Concentration of methylmercury in natural waters from Mississippi using a new automated analysis system

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Mercury is a global health concern due to its toxicity, potential to bioaccumulation up the aquatic food chain, and global dispersion through atmospheric pathways. Mercury is mobilized through natural (e.g., volcanism, erosion) and anthropogenic (e.g., combustion of fossil fuels) means. Elemental mercury (Hg0), the most long-lived and stable form of mercury in the atmosphere, undergoes photochemical oxidation to the more soluble ionic mercury species (Hg2+), which falls to terrestrial and aquatic systems through wet and dry deposition. Sulfate-reducing bacteria, found primarily in low-oxygen aquatic environs, are capable of converting inorganic mercury to the neuro-toxic methylmercury (MeHg) form, which readily concentrates up the aquatic food chain. Human exposure to mercury is primarily through consumption of contaminated fish. In this study, results from a new methylmercury analyzer (Tekran 2700) will be presented. The system uses aqueous phase ethylation, gas chromatography, and atomic fluorescence detection. Samples were collected using clean techniques from areas in the Gulf Coast impacted by the oil spill, and from wetlands and groundwater in northern Mississippi. This poster will present relevant background, an overview of the instrumentation, and compare and contrast results for the saltwater and freshwater samples.

Key words: Methods, Surface Waters, Wetlands

Introduction

Mercury is a global health concern due to its toxicity, potential bioaccumulation, and global dispersion through atmospheric pathways. The element is mobilized through natural means (e.g., volcanism, erosion) and anthropogenic means (e.g., combustion of fossil fuels) [1]. Elemental mercury (Hg^0), the predominate form of mercury in the air, slowly undergoes photochemical oxidation to more soluble oxidized species (e.g., HgX_2), which deposit to terrestrial and aquatic systems through wet and dry deposition. Sulfate-reducing bacteria, found primarily in low oxygen aquatic environs, are capable of converting inorganic mercury to methylmercury (MeHg), which readily concentrates up the aquatic food chain [2, 3]. Humans are exposed to the adverse health effects of MeHg primarily through consumption of contaminated fish and shellfish [4, 5].

A recent report from the National Science and Technology Council Committee on the Environment and Natural Resources on MeHg in the Gulf of Mexico stated that it is critical to continue and expand research and monitoring efforts to better understand the chemical and biological processes that control the bioaccumulation of MeHg and its concentration in fish and shellfish [6]. Moreover, MeHg accumulation in freshwater systems in the southeast US (i.e., Mississippi) are often found to be elevated compared with other regions because of biogeochemical conditions favorable to methylation (e.g., high dissolved organic carbon, anoxic sediments, low pH, and proliferation of sulfate reducing bacteria) [7].

Whereas analysis of total mercury in water is relatively routine, mercury speciation is more difficult. Levels of MeHg, often ng/L or parts-per-trillion (ppt) or less, are generally an order of magnitude lower than inorganic (Hg^{+2}) concentrations. In addition, the MeHg must be separated from other forms of mercury prior to analysis. A number of analytical approaches have been used to measure MeHg, including liquid chromatography with cold vapor atomic fluorescence detection (LC-CVAFS) [8], LC coupled with inductively coupled plasma mass spectrometry (LC-ICPMS) [9], and gas chromatography (GC) [10].

In this study, we analyzed water collected using clean techniques from areas in the Gulf Coast impacted by the oil spill, and from the Yocona River in northern Mississippi. Both the Yocona River and the Enid Reservoir, which the Yocona River flows into, are impaired by mercury; and the Mississippi Department of Health has issued a fish consumption advisory for these waterbodies [11]. The samples were analyzed using a new MeHg analyzer. The system employs aqueous phase ethylation, gas chromatography, and cold vapor atomic fluorescence spectrometry (CVAFS). An in-vial purging technique was also tested. The system is described in more detail in the Methods section.

Methods

Freshwater Sampling and Preservation. Freshwater was sampled from the Yocona River located in north Mississippi (Fig. 1). Samples from the river were collected into acid-washed amber glass bottles just below the water surface. Samples were placed in a cooler with ice and transported to the lab for analysis. Conductivity, pH, oxidative reducing potential (ORP), chloride, and dissolved oxygen (DO) were measured in the field using an YSI multi-meter. At the lab, a portion of the sample was passed through a quartz silica (0.45 µm) glass fiber filter and both filtered and unfiltered samples were preserved to 0.5% HCl.

Saltwater Sampling and Preservation. Samples were collected from eight stations located in the Gulf of Mexico just south of Bay Saint Louis, MS (Fig 2). Samples were collected using either a teflon-coated external spring Niskin bottle or the ship's rosette sampler with metal clean GoFlo bottles. The water was then transferred to acid washed Teflon bottles and shipped overnight to the lab for analysis. The samples were passed through a 0.45 µm glass fiber filter and both filtered and unfiltered samples were preserved to 0.5% H_2SO_4.

Methylmercury Analyzer. The samples were analyzed using a new automated MeHg analyzer (Tekran 2700; Toronto, Canada). A schematic of the instrument is shown in Figure 3. In short, a 45-mL or 30-mL (for in-vial purging) sample aliquot is placed in an I-Chem® glass vial with an acetate buffer and ethylated in the vial by the addition of sodium tetraethyl borate ($NaBEt_4$); volatile mercury species are formed (methyl-ethyl-mercury for $MeHg^+$ and diethylmercury for Hg^{+2}). The ethylated forms are then separated from the solution by purging with argon onto a Tenax carbon trap. After preconcentration the trapped species are thermally desorbed and carried into a GC where the species are separated. The volatile species are then passed through a pyrolytic decomposition column, which converts organo-Hg forms to Hg^0, and further into the cell of a CVAFS for detection. The combination of low background (the detector is 90˚ to the Hg lamp excitation source) and high sensitivity (photomultiplier detection) allows for extremely low detection limits, which is required for the low-levels of MeHg found in the environment.

Quality Assurance. Samples were analyzed following EPA Method 1630 "Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and CVAFS", without the distillation step which others have found to be unnecessary under certain conditions [12]. Calibration curves had r^2 values of 0.995 or higher. Reproducibility was generally ± 25%. Accuracy was checked by sample spiking and later by analysis of a fish tissue certified reference material (CRM), DORM-2 and later DORM-3 obtained from the National Research Council of Canada. The CRM was digested using two methods: a 25% m/v mixture of KOH/Methanol following a procedure by the Florida Department of Environmental Protection [12], and by 25% tetramethylammonium hydroxide (TMAH). The digests were

diluted and analyzed along with the samples; recoveries were between 80-120%.

Results and Discussion

Instrument evaluation. In addition to the quality assurance testing discussed above, a new instrument configuration, in which volatile species are purged directly from the vial (rather than transferring the liquid to a sparger), was evaluated. The in-vial purging method yielded similar results and met EPA quality assurance requirements; the method detection limits (MDL), calculated using the 3 sigma criteria, were 0.014 ppt (external sparging) and 0.018 ppt (in-vial sparging). The new approach is considered advantageous because: there is no transfer of liquids, minimizing carryover between samples; liquid waste is reduced; analysis time is faster (~7 min per sample); and reliability is improved through elimination of the sparger, syringe pump, and liquid switching valves.

Recently, we tested the instrument's capability to determine inorganic (Hg^{+2}) simultaneously with MeHg. Calibration curves and recoveries for reference materials for both species of mercury were good, suggesting that both could be quantified in the same sample. Together the data could be used to estimate total mercury concentrations because other forms of mercury (e.g., Hg0) are expected to be negligible. However, sample chromatograms should be checked for the presence of other peaks which may represent unusual forms of mercury. For the freshwater and saltwater samples discussed below, only MeHg was determined.

Freshwater. For the Yocona River, samples were collected on October 24, 2010 following a period of drought ("low" flow) and on October 25, 2010 after a rain event ("high" flow) (Fig. 4). Results for the filtered and unfiltered samples are shown in Figure 5. Concentrations ranged from about 0.018 to 0.050 ppt (ng/L). Whereas MeHg concentrations were similar for filtered and unfiltered samples, there was a substantial difference between the low and high flow conditions, with the "high" flow exhibiting lower MeHg levels. Water quality also differed, with lower conductivity, pH, ORP and chloride concentration and higher DO for the "high" flow condition (Table 1). This may be attributed to dilution from rainwater. However, the rain event was not large enough to introduce large quantities of soil via erosion processes. It was also not large enough to cause overflow of our test wetlands, which are known MeHg sources.

Saltwater. For the saltwater samples, concentrations ranged from 0.012 to 0.051 ppt (ng/L) (Fig. 6). These levels do not appear to be elevated compared with what others have found in seawater (outside the Gulf) [13]. There were no distinctive spatial trends (across the transect), except for high levels for the filtered sample from station 5 (which was perhaps contaminated).

Whereas the levels of MeHg in the Gulf samples were not particularly high, it should be stressed that the impact of the Deep Water Horizon oil spill in the Gulf of Mexico on the distribution and cycling of MeHg is of continued interest. Over time the oil and dispersants may alter the element's complex biogeochemical cycle due to:

- proliferation of hydrocarbon-degrading- and possibly methylating- microorganisms
- changes in dissolved oxygen (redox conditions) as a result of increased microbial activity
- higher levels of dissolved organic carbon, a factor known to affect Hg bioavailability
- microscopic oil particle plumes layered within the water column, an unknown factor
- the shear amount of Hg introduced into the ecosystem from the oil itself

Conclusions and Future Work

Water samples were collected from the Yocona River and Gulf of Mexico and were analyzed for MeHg using a new automated CVAFS system. Concentrations for the Yocona River were lower under high flow conditions than low flow. Concentrations of MeHg in the Gulf of Mexico do not, at this point, appear to be impacted by the Deepwater Horizon Oil Spill. Concentrations at both sites are lower than

wetlands in northern MS [data not shown]. Overall, results indicate that the new CVAFS system is capable of reliably measuring the low levels of MeHg found in natural waters.

Future plans include measuring MeHg and total-Hg in wetlands in the Little Tallahatchie and Yocona watersheds, and in Enid and Sardis reservoirs. The data, together with estimates of stream discharge, will be used to estimate the MeHg loadings to Enid Lake. The distribution and cycling of mercury species will be studied (spatially and temporally) to better understand the dynamics and importance of these species in the impaired waterbodies. In addition, new samples from the Gulf Coast will be analyzed. As noted earlier, both basic research and long-term monitoring efforts for MeHg at strategic locations in the Gulf should be a high priority given that the influence of the oil and dispersants on the formation and fate of MeHg is not known.

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Table 1. Water quality parameter Yocona River samples						
Date	**Flow**	**Conductivity (µS/cm)**	**pH**	**ORP (mV)**	**Cl (mg/L)**	**DO (mg/L)**
10/24/2010	"low"	192	7.1	152	20	8.0
10/25/2010	"high"	67	5.8	66	8	9.1

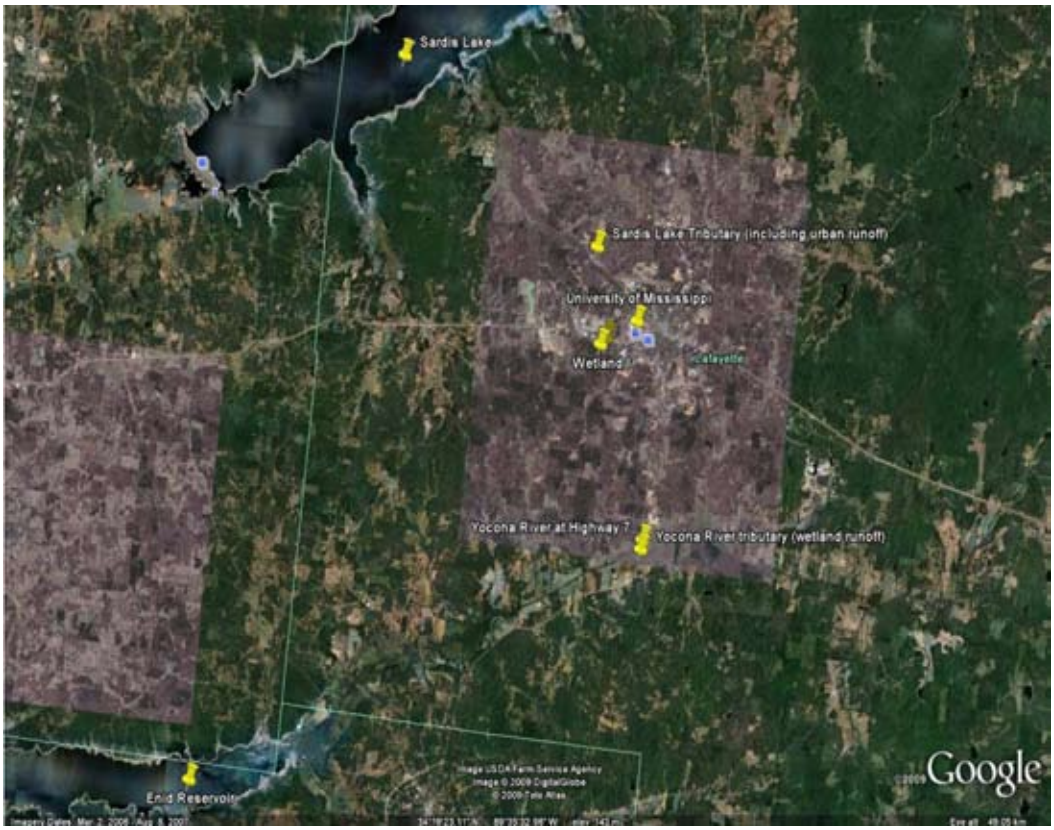

Figure 1. Study area in north Mississippi.

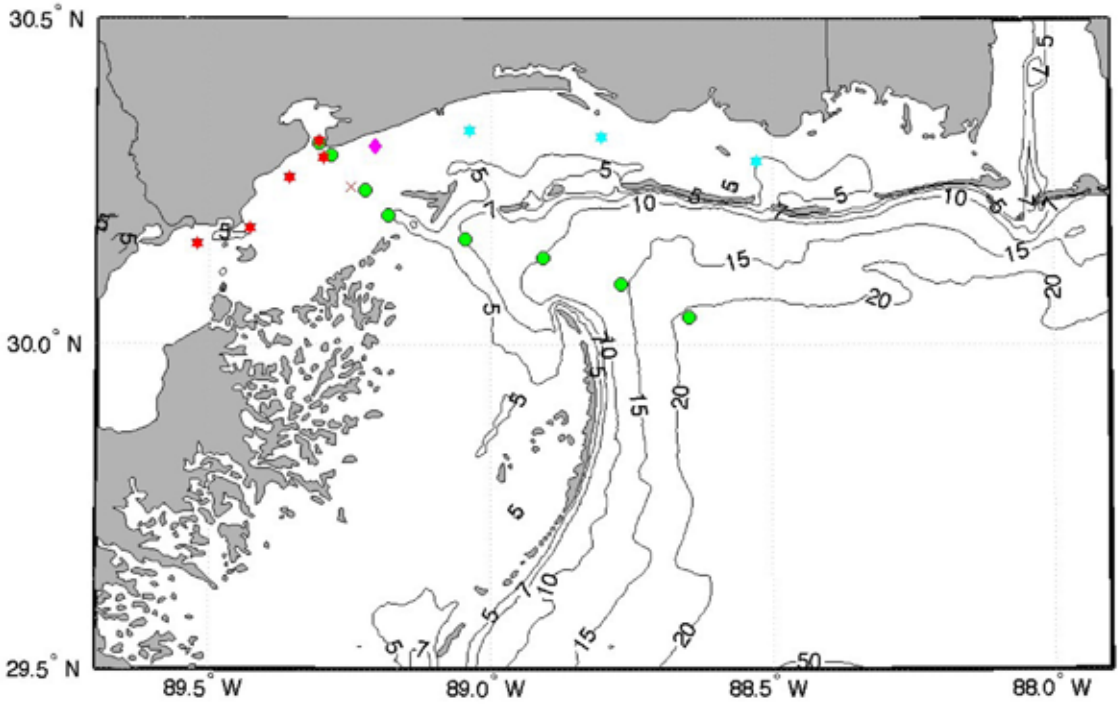

Figure 2. Map showing the Mississippi Gulf coast (near Bay St. Louis) and samples areas (green circles).

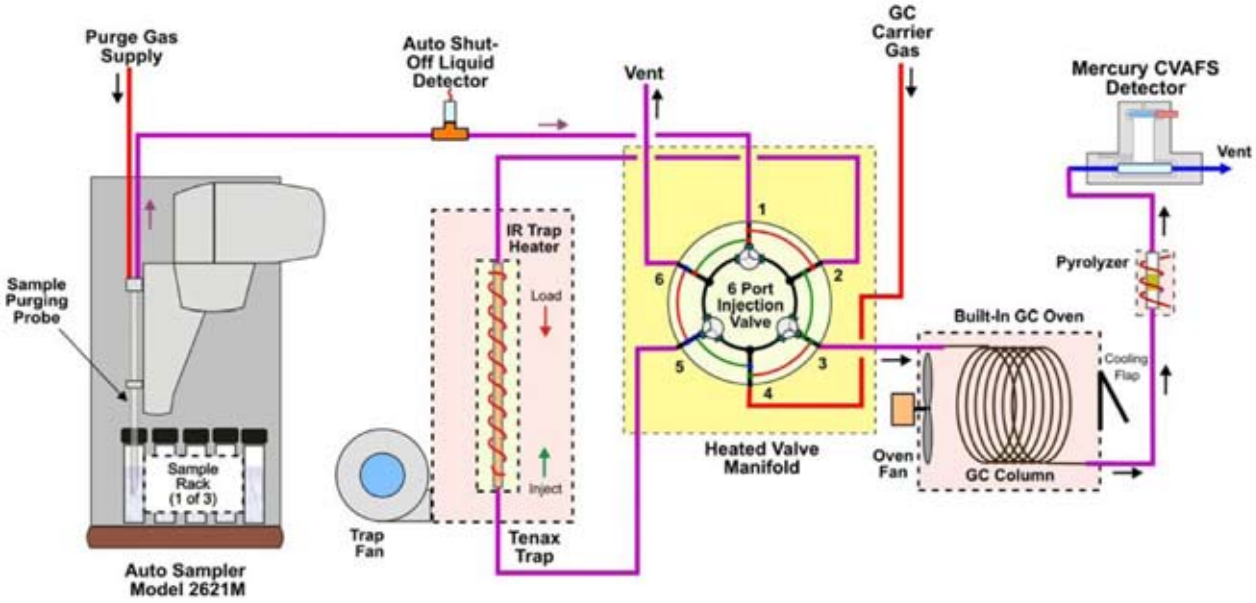

Figure 3. Flow diagram for the methylmercury analyzer (Tekran 2700).

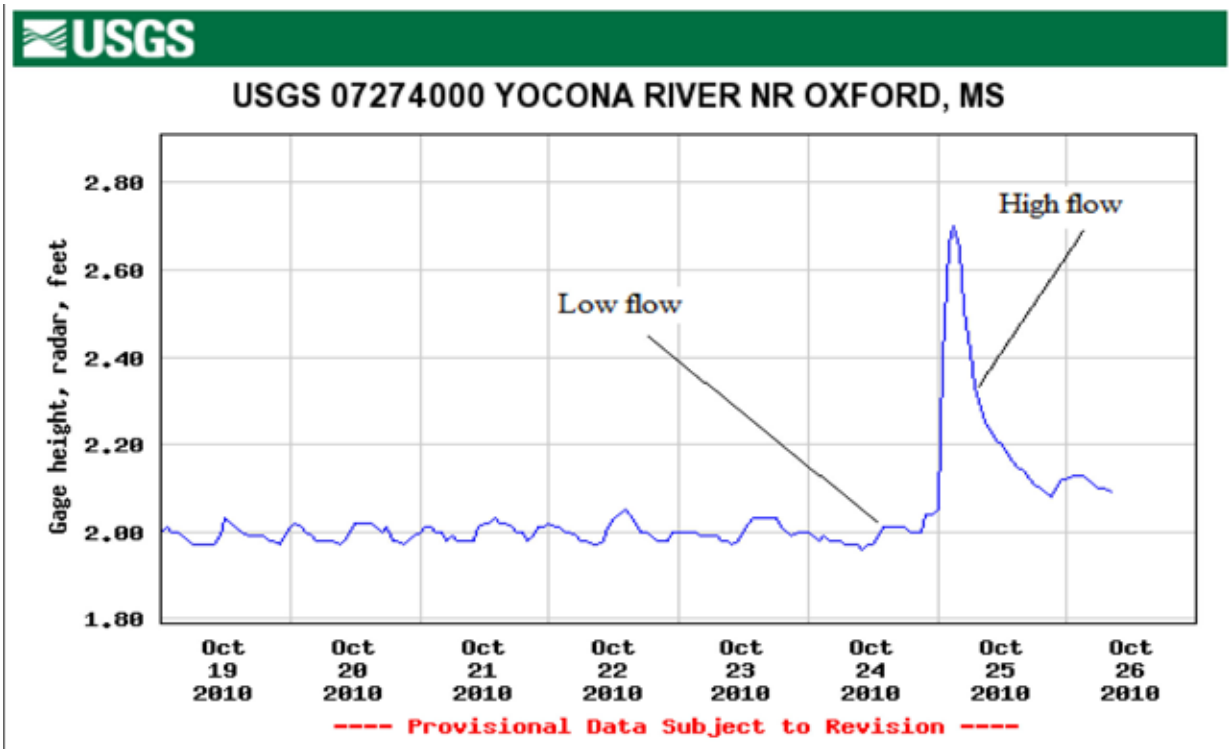

Figure 4. USGS stream gauge data showing the relative height of the Yocona River at Highway 7 near Oxford, MS. Samples were collected at low and high flows as indicated.

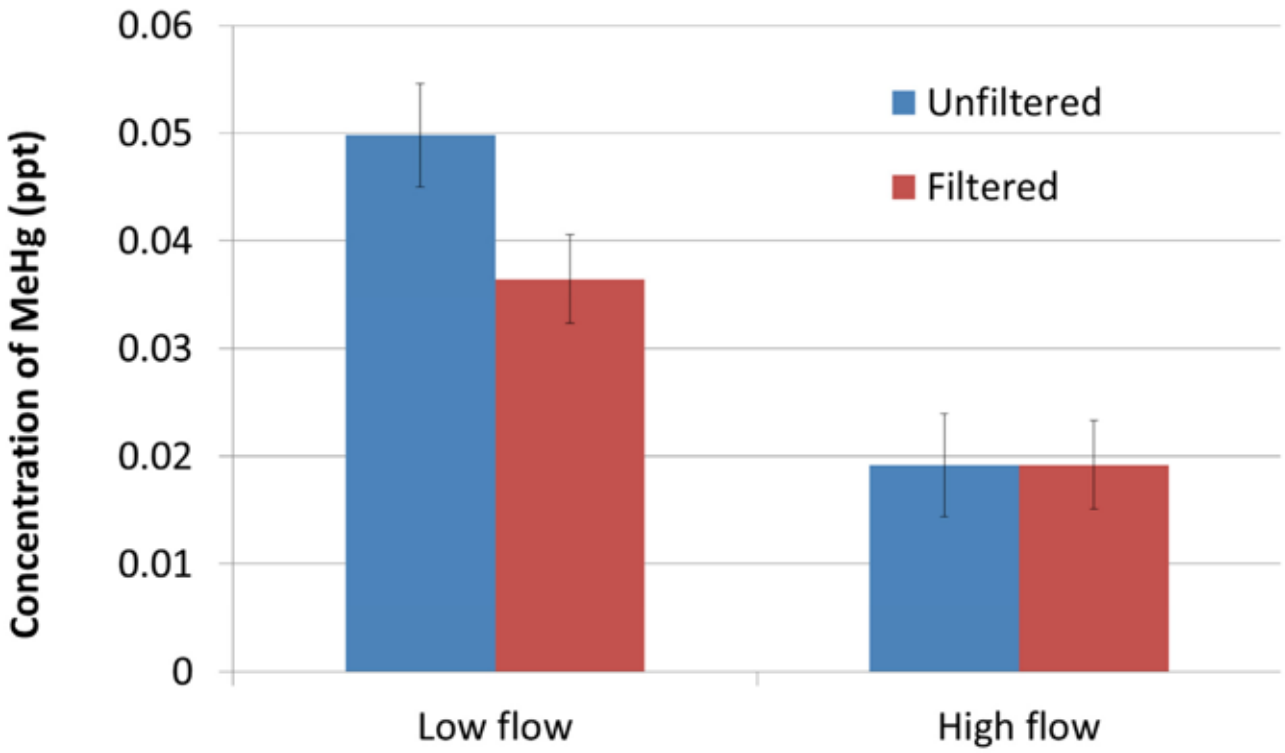

Figure 5. MeHg in the Yocona River during different flow regimes.

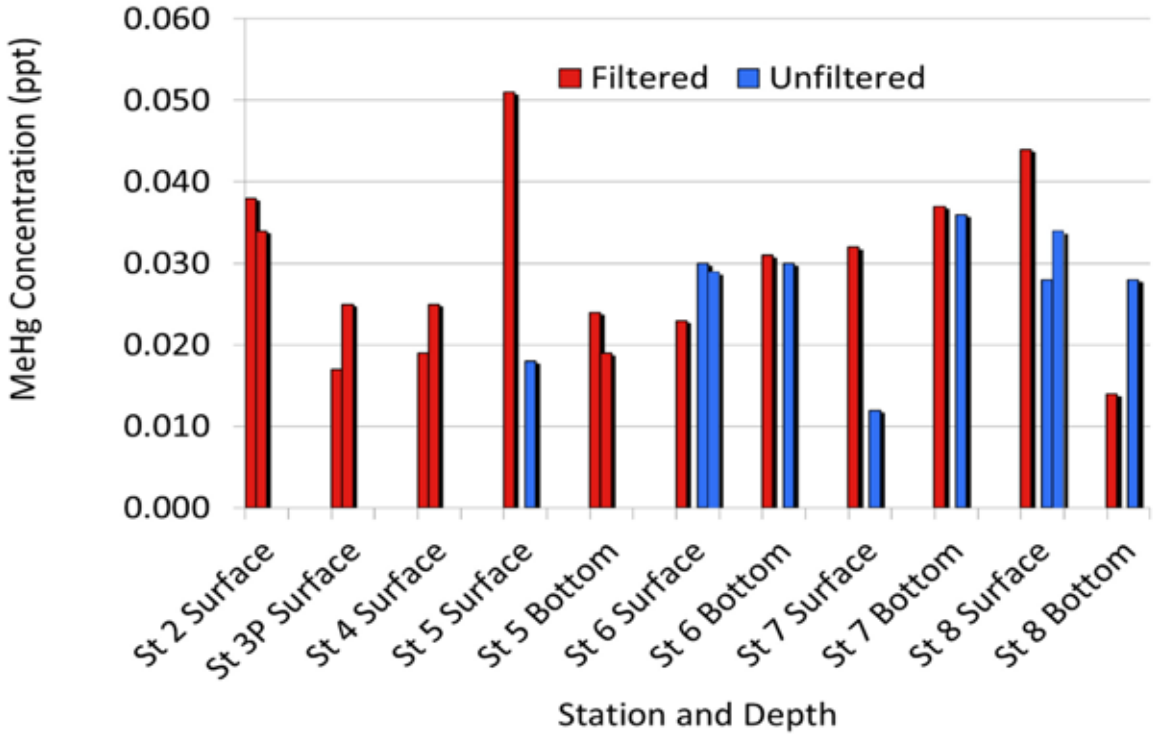

Figure 6. MeHg in the Gulf of Mexico near the site of the Deep Water Horizon oil spill.