Diel Variation in the Atmospheric Mercury Isotopic Composition at Mount Bachelor, Oregon, USA

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Measurements of mercury (Hg) isotopic composition in atmospheric Hg species are key to understanding the global pools and cycling of Hg. Here we present 12-hr Hg isotopic measurements of total gaseous mercury (TGM) at 2700 m elevation on Mount Bachelor (near Bend, Oregon, USA) and from Storm Peak at 3213 m elevation (near Steamboat Springs, Colorado, USA). Finally, we present the first Hg isotopic measurements of particulate bound mercury (PBM) collected from an aircraft at high altitude (>8500 m). Hg isotopic compositions of TGM at Mount Bachelor show strong diel variation with higher Δ^{199}Hg and Δ^{201}Hg during the day (avg. Δ^{199}Hg=-0.22‰ and avg. Δ^{201}Hg=-0.17‰, n=6) than at night (avg. Δ^{199}Hg=-0.35‰ and avg. Δ^{201}Hg=-0.30‰, n=7). δ^{202}Hg displays lower values during the day (avg=0.34‰, n=6) than at night (avg=0.58‰, n=7). Both Δ^{200}Hg and Δ^{204}Hg display limited variation during the sampling campaign. Diel samples from Storm Peak show the oposite trend in δ^{202}Hg between day (0.24‰, n=1) and night samples (-0.13‰, n=1). All other Hg isotope ratios measured at Storm Peak show no diel variation outside of analytical error. Storm Peak is below tree line and we suggest that the vegetation in the area may influence the diel variation in δ^{202}Hg due to the uptake of Hg during the day and release at night. Mount Bachelor is located above tree line and this may lead to different diel variations observed at this site. The high altitude measurements of PBM display high magnitude positive Δ^{199}Hg and Δ^{201}Hg (avg. Δ^{199}Hg=0.88‰ and avg. Δ^{201}Hg=0.66‰, n=3). This may indicate the influence of a high Δ^{199}Hg and Δ^{201}Hg free tropospheric pool of Hg on the night samples taken at Mount Bachelor. Increased UV radiation drives increased photoreduction at high altitudes and could cause positive odd-MIF in PBM while leaving TGM with more negative values. Photochemical reactions may have also been influenced by a nearby forest fire toward the end of the sampling period at Mount Bachelor.