zhao<sup>1</sup>, K. Strong<sup>1</sup>, C. Adams<sup>1,2</sup>, X. Yang<sup>3</sup>, U. Friess<sup>4</sup>, R. Schofield<sup>5</sup>, A. Richter<sup>6</sup>, and A. Blechschmidt<sup>6</sup>

<sup>1</sup>University of Toronto, Canada; <sup>2</sup>now at: University of Saskatchewan, Canada; <sup>3</sup>British Antarctic Survey, UK; <sup>4</sup>University Heidelberg, Germany; <sup>5</sup>University of Melbourne, Australia; <sup>6</sup>University of Bremen, Germany

Ozone depletion events in the polar troposphere have been linked to extremely high concentrations of bromine, known as bromine explosion events. On April 4-5, 2011, we observed such an event in the Canadian High Arctic at the Polar Environment Atmospheric Research Laboratory (PEARL, 86.4°W, 80.1°N), with measurements made by a UV-visible spectrometer showing that the surface volume mixing ratio of BrO increased from ~1 to ~20 pptv. Ozone, measured by ozone sondes, was depleted to ~1 ppbv from the surface to 720 m during this event. Zenith Scattered Light Differential Optical Absorption Spectroscopy (ZSL-DOAS) and Multi-Axis DOAS (MAX-DOAS) data have been used to retrieve stratospheric and tropospheric BrO profiles and partial columns. GOME-2 tropospheric columns of BrO have been used to complement the ground-based measurements.

The HYSPLIT back-trajectory model and GOME-2 data confirmed that this event originated over the Beaufort Sea on March 31, 2011. The interim reanalysis meteorological data from the European Centre for Medium-Range Weather Forecasts (ECMWF), indicates that the 10-m wind increased from 5 to 24 m/s and the boundary layer height surged from 180 to 610 m over Beaufort Sea during the bromine explosion event, suggesting that it was generated from unstable boundary layer meteorological conditions. Further evidences show this long distance (over ~1,800 km) transport event lasted for more than four days, which indicates a strong recycling of BrO within the bromine cloud. The observed bromine explosion event was captured by the UMUKCA chemistry-climate model, which calculated a surface bromine surge to ~10 pptv and surface ozone depletion to ~1 ppbv at PEARL. Comparisons between the measurements and model show that the bromine depletion factor used in the blowing snow bromine release mechanism requires further investigation.

**P02      Polar sea-ice emissions and sea-salt aerosol recycling of bromine in a global chemistry-climate model**

Alfonso Saiz-Lopez<sup>1</sup>, R. Fernandez<sup>1</sup>, C. Ordoñez<sup>2</sup>, D. Kinnison<sup>3</sup>, and J.-F. Lamarque<sup>3</sup>

<sup>1</sup>CSIC, Madrid, Spain; <sup>2</sup>Met Office, Reading, UK; <sup>3</sup>National Center for Atmospheric Research (NCAR), USA

A halogen polar module has been coupled to the CAM-Chem chemistry climate model, including the following processes:

- An inorganic bromine source from sea-ice, with a twofold dependence on both solar zenith angle and local sea-ice cover.
- A sea-salt recycling scheme including the uptake of halogen species on sea-salt aerosols.

Results show that the BrO total columns are in agreement with BrO VCDs measurements from GOME2 and SCIAMACHY. This communication will also explore the modelled vertical distribution of bromine arising from the described parametrization.

**P03      Sources of reactive bromine in polar regions and its implications for ozone in the troposphere**

Paul T. Griffiths<sup>1</sup>, A. T. Archibald<sup>1</sup>, X. Yang<sup>2</sup> and J.A. Pyle<sup>1</sup>

<sup>1</sup>Cambridge University, UK; <sup>2</sup>British Antarctic Survey, UK

In the last two decades, significant depletion of boundary layer ozone (ozone depletion events,



ODEs) has been observed in both Arctic and Antarctic spring. ODEs are attributed to catalytic destruction by bromine radicals (Br plus BrO), especially during bromine explosion events (BEs), when high concentrations of BrO periodically occur. The source of bromine and the mechanism that sustains the high BrO levels are still the subject of study. Recent work by Pratt et al. (2013) posits Br<sub>2</sub> production within saline snow and sea ice, which leads to sudden ODEs. Alternatively, sea salt aerosol could act as a source of bromine via acid displacement.

The aerosol loading over Antarctica shows a seasonal cycle, which has a maximum in winter at many coastal sites [Wagenbach et al., 1998], which is surprising given the fact that the nearest open water is often hundreds of km more distant in that season because of the extension of sea ice. More generally, studies over the last decade have generally concurred that a large proportion of sea salt aerosol in the atmosphere over the Antarctic continent and the surrounding sea ice zone, and in the Antarctic ice sheet, derives ultimately from the sea ice surface.

In light of these facts, Yang et al. (2008) suggested snow could provide a source of (depleted) sea-salt aerosol if wicked from the surface of ice. They suggest that rapid depletion of bromide via acid displacement from the aerosol will constitute a source of photochemical Br<sub>y</sub>. Given the large sea ice extent in polar regions, this may constitute a significant source of gas phase bromine in the polar lower atmosphere. While bromine release from blowing snow is perhaps less likely to trigger sudden ODEs, it may make a contribution to regional scale processes affecting ozone levels.

Currently, the model parameterization of Yang et al. assumes that rapid release of bromine occurs from fresh snow on sea ice during periods of strong wind. The parameterization depends on an assumed sea-salt aerosol distribution generated via sublimation of the snow above the boundary layer, as well as taking into account the salinity of the snow.

In this poster, we consider the production of bromine from sea-salt aerosol from a mixture of snow and sea ice during periods of strong wind. We present results from the recent reimplementation of Yang's blowing snow mechanism as a component of the UK Met Office Unified Model, in the United Kingdom Chemistry and Aerosols model UM-UKCA) and its deployment on the UK supercomputer facility, HECToR.

We present results from a combination of box models and the UM-UKCA to quantify the effect of bromine release in the boundary layer and its effect on ozone at the regional scale. This work is performed as part of the NERC-funded BLOWSEA project which in later stages will draw on new data from the recent Polarstern cruise by members of the British Antarctic Survey.

#### References:

- [1] Yang, X., et al. (2008), Sea salt aerosol production and bromine release: Role of snow on sea ice, *Geophys. Res. Lett.*, 35(16), L16815, DOI:10.1029/2008gl034536.
- [2] Wagenbach, D., et al. (1998), Sea salt aerosol in coastal Antarctic regions, *J. Geophys. Res.*, 103 (D9), 10961-10974
- [3] Pratt, K., et al. (2013), Photochemical production of molecular bromine in Arctic surface snowpacks, *Nature Geoscience*, 2013, DOI:10.1038/NGEO1779

#### **P04                    On the significance of blowing snow above sea ice as a source of polar sea salt aerosol**

Markus Frey<sup>1</sup>, P. S. Anderson<sup>2</sup>, I.M. Brooks<sup>3</sup>, K. Nishimura<sup>4</sup>, A.E. Jones<sup>1</sup>, and E. W. Wolff<sup>5</sup>

<sup>1</sup>British Antarctic Survey, UK; <sup>2</sup>Scottish Association for Marine Science, UK; <sup>3</sup>University of Leeds, UK; <sup>4</sup>Nagoya University, Japan; <sup>5</sup>University of Cambridge, UK

The sublimation of saline blowing snow above sea ice has recently been suggested to generate more sea salt aerosol (SSA) than is produced from a similar area of open ocean. SSA influence climate, both directly and indirectly, and can impact the lifetime of methane, ozone or mercury through the photochemical release of reactive halogens. Furthermore, knowing the origin of SSA measured in ice cores will help to develop a quantitative proxy of past sea ice extent. A winter cruise of the German research vessel 'Polarstern' through the Weddell Sea in June-August 2013 provided unique access to a potential source region of SSA in the Antarctic sea ice zone during a time of year when it is thought to be most active. Reported are measurements of snow particle as well as aerosol concentrations and size distributions during blowing snow events above the sea ice. We show for the first time evidence of significant SSA production

during and after blowing snow events. The aerosol flux is discussed with respect to observed snow salinities as well as atmospheric conditions and compared to the open ocean source.

**P05            Refining the parameterisation of sea salt aerosol production from blowing snow on sea ice based on data collected in the Weddell Sea**

Xin Yang<sup>1</sup>, M.M. Frey<sup>1</sup>, J.G. Levine<sup>2</sup>, I.M. Brooks<sup>3</sup>, P.A. Anderson<sup>4</sup>, A.E. Jones<sup>1</sup>, and E.W. Wolff<sup>5</sup>

<sup>1</sup>British Antarctic Survey, UK; <sup>2</sup>University of Birmingham, UK; <sup>3</sup>University of Leeds, UK; <sup>4</sup>Scottish Association for Marine Science, UK; <sup>5</sup>University of Cambridge, UK

The hypothesis of blowing snow lifted snow particles, via a subsequent sublimation process, as a significant sea salt aerosol (SSA) source over sea ice has recently been strongly supported by a winter cruise through the Weddell Sea during June-August 2013. The newly collected data, including both physical and chemical components, provide a unique way to test and validate the parameterisation used to date.

The observed salinity of surface and blowing snow is very low; on average more than an order in magnitude smaller than column mean value. Here we apply a low salinity of 0.27 PSU (representing an average of the top 10cm of snow plus blowing snow samples) in the p-TOMCAT model to test its effect on sea salt concentrations reaching the Antarctic. The comparison with previous model output (using column mean salinity) shows that SSA concentration in central Antarctica is insensitive to change in snow salinity, due to the compensating effect of increasing fine SSA partitioning upon reducing the salinity. We also investigate the impact of changing the number of SSA particles formed from each snow particle on SSA concentration and size distribution. Applying a ratio of 10 SSA particles per blowing snow particle, rather than one as assumed to date, greatly increases the amount of sub-micrometer SSA reaching central Antarctica. Without applying blowing snow related SSA production in the p-TOMCAT model, the observed elevated SSA in the Weddell Sea could not be reproduced.

**P06            Halogens in ice cores as sea ice proxies**

Niccolò Maffezzoli<sup>1</sup>, and P. Vallelonga<sup>1</sup>

<sup>1</sup>Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Denmark

The halogen elements Bromine (Br) and Iodine (I) show great promise as proxies of polar sea ice extent. Bromine is emitted as bromide ions in sea-salt aerosol from the seawater surface and is actively involved in polar ozone destruction chemistry, due to auto-catalyzed reactions with ozone called “Bromine explosions”, which occur above seasonal sea ice. Iodine has also been linked to sea ice variability: it is produced by algal colonies residing on the underside of sea ice, which is subsequently percolated up to the sea ice surface and emitted to the polar atmosphere. I will present an outline of my PhD project, which started in September 2014. I plan to develop techniques for the measurement of established sea ice proxies (Sodium and MSA) as well as potential ones (Bromine and Iodine) in polar ice cores. Analyses of Bromine and Iodine will be conducted in collaboration with the University of Venice. The project will take advantage of a number of recently drilled or planned ice core projects, including Renland (East Greenland) and Aurora Basin (East Antarctica). Other polar ice cores may be studied according to availability and relevance to the project goals.

**P07            Drivers of sea salt variability measured in ice cores: a model study**

Hazel Hartman Jenkins, Cambridge University, UK

Salt aerosols are produced by snow on sea ice; we model atmospheric concentrations of salts using this newly-discovered mechanism. Concentrations over Antarctica are affected by both sea-ice extent and winds, according to our model (p-TOMCAT). The winds transporting salt poleward are a major source of interannual variability. Wind-caused variation in aerosol production is less important. We model that some ice core sites receive salt from a broad area of

ocean, while other core sites reflect a much narrower area; unsurprisingly, sites generally receive more salt from nearby latitudes and from the west. Since this broad pattern seems likely to hold even in quite different climates, coring sites could be chosen to tell us about past sea-ice extent in specific areas.

**P08                    What can be learnt about past Sea Ice extent from the Roosevelt Island Ice core?**

Helle Astrid Kjaer<sup>1</sup>, P. Vallelonga<sup>1</sup>, M. Simonsen<sup>1</sup>, P. Neff<sup>2</sup>, N. Bertler<sup>2</sup>, and A. Svensson<sup>1</sup>

<sup>1</sup>Centre for Ice and Climate, Niels Bohr Institute, University of Copenhagen, Denmark;

<sup>2</sup>Antarctic Research Centre, Victoria University of Wellington, New Zealand,

The Roosevelt Island ice core (79.36°S, 161.71°W) was drilled in 2011-13 at the top of the Roosevelt Island ice dome, a location surrounded by the Ross ice shelf. The RICE ice core provides a unique opportunity to look into the past evolution of sea ice in the area of West Antarctica. Further the site has high accumulation; 0.26 m of ice equivalent is deposited annually allowing sub-annual layer determination for many chemical parameters. The RICE core was drilled to bedrock and has a total length of 763 m. Preliminary results derived from water isotopes suggest that the oldest ice reaches back to the Eemian, with the last glacial being compressed in the bottom 60 m. The core was analyzed at the New Zealand National Ice Core Research Facility at GNS Science in Wellington.

We present preliminary results from the RICE ice core including continuous measurements of acidity using an optical dye method, insoluble dust particles, conductivity and calcium. The analytical set up used to determine climate proxies in the ice core was a modified version of the Copenhagen CFA system (Bigler et al., 2011). Key volcanic layers have been matched to those from the WAIS record (Sigl et al., 2013) with success. A significant anti-correlation between the continuous record of acidity and calcium was seen in the Holocene part of the record. Due to the proximity to the ocean a large fraction of the calcium originates from sea salt and is in phase with total conductivity and sodium. In combination with the insoluble dust record, calcium has been apportioned into ocean-related and dust-related sources. Variability over the Holocene is presented and attributed to changing inputs of marine and dust aerosols.

**P09                    Arctic atmospheric particle chemistry and influences on snow chemistry**

Kerri Pratt<sup>1</sup>, R. Kirpes<sup>1</sup>, A. Bondy<sup>1</sup>, M. Weber<sup>1</sup>, N. May<sup>1</sup>, A. Laskin<sup>2</sup>, and A. Ault<sup>1</sup>

<sup>1</sup>University of Michigan, USA; <sup>2</sup>Pacific Northwest National Laboratory, USA

Rapid transformation and loss of sea ice due to climate change is already causing observable changes in the Arctic region. Due to feedbacks between the Arctic Ocean surface and the atmosphere, there is an urgent need to characterize the unique atmospheric chemistry due to interactions at the frozen snow-covered sea ice surface. Furthermore, few studies have been conducted prior to polar sunrise at a time when aerosol impacts on clouds are suggested to be particularly significant. Atmospheric particle and snow samples were collected near Barrow, Alaska during January and February 2014 to examine the impact of open leads on local sea spray and deposition to the tundra snow surface. Atmospheric particle morphology and elemental composition were characterized using computer-controlled scanning electron microscopy with energy dispersive X-ray spectroscopy, and snow chemistry was examined using ion chromatography. The mixing state and extent of atmospheric aging of sea spray particles will be discussed, as well as the relative abundance of long-range transported particles.

**P10                    Local pollution influences in the Arctic –perspectives from the ACCESS aircraft campaign and opportunities for future research**

Jennie Thomas<sup>1</sup>, K. S. Law<sup>1</sup>, L. Marelle<sup>1</sup>, J.-C. Raut<sup>1</sup>, J.-P. Jalkanen<sup>2</sup>, L. Johansson<sup>2</sup>, A. Roiger<sup>3</sup>, H. Schlager<sup>3</sup>, J. Kim<sup>3</sup>, B. Weinzierl<sup>3,4</sup>, A. Reiter<sup>3</sup>, J. Fast<sup>5</sup>

<sup>1</sup>UPMC Univ. Paris 06; Université Versailles St.-Quentin; CNRS/INSU, LATMOS-IPSL, Paris, France; <sup>2</sup>Finnish Meteorological Institute, Helsinki, Finland; <sup>3</sup>Institut für Physik der Atmosphäre, Deutsches Zentrum für Luft- und Raumfahrt (DLR), Germany; <sup>4</sup>Meteorologisches Institut, Ludwig-Maximilians-Universität, München, Germany; <sup>5</sup>Pacific Northwest National Laboratory, Richland, WA, USA

The Arctic is undergoing rapid, and potentially irreversible changes, such as a dramatic reduction in sea ice. As a result of increased access to the region the levels of atmospheric pollution are expected to rise dramatically due to the emergence of local pollution sources including shipping and oil/gas extraction. In summer 2012, the ACCESS aircraft campaign was conducted using the DLR Falcon aircraft and focused on studying increasing Arctic pollution sources of the coast off northern Norway. The main aims included quantification of emissions from shipping and offshore extraction platforms in the Norwegian Sea. To complement these measurements, a regional chemical transport model (WRF-Chem - The Weather Research and Forecasting Model with Chemistry), which simulates gas and aerosols simultaneously with meteorology, is used to study the impact of these pollution sources on gas and aerosol concentrations (and their atmospheric transformation) in the region. For example, shipping emissions from July 2012 from the STEAM (Ship Traffic Emission Assessment Model) inventory are included in WRF-Chem and compared with aircraft measurements made by the DLR Falcon during ACCESS. Perspectives on how the increasing anthropogenic emissions associated with industrialization of the Arctic region may connect to air-snow interactions will be discussed.

#### **P11            The preservation of long-range transported nitrate in snow at Summit, Greenland**

Jack E. Dibb<sup>1</sup>, M.G. Hastings<sup>2</sup>, D.L. Fibiger<sup>3</sup>, D. Chen<sup>4</sup> and L.G. Huey<sup>4</sup>

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Deposition of nitrate to snow surfaces results from reactions of nitrogen oxides (NO<sub>x</sub>) with oxidants in the atmosphere, producing HNO<sub>3</sub> that is incorporated into precipitation or reacts on the surface of particles. Several factors motivate studying nitrate in snow, including interpretation of nitrate ice core records to reconstruct past levels of NO<sub>x</sub>, tropospheric oxidant concentrations and natural variability in NO<sub>x</sub> sources. The link between the atmospheric concentration of NO<sub>x</sub> and nitrate concentration in snow is problematic, however, because post-depositional processing, such as photolysis and evaporation, can impact the nitrate. Isotope ratios found in nitrate (<sup>15</sup>N/<sup>14</sup>N, <sup>18</sup>O/<sup>16</sup>O, <sup>17</sup>O/<sup>16</sup>O) can indicate the degree of post-depositional loss and recycling of nitrate.

A number of studies at Summit, Greenland [72°35'N, 38°25'W] have shown emission of NO<sub>x</sub> and HO<sub>x</sub> species from the snow, adding an important component to the local oxidizing environment. Additionally, halogen compounds, such as BrO and soluble Br<sup>-</sup> are frequently present at pptv levels above the snow and Br chemistry is expected to have an important influence on NO<sub>x</sub> and HO<sub>x</sub> cycling at Summit. We undertook two intensive field campaigns during 2010 and 2011, combining measurements of gas phase species (NO, NO<sub>y</sub>, BrO), concentrations of soluble gases (HNO<sub>3</sub>, HONO, Br<sup>-</sup>), and the isotopic composition of nitrate (δ<sup>15</sup>N, δ<sup>18</sup>O, Δ<sup>17</sup>O) in the air and in surface snow.

Based on the isotopic composition of nitrate in the air and in the snow compared with concentrations of a suite of gas phase species, we found that nitrate in snow at Summit is not influenced by significant loss nor by local recycling. A striking correlation between Δ<sup>17</sup>O and δ<sup>18</sup>O (r<sup>2</sup>>0.9) is found in surface snow nitrate throughout both field seasons, with a slope ~0.5. Significant loss or local processing of nitrate in the surface snow cannot explain this relationship. Furthermore, the isotopic composition of nitrate in the air (i.e. HNO<sub>3</sub> collected in a mist chamber) at Summit is significantly different than that in the snow. In both years, the δ<sup>15</sup>N

is significantly lower in the air than that found in surface snow, which would be expected if the  $\text{HNO}_3$  was produced from snow-sourced  $\text{NO}_x$ . In contrast, the  $\delta^{18}\text{O}$  in the air varies -- significantly lower values were found in the air than in the snow in 2010, but significantly higher values were found in the air than in the snow in 2011. The lower  $\delta^{18}\text{O}$  in 2010 occurs when BrO levels are notably higher, opposite of what we would expect if local formation of nitrate influenced by Br chemistry was the dominant source of the measured  $\text{HNO}_3$ . Further, the disconnect between the isotopic composition in the snow and in the air suggests that recycled  $\text{HNO}_3$  from snow-sourced  $\text{NO}_x$  can only be a very small component of the snow nitrate budget. Overall, our results suggest that 1) nitrate at Summit is largely preserved in surface snow during photoactive periods, and that 2) nitrate in snow at Summit is representative of long-range transported  $\text{NO}_x$ /nitrate. Interestingly, comparison of the  $\delta^{15}\text{N}$  data with  $\Delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  suggest mixing between three pools of nitrate with distinct isotopic compositions ( $\delta^{15}\text{N}$ ,  $\Delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$ ): (1) -10, 29, 78‰ (2) 5, 39, 100‰ and (3) 16, 4, 23‰.

## **P12 Snow Nitrate Photochemistry in the Uintah Basin, Utah**

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The surface  $\text{O}_3$  concentrations in the Uintah Basin in northeastern Utah frequently exceed the 8-hour average EPA limit during winter. VOC and  $\text{NO}_x$  emissions associated with oil and natural gas drilling activities coupled with a shallow boundary layer and enhanced surface radiation resulting from a snow-covered surface is likely responsible for the high  $\text{O}_3$  concentrations. Nitrate and nitrite photolysis in snow may also provide a source of reactive nitrogen ( $\text{NO}_x$ , HONO) to the atmosphere.

Here we report measurements of nitrate concentration and isotopic composition in the boundary layer and snow during the Winter Ozone Study in the Uintah Basin in January to February 2014 (UBWOS 2014). During UBWOS 2014, vertical profiles of the concentration and isotopic signature ( $\delta^{15}\text{N}$ ,  $\Delta^{17}\text{O}$ ) of nitrate, light absorbing impurities (LAI), snow grain radii, and snow density were measured in snow. Snow nitrate and LAI (mainly dust) concentrations are several orders of magnitude larger than concentrations of these species in Antarctic snow and the highest nitrate concentrations are located in the dustiest layers. The lowest  $\delta^{15}\text{N}$  values are located near the bottom of most snow pits, except on days with fresh snowfall, when the lowest  $\delta^{15}\text{N}$  values are found at the surface. The observations suggest that the flux of reactive nitrogen from the snowpack was most important after a fresh snowfall, and decreased over the course of several days; likely due to the large amount of dust deposition to the surface snow. Dust will reduce the photolysis of snow nitrate by absorbing UV radiation and by decreasing the acidity of the snow. The  $\delta^{15}\text{N}$  of atmospheric nitrate (particulate nitrate plus gas-phase  $\text{HNO}_3$ ) reveal that reactive nitrogen from anthropogenic sources dominate the local nitrate burden in the boundary layer during most of the field campaign. However, relatively low  $\delta^{15}\text{N}$  values of atmospheric nitrate after fresh snowfall suggest that the snow-sourced nitrate became more important after fresh snowfall. These observations are incorporated into a snow chemistry column model linked to a 4-stream snowpack radiative transfer model to calculate the flux of reactive nitrogen from the snow. Preliminary results from these calculations will be presented.

## **P13 The deposition and fate of perfluoroalkyl substances (PFAS) in the seasonal snowpack: implications for spring runoff**

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Per- and polyfluoroalkyl substances (PFAS), a group of highly persistent chemicals of industrial origin, were measured systematically in a snowpack in northern Sweden to determine chemical behaviour during seasonal melt. Average PFAS concentrations were generally low, but displayed a wide range with median (range) concentrations of PFOA and PFOS of 66.5  $\text{pg L}^{-1}$  (ND-122) and 20.5  $\text{pg L}^{-1}$  (2.60-253) respectively. Average concentrations of the shorter chain,

C4 and C5 perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFSAs), were ~10-fold higher. Differences in the PFAS concentrations and profile were observed between surface snow and deeper layers, with evidence of PFAS migration to deeper snow layers as melt progressed. Chemical loads ( $\text{ng m}^{-2}$ ) for C4-9 PFCAs decreased gradually as melt progressed, but increased for C4, C6-8 PFSAs and the longer chain C10-12 PFCAs. This enrichment in the diminishing snowpack is an unusual phenomenon that will affect PFAS elution with meltwater and subsequent entry to catchment surface waters.

**P14            The Ice2Ice project: Does Arctic and sub-Arctic sea ice cover exert important controls on past and future Greenland temperature and ice sheet variations?**

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Here we present the outline of the new Ice2Ice project funded by the European Research Council Synergy Grant. The Ice2Ice project (2014-2016) will investigate how the ongoing rapid demise of Arctic sea ice may instigate abrupt changes on the Greenland Ice Sheet (GIS). Ice cores from the Greenland Ice Sheet show clear evidence of past abrupt warm events with up to 15 degrees warming in less than a decade.

At present, both Arctic Sea ice and the GIS are in strong transformation: Arctic sea-ice cover has been retreating dramatically during most of the satellite era, satellite data also document an increasing loss of GIS ice mass, while the temperature has risen markedly at the GIS summit since 1990.

Strong transient responses in both major Arctic cryospheric entities prompts the question: Is the dramatic decline in Arctic Sea Ice heralding a new phase of abrupt change, similar to those documented in ocean sediments and ice cores?

The main hypothesis of the Ice2Ice project is that Arctic and sub-Arctic sea ice cover exerts important controls on past and future Greenland temperature and ice sheet variations. The Ice2Ice project will approach this complex question by employing an innovative combination of synchronized records of GIS parameters, records of sea ice- and ocean changes as well as model results ranging from global climate models to regional and process models. Here we present the outline of the project, which amongst other investigations include re-drilling the Renland ice core in the coastal East Greenland, marine coring at the East Greenland margin and Eastern Nordic Seas, as well as Global Climate Model (GCM) investigations of the implications of the freshwater flux from the ice sheet to Arctic sea ice cover to investigate the dynamics behind past abrupt transitions in sea ice cover, and in particular the role of ocean stratification and mixing.

**P15            The Origin of Ice in Arctic Boundary Layer Clouds**

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A paucity of observations in the Arctic means that neither aerosol processes nor cloud properties are well understood or well represented within models, with the result that aerosol and cloud-forcing of Arctic climate is poorly constrained.

Research investigating the lower atmosphere of the arctic has found that low cloud dominates the variability in arctic cloud cover. Temperature and humidity profiles show a high frequency of one or more temperature inversions and below these inversions stratus or stratocumulus clouds form. During the arctic summer these low clouds often consist of multiple layers, with a number of theories describing the separation of these clouds. These clouds have been observed during different seasons but the association between temperature and the formation of ice in these clouds is not well understood. Jayaweera and Ohtake (1973) found that the cloud microphysics consisted of very little ice above -20°C but Curry et al., (1996) observed ice clouds at temperatures as high as -14°C. It is possible that the variation in temperatures at which

point glaciated clouds are observed is caused by variation in the number concentration and composition of aerosol.

## Methodology

The ACCACIA project carried out measurement campaigns during spring (March-April 2012) and summer (July 2012) in the region between Greenland and Norway. Measurements were made from both ship and aircraft platforms. Results presented will be confined to those from aircraft, which made the majority of their measurements in the regions around and to the south of the Svalbard archipelago. Two aircraft (the Facility for Airborne Atmospheric Measurement (FAAM) BAe 146 aircraft based in Kiruna Sweden, and the British Antarctic Survey (BAS) Twin Otter, based at Longyearbyen, Svalbard) were deployed during the spring campaign while only one (the BAS aircraft) flew during the summer period. The overarching thrust of ACCACIA is to reduce the large uncertainty in the effects of aerosols and clouds on the Arctic surface energy balance and climate. Key to the work presented is an understanding the microphysical properties of Arctic clouds and their dependence on aerosol properties. During spring the FAAM aircraft was flown within, below, and above the clouds in order to make high-resolution measurements of both the cloud microphysical structures and of the aerosol properties above and below cloud. A full suite of cloud probes was fitted to the 146, making measurements of the cloud drop size distributions (e.g. using a DMT Cloud Droplet probe; CDP) and of the size distribution and shape of ice particles (e.g. using a SPEC-Inc Two-Dimensional Stereoscopic (2D-S) Probe). Aerosol measurements included measurements of size distribution and size resolved chemical composition. Volatile aerosol composition was measured using an Aerodyne compact Time of Flight (c-ToF) aerosol mass spectrometer (AMS) and non volatile components were measured by offline ESEM analysis of filter samples. During the summer campaign the BAS Twin Otter aircraft was also equipped with CDP and 2D-S probes, alongside aerosol sampling equipment.

## Results

Two cases from the winter campaign (FAAM flights B761 and B768) are presented. B768 was influenced by pollution aerosol with higher sulphate loadings advected from Northern Europe, while B761 was carried out in much less polluted conditions. B768 contained many more cloud droplets, attributable to the higher concentration of aerosols ( $\sim 400 \text{ cm}^{-3}$  compared to  $\sim 70 \text{ cm}^{-3}$  for B761) many of which were acting as Cloud Condensation Nuclei (CCN). However, the numbers of ice crystals observed was very similar ( $\sim 0.5 \text{ L}^{-1}$ ) and close to the number of ice nuclei that would be expected based on the aerosol measurements (of aerosols greater than  $0.5 \mu\text{m}$  in size). In both cases, cloud base temperatures were about  $-10^\circ\text{C}$  and cloud top temperatures about  $-20^\circ\text{C}$ . An example from the summer campaign is also presented. case in this case the droplet number concentration was similar to the clean winter case (around  $90 \text{ cm}^{-3}$ ). Cloud base and cloud top temperatures (around  $-2^\circ\text{C}$  and  $-10^\circ\text{C}$  respectively), were much higher, and the number of ice crystals present (with a median value of around  $3 \text{ L}^{-1}$ ) was also higher than observed during the winter cases. The observed ice crystal concentration enhancement, at temperatures between  $-2^\circ\text{C}$  and  $-10^\circ\text{C}$  in the summer case, is consistent with a process of secondary ice particle production by the Hallett-Mossop process which is most active in the temperature zone around  $-6^\circ\text{C}$ . Further evidence for this was observed by the presence of riming ice particles and many small columnar crystals.

## Conclusions

In winter there were frequent incursions of polluted aerosol in layers, generally advected from continental Europe and Russia, which were observed lofted above the arctic boundary layer. However, enhancements of ice nuclei, which are often associated with the larger particles, were not present in the cases examined. The boundary layer stratocumulus clouds contained substantial amounts of supercooled water at all times. In spring, the ice crystal concentrations were controlled by the number of primary ice nuclei. In summer, there were fewer incursions of polluted air, and the often multi-layered clouds again consisted predominantly of supercooled water. However, at this time of year pockets of glaciation were present (produced by secondary ice particle production), in which ice crystal concentrations exceeded those observed in the colder winter clouds.

**P16 Rapid Changes in Surface Water CO<sub>2</sub> and Carbonate Chemistry During Antarctic Sea Ice Melt**

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The seasonal cycle of sea surface carbon dioxide (CO<sub>2</sub>) in the Scotia Sea revealed distinct effects of sea ice dynamics on ocean carbon uptake. Waters beneath the pack ice were saturated in CO<sub>2</sub> from entrainment of deep waters rich in dissolved inorganic carbon (DIC) during the winter. During the spring and summer thaw, biological carbon uptake swiftly reduced sea surface CO<sub>2</sub> to create strong sinks for atmospheric CO<sub>2</sub>. Changes in carbonate chemistry at the ice edge confirmed the dominance of biological carbon uptake, which accounted for 38% of the summer DIC depletion in the surface ocean mixed layer. The release of DIC-poor brines from melting sea ice where precipitation of carbonates, such as ikaite (CaCO<sub>3</sub>·6H<sub>2</sub>O), has taken place could have made a minor contribution to summertime DIC deficits in the ocean mixed layer. The effects of carbonate precipitation are superimposed onto the biological carbon uptake and act to pump CO<sub>2</sub> from the atmosphere into the ocean during sea ice melt. Challenges for the future include improving the understanding of ikaite chemistry in Antarctic sea ice and its importance for the carbon pump in the polar oceans.

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**P17 The seasonal cycle of inorganic carbon in the seasonally sea-ice covered water of Ryder Bay, West Antarctic Peninsula**

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Approximately 15 million km<sup>2</sup> of the Southern Ocean is seasonally ice covered and yet the processes affecting carbon cycling in this climatically important region remain poorly understood and poorly represented in models. Here we present two consecutive seasonal cycles of dissolved inorganic carbon (DIC) and total alkalinity (TA) from the Rothera Biological and Oceanographic Time Series (RaTS) on the West Antarctic Peninsula. Samples were taken at 15 m depth 4 km offshore of Adelaide Island, roughly weekly and analysed for DIC and TA at the UEA, Norwich, UK. This unique dataset, together with accompanying physical, chemical, biological and atmospheric data from RaTS, allows detailed investigation of the drivers of the seasonal cycle of inorganic carbon and gives an insight into interannual variability in carbon cycling. We observe a clear seasonal cycle in inorganic carbon: DIC is rapidly drawn down by biological production to a minimum of ~2000 µmol/kg in December/January before gradually rising to a winter maximum of ~2200 µmol/kg due to mixed layer deepening and increasing ice cover. Alkalinity shows a similar pattern, with a sharp spring decrease to summer minima and a winter maximum of nearly 2300 µmol/kg. Significant interannual variability is apparent which appears to be connected to large-scale atmospheric variability. Air-sea CO<sub>2</sub> flux estimates suggest that this region is a net sink of atmospheric CO<sub>2</sub> over an annual cycle and that winter ice cover increases this sink. A better mechanistic understanding of carbon cycling in the Southern Ocean, particularly the impact of sea ice on CO<sub>2</sub> uptake, will help us to predict better the Southern Ocean's response to climate change in the coming decades and centuries.

**P18 How does snow affect air-sea ice CO<sub>2</sub> fluxes?**

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Sea ice is a significant contributor to the sink of atmospheric CO<sub>2</sub> by polar oceans. Physical and biogeochemical sea ice processes affect partial pressure of CO<sub>2</sub> within sea ice, that in turn controls the way and magnitude of air-sea ice CO<sub>2</sub> fluxes. Snow cover appears to affect the magnitude of the fluxes. In order to understand the role of snow, we compared chamber and micrometeorological measurements of air-ice CO<sub>2</sub> fluxes over snow covered and uncovered sea ice (land fast and pack ice) in both the Arctic and the Antarctic. We observed significant differences between fluxes over uncovered and covered sea ice. In addition chamber and micrometeorological measurement show different patterns that are partially due to snow cover. By gathering these observations, we observed at least three effects of snow on air-ice CO<sub>2</sub> fluxes. Snow appears to (i) act as a transient CO<sub>2</sub> reservoir (ii) affect thermal properties of the ice surface (iii) control gas transfer depending on snow structure (superimposed ice, slush).

**P19 Bromoform and inorganic bromine in a global chemistry climate model**

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We present global simulations of bromocarbons, including bromoform, and inorganic bromine using the chemistry climate model EMAC. Emissions of bromocarbons are calculated in our model simulations from prescribed surface ocean water concentrations derived from a climatology of measurements and a parameterization of air-sea exchange. The model takes into account state-of-the-art gas phase bromine chemistry, but currently does not yet consider specific atmosphere-snow-sea-ice chemical interactions. Modeled bromocarbons are compared with surface observations from a number of polar sites in the Arctic and Antarctic. While the model is able to reproduce observed bromoform and other halocarbons generally well, there are instances where observed bromoform at high latitudes greatly exceeds modeled values and possible implications are discussed.

**P20 Model examination of new Antarctic sea-ice, DMS derived, aerosol to the Southern Ocean region**

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Recent measurements in the sea-ice region of East Antarctica have led to the discovery of a large scale aerosol formation mechanism that could be a significant source of cloud condensation nuclei (CCN) to the Southern Ocean and Antarctic region. The chemical-transport mechanism is intimately linked to the Antarctic Polar Cell circulation. Detailed analysis of the circulation revealed a well-defined downward draft that brings upper-tropospheric air to the sea ice surface that is almost circumpolar (except for the Amundsen Sea quadrant), yet doesn't seem to influence coastal stations. Aerosol formation occurs within this circulation, transporting precursors emitted in the sea ice region to the upper troposphere where they are oxidized, prompting nucleation and growth. Exhaustion of the precursor reservoir halts aerosol nucleation and growth, and the new aerosol populations are transported in the circulation down to the sea ice surface. It is here that the air-mass is replenished with precursor species and a large fraction of the air mass rises above the boundary layer and travels north to the Southern Ocean and mid-latitudes, where, after growth via condensation of precursors and coagulation, aerosols grow to climate-relevant sizes.

Here we quantify this process using a state-of-the-art Earth system model to examine the aerosol number concentrations in the sea ice region. The Earth system model utilized here, HadGEM3, includes the UKCA composition module, with the aerosol microphysics model GLOMAP.

Currently, UKCA's treatment of DMS assumes zero flux from sea ice surfaces. We perturb the system by allowing a sea-ice DMS flux based on values obtained from the literature. The effect of these DMS perturbations on aerosol nucleation and CCN in the Antarctic and Southern Ocean regions is then assessed. This work could help to explain a missing component of the Southern Ocean CCN budget currently present in global models as well as lend support to the model derived from experimental data.

**P21                    Boundary Layer and Temperature Effects on NO Concentrations at the South Pole**

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A series of experiments have explored the behavior of NO concentrations at the South Pole as part of the ISCAT (1998, 2000) and ANTCI (2003, 2005, 2006-7) field programs [Davis et al., 2008]. The relationship between NO and boundary layer depth (BLD) proposed by [Davis et al., 2004] was verified by [Neff et al., 2008] using direct sodar measurements of BLD during the period November-December 2003. A longer time series of NO<sub>x</sub> was generated in the ANTCI program from sunrise in 2006 into summer 2007. However, no direct BLD measurements were available. To address this deficiency, we used multiple linear regression on data from 2003 where both directly observed BLD and meteorological variables were recorded. This analysis showed that the three most important variables were wind speed ( $r^2=0.56$ ), Delta T2-22m ( $r^2=0.32$ ), and wind direction ( $r^2=0.10$ ). The strong dependence on wind speed is consistent with the results of [Neff et al., 2008] showing the dependence of BLD on surface stress (representing turbulent mixing of momentum to the surface). The dependence on wind direction may be unique to the South Pole because of the constancy of surface winds from the northeast that are weakly perturbed by synoptic weather systems: winds from grid east tend to be light, colder, and with shallower BLD whereas those from grid north are stronger, warmer, and have greater BLD. To further test these regression results, we used lower resolution sodar data from the austral spring of 1993 (e.g., October/ November). From these data we found that applying the 2003 regression analysis results to 1993 data, ~32% of the variance could be accounted for, despite the coarseness of the 1993 observations. The latter result provided the justification for applying the 2003 BLD regression analysis to our estimating BLDs on the 2006-7 NO<sub>x</sub> data set.

As found in the 2003 data set, the general trend in the 2006-7 data showed that predicted shallow BLDs consistently correlated with higher concentrations of NO<sub>x</sub>. One of the unique features of the 2006-7 data set was the capture of the full transition from winter to summer in terms of insolation, temperature, and a wide variety of weather regimes. As a result, an important new finding from this analysis was the apparent dependence of the level of observed atmospheric NO<sub>x</sub> on local temperature as proposed by Davis et al., 2010. These authors have further suggested two possible mechanisms that might explain this trend. The first of these involves the local availability of high concentrations of HO<sub>2</sub>NO<sub>2</sub> at South Pole (SP) as reported by [Davis et al., 2008]. This reflects the fact that HO<sub>2</sub>NO<sub>2</sub> is stable only at very low temperatures. As a result it represents a significant loss process for atmospheric NO<sub>x</sub> at this site. However, since HO<sub>2</sub>NO<sub>2</sub> also has a much larger photochemical absorption cross-section in ice versus HNO<sub>3</sub> (a molecule also involved in the removal of NO<sub>x</sub>), it defines a much more efficient recycling mechanism for returning nitrate to the atmosphere. A second hypothesis put forward by Davis et al. 2010, involves the possible role of ice-surface adsorbed HNO<sub>3</sub>. In this scenario the density of isolated HNO<sub>3</sub> molecules on ice crystals is strongly influenced by the levels of atmospheric water vapor. The latter, of course, is a strong function of temperature. Higher temperatures would lead to elevated H<sub>2</sub>O thus leading to enhancements in the burial rate of surface adsorbed HNO<sub>3</sub>. The latter mechanism could be of critical importance since surface adsorbed HNO<sub>3</sub> would have a much higher quantum yield for photochemical production of NO<sub>2</sub> than in-situ bulk ice HNO<sub>3</sub> which when photolyzed experiences significant cage effects that greatly reduced its recycling efficiency.

Using our BLD estimation technique, we stratified the NO<sub>x</sub> -Temperature relationship reported by [Davis et al., 2010] by boundary layer depth. What was found was that NO<sub>x</sub> concentrations systematically decreased with both increasing BLD as well as temperature. As noted by Davis et al. (2010), virtually no other global polar site has shown the high levels of NO<sub>x</sub> that are

routinely observed on the plateau during the Austral spring/summer time period, particularly as recorded at SP. Of particular note are the recent spring/summer observations at Summit Station Greenland [Van Dam et al., 2013]. These data revealed very low levels of NO (typically less than 20 pptv) and no BLD height dependence. Thus, they would appear to be consistent with the hypotheses of Davis et al. 2010, since the temperatures there were typically greater than -25°C.

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## P22 Estimating NO<sub>x</sub> fluxes from snow-packs at Halley, Antarctica.

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Atmospheric concentrations of NO<sub>x</sub> (NO and NO<sub>2</sub>) were measured year-round in 2007 at Halley research station (75°S 26°W) in coastal Antarctica using a 2-channel Chemiluminescence Detector (CLD). During periods of about a week for each season of the year, NO<sub>x</sub> was measured at 2 levels, 0.01 and 7m, above the snow pack, respectively. Measurements of meteorological variables like temperature (at 1.5m above surface), pressure (at 30 m above surface), wind (velocity and direction at 10m above surface), and relative humidity w.r.t water (at 1.25m above surface) were carried out throughout the year at AWS (Automated Weather Station) at Halley. Measurement of three dimensional wind vectors (u, v, w) and temperature (T) at 40 Hz was made using a sonic anemometer about 4m above the snow surface. These three wind components along with their cross-products were used to compute atmospheric turbulence parameters such as friction velocity (u\*), L (Monin-Obukhov length), K<sub>h</sub> (turbulent diffusivity for heat) and Φ<sub>h</sub> (stability function for heat). Additionally, atmospheric boundary layer profile measurements were also carried out using a Doppler SODAR system throughout the year.

The NO<sub>x</sub> mixing ratios were filtered to exclude pollution from station and the flux was then computed based on the flux-gradient method. The 10-min median flux (in molecules/m<sup>2</sup>/sec) during various periods of 2007 were 1.1 x 10<sup>11</sup> ± 1.3 x 10<sup>11</sup> (21-24 Feb); 4.8 x 10<sup>11</sup> ± 4.5 x 10<sup>11</sup> (4-5 March); 7.3 x 10<sup>10</sup> ± 8.2 x 10<sup>10</sup> (6-7 March); 1.5 x 10<sup>10</sup> ± 5.2 x 10<sup>10</sup> (11-13 June); 7.0 x 10<sup>11</sup> ± 7.5 x 10<sup>10</sup> (12-15 October) and 6.4 x 10<sup>11</sup> ± 5.1 x 10<sup>10</sup> (16-19 December), indicating a clear increase in NO<sub>x</sub> flux during austral spring (October) and very low values during winter (June). Clear diurnal patterns of NO<sub>x</sub> flux were observed in spring (mid-October), with fluxes predominantly being positive (emission) during summer and negative (deposition) during autumn. During winter (11-14 June) the average NO and NO<sub>2</sub> mixing ratio remained below the limit of detection of the instrument (LOD is 1pptv for NO and 5pptv for NO<sub>2</sub>).

Here, we discuss the role of key atmospheric drivers such as atmospheric boundary layer height, turbulent diffusivity, temperature, as well as the strength of the photochemical snow source in governing the NO<sub>x</sub> fluxes from snow-packs at Halley. The seasonal variability of NO<sub>x</sub> flux will improve our understanding of the influence of the coastal snow pack on tropospheric NO<sub>x</sub> and ozone production during different times of the year. We contrast our findings to observations at Dome C, a site at the same latitude but located on the high East Antarctic Plateau.

P23

**Nitrate post-depositional processes in Svalbard coastal surface snow**

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The snowpack acts as a sink for atmospheric reactive nitrogen. However, the snowpack is not a final reservoir for this nitrogen, where several post-depositional processes have been confirmed to alter the concentration and isotopic composition of snow nitrate. This has implications for the atmospheric boundary layer chemistry, ice core records and terrestrial ecology following snow-melt. Here we present nitrate data from coastal surface snow during winter (11–15 February, 2010) and spring-time (April 9–May 5, 2010) near Ny-Ålesund, Svalbard. The data reveals a complex pattern of processes within the snowpack. At this site nitrate dry deposition was found to dominate over loss processes (deposition rate =  $0.62 \mu\text{mol m}^{-2} \text{d}^{-1}$ ). At Ny-Ålesund, such surface dry deposition can either result from long-range atmospheric transport of  $\text{NO}_{x,y}$  or include the re-deposition of photolytic/bacterial emission originating from deeper snow layers. The data also confirms earlier findings of  $^{15}\text{N}$ -depleted nitrate air masses arriving from the polar basin, while high nitrate  $\delta^{18}\text{O}$  values only occur with ozone-depleted air, signatures that are reflected in the deposited nitrate. Ozone-depleted air is usually attributed to an active halogen chemistry occurring prior to the air-masses arrival to Svalbard. However, here the Ny-Ålesund surface snow was found to have an active role in the halogen dynamics, as indicated by declining bromide concentrations and increasing nitrate  $\delta^{18}\text{O}$  within the surface snow, when air mass trajectories were stagnant around Svalbard and total column BrO content was low.

P24

**The impact of parameterising light penetration into snowpack on the photochemical production of nitrogen oxide and OH radicals**

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This modeling study evaluates the impact of simplifying actinic flux profile within snowpack on the calculation of depth-integrated photolysis rate constant for of nitrogen oxide from nitrate and nitrite and OH radical from hydrogen peroxide within the snow and gas phase nitric oxide from nitrogen dioxide in the snowpack interstitial air. We evaluated the sensitivities of depth-integrated photolysis rate constant to snow type - density, grain size and light absorbing impurities (black carbon). A depth-integrated photolysis rate constant ratio was determined to compare the difference between calculation done with a coupled atmosphere-snow radiative transfer model (TUV 4.4) and by e-folding depth, the depth that the intensity of radiation has dropped to  $1/e$  of its initial value and it is commonly used as approximation of radiation profile in the snowpack. TUV, however, models more detail in the physics of radiation transfer. Simplification causes largest error in the approximation of depth-integrated photolysis rate constant for gas phase nitrogen dioxide then for nitrite, and least for nitrate and hydrogen peroxide. In most cases, the e-folding depth approximation leads to underestimation when sun is/nearly direct overhead and causing overestimation at high solar zenith angle. The depth-integrated photolysis rate constant ratio is mildly sensitive to density and black carbon content but responsive to scattering-cross section. A simple algorithm has been developed to improve the approximation of depth-integrated photolysis rate constant using e-folding depth, reducing the difference between the two methods from +35% & -18% to +6% to -3%, respectively.

P25

**Incorporation of snow nitrate photochemistry into a global chemical transport model: Impact on boundary layer chemistry and ice core records in Antarctica**

The formation and cycling of reactive nitrogen in the atmosphere has important implications for air quality and the oxidation capacity of the atmosphere. Snowpack nitrate photolysis provides a source of oxidants (e.g. OH, O<sub>3</sub>) and oxidant precursors (e.g. NO<sub>x</sub>) to the overlying boundary layer in remote, snow-covered regions. We have developed a parameterization for calculating the depth dependence of actinic flux in snowpack, and have incorporated it into a global chemical transport model, GEOS-Chem. We use the model to estimate the flux and redistribution of nitrogen in Antarctic snowpack due to snow nitrate photolysis, and examine the implications for ice core nitrate concentration and isotope observations.

The modeled potential flux of NO<sub>x</sub> from Antarctic snow ( $3\text{--}8 \times 10^8$  molecule cm<sup>-2</sup> s<sup>-1</sup>) and e-folding depths of ultraviolet actinic flux (26–80 cm) are comparable to observations. Antarctic boundary layer total nitrate (HNO<sub>3</sub>+NO<sub>3</sub><sup>-</sup>), NO<sub>x</sub>, and OH concentrations are increased by an order of magnitude and boundary layer O<sub>3</sub> concentrations are roughly doubled when snowpack photodenitrification is included in GEOS-Chem. The modeled calculated nitrogen recycling factor (NRF) suggests that nitrate is recycled multiple times per year over the majority of the Antarctic continent. Nitrate remains in the snow photolytic zone for at least 0.65 to 24 years, and depends on the snow accumulation rate. GEOS-Chem is also used to compare primary deposition of nitrate to the snow surface originating from long-range transport (FPRI), the re-deposition of photo-produced NO<sub>x</sub> to the snow surface (FPD), and the upward flux of NO<sub>x</sub> from the snow (FNO<sub>x</sub>) to examine nitrogen recycling and redistribution across Antarctica. FPD is larger than FPRI across much of Antarctica, suggesting large-scale redistribution of nitrogen across the entire continent. The model-calculated flux of nitrate transported off the continent ( $5 \times 10^7$  kg nitrate yr<sup>-1</sup>) is in agreement with a previous estimate. The utility of δ<sup>15</sup>N measurements in Antarctic ice cores in assessing the degree of post-depositional processing across the Antarctic continent is also investigated.

**P26            The enhanced iodide oxidation in frozen environment and the following release of gaseous iodine molecules (I<sub>2</sub>) to the atmosphere**

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Active halogens play a significant role in Earth's environmental systems. Especially, iodine species are known to be related to perturbation of HO<sub>x</sub>/NO<sub>x</sub> cycles, ozone depletion event, formation of CCN (cloud condensation nuclei), controlling the atmospheric oxidizing capacity. However, the mechanism for abiotic generation of iodine compounds is still not clear. Although the reaction processes taking place in the ice matrix are greatly different from those in aqueous solution, chemical reactions of halogens in frozen condition have been rarely investigated compared to those in water. In this work, we investigated the formation of tri-iodide (I<sub>3</sub><sup>-</sup>) through iodide oxidation in ice phase under UV irradiation ( $\lambda > 300$  nm) and in the dark. The oxidative formation of I<sub>3</sub><sup>-</sup> through iodide oxidation, which is very slow in aqueous solution, was significantly accelerated in polycrystalline ice even in the absence of UV irradiation. The following release of gaseous iodine molecule (I<sub>2</sub>) to the atmosphere was also monitored by CRDS (cavity ring-down spectroscopy). We suspect that the highly enhanced oxidation of iodide in ice is due to the freeze concentration of iodides, protons, and dissolved oxygen in the ice crystal grain boundaries. The outdoor experiments carried out under ambient solar radiation of the Antarctic region King George Island (62 °S 58 °W, sea level) also confirmed that the generation of I<sub>3</sub><sup>-</sup> via photooxidative processes is enhanced when iodide is trapped in ice. The observed authentic redox transformation of iodide in ice phase suggests a previously unknown generation pathway for considerable release of reactive halogen compounds to the atmosphere consequently influencing O<sub>3</sub> and Hg depletion events, perturbation of HO<sub>x</sub>/NO<sub>x</sub> cycles, and DMS oxidation to form CCN.

**P27            Accelerated dissolution of iron oxides in ice media and its environmental effects**

The dissolution of iron from mineral dusts and soil particles is crucial for the bio-availability of iron in various environmental media. The bio-availability of iron has been regarded as a crucial limiting factor for the phytoplankton productivity and involved in the sequestration of atmospheric carbon dioxide ( $\text{CO}_2$ ), especially in HNLC (High Nutrients Low Chlorophyll) regions such as the Southern Ocean. Although the bioavailability and fate of iron in aquatic environments has been intensively investigated, those in frozen environments have rarely been studied. In this study, the dissolution of iron oxide particles trapped in ice was investigated as a new pathway of iron supply both in the absence and presence of irradiation. The dissolution of iron oxides in frozen sample was significantly accelerated compared to those in aqueous solution. The outdoor experiments carried out under ambient solar radiation of Ny-Alesund (Svalbard,  $78^\circ 55' \text{N}$ ) and King George Island ( $62^\circ \text{S } 58^\circ \text{W}$ , sea level) also confirmed that the production of bio-available iron species is enhanced when iron oxides are trapped in ice. We speculated that the freeze concentration of iron oxide particles, protons, and organic ligands in ice grain-boundaries could be the plausible reason for the enhanced dissolution of iron oxides in the ice phase. Our research implies that the frozen atmospheric ice with iron-containing dust particles in the upper atmosphere may provide bioavailable iron to the ocean surface when they thaw.

**P28 Re-evaluating the reactive uptake of HOBr in the troposphere**

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The reactive uptake of HOBr promotes the formation of BrO through its conversion of  $\text{Br}^-_{(\text{aq})}$  into di-halogens ( $\text{Br}_2$ ,  $\text{BrCl}$ ). Its quantification is thus important for understanding BrO events, and impacts of reactive halogen chemistry on tropospheric oxidants and mercury deposition. We present a new evaluation of HOBr reactive uptake coefficients in the context of the general acid assisted mechanism, highlighting limitations of the termolecular kinetic approach assumed in numerical model studies to date. Our study reconciles for the first time the different reactive uptake coefficients reported from laboratory experiments. The re-evaluation confirms HOBr reactive uptake ( $\gamma_{\text{HOBr}}$ ) is rapid on moderately acidified sea-salt aerosol (and slow on alkaline aerosol), but predicts low reactive uptake coefficients on highly-acidified submicron particles. This is due to acid-saturated kinetics combined with low halide concentrations induced by acid-displacement reactions (affecting  $\text{Cl}^-$ ) and also dilution effects of  $\text{H}_2\text{SO}_4(\text{aq})$  (affecting  $\text{Br}^-$ ). Thus, our re-evaluation of HOBr kinetics suggests the reactive uptake of HOBr on  $\text{H}_2\text{SO}_4$ -acidified particles is over-estimated, highlighting implications for modeling of BrO chemistry in both marine boundary layer and volcanic environments. Uncertainties in fully constraining HOBr general acid-assisted kinetics with temperature remain, and at very high acidity (high wt%  $\text{H}_2\text{SO}_4$ ) the mechanism instead likely occurs via an initial protonation step. Nevertheless, the re-evaluated HOBr reactive uptake coefficients present a framework towards improved understanding of BrO events also in an Arctic context, where HOBr reactions on snow surface layers, blowing snow, and Arctic haze particles have been implicated.

**P29 Haloalkanes at the air – water and air – ice interfaces: A molecular picture**

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Halogenated organics are emitted into the atmosphere from a variety of natural and anthropogenic sources. Uptake of these molecules onto the surface of aqueous atmospheric aerosols and ice particles can affect their reactivity, for example in processes which lead to release of reactive chlorine, bromine and iodine radicals into the atmosphere. Classical molecular dynamics (MD) simulations are carried out to investigate the interaction of

haloalkane molecules of atmospheric relevance with the surface of crystalline ice at a temperature of approximately -15°C, and with the surface of liquid water at room temperature. The results of the MD simulations provide insight into the adsorption behavior of haloalkanes on water and ice, such as the adsorption energy, surface-residence times, interfacial orientation etc., depending on the number and identity of the halogen atoms and the length of the alkyl chain.

**P30                      Air-snow exchange modeling in elevated watersheds**  
Amir Yadghar, Concordia University, Canada

Snow is an important part of the hydrological cycle in highly elevated watersheds and river basins. Water balance in the watershed and surface energy are directly affected by the quantity of snow in the area. A model has been developed for air snow exchange and snow accumulation based on measuring the snow interception. The model has been tested and verified in a study domain in Canada. The model calculates the snow water equivalent in different conditions. Simulation outputs are close to observations in non-urban areas. The model may be calibrated for a case and used for other similar cases.

**P31                      Investigation of Microcrystalline Cellulose as Ice Nucleus in Immersion Freezing Processes**  
Thomas Häusler<sup>1</sup>, L. Felgitsch<sup>1</sup>, and H. Grothe<sup>1</sup>  
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Clouds play an important role in the earth's climate system. So it is crucial to research the microphysical processes in a cloud and to understand their behavior like cloud albedo, lifetime or precipitation properties. In all these processes, aerosol particles play a crucial role by acting as cloud condensation nuclei for liquid droplets and/or as ice nuclei for the formation of ice particles. Previous research in our group has been related to biological ice nucleation [1, 2]. Here, we present a proxy for many biological macromolecular substances, i.e. microcrystalline cellulose. Several types of microcrystalline cellulose were analyzed and investigated due to their physico-chemical properties. Immersion freezing experiments were carried out in a unique reaction gadget. In this device a water-in-oil suspension (with the cellulose suspended in the aqueous phase) was cooled till the freezing point and observed through a microscope. The results of the immersion freezing experiments of the different cellulose types showed variable ice nucleation activities depending on their type and their concentration. Further analysis methods as scanning electron microscope (SEM) and small angle x-Ray scattering (SAX) were carried out to completely describe the cellulose and their ice nucleation activity.

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**P32                      Acidic trace gas adsorption on ice: XPS and NEXAFS analysis with the new NAPP solid chamber at SLS**  
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Acidic trace gases, such as HCl, HNO<sub>3</sub> and formic acid, play an important role in tropospheric chemistry. The presence of ice in form of cirrus clouds or of snow disturbs this chemistry. The underlying processes, especially on the molecular level, are not fully understood yet (1). One crucial step in these processes is the interaction of the trace gases with the ice surfaces upon adsorption. The understanding of how dopants can modify the structure of the ice's water

molecules network is herein of fundamental importance. Pioneering laboratory based studies have indicated that the surface of ice can become increasingly disordered upon adsorption of acids at temperatures of less than 243 K. It was further shown that the uptake of acidic gases significantly increased in presence of this disordered surface layer, also called quasi-liquid layer (2).

Here, we present first molecular level data on the uptake of formic acid to ice surfaces gained by surface sensitive core-electron Near Ambient Pressure Photospectroscopy (NAPP) at PSI/SLS. Partial auger yield Near Edge x-ray Absorption Fine Structure (NEXAFS) was used to observe the hydrogen- bonding network of ice upon adsorption. X-ray Photoelectron Spectroscopy (XPS) delivers the quantitative surface coverage of the dopant (< 0.5 ML) and probes the depth profiles (1 - 7 nm) and the dissociation degree of the dopant. Combined, these preliminary data allow to gain a complete picture of the trace-gas ice interaction. These data further illustrate the advantages of the newly designed experimental chamber, such as the ability to analyze stable ice films up to temperatures close to the melting point (-5°C), to dose trace gases at low concentrations, and to operate at different beam lines. Results are compared to other techniques probing the dissociation of acids in ice such as laser- induced fluorescence (3), or the hydrogen bond structure such as elipsimetry (2).

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#### **P33                    Model simulations for gas adsorption on ice surfaces with combined ice bulk diffusion around 200 K**

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A kinetic and thermodynamic multi-phase model has been developed to describe the adsorption of gases on ice surfaces followed by diffusional loss of the gases in the ice bulk phase. This model consists of a gas phase, a solid surface, a sub-surface layer and the ice bulk; the associated processes are gas adsorption on the surface, solvation into the sub-surface layer and diffusion in the bulk. It is assumed that the gases dissolve according to Henry's law while the surface concentration follows the Langmuir adsorption equilibrium. The flux of molecules from the sub-surface layer into the ice bulk is treated according to Fick's second law.

Kinetic and thermodynamic quantities as applicable to the uptake of small carbonyl compounds on ice surfaces at temperatures around 200 K have been estimated and used to perform model calculations and corresponding sensitivity tests. These tests have been differentiated to account for open and closed gas phase systems, which correspond to situations of constant and time dependent gas phase concentrations, respectively. It is shown that in each case and for shorter exposure times the loss of molecules from the gas phase is only determined by adsorption onto the surface and the solvation into the sub-surface layer. Diffusional loss into the bulk, on the other hand, is only important at longer exposure times.

A comparison experimental data obtained from measurements for the uptake of acetic acid on ice surfaces using a coated wall flow tube (CWFT) reactor coupled to a QMS will be presented.

#### **P34                    Multi-component Continuous Flow Analysis of ice cores: a tool for understanding changes to the chemical composition of the atmosphere**

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Continuous flow analysis (CFA) allows the multi-component study of various particulate matter and chemical properties of firn and ice cores from polar regions. The system presented here (CFA-FIC-TE) is the first, to our knowledge, to comprise Fast Ion Chromatography (FIC) to provide potential sea ice proxies in  $\text{MSA}^-$  and  $\text{Cl}^-$  and the important  $\text{SO}_4^{2-}$  seasonal cycle and volcanic indicator component; along with the trace elements (TE) Na, Ca, K, Mn, Mg, Al, Fe measured by ICPMS.  $\text{NO}_3^-$  is measured by both UV absorbance and FIC allows for cross-calibration of the record. The difficulties in interpreting nitrate records from ice cores is widespread due to poor understanding of post-depositional processes. However, it is only through multi-proxy studies to reveal local oxidative capacity and acidity changes over time that this may be effectively interpreted. High resolution  $\text{H}_2\text{O}_2$  measurements provided by a fluorometric channel from high accumulation, low annual mean temperature sites as described in this work, provide seasonal resolution to the chronology of the cores and also reveal variations in tropospheric ozone concentration and in ozone photolysis rates ( $\text{J}(\text{O}^1\text{D})$ ) over recent decades. We demonstrate the potential for addition of further analyte channels to the CFA-FIC-TE system, particularly for organic compounds and halogen species, allowing highly resolved, well-calibrated signals to be retrieved whilst avoiding contamination.

### **P35 Development of a New Generation of Environmental Molecular Beam method**

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The Environmental Molecular Beam (EMB) technique is a useful bridge connecting simulations (e.g. molecular dynamics simulations) with macroscopical experimental results and field observations, thanks to its sensitivity in a molecular level. In previous studies, the EMB has been employed to investigate ice and organic surfaces properties at temperatures up to 210 K, e.g. ice formation and morphology<sup>1</sup>, water accommodation coefficients and precursor kinetic model<sup>2</sup>, phase transformation of organic surfaces<sup>3</sup>, etc. The structure of ice surfaces changes significantly when temperatures approach to the melting point, so it is difficult to extrapolate the found mechanisms to higher temperature ranges. Moreover, the current literature results are also very controversial. It is therefore strongly desirable to design and construct a new generation of EMB to allow directly measurements of ice surfaces at high temperatures.

The development and application of the new generation EMB setup for studies of gas-ice interactions at pressures in the  $10^{-1}$  mbar range has been described. Direct Simulation Monte Carlo (DSMC) calculations have been applied to optimize the experimental design with respect to gas transmission through the high pressure zone outside the ice surface and pressure along the surface plane. Different designs were evaluated according to three criteria, which are 1) high beam transmission; 2) absolute pressure above the surface (in the  $10^{-1}$  mbar range); 3) even pressure distribution along the surface. In a first application of the new setup with best design, molecular beams (helium, argon and  $\text{D}_2\text{O}$ ) and light scattering have been used to study the formation of water on a graphite surface in the temperature range up to 240 K. This new EMB technique enables us to directly probe how ice surface pre-melting influences molecular collision dynamics and gas adsorption/desorption kinetics on surfaces, which are crucial to quantify the atmospheric ice particles formation and growth.

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# Eating in Cambridge

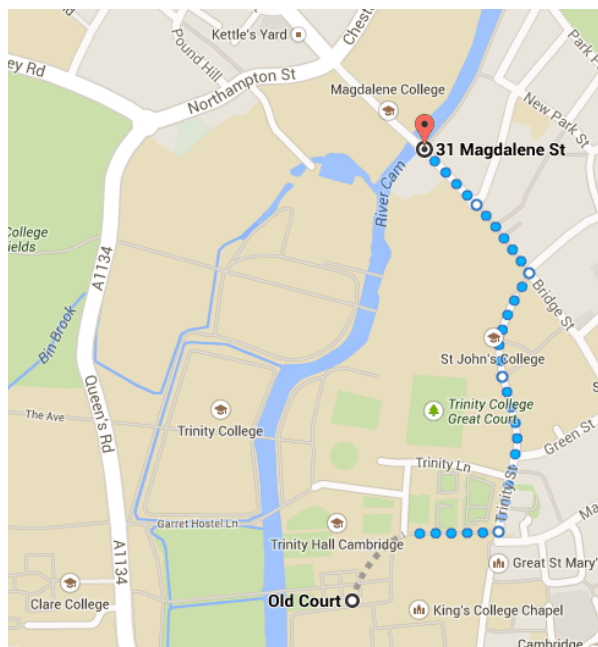
Cambridge boasts a large number of restaurants and pubs. As a guide we recommend that you browse through the different parts of the city. We offer just a few suggestions (not necessarily recommendations!) but please do explore.

## Magdelene/Bridge Street area *to the north of the City Centre:*

Wildwood – Italian  
Prezzo - Italian  
Cote Brasserie – French  
Café Rouge - French  
The Galleria Restaurant – Modern bistro  
The Riverbar Steakhouse and Grill  
The Pickeral Inn – Traditional Pub  
La Tasca – Spanish Tapas  
The Mitre – Pub  
Curry King – Indian  
St John's Chophouse – British for meat lovers (on Northampton Street, go straight up Queens Rd)

### *General Directions (from Google):*

From old Court, head east (via Senate House Passage) towards Trinity Street, turn left, continue onto St Johns Street, turn left onto Bridge Street.

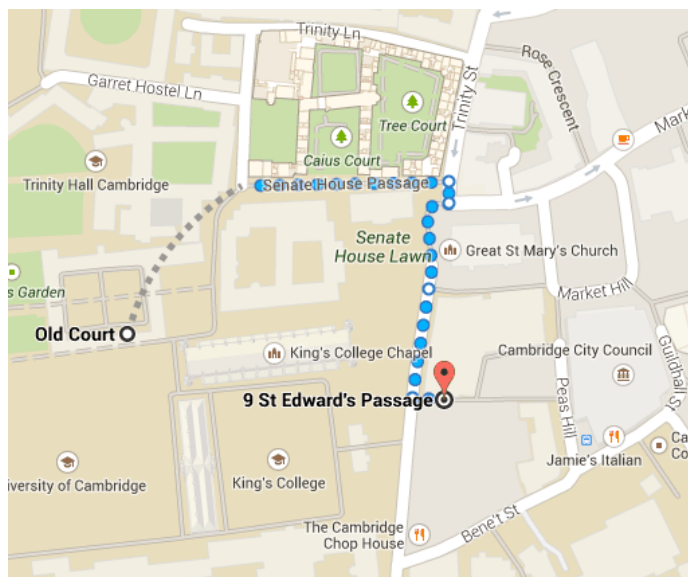


## King's Parade and the centre

Rainbow Vegetarian Café  
The Copper Kettle – Mediterranean café  
The Cambridge Chop House – British for meat lovers  
Zizzi – Pizza and Pasta  
The Eagle – historic pub (Watson and Crick)  
Jamie's Italian  
YO Sushi  
Carluccio's – Italian café

### *General Directions (from Google):*

From old Court, head east (via Senate House Passage) towards Trinity Street, turn left, turn right onto Senate House Hill, continue onto King's Parade (explore the surrounding roads).

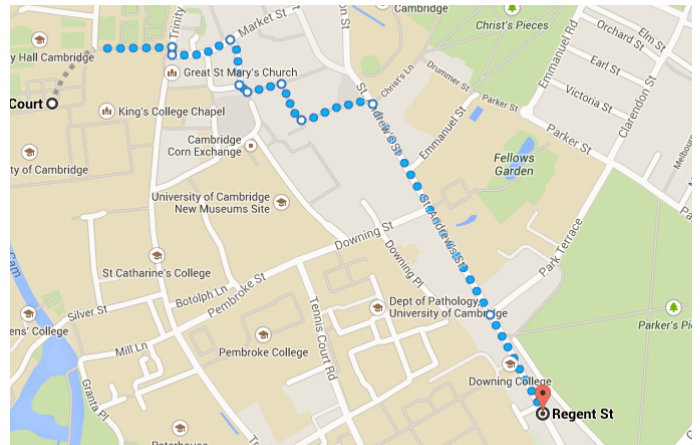


## Regent Street *to the south of the city*

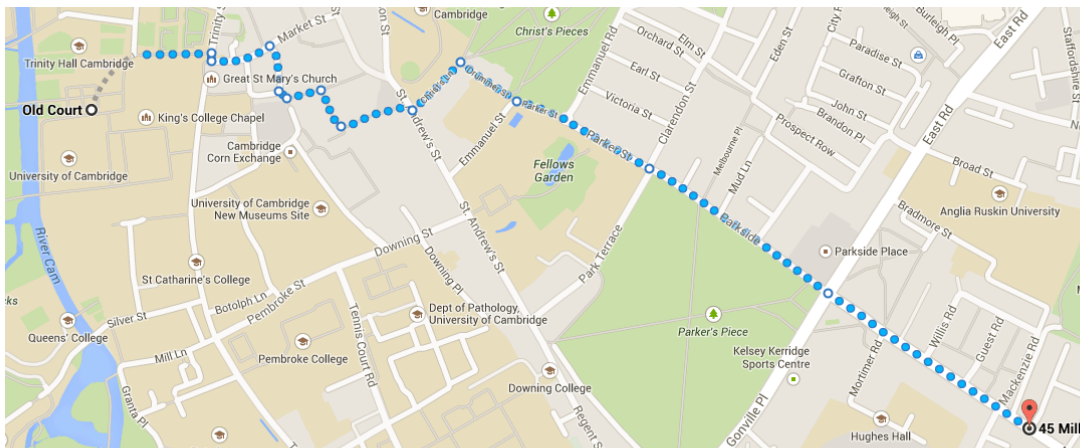
Restaurant 17 – Mediterranean  
The Olive Grove – Greek  
Shiraz – Persian  
The Oak Bistro – British & Continental

### ***General Directions (from Google):***

From old Court, head east (via Senate House Passage) towards Trinity Street, turn right, turn left onto St. Mary's Street, turn right onto Market Hill, turn left toward Petty Cury & turn left, turn right into the Grand Arcade and follow through to the far exit (past John Lewis) turn right onto St. Andrews's Street and continue on.



### ***Mill Road to the east of the city***



Kingston Arms – pub food

Devonshire Arms – pub food

Bedouin – Algerian

Curry Queen – Indian

Rockers Steak house

### ***General Directions (from Google):***

Follow directions to Regent Street as far as St Andrew's Road, then go straight across up Emmanuel Street. Turn right onto Parker Street, continue straight on along Park Side, Continue onwards

### ***Suggested Pubs***

The Clarendon Arms – Clarendon Street (food)

Elm Tee Pub – Orchard Street

The Free Press – Prospect Row (food)

The Tram Depot – Dover Street (food)

Kingston Arms – Kingston Street (food)

Devonshire Arms – Devonshire Road (food)

The Cambridge Blue –Gwydir Street (food)

Live & Let Live – Mawson Road (food)

The Cambridge Brew house – King Street (food)

The Mill - Mill Lane (food)

The Granta – Newnham Road (food)

The Pickeral – Bridge Street (food)

The Fort Saint George –riverside (food)