

## High Sensitivity Chemical Ionization Mass Spectrometry for the Direct Measurement of Gas Exchange and Reaction at the Ocean Surface.

海洋表面における反応の直接測定のための高感度化学イオン化質量分析計の開発

Timothy H. BERTRAM

Chemical reactions at the air-sea interface have been shown to alter oxidant concentrations in the atmosphere. To date, limitations in trace gas measurement technology have prohibited the direct in situ measurement of air-sea exchange for all but a select number of gases. Here, we describe the application of high sensitivity Chemical Ionization Mass Spectrometry (CIMS) for the selective measurement of trace gas deposition via eddy covariance. We show that eddy covariance techniques, when coupled with high sensitivity CIMS measurements have the sensitivity to directly determine vertical fluxes of reactant and product pairs such as  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$ <sup>[1]</sup>. The eddy covariance studies permit a direct assessment of the importance of the air-sea interface as a net source or sink for reactive trace gases in marine environments, while serving to connect mechanistic investigations conducted on the laboratory scale to ambient conditions.

### Introduction

Atmospheric chemistry plays a critical role in governing both the abundance and distribution of greenhouse gases, air pollutants and aerosol particles. The skill with which climate and chemistry models represent the current state of the atmosphere and respond accurately to chemical and physical perturbation is limited by our understanding of the underlying chemical processes. Direct ambient observations, supported by detailed laboratory investigations, provide unparalleled constraints for, and confidence in climate and chemistry simulations and ultimately the policy recommendations derived from them. In the following research statement, I outline my group's current research objectives in the development for the next generation of atmospheric chemistry measurements that provide direct observation based constraints on trace gas abundances, with the specific application of studying air-sea exchange of reactive trace gases.

The production rate of tropospheric ozone ( $\text{O}_3$ ), a criteria air pollutant, depends critically on the concentrations of nitrogen oxides ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ), Volatile Organic Compounds (VOCs), trace oxidants (e.g., OH,  $\text{NO}_3$ , and Cl) and the wavelength dependent actinic flux. Accurate

model representation of  $\text{O}_3$  mixing ratios and the sensitivity of  $\text{O}_3$  to changes in  $\text{NO}_x$  and VOC emissions rely heavily on a complete description of the factors that control  $\text{NO}_x$  lifetimes and in turn the concentrations of atmospheric oxidants. Modelling studies, constrained by laboratory and field observations, have shown that heterogeneous and multi-phase reactions play an important role in regulating the loss rate of reactive nitrogen compounds. As an example, it has been shown that the heterogeneous reaction of  $\text{N}_2\text{O}_5$  on chloride containing aerosol particles<sup>[2, 3]</sup> serves as both an efficient  $\text{NO}_x$  recycling and halogen activation mechanism *via* the production of photo-labile nitryl chloride ( $\text{ClNO}_2$ ) in both coastal<sup>[4]</sup> and continental airmasses<sup>[5]</sup>. In what follows, we focus on the role of the ocean surface as a reactive medium for the net loss of reactive nitrogen compounds and the potential production of reactive halogen compounds (Figure 1).

### Research Statement

#### Chemical Ionization Time-of-Flight Mass Spectrometry (CI-ToFMS)

Direct, simultaneous measurements of a wide array of trace gases has been made possible by the recent development of a new chemical ionization time-of-flight

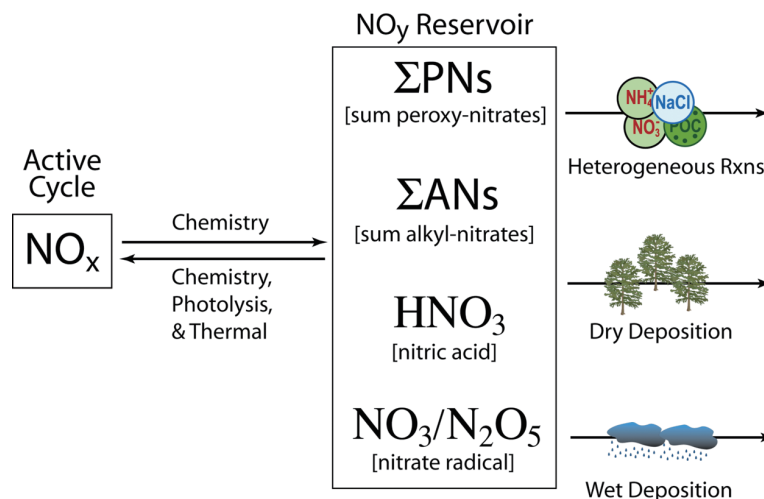
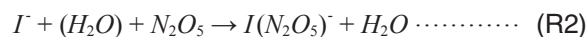
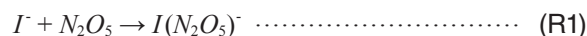


Figure 1 Schematic representation of the conversion of nitrogen oxides ( $\text{NO}_x \equiv \text{NO} + \text{NO}_2$ ) to total reactive nitrogen ( $\text{NO}_y \equiv \text{NO}_x + \text{peroxy-nitrates, alkyl-nitrates, nitric acid, dinitrogen pentoxide, and others}$ ). The integrated ozone production rate is critically dependent on the lifetime of  $\text{NO}_x$  in the atmosphere. As such, it is critical that chemical models of the atmosphere accurately represent both  $\text{NO}_x$  lifetime and the mechanisms with which  $\text{NO}_x$  and  $\text{NO}_y$  interconvert and are removed from the atmosphere.

mass spectrometry applications<sup>[6]</sup>. As applied to trace acids, the sensitivity ( $> 300$  counts  $\text{pptv}^{-1}$ ) is an order of magnitude better than that reported for similar quadrupole based instruments<sup>[7]</sup>, which we attribute to advances in the high pressure interface described below. In the laboratory we have used a host of reagent ions (e.g.,  $\text{C}_6\text{H}_6^+$ ,  $\text{NO}^+$ ,  $\text{H}_3\text{O}^+$ ,  $\text{I}^-$ , and  $\text{CH}_3\text{C}(\text{O})\text{O}^-$ ) to demonstrate the versatility of the system toward detection of a wide array of target molecules. Details of the instrument can be found in Bertram et al., 2011.

In the work described here, we use iodide ions ( $\text{I}^-$ ) for the selective detection of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  via the following

ion-molecule reactions as described in Kercher et al. 2009 (Figure 2).



#### Atmospheric Measurements of $\text{N}_2\text{O}_5$ and $\text{ClNO}_2$

Dinitrogen pentoxide ( $\text{N}_2\text{O}_5$ ) and nitryl chloride ( $\text{ClNO}_2$ ) concentrations were measured continuously for a period of two weeks at the Scripps Institution of Oceanography's Pier. The pier extends 300 m from the coast and is 10 m off the water. We position our inlet manifold on an

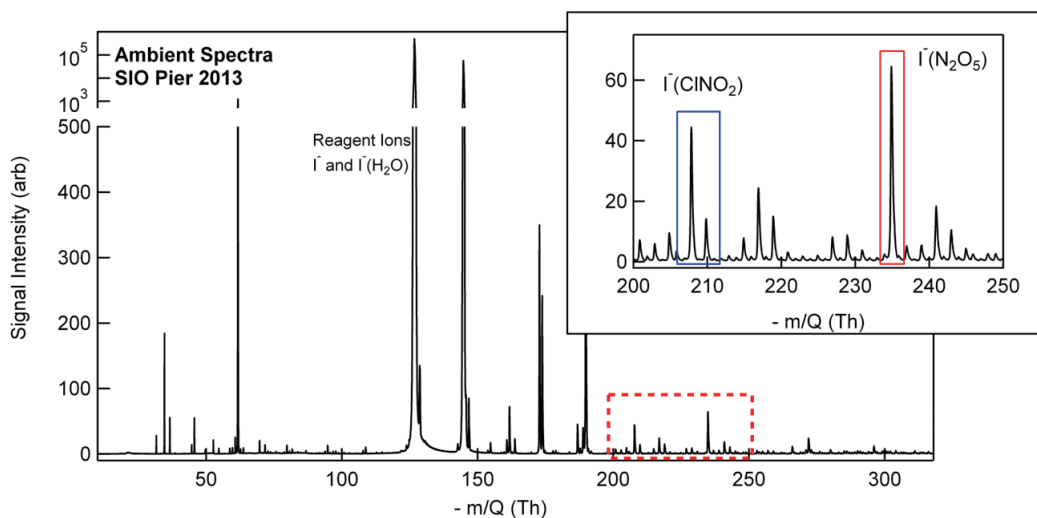


Figure 2 Time of flight mass spectrum taken at the Scripps Institution of Oceanography (SIO) pier in La Jolla, CA. During this period the CIMS was operated using  $\text{I}^-$  ions for the selective detection of  $\text{I}^-(\text{N}_2\text{O}_5)$  and  $\text{I}^-(\text{ClNO}_2)$  as shown in the inset figure.

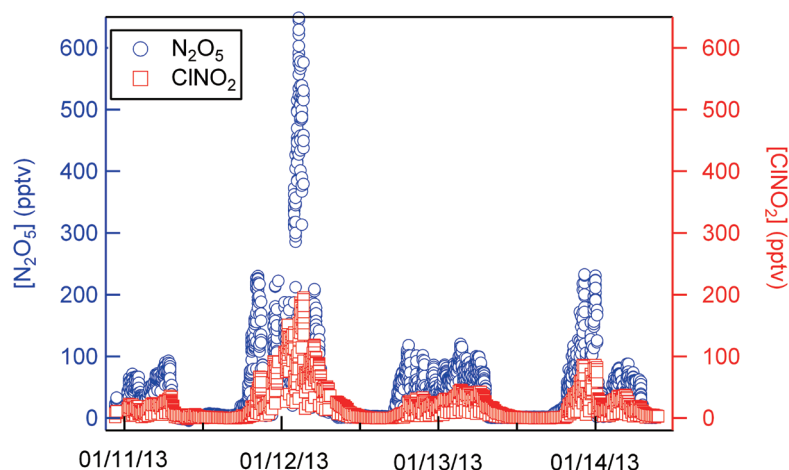


Figure 3 Time series of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  measurements made from the Scripps Institution of Oceanography (SIO) pier in La Jolla, CA. As shown,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  are primarily nocturnal compounds, where peak concentrations occur close to midnight between 100 and 500 pptv.

instrumentation boom that extends an additional 10 m off the end of the pier, and our instrument in an existing instrument van at the end of the pier. As shown in Figure 3,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  mixing ratios are near zero during the day, reflecting the short photolysis lifetime for nitrate radicals ( $\text{NO}_3$ ), which limits  $\text{N}_2\text{O}_5$  production and moderate photolysis lifetime for  $\text{ClNO}_2$  ( $\tau(\text{ClNO}_2) = 3\text{hr}$ ) that limits  $\text{ClNO}_2$  production. As expected,  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  concentrations peak close to midnight between 50–500 ppt dependent primarily on local meteorology.

In order to accurately assess the impact of nocturnal nitrogen oxide chemistry on tropospheric ozone production, it is critical that we properly constrain not only the production rates for  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  in polluted coastal environments, but also loss rates. At present, the production rate for  $\text{N}_2\text{O}_5$  is well constrained in regional and global chemical transport models as it is primarily dependent on the concentrations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$ , all three of which are measured and well constrained. However, the loss rate of  $\text{N}_2\text{O}_5$  and the production rate of  $\text{ClNO}_2$  at aqueous interfaces. At present, our understanding of these mechanisms is based on laboratory work using mimics for atmospheric interfaces such as the air-particle and air-sea interface. This is a challenge as real atmospheric interfaces are both chemically and physically complex and not easily replicated in the laboratory.

#### Chemical Reactions at the Air-sea Interface as Measured using CI-ToFMS

To date, study of the impact of nocturnal processes on the lifetime of  $\text{NO}_x$  and the production of reactive halogen species in the marine boundary layer has concentrated on gas-phase reactions and heterogeneous and multiphase processes occurring on/within aerosol particles, with little

attention paid to reactions occurring at the air-sea interface. We recently demonstrated the first direct measurements of the vertical flux of  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  obtained *via* eddy covariance at a polluted coastal site to provide observation-based constraints on the role of the air-sea interface in setting the lifetime of reactive nitrogen and the production rate of reactive halogens in the marine boundary layer<sup>[1]</sup>. We measure rapid  $\text{N}_2\text{O}_5$  deposition to the ocean surface ( $V_{\text{ex}} = -1.66 \pm 0.60 \text{ cm s}^{-1}$ ), which is limited solely by atmospheric transport to the air-sea interface. Surprisingly, we find no evidence for  $\text{ClNO}_2$  production from the ocean in this study. This result suggests that either aqueous phase reactions of  $\text{ClNO}_2$  at the ocean surface are competitive with volatilization, or that  $\text{ClNO}_2$  production is suppressed due to rapid reactions of  $\text{NO}_2^+$  (a product of  $\text{N}_2\text{O}_5$  hydrolysis) with organic molecules enhanced at the air-sea interface. Comparison with determinations of the  $\text{N}_2\text{O}_5$  loss rate to aerosol at the same sampling location indicates that the ocean surface removes as much as 50% of  $\text{N}_2\text{O}_5$  in the marine boundary layer under the conditions sampled here.

#### Future Directions

In our recent paper we demonstrated that CI-ToFMS when using  $\Gamma$  as the reagent ion had the sensitivity at 10Hz acquisition rates to directly measure  $\text{N}_2\text{O}_5$  and  $\text{ClNO}_2$  vertical fluxes<sup>[1]</sup>. This was the first measurement of a chemical reaction at the air-sea interface probed directly by eddy covariance. As such, we expect that further advances in CI-ToFMS sensor technology will enable us to greatly expand the observational database on trace gas deposition and reaction at the air-sea interface. Specifically, we aim to address the following hypotheses:

- 1) The chemical composition of the sea-surface microlayer

dictates whether the ocean surface serves as either a source or sink for photo-labile halogen molecules such as ClNO<sub>2</sub>.

- 2) Eddy covariance coupled with chemical ionization time-of-flight mass spectrometry can be used to directly measure the exchange of oxygenated volatile organic compounds such as acetone and methanol.
- 3) The reactive uptake of ozone (O<sub>3</sub>) results in the production of HOI, a critical component in the reactive halogen cycle in the marine boundary layer.

## Acknowledgements

Specific details of this project can be found in Kim et al., 2014<sup>[1]</sup>. This is a collaborative project with Delphine Farmer (Colorado State University) and Michelle Kim (a Ph.D. student in my research group at UC San Diego). The work described here is supported by the National Science Foundation CAREER Award (Grant No. AGS-1151430, Bertram (PI)).

## References

- [1] Kim, M., Farmer, D., Bertram, T.H., "A controlling role for the air-sea interface in the chemical processing of reactive nitrogen in the coastal marine boundary layer", PNAS, 2014.
- [2] Behnke, W., George, C., Scheer, V., and Zetzsch, C., "Production and decay of ClNO<sub>2</sub>, from the reaction of gaseous N<sub>2</sub>O<sub>5</sub> with NaCl solution: Bulk and aerosol experiments", *J Geophys Res-Atmos*, **102**, 3795, Doi 10.1029/96jd03057 (1997)
- [3] Finlayson-Pitts, B. J., Ezell, M. J., and Pitts, J. N., "Formation of chemically active chlorine compounds by reactions of atmospheric NaCl particles with gaseous N<sub>2</sub>O<sub>5</sub> and ClONO<sub>2</sub>", *Nature*, **337**, 241, Doi 10.1038/337241a0 (1989)
- [4] Osthoff, H. D., Roberts, J. M., Ravishankara, A. R., Williams, E. J., Lerner, B. M., Sommariva, R., Bates, T. S., Coffman, D., Quinn, P. K., Dibb, J. E., Stark, H., Burkholder, J. B., Talukdar, R. K., Meagher, J., Fehsenfeld, F. C., and Brown, S. S., "High levels of nitryl chloride in the polluted subtropical marine boundary layer", *Nature Geoscience*, **1**, 324, Doi 10.1038/Ngeo177 (2008)
- [5] Thornton, J. A., Kercher, J. P., Riedel, T. P., Wagner, N. L., Cozic, J., Holloway, J. S., Dube, W. P., Wolfe, G. M., Quinn, P. K., Middlebrook, A. M., Alexander, B., and Brown, S. S., "A large atomic chlorine source inferred from mid-continental reactive nitrogen chemistry", *Nature*, **464**, 271, Doi 10.1038/Nature08905 (2010)
- [6] Bertram, T. H., Kimmel, J. R., Crisp, T. A., Ryder, O. S., Yatavelli, R., Thornton, J. A., Cubison, M. J., Gonin, M., and Worsnop, D. R., "A field-deployable, chemical ionization time-of-flight mass spectrometer", *Atmos. Meas. Tech.*, **4**, 1963 (2011)
- [7] Veres, P., Roberts, J. M., Warneke, C., Welsh-Bon, D., Zahniser, M., Herndon, S., Fall, R., and de Gouw, J., "Development of negative-ion proton-transfer chemical-ionization mass spectrometry (NI-PT-CIMS) for the measurement of gas-phase organic acids in the atmosphere", *Int J Mass Spectrom*, **274**, 48, DOI 10.1016/j.ijms.2008.04.032 (2008)



**Timothy H. BERTRAM**

Department of Chemistry and Biochemistry  
University of California, San Diego  
Assistant Professor  
Ph. D