Processes Controlling Mercury Concentration and Speciation in Yellowstone Thermal Waters

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Thermal waters in Yellowstone National Park have a wide range of total unfiltered mercury (7 ng THg L^{-1} to 159 µg THg L^{-1}) and methylmercury (<0.04 to 5 ng MeHg L^{-1}) concentrations that are a function of temperature/pH gradients, mixing of meteoric and deeper hydrothermal waters, volatilization, and boiling. For the majority of acid waters (pH<6) analyzed, over 95 percent of the THg is in the >0.45µm size fraction, operationally defined as colloidal or sediment mercury. Total unfiltered THg concentrations increase with decreasing pH. While there is no correlative relationship with pH, MeHg concentrations are greater in springs with pH<3, with concentrations below detection (<0.04 ng MeHg L^{-1}) in neutral to basic waters. Beryl Spring (33 ng THg L^{-1}; <0.04 MeHg L^{-1}) is regarded as a hydrothermal only endmember water, with approximately 25 percent of the total mercury in the <0.45µm fraction. Basic (8.2 to 9.2 pH) chloride-dominated waters in the Upper and Midway Geyser Basins (7-102 ng THg L^{-1}; <0.04 MeHg L^{-1}) form through mixing meteoric water with this hydrothermal end-member fluid. Volatile species of mercury (e.g., Hg^0_g, MeHgCl) are distilled in the subsurface through boiling and hot gas discharge. Distillation in this functionally closed system has resulted in greatly increased mercury and methylmercury concentrations. This process magnifies mercury and methylmercury concentrations in meteoric-derived acid sulfate waters (12 to 159 µg THg L^{-1}; 2.9 to 5 ng MeHg L^{-1}) as well as hydrothermal-derived waters (28.5 µg THg L^{-1}; 0.29 mg MeHg L^{-1}). Mixing between these fluid types results in the broad range of mercury and methylmercury concentrations in Yellowstone thermal waters.