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The coupled diurnal cycles of bromine and reactive gaseous mercury in the marine boundary layer

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Large uncertainties remain in the global atmospheric budget of mercury, a toxic metal of increasing societal concern. In particular, the rapid cycles of oceanic emissions of Hg^0, oxidation of Hg^0 to reactive gaseous mercury (RGM) in the marine boundary layer (MBL), and deposition of RGM are poorly understood.

Here we examine the redox chemistry of mercury that controls these large fluxes on a diurnal scale in the MBL using datasets of RGM and Hg^0 collected at a coastal site in Okinawa, Japan and during cruises in the Atlantic and Pacific Oceans. The diurnal cycles of RGM have amplitudes of 55-300% relative to 24-hour mean concentrations; abundances peak, with varying sharpness, at noon and decline in the afternoon and evening to near the detection limit. The fastest rate of RGM formation occurs around local sunrise at all sites, suggesting that halogen oxidants of Hg^0, possibly Br or BrO, are major sources of RGM in the marine boundary layer. MBL box models with only OH and O_3 oxidants of Hg^0 do not reproduce the relatively early peak hour of RGM, while models with Br and BrO can. If atomic Br is the primary oxidant of Hg^0 in the early morning, the amplitude of the diurnal cycle is consistent with atomic bromine abundances of $1\text{-}30\times10^5$ cm^{-3} at sunrise (range due to reported rate constants for Hg-Br reactions). As these concentrations are large relative to current estimates from MBL halogen models, we are therefore investigating other redox pathways and the constraints on the sink for RGM imposed by the afternoon decline in concentration. This work supports the growing consensus that mercury-bromine chemistry is important in the mercury cycle at mid-latitudes, and refines our understanding of RGM sources and sinks in the MBL.