263h Indirect Determinations of Integrated Br and CL Concentrations in Barrow, Alaska

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Halogen radicals play an active role in springtime Arctic atmospheric chemistry and over saline bodies of water in lower latitudes as well. Proper understanding of how atmospheric halogen levels are regulated has impact beyond the Arctic springtime surface layer, for example, for regional and hemispheric mercury budgets, and for global marine chemistry. Current chemical models simulate [Br]/[Cl] ratios that exceed by an order of magnitude the ratios inferred from measurements of hydrocarbon loss rates in the Arctic. Either quantitation of Br and Cl from relative hydrocarbon loss rates is subject to some currently unappreciated interference, or an unknown source of Cl exists, or current understanding of the gas-phase chemistry regulating halogen atom concentrations is inadequate.

During February - April 2005, we undertook a field campaign in Barrow, Alaska whose objective is to simultaneously measure the [Br]/[Cl] ratio by two independent methods and to use the resulting data to investigate the reason for the order-of-magnitude gap between halogen concentrations inferred from hydrocarbon decay, and halogen levels simulated by currently-understood chemical mechanisms. This presentation of preliminary results focuses on the traditional relative hydrocarbon loss method for inferring [Br]/[Cl]. The relative hydrocarbon loss method relies on the fact that hydrocarbons differ in their relative reactivity towards the radicals OH, Br, and Cl. A change in the ratio of two hydrocarbons indicates preferential loss of one species due to more rapid reaction with a particular radical. This method was described by Jobson and coworkers in 1994 [Jobson, Niki, Yokouchi, Bottenheim, Hopper, and Leaitch, J. Geophys. Res. 99(D12), 25355-25368, 1994] and has been used frequently since.

About fifty samples were analyzed for hydrocarbons at Ohio University, and additional complementary measurements, including continuous monitoring of ozone, were made at the same site during the same time period. Conditions at Barrow as described in the literature (high alkene levels, high NOx) were expected to result in unusually good reliability for inferring [Br]/[Cl] ratios from changes in hydrocarbon ratios. Generally, when this method has been used, [Cl] can be inferred from several hydrocarbon species, but [Br] (and [Br]/[Cl]) relies completely on measurements of acetylene, the only hydrocarbon vulnerable to reaction with Br which is also consistently present above the quantitation limit. Hydrocarbon measurements from seven samples published in 1992 [Doskey and Gaffney, Geophys Res Lett 19(4), 381-381, 1992] indicate that levels of ethylene, propylene, and acetylene are unusually high at Barrow. It was our hope that this would make it possible to more accurately quantify [Br]/[Cl] by measuring hydrocarbon ratios during episodes of active halogen chemistry.

In this presentation, we will show the hydrocarbon mole fractions measured at Barrow over the course of the transition from 24-hour darkness to 24-hour daylight, and discuss the [Br] and [Cl] inferred from these mole fractions during different time periods. This is the first characterization of springtime hydrocarbon levels in Barrow for more than a decade, and the most comprehensive.