New York State Energy Research and Development Authority

Geographic Variation of Methylmercury Bioaccumulation in the Hudson River

Final Report

January 2014

Report Number 14-25

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Geographic Variation of Methylmercury Bioaccumulation in the Hudson River

Final Report

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NYSERDA Report 14-25 NYSERDA Contract 16297 January 2014

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Acronyms and Abbreviations

Bq	Bequerel, where 1 Bq = 1 nuclear disintegration per second
DOC	dissolved organic carbon
MeHg	methylmercury

Executive Summary

To help understand the geographic variation in fish concentrations of methylmercury (MeHg) in the Hudson River and its tributaries, the authors reasoned that it is necessary to first understand the bioaccumulation of MeHg in resident phytoplankton, which are at the base of the aquatic food webs. Animals are known to accumulate MeHg almost exclusively through their diet, and MeHg levels in aquatic organisms that could serve as the diet for fish are ultimately dependent on MeHg uptake by phytoplankton. The project evaluated the dependence of MeHg uptake in phytoplankton on the variation in the dissolved organic carbon (DOC) in the water in different regions of the Hudson. Most of the waters that we examined, primarily freshwater, did not vary enormously in DOC concentration, but nevertheless there appeared to be a clear inverse relationship between bioconcentration factors of MeHg in diatoms and external DOC concentration. These data are entirely consistent with prior work for fresh waters in the California Bay-Delta region near the Sacramento River. Also, it appears that MeHg displays somewhat greater bioavailability for diatoms in saline waters than in purely fresh waters. While uptake of MeHg in phytoplankton would appear to be affected by total DOC concentrations (and most likely DOC rich in thiols), this detail may have a smaller effect on the amount of MeHg that is transferred trophically to fish than the total MeHg concentration in the water. There was no pronounced relationship between killifish concentrations of MeHg and ambient DOC.

1 Introduction and Rationale

This project examined factors that influence the bioaccumulation of methylmercury (MeHg) in phytoplankton in the Hudson River and its tributaries. Specifically, this project addressed biogeochemical processes affecting MeHg uptake in aquatic food chains, with an eye toward understanding the geographic variation observed in mercury concentrations in fish in the Hudson River watershed. Particular attention was paid toward determining the effects of naturally occurring dissolved organic carbon (DOC) on MeHg uptake in phytoplankton. The rationale for this approach is that although MeHg displays food chain biomagnification, the largest bioconcentration step by far of MeHg in aquatic food chains occurs from the aqueous phase to phytoplankton, which serve as the base of most aquatic food webs. The authors measured the trophic transfer of MeHg from phytoplankton to zooplankton to killifish (*Fundulus*) and assessed the influence of DOC on the build-up of MeHg in aquatic food chains for different batches of water from different locations in the Hudson River. We believe that the results of this study should be applicable to other bodies of water.

Mercury is released into the environment by a number of natural and human processes. Anthropogenic activities that especially contribute mercury (Hg) include coal burning electric power generation and, increasingly rare, chloralkali plants. Once Hg is released by these activities, a small fraction of it can eventually be methylated by aquatic bacteria (thought primarily to be sulfate-reducers, but not exclusively) and then released into ambient water and sediment. Both inorganic mercury (HgII) and MeHg are greatly concentrated from ambient water by phytoplankton. However, MeHg displays very different biological behavior than HgII. In particular, MeHg tends to display biomagnification in freshwater and marine food chains, and can act as a more effective nerve poison than inorganic Hg because it is assimilated in animal tissues and crosses the blood-brain barrier. As a consequence, MeHg can arguably be considered the single most detrimental pollutant in aquatic systems, both to aquatic life and to human consumers of seafood, which supply the large preponderance of total mercury uptake in people.

It has commonly been observed that fish, including in New York State's waters, display considerable geographic variation in their MeHg concentrations, yet explanations are not fully apparent (Levinton and Pochron 2008). Importantly, fish tissue concentrations generally reflect the loading of natural waters by mercury, usually via atmospheric fallout. However, within a watershed, there can remain considerable variability, even for the same fish species (of the same size and age). For those fish that tend to have small swimming ranges, this variability is most likely attributable to water chemistry differences between regions.

This work extended some recent discoveries that demonstrated that MeHg uptake is greatly influenced by dissolved organic carbon (DOC) that occurs in natural waters at environmentally realistic concentrations. We explored how DOC variability in water in different areas of the Hudson River and its tributaries can affect the introduction of MeHg into food chains in those waters. We also assessed the significance that this introduction has for transfer of the planktonic MeHg to killifish. Killifish were used as a model fish for several reasons: they are euryhaline and ubiquitous throughout the Hudson; they are important prey for larger game fish that are caught for human consumption; they display very limited swimming ranges, and hence have been used as bioindicators of contamination that are quite site-specific; and there is already a large and growing literature on their sensitivity to Hg. Further, recent work in our laboratory has evaluated such key factors as salinity and DOC concentrations on MeHg uptake by these fish directly from the aqueous phase. However, because dietary sources are the dominant source for MeHg uptake in these (and other) fish, this work emphasized the influence of DOC on the bioaccumulation of MeHg on phytoplankton and its subsequent trophic transfer to fish.

Virtually alone among the metals, Hg displays biomagnification throughout aquatic food chains, reaching concentrations in fish that can be greater than or equal to 10^6 times higher than surrounding waters (Mason et al. 1996). Key to understanding this pattern is the biological behavior of methylmercury (MeHg), an organic form that is more readily accumulated and stored in cells than inorganic HgII (Mason et al. 1996; Pickhardt and Fisher 2007), and is lost from fish at extremely slow rates (Pickhardt et al. 2006). This observation helps account for the fact that higher MeHg concentrations are typically found in upper level carnivores with relatively long life spans.

1.1 Mercury in the Hudson River and Its Fishes

In the Hudson, MeHg accumulates in fish to concentrations high enough to warrant human health concerns. In the northern end of the Hudson, from Corinth Dam to the dam in South Glen Falls, high Hg concentrations are responsible for fish consumption advisories in smallmouth bass (New York State Department of Health 2008). In the southern end of the Hudson and NY Harbor, anglers who consumed local fish had higher blood concentrations of Hg than those who did not (Gobeille et al. 2006). Mercury concentrations reach levels that would warrant posting in other regions. For example, concentrations of Hg in striped bass in the lower Hudson River ranged from 0.07 to 0.68 ppm (A. Forti, NYS Department of Health, personal communication). In California, the Regional Water Quality Control Board set screening values of 0.2 ppm for Hg in fish in the San Francisco Bay (SFEI 2000). High Hg concentrations are especially a concern for pregnant women because mercury may affect fetal brain development and result in neuromotor, visual, and sensory impairments in developing fetuses (Mahaffey 2000).

Despite the high concentrations of Hg in fish from the estuary, there remains considerable uncertainty about the factors governing Hg distributions and bioavailability in fish. In previous research, Levinton and Pochron (2008) found that there was a spatial pattern in fish Hg concentrations, with levels increasing as they moved north in the Hudson River from New York City. However, they were unable to determine if this pattern was due to a point source or due to variations in water chemistry, especially from the Adirondack watershed that empties into the northern Hudson. Balcom et al. (2008) found that fluvial inputs were the dominant MeHg source to NY Harbor, but were unable to quantify the exact magnitudes.

As previously noted, the goal of this research was to determine some of the key factors responsible for MeHg bioaccumulation in the Hudson River. To accumulate a contaminant, fish must acquire it from either dietary uptake or direct, aqueous exposure or both. For MeHg, more than for any other metal, dietary uptake is the primary route of exposure (Mathews and Fisher 2008), making MeHg accumulation by phytoplankton a critical first step. Moreover, concentration factors for MeHg in phytoplankton can be greater than 10^5 (Pickhardt and Fisher 2007), indicating that algal cells are enriched in MeHg by that amount over ambient water. Differences in MeHg concentrations between plankton and animals higher in the food chain are typically far smaller, often by a factor of only 2 or 3 (IAEA 2004). Therefore, this research focused on understanding the parameters that affect MeHg accumulation by phytoplankton and evaluating how that mercury is then transferred up the food chain.

One variable that may be particularly important for understanding how MeHg is accumulated in phytoplankton is dissolved organic carbon (DOC) in the water. It has long been recognized that phytoplankton cells respond to free metal ion activity rather than total ambient metal, and that metals complexed by DOC in natural waters are generally less bioavailable than free metal ions to phytoplankton. Most studies that have examined the influence of DOC on metal-biota interactions have considered metal ions and inorganic metal complexes; the influence of DOC on the bioavailability of methylated metals such as MeHg has received considerably less attention.

Although MeHg uptake by phytoplankton in the Hudson River has not been previously assessed, several studies of other locations point to the potential importance of DOC in controlling MeHg partitioning and bioavailability. MeHg and Hg(II) may bind to the DOC through complexation to reduced sulfur groups (e.g., thiol groups) on amino acids and humic substances (Amirbahman et al. 2002). In culture studies with water collected from two sites in the San Francisco Bay Delta, Pickhardt and Fisher (2007) found that phytoplankton grown in water with a DOC concentration of 280 μM C accumulated at least twice as much MeHg as phytoplankton grown in water with a DOC concentration of 177 μM C. They hypothesized that the phytoplankton actively took up some components of the DOC, such as amino acids, and inadvertently acquired the MeHg associated with that organic matter.

Recent studies in our laboratory with organic matter isolates from the San Francisco Bay Delta suggest that organic matter significantly decreases the availability of MeHg to phytoplankton, with the most pronounced declines in MeHg bioconcentration in response to additions of DOC below 350 μM C (Luengen et al. 2012). Our result was consistent with work by Gorski et al. (2008), which compared water from a variety of field sites, including the San Francisco Bay Delta, river water, and lake water, and found that phytoplankton grown in water with low DOC concentrations, particularly rainwater, had the highest accumulation of MeHg. They hypothesized that MeHg bonding to DOC reduced MeHg bioavailability. Similarly, in a field study of 15 Wisconsin lakes, Watras et al. (1998) found negative correlations between DOC and MeHg concentrations for seston, zooplankton, and fish, suggesting that DOC reduced MeHg uptake by phytoplankton and resulted in lower fish concentrations. In a study of Adirondack lakes, Driscoll et al. (1995) found that the effect of the DOC depended on its concentration: at high DOC concentrations, DOC limited MeHg concentrations in fish, whereas at low DOC concentrations, DOC was positively correlated with MeHg concentrations in fish.

2 Research Performed

2.1 Approach Used

Water was collected from a range of different Hudson River (and tributary) sites, most of which were entirely freshwater. The chemical composition of the water at each site was determined, focusing principally on the DOC concentration. Where possible killifish were also collected and analyzed for Hg concentration. For each batch of water from each field site, the uptake of MeHg by phytoplankton was assessed using the gamma-emitting radioisotope ^{203}Hg. Me^{203}Hg was added to water obtained from different locations within the Hudson River, each with its own DOC content, and allowed to equilibrate before inoculating with phytoplankton cells. The phytoplankton were exposed to the Me^{203}Hg for several days during which cells were periodically filtered out of their radioactive water and analyzed for radioactivity. The Me^{203}Hg uptake rates and concentrations factors were determined for each batch of water.

2.2 Water Samples

Water samples for chemical analyses, the growth experiments, and the analysis of dissolved organic carbon were taken at a series of mid-river stations using the Cary Institute boat, which is a 20-foot Whaler. Samples from some of the major tributaries were obtained by boat. , Where the water was shallow, other samples were obtained by kayak. Chemical analyses followed the Cary Institute protocol for the Hudson River as in Lampman et al. (1999) and Goodwin et al. (2008). Samples were kept in a cold cooler (about 4 to 8 ^{o}C) until they were returned to the lab. For dissolved constituents including DOC, samples were filtered through Whatman GF/F filters.

Dissolved oxygen and temperature were measured in the field at 0.5 m depth using a YSI Pro-ODO oxygen meter with an optical probe, and pH was measured using a Accumet AP61 pH meter with 13-620-AP60A probe pH meter. Chloride was measured in the field as a proxy for salinity using an Accumet 13-620-526 chloride probe. Conductivity was measured in the field, corrected for temperature, using a YSI EC 300 conductivity meter. All of the probes were calibrated in the field prior to use.

Total DOC was measured using a Shimadzu TOC-V Carbon, Sulfur, Hydrogen analyzer. This machine uses a high temperature oxidative combustion with a platinum catalyst and the evolved CO_2 is measured by infrared analysis. For the Specific Ultra Violet Absorbance (SUVA) analysis of DOC, we used Perkin Elmer LS50B luminescence spectrometer and followed the procedures of McKnight et al. 2001) and Cory et al. (2007). We used 350 nanometers (nm) as the excitation wavelength and measured emissions at both 450 and 500 nm. The ratio of these two emissions bands is used as the SUVA ratio (McKnight et al. 2001)

Fish for mercury analysis and for stable isotopes were obtained in shallow water using beach seines. Our goal was to obtain banded killifish (*Fundulus diaphanous*) at all sites for facilitate comparison. We were only partially successful in this collection, and substituted other small, littoral fishes where no killifish could be obtained.

The sites where samples were taken and where water was obtained are shown in Tables 1 and 2. Table 1 and Figure 1 show the sites in the main stem of the Hudson River; Table 2 shows the tributary and other sites. To increase the DOC gradient, we also sampled one pond (Old Man McMullen Pond; OMM) in Litchfield, Connecticut. (Latitude: 41.9575342; Longitude: 73.2505967). To prepare water for one of the Hg uptake experiments, we added 1.5 g of sodium bicarbonate to 18 L OMM water and added 2 L of water from the Hudson River at Kingston. The idea was to create high DOC concentrations in a matrix that was similar in pH and cations to that of the Hudson. Of these sites, only Dykman St., the most southerly site, was partially saline; the other sites were essentially freshwater or slightly brackish. Specific conductance from near 0 to greater than 3000 with three sites (Dykman St., Yonkers and Dobbs Ferry) with conductance above 400. Most sites had DOC concentrations in the 3-4 milligrams per liter (mg/L) range, although the Walkill (6.8 mg/L), Swarte Kill (9.4 mg/L), and Old Man McMullen sites (10.6 mg/L) had significantly higher DOC concentrations (Tables 1 and 2). The pH of all of the riverine and tributary sites were all cirumneutral to slightly alkaline, only Old Man McMullen pond had acidic water. While the DOC concentrations varied, the SUVA ratios were in a tight range between 1.5 and 1.9 (Table 1). These ratios are indicative of a largely terrestrial origin of the DOC and consistent with the isotopic work in Cole and Solomon (2012).

Figure 1. Map of the Hudson River showing the locations of the stations sampled in this study

For station locations, we used river kilometers (Rkm), with Battery Park, at the southern tip of Manhattan defined as 0 Rkm. Rkm run north from Battery Park. The details about the stations sampled are shown in Table 1. Not every station in Table 1 is shown on the map but its location can be determined by interpolating between the Rkm shown.

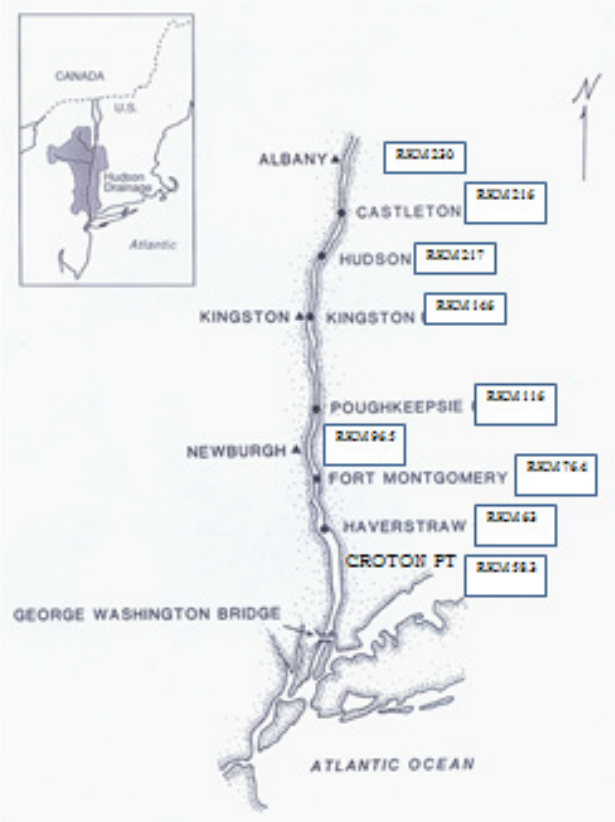


Table 1. Sites and chemical characteristics of water in this study from sites in the main stem of the Hudson River

River km are km north from the southern tip of Manhattan Island. This is a standard way to report location for Hudson River sites.

Site name	River km	Date collected	temp C	pH	DO % sat	conductivity (uS/cm)	Cl mg/l^{-1}	DOC mg C l^{-1}	Color (440 nm)	SUVA (450 nm)	SUVA (500 nm)	SUVA (ratio)
Dykman St	25.1	5/25/11	13.4	8.11	97.8	3146.00		3.31	0.097	8.813	5.176	1.703
Yonkers-JFK	34.8	5/25/11	19.3		96.5	892.00		3.54	0.082	7.617	4.352	1.750
Dobbs Ferry	41.5	5/25/11	19.5	7.73	99.8	437.80		3.72	0.095	8.652	4.956	1.746
Croton Pt.	58.3	5/25/11	19.9		120.7	201.00		3.30	0.087	7.247	4.535	1.598
Newburgh	96.5	4/15/11		7.92	102.3	272.20		3.19	0.099	7.914	4.202	1.888
Rhinecliff	144.4	6/23/10				321.00	29.1		0.006	7.396	3.813	1.961
Kingston	146.4	5/19/11	14.5	7.32	95.6	150.70		3.14	0.081	9.018	5.359	1.684
Charles Ryder	150	8/2/10	25.6	7.64	90.7	246.00	22.3	3.44	0.031	7.659	3.990	1.916
Charles Ryder	150	6/23/10				256.00	27.4		0.008	6.749	3.769	1.793
Schodack	213	7/23/10										
Schodack	213	6/25/10				253.00	23.9		0.015	8.768	5.073	1.728
Henry Hudson	217.5	8/3/10	21.2	7.89	99.4	305.00	27.1	3.93	0.023	9.593	5.274	1.828
Albany	230.5	6/29/10				230.00	21.7		0.013	8.629	4.849	1.784

Table 2. Sites where water was taken in tributaries of the Hudson River and for Old Man McMullen Pond (OMM) in Connecticut

Site	River or system	Date	T °C	pH	DO % sat	cond	Cl mg/L	DOC mg CL^{-1}	Color 450 nm	SUVA 450 nm	SUVA 500 nm	SUVA ratio
Wallkill	Wallkill/Roundout	7/16/10					39.8		0.013	11.98	6.44	1.88
Wallkill	Wallkill/Roundout	8/2/10	25	7.69	69.5	280	37.9	3.6	0.015	9.56	5.14	1.87
Mohawk	Mohawk	7/1/10					28.2		0.014	9.44	5.45	1.75
Lock 6	Mohawk	8/3/10	24.9	7.89	94.1	215	20.5	4.8	0.008	11.94	6.73	1.78
proper	Wallkill	4/15/11	11.9	7.95	96.2	339		6.8	0.107	23.50	13.32	1.77
Swarte Kill	Swarte Kill	4/15/11	13.2	7.27	90.6	235		9.4	0.107	27.36	18.32	1.49
OMM	Old Man McMullen	5/20/11	15.6	4.86	101.5	20.2	0.0	10.6	0.143	18.43	11.90	1.55

2.3 Laboratory Experiments

Laboratory experiments were conducted to evaluate the biological uptake of MeHg into phytoplankton and the subsequent trophic transfer to amphipods and fish using waters from different salinity and DOC combinations and locations in the Hudson watershed. Water from field sites in the Hudson River estuary were collected with existing sampling efforts by author Jonathan Cole.

In fall 2010, the four sites chosen were Charles Ryder (CR), Wallkill (WK), Henry Hudson (HH), and Mohawk (MH). Forty liters from each site was 45 µm course Nitex filtered in the field.

The gamma-emitting radioisotope $^{203}HgCl_2$, purchased from Eckert & Ziegler Isotope Products, Valencia, CA, was used to synthesize $CH_3{}^{203}HgOH$ ($^{203}MeHg$) by following established methods (Rouleau and Block 1997; Pickhardt and Fisher 2007).

The $^{203}MeHg$ concentrations were followed in water and phytoplankton cells over a period of three days. MilliQ water was filtered through 0.2-µm sterile cartridges to make amended fresh water media, WCL-1. Then it was inoculated with the diatom *Cyclotella meneghiniana* (clone UTEX LB 2611) for the phytoplankton uptake and to label the fresh water laboratory reared amphipod, *Hyalella azteca*, acquired from Aquatic Research Organisms in Hampton, NH.

The four site waters were filtered with 0.2-µm sterile cartridges, used to make amended WCL-1 media, and distributed in 100-millilter (mL) volumes to each experimental 250-mL ground glass trace metal clean Erlenmeyer flask with glass stopper. Triplicates were made for each site in addition to triplicate controls. An initial density of 2×10^5 cells/mL was used, and the triplicate flasks for each site were inoculated with the phytoplankton that was resuspended from a 1 µm pore size 47 mm diameter sterile polycarbonate filter. The control triplicate flasks contained no phytoplankton.

$^{203}MeHg$ was added to each flask (29.6 killiBequerels, or kBq, total for 24 flasks) and a 1-mL unfiltered sample (T=0) was taken for confirmation of the radioactivity. The sample time points were T=2, T=5, T=10, T=24, T=48, and T=72 hours. For the flasks containing phytoplankton sampling consisted of 2 mL preserved with Lugol's solution for cell counts, 1 mL unfiltered, and 10 mL filtered on a 1 µm pore size 25 mm diameter polycarbonate sterile filter with two 5 mL rinses of filtered, unradioactive MilliQ water adjusted to pH 7 via NaOH. For the control flasks, 1 mL unfiltered and 10 mL filtered on a 1 µm pore size 25 mm diameter polycarbonate sterile filter were sampled. Cells were counted using a Beckman Coulter Multisizer 3 Counter. The fractionation of the $^{203}MeHg$ was

determined by dividing the radioactivity on washed particles caught by 1-µm filters by the radioactivity in the aqueous phase (that is, passing through the 1-µm filters. To normalize the particulate radioactivity to cellular biomass, volume/volume concentration factors were determined by dividing the radioactivity per cubic micrometer of cellular material by the dissolved radioactivity in the same volume of ambient water.

^{203}MeHg was used to conduct trophic transfer experiments using protocols established to determine the efficiency with which the ^{203}MeHg in the phytoplankton can be assimilated by animals feeding on them. MilliQ water that was filtered with a 0.2-µm sterile cartridge and used to make amended WCL-1 media was distributed in 150 mL volumes to four glass beakers for the *H. azteca* distribution and four other glass beakers contained amended WCL-1 media for controls. The *H. azteca* were starved for 24 hours prior to the experiment.

The experimental design for the *H. azteca* labeling used a 0.2 µm sterile cartridge to filter the four site waters and distributing 150 mL volumes to eight 250-mL ground glass TM clean Erlenmeyer flasks with ground glass stoppers for the radiolabeled phytoplankton addition and for controls. An initial cell density of 2×10^5 cells/mL was used and four flasks were inoculated with *C. meneghiniana*. The control flasks contained no phytoplankton. ^{203}MeHg was added to each flask (82.51 kBq total for eight flasks) and a 1 mL unfiltered sample (T=0) was collected for confirmation of the initial radioactivity. The radiolabeled phytoplankton were exposed to the radiolabeled MeHg for 48 hours.

After 48 hours, samples of 1 mL unfiltered water and 10 mL filtered cells on a 1 µm pore size 25 mm diameter polycarbonate filter were taken in addition to a 2 mL sample for cell counts. The phytoplankton cells were then filtered out and resuspended onto 1 µm pore size 47 mm diameter polycarbonate filters into the beakers containing the *H. azteca* where they were allowed to feed for four days. Then they were removed, counted in a NaI gamma well detector, and transferred for trophic transfer to the killifish, *Fundulus heteroclitus*.

The control cells were filtered using 1 µm pore size 47 mm diameter polycarbonate sterile filters, rinsed with MilliQ water at pH 7, and resuspended to the control beakers containing amended WCL-1 media. The cells were left for four days, which was the same duration as the *H. azteca* feeding in treatments. Then the cells were filtered out and discarded. A 1-mL unfiltered sample was counted for an aqueous control because it had whatever ^{203}MeHg was desorbed from the radiolabeled cells during feeding. *H. azteca* were added to the same water, left for four days, removed, and counted to measure how much of their ^{203}MeHg could be attributed to aqueous exposure so that the differences in *H. azteca* accumulation could be explained by the phytoplankton and not by acquisition from the aqueous phase.

Juvenile killifish, *F. heteroclitus*, approximately 2.5 cm in length were field collected and purchased from Aquatic Research Organisms, Hampton, NH. They were housed in glass aquaria with aged tap water and corner box floss filtration and aeration and fed a diet of frozen blood worms. The four site waters were 0.2 µm sterile cartridge filtered and distributed in 600-mL volumes to 1-L glass beakers. The fish received a 20% water change daily.

There were six replicates for each site and one *F. heteroclitus* was placed in each beaker 36 hours in advance to starve prior to experimentation. Five radiolabeled *H. azteca* were placed in each treatment for the fish to consume. Each fish was fed three individual non-labeled *H. azteca* daily. *F. heteroclitus* were rinsed with filtered site water and counted by nondestructive manner in a NaI(Tl) gamma well detector in 30 mL of water. A T=0 hours was counted one half hour post ingestion. The time points consisted of T=4, T=10, T=24, T=48, T=72, T=96, and T=144 hours.

Additional experiments were conducted in the fall of 2010 to evaluate phytoplankton uptake from two systems with varying DOC levels. Natural site water was field collected from Old Man McMullen Pond (POND), Great Mountain Forest, Norfolk, CT, by author Jonathan Cole. The mid 5 pH was adjusted to pH 7 with $NaHCO_3$. The second treatment consisted of an artificial mix of the Charles Ryder (CR) site with Old Man McMullen Pond (MIX) and the pH adjusted to 7.5 via $NaHCO_3$.

The ^{203}MeHg concentrations were followed in water and phytoplankton cells over a period of three days. MilliQ water was filtered with a 0.2-µm sterile cartridge to make amended fresh water media WCL-1. Then it was inoculated with *C. meneghiniana* for the phytoplankton uptake.

The two water treatments were filtered with a 0.2- µm sterile cartridge, used to make amended WCL-1 media, and distributed in 100-mL volumes to each experimental 250-mL ground glass TM clean Erlenmeyer flask with glass stopper. Triplicates were made for each site in addition to triplicate controls. An initial cell density of 2×10^5 cells/mL was used and the triplicate flasks for each site were inoculated with the phytoplankton that was resuspended from a 1-µm sterile polycarbonate filter. The control triplicate flasks contained no phytoplankton.

^{203}MeHg was added to each flask (28.49 kBq total for 12 flasks) and a 1 ml unfiltered sample (T=0) was collected for confirmation of the radioactivity. The time points were T=2, T=5, T=10, T=24, T=48, and T=72 hours. For the flasks containing phytoplankton, sampling consisted of 2 mL preserved with Lugol's solution for cell counts, 1 mL unfiltered, and 10 mL filtered on a 1 µm pore size 25 mm diameter polycarbonate sterile filter with two 5-mL rinses of filtered unradioactive MilliQ water adjusted to pH 7 via NaOH. For the control flasks, 1 mL unfiltered and 10 mL filtered on a 1 µm pore size 25 mm diameter polycarbonate sterile filter were sampled. Cells were counted using a Multisizer 3 Coulter Counter.

In summer 2011, the four sites chosen were Wallkill Proper (WR), Swarte Kill (SK), Dykeman Street (DS) and Croton (CR). A separate batch of ^{203}HgCl2 was purchased, due to radioactive decay of the first batch, and was used to synthesize a fresh batch of ^{203}MeHg. To determine trophic transfer of the MeHg, *C. meneghiniana* and *H. azteca* were exposed to the freshly synthesized ^{203}MeHg following the previously described protocol using radioactivity levels of 247.75 kBq for 24 flasks. The radiolabeled amphipods were fed to *F. heteroclitus* as previously described. Uptake of ^{203}MeHg by *C. meneghiniana* was followed using 82.51 kBq total added to eight flasks. For the *F. heteroclitus* experiments, the four site waters were filtered with a 0.2-µm sterile filter and distributed in 600-mL volumes held in 1-L glass beakers. The fish received a 20% water change daily. There were six replicates for each site and one *F. heteroclitus* was placed in each beaker 36 hours in advance to starve. Five radiolabeled *H. azteca* were placed in each treatment for the fish to consume. Each fish was fed three individual nonlabeled *H. azteca* daily. *F. heteroclitus* were counted by nondestructive manner in a NaI gamma well detector in 30 mL of water.

3 Results and Discussion

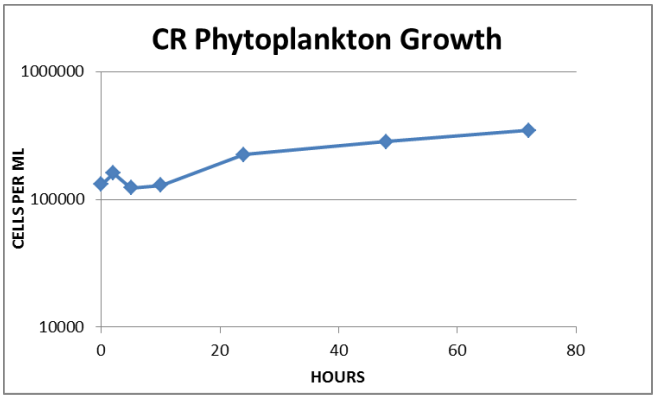
3.1 Phytoplankton Exposures to MeHg

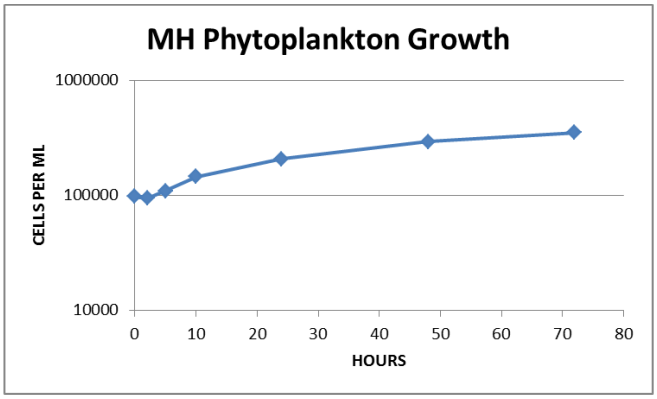
Growth of the diatom *Cyclotella meneghiniana* in different batches of Hudson River water collected in 2010 is depicted in Figure 2. It was necessary to assess growth in order to determine volume-normalized mercury uptake by the cells. Depending on the site and the extent of diatom growth, the extent to which ^{203}MeHg was associated with cells ranged up to about 75% (Table 2). Generally, there were only modest differences between diatom uptake of the ^{203}MeHg in different batches of water, although some exceptions were noted (Figure 3). Calculated volume/volume concentration factors (VCFs) ranged from less than 5×10^3 to about 40×10^3 (Figure 4). The lowest VCFs were clearly noted for cells exposed to waters from Pond and Mix sites (Figure 4). These waters had DOC concentrations of 10.6 mg/L and an estimated 7 mg/L (Tables 1 and 2). Thus, there appeared to be an inverse relationship between MeHg VCFs and DOC concentrations in the water (Figure 4).

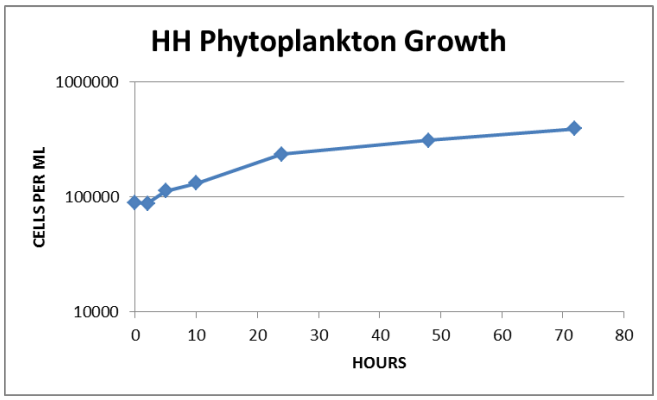
Growth of *C. meneghiniana* in water collected in 2011 is shown in Figure 5 and fractionation of ^{203}MeHg on the cells in these waters is shown in Figure 6. As with previous exposures, the percentage of MeHg on cells ranged from about 40% to about 80%. Once again, there was an inverse relationship between VCFs (which ranged from 5-30 $\times 10^3$) and DOC concentrations (Figure 7). Another interesting finding was the VCF for MeHg was about double in water from Dykman St., which was saline (about 3 ppt) compared to Croton Pt. a freshwater site, though both contained the same amount of DOC (3.3 mg/L).

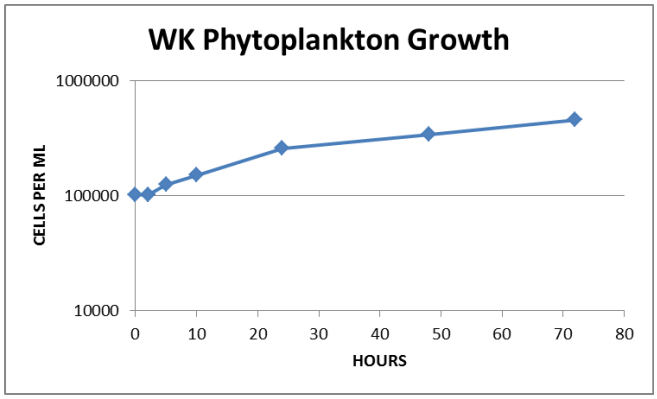
Figure 2. Growth of the diatom *Cyclotella meneghiniana* over time in water collected from different Hudson River sites in 2010

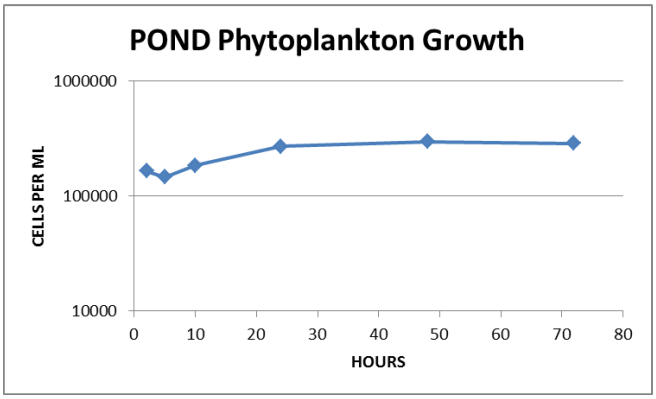
HH: Henry Hudson; CR: Charles Ryder; POND: Old Man McMullen Pond; MH: Mohawk; WK: Walkill; MIX: CR + POND.











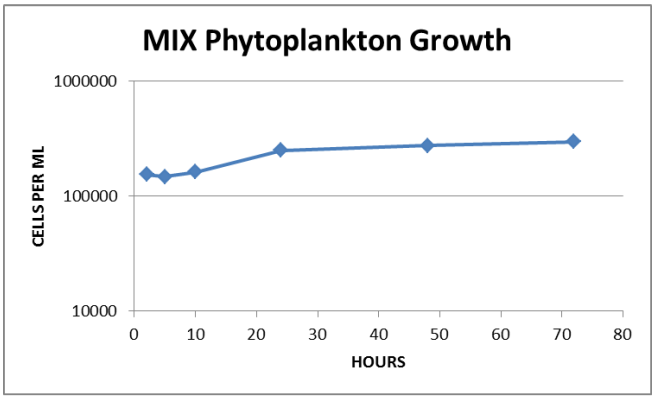


Figure 3. Percent of total water column ^{203}MeHg associated with diatoms after exposure in water from different Hudson River sites in 2010

HH: Henry Hudson; CR: Charles Ryder; POND: Old Man McMullen Pond; MH: Mohawk; WK: Walkill; MIX: CR + POND.

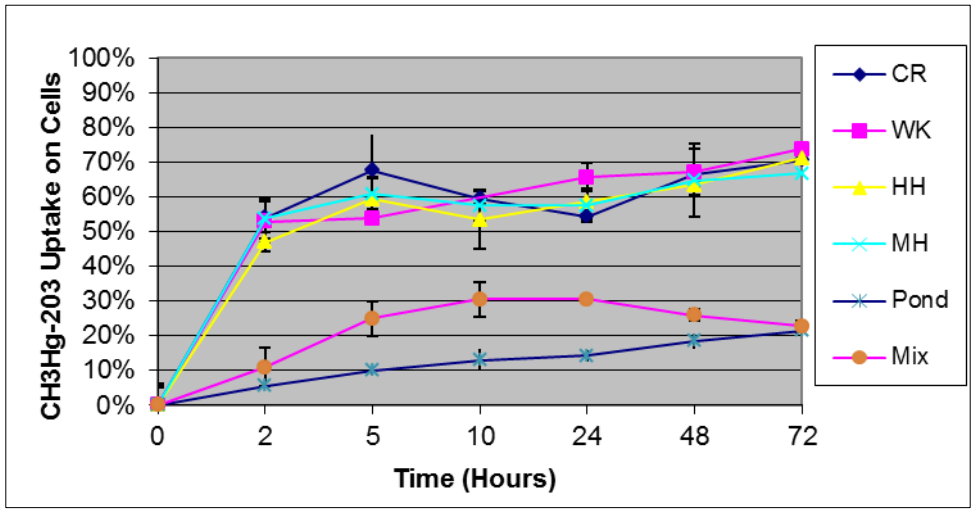


Figure 4. Mean volume/volume concentration factors (VCFs) of ^{203}MeHg in diatoms

Calculated after 24 hours of exposure in 6 Hudson River sites, related to the DOC concentration at each site. Data are from 2010 sampling sites.

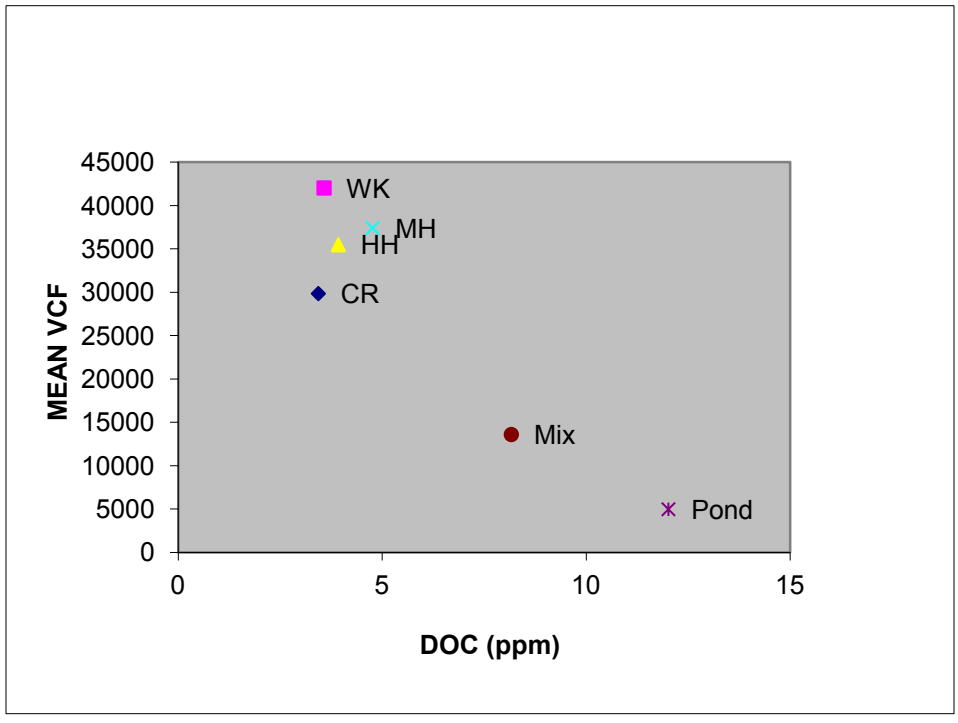


Figure 5. Growth of the diatom *Cyclotella meneghiniana* over time in water collected from 10 different Hudson River sites in 2011

HH: Henry Hudson; CR: Charles Ryder; POND: Old Man McMullen Pond; MH: Mohawk; WK: Walkill; SK: Swarte Kill; DS: Dykman Street; Croton: Croton; WR: Walkill Roundout; MIX: CR + POND.

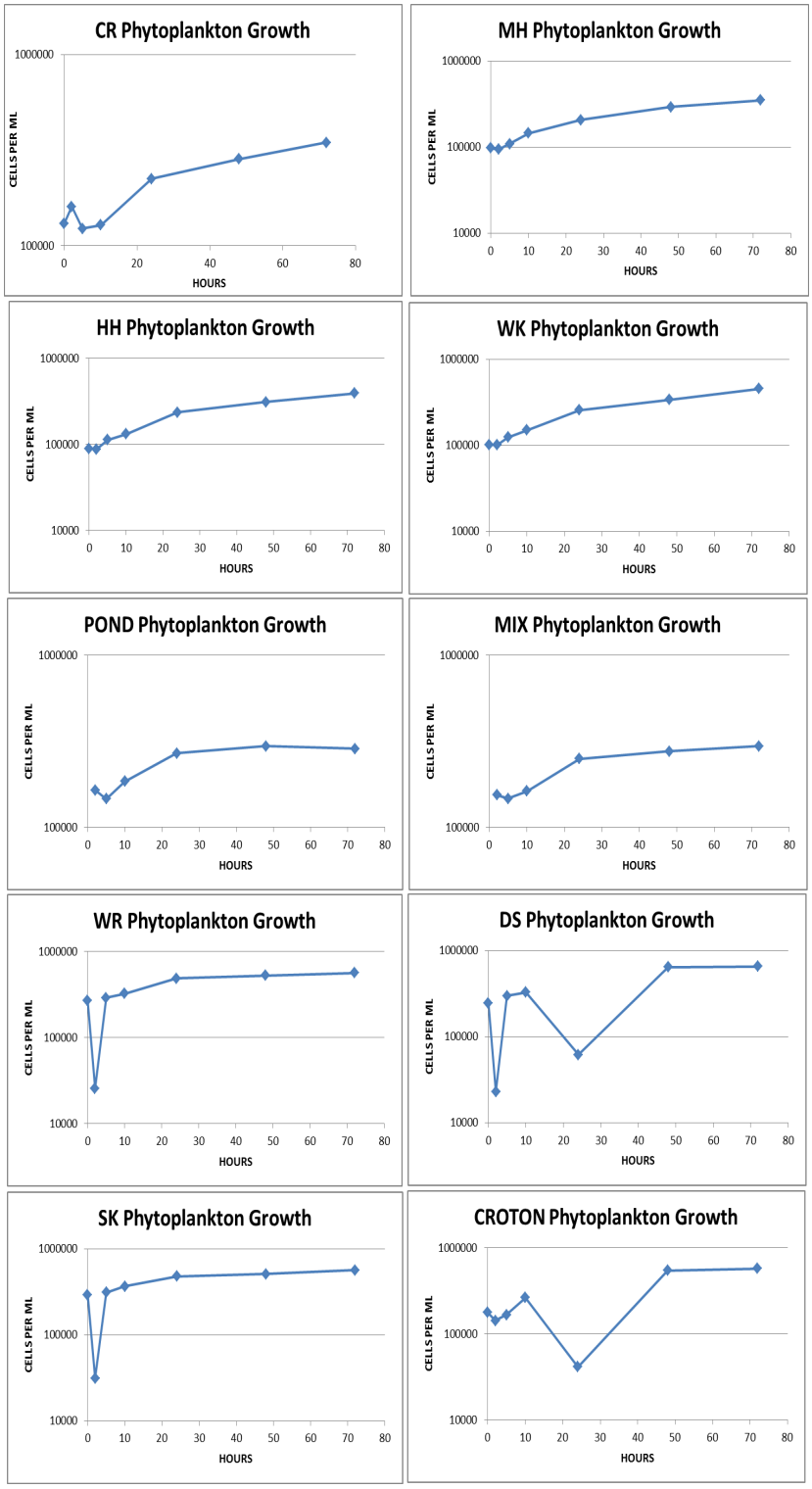


Figure 6. Percent of total water column ^{203}MeHg associated with diatoms after exposure in water from different Hudson River sites in 2011

WR: Walkill Roundout; DS: Dykman Street; CR: Croton; SK: Swarte Kill

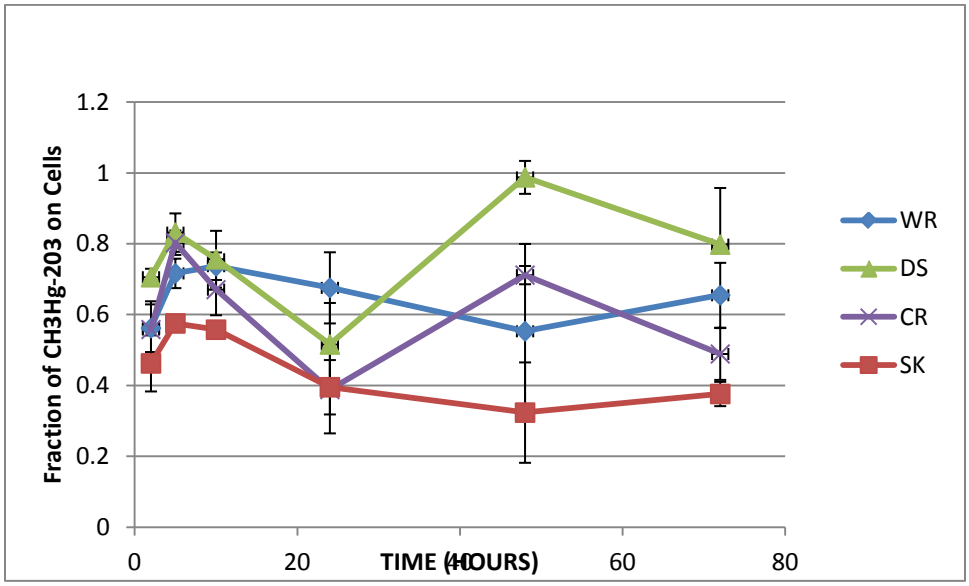
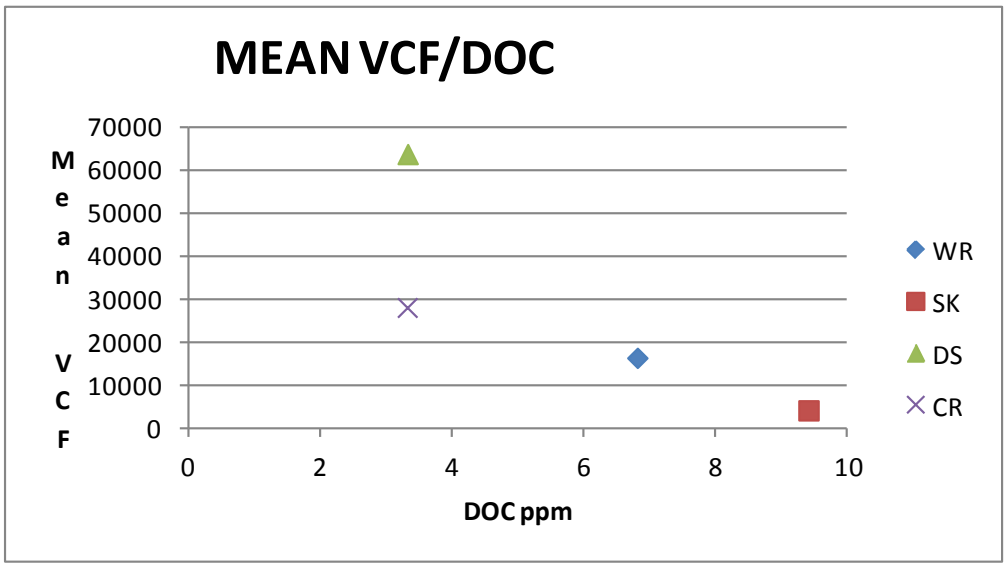


Figure 7. Mean volume/volume concentration factors (VCFs) of ^{203}MeHg in diatoms

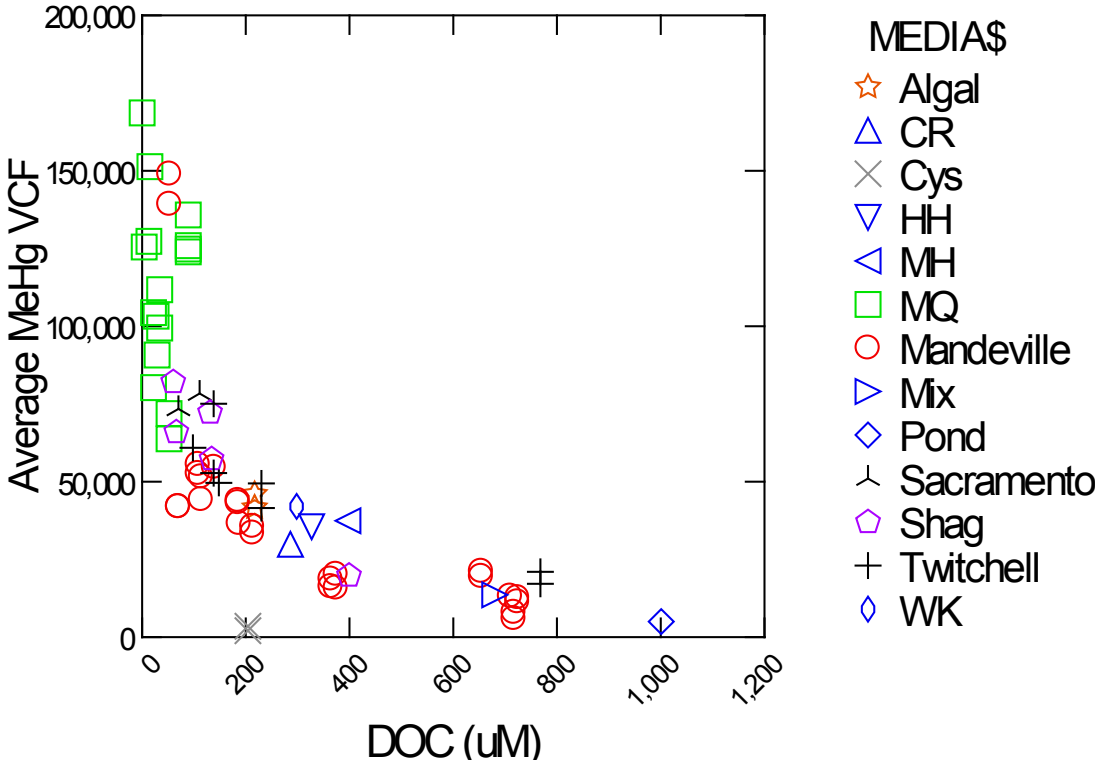
Calculated after 24 hours of exposure in 6 Hudson River sites, related to the DOC concentration at each site. Data are from 2011 sampling sites.



The inverse relationship between DOC concentration and MeHg VCFs was virtually identical to that found by Luengen et al. (2012). Figure 8 displays the data from both this study and that of Luengen et al. superimposed on one another, showing remarkable agreement between the two studies, despite the fact that this is essentially a comparison of the influence of DOC extracted from waters from the California Bay Delta area with that in the Hudson River system.

Figure 8. Mean VCFs of MeHg in two data sets

The diatom *Cyclotella meneghiniana* was exposed to deionized water containing varying amounts of added DOC extracted from natural fresh waters in the San Francisco Bay Delta region (Luengen et al. 2012), or in unamended Hudson River water with varying levels of natural DOC (this study). The influence of cysteine (Cys) is also shown for comparison.



Once radiolabeled amphipods were fed to *Fundulus heteroclitus*, the retention of the ^{203}MeHg in these fish did not vary among the various water sites tested (Figure 9). Note that extremely little loss of MeHg was observed from *F. heteroclitus* in any of the sites, suggesting that the assimilation efficiencies of the MeHg were extremely high (greater than 90%) for all sites tested. While the assimilation efficiencies of MeHg were high, as expected, the fact that no differences existed in different batches of water suggests that the extent to which MeHg builds up in these fish is a function solely of the extent to which it is associated with the phytoplankton at the base of the food web. After that, the assimilation efficiency of ingested MeHg is not affected by the ambient water chemistry (e.g., DOC). Thus, the presence of DOC will moderate the bioavailability of the MeHg for phytoplankton and the presence of salinity would appear to enhance the MeHg bioaccumulation in phytoplankton, probably because the

zero-charge chloro-complex has a greater octanol-water partition coefficient than the uncomplexed mercury (Mason et al. 1996), leading to greater penetration across cell membranes and thus greater uptake by the phytoplankton. Field-collected fish were either killifish (most of the samples) or satinfin shiners (samples from only four sites). The killifish, from six locations, ranged in Hg concentrations from 88 to 560 nanograms per gram (ng/g) and averaged 214 ng/g in waters where the DOC concentration had a narrow range, from 3.0 to 3.9 mg/L (Table 3). The shiners were from waters with essentially identical DOC concentrations (all sites had 3.6 mg/L), and yet Hg concentrations in their tissues ranged from 319 to 537 ng/g. Given the relatively narrow range of DOC in these waters, one would not expect to see a significant relationship between Hg and DOC, and indeed no significant relationship was apparent. Differences in Hg concentrations in these fish tissues from one location to another may well have been due to different Hg loadings into each of the individual water bodies, although this was not assessed in the current project.

Figure 9. Retention of ^{203}MeHg in *Fundulus heteroclitus* after feeding on radiolabeled amphipod food

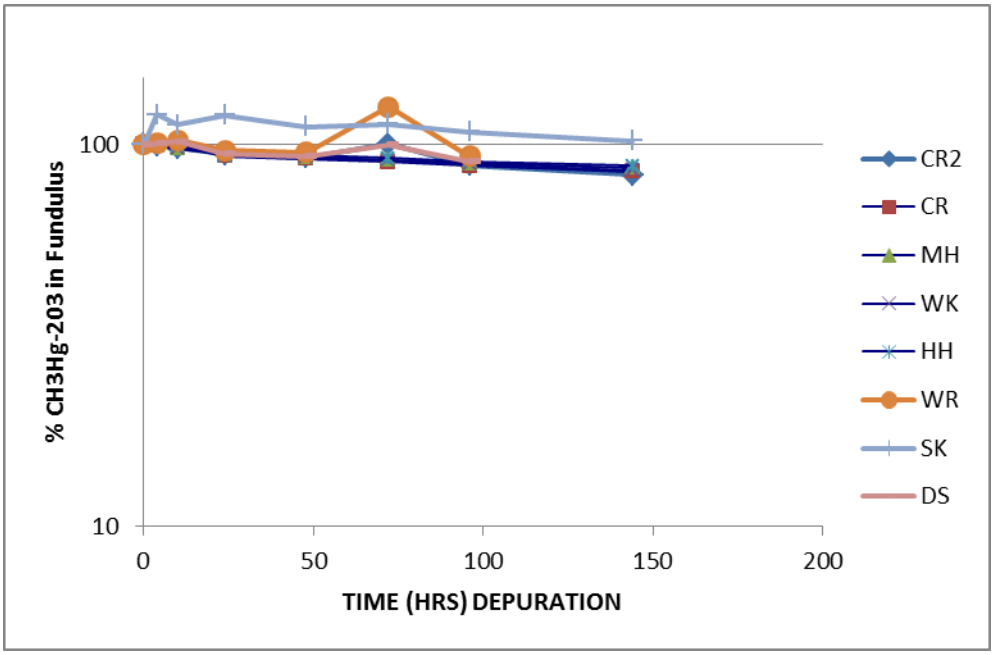


Table 3. Hg concentrations in satinfish shiners and killifish in different Hudson River sites

Also shown are $\delta^{13}C$ and $\delta^{15}N$ of the fish and the DOC concentrations of the sample sites. Note that DOC showed little variation among the sample sites

Site	Date Collected	Species	Hg ppb (ug/kg)	δD (‰)	dup dD (‰)	d13C (‰)	dup d13C (‰)	d15N (‰)	dup d15N (‰)	DOC mgC/L
wallkill	7/16/10	satinfin shiner	527.28	-142.80		-26.42		10.58		3.6
wallkill	7/16/10	satinfin shiner	536.93	-134.23		-25.91		10.94		3.6
wallkill	7/16/10	satinfin shiner	412.67	-155.35	-154.61	-27.94	-27.90	11.09	11.22	3.6
wallkill	7/16/10	satinfin shiner	319.41	-150.09	-152.76	-27.01	-26.99	10.90	10.82	3.58
rhinecliff	6/23/10	killifish	91.13	-150.10		-24.69		12.60		3.03
rhinecliff	6/23/10	killifish	145.32	-144.78		-22.96		13.44		3.03
rhinecliff	6/23/10	killifish	195.58	-144.64		-24.40		14.06		3.03
rhinecliff	6/23/10	killifish	139.67	-146.66		-28.21		13.45		3.03
charles ryder	8/2/10	killifish	154.76	-154.36		-25.98	-25.78	14.74	14.65	3.44
charles ryder	6/23/10	killifish	336.76	-134.85		-25.24		14.16		3.03
charles ryder	6/23/10	killifish	254.02	-137.00	-134.12	-24.89		13.57		3.03
charles ryder	6/23/10	killifish	155.42	-148.77		-25.86		13.62		3.03
charles ryder	8/2/2010	killifish	88.54							3.44
lock 6	8/3/10	killifish	165.14	-144.93		-27.21		11.59		3.00
lock 6	8/3/10	killifish	131.52	-151.40		-27.42		11.24		3.00
lock 6	8/3/10	killifish	185.23	-150.21		-27.11		12.63		3.00
schodack	7/23/10	killifish	261.15	-136.96		-25.40		12.77		3.93
schodack	7/23/10	killifish	339.22	-150.98		-22.00		12.64		3.93
schodack	7/23/10	killifish	274.04	-163.40		-22.18		13.25		3.93
schodack	7/23/10	killifish	559.85	-138.82		-21.78	-21.93	12.91	12.95	3.93
schodack	6/25/10	killifish	231.25	-147.65		-24.85	-24.61	13.36	13.31	3.43
schodack	6/25/10	killifish	178.07	-157.18		-25.03		12.89		3.43
mohawk	7/01/10	Killifish	173.40							4.8

3.2 Dissolved Organic Carbon in the Hudson River

The tidal-freshwater Hudson is a strongly net-heterotrophic ecosystem and is dominated by watershed inputs of organic matter (Howarth et al. 1996). This freshwater section of river does not receive either salt or nutrients or organic matter from New York City, which is in the saline part of the estuary. The lower estuary and harbor receive inputs from upstream as well as a substantial input of material from New York City. In the tidal fresh water portion, the Hudson River is both turbid and well mixed; therefore, the phytoplankton are strongly light limited and primary production is low (Cole and Caraco 2006). Since the invasion of the zebra mussel in 1992, phytoplankton consist mainly of large diatoms with sporadic blooms of *Microcystis* and other cyanobacteria in late summer (Fernald et al. 2007). Mean annual chlorophyll a values are below 5 mg/L and peak values rarely exceed 10 mg/L (Pace et al. 2010). The situation in the lower estuary is more complex with partial stratification and much high primary production from phytoplankton (Swaney et al. 1999; Howarth et al. 2006).

For the freshwater portions, the major input of organic carbon to the Hudson is from the watershed at 650 gC/m^2 yr, which is more than six times larger than estimates of net primary production (NPP) of the sum phytoplankton, macrophytes and periphyton.The dominant macrophytes in the Hudson are the submergent *Vallisneria americana* and the floating leafed *Trapa natans*. Total macrophyte NPP is estimated at 42 g C/m^2 yr. Traditional estimates of NPP of phytoplankton using ^{14}C incubations give about 70 g C/m^2 yr. These values do not include the respiration of phytoplankton in the dark, which can be quite large in this well-mixed and poorly lit system. Thus, the true NPP of phytoplankton may be even lower (Cole and Caraco 2006). The production of benthic algae is poorly known but is probably 2 g C/m^2 yr (Cole and Caraco 2006). Heterotrophic respiration, dominated by pelagic bacteria (116 g C/m^2 yr) and zebra mussels (83 g $C/^{-2}$ yr), are together larger than autochthonous primary production. Thus, at the ecosystem scale respiration exceeds gross primary production results in generally undersaturated dissolved oxygen and supersaturated CO_2 concentrations (Raymond et al. 1997; Caraco et al. 2000; Cole and Caraco 2001).

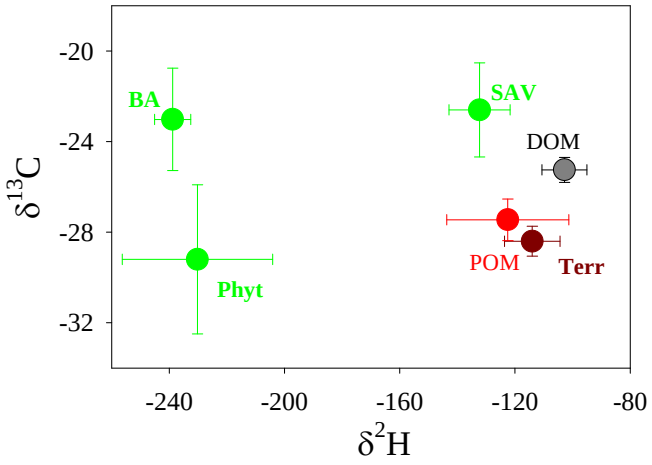
DOC is the largest pool of organic matter in the water column of the Hudson River and its major tributaries. The samples taken for this project are fairly typical for the river in general. The tributaries tend to be more variable in DOC concentration than the main stem of the river with some tributaries, particularly the Walkill that sometimes havs DOC in excess of 10 mg C/L. For the main river and tributary stations sampled for this project, DOC averaged 4.35 mg $C^{/L}$ with an standard deviation of 1.9 mg C/L. The highest concentration found for this project was 9.5 mg C/L in the Swartekill (Table 1).

The stable isotope ratios of dissolved organic matter (DOM) reflects its largely terrestrial origin in the Hudson River. The δ^2H values at a mean of -102 per mil are enriched, and more similar to terrestrial organic material (-114 per mil) than to any of the in river sources (phytoplankton -230; periphyton -238; *Vallisneria* -132). The $\delta\ ^{13}C$ values of DOC (-25.2) are more enriched than phytoplankton (-29.2) but lower than those of periphyton (-23) or Vallisneria (-22.6) (Figure 10). Using a Bayesian isotope mixing model, Cole and Solomon (2012)

estimated that on average DOM in the Hudson River consists of a mixture of about 65% terrestrial and 30% submersed macrophytes with trivial contributions from phytoplankton or periphyton. This composition could be correct, but it is difficult to imagine how submersed macrophytes can be such a large source of DOM considering their low primary production relative to terrestrial loading. It is possible that some of the enriched ^{13}C in the DOM comes from the loading of sewage, but this is speculation at this point. That the SUVA values were in a tight range among stations and times (1.83 + 0.07) suggests a similar amount of aromacticity for the DOC at all the sites. These relatively high values are in concert with the DOM being largely of terrestrial origin.

Figure 10. Isotope bi plot showing the terrestrial character of dissolved organic matter (DOM; filled gray circle) and particulate organic matter (filled red circle) in the Hudson River

The X axis shows the δ^2H and the Y axis shows the $\delta^{13}C$ of terrestrial material (Terr- solid brown circle) and the riverine primary producers (BA-algae, SAV-*Vallisneria*; Phyt-phytoplankton). Note that both the POM and DOM fall near the terrestrial end-member and not near either phytoplankton or benthic algae. Isotope mixing models show that the DOM is largely of terrestrial origin (see text).



In conclusion, it would appear that geographic variation in fish concentrations of MeHg would track the extent to which the MeHg is taken up by phytoplankton at the base of the food web and that this is in turn attributable to the variation in the quantity and perhaps quality of the DOC in the water in different regions. It would also appear that MeHg would display somewhat greater bioavailability in saline waters than in purely fresh waters. While uptake of MeHg in phytoplankton would appear to be affected by total DOC concentrations (and most likely DOC rich in thiols), this composition may have a smaller effect than the total MeHg concentration in the water. The latter is due to both loadings of inorganic mercury and to the methylation rates, which are known to be affected by diverse environmental factors, including iron concentrations, DOC levels, and of course the microbial consortia present in those waters. This study did not evaluate mercury loadings, microbial consortia, or methylation rates in the various water bodies. Thus, while we saw no significant relationships between fish concentrations of MeHg and DOC in ambient water, it is difficult to assess whether such a relationship exists based on the present work because the range of DOC concentrations was surprisingly small across the various sampled sites.

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Final Report
January 2014

Report Number 14-25

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