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Atmospheric transformation of elemental mercury upon reactions with halogens

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Abstract

Rapid depletions of atmospheric mercury (Hg^0) and ozone have recently been observed in several regions of high- and sub-Arctic, as well as Antarctica. There are a large body of ground based and satellite observations implicating the reactions of halogens, during these depletion events. In our laboratory, we have performed extensive kinetic and product studies on the oxidation reactions of elemental mercury with atmospheric oxidants, along with complementary thermochemical studies based on our kinetics and product studies of reactions of gaseous Hg^0 with molecular and atomic halogens. In this study, we incorporated our laboratory data in a chemical box model (MOCCA). Our results on the potential importance of some key molecular and atomic halogen reactions in depletion of mercury within atmospheric boundary layer, will be discussed.

1. INTRODUCTION

Mercury is one of the most toxic elements in nature. Its dominant form in the atmosphere is Hg^0 . It has been three years since Schroeder *et al.* [1] reported surprisingly rapid depletion of Hg^0 from the atmospheric boundary layer during spring in the high Arctic at Alert, Canada. Since then, there has been a growing body of observational evidence reporting Hg^0 depletion throughout the Arctic [2], and sub-Arctic [3] as well as Antarctica. These phenomena are associated with enhanced mercury deposition in surface snow and ice. [4] These episodes of mercury depletion coincide with an ozone hole at the ground driven by photochemistry and bromine atoms derived from reactions of atmospheric reactive halogen gases with surfaces of snow and ice. [5-7]. It is noteworthy that some mercury derivatives are of bio-accumulative nature. In our laboratory, we provided the first kinetic and mechanistic information on reactions of elemental mercury with halogens [8]. We herein incorporated our novel kinetic data set in an atmospheric chemical box model to evaluate the importance of atomic and molecular halogen chemistry (chlorine and bromine) in near complete destruction of boundary layer elemental mercury.

2. MODEL DESCRIPTION

We used Mocalce (Model Of Chemistry Considering Aerosols in Cold Environment) to investigate the chemistry of molecular and atomic halogens during the Arctic tropospheric mercury depletion events. Previously used for the marine air at mid-latitudes (9), Mocalce has now been modified to include the chemistry of mercury. Mocalce contains 157 reactions in the gas phase, 102 in aerosol particles. The number of chemical species is 83 in the gas phase and 68 in the aqueous phase. Since the Arctic air mass is very stagnant during ozone depletion (coinciding mostly with mercury depletion events), the boundary layer can be treated as a “smog chamber” reactor. The reactions of mercury with HO, O_3 , Cl_2 , Br_2 , Cl and Br are parameterized in the model considering the initial attack. The model runs start at Julian day (JD) 90 (JD 1 = January 1) with initial concentrations set to typical values for the Arctic Spring. The daytime concentrations of HO, Cl, and Br are approximately 10^{-5} cm^{-3} , 10^{-4} cm^{-3} , and 10^{-7} cm^{-3} , respectively.

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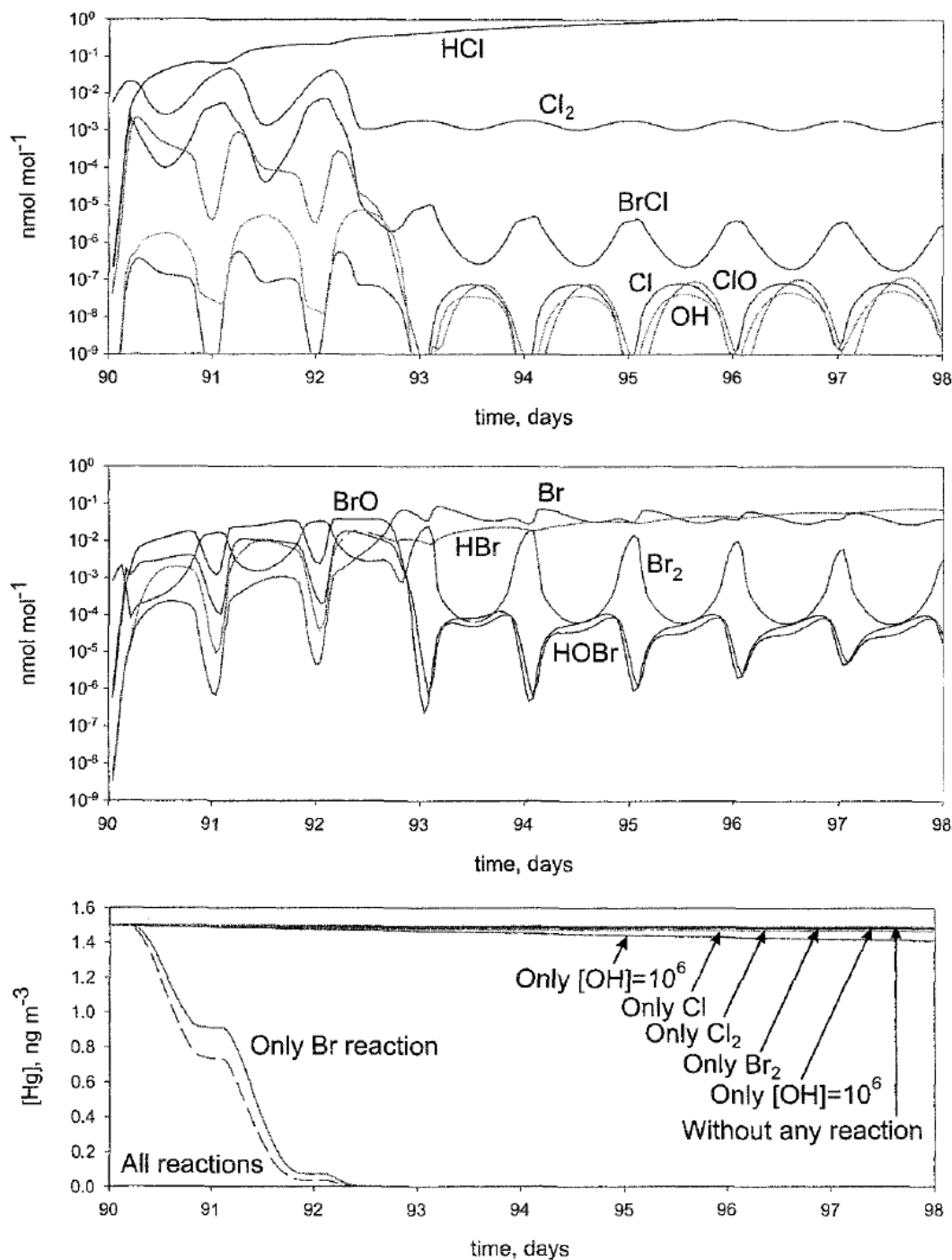


Figure 1. Time-series simulations of selected atmospheric oxidants: the bottom graph depicts the concentration changes of mercury upon the reactions with atmospheric oxidants.

3. RESULTS AND DISCUSSION

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Figure 1 depicts an example model run, in which we attempted to evaluate the boundary layer importance of halogen reactions of mercury in light of our laboratory kinetic studies. Similar to the reaction of O₃ with Hg⁰, the reactions of Cl₂ and Br₂ with Hg⁰ are far too slow to be important atmospheric “sinks” for mercury. At hydroxyl radical concentrations of 10 or even 10 molecule cm⁻³, to account for potential high concentration of HO within the boundary layer, observed mercury depletion could not be reproduced. Despite the fast rate coefficient of Cl-atom initiated reaction of mercury measured the inferred concentration of chlorine atoms^{6,7} is far too low to play a significant role in the destruction of mercury. The Br atom reaction, however, is sufficiently fast, and Br is present in high enough concentrations to exclusively destroy mercury completely within a couple of days, as observed in the Arctic. Formation of condensed products in the gas-phase reactions of halogens with mercury is consistent with the observation of the increase in concentrations of oxidized mercury in aerosols and snow surfaces in the Arctic⁴. Of particular concern is the deposition of mercury derivatives, since the transformation products of halogen-initiated reactions of elemental mercury identified in our experiments are much more water-soluble than Hg⁰. Their ecological impact at the onset of peak biological activities, over a large part of the Northern Hemisphere ought to be carefully considered.

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