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Bromine-induced Atmospheric Mercury Depletion Events (AMDEs) at the Dead Sea: magnitude, frequency, spatial extent, and modeled reaction pathways

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Strong Atmospheric Mercury Depletion Events (AMDEs) driven by high levels of reactive bromine species were observed recently in the warm Dead Sea boundary layer. We present a detailed summary of results from (i) two field measurement campaigns at the Dead Sea where we simultaneously quantified the major forms of atmospheric mercury (elemental Hg(0), gaseous and particulate-bound oxidized Hg(II)), bromine oxide (BrO), ozone (O_3), and auxiliary chemical and meteorological variables; (ii) Hg(0) and O_3 measurements at a second location some 400 m above the Dead Sea water to assess spatial and temporal patterns of AMDEs in the region; and (iii) numerical simulations using the MECCA box model to evaluate how reactive bromine and other halogens relate to AMDEs.

Results from measurements at the Dead Sea shore showed frequent, near-complete conversion of Hg(0) to Hg(II) producing among the highest Hg(II) levels (>900 pg m^{-3}) ever observed. Hg(II) formation and Hg(0) depletion temporally coincided well with high BrO levels and O_3 depletion. Higher BrO concentrations in the summer led to larger and more frequent AMDEs; in summer, we observed Hg(0) depletion below 1 ng m^{-3} on 20 of 29 days, while this occurred in winter only on 8 of 20 days. In spite of frequent pronounced AMDEs, we found negligible amounts of total and methylated Hg in Dead Sea water indicating that little AMDE-induced Hg deposition was retained in the water.

We observed frequent Hg(0) and O_3 depletions also at a second site some 400 m above the Dead Sea, indicating that AMDEs are widespread throughout the region and not limited to close proximity of the water surface. At this second site, we observed Hg(0) and O_3 depletions lasting well into the night, suggesting transport and resilience of depleted air masses for several hours and over significant transport distances. Further, Hg(0) depletions were not always accompanied by corresponding O_3 depletions, suggesting that Hg(0) depletions can occur without corresponding O_3 depletions.

Model results using MECCA demonstrate that BrOx (i.e., Br+BrO) was responsible for more than 90 percent of Hg(0) depletion at the Dead Sea. Unexpectedly, we found that BrO was the dominant oxidant with contributions above 80 percent. Best agreements between simulations and observations were achieved using rate constants for kHg+Br and kHg+BrO of 2.7E-13 cm^3 $molecule^{-1}s^{-1}$ and 1.5E-13 cm3 cm^3 $molecule^{-1}s^{-1}$, respectively.