Mercury stable isotopes in sediments and largemouth bass from Florida lakes, USA
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HIGHLIGHTS
► Mercury isotope ratios were measured in sediments and bass from 20 lakes in Florida.
► Isotopic compositions of fish indicated sediments were the primary Hg source.
► Mercury recently emitted by a local source did not preferentially enter the fish.
► Declines in fish Hg concentrations may take decades to centuries.

ABSTRACT
Humans and wildlife can be exposed to mercury (Hg) through the consumption of fish with elevated concentrations of methylmercury (MeHg). Studies have shown that increased atmospheric deposition of Hg often leads to increased MeHg concentrations in aquatic organisms. However, depending on the ecosystem characteristics, reductions in Hg emissions may not always lead to immediate decreases in fish MeHg concentrations. Measurements of natural abundance Hg stable isotope ratios may enable a better understanding of these complex relationships. To gain insight into the sources of Hg to sport fish in central Florida, we measured the Hg isotopic compositions of surface sediments and largemouth bass from freshwater lakes. We found that fish collected from lakes located near the large Crystal River coal-fired power plant did not display evidence of anomalous negative δ202Hg values that were observed in nearby precipitation. This suggests that Hg recently deposited from the atmosphere is not preferentially methylated and bioaccumulated in these lakes relative to previously deposited Hg accumulated in the lake sediments. We also observed significant positive Δ199Hg values in the fish that were correlated with light penetration depth in the lakes from which they were collected. This indicates that a significant amount of photochemical degradation of MeHg (up to ~40%) occurred prior to uptake of the remaining MeHg into the food webs. These results suggest that depending on physical lake characteristics and biogeochemical factors, decreased atmospheric Hg deposition may not lead to immediate short-term reductions in fish MeHg concentrations. Instead, recovery of some freshwater fish populations to baseline MeHg concentrations may take decades to centuries.

1. Introduction
Methylmercury (MeHg) is a neurotoxin that threatens human and wildlife health mainly through the consumption of aquatic organisms with elevated MeHg concentrations (Clarkson and Magos, 2006; Evers et al., 2008; Mergler et al., 2007; Scheuhammer et al., 2007). In aquatic systems, inorganic mercury (Hg) is methyalted to MeHg, which is subsequently bioaccumulated (Mason et al., 1995), often reaching concentrations that exceed recommended human consumption levels (0.1 μg/kg body weight/day) in high trophic level fish (U.S. EPA, 2012a; Mergler et al., 2007). Exposure to MeHg can result in decreased reproductive success, central nervous system damage, and deleterious behavioral changes in piscivorous birds, fish, and mammals (Adams et al., 2010; Evers et al., 2008; Scheuhammer et al., 2007; Wolfe et al., 1997).

Depending on lake characteristics, Hg can be methylated both biotically and abiotically in surface sediments (Gilmour and Henry, 1991; Ullrich et al., 2001), biotically (Eckley and Hintelmann, 2006) and abiotically in the water column (Celo et al., 2006; Siciliano et al., 2005), and within periphyton and algal mats (Cleckner et al., 1999; Desrosiers et al., 2006). MeHg can also be produced in wetlands and transported to nearby lakes (Branfireun et al., 2005). In most oxygenated, well-mixed freshwater lakes, sulfate-reducing bacteria at the oxic/anoxic boundary layer in surface sediments account for the majority of biotic, in-lake methylation (Benoit et al., 2003; Berman and Bartha, 1986; Compeau and Bartha, 1985; Fleming et al., 2006; Korthals and Winfrey, 1987; Krabbenhoft et al., 1998;
Munthe et al., 2007). After it is produced, MeHg can be demethylated biotically (Marvin-DiPasquale et al., 2000; Marvin-DiPasquale and Oremiand, 1998; Robinson and Tuovinen, 1984) and abiotically through photochemical reactions involving visible and ultraviolet (UV) radiation (Black et al., 2012; Hammerschmidt and Fitzgerald, 2006a; Lehnerr and St. Louis, 2009; Sellers et al., 1996). A number of factors can impact MeHg production and degradation including lake acidity (Gilmour and Henry, 1991; Lange et al., 1993; Xun et al., 1987), nutrient concentration (Kelly et al., 2006; Lange et al., 1993), dissolved organic carbon (DOC) concentration and composition (Miskimmin et al., 1992; Ulrich et al., 2001; Zhang and Hsu-Kim, 2010), sulfide and sulfate concentration (Gilmour et al., 1992; Ulrich et al., 2001), and light intensity and depth of light penetration (Burns et al., 2012; Lehnerr and St. Louis, 2009). Methymercury that is not degraded can be taken up by benthic organisms (Boudou and Ribeys, 1997) or exported into the overlying water column where it can enter the pelagic food web (Mason et al., 1995; Orihel et al., 2008). Unlike inorganic Hg, MeHg is rapidly assimilated into the tissues of organisms and is not readily excreted (Mason et al., 1995, 1996). As a result, MeHg bioaccumulates through food webs, and in most cases, nearly all (> 90%) of the Hg in fish muscle tissue is MeHg (Bloom, 1992; Grieb et al., 1990; Pentreath, 1976; Pickhardt et al., 2006; Trudel and Rasmussen, 1997; Wang and Wong, 2003).

Concentrations of MeHg in freshwater fish are controlled by a number of variables including supply of bioavailable MeHg, physical water body characteristics, food web structure, and fish characteristics such as feeding strategy, age, and growth rate (Lange et al., 1993; Macrury et al., 2002; Munthe et al., 2007; Orihel et al., 2008; Trudel and Rasmussen, 1997, 2006; Ward and Neumann, 1999). Recent studies indicate that the amount of Hg that is deposited from the atmosphere to a water body can also significantly influence fish MeHg concentrations (Hammerschmidt and Fitzgerald, 2005, 2006b; Harris et al., 2007; Paterson et al., 2006). However, the relationships between Hg deposition and MeHg concentrations in fish are complex (Munthe et al., 2007; Orihel et al., 2008). Although some studies suggest that decreased atmospheric deposition of Hg may result in rapid reductions in freshwater fish MeHg concentrations (Harris et al., 2007; Hrabik and Watras, 2002), lake sediments contain accumulated Hg that may continue to be methylated. As a result, depending on the characteristics of the aquatic system, fish MeHg concentrations may remain elevated for decades to centuries after atmospheric Hg deposition decreases (Kannan et al., 1998; Knights et al., 2009; Munthe et al., 2007; Orihel et al., 2008; Paterson et al., 2006; Sunderland et al., 2010). It is necessary to better characterize the biogeochemical relationships in aquatic systems to more accurately predict and assess the impacts of Hg emissions regulations on fish MeHg concentrations.

Elevated concentrations of Hg in precipitation, fish, and other wildlife have been observed across the state of Florida (FL; U.S.A.) for more than two decades (Axelrad et al., 2011; Dvonch et al., 1998, 2005; Frederick et al., 2002; Hand and Friedemann, 1990; Lange et al., 1993, 1994; Royals and Lange, 1990). Largemouth bass are common sport fish in FL, but due to their high MeHg concentrations, the FL Department of Health currently maintains limited consumption advisories for largemouth bass in more than 325 water bodies in FL (Florida Department of Health, 2012). Additionally, the FL Department of Health recommends that women of childbearing age restrict consumption of largemouth bass to 170 g (6 oz.) per month from all untested lakes (Florida Department of Health, 2012). Although MeHg concentrations in largemouth bass have recently decreased in some parts of FL (such as the Water Conservation Areas in south FL; Axelrad et al., 2011), these trends do not appear to be consistent across the state.

Recent studies have demonstrated that measurement of natural abundance Hg stable isotope ratios in environmental samples can be used to differentiate the sources of Hg to fish populations and to better understand Hg cycling within aquatic systems (Gantner et al., 2009; Gehrke et al., 2011; Perrot et al., 2010; Senn et al., 2010). There are seven stable isotopes of Hg (196 to 204 amu), and mercury stable isotope ratios are reported using delta notation as:

$$\delta^{198}\text{Hg} = \frac{\left(\frac{^{198}\text{Hg}}{^{201}\text{Hg}}\right)_{\text{sample}}}{\left(\frac{^{198}\text{Hg}}{^{201}\text{Hg}}\right)_{\text{SRM 3133}}} - 1 \times 1000$$

(1)

where $^{198}\text{Hg}$ is an isotope of Hg and SRM 3133 is a National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) for Hg (Blum and Bergquist, 2007). Mass-dependent fractionation (MDF) of Hg isotopes occurs during a number of biotic and abiotic processes including methylation (Malinovsky and Vanhaecke, 2011; Rodriguez-Gonzalez et al., 2009) and MeHg degradation (Bergquist and Blum, 2007; Kritee et al., 2009). Mercury stable isotopes can also undergo mass-independent fractionation (MIF), which is reported as the deviation of a measured isotope ratio from that which is theoretically predicted to result due to MDF:

$$\Delta^{198}\text{Hg} = \delta^{198}\text{Hg} - \left(\delta^{202}\text{Hg} + \beta\right)$$

(2)

For kinetic reactions, $\beta$ is equal to 0.252 for $^{199}\text{Hg}$, 0.502 for $^{200}\text{Hg}$, and 0.752 for $^{201}\text{Hg}$ (Blum and Bergquist, 2007). A high degree of MIF can occur due to the magnetic isotope effect during photochemical reactions that involve the formation of long-lived radical pairs (Bergquist and Blum, 2007; Buchachenko, 2001; Turro, 1983). Only the odd-mass-number isotopes of Hg have unpaired nuclear spin and are magnetic. As a result, during these reactions, radical pairs involving odd-mass-number isotopes of Hg recombine at different rates than those involving even-mass-number isotopes of Hg. This process has been shown experimentally to occur during the photochemical degradation of MeHg in aquatic solutions containing DOC and result in a $\Delta^{198}\text{Hg}/\Delta^{201}\text{Hg}$ ratio of 1.36 ± 0.02 (2 s.e.) (Bergquist and Blum, 2007). A number of recent studies have observed significant positive MIF in fish along with similar $\Delta^{198}\text{Hg}/\Delta^{201}\text{Hg}$ ratios of between 1.2 and 1.3 (Bergquist and Blum, 2007; Das et al., 2009; Gantner et al., 2009; Gehrke et al., 2011; Kwon et al., 2012; Laffont et al., 2009; Perrot et al., 2010; Point et al., 2011). It has been hypothesized that photochemical demethylation of MeHg in the water column prior to incorporation of the remaining MeHg into the food web causes the observed MIF of Hg isotopes in fish (Bergquist and Blum, 2007; Gantner et al., 2009; Gehrke et al., 2011; Kwon et al., 2012; Laffont et al., 2009; Perrot et al., 2010; Point et al., 2011; Senn et al., 2010). In this study we measured the Hg isotopic compositions of surface sediments and largemouth bass from freshwater lakes in central FL to characterize the sources of Hg to these sport fish and to explore the influence of lake characteristics on the measured Hg isotope ratios.

2. Materials and methods

2.1. Sample collection

Water samples, sediments and largemouth bass were collected between October 2008 and December 2011 by the FL Department of Environmental Protection (FDEP) and the FL Fish and Wildlife Conservation Commission in collaboration with a statewide study conducted to understand Hg deposition patterns and model Hg concentrations in fish populations. Water samples, sediments, and largemouth bass were collected from 20 lakes in central FL (Fig. 1). Five of these lakes (Lake Rousseau, Little Lake Henderson, Lake Davis, Lake Panasoffkee, and Lake Bonable) are within 50 km of one of the largest anthropogenic point sources of Hg in FL, the 2267 MW Crystal River coal-fired utility boiler (CFUB). Of these lakes, four are located in the Withlacoochee River watershed (Fig. 1). This large watershed (5440 km$^2$) contains numerous lakes and wetlands that are hydrologically connected to the Withlacoochee River (Trommer et al., 2009). The closest lake to the...
Crystal River CFUB, Lake Rousseau (L1557), is a damned lake at the downstream end of the Withlacoochee River. One of the other large lakes in the watershed, Lake Tsala Apopka, is comprised of connected lakes, including Little Lake Henderson (L732) and Lake Davis (L72), in which water levels and flow are maintained using control structures (Trommer et al., 2009).

Water quality parameters including light penetration depth and pH were measured in each lake. Light penetration depth was measured manually at approximately the deepest part of the lake using a Secchi disk attached to a rope marked with 0.1 m increments. Over the course of the study, light penetration depths were measured one to three times in each lake. Water samples were collected using trace metal-clean techniques (Gill and Fitzgerald, 1985; Hurley et al., 1996) from the open surface water of each lake and taken to the FDEP Central Laboratory for analysis. These samples were collected 1.0 m below the water surface except in lakes that were less than 1 m deep or when equipment constraints did not allow sampling at depth (Table 1). Water sampling equipment rinse blanks (deionized water) were collected throughout the field sampling campaign (n = 22) and these blanks generally did not contain detectable amounts of total Hg or MeHg (Appendix A). Total Hg concentrations were determined using cold vapor atomic fluorescence spectrometry (CVAFS) according to U.S. Environmental Protection Agency (U.S. EPA) Method 1631-E (U.S. EPA, 2002). Methylmercury concentrations were determined using CVAFS after ethylation, gas chromatographic separation, and pyrolysis according to a modified version of U.S. EPA Method 1630 (U.S. EPA, 1998; Bloom, 1989). Alkalinity (as mg of CaCO3 per liter) was determined with an automatic titration instrument (PC-Titrate™) and DOC concentrations were measured using a total organic carbon analyzer (Shimadzu TOC-V).

Sediments (upper 8 to 10 cm) were collected from each lake with a Wildco® Ponar dredge using trace metal-clean methods. Three dredge samples were taken in each lake from the location of the deepest water depth. These samples were homogenized together into pre-washed high-density polyethylene bottles (I-CHEM®) and kept frozen at −25 °C until analysis at the University of Michigan Biogeochemistry and Environmental Isotope Geochemistry Laboratory. The dredge was cleaned between samples with deionized water. Five dredge rinse
blanks (deionized water) were collected after cleaning and these blanks did not contain detectable quantities of Hg.

Adult largemouth bass (>178 mm in length) were collected from each lake using electro-fishing methods. Fish length, weight, sex, and age (determined using sagittal otoliths; Taubert and Tranquilli, 1982) were recorded (Appendix B, Table B.1). Right-side dorsal muscle fillets were taken from each individual using trace metal-clean methods. Fish MeHg concentrations were not measured during this study. However, previous work indicates that >90% of the Hg in the fish muscle was likely MeHg (Bloom, 1992; Grieb et al., 1990). The fish samples were stored frozen at −25 °C until shipped.

2.2. Sample processing

The Hg isotopic compositions of sediment samples from all 20 lakes and largemouth bass from a subset of the lakes (n = 11) were analyzed (Fig. 1). The 11 lakes for fish analyses were chosen based on their locations and water quality characteristics to represent a wide variety of conditions. Two fish each from Mill Dam Lake (L440) and Lake Kerr (L374) and three fish from each of the other lakes were analyzed for Hg isotopes. Over the course of the study, replicate analyses (total Hg concentration and Hg isotopic composition) were made of individual fish (n = 10) and sediment samples (n = 3).

To prepare the samples, the frozen sediments and fish were freeze-dried for 48 to 72 h (VirTis® Sentry Freezeemobile 12SL). The dry samples were then homogenized and ground to a fine powder using an alumina ball mill mixer (SPEX SamplePrep® Mixer/Mill). Between samples the ball mill was cleaned by repeatedly grinding silica sand that had been baked at 750 °C for 8 h to remove any Hg. Small aliquots of baked silica sand (50 to 60 mg) were processed periodically between samples and analyzed as grinding blanks using atomic absorption spectrometry (Nippon® Instruments MA-2000). The ground silica sand blanks did not contain significant amounts of Hg (mean = 86 pg of Hg per grinding blank, 1 s.d. = 42 pg, n = 4). After grinding, the samples were weighed into ceramic boats and Hg in the samples was thermally released using previously published methods (Sherman et al., 2012). Briefly, each sample was placed in a two-stage furnace where the temperature of the first furnace was incrementally increased to 750 °C and the second furnace was maintained at 1000 °C. The released Hg$^{0}(g)$ was carried in a stream of Hg-free O$_2$ and bubbled into 25 g of acidic 1% (w/w) KMnO$_4$ solution (KMnO$_4$ in 1.8 M trace metal grade H$_2$SO$_4$). To concentrate the Hg and separate it from any combustion products present in these solutions, the Hg was subsequently transferred into secondary 1% KMnO$_4$ solutions. To do this, the primary solutions were first reduced with 2% (w/w) of 30% NH$_2$OH·HCl and then divided into 5 ml aliquots. Mercury in each aliquot was reduced with 0.3 ml of 20% SnCl$_2$ and 0.3 ml of 50% H$_2$SO$_4$ and then bubbled into a secondary 1% KMnO$_4$ solution using a modified autosampler. Mercury concentrations were measured in these final solutions by atomic absorption spectrometry and used to determine total Hg concentrations in the sediments and fish tissue samples. Mercury standards (NIST SRM 3133) measured during concentration analyses were replicable to within ±5%. Sediment total Hg concentrations are reported as dry weight concentrations and fish total Hg concentrations are reported as wet weight concentrations (Appendix B, Table B.1). Total Hg concentrations in replicate sediment and fish samples generally agreed within reported analytical uncertainty (mean relative percent difference = 8.6%, 1 s.d. = 7.8%, n = 13).

Procedural standards and blanks were processed using the same methods. Over the course of this study, six sediment procedural standards (NIST SRM 1944), 16 fish procedural standards (seven CRM DORM-3 and nine ERM CE-464), and nine procedural blanks were analyzed. All of the procedural blanks contained negligible amounts of Hg attributable almost entirely to the Hg blank of the 1% KMnO$_4$ solutions (mean = 0.02 ng of Hg per g solution, 1 s.d. = 0.02 ng Hg per g solution, n = 9). Mercury recoveries in the procedural standards were determined after processing based on the amount of Hg that was originally combusted and the measured Hg concentration in the final 1% KMnO$_4$ solution. For the sediment standards, mean Hg recovery was 95% (1 s.d. = 15%, n = 6); for the DORM-3 fish standards, mean Hg recovery was 90% (1 s.d. = 10%, n = 7); for the ERM CE-464 fish standards, mean Hg recovery was 96% (1 s.d. = 9.9%, n = 9).

2.3. Stable isotope ratio analyses

Mercury stable isotope ratios were measured in samples and standards using cold-vapor multi-collector inductively-coupled plasma mass spectrometry (Nu® Instruments) according to previously published
methods (Bergquist and Blum, 2007; Blum and Bergquist, 2007). The < 100% yields during combustion and purification for some of the procedural standards did not cause any systematic isotope fractionation. However, the measured isotopic compositions of these procedural standards were more variable than those of the secondary University of Michigan Almadén standard that was measured ~5 times during each analytical session. For this reason, sample analytical uncertainty for each isotope ratio is estimated as 2 times the standard deviation of the same ratio measured in the relevant procedural standards. Mercury isotope ratios measured in replicate fish (n = 10) and sediment samples (n = 3) were reproducible within these uncertainties (Table B1).

Carbon (δ13C, relative to Vienna Pee Dee Belemnite) and nitrogen (δ15N, relative to air N2) stable isotope ratios were also measured in the largemouth bass samples at the University of Michigan Stable Isotope Laboratory. Approximately 700 μg of powdered material per sample was loaded into tin weigh boats. The samples were analyzed using an elemental combustion system (Costech ECS 4010) coupled to an isotope ratio mass spectrometer (Finnigan Delta V Plus). International standards (IAEA 600, IAEA-CH-6, IAEA N2, and USGS 25) were used to normalize on a per-run basis and maintain precision of δ13C and δ15N values of better than ±0.12‰ (1 s.d.).

2.4. Statistical analyses

The relationship between fish tissue sample Δ199Hg and Δ201Hg values was analyzed using a York regression (York, 1966). This iterative regression method considers error in both the dependent and independent variables. The relationships between Secchi depth, DOC concentration, and Δ199Hg values measured in the fish tissue samples were assessed using linear regression. The relationship between bulk sediment δ201Hg values and estimated sediment MeHg < δ201Hg values was also assessed using linear regression.

3. Results and discussion

3.1. Water quality parameters

Water quality measurements for the studied lakes are shown in Table 1. Florida generally has warm wet summers and cooler dry winters. As a result, characteristics of these lakes can vary seasonally (Griffith et al., 1997) and the measurements made during this study may not represent average yearly conditions. The studied lakes are generally shallow, well mixed, and fully oxic. As a result, although it is likely correlated with, but more rapidly attenuated than visible light penetration depths, it is probably negatively correlated with DOC concentration (slope = −0.05 ± 0.02, 1 s.e.; p = 0.01; r² = 0.31; n = 20). In lakes with high light penetration and low DOC concentrations, it is likely that rates of photochemical demethylation of MeHg are enhanced (Krabbenhoft et al., 2002; Lehnher and St. Louis, 2009; Sellers et al., 1996).

3.2. Mercury concentrations

Previous studies have measured sediment accumulation rates in FL wetlands of between 0.16 cm/yr and 0.33 cm/yr (Breder et al., 2001; Craft and Richardson, 1993). Similar accumulation rates (up to 0.40 cm/yr) have been measured in organic-rich FL lake sediments (Binfold et al., 1992; Brenner et al., 2001; Brezonik and Engstrom, 1998). Based on these accumulation rates, we expect that the upper 10 cm of sediment in the study lakes represents accumulation over the past ~25 and ~60 yr. However, it is likely that sediment accumulation rates in these shallow lakes are spatially and temporally variable as a result of sediment redistribution, mixing, and focusing into deeper areas (Brezonik and Engstrom, 1998; Whitmore et al., 1996). Therefore, although it is likely that the sampled sediments represent accumulation of less than 100 yr, it is possible that they contain a mixture of pre-anthropogenic and anthropogenic Hg.

Total Hg concentrations in sediment samples ranged from 13.3 ng/g to 307 ng/g (mean = 153 ng/g), 1 s.d. = 81.9 ng/g (n = 20) (Appendix B). These concentrations are similar to those measured previously in FL (Kanan et al., 1998; Rood et al., 1995). A study of sediment cores from the FL Everglades indicated that historic sediments (pre-1900) generally had Hg concentrations of <100 ng/g whereas recent sediments (post-1985) had Hg concentrations of >100 ng/g (and up to 400 ng/g) (Rood et al., 1995). Although lake sediments collected during this study may contain a mixture of pre-anthropogenic and anthropogenic Hg, most of the sediments had Hg concentrations elevated above those background levels (i.e., >100 ng/g) and likely include significant amounts of anthropogenic Hg (Dvorch et al., 1999; Fitzgerald et al., 1998; Rood et al., 1995).

Total Hg concentrations in fish tissue samples ranged from 43.7 ng/g to 1190 ng/g (mean = 361 ng/g; 1 s.d. = 291 ng/g; n = 31). Fish analyzed during this study do not necessarily represent the range or average Hg concentrations in adult largemouth bass in the study lakes. However, the Hg concentrations measured during this study are similar to those previously observed in FL largemouth bass (Hand and Friedmann, 1990; Lange et al., 1993, 1994). There are no clear correlations between total Hg or MeHg concentrations in water, sediments, or fish from these lakes. Total Hg concentrations in the lake sediments are not correlated with total Hg concentrations in the water column. In addition, total Hg concentrations in fish are not correlated with total Hg concentrations in the sediments, total Hg concentrations in the water, or MeHg concentrations in the water. However, because only a limited number of samples were analyzed from each lake, these samples may not be fully representative of average total Hg or MeHg concentrations.

3.3. Carbon and nitrogen isotope ratios

Carbon and nitrogen isotope ratios in the fish tissue samples are presented in Appendix B (Table B1). Carbon isotope ratios are often used to determine the carbon source to the base of food webs (DeNiro and Epstein, 1978). In contrast, because nitrogen isotope ratios increase by ~3‰ per trophic level, δ15N values are often used to estimate consumer trophic position (Fry, 1991; Fry et al., 1999; Peterson and Fry, 1987). Measured δ13C values in the largemouth bass ranged from −16.2 to −30.0‰ (mean = −24.5‰; 1 s.d. = 3.8‰; n = 31) and δ15N values ranged from 7.88 to 16.3‰ (mean = 11.8‰; 1 s.d. = 2.1‰; n = 31). Largemouth bass collected from the same lakes displayed similar δ13C and δ15N values and within lake isotopic variability (δ13C mean 1 s.e. = −0.56‰; δ15N mean 1 s.e. = 0.22‰) was less than between lake isotopic variability (δ13C mean 1 s.e. = 1.13‰; δ15N: mean 1 s.e. = 0.63‰). It is possible that some of the variability
between individuals in a given lake is due to differences in tissue lipid content (Focken and Becker, 1998; Gaye-Siessegger et al., 2004) or to differences in individual fish feeding behavior (Fry et al., 1999; Gu et al., 1996). Largemouth bass are opportunistic top predators that generally eat a variety of small aquatic invertebrates when they are young but switch to a diet of crayfish, larger invertebrates, and other fish as adults (MacRury et al., 2002; Soupir et al., 2000; Wheeler and Allen, 2003). As a result, older largemouth bass may be feeding on a higher proportion of benthic organisms and at a higher effective trophic level than smaller largemouth bass. However, overall the largemouth bass Δ2H values were not correlated with fish length (\( r = 0.28, r^2 = 0.04 \)), fish age (\( r = 0.66, r^2 = 0.01 \)), or total Hg concentration (\( r = 0.11, r^2 = 0.08 \)) (Appendix B, Table B.1). Therefore, it is not likely that ontogenetic dietary shifts leading to differences in effective trophic level can explain the between lake variability in Δ2H values. Instead, it is more likely that the variations in Δ2H values are due to differences in δ15N at the base of the food web. Similarly, it is likely that differences in δ13C values between lakes are a result of differences in the carbon isotopic composition at the base of these food webs (Fry et al., 1999).

### 3.4. Mercury stable isotope ratios

The proportion of atmospheric Hg deposition at a given location that results from local, regional, and long-range emissions is location-specific (Mercury Atmospheric Processes, 1994; Lindberg et al., 2007; White et al., 2009) but a number of studies have observed enhanced Hg deposition near point sources and urban areas (U.S. EPA, 2005; Dvonch et al., 1999; Landis et al., 2002; Lohman et al., 2006; White et al., 2009). Sherman et al. (2012) found that in July 2009, Hg emitted by the Crystal River CFUB was deposited locally in precipitation and displayed anomalous negative δ202Hg values (mean = −2.56‰, 1 s.d. = 1.10‰, \( n = 28 \)). After the time of sample collection for the Sherman et al. (2012) study, in 2009 and 2010, selective catalytic reduction units and flue gas desulfurization units were installed on two of the Crystal River CFUB's four units (U.S. EPA, 2012b). Although these air pollution control devices are known to decrease Hg emissions (Srivastava et al., 2006), Hg emissions from the CFUB estimated by the U.S. EPA Toxic Release Inventory did not change significantly between 2009 and 2011 (U.S. EPA, 2009–2011). Coal combusted at the CFUB was sourced from mines in the same regions of Kentucky and West Virginia from 2009 to 2011 (U.S. Energy Information Administration, 2009–2011). Therefore, although we did not collect precipitation near the CFUB after July 2009, we suggest that the isotopic composition of combusted coal powder likely remained relatively constant and that reactive Hg emitted by the CFUB and deposited locally in precipitation throughout this study likely displayed extreme negative δ202Hg values similar to those observed by Sherman et al. (2012).

To investigate the relationship between Hg emitted by the Crystal River CFUB and Hg in lake sediments and largemouth bass, we divided the study lakes into two categories: those located close to the CFUB (<50 km away, 5 lakes; fish were analyzed from three of these lakes) and those located farther from the CFUB (>50 km away, 15 lakes; fish were analyzed from eight of these lakes). Although the spatial distribution of Hg deposition near a point source depends on many factors, we hypothesized that reactive Hg species emitted by the CFUB would be more likely to be deposited to lakes within 50 km of the utility than to those located farther away (Mercury Atmospheric Processes, 1994; Dvonch et al., 1999; Lindberg et al., 2007; White et al., 2009). We used these samples to 1) assess whether Hg recently deposited from the atmosphere was preferentially methylated and bioaccumulated compared to previously deposited Hg accumulated in lake sediments and 2) explore the influence of physical lake characteristics and biogeochemical processes on the Hg isotopic compositions of largemouth bass. The Hg isotopic compositions of all analyzed samples and standards are presented in Appendix B (Table B.1).

**3.4.1. Lakes closer to (<50 km) the Crystal River CFUB**

Results of the Mercury Experiment to Assess Atmospheric Loading in Canada and the United States (METAALICUS) spike addition study suggest that recently deposited Hg can be rapidly methylated and bioaccumulated in aquatic food webs (Harris et al., 2007). If these results are applicable to FL lakes, we hypothesized that Hg emitted by the Crystal River CFUB and deposited to the nearby lakes would be preferentially methylated and bioaccumulated up the food web to the largemouth bass. Further, assuming that the extreme negative δ202Hg values observed in precipitation collected near the Crystal River CFUB (Sherman et al., 2012) are representative of local Hg recently deposited from the atmosphere, we hypothesized that the largemouth bass collected from lakes close to the CFUB would display evidence of those negative δ202Hg values. Based on the average δ202Hg values of sediments from these lakes (mean = −0.84‰, 1 s.d. = 0.19‰, \( n = 5 \)) and precipitation (mean = −2.56‰, 1 s.d. = 1.10‰, \( n = 28 \); Sherman et al., 2012), isotopic mass balance can be used to estimate the expected δ202Hg values in the fish depending on the proportion of Hg in the fish that is derived from recent atmospheric deposition. For example, if only ~2% of the Hg in the fish was derived from recent atmospheric deposition, δ202Hg values in these fish would be ~0.05‰ lower than sediment δ202Hg values. This amount of deviation would not be distinguishable from analytical uncertainty. However, if ~10% to ~30% of the Hg in the fish was derived from recent atmospheric deposition, δ202Hg values in the fish would be ~0.25 to ~0.55‰ lower than sediment δ202Hg values. Deviations of this magnitude would be distinguishable from analytical uncertainty and from the isotopic variability between individual fish.

We did not observe lower δ202Hg values in fish compared to sediments in these lakes that we could attribute to recent deposition of Hg emitted by the Crystal River CFUB. Sediments from lakes close to the CFUB had δ202Hg values ranging from −1.11 to −0.63‰ (±0.12‰, 1 s.d. = 0.19‰, \( n = 5 \)). The δ202Hg values in these sediments were close to 0‰ (mean = 0.00‰, 1 s.d. = 0.17‰, \( n = 5 \)). A similar lack of MIF of Hg isotopes in lake and coastal sediments has been observed in previous studies (Gantner et al., 2009; Gehrke et al., 2010; Perrot et al., 2010; Senn et al., 2010). Largemouth bass from these lakes displayed δ202Hg values ranging from −0.57 to −0.22‰ (±0.15‰, 2 s.d.; mean = −0.84‰, 1 s.d. = 0.19‰, \( n = 5 \)) and precipitation (mean = −2.56‰, 1 s.d. = 1.10‰, \( n = 28 \)). As shown in Fig. 2, these Hg isotopic compositions were similar to those of sediments and fish collected from the lakes located >50 km from the Crystal River CFUB.

There are several possible explanations for the lack of lower δ202Hg values in fish collected from lakes located near the Crystal River CFUB. First, it is possible that the negative δ202Hg values measured in precipitation during July 2009 near the Crystal River CFUB (Sherman et al., 2012) were not representative of Hg deposition in the area. However, as described previously, because estimated Hg emissions and the origin of the combusted coal did not change throughout the study period, we suggest that these values are a good estimate of the isotopic composition of Hg emitted by the CFUB and deposited locally. Second, it is possible that MDF occurring in the water column (e.g., due to adsorption to DOC or suspended particles or due to photochemical reduction) or during biotic processes in the sediments (e.g., methylation and demethylation) may have altered and somewhat obscured the negative δ202Hg values (Bergquist and Blum, 2007; Kritee et al., 2009; Rodriguez-Gonzalez et al., 2009). However, it is likely that these processes occur to a similar degree in the lakes both near to and far from the CFUB. Therefore, even if these processes obscured the lower δ202Hg values, we would have expected to observe a measurable offset between fish from the two areas.

Finally, it appears most likely that recently deposited Hg is not preferentially methylated and bioaccumulated compared to previously accumulated Hg in the sediments. Previous studies have similarly found that although a portion of recently deposited Hg can be rapidly
In addition to understanding the sources of Hg to largemouth bass in these lakes, the data collected in this study can be used to explore other hypotheses. One hypothesis proposed to explain the positive $\Delta^{199}$Hg values observed in fish populations is that they are caused by photochemical demethylation of MeHg (Das et al., 2009; Jackson et al., 2008) or photochemical demethylation of MeHg prior to uptake into organisms (Rudolph et al., 2004; Schade et al., 2005; Laffont et al., 2007). It is likely that Hg transported through the watershed in association with suspended solids and sediments provides an influx of previously deposited Hg to these lakes (Babiarz and Andren, 1994; Brigham et al., 2009; Hurley et al., 1995). Our data suggest that in these lakes recently deposited Hg mixes with previously deposited Hg in the sediments (some of which has been transported through the watershed) and that a portion of it is methylated and enters food webs, the large reservoir of previously deposited Hg in surface sediments can provide a significant source of MeHg to the ecosystem (Oribel et al., 2008; Paterson et al., 2006; Sunderland et al., 2010). If we assume that the sediment sample collected in Lake Rousseau is representative of surface sediments throughout the lake, we can estimate the relative percentages of recently deposited and historically deposited Hg in the sediments. Based on measurements made at a nearby Mercury Deposition Network site (FL05), average annual deposition of Hg during the study period (2008 to 2011) was 14.3 μg/m² (1 s.d. = 1.0 μg/m²) (NADP, 2012). Assuming a dry sediment density of ~1 g/cm³ (St. Johns River Water Management District, 2011; Davis and Ford, 1982), this amount of annual Hg deposition directly to the lake surface represents only ~0.1% of the total Hg in the upper 10 cm of sediments in Lake Rousseau. Therefore, annual atmospheric Hg deposition likely represents a very small percentage of the total Hg in surface sediments of these lakes. This may be especially true for lakes with large watershed such as the Withlacoochee River watershed that do not receive all of their Hg from direct atmospheric deposition (Knightes et al., 2009; Munthe et al., 2007). It is likely that Hg transported through the watershed in association with suspended solids and sediments provides an influx of previously deposited Hg to these lakes (Babiarz and Andren, 1994; Brigham et al., 2009; Hurley et al., 1995). Our data suggest that in these lakes recently deposited Hg mixes with previously deposited Hg in the sediments (some of which has been transported through the watershed) and that a portion of it is methylated and enters the food web.

3.4.2. Lakes farther (>50 km) from the Crystal River CFUB

In addition to understanding the sources of Hg to largemouth bass in these lakes, the data collected in this study can be used to explore the influence of physical lake characteristics and biogeochemical processes on Hg isotopes in fish. Sediments from lakes >50 km from Crystal River, FL had $\delta^{202}$Hg values ranging from $-1.19$ to $-0.46\%$ (±0.12%, 2 s.d.; mean = $-0.72\%$, 1 s.d. = 0.25%, n = 15) and $\Delta^{199}$Hg values close to 0% (mean = $-0.05\%$, 1 s.d. = 0.13%, n = 15). In contrast to the sediments, $\delta^{202}$Hg values of fish from these lakes ranged from $-0.60$ to $0.68\%$ (±0.15%, 2 s.d.; mean = 0.08%, 1 s.d. = 0.38%, n = 22) and $\Delta^{199}$Hg values ranged from 0.18 to 4.43% (±0.07%, 2 s.d.; mean = 1.35%, 1 s.d. = 1.22%, n = 22) (Fig. 2). Similar Hg isotope ratios in fish from lakes and coastal environments have been observed in previous studies (Bergquist and Blum, 2007; Gantner et al., 2009; Gehrke et al., 2010; Perrot et al., 2010; Senn et al., 2010). Largemouth bass Hg isotopic compositions were less variable within each lake than between lakes, especially with respect to $\Delta^{199}$Hg values (within lake 1 s.e. of $\Delta^{199}$Hg values = 0.21%; between lake 1 s.e. of mean $\Delta^{199}$Hg values = 0.48%). This suggests that lake characteristics and/or processes occurring within each lake largely control the observed MIF.

There have been two hypotheses proposed to explain the positive $\Delta^{199}$Hg values observed in fish populations: 1) in vivo MIF occurring in organisms leads to the observation of increasing $\Delta^{199}$Hg with increasing trophic level (Das et al., 2009; Jackson et al., 2008) or 2) photochemical demethylation of MeHg prior to uptake into organisms causes MIF and this isotopic signature is retained during trophic transfer (Bergquist and Blum, 2007; Kwon et al., 2012; Laffont et al., 2009; Point et al., 2011; Senn et al., 2010). Das et al. (2009) observed a correlation between $\Delta^{199}$Hg values and trophic level (based on $\delta^{15}$N values) in a freshwater lake in FL and concluded that MIF likely occurs during metabolic processes within the fish (Das et al., 2009). However, no experimentally studied biotic processes have been shown to produce MIF of Hg isotopes (Kritee et al., 2007, 2009; Rodriguez-Gonzalez et al., 2009) and theoretical calculations suggest that biochemical processes are unlikely to produce MIF of Hg isotopes (Kritee et al., 2009). Natural processes that cause MIF in the absence of light have been shown to produce only $<0.3\%$ of fractionation (Estrade et al., 2009; Ghosh et al., 2012; Zheng and Hintelmann, 2009, 2010). In addition, recent experimental studies by Kwon et al. (2012) demonstrated that no MIF occurs during trophic transfer of MeHg from food to fish. Finally, as has been observed in previous studies, $\Delta^{199}$Hg values measured in largemouth bass tissues during this study do not correlate with trophic position based on $\delta^{15}$N values (Gantner et al., 2009; Point et al., 2011; Senn et al., 2010). Therefore we suggest that it is unlikely that the observed positive $\Delta^{199}$Hg values in the largemouth bass were caused by in vivo MIF.
the remaining MeHg is taken up by organisms. Bergquist and Blum (2007) conducted photochemical demethylation experiments using natural sunlight in aqueous solutions containing 1 mg/L and 10 mg/L of DOC and observed that the $\Delta^{199}$Hg/$\Delta^{201}$Hg ratio of MeHg remaining in the solution was $1.36 \pm 0.02$, 2 s.e. (Bergquist and Blum, 2007). As shown in Fig. 3, we observed a comparable $\Delta^{199}$Hg/$\Delta^{201}$Hg ratio in the largemouth bass samples ($1.30 \pm 0.01$, 1 s.e., $n=31$). These data suggest that photochemical degradation of MeHg prior to incorporation of remaining MeHg into the food web resulted in the observed positive MIF in the fish.

If photochemical degradation of MeHg is responsible for the MIF, then $\Delta^{199}$Hg values of the largemouth bass should be related to the magnitude of photochemical demethylation. It is also possible that an increased degree of photochemical demethylation could result in a measurable depletion of MeHg from the water column. As discussed previously, more photochemical demethylation of Hg is expected to occur in lakes with greater light penetration depths and lower concentrations of DOC (Amyot et al., 1997; Morris et al., 1995). As shown in Fig. 4A, light penetration depth in these FL lakes is positively correlated to $\Delta^{199}$Hg values measured in the largemouth bass ($slope = 0.88 \pm 0.16$, 1 s.e.; $p < 0.0001$; $r^2 = 0.51$, $n=31$). In addition, as shown in Fig. 4B (on a log-log scale) DOC concentrations are negatively correlated with $\Delta^{199}$Hg values in the fish ($slope = -0.45 \pm 0.12$, 1 s.e.; $p = 0.0007$; $r^2 = 0.33$, $n=31$). Finally, although $\Delta^{199}$Hg values in the largemouth bass are only weakly correlated to the percent MeHg in the water column ($p=0.10$, $r^2 = 0.80$, $n=31$), the highest $\Delta^{199}$Hg values (greater than 1.5‰) only occurred in fish from lakes with low percent MeHg (<5%). Although photochemical demethylation has been proposed by several previous studies to explain MIF observed in fish, correlations between MIF, light penetration depth, and DOC concentration have not been previously reported.

Some lakes show significant deviations from the correlations of MIF in the largemouth bass with light penetration depth and DOC concentration. This variability may be due to seasonal differences in light penetration depth and differences in the relationship between DOC concentration and UV radiation absorption (Morris et al., 1995) caused by variations in DOC composition. The fish from Lake Rousseau (L1557) do not fall on the correlation line between DOC concentration and $\Delta^{199}$Hg values defined by fish from the other lakes. If the data from Lake Rousseau are excluded, this correlation is stronger ($slope = 0.80 \pm 0.12$, 1 s.e.; $p < 0.0001$; $r^2 = 0.68$, $n=28$). This may be due to variations in the character of DOC in Lake Rousseau, which is located at the downstream end of the Withlacoochee River watershed. Additionally, the observed $\Delta^{199}$Hg values in largemouth bass from Lake Kerr (L374) are higher than expected based on light penetration depth. Lake Kerr is a deep lake in which light penetration depth can be up to 4.2 m (St. Johns River Water Management District, 2011). If the average annual light penetration depth in Lake Kerr is greater than that measured during this study, increased photochemical demethylation could have resulted in the observed high largemouth bass $\Delta^{199}$Hg values.

In addition to the observed variability between the lakes, in some cases individual fish collected from a given lake display varying magnitudes of MIF. These variations may be partly due to differing rates of MeHg elimination and differences in individual fish feeding habit (Rice et al., 1983; Trudel and Rasmussen, 1997, 2006). As described previously, because the diets of largemouth bass generally switch from aquatic invertebrates to crayfish, larger invertebrates, and other fish as they age (MacRury et al., 2002; Soupir et al., 2000; Wheeler and Allen, 2003), it is possible that older largemouth bass may be feeding on more benthic organisms than younger largemouth bass. This could result in older largemouth bass accumulating more MeHg from the benthic food web that has not been photochemically demethylated to the same degree as the MeHg in the water column and, therefore, displays lower $\Delta^{199}$Hg values. For example, the one-year-old largemouth bass from Mill Dam Lake (L440) displayed a significantly higher $\Delta^{199}$Hg value (individual L72, $\Delta^{199}$Hg = 3.25‰ ± 0.15‰, 2 s.d.) than the two-year-old largemouth bass from the same lake (individual L810.005, $\Delta^{199}$Hg = 1.49‰ ± 0.15‰, 2 s.d.). These differences in feeding habit could also partially explain the observation of similar $\Delta^{199}$Hg values between individuals from lakes with different light penetration depths. However, as described previously, because $\Delta^{199}$Hg values are not correlated to fish age ($p = 0.79$, $r^2 = 0.00$), it does not appear that these differences in feeding habit are present in all of the lakes.

Based on the observed $\Delta^{199}$Hg values in the largemouth bass, we can estimate the proportion of MeHg that was degraded in each of the lakes due to photochemical demethylation. Although DOC

![Image](image-url)
concentrations were variable, the lakes contained 13.5 mg/L of DOC on average (1 s.d. = 9.4 mg/L, n = 20) (Table 1). If we assume that photochemical demethylation experiments conducted with 10 mg/L of DOC in solution (Bergquist and Blum, 2007) are applicable to these FL lakes, we estimate that between ~4% (Lake Thonotosassa, L1790) and ~40% (Lake Kerr, L374) of the MeHg in these lakes was photochemically degraded (see Appendix C for calculations). Point et al. (2011) suggested that the ratio of MeHg to DOC could affect the relationship between photochemical demethylation and MIF of Hg isotopes and extrapolated the Bergquist and Blum (2007) experimental data to lower MeHg/DOC ratios. Application of the calculations made by Point et al. (2011) using MeHg/DOC ratios observed in these FL lakes only negligibly lowers our estimates of percent photochemical demethylation to between ~4 and ~37% (Appendix C).

By using the $\Delta^{199}$Hg values to estimate the amount of MDF that occurred in the water column due to photochemical demethylation, we can estimate the amount of MDF that occurred prior to this in the sediments before the MeHg was exported to the water column. Bergquist and Blum (2007) observed that photochemical demethylation of MeHg resulted in fractionation such that the ratio of $\Delta^{199}$Hg/$\delta^{202}$Hg of MeHg remaining in an aqueous solution as the experiment progressed was 4.8 ± 0.33 (1 s.e.). Assuming that this experiment is relevant to these natural lakes, we can use these data to estimate the $\delta^{202}$Hg values of MeHg in the lake sediments based on the Hg isotopic compositions of the largemouth bass. We additionally assume that no MIF occurs during trophic transfer and that the isotopic compositions of largemouth bass reflect those of MeHg in the water column prior to entry into the food web. Based on the average isotopic composition of largemouth bass from each lake, and the $\Delta^{199}$Hg/$\delta^{202}$Hg relationship observed by Bergquist and Blum (2007), the isotopic composition of MeHg in the sediments prior to photochemical demethylation in the water column was back calculated. These estimated sediment MeHg $\delta^{202}$Hg values are

$$y = 0.88x + 0.17$$
$$r^2 = 0.51$$

$$y = -0.45x + 0.38$$
$$r^2 = 0.33$$

Fig. 4. Light penetration depth and DOC concentration versus MIF in largemouth bass. Largemouth bass from lakes located <50 km of Crystal River are shown as open colored squares; fish from lakes located >50 km from Crystal River, FL are shown as filled colored squares. A). Light penetration depth (m) was measured as Secchi depth. Solid line shows a linear regression model including fish from all of the lakes (slope = 0.88 ± 0.16, 1 s.e.; p < 0.0001, r² = 0.51, n = 31). B). Solid line shows a linear regression model through the log-transformed data including fish from all of the lakes (slope = −0.45 ± 0.12, 1 s.e.; p = 0.0007, r² = 0.33, n = 31). Horizontal dashed line shows the 0 values for the y-axis.
consistently offset from the measured bulk sediment $\delta^{202}$Hg values by an average of 0.45‰ (1 s.d. = 0.19‰, n = 11) (Fig. 5A). The estimated sediment MeHg $\delta^{202}$Hg values are also positively correlated with the measured bulk sediment $\delta^{202}$Hg values (slope = 0.89 ± 0.32, 1 s.e.; p = 0.02; $r^2 = 0.47$, n = 11) (Fig. 5B). Gehrke et al. (2011) observed a similar offset (0.60 ± 0.16‰, 1 s.d.) between bulk sediment $\delta^{202}$Hg values and estimated sediment MeHg $\delta^{202}$Hg values based on the isotopic compositions of young-of-year fish in San Francisco Bay, California. The measured bulk sediment $\delta^{202}$Hg values and estimated sediment MeHg $\delta^{202}$Hg values in Lake Davis (L72) are offset to a lesser degree (0.07‰). In contrast to the other lakes, Lake Davis is one of the shallowest lakes in FL and it was covered with a 10–20 cm thick floc layer during sample collection. It is possible that these characteristics resulted in atypical MDF in the sediments of this lake. If Lake Davis is excluded, the correlation between measured sediment $\delta^{202}$Hg values and estimated sediment MeHg $\delta^{202}$Hg values is stronger (slope = 0.99 ± 0.25, 1 s.e.; p = 0.004; $r^2 = 0.67$, n = 10).

The observed offset between measured bulk sediment and estimated sediment MeHg $\delta^{202}$Hg values (based on the isotopic compositions of the largemouth bass) is likely due to a balance between biotic methylation and demethylation in surface sediments. Experimental studies have demonstrated that the light isotopes of Hg are preferentially methylated and demethylated during biotic processes (Bergquist and Blum, 2007; Kritee et al., 2009; Rodriguez-Gonzalez et al., 2009). The similarity among the lakes in the offset between measured bulk sediment and estimated sediment MeHg $\delta^{202}$Hg values suggests that similar rates of methylation and demethylation occur in lake sediments throughout the region. However, we cannot rule out the possibility that $\delta^{202}$Hg values measured in the bulk sediment samples are not representative of the relatively small fraction of bioavailable Hg in sediments that can be methylated (Bloom et al., 2003; Marvin-DePasquale et al., 2009). If bioavailable Hg has higher $\delta^{202}$Hg values than that measured in the bulk sediments, the observed offset in $\delta^{202}$Hg values between the bulk sediment and our estimated values for MeHg in the
sediments may not reflect net fractionation due to biotic methylation and demethylation.

4. Conclusions

Mercury isotope ratios measured in sediments and largemouth bass from freshwater lakes in central FL suggest that recently deposited atmospheric Hg is not preferentially methylated and bioaccumulated compared to previously accumulated Hg in lake sediments. Furthermore, the Hg isotope data suggest that the majority of the MeHg in largemouth bass is ultimately derived from previously deposited anthropogenic Hg in the lake sediments. We hypothesize that processes occurring in the sediments such as microbial methylation and demethylation cause MDF such that MeHg which is exported to the water column has \( \delta^{199}\text{Hg} \) values ~0.45%o higher than bulk Hg in the sediments. Once in the water column, photochemical demethylation causes significant MIF of the odd-mass-number isotopes of Hg and degradation of a significant portion of the MeHg before the remaining MeHg is incorporated into the food web. The \( \Delta^{199}\text{Hg} \) values of fish tissues are correlated with light penetration depth and DOC concentration and reflect the proportion of MeHg that was photochemically demethylated in each lake.

The results of this study suggest that reductions in atmospheric deposition of Hg to FL lakes may not rapidly result in decreased MeHg concentrations in largemouth bass because the primary source of Hg to the fish is Hg accumulated in the sediments rather than Hg recently deposited to the water column. It is important to consider that the magnitude and timing of changes in fish MeHg concentrations in response to changes in atmospheric deposition are influenced by physical lake characteristics, ecosystem properties, and fish physiological characteristics (Knight et al., 2009; Munthe et al., 2007; Orihel et al., 2008; Sunderland et al., 2010). In lakes with small watersheds that are dominated by direct atmospheric Hg input, fish may respond rapidly to reductions in Hg deposition (Harris et al., 2007). However, in lakes fed by large watersheds, previously deposited Hg can inflow into the lake long after it is deposited from the atmosphere and continuously add to the reservoir of Hg in the sediments that is available for methylation. Therefore, in many lakes, declines in fish MeHg concentrations may be prolonged for decades to centuries after Hg deposition reductions occur.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2012.09.038.

References


