**Title:**

Evidence against oxidation of elemental mercury by ozone

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**Abstract:**

Mercury is a potent neurotoxin, and most mercury pollution is emitted to the atmosphere. Emitted elemental mercury exists in that atmosphere long enough to be transported around the globe. It can, however, undergo oxidation reactions, creating mercury compounds that are rapidly deposited to ecosystems, where they can have a toxic impact. Elemental mercury is known to be oxidized by halogen radicals, especially bromine. These radicals are relatively abundant in the marine boundary layer and the upper atmosphere, but they exist at very low levels in the terrestrial boundary layer. Some experimental evidence indicates that ozone is also an important oxidant of elemental mercury, but theoretical calculations argue against oxidation by ozone. Oxidized mercury cannot be measured as individual chemical species, so deciphering oxidation mechanisms from atmospheric measurements is difficult. Thus, great deal of controversy exists among atmospheric scientists about mercury oxidation mechanisms.

We measured atmospheric elemental and oxidized mercury during winter 2019 in the Uinta Basin, Utah. Local air pollution, along with persistent inversions and abundant snow cover to increase available sunlight, allow ozone to form during some Uinta Basin winters, and it reached concentrations greater than 100 ppb during 2019. Winter inversion conditions provide a strong barrier to separate the surface layer from the atmosphere above, and this allowed us to distinguish oxidized mercury that originated in the upper atmosphere (i.e., oxidized mercury that may have been formed from reactions with halogen radicals) from oxidized mercury generated via surface-level photochemical pollution.

Our measurements showed that oxidized mercury was consistently low during winter 2019 and was weakly negatively correlated with ozone and total reactive nitrogen (NOy), providing evidence that ozone did not oxidize elemental mercury. Oxidized mercury was instead correlated with colder temperatures and lower humidity, which conditions tended to occur after storm fronts passed and before multi-day inversion conditions formed. We are now conducting chemical box modeling to verify these findings.