

Introduction: To better understand the impact of global climate change and the effects of increased biogenic and anthropogenic emissions, more research is needed into the unique photochemical processes that take place in the Arctic atmosphere. Although geographically remote, the Arctic has a significant impact on globally important feedbacks to climate change. Since ozone (O_3) is the precursor for most of the oxidizing, or self-cleaning, capacity in the troposphere, it generally controls the oxidation potential of the atmosphere. Similar to the discovery of stratospheric ozone depletion, observations of ozone depletion events (ODEs) in the polar boundary layer (BL) were surprising.

Springtime episodic depletions of tropospheric O_3 , and the characteristic photochemistry involved, are current areas of considerable research. These sudden and recurrent ODEs during late winter and spring are associated with elevated concentrations of halogenated radicals. The conversion of inert halide salt ions into reactive halogenated species has been shown to deplete O_3 following the onset of Polar Sunrise [e.g. 1,2]. While it is widely accepted that bromine is the primary driver of ODEs via photochemical reactions, the role of iodine chemistry in ozone destruction and oxidizing strength of the atmosphere is not well understood [e.g. 3,4]. The dominance of bromine in Arctic ODEs appears to be a function of its abundance only, as even small perturbations in the iodine concentration significantly impact the rate of ozone depletion in recent models [5]. These models have also shown that interactions with iodine may double the efficiency of bromine in ozone depletion [6].

Problem Statement: To date, few successful in-situ measurements of iodine compounds have been achieved in the Arctic due to the lack of analytical methods. As a result, iodine chemistry is often omitted from current climate models that simulate Arctic ODEs, which may significantly underestimate the rate of ozone depletion. *Research Objectives:* This study proposes the exploration of new technologies and methods for the selective, quantitative chemical detection of iodine compounds that may play an important role in Arctic ODEs. In this study, I propose to investigate new analytical procedures and instrumentation to observe and quantify I_2 and IO during springtime Arctic ODEs. This work will then allow iodine chemistry to be incorporated with reduced uncertainty into kinetic analyses and computer model simulations.

Method Development: To complete these objectives, I will work with Prof. Paul Shepson of Purdue University, a leading scientist in the field of atmospheric halogen chemistry in the Arctic. I will design new laboratory techniques to study the reaction mechanics of Arctic iodine species using chemical ionization mass spectrometry (CIMS), and inductively coupled Argon plasma mass spectrometry (ICP-MS). CIMS has not yet been used to detect I_2 /IO in the High Arctic, however, the Shepson lab has adapted a CIMS for the field and I plan to expand the capabilities of that instrument to detect I_2 and IO in-situ, using SF_6 gas as the ion source.

Study Site and Field Observations: Field observations of I_2 and IO using CIMS and filter sampling will take place in Barrow, Alaska where Beaufort meets the Chukchi Sea in the Arctic Ocean. This site is ideal for studying an Arctic maritime environment as it is coastal, surrounded by first-year sea ice, and the predominantly northeasterly winds come from clean, undisturbed snow over the sea ice. This ensures that our measurements include only halogenated compounds from the natural environment. Filtered samples from the field site will be transported and analyzed using ICP-MS at the Mass Spectrometry Center at Purdue University.

Modeling: Initial models established in the Shepson lab will be expanded to include observations of reactive iodine species (I, IO, HI, HOI, I₂O₂, INO_x) significant to ODEs in the Arctic. Improvements will be made to a multiphase, zero-dimensional model used previously to study Br and Cl radicals [6], in order to predict the chemistry of iodine species and their involvement during ODEs. Developments to the model needed to expand on the heterogeneous iodine production mechanism and provide a better representation of snowpack and aerosol chemistry are as follows: nitrate and sulfate chemistry will be included; pH, temperature and the availability of oxidants will be varied; and finally, vertical mixing rates will be updated to include a better parameterization of the transfer of halogenated compounds between snow, interstitial air and the boundary layer. This model will aim to quantify the fraction of O₃ depleted by iodine during ODEs, the impact of iodine on the rate and timescale of O₃ depletion, and the effect of iodine on other important atmospheric oxidants such as HO_x and NO_x.

Intellectual Merit: Significant opportunities exist in this proposal to discover fundamental knowledge related to the kinetics of Arctic iodine species and their relationship to ODEs. In addition to the development of a sensitive and selective method for quantifying reactive iodine species from the High Arctic during an ozone depletion event, this research will produce a model of Arctic ozone photochemistry that incorporates the effects of I₂/IO chemistry in addition to those of Br and Cl. This will lead to a better understanding of the role of iodine chemistry in ODEs and other tropospheric chemical cycles important to the future of global climate change.

My previous experience with analytical instrumentation has provided me with a strong foundation for success in developing this method. Undergraduate research and my current position as a lab and field technician have prepared me well for conducting research in an academic setting as well as in the field (see previous research essay). Working in the Shepson lab will be central to the growth of my knowledge about environmental modeling. Having presented multiple research projects, in addition to preparing a manuscript and following it through submission and revision, I am trained in effectively communicating the results of my research.

Broader Impacts: I will share this research via publications in peer-reviewed journals for general and specialized audiences, and presentations at both national and international conferences. I will continue my involvement with the ACS and AXΣ (see personal statement) via the ACS Student Affiliates and the AXΣ-Beta Nu chapter at Purdue. In each phase of this project, I will actively recruit high school and undergraduate students from underrepresented groups to gain valuable research experience in our lab. I will encourage students from the ACS Project SEED and the NSF REU program to apply for these positions. The interdisciplinary nature of this research will significantly broaden their scientific experience and enhance their understanding of the importance of chemistry in the Arctic to global climate change. I also plan to be in close contact with the PolarTREC program so that I may host a high school teacher during my field campaign in the Arctic. I plan to partner with them to connect directly to their students back home via a cyber-based platform so that we may share our experiences in the field. Through digital storytelling, I will also be able to communicate the importance of this research to the broader public via a website that Dr. Shepson has previously developed (www.arcticstories.net).

Literature Citations: [1] Bottenheim, J.W., et al. (2002) *Atmos. Environ.*, 36, 2535-2544 [2] Helmig, D., et al. (2012) *J. Geophys. Res.*, 117, D20303 [3] Barrie, L.A.; Platt, U. (1997) *Tellus* 49B,450-454 [4] Mahajan, A., et al. (2010) *J. Geophys. Res.*, 115, D20303 [5] Calvert, J.G.; Lindberg, S.E. (2004) *Atmos. Environ.*, 38, (30), 5087-5104 [6] Stephens, C.R. (2012) *PhD Dissertation*, Purdue University