Diel mercury-concentration variations in a mercury impacted stream

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Diel concentrations of filtered and particulate mercury (Hg) and methylmercury (MeHg), and associated water quality parameters, were evaluated bi-hourly for a 30-hr period during the summer and winter seasons in a creek contaminated with high levels of inorganic Hg (baseflow unfiltered Hg ~70 ng/L) to determine if biogeochemical Hg and MeHg cycles respond to the daily photocycle. Results from the summer field campaign revealed a doubling of particulate Hg and MeHg concentrations during the nighttime periods concurrent with increases in total suspended sediment; diel changes in the activity of macrobiota affecting the suspension of contaminated sediments is likely responsible for these patterns. There were no diel patterns in filtered Hg (~11 ng/L) or dissolved organic carbon quantity (~2 mg/L) or quality ($SUVA_{254}$ ~2.7 L mg C^{-1} m^{-1}). Dissolved gaseous Hg (Hg^0) concentrations, measured on a subset of samples, peaked mid-day (0.45 ng/L) with a minimum measured just prior to sunrise (0.20 ng/L) likely reflecting the effects of Hg photo-reduction. Concentrations of filtered MeHg varied, with daytime increases of ~50% over nighttime concentrations (nighttime low of 0.22 to a mid-day maximum of 0.31 ng/L) representing about one third of the variability observed over the annual cycle (from 0.1 to 0.4 ng/L). As Hg^0 and filtered MeHg represent small fractions (2-4%) of filtered Hg and have offsetting patterns, no diel pattern was detectable in the gross Hg measurement. The large amount of dissolved MeHg variability, which appears to be correlated with the daily photocycle, implies key controls on net methylation occur within the stream or on the stream bed and include factors such as small scale temperature changes in the water column and photosynthetic activity of stream biofilm. Periphyton biofilms in wetlands and lakes and epiphytic microbial communities on a dominant filamentous alga in one stream system have been implicated in methylmercury production; however, further research is required to determine the role of in-stream biofilms to MeHg patterns in this stream system.