(14-240327-A) Iodine May Rival Bromine as a Mercury Oxidant in the Free Troposphere

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In June 2020, the World Health Organization named mercury on its list of ten chemicals of public health concern due to its global ubiquity and potent neurotoxicity. In humans, there is no known safe level of mercury exposure. The atmospheric oxidation of gaseous elemental mercury, Hg⁰, is thought to proceed mostly by bromine atoms (Br) or hydroxyl radicals (OH) to form Hg¹ species; iodine atoms (I) also warrant consideration in light of the recent realization that Hg¹ is more rapidly oxidized than previously thought by ozone (O₃) to form water-soluble and longer-lived Hg^{II} species. The atmospheric deposition of Hg^{II} species is the primary source of mercury to aquatic ecosystems, where mercury bioaccumulates in the food chain. Interestingly, particulate mercury in the upper troposphere correlates with iodine for reasons that are currently not understood, and iodine is currently not considered as an oxidant of Hg⁰ in atmospheric models. Here we present co-located measurements of Hg^{II} and iodine, and show that atmospheric models systematically underestimate the amount of iodine and Hg^{II} observed in the free troposphere. Ours are the first ground-based observations of tropospheric iodine radicals over the central continental United States. At the observed levels, iodine may rival bromine as an oxidant of Hg⁰, especially at cold temperatures; this may explain previously observed particulate mercury-iodine correlations in the upper troposphere. We briefly discuss the atmospheric implications and future research needs to reduce uncertainties in our understanding of the mercury geochemical cycle.

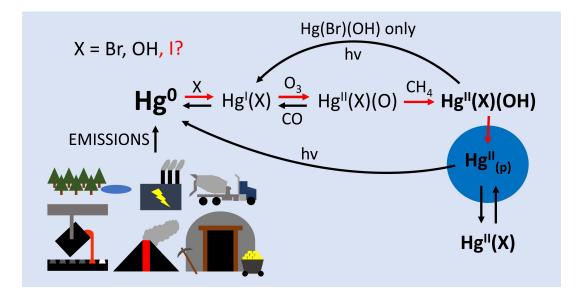


Figure 1. Bromine atom (Br) and hydroxyl radical (OH) are major oxidants of gaseous elemental mercury throughout the atmosphere. Iodine atom (I) is largely unexplored as a mercury oxidant but may rival bromine in the free troposphere.