Developing a novel system for measuring atmospheric fluxes of organic compounds by eddy covariance using a Time of Flight Chemical ionization Mass Spectrometer

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Introduction:

There are a huge number of organic compounds present in the atmosphere. They are emitted from a wide range of sources that are both natural and man-made. Once in the atmosphere the compounds play a significant role in the oxidation chemistry of the atmosphere and may, in the presence of oxides of nitrogen produce significant amounts of ozone. Many of the products of this oxidation have lower volatility and are more polar and soluble and so may be deposited to the surface or into cloud droplets, may condense onto and grow existing atmospheric particulate matter or nucleate new particles. Many of these compounds are important tracers, are important indicators of particular sources, or are key components in the atmospheric cycle of nitrogen or sulphur. Some molecules, particularly from made sources may be toxic to humans. Considerable uncertainty surrounds many of these properties and processes and it is therefore very important to understand and quantify both the atmospheric burden of these and their emission or removal rates to and from the atmosphere.

Recent advances that combine chemical ionization with high-resolution time-of-flight mass spectrometry can now provide sensitive, real-time identification and quantification of a large number of gas-phase compounds in sampled air. Chemical ionisation provides selective detection based on the employed reagent ion chemistry and new orthogonal extraction time of flight mass spectrometers provide very sensitive detection systems. A number of these instruments are now in operation and are being used to sample atmospheric concentrations of a wide range of compounds. An instrument at the forefront of such developments is the Aerodyne Inc. CI-ToFMS which is being developed and used by a number of research groups world-wide, including Manchester. Manchester has extensive experience of measuring fluxes of atmospheric components by eddy correlation, a method which relies on rapid sampling of the parameter of interest being correlated with the instantaneous vertical wind speed. By combining the CI-ToF with Eddy Correlation you will not only be able to measure the atmospheric burden of a wide range of compounds but will be able to measure their emission rates in to the atmosphere and their removal rates from it and as a result will be able to examine our understanding of the atmospheric lifecycle of many key organic components.

Project Summary:

To develop this novel and exciting measurement system, you will learn to operate the Manchester CI-ToF-MS and eddy correlation techniques. By working closely with colleagues at Aerodyne research Inc. and Tofwerk, the company that manufactures the mass spectrometers used in the Aerodyne system, you will combine these two systems and enable the mass spectrometer data to be recorded in a way that can be correlated with rapid measurements of vertical windspeed. You will then deploy the system in a number of field studies, targeted at particular compounds or groups of compounds, characterizing the system and demonstrating its capability. You will need to calibrate the mass spectrometer for the compounds of interest and will then deploy the instrument in a number of studies. It is expected that you will spend extended periods of time with the industrial partner at Aerodyne Research Inc.

References

Bannan, T.J., Booth, A.M., Bacak, A., Muller, J.B.A., Leather, K.E., Le Breton, M., Jones, B., Young, D., Coe, H., Allan, J., Visser, S., Slowik, J.G., Furger, M., Prevot, A.S.H., Lee, J., Dunmore, R.E., Hopkins, J.R., Hamilton, J.F., Lewis, A.C., Whalley, L.K., Sharp, T. Stone, D., Heard, D.E., Fleming, Z.L., Leigh, R., Shallcross, D.E., and Percival, C.J. The first UK measurements of nitryl chloride using a chemical ionization mass spectrometer in central London in the summer of 2012, and an investigation of the role of Cl atom oxidation (2015), J. Geophys. Res., 120(11), pp: 5638-5657, DOI: 10.1002/2014JD022629

Yatavelli,R.L.N., Lopez-Hilfiker, F., Wargo, J.D., Kimmel, J.R., Cubison, M.J., Bertram, T.H., Jimenez, J.L., Gonin,M., Worsnop, D.R., and Thornton, J.A., A Chemical Ionization High-Resolution Time-of-Flight Mass Spectrometer Coupled to a Micro Orifice Volatilization Impactor (MOVI-HRToF-CIMS) for Analysis of Gas and Particle-Phase Organic Species, Aerosol Science and Technology, 46:1313–1327, 2012, DOI: 10.1080/02786826.2012.712236

Coe H. and Gallagher M.W., Measurements of Fluxes of NO2 to a Dutch Heathland. (1992) Atmos. Environ., 118, pp. 767-786.

Glasius, M. and Goldstein, A.H., Recent Discoveries and Future Challenges in Atmospheric Organic Chemistry, Environ. Sci. Technol. 2016, 50, 2754−2764, DOI: 10.1021/acs.est.5b05105.