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Atmospheric Mercury: Successes and Failures with Measurements in the Parts-Per-Quadrillion Range

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Mercury is a potent neurotoxicant. Human exposure to mercury most often occurs from consumption of contaminated fish, but most mercury pollution is emitted to the atmosphere. Once emitted, mercury can be chemically transformed and transported around the globe. Except in some highly-contaminated industrial areas, concentrations of atmospheric mercury are too low to be a direct health hazard. Instead, atmospheric mercury deposits to ecosystems, allowing it to bioaccumulate and biomagnify up aquatic and other food chains. Elemental mercury makes up the vast majority of what is in the atmosphere, with typical concentrations in the range of 1-2 ng m^{-3} (100-200 ppq). Measurements of oxidized mercury compounds are much less certain and vary more with location, meteorology, and chemistry, but typical measurements are in the range of 0-200 pg m^{-3} (0-15 ppq). Several robust, well-verified methods exist to measure gas-phase elemental mercury. Pre-concentration on gold traps followed by atomic fluorescence is the most common method, and it is very sensitive and stable. Measurements of oxidized mercury are fraught, however. Low concentrations typically require lengthy pre-concentration, but oxidized mercury compounds are so reactive that they are not usually able to survive pre-concentration, leading to measurement bias. Also, no established method exists that can measure oxidized mercury compounds directly, so it must be pyrolytically reduced to elemental mercury for analysis. This makes it impossible to know with certainty what oxidized mercury compounds exist in the ambient atmosphere. Finally, oxidized mercury compounds are semivolatile, and dynamic partitioning between the gas-phase and particle-phases makes quantitative separation of the phases extremely challenging. Commercial oxidized mercury measurement systems exist, but they suffer from all of these problems and have repeatedly been shown be biased. Several research groups are working to improve measurements of oxidized mercury. These improvements include (1) development of methods to measure specific oxidized mercury compounds, and (2) development of methods to measure total oxidized mercury in an accurate way, both with better measurement methods and with reproducible calibration systems. To our knowledge, no work is currently being done to develop quantitative measurement systems that accurately differentiate between particle-phase and gas-phase oxidized mercury.