Field validation of DNA-based biosensors for quick detection of ultra-trace mercury(II) in natural waters: Significance for early warning of mercury pollution

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Mercury (Hg) remains a significant pollutant of global concern. In particular, contamination of surface water and groundwater by Hg poses severe threats, unrecognized in many cases, to the drinking water safety of numerous, often economically challenged, communities in the world. While the speciation of aqueous Hg varies depending upon the environmental factors, inorganic Hg(II) represents a primary regulator of its fate and bioavailability in natural waters. In this regard, both the public sectors and private families are soliciting water quality sensors able to detect aqueous Hg(II) down to the ultra-trace level (below the drinking water limit) sensitively, reliably and quickly. Here, we present a summary of the development of DNA-based biosensors for Hg(II) that incorporates recent advance in the field deployment of two forms of the DNA-functionalized biosensing tools. The first form is the DNA-functionalized hydrogel sensor that can be readily applied through direct immersion in solution and water. The second setup is the DNA-DGT sensor that integrates the DNA-functionalized hydrogel with the diffusive gradients in thin films (DGT) technique to unlock more versatile applications in water, soils and aquatic sediments. These two types of Hg(II) sensors were tested with hydrochemically diverse ground and surface waters from the Datong Basin, northern China and the Great Lakes region, North America. The results indicate that the DNA-functionalized hydrogel sensor was able to measure total dissolved Hg(II) quickly (within few hours), yet inapplicable to Hg(II) concentrations below 10 nM especially in the presence of interfering components (e.g., Cl- and natural dissolved organic matter). In contrast, the DNA-DGT sensor could detect variably ultra-trace Hg(II) (even <1 nM) depending upon the deployment time. In combination with equilibrium species calculations, the DNA-DGT sensor shows the capacity to differentiate the partitioning of Hg(II) between various aqueous species and to calibrate the interferences by water temperature and natural dissolved organic matter. It reveals that the bioavailability of Hg(II), even at the ultra-trace levels, to the water organisms varies significantly depending upon the environmental conditions. Furthermore, the sensor measurements together with results of hydrochemical analyses suggest that the transformation of Hg(II) is linked to the biogeochemical cycling of sulfur in the groundwaters. Overall, our DNA-based sensors represent ultra-sensitive, field-deployable detection methods that can unravel the mobility of Hg(II) in natural waters and early warning of Hg pollution to the drinking water.