Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades

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Abstract. Methylmercury (MeHg) concentrations and production rates were examined along with sulfur biogeochemistry in Everglades sediments in March, July and December, 1995, as part of a large, multi-investigator study, the Aquatic Cycling of Mercury in the Everglades (ACME) project. The sites examined constitute a trophic gradient, generated from agricultural runoff, across the Everglades Nutrient Removal (ENR) Area, which is a re-constructed wetland, and Water Conservation Areas (WCA) 2A, 2B and 3 in the northern Everglades. MeHg concentrations and %MeHg (MeHg as a percent of total Hg) were lowest in the more eutrophic areas and highest in the more pristine areas in the south. MeHg concentrations ranged from <0.1 ng gdw^{-1} sediment in the ENR to 5 ng gdw^{-1} in WCA3 sediments; and MeHg constituted $<0.2\%$ of total Hg (Hg$_T$) in ENR, but up to about 2% in two sites in WCA2B and WCA3. Methylation rates in surficial sediments, estimated using tracer-level injections of ^{203}Hg(II) into intact sediment cores, ranged from 0 to 0.12 d^{-1}, or about 1 to 10 ng g^{-1} d^{-1} when the per day values are multiplied by the ambient total Hg concentration. Methylation was generally maximal at or within centimeters of the sediment surface, and was never observed in water overlying cores. The spatial pattern of MeHg production generally matched that of MeHg concentration. The coincident distributions of MeHg and its production suggest that *in situ* production controls concentration, and that MeHg concentration can be used as an analog for MeHg production. In addition, the spatial pattern of MeHg in Everglades sediments matches that in biota, suggesting that MeHg bioaccumulation may be predominantly a function of the *de novo* methylation rate in surficial sediments.

Sulfate concentrations in surficial pore waters (up to 400 μm), microbial sulfate-reduction rates (up to 800 nm cc^{-1} d^{-1}) and resultant pore water sulfide concentrations (up to 300 μm) at the eutrophic northern sites were all high relative to most freshwater systems. All declined to the south, and sulfate concentrations in WCA2B and in central WCA3 resembled those in oligotrophic lakes (50–100 μm). MeHg concentration and production were inversely related to sulfate reduction rate and pore water sulfide. Control of MeHg production in the northern Everglades appears to mimic that in an estuary, where sulfate concentrations are high and where sulfide produced by microbial sulfate reduction inhibits MeHg production.

Introduction

Certain aquatic ecosystems tend to have high levels of methylmercury (MeHg) production and bioaccumulation, including wetlands (e.g. St. Louis et al. 1994, 1995; Hurley et al. 1995; Branfireun et al. 1996). Approximately 1 million acres of the Everglades system contains large mouth bass with mercury (Hg) concentrations above 2 mg kg^{-1} (Florida DEP 1994; Ware et al. 1990), double the FDA limit for human consumption. More than 20 years ago, Andren & Harriss (1973) measured relatively high %MeHg (MeHg as a percent of total Hg) in Everglades sediments, noting that samples from the Everglades were comparable to Hg-contaminated Mobile Bay sediments.

What drives the high levels of MeHg in fish and other biota in the Florida Everglades? Is increased loading of Hg the more important factor, or are biogeochemical controls on net MeHg production and bioaccumulation more critical? The rate of *in situ* MeHg production is a key factor in MeHg bioaccumulation. Detailed studies of Hg cycling in experimentally and atmospherically acidified lakes show that sulfuric acid acidification alone can result in increased net MeHg production (Gilmour et al. 1992) and subsequent bioaccumulation in fish (Weiner et al. 1990), without increased Hg input to the lake (Watras et al. 1994). High rates of microbial MeHg production, driven by high organic matter inputs and flows of nutrient bearing water, are the probable cause of Hg bioaccumulation in reservoirs (Bodaly et al. 1984; Kelly et al. 1996) and wetlands (St. Louis et al. 1994; Krabbenhoft et al. 1995; Branfireun et al. 1996).

The objectives of our work in the Everglades are to determine the importance of Hg methylation in controlling MeHg levels in the Everglades, and to understand the factors such as water chemistry, Hg loading, eutrophication, and hydroperiod that in turn control the methylation process in this wetland. We began work with the hypotheses that sulfate-reducing bacteria (SRB) mediate Hg methylation (Compeau & Bartha 1985; Gilmour et al. 1992), and that the primary site of methylation is at the oxic/anoxic interface, which is often near the sediment surface (Korthals & Winfrey 1987; Watras et al. 1995b) within Everglades sediments. In this paper, we present an overview of the distribution of Hg and MeHg concentration and MeHg production in Everglades sediments in 1995, the first year of a multi-year study. We also present preliminary information on the chemical and biological controls on Hg methylation, with a focus on sulfate and sulfide concentration. The quantitative relationships between total Hg concentration, speciation, and MeHg production within and across aquatic ecosystems remain poorly understood. Recent and continuing development of methods for estimating MeHg production *in situ* (Gilmour & Riedel 1995; Stordal & Gill 1995; Hintelmann & Evans 1997) has been useful in better quantifying this process.

In the work presented below, tracer-level additions of ^{203}Hg(II) are made to intact sediment cores in order to best approximate ambient gross methylation rates.

This work is being conducted as part of a larger, process-oriented project, "Aquatic Cycling of Mercury in the Everglades" (ACME). Information on Hg biogeochemistry along this transect from other research groups is presented in this volume in three companion papers (spatial distribution and partitioning behavior in surface waters and canals, Hurley et al. this vol.; diurnal cycling in surface waters, Krabbenhoft et al. this vol.; trophic transfer, Cleckner et al. this vol.).

Sampling locations

A trophic gradient across the northern Everglades was chosen for study (Figure 1). The transect runs roughly north to south, with the most eutrophic sites in the north. Sampling sites were within four hydrologically distinct units, the Everglades Nutrient Removal Area (ENR), and Water Conservation Areas (WCA) 2A, 2B and 3A. The trophic gradient is driven by discharge of agricultural runoff from the Everglades Agricultural Area to canals and inflow structures along the northern edges of WCA-2A and WCA-3A, creating a roughly north to south nutrient and vegetation gradient across the area (DeBusk et al. 1994). Agricultural runoff is also pumped into the ENR for treatment. The ENR is being examined both as a high nutrient end point in the gradient, and as part of a larger investigation into how Hg will behave in this re-created wetland. Many of the study sites were established by the South Florida Water Management District (SFWMD) as part of their studies on nutrients in the Everglades. A detailed description of the WCAs and sites studied is given in Hurley et al. (this volume).

Methods

Sampling and sediment processing. Sampling was conducted contemporaneously with collaborating ACME researchers during three intensive trips in March, July and December 1995. On a given date, all cores were sampled within a few m^2, however, sampling sites were moved at least 10 m from date to date. Replicate or more cores from each site were taken for bulk and pore water Hg and MeHg concentration, and a suite of biogeochemical parameters including Hg methylation rate; pore water sulfate, sulfide and pH; microbial sulfate reduction rate; and bulk acid-volatile and chromium-reducible sulfides. A much larger suite of parameters was measured by the ACME team
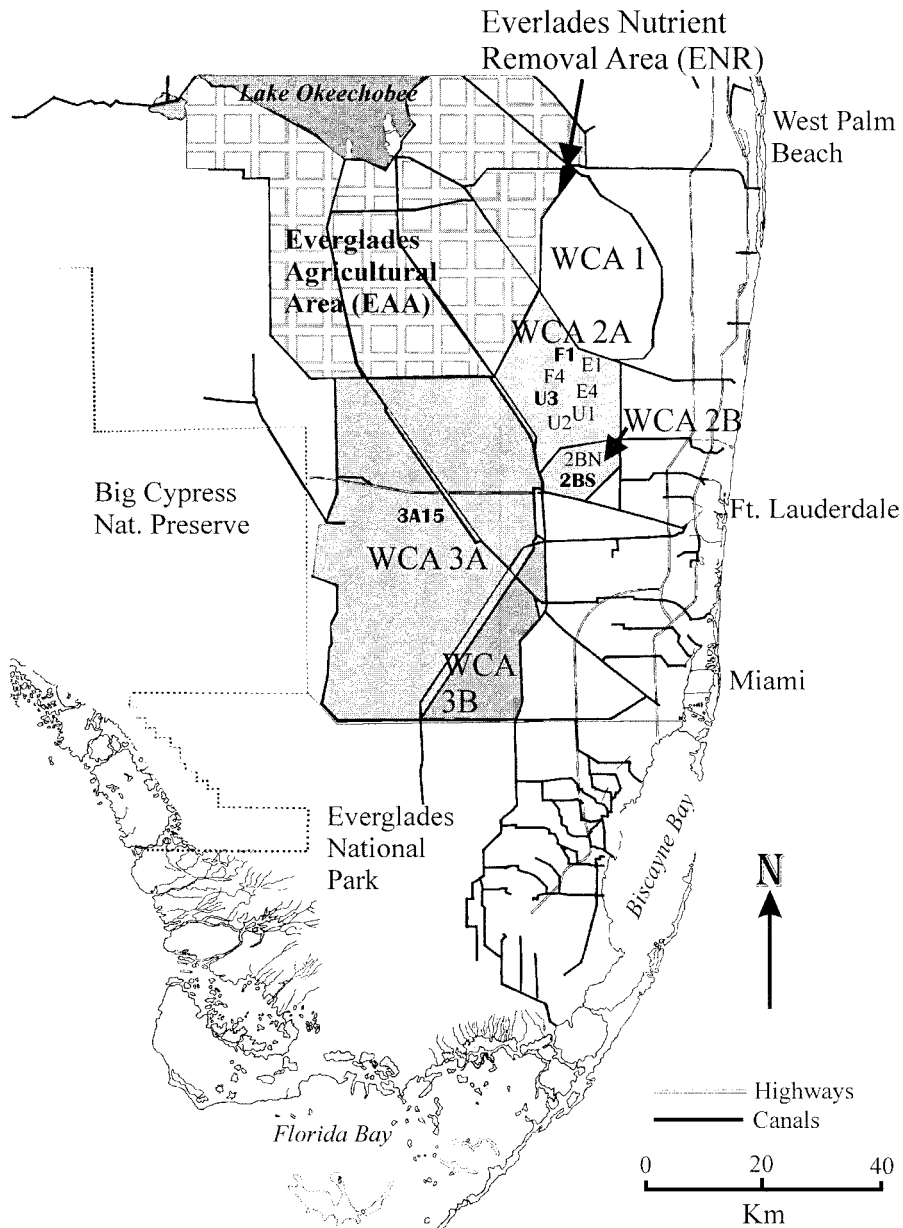
Figure 1. Map of site locations in the northern Everglades.

as whole, but the work presented in this preliminary paper is limited to data collected by the authors. Sediment cores were collected by hand into 25 cm lengths of clear acid-leached PVC tubing, with one end sharpened to help

cut through root material. An "intact sediment core" is defined here as all the material gathered when the core tube is manually pushed into the solid substrate. In this system, that generally included a layer of 2–20 cm of flocculent material and/or periphyton (as defined in Browder et al. 1994) over fairly solid peat.

Pore waters for all analyses were separated from sediments in a field laboratory by direct filtration of bulk sediment sections on disposable Nalgene filter apparatus (0.2 μm pore-size polycarbonate). Filters were rinsed with 10% HCl and low-Hg deionized water immediately before use. Sediments were sectioned and filtered inside a N_2-filled glove bag. Alternatively, redox-sensitive components were measured from pore waters collected by Krabbenhoft and others using an *in situ* interstitial pore water sampler with an in-line 0.45 μm filter (Krabbenhoft et al. submitted). All surface water samples were filtered in the field to 0.2 μm.

Hg and MeHg analyses. Non-contaminating, low-level trace metal techniques (e.g. Gill & Fitzgerald 1987) were employed during all stages of sample collection, handling and analysis. Sediment samples were digested with a 5:2 mixture of HNO_3:H_2SO_4, and analyzed for total mercury Hg_T following Gill & Fitzgerald (1987) and Bloom & Fitzgerald (1988). Pore waters were preserved in 1% HCl and digested with BrCl prior to analysis for Hg_T. Methylmercury analysis in both porewaters and sediments was carried out by distillation (Horvat et al. 1993a,b), then aqueous phase derivitization (Bloom 1989). A matrix modifier (diethyldithiocarbamate) was added during distillations of liquid samples (Bloom & Von der Geest 1995). Wet and dry weights were measured individually on each sample analyzed. The percent dry weight of samples was small, and was highly variable both spatially and with depth in sediments.

During analysis of the 1995 Everglades samples, the average recovery of MeHg spikes into sediment samples (at 100 to 200 pg spike per 1 g wet weight sample) was 81$\pm$19% ($n = 35$). The detection limit, based on $3\times$ the standard error of sample blanks, averaged 6 pg gdw^{-1}. Duplicate analysis of 29 samples (avg. MeHg concentration 155 pg gdw^{-1}) yielded an average relative percent difference (RPD; or the absolute value of the difference between duplicates divided by their average, expressed as a percentage) of 35%. Although the RPD between duplicates is generally higher for MeHg analysis than for total Hg analysis (see below), much of the sample RPD reflects inhomogeneity in subsampling wet peat samples, rather than analytical error. The average RPD for MeHg analysis of dry standard reference materials (SRM) was <10%. BEST (Beaufort Sea sediment, NRC, Canada) was used as an SRM for MeHg; we measured an average concentration of 167$\pm$30 pg g^{-1} ($n = 7$) compared

to 160±54 reported in Horvat et al. (1993). We also participated successfully in an international intercalibration for MeHg in water (Bloom et al. 1995b). Bloom et al. (1997) has noted the production of MeHg from inorganic Hg in samples during distillation. However, we did not observe MeHg production, above the error in the method, from inorganic Hg spikes into Everglades sediment samples. The average concentration of MeHg in a set of 9 samples spike and unspiked samples was the same (29 pg g^{-1}). Samples were analyzed with and without 100 ng $HgCl_2$ per 1 g sample, added just before distillation. In addition, the RPD between spiked and unspiked samples was the same as the running RPD between duplicates for all samples.

Spike recoveries for total Hg (100 ng per 1 g wet weight sample) averaged 103±15% ($n = 33$). Analysis of 29 samples in duplicate yielded an average RPD of 19. The detection for Hg_T in sediments was 10 pg gdw-1 based on 3× the standard error of sampling blanks. Two SRMs were used during analysis of these samples. Our analysis of BEST yielded 80±9 ng g^{-1} ($n = 4$) compared to a certified value of 92±9; BCSS (estuarine sediment from the Gulf of St. Lawrence, NRC, Canada) was 153±25 ($n = 8$) in our lab compared to 180±71. During 1995 we participated successfully in the ninth round of NOAA/NRC metals intercalibration trials (Willie & Berman 1995).

Hg methylation. Methylation within sediments was estimated by the conversion of tracer additions of ^{203}Hg(II) into Me^{203}Hg in intact sediment cores as shown in Figure 2. High specific-activity ^{203}HgCl$_2$ was produced for this work by custom synthesis from ^{202}Hg(II)O obtained from Oak Ridge National Labs. Isotope processing was performed by the Buffalo Materials Research Center, Buffalo, NY. Two batches were used in this work, with specific activities of 33 (March) and 37 (October) mCi mg^{-1}. The goal of this method is to use ^{203}Hg(II) of specific activity sufficient to act as a tracer in natural sediments and waters. Stock solutions of ^{203}Hg(II)Cl$_2$ were maintained in 1% HCl until use. Stock was diluted into 0.2 μm filtered surficial pore water at least an hour before injection into cores to allow formation of dissolved Hg complexes. The speciation of added ^{203}Hg(II) in working dilutions should therefore have resembled that of Hg(II) in aqueous phase of the sediments being examined. Dilutions were high enough that the pH of working solutions was the same as ambient pH (range 7.1–8.3).
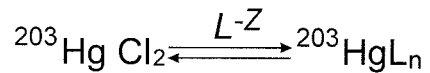
Working dilutions were injected into intact sediment cores at 1 cm depth intervals within 6 h of collection. Water overlying cores was gently changed before addition of ^{203}Hg(II) to prevent depletion of electron acceptors. Sediment core tubes of 3.5 cm inner diameter had holes drilled at 1 cm intervals and filled with silicone sealant. For each 1 cm interval, about 0.5 μCi of ^{203}Hg(II) was injected in a volume of 25μl. Injections were made along three

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Measurement of gross Hg methylation rate using tracer-level ^{203}Hg
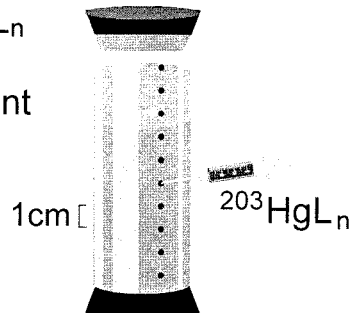
1. Synthesize ^{203}Hg

$$^{202}Hg \xrightarrow{\text{irradiate}} {}^{203}Hg$$
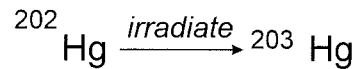
2. Equilibrate with pore water ligands

$$^{203}Hg\ Cl_2 \underset{L^{-Z}}{\overset{L^{-Z}}{\rightleftharpoons}} {}^{203}HgL_n$$

3. Spike $^{203}HgL_n$ into sediment cores

4. Incubate under in situ conditions 2 to 48 hours

1cm [ ] $^{203}HgL_n$

5. Cut and slice sediment cores

6. Extract Me^{203}Hg from sediments and count

Calculation for each sediment depth interval:

$$\frac{[Me^{203}Hg]_{formed}}{[^{203}Hg]_{added}} \times \frac{[Hg]_{ambient}, (ng\ cc^{-1})}{\text{hours incubation}} = \text{gross MeHg produced} \ (ng\ cc^{-1}h^{-1})$$

Calculation for surface area of sediment :

$$\frac{\text{MeHg produced}}{(ng\ m^{-2}\ d^{-1})} = \overset{\text{depth interval}}{\underset{}{\Sigma}} (MeHg\ produced, \ ng\ cc^{-1}\ d^{-1}) * 1000$$

Figure 2. Measurement of gross Hg methylation rate using tracer-level ^{203}Hg.

lines radiating from the injection site. Cores were incubated at *in situ* marsh temperatures in the dark. After incubation, cores were sliced and frozen until analysis.

Me^{203}Hg was extracted from aliquots of thawed sediment and quantified as described in Gilmour & Riedel (1995). The ambient methylation rate was calculated by multiplying the fraction of added ^{203}Hg methylated per day by the ambient total Hg concentration in the horizon of interest. This calculation assumes that ^{203}Hg is added as a tracer, and that the speciation and sediment/water partitioning of added Hg(II) mimic that of ambient Hg(II). The tracer assumption was met in most cases, with ^{203}Hg additions of 1 to 4 ng cm^{-3} compared to ambient concentrations of 1 to 40 ng cm^{-3}. The second assumption was tested by measuring the time course of ^{203}Hg partitioning onto the solid phase. Partitioning was generally complete within a hour. Whether 1) sorption to the solid phase is rapid enough relative to methylation to provide good estimates of ambient rates, and 2) the speciation of ^{203}Hg newly sorbed to sediments adequately reflects ambient speciation with regard to availability for methylation are subjects of continuing research in our laboratory. To ensure that demethylation of newly formed Me^{203}Hg did not occur to any significant extent, the time course of Me^{203}Hg production was examined, using replicate intact sediment cores. At station U3 in December, the amount of Me^{203}Hg produced increased approximately linearly through 8 h, after which time the amount of Me^{203}Hg in the sediment cores began to decline. Therefore, most methylation assays were incubated for 2–4 h. The linearity of methylation through 8 h also suggests that the bioavailable fraction of the added ^{203}Hg(II) does not change over this time period.

Other analyses. Dissimilatory sulfate-reduction was measured by the reduction of ^{35}SO$_4$ spiked into intact sediment cores at 1 cm intervals as described above for ^{203}Hg(II). Carrier-free ^{35}SO$_4$ was diluted with cold sulfate to 400 μCi μm^{-1}, and a total sulfate concentration of 100 μm, before addition to sediments. A time course of sulfate reduction in U3 sediments in December showed linearity through only 4 h; most incubations were carried out for 1–2 h. Sulfate reduction into both acid-volatile (AVS) and chromium-reducible (CRS) reduced sulfur phases was analyzed and summed (Fossing & Jorgenson 1989). A sulfide anti-oxidant buffer (SAOB; Brouwer & Murphy 1994) was used to preserve sulfide in water samples for up to 36 h. The SAOB buffer was prepared daily, using deoxygenated water. Sulfide was quantified with a detection limit of about 100 nM, using an ion-specific electrode and a sulfide standard curve made daily in SAOB.

Amendment studies. To study the control of methylation, sets of individual intact sediment cores were amended with a suite of compounds that might affect various processes involved in methylation. Additions, and their approximate final concentration in porewater were: MoO_4^{2-}, 20 mM; bromoethane sulfonic acid (BES), 20 mM; SO_4^{2-}, 2.5 mM; sulfide, 50 μM; NO_3^-, 100 μM; NH_4^+, 10 μM; PO_4^{2-}, 10 μM; and Fe(III) citrate, 2.5 mM. All amendments were made using pH 7 solutions. For each study, each amendment was made to duplicate cores, and four unamended control cores were used. Cores were incubated with amendments for 1 h before injection of ^{203}Hg(II). Hg methylation was measured in the top 4 cm of sediments as described above, with ^{203}Hg and amendments injected at 1 cm intervals to 5 cm depth into sediment cores. Cores were sliced and frozen after a 4–6 h incubation in the dark at *in situ* marsh temperature.

Results and discussion

Spatial patterns of Hg$_T$, MeHg and Hg methylation. Total Hg concentrations were lowest at the most eutrophic sites, and increased somewhat as nutrient concentrations decrease (Figure 3). This pattern was observed by Rood et al. (1995), and may be explained by higher total sedimentation rates in more eutrophic areas diluting the Hg accumulating in sediments. Methylmercury concentrations and %MeHg increased dramatically to the south, with MeHg concentrations and %MeHg in the southern part of the transect comparable to sulfuric acid-impacted freshwater systems (Gilmour & Henry 1991; Gilmour et al. 1992; Gilmour & Riedel 1995; Krabbenhoft et al. submitted). The increase in MeHg to the south is driven primarily by factors other than total Hg concentration. While Hg concentrations increased by a factor of 3 to 4 over the gradient studied, MeHg concentrations increased by a factor of about 25.

A sub-set of sites was studied more intensively, including measurements of Hg methylation and sulfate reduction rate with depth. Like %MeHg, methylation rates generally increased to the south (Figure 4). The coincident distributions of MeHg and its production suggest that MeHg concentrations in sediments are controlled by *in situ* methylation. Methylation rates appeared to follow the same trend as MeHg, with methylation rates increasing toward the south, during the March and July sampling periods. Methylation rates were lowest and most uniform among sites in December. Mid-day mid-water column temperatures at the sites sampled averaged 25 °C in March, 28 °C in July and 18 °C in December. Lower temperatures and senescent vegetation during winter may lower overall bacterial activity and hence methylation. Higher rates of net Hg methylation and MeHg accumulation in summer are
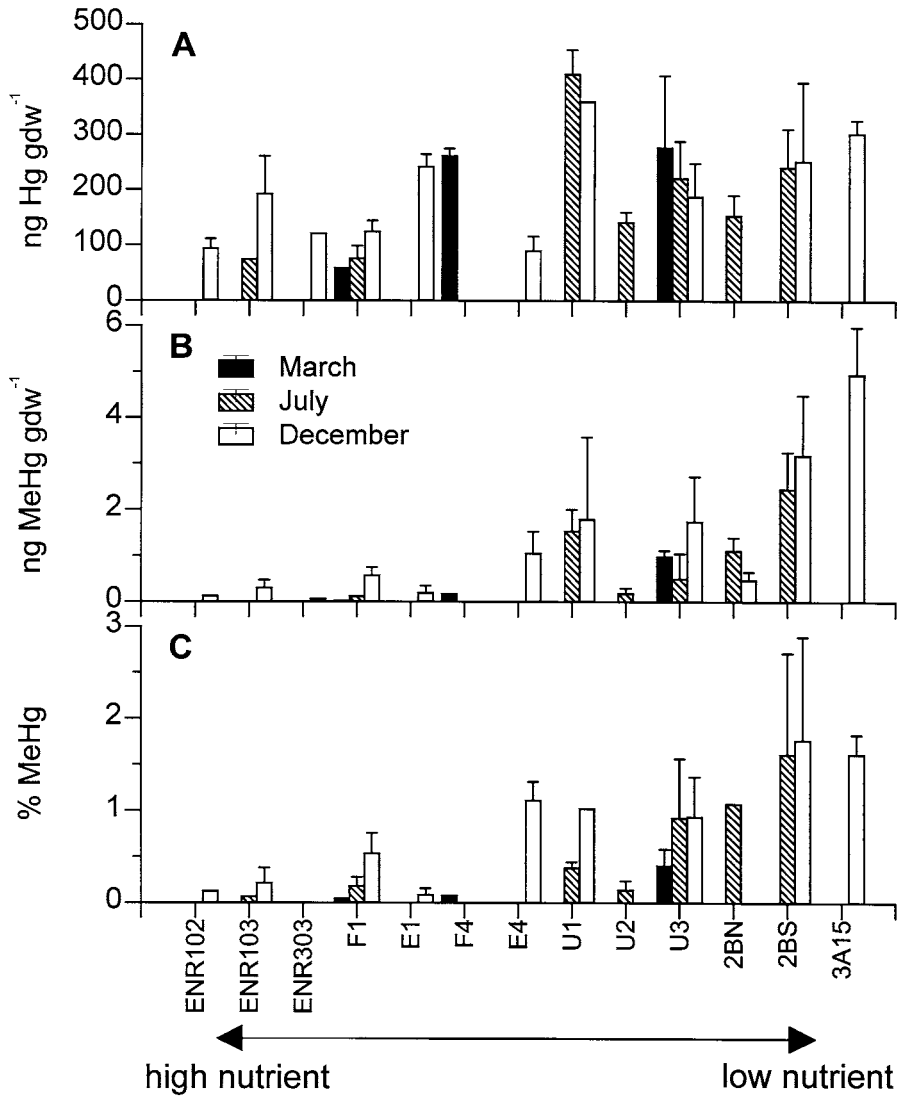
Figure 3. Total Hg (A) and MeHg (B) per gram dry weight sediment, and MeHg as a percentage of total Hg (C) for three dates in 1995. The sites represent a trophic gradient in the northern Everglades, and are arranged from left to right roughly in order of nutrient concentration, and from north to south. Error bars represent the SD among the top 4 cm of 2 to 5 separate cores taken at each site at each date.

consistent with studies in Canadian Shield lakes where methylation in surficial sediment was favored over demethylation at warmer temperatures (Ramlal et al. 1993).
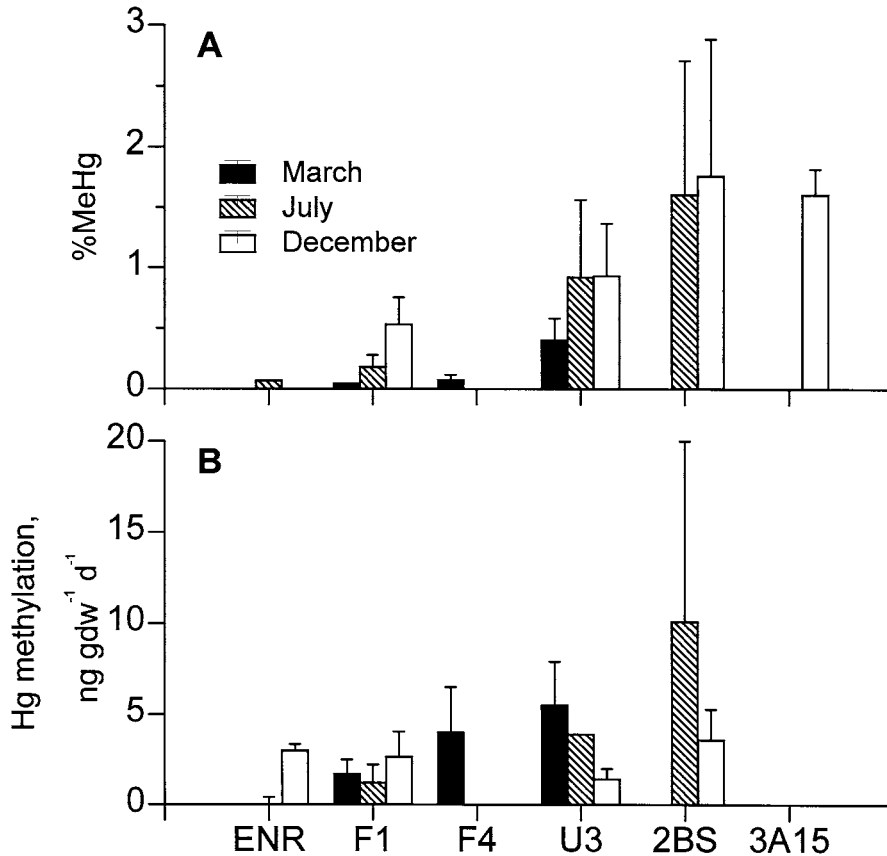
Figure 4. %MeHg (A) and methylation rate (B) for intensively studied Everglades sites across the trophic gradient. Error bars represent the SD for 2 to 5 separate sediment cores.

Methylation rates shown in Figure 4 are the product of the fraction of added ^{203}Hg(II) methylated and the ambient concentration of Hg_T, as described in Figure 2. The fraction of ^{203}Hg(II) methylated ranged from 0 to 0.12 d^{-1} in surficial (0–4 cm) sediments, and averaged 0.02 d^{-1} across all sites and dates in 1995. MeHg appeared to accumulate in Everglades surface sediments over the course of the year at the intensively studied sites (Figure 3). Nevertheless, the majority of MeHg produced must be accounted for by other loss processes; otherwise, methylation rates were overestimated. MeHg may be lost from sediments via advection or bioaccumulation, or via microbial (Oremland et al. 1995) or photochemical demethylation (Sellers et al. 1996). Ongoing ACME studies are examining the importance of these loss terms, as well as methodology for gross and net methylation.
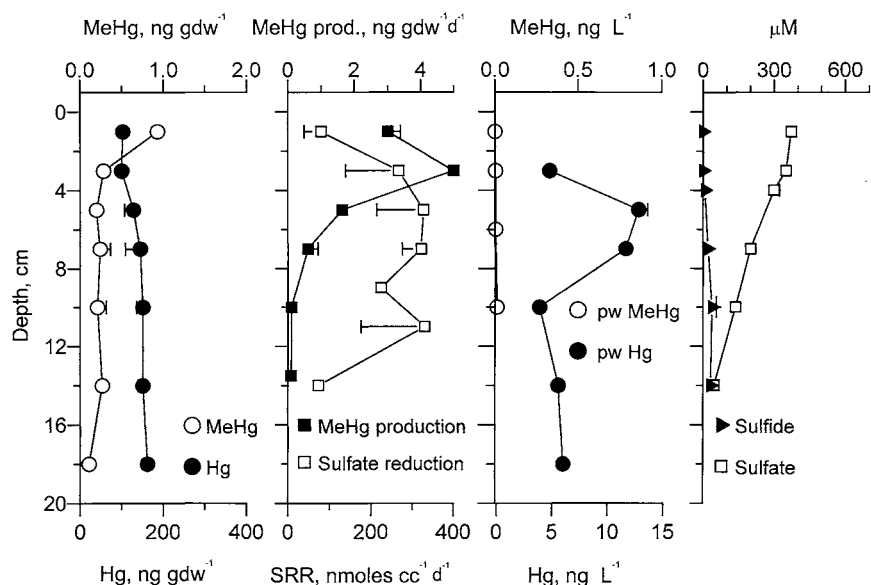
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Figure 5. Depth profiles of a number of parameters in sediments and sediment pore waters at site F1 in WCA-2A in December 1995. Error bars show the SD between duplicate cores.

As in other aquatic systems (Korthals & Winfrey 1987; Gilmour et al. 1992; Ramlal et al. 1993), methylation rates were generally highest at or within a few cm of the sediment surface. Profiles of a number of parameters with depth are shown for sites F1 (Figure 5) and U3 (Figure 6) in December, 1995. In these profiles, "0 cm" refers to the solid/water interface, whatever the composition of the solid at the surface of the core may be. The profile of MeHg concentration generally reflects the methylation profile, i.e. both are highest near the surface. However, the distribution of methylation rate with depth does not follow Hg_T, either in bulk phase or in pore waters. Methylation rate in the water above sediment was routinely assayed in early 1995; however, none was ever detected. In most cases, sulfate was depleted with depth in the Everglades sediments examined. However, the profile of $^{35}SO_4$ sulfate reduction did not always match the sulfate concentration profile, nor the methylation profile. Sulfate reduction profiles may reflect strong internal recycling of S within sediments, possibly fueled by transport of O_2 through root systems of emergent macrophytes.

Control of methylation. In order to examine the biogeochemical control of methylation, amendment experiments using potential stimulants or inhibitors of methylation were performed using intact sediment cores. An example is given in Figure 7, for F1 in December 1995. Amendment experiments were
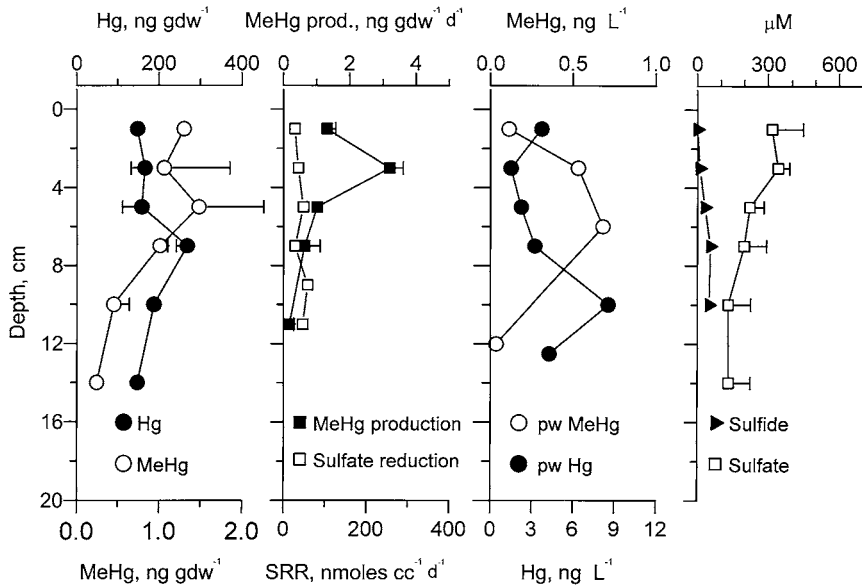
Figure 6. Depth profiles of a number of parameters in sediments and sediment pore waters at site U3 in WCA-2A in December 1995. Error bars as in Fig. 5.

also performed at site F1 and U3 in July 1995. In all amendment studies performed to date in the Everglades, the addition of molybdate, an inhibitor of sulfate reduction, inhibited methylation; and addition of BES, an inhibitor of methanogenesis, had either no effect of stimulated methylation. However, response to sulfate and sulfide amendments has been mixed across sites and seasons. In the experiment shown in Figure 7, the addition of 50 μM sulfide to sediments with ambient pore water sulfide concentration of about 200 μM significantly inhibited the $Me^{203}Hg$ production. Sulfate, injected to a final pore water concentration of 2.5 mM with depth into sediments did not significantly affect methylation. However, in the other amendment experiments conducted in the sediments from WCA-2A, methylation was not inhibited by sulfide additions but was stimulated by sulfate additions. In no case have we see a response in methylation rate to the direct addition of nitrate or phosphate. The responses to molybdate and BES additions suggest that sulfate-reducing bacteria are mediators of Hg methylation in Everglades sediments (including floc, periphyton and peat), however, methylation rates may be controlled by either sulfate or sulfide depending on site and season.

Sulfur biogeochemistry. Sulfate concentrations in surficial pore waters (0–4 cm) changed dramatically along the transect studied. Concentrations were highest within WCA-2A and ENR. However, sulfate levels in WCA-2B were
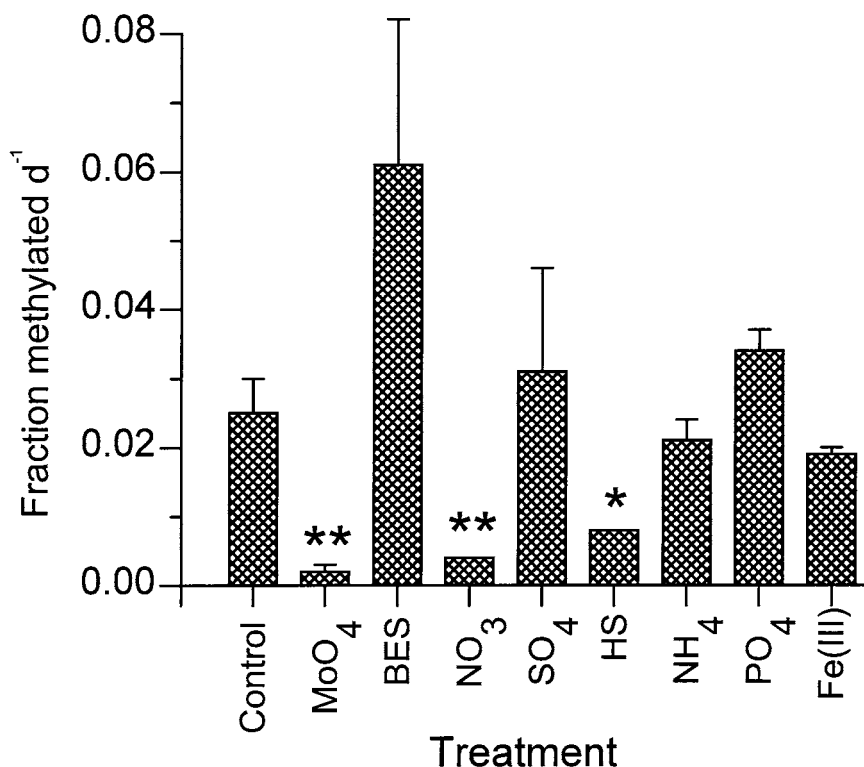
Figure 7. Effect of amendments on Me²⁰³Hg production in the top 4 cm of intact sediment cores, Site F1, December, 1995. Each bar represents the fraction of added ²⁰³Hg(II) methylated per day in the top 0–4 cm of replicate intact sediment cores, ±SE (n = 2 except n = 4 for controls). Treatments significantly different from controls are marked ⋆⋆ ($\alpha < 0.05$) or ⋆ ($\alpha < 0.10$), based on a two-tailed Dunnett's test.

as low at 50 μM, probably reflecting rain water sulfate concentrations and the lack of agricultural discharge in this hydologically separate area. Limestone underlying peat may be a source of sulfate in addition to agricultural and atmospheric sources of sulfate to the Everglades. However, sources of sulfate to the Everglades appear to be poorly characterized.

Sulfate reduction rates (SRR) were fairly high for a freshwater system (10–60 mmol m^{-2} d^{-1}) across the entire transect studied, even given the high sulfate concentrations in the north (Marnette et al. 1992; Urban et al. 1994). High availability of organic carbon, high temperatures and high sulfate concentrations favor sulfate reduction in the eutrophic northern Everglades, and phosphate-driven eutrophication of the northern WCA-2A results in more anaerobic sediments (Amador & Jones 1995). Rates in the most eutrophic areas compare to those found in marine and estuarine sediments and temperate

salt marshes, where surface water sulfate concentrations can be 50 times higher than in the northern Everglades. Drake et al. (1996) found higher numbers of culturable SRB in sediments at station F1 than at a more pristine site in WCA-3A. However, SRR appears to remains fairly high even at low sulfate concentrations. Internal reoxidation of reduced sulfur under the less reducing conditions found in the more pristine sediments may account for this. Microbial sulfate reduction appears to be the most important mechanism for reduced S storage in Everglades peats. Stable isotope signatures (E. Spiker, personal communication) show that the majority of reduced S stored in Everglades sediments, at both eutrophic and more pristine sites, arises from dissimilatory sulfate reduction rather than assimilation by plants.

The distribution of sulfide in Everglades pore waters (Figure 8B) generally followed the distribution of sulfate. High concentrations at the high nutrient end of the transect reflect high dissimilatory sulfate-reduction rates. Sulfide concentrations in surficial northern Everglades peats were high, up to 300 μM; and during the warmer months surface waters were also sulfidic (data not shown). Like sulfate, sulfide concentrations were dramatically lower in WCA-2B, generally <10 μM.

Conclusions

Methylmercury concentrations in surficial Everglades sediments and MeHg as a percent of Hg_T (%MeHg) increased dramatically from north to south, opposite the gradients in nutrient, sulfate and sulfide concentrations. Although fewer data have been collected, MeHg production rates also appear to increase toward the south. As in most other aquatic sediments, methylation occurs mainly near the surface of sediments and appears to be mediated by sulfate-reducing bacteria. Methylation did not occur in water overlying sediments. The coincident distributions of MeHg and its production suggest that *in situ* production controls concentration. The spatial pattern of MeHg in sediments was reflected in other matrices examined by ACME investigators, including water, periphyton and biota, in some but not all seasons (Hurley et al. this vol.; Cleckner et al. this vol.). The amount of MeHg accumulation in biota may therefore be a function of the *de novo* methylation rate in surficial sediments.

Methylmercury production in the eutrophic northern Everglades appears to mimic that in an estuary, where sulfate and sulfate reduction rates are high and sulfide produced by sulfate reduction inhibits MeHg production (Compeau & Bartha 1985; Choi & Bartha 1994). Levels of sulfate and other conditions in the more pristine southern areas appear sufficient to support high sulfate reduction rates, without high sulfide accumulation, a balance that favors higher rates of Hg methylation. The relationship between %MeHg
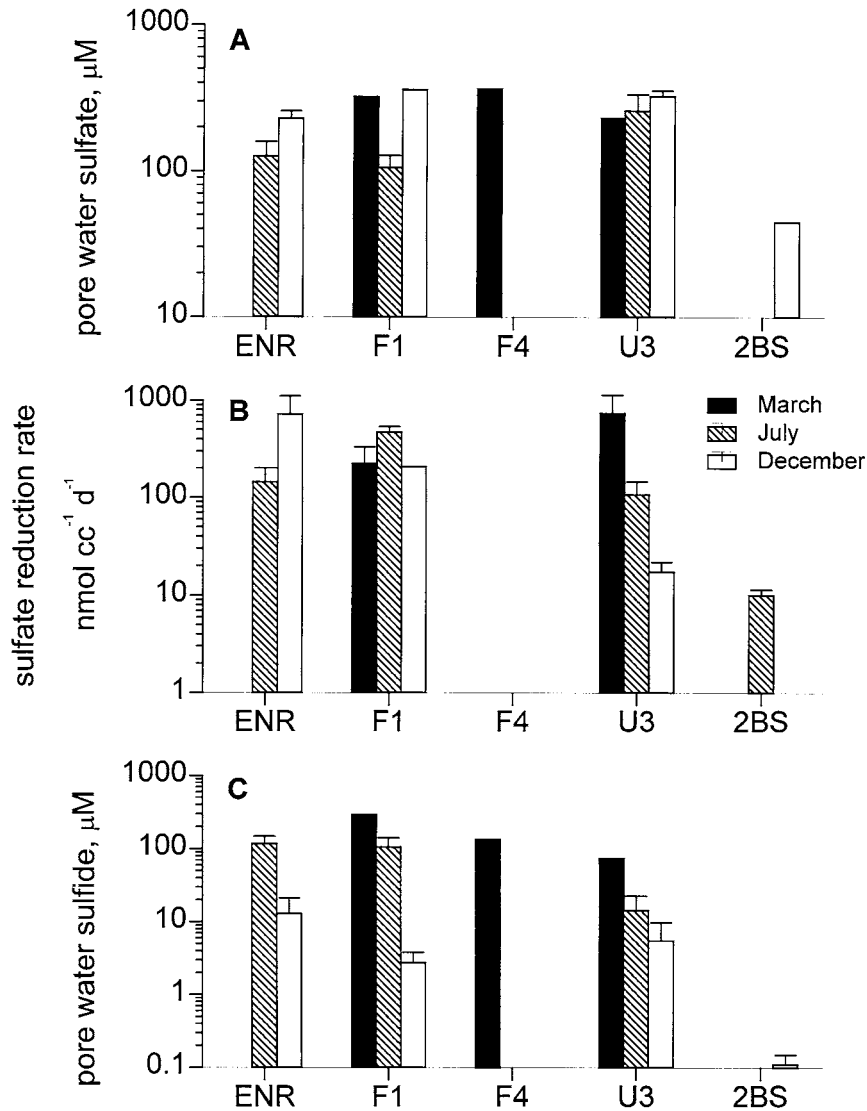
Figure 8. Dissolved sulfate concentrations (A) sulfate reduction rates (B) and dissolved sulfide concentrations (C) in the top 4 cm of sediment at intensively sampled sites across the nutrient transect.

and surface water sulfate for a number of ecosystems, including the northern Everglades, is shown in Figure 8 of Benoit et al. (this volume). This pattern suggests that %MeHg in the Everglades may be higher south of the sampling sites studied to date. Sources and cycling of sulfate in the nutrient impacted

Everglades and in the more pristine areas to the south will be important in modeling MeHg production and bioaccumulation in this system.

Acknowledgements

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