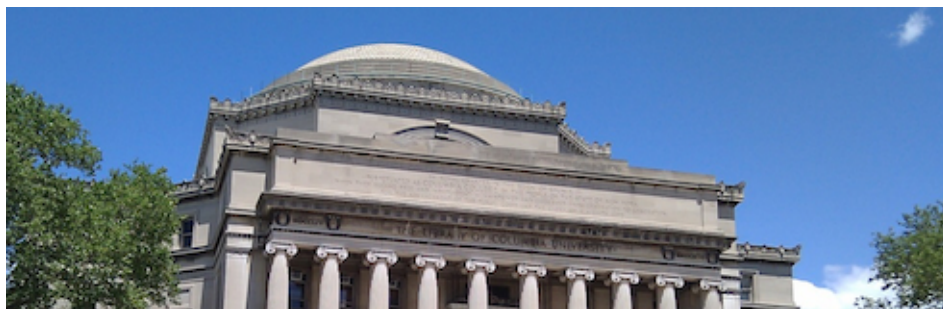


Third workshop on Air-Ice Chemical Interactions (AICI)

Monday, 6 June 2011 - Wednesday, 8 June 2011

Columbia University



Book of Abstracts

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Modeling Workshop / 1**Investigating the Impact of Snowpack Photodenitrification on Antarctic Atmospheric Chemistry Utilizing Results from a Snowpack Radiative Transfer Model in a Global Chemical Transport Model****Author:** Maria Zatzko¹**Co-authors:** Becky Alexander¹; Thomas Grenfell¹¹ *University of Washington***Corresponding Author:** mzatzko@uw.edu

The photolysis of nitrate (NO₃⁻) in snowpack is a source of NO_x to the overlying atmosphere, with implications for the oxidizing capacity of polar atmospheres and the preservation of chemicals in the ice core record. A snowpack radiative transfer model with updated optical properties in the UV [Warren and Clarke, 2008] leads to an e-folding depth of actinic flux in snowpack of 60 cm [Grenfell, 1991]. The snowpack radiative transfer model is used to determine the vertical profile of actinic flux in Antarctic snowpack at South Pole, Dome C, and Neumayer. The NO_x ventilation depth in snowpack is determined by comparing the ventilation lifetime of NO₂ out of the snowpack by diffusion and wind pumping to the chemical lifetime of NO₂ in the snowpack. Chemical sinks for NO₂ in the snowpack include conversion to HNO₃, BrNO₃ and INO₃. Below the ventilation depth, 42 ± 27 cm at South Pole, 38 ± 11cm at Dome C, and 34 ± 26 cm at Neumayer, Antarctica, the NO_x produced through NO₃⁻ photolysis does not escape into the atmosphere. Preliminary results of this study show that photodenitrification can occur tens of centimeters deeper in the snowpack than previously determined. The flux of NO_x from South Pole (1.4-4.4E8 molec cm⁻² s⁻¹) and Neumayer (1.2-3.9E8 molec cm⁻² s⁻¹) snowpacks are computed and are in good agreement with observed NO_x fluxes at South Pole (2.2-3.9E8 molec cm⁻² s⁻¹) and Neumayer (1.3-2.5E8 molec cm⁻² s⁻¹). The results of this study will be used in a global chemical transport model, GEOS-Chem, to estimate the impacts of snowpack photodenitrification on polar nitrogen budgets.

Please list some keywords:snowpack photodenitrification, Antarctica, e-folding depth, ventilation depth, NO_x flux, GEOS-Chem**Modeling Workshop / 2****How different would tropospheric oxidation be over an ice-free Arctic?****Author:** Apostolos Voulgarakis¹**Co-authors:** John Pyle²; Xin Yang²¹ *NASA Goddard Institute for Space Studies at Columbia University, New York, USA*² *NCAS-Climate, Centre for Atmospheric Science, Department of Chemistry, University of Cambridge, UK***Corresponding Author:** avoulgarakis@giss.nasa.gov

Climate projections suggest that a complete Arctic sea-ice retreat is likely in the future during summer. Less ice will cause less light reflection and slower tropospheric photolysis. We use a tropospheric chemistry model to examine how oxidation may differ over an ice-free Arctic. We find that late-summer OH concentrations can decrease by 30–60% at polar latitudes, while effects on local ozone and global oxidant abundances are small. Ozone changes

become larger in the more extreme case where sea-ice is also removed in spring and early summer. In this case, we find large spring ozone increases (up to 50–60%) over the Arctic, and even over inhabited high latitude regions (up to 20%), due mainly to a reduction in the impact of bromine chemistry, caused by the sea-ice retreat. Annual mean ozone also increases in the run with the summer/spring sea-ice removal, but not in the simulation including only late-summer sea-ice removal.

Please list some keywords:

sea-ice retreat, photolysis rates, hydroxyl radical, bromine, tropospheric ozone

Lunch and Poster / 3

Interactions of hydroxyl radicals with ice: A molecular dynamics study

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Molecular dynamics (MD) simulations were used to investigate the behaviour of hydroxyl radicals at air-water and air-ice interfaces. Parameters such as orientation at the surface and duration of interactions with the surface varied in expected ways as a function of temperature. This is in contrast to compounds such as aromatic species which have been shown experimentally and theoretically to interact very differently with ice and water surfaces at identical temperatures. The results were used to predict uptake coefficients including mass accommodation and reactive uptake. The predicted reactive uptake coefficients were higher on ice surfaces than on liquid water surfaces at the same temperature. This suggests that recombination of OH to form hydrogen peroxide might be much more rapid on ice; this could be an important sink for OH in snow and ice, and could help to explain recent experimental results which indicate that OH is unreactive toward some organic species at air-ice interfaces.

Please list some keywords:

ice, water, quasi-liquid layer, hydroxyl radicals (OH), hydrogen peroxide (H₂O₂), uptake coefficient

4

On or in? Where does atmospheric ice chemistry occur?

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Chemical reactions of importance to the atmosphere are generally assumed to take place at the air-ice interface, where a combination of atmospheric deposition and solute exclusion are thought to give rise to high reagent concentrations. Using glancing-angle fluorescence and Raman spectroscopies we have made direct measurements of photochemical and bimolecular kinetics at this interface, and compared the results with those obtained using more traditional techniques. We find that the ice and liquid water surfaces show very different reactive natures. The liquid surface and bulk kinetics are consistent with bulk ice results and the ice surface typically different by up to an order of magnitude. As well, we have shown that solute exclusion to the air-ice interface is neither complete, nor always well predicted by the relevant phase diagram.

Please list some keywords:

chemical kinetics, heterogeneous chemistry, ice surface, photochemistry

5

The Applicability of Artificial Snow for Environmental Studies

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The freezing of aqueous solutions of most of the organic (and inorganic) compounds causes ice and solute molecules to separate. It results in their increased local concentrations in a liquid (or quasi-liquid) phase covering the ice crystal surface or residing in a limited volume, referred to as micropockets, at the boundary of solid ice. Contrary to this, a shock freezing preparation technique can produce artificial snow grains which grow freely without the physical restrictions. Recently we investigated the surface coverage of artificial snow grains by organic contaminants in relation to their surface self-association, diffusion, and bimolecular reactions. Our study revealed that hydrophobic organic molecules can be located on the surface of snow grains in associations rather than as isolated species even at very low concentrations. It is demonstrated that snow represents a readily available study matrix that can be used to emulate the natural chemical processes of trace contaminants occurring in natural snow and stratospheric cloud particles.

Please list some keywords:

Ice; artificial snow; photochemistry; radical recombination; self-association.

6

Speciation, location, and reactivity of aldehydes in snow

Author: Florent Domine¹

Co-authors: Alan Fried ²; Didier Voisin ¹; Dirk Richter ²; James Walega ²; Jean-Charles Gallet ¹; Manuel Barret ¹; Petter Weibring ²; Stephan Houdier ¹

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Aldehydes are key reactive species produced by photochemical processes in the snow. They have the potential to be released to the atmosphere, affecting its oxidative capacity. We have performed measurements of formaldehyde, acetaldehyde, glyoxal and methylglyoxal in polar snow, and in particular at Barrow, Alaska, where atmospheric mixing ratios of formaldehyde were also measured. The predominant aldehyde is formaldehyde, HCHO. Based on recent laboratory studies of HCHO diffusion and solubility in ice, we demonstrate that HCHO forms a solid solution with ice and that the variations of its concentrations in snow can be explained by solid state diffusion in and out of snow grains. Events are observed where HCHO concentrations in snow increase, while HCHO is also emitted by snow, demonstrating a photochemical source of HCHO in the snow. Acetaldehyde, glyoxal and methylglyoxal concentrations are correlated to those of formaldehyde. However, the lack of basic data on the interactions of those species with ice, and the absence of measurement of their atmospheric mixing ratios prevents a detailed quantitative interpretation of their concentrations. Together, these three species can be as abundant as formaldehyde, so that their role can be important and warrant further studies.

Please list some keywords:

aldehydes, formaldehyde, air-snow exchange, solid solution, diffusion in ice, snow photochemistry

Lunch and Poster / 7

Ice Photochemistry Mediated by Dissolved Organic Matter: Degradation of Persistent Organic Pollutants

Author: Amanda Grannas¹**Co-authors:** Brittany Pierce ¹; Rachel Bobby ¹¹ Villanova University**Corresponding Author:** amanda.grannas@villanova.edu

Contamination and accumulation of persistent organic pollutants (POPs) in the Arctic, an area previously considered as pristine and removed from human influence, has become a growing concern. Volatile and semi-volatile contaminants from lower latitudes are transported to the Arctic through a process known as global distillation. The polar regions are unique in that they sit in darkness during the winter until polar sunrise. These conditions allow pollutants to accumulate during winter and then undergo 24-hours of continuous irradiance in sunlit conditions. Photochemical degradation may thus be an important pathway to consider in the spring/summer Arctic season.

Aldrin and dieldrin, globally distributed pesticides, are of particular environmental concern due to bioaccumulative properties, known persistence in the environment, and ability to degrade into environmentally persistent products. To investigate the potential photochemical degradation of these compounds, aqueous solutions in liquid and frozen phases were irradiated under Q-Panel 340 lamps to simulate the UV radiation profile of natural sunlight. Following irradiation, samples were extracted with organic solvent containing an internal standard for GC-ECD analysis. Aldrin degraded quickly in the presence of natural organic matter, with frozen samples degrading more quickly than liquid samples. Dieldrin also showed photochemical reactivity, albeit on a much slower timescale. We report here the differences in liquid and frozen reactivity, the influence of different sources of natural organic matter, and the effect of temperature on degradation half lives.

Please list some keywords:

snow, photochemistry, dissolved organic matter, persistent organic pollutants

8

Organics in Snow and Ice: Recent Findings from Field and Modeling Studies

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It has become increasingly apparent that snow and ice are important media for both homogeneous and heterogeneous environmental chemical reactions. A variety of chemistry occurs in/on snow and ice, including photochemical, redox and biologically-mediated reactions. Organic components play an important role in many of these processes. Organics can be the reactive chromophore or a photosensitizer in photochemical processes; they may take part in electron shuttling for redox processes; or they can serve the role of carbon source for biological metabolism. These myriad processes all play an important role in the exchange of reactive species between snow and the atmosphere. This presentation will focus on the state of the science with respect to identifying and characterizing organic materials present in snow and ice, and the interactions of snow and ice in the environment with VOCs, from a field and modeling perspective.

Please list some keywords:

snow, ice, VOCs, organics, photochemistry, atmospheric exchange

Lunch and Poster / 9

The Effect of the Novel HNO₃(g) Production

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It is well established that the reaction of HO₂ with NO plays a central role in atmospheric chemistry by way of OH/HO₂ recycling and reduction of ozone depletion by HO_x cycles in the stratosphere and in ozone production in the troposphere. In the stratosphere this reaction moderates the effectiveness of the cycle involving HO_x radicals, which is an important removal mechanism of ozone. In the troposphere this reaction plays a key role in controlling the interconversion between HO₂ and OH radicals through cycles involving CO and volatile organic compounds (VOCs); these chemical cycles serve as a secondary source of OH radicals as well as a major source of tropospheric ozone. Utilizing a photochemical box model, we investigate the impact of the recently observed HNO₃ production channel (HO₂ + NO → HNO₃) on NO_x (NO + NO₂), HO_x (OH + HO₂), HNO₃, and O₃ concentrations in the boundary layer at South Pole, Antarctica. The inclusion of the new reaction channel decreases peak O₃, NO, NO₂, and OH by 3 ppbv, 200 pptv, 125 pptv, and 0.3 pptv, respectively, from their peak concentrations, while peak HNO₃ increases by 125 pptv; the peak HO₂ amount is unaffected by the new chemistry. The decrease in O₃ from 37 to 34 ppbv worsens the agreement between the model and the highest O₃ concentrations observed at the South Pole (45

ppbv). As the mean concentration of OH at the South Pole is 2.5×10^6 molecules cm^{-3} , our simulations bring mean OH into better agreement with observations as OH is reduced from 3×10^7 to 1×10^7 molecules cm^{-3} . HO₂ are incongruent with maximum and mean concentrations of HO₂ measured at the South Pole, $\sim 7 \times 10^7$ and $\sim 1 \times 10^6$ molecules cm^{-3} , respectively. Given that peak measured HNO₃ concentration measured at the South Pole is 70 pptv, our simulations still over-predict it by an additional ~ 130 pptv. The reduced concentrations of NO_x as a result of the application of the new channel are consistent with expected decreases in atmospheric NO_x lifetime as a result of increased sequestration of NO_x into HNO₃. Without this new channel current models will tend to underestimate NO_x losses. This has important implications: 1) given that previous studies investigating snowpack emissions of NO_x have relied upon accurate and comprehensive determinations of NO_x losses in this environment, our result implies that NO_x snowpack emissions are larger than currently reported; 2) current estimates of the nitrate recycling factor again rely upon accurate characterization of NO_x lifetime, and, therefore, current estimates of the nitrate recycling factor are likely too low. Although we show that the inclusion of the novel HNO₃ production channel brings better agreement for HO_x with field measurements, the modeled ozone and HNO₃ are worsened, and the changes in NO_x lifetime imply that snowpack NO_x emissions and snowpack nitrate recycling must be re-evaluated.

Please list some keywords:

snowpack, sea-ice, ice photochemistry

Modeling Workshop / 10

Comparative molecular dynamics study of vapor-exposed basal, prismatic and pyramidal surfaces of ice

Author: Martina Roeselova¹

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We present the results of molecular dynamics simulations in which ice Ih slabs with free basal, prismatic, 28 degrees pyramidal, and 14 degrees pyramidal facets are exposed to vapor. All simulations were carried out at 250 K using a six-site intermolecular potential. Characteristics common to all facets include spontaneous development of a quasi-liquid layer (QLL) within ~ 10 ns, and QLL stratification into outer and inner sublayers having on average two and three hydrogen bonds, respectively. Vapor pressure, based on the rate of sublimation of molecules from the ice surface to the vapor phase, is found to be greatest for the 14 degrees pyramidal and basal facets (~ 230 Pa), while significantly lower values are obtained for the prismatic and 28 degrees pyramidal facets (~ 200 Pa). E-folding lifetimes and layer-specific bulk ice accommodation coefficients indicate much more frequent exchange between the QLL and inner ice layers for pyramidal surfaces compared to basal and prismatic surfaces. The free prismatic facet and 28 degrees pyramidal facets exhibit significant anisotropic diffusivity, in-plane motion being faster in the trans-prismatic direction than in the basal-to-basal direction. Implications of these molecular-level findings for the growth of ice crystals by vapor deposition and for adsorption of gas phase species of atmospheric relevance onto ice will be discussed.

Please list some keywords:

ice surface, vapor pressure, surface diffusivity, surface lifetime, basal, prismatic, pyramidal

Lunch and Poster / 11**Overview of the NITEDC (NItRate Evolution in Dome C snow) program and presentation of its preliminary results****Author:** Joel Savarino¹**Co-authors:** Florent Dominé ¹; James France ²; Jean-Charles Gallet ³; Joseph Erbland ¹; Markus Frey ⁴; William Vicars ¹¹ LGGE/CNRS/Université Joseph Fourier, Grenoble, France² Royal Holloway University, Surrey, UK³ Norwegian Polar Institute, Tromsø⁴ British Antarctic Survey**Corresponding Author:** maey@bas.ac.uk

The interpretation of nitrate profiles recorded in deep ice cores is hindered by surface post depositional processes. Deciphering the atmospheric information embedded in these profiles should greatly enhance our understanding of the chemical state of paleo-atmospheres as nitrate potentially contains information about the NO_x chemistry. Furthermore, there is now consensus that photodissociation of nitrate in snow drives emissions of NO_x from snow surfaces and thereby significantly impacts the NO_x, and HO_x budgets over ice-sheets during the summer season, altering the oxidative capacity of the polar boundary layer.

Concordia station at Dome C (Antarctica) is the third year-round research base (after South Pole and Vostok) located in the interior of the Antarctic continent (75°06'S, 123°20'E, alt. 3306m asl). Contrary to the other inland stations, Concordia is at the summit of a dome and consequently experiences more stratified air with very shallow boundary layers associated with strong temperature inversion and low average wind speeds. Furthermore, its position at 75°S produces strong diurnal variations of radiation and temperature during the summer season capable of revealing the relative action of photochemistry and boundary dynamic in this environment. Another positive point is that the permanent presence of technicians and scientific at the station allows year-round study of change of the physical and chemical characteristic of snow and air.

The NITEDC program was dedicated to study the evolution of atmospheric and snow nitrate/nitric acid in this harsh environment. It is the first East Antarctic Plateau study outside of South Pole investigating the cycling of reactive nitrogen between atmosphere and snow. Both physical and chemical aspects were studied.

The specific surface area of snow (SSA = Surface of snow/Mass of snow) which governs the surface available for air-snow exchange was measured in different snow pits and along the Dome C-Dumont d'Urville (the coastal French station). Strong vertical and horizontal gradients were observed. Higher SSA were observed at the surface (~38 m² kg⁻¹), decreasing monotonically to ~14 m² kg⁻¹ at 15 cm depth. Closer to DDU, the SSA of the top 5 cm was 23 m² kg⁻¹, decreasing to 19 m² kg⁻¹ at 50 cm depth.

UV/Vis light penetration was measured directly at different snow depths with a multiprobe spectrometer. Depth characteristic of light penetration is a function of the type of snow encountered at DC with e-folding ranging from 10 cm for windpack layers and ~20 for depth hoar layers at 400 nm wavelength.

Nitrogen dioxide (NO/NO₂) concentrations were followed during the 09-10 summer season, showing a repeatable, strong diurnal cycle, with a minimum at noon and a maximum in the early evening. Further analysis shows that the diurnal variability results from a combination of the strength of the snowpack source (i.e. radiation) and the mixing properties of the atmospheric boundary layer.

Finally and for the first time, snow and atmospheric nitrate were simultaneously analyzed for both concentration and N and O isotope compositions. The comparison between surface snow and atmosphere reveals the intense recycling between these two nitrogen pools. Intense negative nitrogen but positive oxygen fractionations found in snow pits strongly suggest that photodissociation (moderated by the interplay of accumulation rate and actinic flux) is the driving force that controls the nitrate concentration in snow (and not HNO₃ desorption). However, laboratory experiments demonstrate that liquid phase photodecomposition of nitrate is unable to explain the observation isotopic fractionations and that photodissociation of nitrate/nitric acid in solid or adsorption phase should be considered firstly. Tests are currently underway in our laboratory to find the location of nitrate in Antarctic snow as well as incorporating of these findings in a semi empirical photochemical model.

Please list some keywords:

reactive nitrogen; atmosphere-snow exchange; snow photochemistry; stable nitrate isotopes; Antarctica

12

Exploring new pathways on ice

Author: John Sodeau¹

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Snow-packs, cirrus clouds, polar stratospheric clouds, frost flowers and sea-ices can all be viewed as part of the Earth's Cryosphere. Not mere spectators on chemistry in the atmosphere, ices often play an active role due to the presence of their surfaces, triple points and internal pores. The effects manifest as rate changes for known chemical processes as well as the promotion of "unexpected" pathways. Therefore in this talk some new results on a number of systems relevant to atmospheric processing on ice surfaces will be discussed.

The first topic concerns the influence of freezing on the chemical composition of halide ions in dilute aqueous solutions. The "freeze-enhanced" chemistry discussed is particularly relevant to the anomalously high levels of halogen oxides observed in the Polar troposphere. The focus then moves to investigations of the low-temperature reactivities of sulfur dioxide on/within ices using FT-RAIRS and TPD as probes of the chemistry. Similar methodologies are adopted for an investigation of the low-temperature photochemistry of organo-nitrates in the presence of water-ice surfaces. The question to be answered here is: are these long-lived compounds, which are mainly anthropogenic in origin, transformed by heterogeneous processing on cryospheric ice surfaces? Finally the dark oxidation of dissolved gaseous mercury in ice will be illustrated from experiments based on atomic fluorescence detection. Very few results on the chemical interaction between mercury and water-ices are available to the atmospheric chemistry community currently and the data obtained in this work clearly show that freezing does play an effect on the oxidation processes studied.

Please list some keywords:

ice, oxidation,

Modeling Workshop / 13

Microstructural Modeling of Snow- and Firn Processes

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The micro-structure of a sintered and porous material impacts its chemical and physical properties. In particular, sintering ice-crystals evolving from snow to firn alter the characteristics of the snow-pack. We study the link between micro-structure and properties by numerical modeling based on

experimental X-ray micro-tomography data or using discrete element model (DEM) snow as geometrical input. We use phase-field techniques to solve the two-phase (ice and air) heat and mass transfer problem in snow and to predict heat conductivity, evaporation-condensation, and sintering rates. We analyze mechanical behavior within the DEM framework, flow using Lattice-Boltzmann simulations, and study optical properties by Monte Carlo ray tracing techniques. The coupling with chemical models presents particular challenges.

Please list some keywords:

snow micro-structure, modeling, X-ray micro-tomography, phase-field, discrete elements

Lunch and Poster / 14

Photochemistry of Model Organic Matter in Ice

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The organic matter present in ice and snow is composed of humic-like substances and the transported degradation products of anthropogenic and biogenic emissions. Our research explores the direct photochemistry and thermal reactions of model organic matter in ice and water. Pyruvic (PA) and benzoylformic acids (BA) are used as surrogates for the species present in the polar environment. Several experimental techniques are used to propose and contrast a reaction mechanism: TOC, and EPR, NMR, UV, FTIR, and fluorescence spectroscopies. Control dark experiments confirm that PA and BA are thermally stable below -5 °C. LC-ESI-MS detection and 2H- and 13C-isotope labeling experiments were used to identify oligomeric products. Our results support the facts that simple dicarbonyls can undergo photochemical reactions in ice to produce carbon dioxide and regenerate polyfunctional products.

Please list some keywords:

dicarbonyl; hydration equilibrium; ice, snow, ketocarboxylic acid, oligomer,

Lunch and Poster / 15

Pernitric and nitric acid in a coastal Antarctic boundary layer –a winter time study

Author: Anna Jones¹

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It has been mooted that pernitric acid (HO₂NO₂) might play an important role in low altitude photochemistry of the polar regions. This potential arises from the intrinsic link between PNA and atmospheric NO_x and HO_x radicals. For example, gas-phase production and destruction reactions are, respectively, sinks and sources of NO_x and HO_x. Further, like HNO₃, PNA can adsorb to ice/snow

surfaces, so has the potential to form reservoirs of radicals associated with the condensed phase, either temporary or longer-term. Previous measurements at the South Pole detected significant amounts of boundary layer PNA with a lifetime controlled predominantly by dry deposition and thermal decomposition. No observations at relatively warmer, coastal, Antarctic sites have yet been reported.

As part of a year-round field campaign at the British Antarctic Survey station, Halley, in coastal Antarctica, measurements of PNA and HNO₃ were made using a Chemical Ionisation Mass Spectrometer (CIMS). Observations extended from March (austral autumn) through to September (austral spring) with further periods in late spring and summer. Concurrent measurements of NO and NO₂ were obtained by a chemiluminescence analyser.

Here we present the winter time observations. Both PNA and HNO₃ were present in the winter time boundary layer at Halley. Considerable variability in mixing ratios was evident, between instrumental detection limits and ~20 pptv, and with the same variability patterns reflected in both PNA and HNO₃. The majority of these measurements were made during polar night, so little or no photolysis was active (indeed, [NO] and [NO₂] were below detection limit throughout the measurement period). Instead, the variability in PNA and HNO₃ appears to have been controlled by transport and physical exchange processes. We explore case studies that suggest higher PNA and HNO₃ was associated with air mass transport from the polar plateau and linked to changing temperatures, which in turn would drive air/ice adsorption and desorption processes.

Our data thus suggest that PNA and HNO₃ from Plateau snow is feeding into coastal areas under specific environmental conditions. While such events are infrequent at Halley, the process would likely be more important in areas with katabatic outflow. If correct, this would be a new mechanism affecting the nitrogen budget (both air and snow) and radical recycling potential across Antarctica.

Please list some keywords:

Pernitric acid, nitric acid, air/snow physical exchange, coastal Antarctica, winter boundary layer

Lunch and Poster / 16

Investigating Brine on Frost Flowers with Absorption Tomography

Author: Peter Peterson¹

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Because of the ubiquitous nature of ice, chemistry taking place on ice surfaces can have a substantial effect on the environment, particularly in the polar regions, through processes such as ozone depletion and mercury deposition. Frost flowers are an ice form found on newly formed sea ice that have the potential to play a role in halogen activation due to their high salinity. Current understanding of the role of frost flowers in these processes is inhibited by a lack of knowledge of the impurity distribution in relation to the ice surface. One way of obtaining this information is through the use of X-ray microtomography. This technique allows for visualization and quantitative analysis of the brine distribution. Analysis of the data shows that while brine is concentrated near the surface of the frost flower, it is unevenly distributed over the surface indicating that not all of the surface area is chemically active. The data also show brine pockets in the overall structure that are unavailable to react with the atmosphere, indicating that a knowledge of bulk chemical composition of reactive ice is insufficient to accurately determine the effects of ice surface chemistry on the atmosphere.

Please list some keywords:

Brine, Ice Surface, Frost Flower, Tomography

17

The ice - air interface in snow - the molecular to micron scale perspective

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Ice is a high temperature material in the sense that under environmental conditions it is close to its melting temperature. This leads to peculiarities that determine the physical and chemical properties of the ice - air interface but also the larger scale snow structure. While this is reasonably well understood for pure ice, contaminants present in environmental snow interact with the structure of ice and are believed to significantly alter the ice surface. This overview presents results of novel spectroscopic experiments that directly probe this interface in presence of a number of different contaminants. It highlights that the molecular environment around soluble species at the surface is resembling that of a concentrated solution containing this solute. The surface energy is minimized by accommodating the trace species into a local solution like environment. Therefore, at low contaminant levels, the elusive quasi-liquid layer is not extending over larger scales than the hydration shells of solutes present at the surface, and the majority of the ice surface remains ice-like. Whether such hydrated species prefer the ice - air interface or grain boundary remains an open question. In contrast, if solutes may form a stable solution in equilibrium with ice, they form a separate phase. For halides, such brines tend to be excluded to the ice surface, while their surface chemical properties are consistent with the halide - water - ice phase diagram. These features of the contaminated ice surface govern the chemical properties and thus reactivity. When scaled up to the level of snow, the continuously evolving structure of snow becomes important, as it determines in what way the contaminant species are exposed to the interstitial air or the transport processes into and out of the snowpack

Please list some keywords:

snow, ice, quasi-liquid layer, nitrate, sea salt,

18

Atmospheric nitrogen oxides (NO and NO₂) at Dome C: first observations & implications for reactive nitrogen cycling above the East Antarctic Ice Sheet

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The nitrogen oxides NO and NO₂ (NO_x) play a key role in determining the oxidizing capacity of the boundary layer in high latitudes. Previous Arctic and Antarctic field campaigns have demonstrated that the polar snow pack can release significant amounts of NO_x and that one of the major driving

mechanisms is UV-photolysis of snow nitrate (NO_3^-). Unusually high levels of NO observed at South Pole and on an airborne campaign suggested that the East Antarctic Ice Sheet (EAIS) can be perceived as a gigantic chemical reactor, processing many chemical trace species at the surface and thereby modifying their concentration eventually preserved in ice cores. However, the database for a quantitative understanding of reactive nitrogen recycling across Antarctica is still weak.

First measurements of atmospheric NO_x mixing ratios at Dome C (DC), East Antarctica (75.1°S 123.3°E, 3233 m) during austral summer 2009/2010 yield new insights: NO_x mixing ratios were large, ranging between 3 pptv and >1000 pptv, but unlike at South Pole showed a strong diurnal variability. Concentration maxima in ambient air at 0.01, 1.0 and 4.0m above the snow occurred in the evening hours. They coincided with the strongest concentration gradients between the snow surface and 4.0 m, highlighting the importance of the interplay between snow pack source strength and the evolution of the boundary layer diffusivity profile. Conversely, near-surface firn air levels of NO_x varied in phase with solar radiation, consistent with a photolytic source in the near-surface snow.

Steady-state analysis shows strong increases in the Leighton ratio around solar noon, confirming the importance of oxidants other than ozone, i.e. hydroxyl radicals. Comparison of observations with a potential NO_2 flux based on a radiation transfer model (TUV-snow) allows to improve the parameterization of NO_x emissions in a quantitative model of reactive nitrogen recycling above Antarctica.

Please list some keywords:

NO_x snow emissions, nitrate photolysis, Antarctica, oxidation capacity

Lunch and Poster / 19

Post-depositional fractionation of nitrate stable isotopes in Antarctic snow: towards an ice core proxy of surface UV

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Recent studies on atmospheric particulate nitrate (NO_3^-) have shown that the nitrogen and triple oxygen stable isotopic composition of NO_3^- allows constraining atmospheric sources and sinks, in particular oxidation pathways of reactive nitrogen. However, extending this tool to past atmospheres using ice cores can be complicated by post-depositional mass loss and fractionation via UV-photolysis and evaporation. In regions, where these alterations are strong, we propose that the post-depositional process itself leaves a specific isotopic fingerprint in the snow, which can be related to past environmental surface conditions.

From this point of view we discuss a new 60-yr firn record of $^{15}\text{N}/^{14}\text{N}$ ratios in NO_3^- from Dome C, Antarctica (75° S, 123° E), which shows strong fractionation compared to the atmospheric signal. Recent estimates of the photolytic fractionation constant for the nitrogen isotope ^{15}N in snow based on a simple Zero-Point-Energy (ZPE) shift model are consistent with field and laboratory observations. This suggests that the isotopic enrichment observed is largely caused by post-depositional UV photolysis of nitrate. Therefore, the extent of isotopic enrichment is expected to depend on two factors: a) the residence time of a given snow layer within the photolytic zone of the upper snow pack, which in turn is controlled by accumulation rate variability and b) the spectrum of incident UV radiation. The latter depends mostly on the ozone over-head column, which has undergone significant changes over the past decades. Indeed, we find a strong correlation between nitrogen isotopic ratios and modeled annual UV radiation ($r = 0.7$, $p < 0.001$). We then discuss sensitivities of isotopic

fractionation to the variability in accumulation rate and timing. Past accumulation rate variability will introduce uncertainty in the use of the nitrogen stable isotope as a proxy of past UV radiation, but is among the parameters typically derived from ice core measurements.

Please list some keywords:

nitrate photolysis, nitrate stable isotopes, Antarctica, ice core proxy, UV radiation

Lunch and Poster / 20

The depth of UV light extinction (e-folding depths) at Summit, Greenland

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The depth of illumination of UV light in snow is a critical measurement in the study of snow photochemistry. This depth defines the zone where chemical impurities in the snow can photolyze and release reactive trace gases into the atmosphere. Although numerous studies have measured the depth of UV illumination, the physical properties of snow that control snow optics and light extinction are not well understood. Snow specific surface area (SSA), the ratio of snow crystal surface area to mass, likely has strong control over snow optics and is a more accurate and sensitive way to characterize snow structure than traditional snow density and grain size measurements. The objective of this research is to measure the depth of UV illumination in snow simultaneously with measurements of snow SSA to determine the relationships between physical snow structure and snow optics that control light extinction. I am using new techniques including infrared photography and contact spectroscopy to measure snow SSA during May, 2011 field work at Summit, Greenland. I hypothesize that SSA will have strong optical controls on UV light in snow, and will be an important indicator of the potential depth of light extinction that will vary significantly with different snow conditions. Coupled with snow and air chemistry results from other workers, this research will lead towards a better understanding of the physical properties that control the photochemical zone in the uppermost snowpack.

Please list some keywords:

e-folding depth, snow specific surface area, snow properties, Summit

21

The Importance of Sea Ice for Halocarbon and Mercury Chemistry

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Sea ice is thought of as being a barrier for the transportation of dissolved gases between the ocean and the atmosphere. However, sea ice as a source of gases has not been considered to any larger extent. The gaseous fluxes of halocarbons and mercury in polar waters are poorly known, particularly in regards to the role of sea ice. The fluxes are predicted to change in accordance with changes in the biological processes and by melting of sea ice resulting in more open water. The ice is a habitat for a number of autotrophic and heterotrophic organisms. It is a highly variable ecosystem governed by salinity, temperature, limitation in nutrients as well as light conditions. Sea ice is also a barrier to light transmission, and, therefore, ice algae must be physiologically adapted to low light conditions. It has been shown that their photosynthetic systems are saturated at relatively low light intensities, and have high photosynthetic efficiencies. A consequence of such high activity is an increase in pH as well as a depletion of inorganic carbon.

We have measured the distribution of halocarbons and mercury in sea ice and snow during expeditions to the Amundsen Sea, Antarctica, with the Swedish icebreaker Oden. Our results indicate sea ice as a source of halocarbons, in particular iodinated compounds. For the latter ones the contribution to the atmosphere is in the same order of magnitude as that of seawater.

The importance of irradiance for the distribution of dissolved gaseous mercury in ice cores was also studied. The difference in concentrations of volatile mercury was significantly altered due to different light conditions. This indicates that photo reduction of oxidized mercury is occurring in ice, possibly in the aqueous fractions, brine, within the ice structure.

Please list some keywords:

halocarbons, mercury, gaseous fluxes, Amundsen Sea, Antarctica, photo reduction of oxidized mercury

Lunch and Poster / 22

Freeze-Induced Reactions: Formation of Iodine–Bromine Inter-halogen Species from Aqueous Halide Ion Solutions

Author: Daniel O'Sullivan¹

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The presence of gaseous halogens in the polar troposphere is of considerable interest to researchers as it is known that these highly reactive species can alter the oxidative capacity of the Polar atmosphere. Perhaps the most well known Polar tropospheric phenomenon to which halogens have been linked are sudden ozone depletion events (ODEs), observed to occur within the boundary layer during Polar sunrise. More recently researchers have identified other atmospherically relevant processes influenced by the presence of gaseous halogens, such as the formation of cloud condensation nuclei or the removal and deposition of gaseous elemental mercury to the snowpack. However, questions on how these halogen species are initially released to the Polar troposphere remain.

During this research, interhalide ions of the type I₂Br⁻ and IBr₂⁻ are generated by freezing dilute solutions containing components found in Polar marine environments. These interhalide species have previously been shown to be precursors of iodine monobromide, IBr, which may diffuse from solution, thus releasing reactive halogens to the gas phase. The freezing process itself is shown to stimulate interhalide formation in dilute solutions containing bromide, iodide and hydrogen peroxide, under acidic conditions. The reaction mechanisms that lead to the formation of IBr₂⁻ under freezing conditions are explored, and the chemistry subsequently modified in order to mimic naturally occurring conditions more closely. By modification of the initial ratios of bromide to iodide in solution, interhalide formation is shown to become favourable at pH 5, an acidity comparable to that found in natural snowpack.

Please list some keywords:

Halogens, Sea salt, Freeze-induced Reactions

Lunch and Poster / 23**Model simulations of polar boundary layer ozone depletion events in spring****Author:** Xin Yang¹**Co-authors:** Anna Jones ²; John Pyle ¹¹ *University of Cambridge*² *British Antarctic Survey***Corresponding Author:** xy214@cam.ac.uk

In the last several decades, significant depletion of boundary layer ozone (ODEs) has been observed in both Antarctic and Arctic, especially over sea ice zones. ODEs are attributed to catalytic destruction by bromine radicals (Br and BrO), especially during bromine explosion events (BEs), when high concentrations of BrO periodically occur. However, neither the exact source of the bromine nor the mechanism of the formation of ODEs is completely understood. Here, by considering an additional bromine source from sea ice (through blowing snow events), we can successfully reproduce some of observed BEs in a 3D global transport model, pTOMCAT. Modelled tropospheric BrO compares well, in general, with the tropospheric BrO column retrieved from the GOME satellite instrument. Observed surface ozone data, e.g. at Halley, are also compared with the simulations to further validate the mechanism of bromine release and investigate the condition for surface ODEs. Cases with large BEs over Weddell Sea are chosen for specific comparison.

Please list some keywords:

Model ozone depletion bromine explosion blowing-snow

Lunch and Poster / 24**BRDF measurements of the spectral reflectivity of Antarctic sea-ice: The first results from the deployment of the GRASS system.****Author:** Martin King¹**Co-authors:** Alasdair MacArthur ²; Corrado Fragiaco ³; Flavio Parmiggiani ⁴; Holly Reay ⁵; Nigel Fox ⁶; Zirbordi Giuseppe ⁷¹ *Royal Holloway University of London*² *NERC FSF, Edinburgh, UK*³ *OGS, Trieste, Italy*⁴ *ISAC-CNR Bologna, Italy*⁵ *RHUL*⁶ *National Physics Laboratory, UK*⁷ *GEMU, JRC, Ispra***Corresponding Author:** m.king@es.rhul.ac.uk

Spectral BRDF visible measurements of the Antarctic sea-ice around Terra Nova bay, Antarctica are presented. The BRDF is compared to the physical structure and chemical content of the ice. Satellite observations allow for the synoptic observation of large areas of the globe. However, the reflectance of natural surfaces is not isotropic. The reflectance varies with the illumination and viewing geometries, and consequently impacts satellite observations. Thus the bi-directional reflectance (BRDF) of natural surfaces is a pre-requisite for use of satellite data. Sea-ice is a strong potential calibration

target. BRDF of snow surfaces is also important for the calibration of optical space sensors, and the Antarctic continent is a proposed calibration site. The results presented here are some of the first results from the new GRASS system (Gonio Radiometer Spectrometer System) built by NPL, loaned from NERC FSF, and to be field deployed at DOME C next year. The sea-ice has a strong forward scattering component, which is weaker for bare ice.

Please list some keywords:

sea ice snow reflectivity satellite BRDF albedo black carbon

Lunch and Poster / 25

Can HULIS and Black carbon explain the absorption properties of Polar snows and their effects on the rate of photo-production of radicals in the snowpack?

Author: Martin King¹

Co-authors: Alasdair MacArthur²; Cort Anastasio³; Didier Voisin⁴; Florent Domine⁴; Ghislain Picard⁴; Hans-Werner Jacobi⁵; Harry Beine³; Holly Reay⁶; J Erbland⁴; James France⁶; Joel Savarino⁴; Julia Lee-Taylor⁷; Markus Frey⁸

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The climatology and photochemistry of snowpack is dependent on the optical properties of snowpack. Nanogram quantities of light absorbing compounds in a single gram of snow can reduce the albedo, light penetration depth and photochemical production of chemicals such as hydroxyl radicals and nitrogen dioxide within the snowpack. We will present results from the Arctic (Barrow) and Antarctic (Dome C) demonstrating that the light absorbing compounds in snowpack are consistent with a HULIS/HUMIC component and a black carbon component. The contrast between the clean Dome C (Antarctica) and the dirty Barrow (Arctic) snowpacks is striking, but the same components can explain all the absorption behavior. We will demonstrate how increasing or decreasing the black carbon content of the snow reduces snow photochemical production, albedo and light penetration depth for shortwave solar radiation. The work is from two papers that are to be shortly submitted

Please list some keywords:

photochemistry nitrate hydrogen peroxide black carbon HULIS absorption radiative-transfer hydroxyl

Lunch and Poster / 26

Investigation of boundary layer photochemistry at the WAIS-Divide site through measurement of major photochemically active species in snow and air

Author: Sylvain M. Masclin¹

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Interactions between the polar snowpack and the overlying troposphere impact boundary-layer photochemistry and preservation of deposited atmospheric chemical species in snow. The potential of the polar snowpack to act as an H₂O₂ reservoir and its potential to emit NO_x (NO+NO₂) from nitrate photolysis in the near-surface snowpack were recently suggested as important factors in altering the oxidative composition of the lower portion of the overlying troposphere.

Measurements of major photochemically active species: nitric oxide (NO), ozone (O₃), hydrogen peroxide (H₂O₂), nitrate (NO₃⁻) were made during the 08-09 WAIS-Divide campaign. Overall values were in the range of those measured above the West Antarctic Ice Sheet during the ITASE traverses. Measured NO levels confirmed those estimated by previous photochemical box model runs (Frey et al., 2005).

Assuming a boundary-layer height of 100 m, we estimated a NO_x flux from the snowpack and compared the result with our atmospheric record. We found that NO_x emission from the snowpack contributes to up to 40% of the atmospheric nitric oxide at the WAIS-Divide site. Observed specific ozone events at WAIS Divide and at South Pole combined with back-trajectory analyses suggest that outflows from the East Antarctic Plateau also significantly impact the boundary-layer chemical composition at WAIS Divide.

Please list some keywords:

Photochemistry; Antarctica; WAIS-Divide; NO_x; NO₃; H₂O₂; Ozone; Snow emissions; Troposphere

Lunch and Poster / 27

The Effect of Liquid-Like Layers on the Interaction of Nitric Acid with Ice Surfaces

Author: Samar Moussa¹

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¹ *Columbia University*

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The “quasi-liquid layer”(QLL) is a nanoscale region of surface disorder that exists near the melting point of ice (-30°C). The presence of this layer is believed to affect gas-ice interactions, uptake coefficients and heterogeneous chemistry in the polar regions. It is also believed that gas-ice interactions can modulate the QLL thickness and induce its formation at temperatures below -30°C.

Characterization of gas-QLL interactions is a prerequisite for a better understanding of chemistry in the polar regions and gives more accurate insights to polar atmospheric and climate models. We report results for the interaction of HNO₃ with zone-refined ice. The QLL layer formation and thickness were determined using ellipsometry. Uptake coefficients were determined using a coated-wall flow tube coupled with chemical ionization mass spectrometry. Experimental data were tested

against a thermodynamic model developed in our lab for the QLL on pure ice and on ice with impurities.

Please list some keywords:

Zone refined ice, QLL, BL, nitric acid, ellipsometer, thickness

Lunch and Poster / 28

Modelling of the interaction of halogenated molecules with the ice surface

Author: Céline TOUBIN¹

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The interaction between ice and halogenated species has received much attention in the past few years in the context of atmospheric chemistry and ozone depletion. Much theoretical and experimental work has been carried out in order to understand the HX (X=Cl, Br···) behaviour (adsorption or ionization) at the ice interface. Up to now, very few studies have been dedicated to photolytic processes occurring at the interface.

The work we present here concerns the dynamics and the photodissociation of halogenated molecules (HCl, Cl₂, CH₃Cl···) adsorbed at the ice surface by means of classical and quantum dynamical calculations.

Please list some keywords:

modelling, halogens, dynamics, photodissociation, adsorption

Lunch and Poster / 29

Exploring high resolution measurements of ozone depletion chemistry in coastal Antarctica through use of a 1D marine boundary layer chemistry model (MISTRA)

Author: Zak Buys¹

Co-authors: Anna Jones ¹; David Tanner ²; Greg Huey ²; Neil Brough ¹; Roland von Glasow ³

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Tropospheric Ozone Depletion Events (ODEs) have been known, for over 20 years, to occur in polar regions. During such events, ozone concentrations can fall from background amounts to below instrumental detection limits within a few minutes and remain suppressed for on the order of hours to days. The chemical destruction of ozone is driven by halogens (especially bromine radicals) that

have a source associated with the sea ice zone. Although our knowledge of ODEs has increased greatly since their discovery, some of the key processes involved are not yet fully understood.

In 2007, year round measurements were made at the British Antarctic Survey station Halley, in coastal Antarctica, using a Chemical Ionisation Mass Spectrometer (CIMS). During specific periods in the spring the CIMS was configured to measure concentrations of BrO, Br₂ and BrCl. In addition, concurrent measurements of surface ozone and local meteorology were made.

A 1D Marine Boundary Layer (MBL) chemistry model (MISTRA; von Glasow et al, 2002) has been modified to be representative of Antarctic conditions by implementing measurements from Halley station which include; aerosol size distribution and composition (Rankin and Wolff, 2003), local meteorology (Anderson et al., 2008), and chemistry in the model.

We present here an analysis of these datasets in terms of the broader meteorological situation at play during the onset and termination of ODEs, in a move towards developing a generalised picture for ODEs at Halley. In order to explore halogen release, we use the MISTRA model (in box model mode) to consider emissions from a specific source region, identified using HYSPLIT air parcel back trajectories.

Please list some keywords:

ozone depletion, halogen, MISTRA, Halley, Antarctica

Lunch and Poster / 30

Reactive nitrogen chemistry in surface snow during the OASIS spring campaign 2009 at Barrow, AK

Author: Hans-Werner Jacobi¹

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It is well known that nitrate in snow is transformed into nitrogen oxides under the influence of solar radiation. However, this process involves multiple physico-chemical steps. One important reactive intermediate is nitrite. To investigate the transformation of nitrate in the snow, we collected surface snow samples every 2 hours for a 36-hour period during the OASIS spring campaign 2009 at Barrow, AK. The samples were analyzed for the compounds nitrate, nitrite, and hydrogen peroxide. Photolysis rates of these compounds in the surface snow were calculated using radiative transfer modeling. We used the photolysis rates to calculate production and destruction rates for nitrite indicating that observed concentrations were significantly higher than expected from simple photostationary state calculation. Under these conditions, nitrite can also constitute an important source of OH radicals in the snow besides the photolysis of hydrogen peroxide and nitrate.

Please list some keywords:

Nitrate - nitrite - Barrow 2009

Lunch and Poster / 31

Chemical composition of the snowpack during the OASIS spring campaign 2009 at Barrow, AK

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During the OASIS spring campaign 2009 at Barrow, AK, the chemical composition of the snowpack was investigated. More than 110 snow samples including all snow types normally encountered in the snowpack of Alaska's Arctic Coastal Plain were collected and analyzed regarding major and minor sea salt components. For all species neither distinct temporal trends nor vertical profiles could be determined. However, a clear relationship between the composition and the snow types becomes obvious. All species show lower concentrations in fresh snow or surface hoar / diamond dust snow samples compared to blowing snow or older deposited snowpack types like windpacked snow or depth hoar. Sea salt components like chlorid, sodium, and potassium exhibit concentration ratios similar to standard seawater ratios throughout most of the samples. Blown and older deposited snow types are depleted in sulfate and enriched in magnesium and calcium compared to standard sea water. While the enrichments are probably due to additional input from continental dust, the sulfate depletion may be caused by the precipitation of mirabilite during sea ice formation. Bromide concentrations are higher than the standard sea water ratio in the fresh snow and surface hoar / diamond dust samples, but also in the depth hoar. A fraction of the deposited snow types show signs of bromine depletion. Nitrate and ammonium concentrations are much less variable compared to the sea salt components. This different behavior of the investigated species point to different sources like sea salt aerosols from marine sources, dust from continental sources, and deposition of volatile species from the gas phase.

Please list some keywords:

Snow types - composition - Barrow 2009

Lunch and Poster / 32

Nitrate and Protons at the Air-Ice Interface

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We used surface-sensitive spectroscopic methods to study the air-ice interface, with a focus on two species: nitrate (NO_3^-) and protons (H^+). Nitrate ions at the surface of frozen $\text{Mg}(\text{NO}_3)_2(\text{aq})$ samples were directly measured using glancing-angle Raman spectroscopy. Protons at the surface of frozen water samples, whose pH was adjusted using HNO_3 , HCl , NaOH or NH_4OH , were indirectly measured using glancing-angle laser-induced fluorescence and the pH-sensitive fluorescent molecule, acridine. Results suggest that although nitrate is excluded to the ice surface, its surface concentration is much lower than that predicted using the bulk phase diagram. The amount of nitrate excluded to the air-ice interface was not temperature dependent over the range 263 - 273 K. Preliminary results also suggest that protons, while present at the air-ice interface, are not excluded there from the bulk: the pH obtained at the air-ice interface of frozen solutions is the same as that of the solution prior to freezing. This study has important implications for understanding a) snowpack nitrate photolysis which leads to fluxes of NO_x and HONO to the overlying boundary layer and b) pH-sensitive heterogeneous processes occurring on ice, such as bromide activation.

Please list some keywords:

ice, snow, surface, nitrate, pH, Raman, laser-induced fluorescence, phase equilibrium

33

1D multiphase modeling of NO_x and halogen photochemistry at Summit, Greenland using MISTRA-SNOW

Author: Jennie Thomas¹

Co-authors: Barry Lefer²; Jack Dibb³; Jochen Stutz⁴; L. Greg Huey⁵; Roland von Glasow⁶

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Motivated by observations of reactive halogens and NO_x at Summit, Greenland in the center of the Greenland ice sheet we have developed a 1D model for snow physics and chemistry. This model has been coupled to the boundary layer model MISTRA, which includes detailed multiphase chemistry in the atmosphere and snow. We have developed the model with the goal of understanding how chemical species evolve with time in the interstitial air and to study the interplay between the chemistry in and above the snow.

Measurements of gas phase bromine species were undertaken as part of the GSHOX field campaign, conducted during summer 2007 and 2008 at Summit Research Station on the Greenland ice sheet. We compare model results with data collected from the field including meteorology, as well as observed NO and BrO mixing ratios. We have found that both ambient NO and BrO mixing ratios can be explained by fluxes out of the snow pack.

The methodology for modeling the multiphase in-snow chemistry will be presented along with results from the model, including vertical profiles of halogens in the snow pack and in the atmosphere along with their evolution in time.

Please list some keywords:

Halogen, chemistry, Greenland, Summit, model, snow

Lunch and Poster / 34

Greenland Summit HO_x/Halogen Experiment: 2007 and 2008

Author: Jennie Thomas¹

Co-authors: Barry Lefer²; Christine Haman³; Donald R. Blake⁴; Jack Dibb⁵; Jin Liao⁶; Jochen Stutz⁷; L. Greg Huey⁶; Steve Brooks⁸

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Reactive halogens in Arctic regions and their impact on ozone levels have been a subject of extensive research since the mid 1980s. In particular, studies have focused on coastal regions close to first-year sea ice. Less is known about halogens in more remote regions, such as the Greenland ice sheet. Motivated by indirect evidence of halogen chemistry, two field campaigns have been conducted at Summit, Greenland (altitude 3.2 km, latitude = 72.55°N), in May/June 2007 and June/July 2008. The purpose of these studies was to measure air and snow properties with a particular focus on halogen and HOx chemistry at Summit.

Measurements of gas phase soluble bromide as well as Differential Optical Absorption Spectroscopy (DOAS) and Chemical Ionization Mass Spectrometer (CIMS) confirm the presence of gas phase reactive bromine at Summit. The most likely source of gas phase bromine is activation of Br⁻ in the snow followed by release of active Br to the overlying air, despite the relatively small concentrations of Br⁻ compared to the coastal Arctic. Mixing ratios of soluble bromide and BrO above the snow were also found to be small (with maxima of ~4 ppt). This amount of bromine can oxidize and contribute to deposition of long-lived gaseous elemental mercury and may perturb HOx partitioning. A complete description of the experimental set up including the micrometeorological situation at Summit during the campaigns will be presented.

In order to understand the chemical and physical processes occurring during these field experiments we have also developed a 1D model for snow physics and chemistry, coupled to the boundary layer model MISTRA. The model indicates that the observed bromine can be explained by photochemical release from the snow pack.

Please list some keywords:

Summit, GSHOX, halogen, NOx, photochemistry, snow

Lunch and Poster / 35

Simulating the fate of cryospheric mercury

Author: Dorothy Durnford¹

Co-authors: Andrei Ryjkov ¹; Ashu Dastoor ²; Daniel Figueras-Nieto ²

¹ *Independent researcher*

² *Environment Canada*

The fate of mercury deposited onto snow- and ice-covered surfaces is of critical importance for atmospheric mercury models. At high-latitudes, springtime Atmospheric Mercury Depletion Events (AMDEs) are accompanied by important deposition of oxidized mercury to the cryosphere. A significant portion of the deposited mercury may revolatilise from the cryosphere rapidly. However, a combination of physical and chemical environmental factors may trap a substantial portion of the deposited mercury within the cryosphere for an extended period of time. During snowmelt, the cryospheric mercury may enter the snowpack's meltwater. The subsequent emission of mercury from the snowpack's meltwater can be an important source of atmospheric mercury. Indeed, it is possible that the high-latitude summertime increase in the concentration of surface-level atmospheric gaseous elemental mercury is caused by significant emission of mercury from cryospheric

meltwater. To simulate these various processes, a new atmosphere/cryosphere parameterisation has been developed for atmospheric mercury models. This parameterisation predicts the concentrations of elemental and oxidised mercury in the snowpack surface layer, the underlying snowpack, and the snowpack meltwater. Emission of elemental mercury from the snowpack and its meltwater to the atmosphere is represented.

In this presentation, we will describe the developed snowpack/meltwater mercury model. This parameterisation has been incorporated into Environment Canada's atmospheric mercury model, the Global/Regional Atmospheric Heavy Metals model (GRAHM). We will discuss the performance of the updated GRAHM. We find that the addition of the snowpack/meltwater model significantly improves the seasonality of GRAHM's simulated surface-level atmospheric gaseous elemental mercury concentrations.

Please list some keywords:

mercury cryosphere emission fate AMDE snowmelt

Modeling Workshop / 36

Reactive halogen release from the polar snowpack and the depletion of ozone and mercury in the air: Insights from 1-D (mechanistic) and 3-D (chemical transport) models

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¹ York University / Environment Canada

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Reactive halogens, especially bromine, are known to play a major role in the rapid loss of both ozone and gaseous elemental mercury (GEM) in the polar boundary layer during the spring. Measurements of relevant chemical species in the field and from satellites have shown that reactive bromine is released to the high-latitude atmosphere extensively and most notably from the ice-covered ocean. However, there are a lot of open questions with regard to (micro-) physical and chemical mechanisms behind the occurrence of the high bromine content in the polar snow and the movement and transformation of bromine (and chlorine and iodine as well) between seawater, sea ice, snowpack and atmosphere.

In this talk, we first present the status of our development of a 1-D mechanistic model (PHANTAS, a model of PHotochemistry ANd Transport in Air and Snowpack), which describes the two-way transport of trace gases between the snowpack and the overlying atmosphere as well as their photochemical reactions in the gas phase and in the condensed phase of aerosols and snowpack. Vertical diffusivity in the lowest hundred meters of the atmosphere is diagnosed empirically from surface wind speed and heat flux. Gas transport in the snowpack interstitial air is represented by a combination of molecular diffusivity and wind-pumping advection. Model simulations show that strong surface winds, as well as promoting turbulent mixing in the boundary layer, also lead to the pumping of air in and out of the snowpack with the consequent release of reactive halogens. Ozone and GEM are both lost rapidly via reactions with bromine atoms in both the atmospheric boundary layer and the snowpack interstitial air while the level of the bromine activation in the snowpack is highly sensitive to the assumed fate of key radical species against gas-to-snow uptake. The effect of dissolved organic matters (DOMs), in reducing the oxidized mercury back into elemental form, is represented by a combination of one-step, first-order photolysis reactions of mercury-DOM complexes of varying stability. The sensitivity of model results to the initial concentration profiles of

halides and DOMs in the snow as well as to the type of DOM–mercury interactions is explored in order to provide insights into the fate of mercury after its deposition to the polar snow.

We also present results from a 3-D model (GEM-AQ) with a simple representation of air-snow chemical interactions to study reactive bromine production and ozone depletion in the Arctic boundary layer (Toyota et al., 2011, ACP). A set of sensitivity experiments have been performed to explore the effects of temperature and the age of sea ice (first-year, FY, versus multi-year, MY) on the release of reactive bromine to the atmosphere. The model simulations capture much of the temporal variations in the surface ozone mixing ratios as observed at stations in the high Arctic and the synoptic-scale evolution of “BrO clouds” in the lower troposphere as estimated from satellite observations. In this work it was suggested that reactive bromine is released ubiquitously from the snow on the sea ice during the Arctic spring while the timing and location of the bromine release are largely controlled by meteorological factors but through the transport of ozone to the surface air over the snow/ice surface. The evaluation of the various simulations indicated, although moderately, the likelihood that physical and/or chemical conditions on the FY sea ice are more advantageous for bromine release relative to the conditions on the MY sea ice, as suggested previously by Simpson et al. (2007). Also, if indeed the surface snowpack does supply most of the reactive bromine in the Arctic boundary layer, it appears to be capable of releasing reactive bromine at temperatures as high as -10 degree Celsius, particularly on the sea ice in the central and eastern Arctic Ocean.

Please list some keywords:

Ozone, bromine, mercury, snowpack, Arctic, Sea ice, GEM-AQ, PHANTAS

Lunch and Poster / 37

Probing the liquid-like surface of frozen salt solutions via infrared spectroscopy

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While the surfaces of ice, snow, and sea ice are known to act as chemical processors that perturb the local atmosphere, the morphology, dynamics, and reactivity of the surface and near-surface regions are not well known. We present a method for studying the near-surface region of frozen aqueous films in the laboratory. Attenuated total reflection infrared spectroscopy (ATR-IR) enables study of the near-surface region of ice near its melting point without interference from water vapor. ATR-IR spectra of frozen NaCl solutions at -8°C show that there is a liquid-like brine layer that increases in depth with NaCl concentration. Additionally, reflection spectra of ice with a liquid layer were modeled from the Fresnel equations. By modeling reflection spectra as well as analyzing the experimental spectra, the thickness of the brine layer as a function of NaCl concentration has been estimated. Furthermore, a method for determining the acidity of the liquid-like layer has been developed, since acidity plays a key role in many reaction mechanisms. Preliminary results for measuring changes in acidity upon freezing for solutions containing nitrate will be presented.

Please list some keywords:

BL, brine layer, interface, depth, acidity, IR

Modeling Workshop / 38

Photolysis rates of nitrate, hydrogen peroxide and nitrite in Arctic and Antarctic snows: A field and modelling study

Author: Martin King¹

Co-authors: Alasdair MacArthur²; Cort Anastasio³; Didier Voisin⁴; Florent Domine⁴; Ghislain Picard⁴; Hans-Werner Jacobi⁴; Harry Beine³; Holly Reay⁵; J Erbland⁴; James France⁵; Joel Savarino⁴; Julia Lee-Taylor⁶; Markus Frey⁷

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Photolysis of chemicals within snowpacks can produce radical species that initiate oxidation reactions within the snowpack and may be responsible for chemical fluxes from the snowpack.

Photolysis rate coefficients as a function of solar zenith angle, snowpack depth and snowpack layer structure are reported using a radiative-transfer model constrained by field measurements of the solar reflectivity and light penetration depth measurements from the Arctic (Barrow) and Antarctic (DOME C). Photolysis rate coefficients and production rates are reported for photolysis of nitrate and hydrogen peroxide to produce OH radicals and nitrogen dioxide. Work will also be presented demonstrating the danger and significant error of not considering photochemistry at depth within the snowpacks. The effect of snow layering on photolysis rate and production rates will be shown for the Antarctic snowpack.

Please list some keywords:

photolysis photochemistry nitrate hydroxyl OH radical radiative transfer modelling

39

Carbonaceous species and Humic Like Substances in Arctic Snow: contribution to the speciation of total carbon and optical properties during OASIS –Barrow 2009 campaign.

Author: D. Voisin¹

Co-authors: A. Grannas ; F. Dominé ; H. J. Beine ; H.-W. Jacobi ; J. -L. Jaffrezo ; M. Barret ; S. Houdier

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Carbonaceous species play critical roles in the interaction of snow with the overlying atmosphere. Elemental or Black Carbon strongly decreases snow albedo, therefore influencing the snow-climate feedback loop. Carbonyls and complex organic molecules such as Humic Like Substances also absorb UV and visible light, therefore influencing photochemistry and light penetration depths in the snowpack. It has been proposed that some of those complex organic molecules, acting as electron donors in photochemical reactions might change the photolysis paths of nitric acid from NO / NO₂ to HONO. Yet, global investigations of the organic matter in arctic snowpack are scarce, and often limited to a few specific species.

During the OASIS campaign in Barrow, 2009, we investigated the global carbonaceous content of continental snowpack. On most samples, analysis included Dissolved Organic Carbon, short chain

mono and di-carboxylic acids (ion chromatography), and some aldehydes (LC-fluorimetry). Additional samples were also analyzed for EC and Water Insoluble Organic Carbon. This enables to discuss the contribution of various carbon fraction to the total carbon load of the snowpack, as a function of snowtypes

A small subset of samples was used to isolate HULIS fraction. Their carbon content was measured together with their UV-Vis absorption spectrum. This enables us to calculate spectral mass absorptivities for HULIS in snow and the contribution of HULIS to the total absorbance measured separately on melted snow samples, and to discuss their potential contribution to snow photochemistry.

Please list some keywords:

organic matter carbon Barrow

Lunch and Poster / 40

Liquid-like layers on ice in the environment: bridging the quasi-liquid and brine layer paradigms

Author: Min H. Kuo¹

Co-authors: Samar G. Moussa ; V. F. McNeill

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Liquid-like layers on ice significantly influence atmospheric chemistry in polar regions. In the absence of impurities a nanoscale region of surface disorder known as the “quasi-liquid layer”(QLL) may exist at temperatures well below the bulk melting point (down to ~-30°C). Surface and bulk impurities are known to modulate the QLL thickness. In aqueous systems containing ionic solutes a liquid brine layer (BL) may form upon freezing due to the exclusion of impurities from the ice crystal lattice coupled with freezing point depression in the concentrated surface layer. Brine layers are conceptually distinct from the QLL, which can exist in the absence of impurities.

We have developed a unified model for liquid-like layers in environmental ice systems that is valid over a wide range of temperatures and solute concentrations, spanning the QLL and BL regimes. The model consists of two coupled modules describing the thickness of the BL and the QLL. The BL module is derived from fundamental equilibrium thermodynamics, whereas the QLL formulation is derived semi-empirically based on statistical mechanical principles and previously published QLL thickness data. The resulting unified model has been tested against experimental data from literature and applied to several environmentally important systems, such as HCl(g)-ice, HNO₃(g)-ice, and frozen sea ice. This model can be used to improve the representation of air-ice chemical interactions in polar atmospheric chemistry models.

Please list some keywords:

QLL brine modeling

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Can detailed oxidation kinetics indicate where reactivity occurs in ice?

Author: Jon Abbatt^{None}

One of the significant challenges to the ice chemistry community is to identify the medium in which reactive chemistry occurs, ie. on a QLL surface, in an associated brine, or in the bulk ice, and how

fast it occurs in each medium. This talk will present the results from two reactive systems which help to identify the location of the reactive chemistry. In particular, detailed kinetics will be presented for: i) the heterogeneous oxidation of bromide by gas-phase ozone in both liquid and frozen salt solutions, and ii) the oxidation of succinic acid in liquid and frozen solutions, by photolytically generated hydroxyl radicals. In the case of ozone/bromide, the kinetics indicate that both a surface and bulk phase reaction occur simultaneously with kinetics very similar between the frozen and liquid solutions. This suggests that brine chemistry is dominant. For the case of succinic acid, the unfrozen solution kinetics are substantially faster than for the frozen solutions, suggesting that the reactants are physically separated in the ice.

Please list some keywords:

halogen oxidation ice

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Welcome & Scope & Reviews

Authors: Jon Abbatt¹; Thorsten Bartels-Rausch²; V. Faye McNeill³

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What the meeting is for, presentation of the 3 review papers, info on local arrangements

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Marcello Guzman: organics - mechanism

Author: Michael Hoffmann¹

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short discussion

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short discussion

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short discussion

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Discussion: Representing physical and chemical processes on the micro scale in models

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Discussion: Radiative transfer and photolysis rates in snow

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L. Ganzevled: Global modeling

Modeling Workshop / 56

Discussion: representing processes in the snow in global models

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Summary + Outlook

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General Discussion and questions

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General Discussion about Review Paper

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Writing teams can meet separately

61

Meeting ends: Summary & Deadlines

63

Perspective on Halogens

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Modeling Workshop / 64

Parameterizing Trace Gas - Ice Interactions: A look into laboratories

Author: Thorsten Bartels-Rausch¹

Co-authors: Markus Ammann¹; Michael Kerbrat¹; Sepp Schreiber¹; Thomas Ulrich¹

¹ *Paul Scherrer Institut*

Corresponding Author: thorsten.bartels-rausch@psi.ch

Recent laboratory experiments that investigated the interaction of atmospheric trace gases with ice surfaces under tropospheric conditions are presented. Key-Questions are

- a) the importance of surface versus bulk uptake of trace gases
- b) the effect of trace gas adsorption on the quasiliquid layer
- c) the influence of the presence of an additional, coadsorbing trace gas on the uptake

I will also shortly address how the laboratory results are usually described mathematically and compare this to the parameterization in recent 1-D snow-pack models.

Please list some keywords:

Langmuir Henry Adsorption QLL

Lunch and Poster / 65

The Adsorption of HO₂NO₂ on Ice

Author: Thomas Ulrich¹

Co-authors: Markus Ammann¹; Samuel Leutwyler²; Thorsten Bartels-Rausch¹

¹ *Paul Scherrer Institut*

² *University of Berne*

Nitrogen peroxides, such as peroxyntic acid (HO₂NO₂) act as reservoir for atmospheric NO_x and HO_x species and thus impact the oxidative capacity of the atmosphere. Mixing ratios of HO₂NO₂ in the range of 76 pptV have been measured in the upper troposphere. The presence of ice in cirrus clouds there may represent a major sink for HO₂NO₂, yet little is known about the partitioning to ice particles of this trace gas.

In this study, the partitioning of HO₂NO₂ between the atmosphere and ice was investigated by coated wall flow tube experiments in the temperature range of -45 °C to -20 °C. The detection was done with a chemical ionization mass spectrometer, using SF₆- as ionizing species, allowing for mixing ratios of HO₂NO₂ of around 2-3 ppbV during the experiments.

The temperature dependence of the equilibrium partitioning constant of HO₂NO₂ between air and ice was determined. The partitioning of HO₂NO₂ between air and ice is compared to the IUPAC recommendations for HNO₃; the partitioning coefficients of HO₂NO₂ were found to be orders of magnitude lower than the ones for HNO₃. The adsorption of HO₂NO₂ on ice proved to be fully reversible, as determined by desorption experiments. Further, the atmospheric implications are discussed.

Please list some keywords:

HNO₄

Modeling Workshop / 66

Development of a mechanistic representation of snow-atmosphere exchange of reactive compounds for implementation in large-scale models

Author: Laurens Ganzeveld¹

¹ *Earth System Sciences - Climate Change group, department of Environmental Sciences, Wageningen University and Research Centre, Wageningen, Netherlands*

Research on snowpack processes and atmosphere-snow gas exchange has demonstrated that chemical and physical interactions between the snowpack and the overlaying atmosphere have a substantial impact on the composition of the lower troposphere. These observations also imply that deposition, e.g. of ozone to the snowpack and the potential release of reactive oxidized nitrogen, NO_x, possibly depends on parameters including the quantity and composition of deposited trace gases, radiation, snow pack physical properties and the substrate below the snowpack. Such dependencies are not yet considered in large-scale models where the representation of snow-atmosphere exchanges is generally ignored or limited to the use of constant uptake rate approaches. The snowpack is deemed by many of the atmospheric chemistry community to be an inert medium only relevant in terms of its albedo and low temperatures. This is also supported by the fact that observed dry deposition velocities, e.g., that of ozone (V_dO₃) are small, typically a factor 40 smaller than removal rate over tropical forests. However, sensitivity analysis using a range of V_dO₃ has demonstrated that simulated surface layer ozone concentrations over snow are highly sensitive to small changes in V_dO₃ due to the long timescales of turbulent transport and chemical transformations.

Results from field campaigns have revealed interesting chemical cycling inside and above the snowpack that should be considered in order to ensure a fair evaluation of the simulated chemistry over the Earth's snow- and ice covered regions. It would require the development of a more mechanistic representation of the exchange of reactive compounds between the snowpack and the atmosphere

as a function of micrometeorological drivers and snowpack physical and chemical properties. However, an essential prerequisite of such a mechanistic snow-atmosphere exchange representation is its simplicity to accommodate its application in large-scale atmospheric chemistry models. Development of such a mechanistic snow-atmosphere exchange model is one of the goals of our current research. This work also includes field observations of in-snowpack and surface layer chemistry and fluxes for O₃ and NO_x at a midlatitude seasonal snow site (Niwot Ridge, CO), a polar site with permanent snow cover (Summit, Greenland) and snow cover over permafrost (Toolik Lake, AK). We will present results from the measurement campaign and model development and application.

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Comparison of Gas and Adsorbed Phase Photoemission Spectra of C₃H_xO on Ice at -45°C

Author: John Newberg¹

Co-author: Hendrik Bluhm¹

¹ *Lawrence Berkeley National Laboratory*

We present results of gas phase and adsorbed phase XPS and NEXAFS spectra of 1-propanol, 2-propanol, acetone, and 1-propanal on ice at -45°C using synchrotron based, ambient pressure X-ray photoemission spectroscopy. Uptake experiments give rise to Langmuirian isotherms. The two alcohols and acetone show little difference in the photoemission spectra between the gas phase and adsorbed phase, suggesting that adsorption occurs molecularly. However, adsorption of 1-propanal shows evidence of oxidation to an organic acid. Further studies are needed to understand this adsorption behavior.

Please list some keywords:

Laboratory, adsorption, trace gas, organics