

solas event report

Report 17 | March 2020

Open Science Workshop on:

Cryosphere and Atmospheric Chemistry (CATCH)

7-8 December 2019

Berkeley, California, USA



From 7th until 8th of December, the workshop of the International Global Atmospheric Chemistry (IGAC) activity Cryosphere and Atmospheric Chemistry (CATCH) sponsored by the Surface Ocean - Lower Atmosphere Study (SOLAS), IGAC, and International Arctic Science Committee (IASC) took place at UC Berkeley, California, USA.

CATCH is a community driven initiative and aims to foster research collaborations across scientific disciplines and national boundaries to advance knowledge on the chemical, physical/biological interactions and feedbacks within the coupled cryosphere-atmosphere system and implications for climate, ecosystems and society (Thomas *et al.*, 2019). The specific aims of this workshop were to discuss research challenges and identify the most urgent scientific needs within the community. Based on this input, community actions and strategies supported by CATCH were aimed to be developed.

In total, 44 scientists - one third being early career researchers - from 14 countries attended the workshop representing a wide range of science

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Figure 1: Participants of the Cryosphere and Atmospheric Chemistry (CATCH) workshop. Workshop organisers: Megan Willis, Jennie Thomas, Markus Frey, Thorsten Bartels-Rausch, Jochen Stutz, Manuel Dall'Osto, Paul Zieger, Daiki Nomura, Kerri Pratt, Jennifer Murphy. Workshop participants: Tomás Rafael Bolaño-Ortiz, Robyn Schofield, Bruno Delille, Nadja Steiner, Foteini Baladima, Louis Marelle, Niccolò Maffezzoli, Muhammad Zeeshan Shahid, Yanisha Manoharan, John Prytherch, Daun Jeong, Michal Segal Rozenhaimer, Peter Peterson, Lynn Russell, Jun Liu, Qianjie Chen, William Swanson, Cort Anastasio, Becky Alexander, Rebecca Michelsen, Yuan Gao, Paul Shepson, Laurence Yeung, Tony Hansen, Lyatt Jaeglé, Ted Hullar, Christopher Holmes, Isabel McCoy, Russ Schnell, Kenji ro Toyota, Mike Lawler, Kevin Worthington, Chi Li. © Kevin Worthington

disciplines (Figure 1). In addition, a remote participation was offered by providing a video link to the workshop. This was very well received and recommended as a standard feature of future workshops to help reduce the carbon footprint.

The workshop programme was divided into five different sessions (Aerosols and clouds, Atmosphere-cryosphere chemical interactions, Knowledge from ice core records, Microscale and process knowledge and Processes in urban and mountain regions). Each session included keynote lectures followed by 5-minute flash presentations on current research highlighting scientific challenges for the wider community. Furthermore, the programme contained oral and poster presentations, discussions in the plenary and in smaller breakout groups to achieve as much interaction and engagement as possible. During the first day, the session topics were further explored in breakout sessions to prioritise research needs and strategies to address them. A selection is summarised below.

Polar aerosol and clouds. To characterise polar aerosol and potential impact on cloud formation basic information is lacking, including chemical composition, properties of cloud condensation nuclei (CCN) and ice nucleating particles (INP), and size distributions; e.g. nanoparticles play a major role as cloud seeds in the Arctic and are partially linked to ice processes, but few measurements are available. Almost no observations exist during wintertime and vertical information is missing to link the surface to atmospheric layers, where clouds are formed. Ways forward should include multi-year measurements of aerosol chemical and CCN/INP properties and better spatial coverage of snow, sea ice, and ocean sampling to characterise surface particle sources. Finding unique tracers for sea ice aerosol origin would further constrain background particle contributions in the warming polar regions. It is agreed that more interdisciplinarity, for example by including ice specialists and atmospheric dynamicists, would benefit the coordination of campaign-based and continu-

ous long-term observations, the design of process-focused cloud-aerosol interaction studies and data interpretation. A linkage to process and climate models needs to be maintained to achieve progress.

Atmosphere-cryosphere chemical interactions. There is an urgent need of advancing science in this area as the cryosphere particularly in the Arctic is changing at a faster rate than scientists can understand the underlying processes that are changing as well. For example, with retreating Arctic sea ice relative contributions from local or remote sources of aerosol and trace gases will change dramatically, the biology of the coupled ocean-ice-air system will undergo change with impacts on direct particle emissions and the coupling between atmosphere and ocean will become more important. In order to achieve reliable model predictions of air quality in the polar environment complete process studies are needed in the field supported by sea ice chamber experiments. Known uncertainties, which need to be addressed include improved measurements of fundamental properties of icy surfaces at the micro-scale such as the pH and the location of impurities and oxidants, as well as an improved process understanding. Only knowing the former will allow to assess e.g. the role of first year sea ice for reactive halogen chemistry and the evolution of polar tropospheric composition and feedbacks with air pollution in the next decades. However, next to halogens also cryosphere-atmosphere chemical cycles of sulfur, mercury and organic compounds need to be studied in depth, not highlighting how they are separate but understanding how they overlap. Sea ice, snow on sea ice but also polluted snow in urban environments will need to be studied. To understand the spatial impact of processes upscaling to regional and larger scales is needed possibly supported by relevant satellite measurements. A role for CATCH and SOLAS to play is to build consensus leading to an interdisciplinary proposal that can target these overlapping questions.

The cryosphere and climate change. The overarching questions are how cryosphere-atmospheric chemistry processes, interactions and feedbacks impact climate change and how their understanding may reduce uncertainties in model predictions of climate in the 21st century. Particular science questions discussed included: are the correct boundary conditions being used for model projections of sea ice and biogeochemistry and what elements are most important? Are all the relevant sources and sinks of aerosols and pollutants captured in models? Cryosphere-climate feedbacks work in both directions, e.g. one needs to ask not only how do sea ice emissions of trace chemical compounds affect climate but also how does climate change affect lifetimes of chemical species? And how does the interaction between a changing Arctic and human activities present its own feedback loop on local climate? Which changes in direct and indirect climate impacts of aerosol matter and can they be quantified using field observations of surface aerosol? It was recognised that involving ice core sciences in CATCH has mutual benefits: a better understanding of the coupling between macro- and microscale processes at present will be very useful to better interpret ice core records of past climate change. And vice versa involving ice core sciences will help understand modern change in comparing to analog changes in the past, at least for parameters, which have been established with some certainty (e.g. paleo-temperature, sea level). Practical approaches to address the above should include integrating “closure studies” with dynamics and radiation, comprehensive model/measurement inter-comparison projects to exploit existing data and to refine understanding, studies of fundamental processes to improve predictions of an uncertain future, and building collaborations of fundamental needs to empower community in front of funding agencies (e.g. SCOR).

From micro-scale chemical, biological and physical processes to regional cryosphere-atmosphere interactions. Fundamental process studies are continued to be needed for the microscale as well as smog-chamber equivalent studies. The key question remains to identify and characterise dominating reaction pathways that drive the large-scale chemical fluxes observed. In addition, well-controlled laboratory studies to characterise chemical processes in complex multiphase snow and ice are needed. Further, how to upscale these findings to models and field data was intensively discussed.

On day 2, workshop participants defined four areas of future CATCH activities and explored in respective breakout sessions specific community actions summarised below:

Field campaigns and long-term observations.

Recommended actions included (i) the planning and delivery of a research cruise by the CATCH and the Biogeochemical Exchange Processes at the Sea-Ice Interfaces (BEPSII) community with a geographic preference for the Southern Ocean/Antarctica and (ii) development of a list of essential and desirable baseline observations, which is shared among existing observatories worldwide.

Models. The need for modelling improvement by going through a hierarchy of models, including box/1-D, regional, and global Earth system models was clearly recognised. The long-term aim should be to develop models, which include the most important processes and couple all relevant domains: ocean, sea ice, snow and atmosphere. The main activities achievable in the short and mid-term that were proposed were (i) development of a CATCH community 1D-model that includes atmosphere/snow chemical interactions and (ii) coupling existing snowpack models with atmospheric models. It became clear that CATCH science is an Earth System science, whereas the CATCH community consists primarily of atmospheric chemists with participation from biogeochemists. Thus, physical cryosphere sciences

and hydrology will need to be involved more closely in order to achieve progress in modelling.

Data. Public data repositories as well as synthesis papers highlighting available parameterisations are hugely important for modellers. The CATCH network is ideally placed to make significant contributions to both resources. In order to make use of existing measurements it is recommended to develop a CATCH meta-repository that lists relevant data from existing national and international data archives.

Outreach. Important stakeholders that were highlighted, include the wider scientific community, the public and national or international funding agencies. It was recognised that it is of utmost importance to explain aims and relevance of CATCH to these stakeholders and a dedicated activity is required, which coordinates social media campaigns, stakeholder workshops or town hall meetings.

The workshop concluded with a final plenary session. There was consensus that the CATCH community is working in the context of rapid cryospheric change, and that there is a scientific and moral imperative to both document and understand that change including its impact on atmospheric composition and climate. Interdisciplinarity is key to address the research challenge, e.g. a 'flux' of information is needed between the communities of polar atmospheric chemistry, sea ice biogeochemistry and ocean sciences to understand the 'flux' of chemicals.

We thank the workshop sponsors, which enabled participation of so many young scientists, and all the participants to have come from near and far to join CATCH, to engage in truly cross-disciplinary and international dialogue and scientific discussions, which often require a lot more patience than talking to your specialist colleague.

The outcomes of this workshop contribute to advance our knowledge of the Core Theme 4 “Interconnections between aerosols, clouds, and marine ecosystems” and Cross-Cutting Theme “Integrated Topics” of the SOLAS 2015-2025 Science Plan and Organisation.

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Event website

<https://sites.google.com/view/catch-science/open-science-workshop>



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Isabel L. McCoy received a Bachelor of Science in physics from the New Mexico Institute of Mining and Technology, New Mexico before pursuing her graduate studies in atmospheric science at the University of Washington, Seattle, United States. Now as PhD candidate, Isabel investigates cloud-aerosol interactions in pristine, marine environments and low cloud feedbacks associated with cloud morphologies.

Are Southern Ocean low-cloud droplet numbers buffered by recently formed particles associated with synoptic uplift?

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Limited knowledge of pre-industrial (PI) aerosol is a leading driver of uncertainty in estimating the change in planetary albedo over the industrial period associated with aerosol cloud interactions (aci) (Carslaw *et al.*, 2013). This aci-associated change in albedo is the leading uncertainty source in inferring Earth's climate sensitivity to increased greenhouse gases from the historical record (Bellouin *et al.*, 2019). One way aerosols change liquid cloud albedo is by modulating the number concentration of cloud droplets (Nd), changing cloud reflectivity without changing cloud macrostructure (Twomey, 1977). Nd is the most direct measure of aci.

Examining the pristine Southern Ocean (SO) helps us to understand the PI state (Hamilton *et al.*, 2014) and to quantify cloud and aci characteristics in a region that has large radiative biases in climate models associated with production of overly-dim low clouds (Bodas-Salcedo *et al.*, 2016). The 2018 SOCRATES (Southern Ocean Cloud Radiation Aerosol Transport Experimental Study) aircraft campaign sampled summertime

clouds and aerosols across varied meteorological environments south of Tasmania (45-62°S), Australia.

Recent particle formation (RPF) was frequently observed in the free troposphere (FT, 3-6km). RPF events contribute to large concentrations of condensation nuclei (>1000/cc, diameter>10 nm) dominated by Aitken mode aerosols (10-100 nm). A novel synoptic-uplift mechanism for FT particle production is identified using observations, Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT) back-trajectories, and European Centre for Medium-Range Weather Forecasts (ECMWF) reanalysis (Figure 2). Air masses rich in dimethyl sulphide (DMS) are lofted through clouds associated with synoptic events, cleansed of aerosols, and released into the FT where DMS oxidises into pre-cursor gases (e.g. sulphuric acid) and gas-to-particle conversion occurs. This and a cumulus-outflow mechanism (Clarke *et al.*, 1998) will generate widespread SO FT particles. How do FT Aitken particles influence SO clouds? Nd (80-100/cc) is controlled by sub-cloud cloud

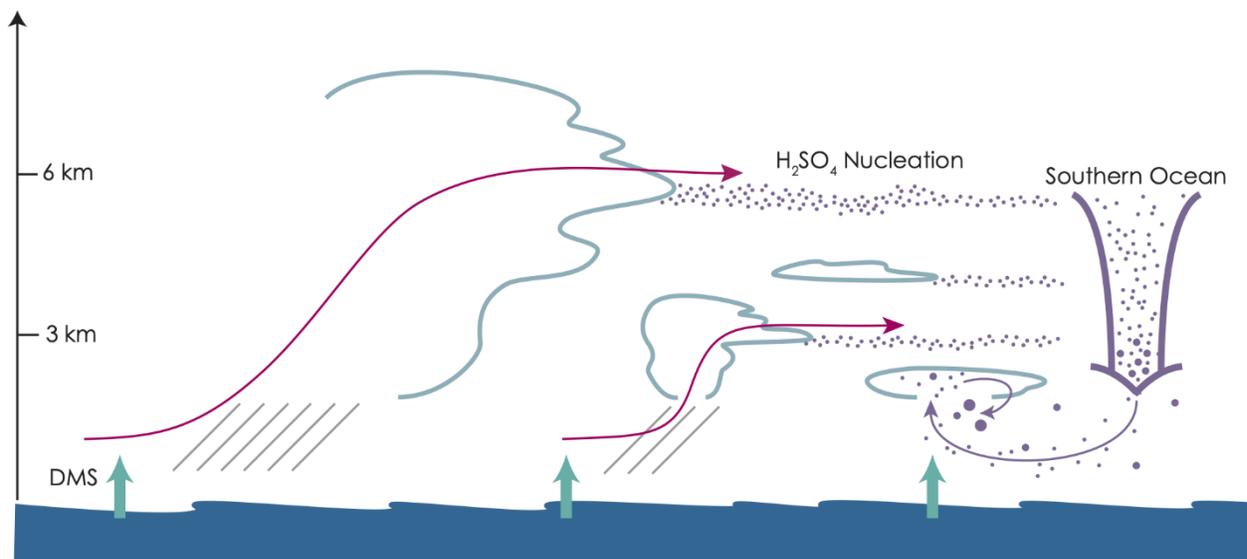


Figure 2: Synoptic-uplift mechanism for particle generation in Southern Ocean free troposphere after Clarke *et al.* (1998). DMS: dimethylsulfide, H_2SO_4 : sulphuric acid.

condensation nuclei (CCN, 100-1000nm), but direct emissions (i.e. sea salt) are not a large CCN contribution. In-, sub-, and above-cloud particle composition is primarily sulphur-based, consistent with growth from FT particles with H_2SO_4 composition signatures. Two hypotheses are developed for future testing: (i) Aitken particles from the SO FT significantly contribute to sub-cloud CCN by growing in- and sub-cloud, and (ii) the FT Aitken reservoir buffers SO clouds against precipitation depletion (i.e. Nd decreases), leading to persistently bright SO clouds.

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Yanisha Manoharan conducted her master studies in surface chemistry at the Swiss Federal Laboratories for Material Science and Technology (EMPA) in Switzerland. She started her PhD at the Paul Scherrer Institute (Switzerland) in 2019. Currently, she is investigating the photochemistry and acid-base chemistry of nitric acid at the air-ice interface.

Probing water and solutes at the air-ice interface using X-ray excited photoelectron spectroscopy

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Photolysis and oxidation of nitrogen oxides (NO_x = nitric oxide (NO) + nitrogen dioxide (NO_2)), that are emitted to the atmosphere by combustion, alter the hydroxyl radical (HO_x = hydroxy ion (OH) + hydroperoxy (HO_2)) budget and ozone production in the troposphere. Ozone in the troposphere has a negative impact on our respiratory system, and contributes to global warming as a greenhouse gas. One product of NO_x oxidation in the troposphere is nitric acid (HNO_3), which is then removed by wet and dry deposition (Finlayson-Pitts and Pitts, 2000). In polar regions, the release of NO_x and nitrous acid (HONO) to the atmosphere from surface snow, to which HNO_3 was deposited is an important process, that affects the HO_x and ozone production in these regions (McFall *et al.*, 2018).

My research work focuses on drawing a link between a detailed surface science investigation of HNO_3 adsorbed to ice with atmospheric chemistry. The scope is to investigate how the dissociation of HNO_3 at the ice surface impacts the interfacial photochemistry. Previous X-ray excited photoelectron spectroscopy (XPS) work from our

group showed that dissociation of acids at the air-ice interface is unique from that in aqueous solution (Křepelová *et al.*, 2013; Bartels-Rausch *et al.*, 2017; Kong *et al.*, 2017; Waldner *et al.*, 2018), illustrated in Figure 3 for the case of hydrochloric acid (HCl).

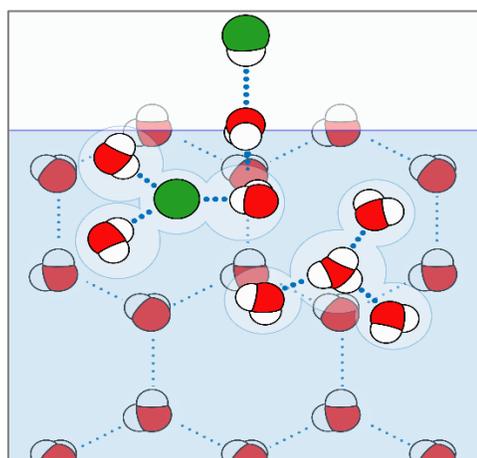


Figure 3: Scheme of the proposed acid-base chemistry at the air-ice interface. Physisorbed molecular hydrochloric acid (HCl), co-exists with solvated chloride ions (Cl^-) deeper in the quasi-liquid layer. Oxygen red, chlorine green, hydrogen white.

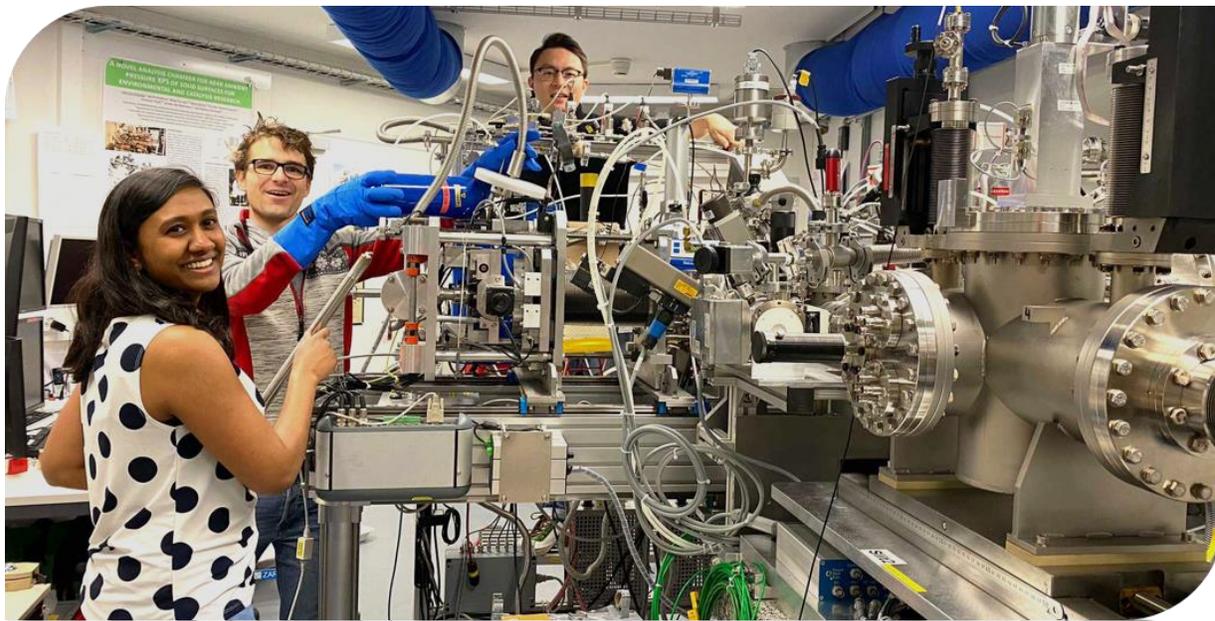


Figure 4: Photo of our team conducting X-ray excited photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) experiments in the solid-gas-interface-chamber at the Swiss Light Source in Switzerland. © Yanisha Manoharan

The dissociation of acids at the air-ice interface has been suggested to drive the strong partitioning of acids to ice surfaces (Zimmermann *et al.*, 2016). In this project, we focus on another impact of high relevance to atmospheric science: The interfacial dissociation.

Figure 4 shows a picture of the chamber at the Swiss Light Source in Switzerland (Orlando *et al.*, 2016), where we conduct our XPS and near-edge X-ray absorption fine structure (NEXAFS) experiments with nitric acid deposited on ice. While the flow tube experiments focus on the kinetics and product yields of the photochemical reactions on ice, surface characterisation is carried out by means of XPS, which allows us to differentiate between HNO_3 and nitrate (NO_3^-). NEXAFS is an established method to investigate the quasi-liquid-layer (QLL) at the ice interface, since the oxygen K-edge NEXAFS spectra of ice provide information about structural changes in the hydrogen bonding network.

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Qianjie Chen obtained his PhD in atmospheric sciences from the University of Washington Seattle, United States in 2017. He is currently a postdoctoral research fellow at the University of Michigan, United States in the laboratory of Prof. Kerri Pratt. His research involves tropospheric sulphur, halogen, and nitrogen chemistry, especially in the remote marine and cold environments. Qianjie has used a variety of techniques in his research, including the Goddard Earth Observing System (GEOS)-Chem global chemical transport model, isotope-ratio mass spectrometry, ion chromatography, and chemical ionization mass spectrometry.

Nitrous acid (HONO) production from snowpack nitrate photolysis in a mid-latitude urban environment

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Nitrous acid (HONO) plays an important role in the oxidative capacity of the atmosphere via photolysis to produce hydroxyl radicals (OH), especially in polluted regions during wintertime when nitrogen oxides are abundant and other photolytic OH sources are weak. In particular, during wintertime, solar intensity is low, and water vapour abundance is reduced at low temperatures, making OH production from ozone (O₃) photolysis inefficient. Yet, few studies have investigated the HONO budget in the mid-latitude snowy wintertime environment (Michoud *et al.*, 2015). Snow-covered ground is often associated with stable and shallow atmospheric boundary layers and high surface albedo for solar radiation, which affects the concentrations of trace gases and photochemical reactions (e.g., HONO photolysis) in the atmosphere. In addition, the snowpack can serve as a significant source of trace gases, including nitrogen oxides (NO_x), HONO, reactive halogens, and organic compounds (Grannas *et al.*, 2007). Snowpack nitrate photolysis has been proposed as an important HONO source in the Arctic (Zhou

et al., 2001). We conducted measurements of atmospheric HONO, particulate nitrite and nitrate, and snow nitrite and nitrate in Kalamazoo, Michigan during January-February 2018. Elevated levels of HONO were observed over snow-covered ground (Figure 5), likely due to emissions of HONO from the snowpack, as well as weak turbulent mixing in the atmospheric boundary layer. The noontime peak in HONO over snow-covered ground suggests significant photochemical snowpack HONO emissions, likely from snow nitrate photolysis, as previously observed in the Arctic (Zhou *et al.*, 2001). This is further supported by high snow nitrite concentrations (0.4±0.3 μM) and the positive correlation between snow nitrite and nitrate concentrations (Figure 6). By assuming HONO in contact with the snowpack undergoes adsorption equilibrium with nitrite at the snowpack surface (Jacobi *et al.*, 2014), HONO mole fractions of 1-10 parts per billion (ppb) are calculated at the snowpack surface, and are much higher than the HONO measured at 1.8 m above the snow-covered ground (60±44 parts per trillion

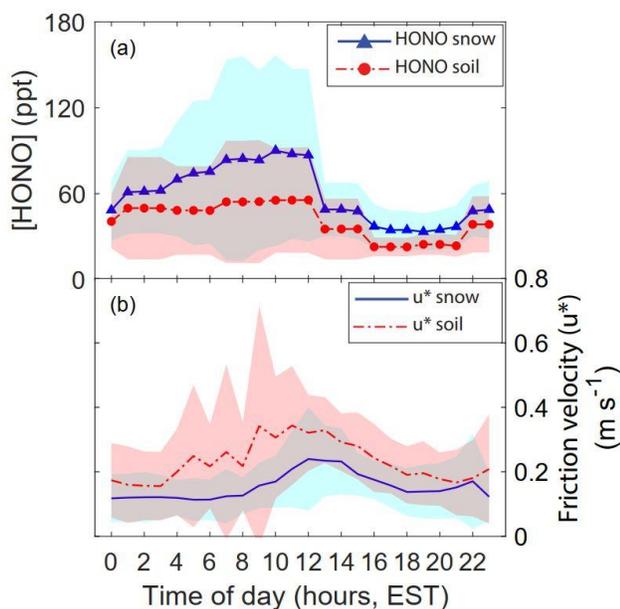


Figure 5: Diurnal patterns of average atmospheric (a) nitrous acid (HONO) mole fractions ([HONO]) and (b) friction velocities (u^*) for periods characterised by snow-covered (blue) and bare-soil ground (red). The standard deviations of [HONO] and friction velocity are shown as shading.

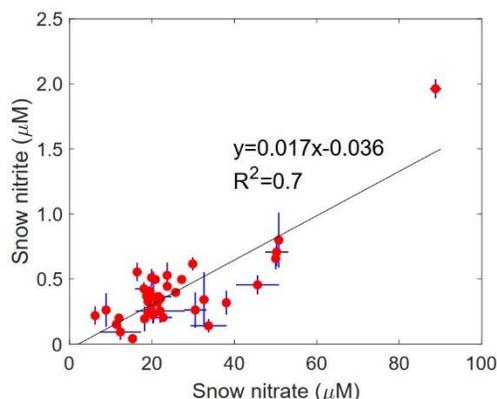


Figure 6: Snow nitrite concentration versus snow nitrate concentration for surface snow samples.

(ppt)), suggesting a large HONO emission from the snowpack to the ambient air.

Wintertime air pollution is often characterised by high fractions of particulate ammonium nitrate, often over snow-covered ground (Stanier *et al.*, 2012). As a consequence, the photolysis of nitrate

in aerosol particles and snowpack are expected to inject significant amounts of HONO and NO_2 into the near-surface atmosphere, thereby significantly influencing the oxidative capacity of the wintertime urban atmosphere. Our results show that the snowpack source is important for the HONO budget in the mid-latitude urban environment, in addition to the remote Arctic, and this suggests that this chemistry is likely important across snow-covered coastal and inland regions across the globe. This work was presented at the 2019 Cryosphere and Atmospheric Chemistry (CATCH) workshop in Berkeley, CA and published in *ACS Earth and Space Chemistry* (Chen *et al.*, 2019).

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