A novel spectroscopic approach for detection of chlorine reservoir species: HCl-TILDAS

John Halfacre[1], Pete Edwards[1], Jordan Stewart[1], Scott Herndon[2], Joseph Roscioli[2], Christoph Dyroff[2], Tara Yacovitch[2], Nicholas Marsden[3], Thomas Bannan[3], Carl Percival[3,4], Hugh Coe[3], Patrick Veres[5], and Steven Brown[5]

[1]University of York, Wolfson Atmospheric Chemistry Laboratories, Department of Chemistry, York, United Kingdom
[2]Aerodyne Research Inc, Billerica, MA, United States of America
[3]University of Manchester, School of Earth, Atmospheric and Environmental Sciences, Manchester, United Kingdom
[4]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, United States of America
[5]Earth System Research Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO, United States of America

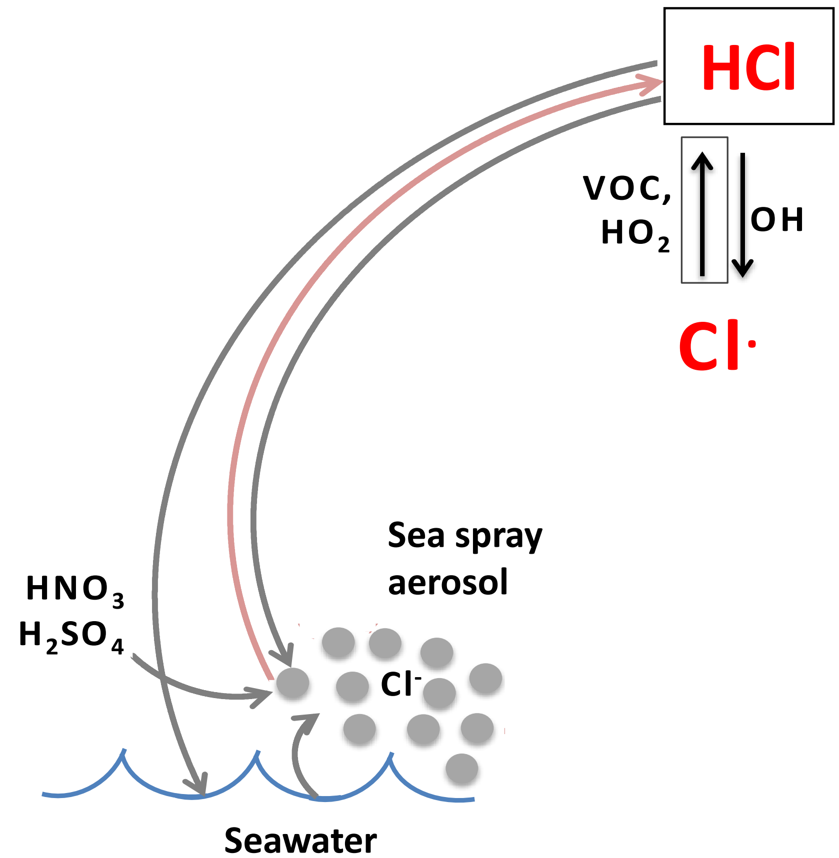
Contact: john.halfacre@york.ac.uk

Motivation – Chlorine's Role in Oxidation

- Chlorine atom - **highly reactive oxidant** of both organic and inorganic compounds[1]
- Thought to play important roles in **tropospheric oxidation**, including[2,3,4]
  - Volatile organic compound (VOC) oxidation (hydrocarbons)
  - Regional ozone production / ozone loss
  - Processing of reactive nitrogen
- Extent of role is highly uncertain as estimated global average concentrations span several orders of magnitude[5]
- Missing observational constraints of inorganic chlorine compounds prevents accurate determination of tropospheric relevance!

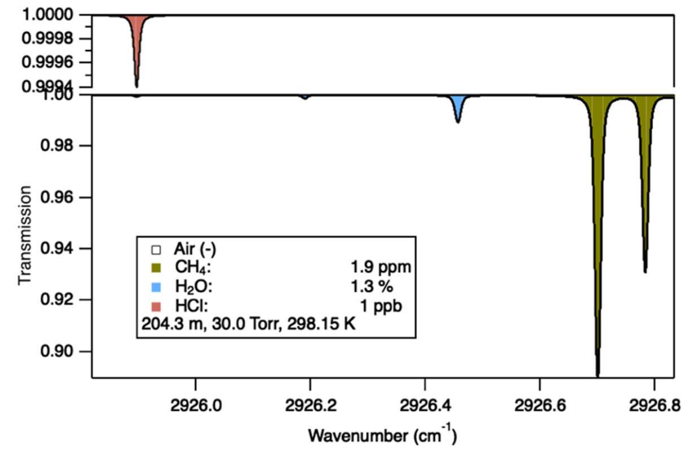
Motivation – Importance of HCl

- **Gas phase chlorine** is found most abundantly **as hydrochloric acid (HCl)** (10^2-10^3 pptv)[1]
- Produced predominantly via acid displacement from **sea salt aerosol,** and as an oxidation product of chlorine radical with **volatile organic compounds**[1]
- **Direct HCl field observations have been traditionally rare** due to sampling difficulties and the burden of complex instrumentation

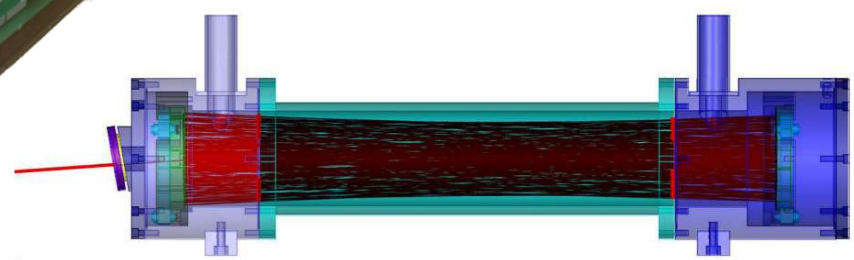


Novel HCl Detection Method

- **HCl-Tunable Infrared Laser Direct Absorption Spectroscopy** (HCl-TILDAS), developed by Aerodyne Research, Inc.
- **Optical technique** that utilizes a mid-IR laser to probe the major HCl rotational-vibrational transition
- **Two-hundred meter absorption pathlength** enabled by astigmatic **Herriott cell**
- **Advantages** of HCl-TILDAS over other HCl-detection methods:
  - **Specificity** for HCl
  - **Absolute** measurement via Beer-Lambert Law
  - > 1 Hz detection frequency



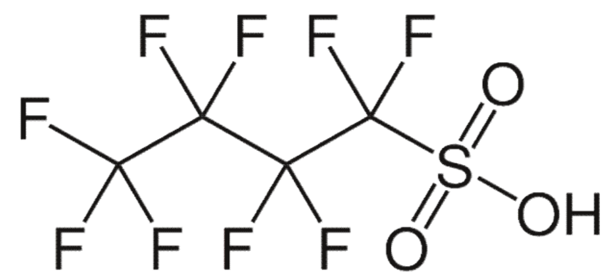
Simulated transmission spectrum for the HCl TILDAS



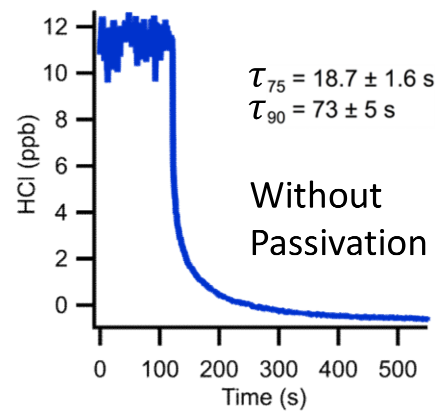
Astigmatic Herriott cell, red lines represent laser travel path

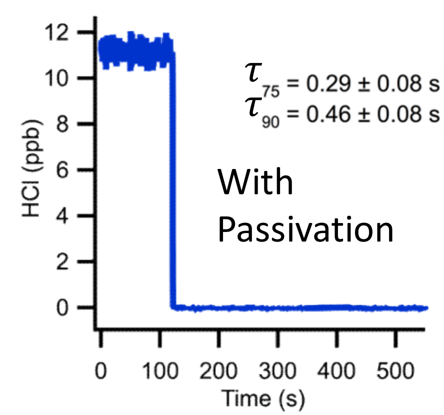
Solving Stickiness - Active Passivation

- The high polarity of HCl results in "**sticky**" character[6], making sampling difficult
- To address this, a small flow (~100 sccm) of **nonafluorobutanesulfonic acid (NFBSA)** is constantly added to the sampling line to **passivate** reactive sites[6]
- NFBSA replaces water / less polar groups bound on interfaces, while its perfluorinated tail creates an **inert environment** and **maximizes HCl transmission** to the absorption cell[6]



nonafluorobutanesulfonic acid (NFBSA)

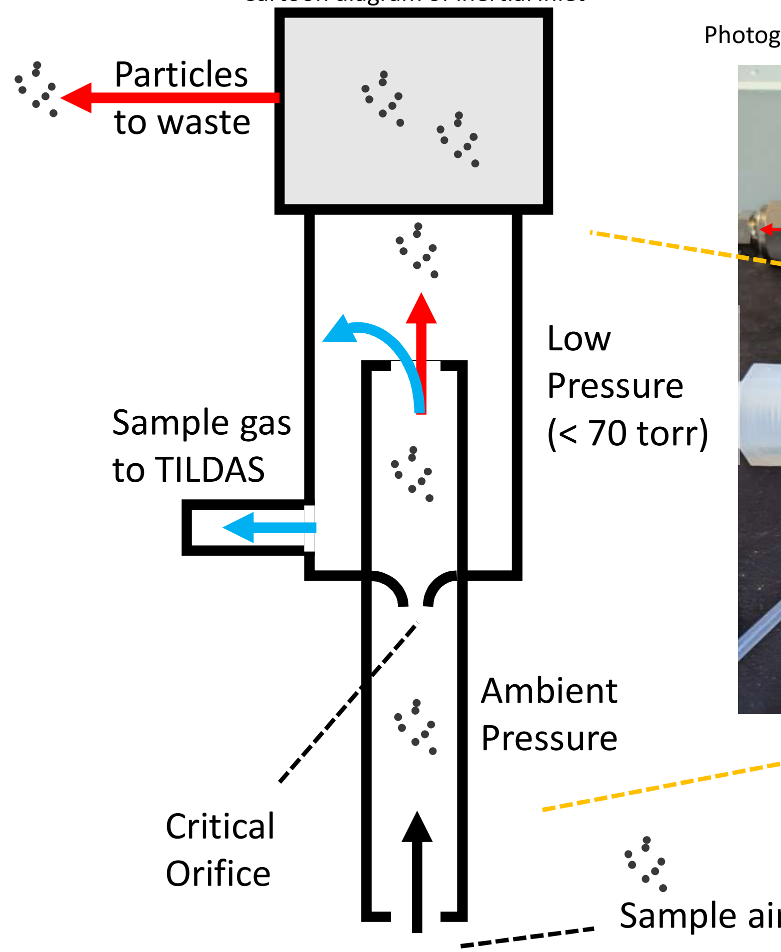




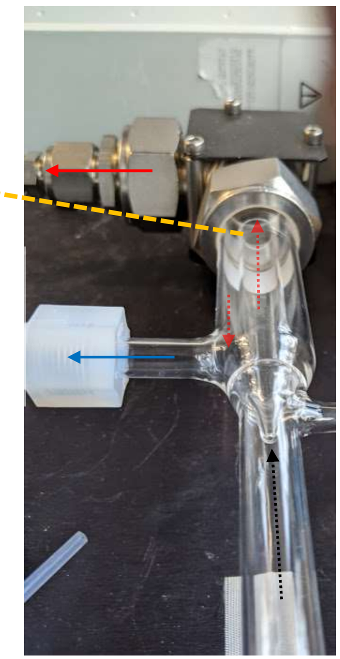
Solving Filtration - Inertial Inlet

- Method requires particle filtration
  - Particles would dirty TILDAS measurement cell mirrors
  - Use of a traditional filter would collect particulates as well as sticky HCl
- Quartz **inertial inlet**
  - Based on virtual impactor
  - Avoids need for filter membrane - **removes** particles > 300 nm diameter to a waste flow due to large forward momentum
  - **Allows** particle-free gas to be drawn from the side
  - Reduces contamination of Herriott cell mirrors

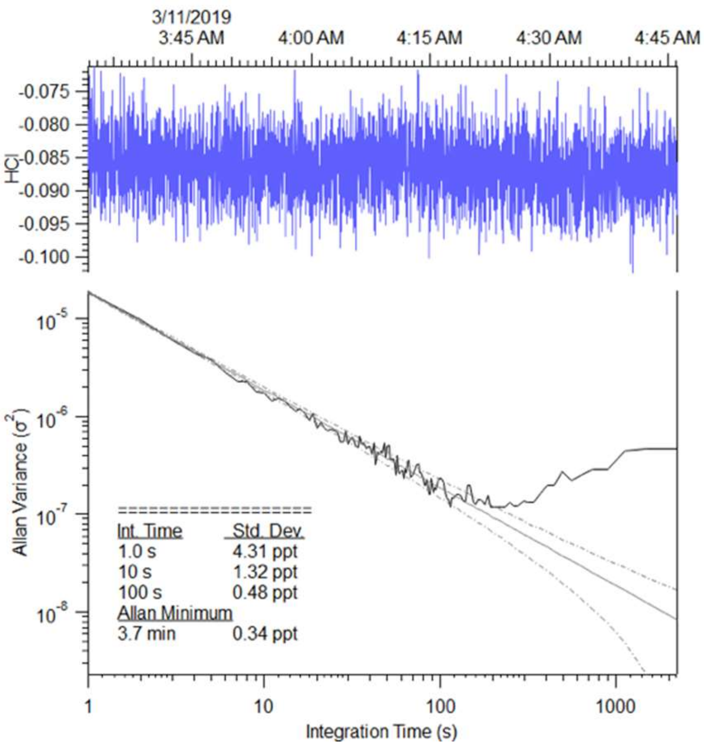
Cartoon diagram of inertial inlet



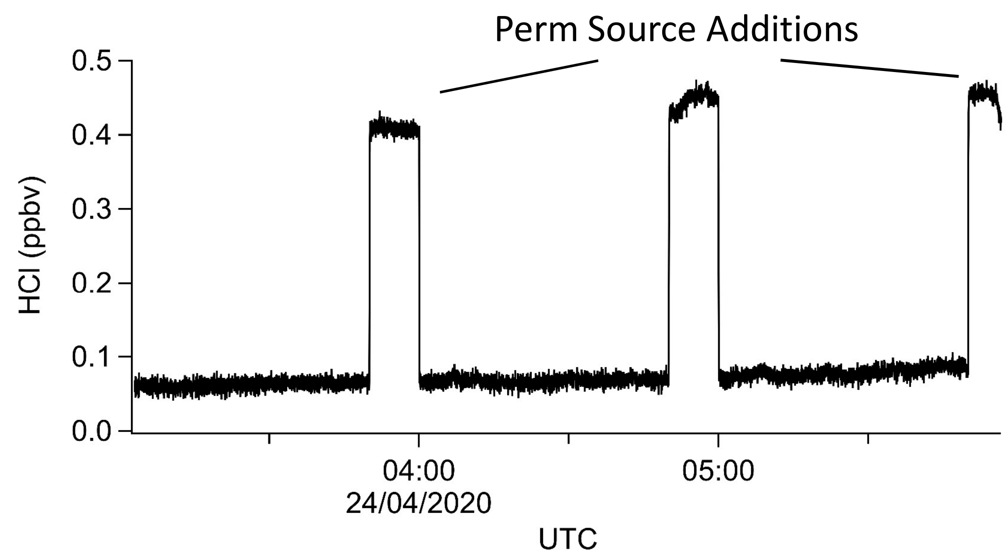
Photograph of actual inertial inlet



Instrument Performance



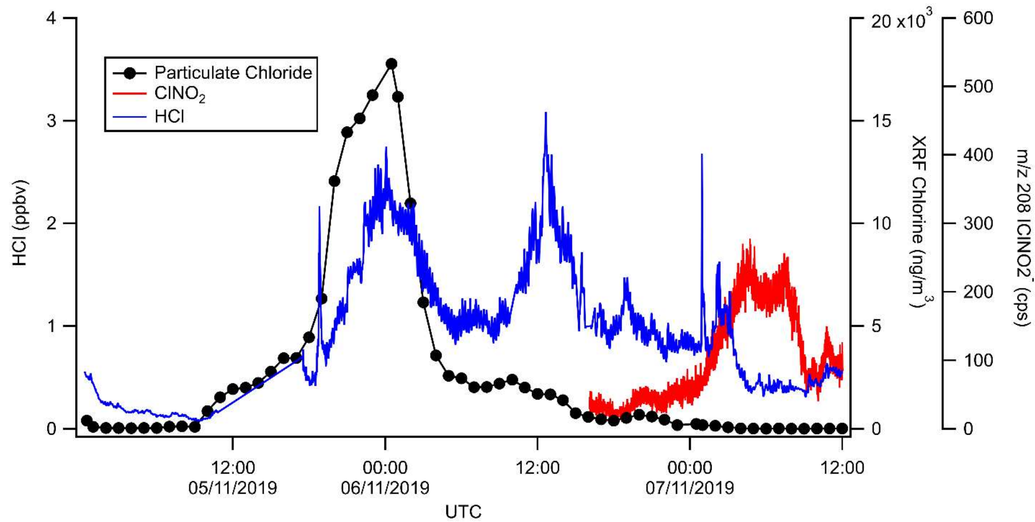
- Precision – 5 pptv (1 sec data)
- 3 sigma LOD - < 20 pptv



Flow from a HCl permeation source is regularly added to the sample stream to assess instrument performance and as a test for line losses.

Future Work and Field Campaigns

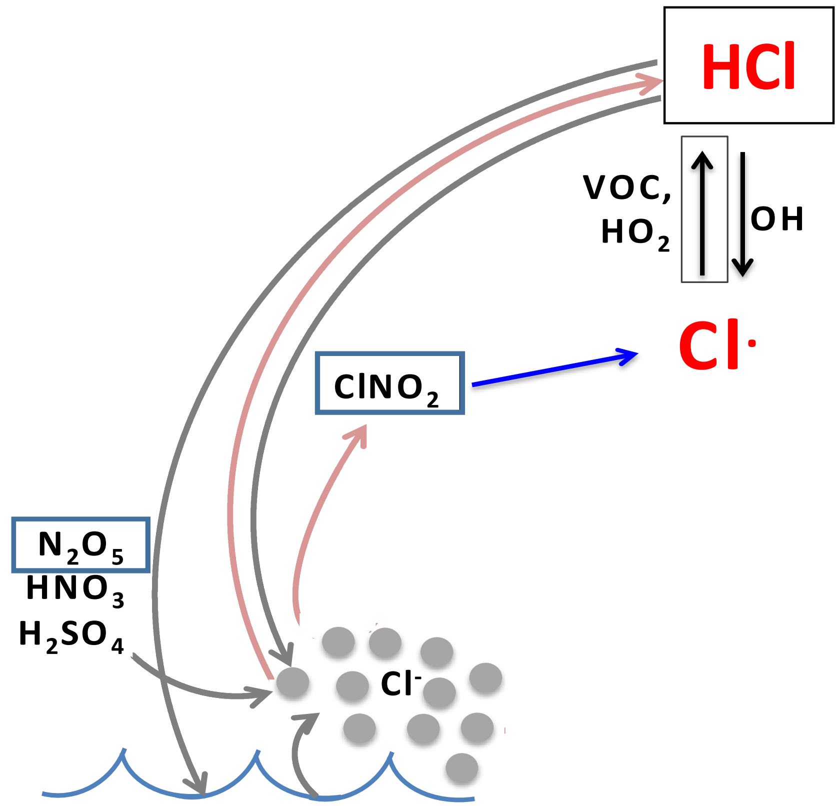
- Examining relationship between TILDAS response and humidity
- Sampling during annual **UK Bonfire Night** fireworks celebration
- Participating in the **2021 UK Clean Air Winter** intensive observation period in **London, UK**
- Extend detection capability to include $ClNO_2$ (next slide)



Plot of preliminary, uncalibrated data during Bonfire Night 2019, including HCl (TILDAS), particulate chloride (X-Ray Fluorescence), and $ClNO_2$ (CIMS)

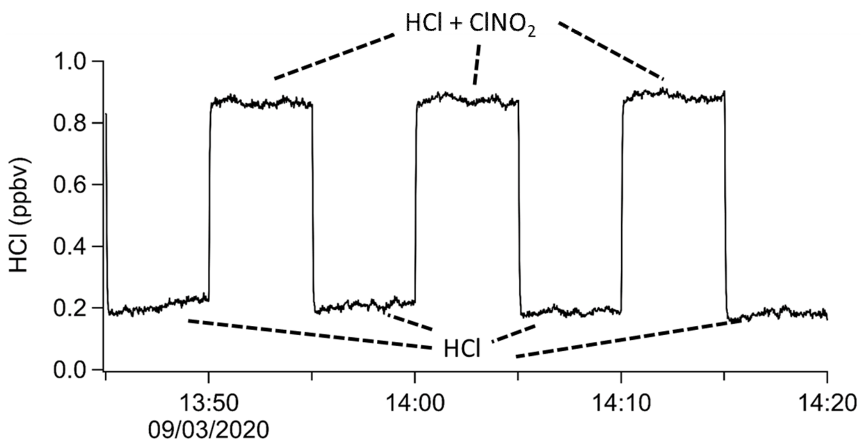
Future Work - TILDAS for $ClNO_2$

- $ClNO_2$ is formed by aerosol uptake of N_2O_5 and its subsequent reaction with Cl^- (aq)
- The first in situ $ClNO_2$ observations were first reported in 2008 at unexpectedly high mixing ratios[7]
- This is significant because $ClNO_2$ acts as
  - Nocturnal reservoir of NO_x
  - Source of reactive chlorine atoms upon morning photolysis
- Currently, all in situ $ClNO_2$ observations have been obtained by CIMS

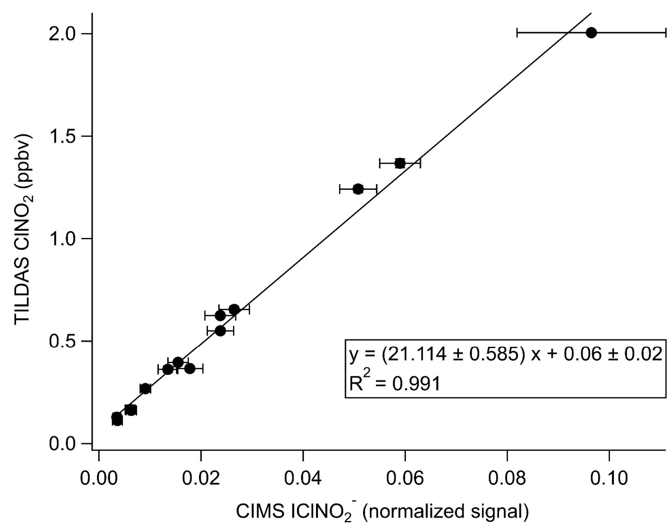


Future Work - TILDAS for $ClNO_2$

- $ClNO_2$ is the only known inorganic chlorine species to thermally dissociate at 450 ^{o}C[8]
    - $ClNO_2$ + heat (>450 ^{o}C) → ●Cl + NO_2
- $ClNO_2$ can be detected by TILDAS if the resulting ●Cl is converted to HCl
    - ●Cl + CH_4/C_3H_8 (100 ppm each) → HCl + products



For detecting $ClNO_2$ by TILDAS, an alternative heated flow path is added to the sample line. Signal from this flow path represents the sum of ambient HCl + $ClNO_2$



Preliminary $ClNO_2$ comparisons with CIMS are linear, but a CIMS calibration is still needed. (Error bars represent 1 standard deviation.)

Summary and Conclusions

- HCl-TILDAS is a powerful technique for detecting HCl and $ClNO_2$
- Provides an independent method of analysis for providing observational constraints on the highly uncertain chlorine budget
- First field campaign measurements are planned for Winter 2020-2021

- Thanks for your interest!

Acknowledgements

- This work is funded through ERC starting grant 802685
- T. VandenBoer and C. Young (York University) for assistance in permeation source fabrication
- NOAA for the SBIR that funded the development of the HCl TILDAS
- Wolfson Atmospheric Chemistry Laboratory

References

1. Simpson, W. R. et al., *Chemical Reviews* 2015 *115* (10), 4035-4062, https://doi.org/10.1021/cr5006638
2. Young, C. J. et al., *Atmos. Chem. Phys.,* 14, 3427–3440, https://doi.org/10.5194/acp-14-3427-2014, 2014.
3. Wang, X. et al., *Atmos. Chem. Phys*., 19, 3981–4003, https://doi.org/10.5194/acp-19-3981-2019, 2019.
4. Kim, M. J. et al., *Proceedings of the National Academy of Sciences* 2014, 111 (11) 3943-3948, https://doi.org/10.1073/pnas.1318694111
5. Sherwen T. et al., *Faraday Discuss.,* 2017, **200**, 75, https://doi.org/10.1039/C7FD00026J
6. Roscioli, J. R. et al., *The Journal of Physical Chemistry A* 2016 *120* (9), 1347-1357 https://dx.doi.org/10.1021/acs.jpca.5b04395
7. Osthoff, H. *et al. Nature Geosci* **1,** 324–328 (2008). https://doi.org/10.1038/ngeo177
8. Thaler, R. D. et al., *Analytical Chemistry* 2011 *83* (7), 2761-2766, https://doi.org/10.1021/ac200055z