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Distribution of Total Mercury and Methyl Mercury in Water, Sediment, and Fish from South Florida Estuaries

K. Kannan,[1] R. G. Smith, Jr.,[1] R. F. Lee,[1] H. L. Windom,[1] P. T. Heitmuller,[2] J. M. Macauley,[3] J. K. Summers[3]

[1] Skidaway Institute of Oceanography, 10 Ocean Science Circle, Savannah, Georgia 31411, USA
[2] U.S. Geological Survey, National Wetlands Research Center-Gulf Breeze Project Office, 1 Sabine Island Drive, Gulf Breeze, Florida 32561, USA
[3] U.S. Environmental Protection Agency, National Health and Environmental Effects Research Laboratory, Gulf Ecology Division, 1 Sabine Island Drive, Gulf Breeze, Florida 32561, USA

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Abstract. Concentrations of total mercury and methyl mercury were determined in sediment and fish collected from estuarine waters of Florida to understand their distribution and partitioning. Total mercury concentrations in sediments ranged from 1 to 219 ng/g dry wt. Methyl mercury accounted for, on average, 0.77% of total mercury in sediment. Methyl mercury concentrations were not correlated with total mercury or organic carbon content in sediments. The concentrations of total mercury in fish muscle were between 0.03 and 2.22 (mean: 0.31) μg/g, wet wt, with methyl mercury contributing 83% of total mercury. Methyl mercury concentrations in fish muscle were directly proportional to total mercury concentrations. The relationship of total and methyl mercury concentrations in fish to those of sediments from corresponding locations was fish-species dependent, in addition to several abiotic factors. Among fish species analyzed, hardhead catfish, gafftopsail catfish, and sand seatrout contained the highest concentrations of mercury. Filtered water samples from canals and creeks that discharge into the Florida Bay showed mercury concentrations of 3–7.4 ng/L, with methyl mercury accounting for $<$0.03–52% of the total mercury. Consumption of fish containing 0.31 μg mercury/g wet wt, the mean concentration found in this study, at rates greater than 70 g/day, was estimated to be hazardous to human health.

Mercury has been one of the contaminants of concern in Florida for several years. Earlier studies have reported high mercury concentrations in inland aquatic systems throughout Florida (Cabbage 1989; Hand and Friedemann 1990; Hord *et al.* 1990; Royals and Lange 1990). The state of Florida issued an advisory in 1989 prohibiting consumption of top-level predatory fish, largemouth bass (*Micropterus salmoides*), bowfin (*Amia calva)*), and gar (*Lepisosteus* spp.) in southern Florida, and the entire Everglades watershed has been closed to hunting of alligators due to excessive mercury in edible tissues (Royals and Lange 1990). Methyl mercury intoxication has been documented in wildlife in southern Florida (Roelke *et al.* 1991; Sundlof *et al.* 1994). While information pertaining to mercury in abiotic and biotic compartments in inland areas of Florida are available, there is less information on the distribution of mercury in estuarine and coastal areas. Concentrations of methyl mercury in sharks collected along the Florida coast often exceeded the U.S. Food and Drug Administration's action level of 1 μg/g (Hueter *et al.* 1995).

In order to understand factors that influence the dynamics of mercury in estuaries, it is necessary to provide information on the concentrations of mercury compounds in various matrices in correspondence with ancillary parameters such as organic carbon and silt contents. Further, simultaneous collection and analysis of sediments and fish will provide information on the extent of bioavailability of sediment-bound mercury compounds. We present information on the distribution, concentrations, and partitioning of mercury between sediment and fish from estuarine and coastal areas of southern Florida. Some preliminary results on mercury concentrations in water flowing into Florida Bay are also presented.

This study is a part of the Environmental Monitoring and Assessment Program (EMAP), created in 1988 by the U.S. Environmental Protection Agency (EPA) in cooperation with other federal agencies to evaluate environmental problems impacting ecological resources. The program is designed to monitor pollutants and environmental changes simultaneously to identify causes of adverse changes. The estuarine component of EMAP (EMAP-E) has monitored the status and trends in the environmental quality of the estuarine waters of the United States since 1990 (Summers *et al.* 1995; Daskalakis and O'Connor 1995). The EMAP-E monitoring program conducted in 1995 in the West Indian Province (South Florida, from Tampa Bay around the southern tip of Florida, including the Florida Keys up the Atlantic coast to near Ft. Pierce; see Figure 1) analyzed water, sediment, and biota for the presence of a variety of organic and inorganic contaminants (Macauley and Summers 1995).

Correspondence to: K. Kannan, 201 Pesticide Research Center, Michigan State University, East Lansing, Michigan 48824; e-mail: kuruntha@pilot.msu.edu

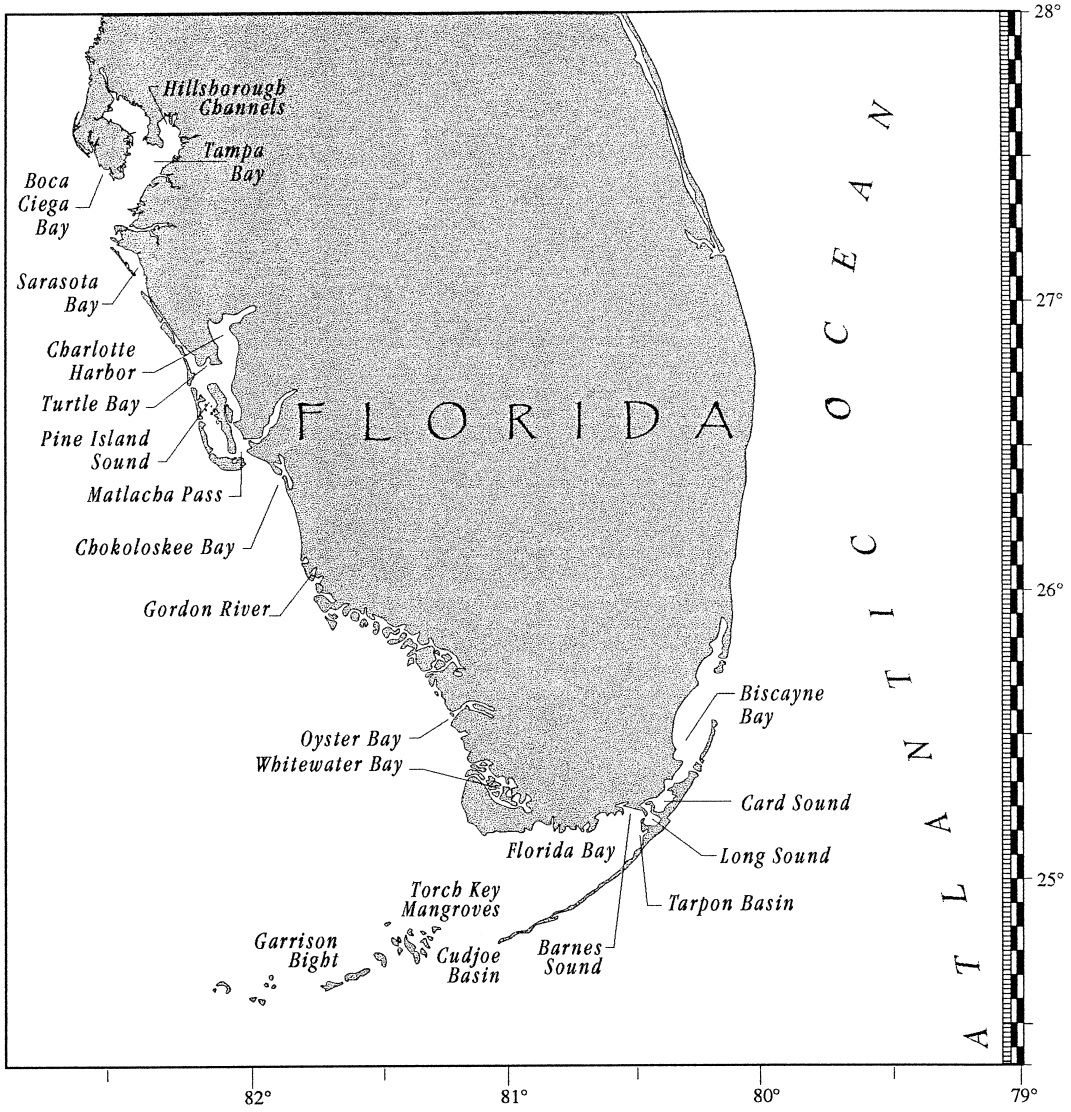

Fig. 1. Locations of sampling in estuaries in southern Florida

Materials and Methods

Sample Collection

Sediment and fish samples were collected in 1995 (Figure 1) in accordance with EMAP's probabilistic sampling protocol (Macauley and Summers 1995). Sediment samples were collected from a vessel with a Van Veen grab sampler. The grab sampled an area of 440 cm^2 with a maximum penetration depth of 10 cm. Clean stainless steel scoops were used to remove the top 2 cm of sediment from the grab. In areas where seagrasses were profuse (such as Florida Bay and Keys), a Kynar® coated posthole digger was used. Sediments from at least three replicate grabs were homogenized and aliquots were placed into high-density polyethylene jars, which were placed on ice immediately and frozen at −20°C within 24 h of collection. Most sediment samples were carbonate sand, except for Tampa Bay sediments which were quartz sand. Organic carbon and mud (silt + clay) contents of sediments were available as ancillary data for the EMAP-E program.

Fish were collected by either trawl net or fish traps deployed at the station overnight and placed in water-tight polyethylene bags and frozen at −20°C. Traps were used in areas that were closed to trawling (e.g., sanctuary areas of Florida Bay and the Everglades National Park). Whole fish were weighed and dissected, the skin removed, and equal amounts of muscle fillets of several individuals of the same species from each location were pooled, homogenized, and analyzed. Fish species analyzed included the following: hardhead catfish (*Arius felis*), white grunt (*Haemulon plumieri*), sand perch (*Diplectrum formosum*), lane snapper (*Lutjanus synagris*), gafftopsail catfish (*Bagre marinus*), pinfish (*Lagodon rhomboides*), spot (*Leiostomus xanthurus*), pigfish (*Orthopristis chrysoptera*), sand seatrout (*Cynoscion arenarius*), and brown shrimp (*Penaeus aztecus*). Fish were collected at most locations where sediments had been taken. An aliquot of sediment and fish muscle were dried in an oven at 80°C to estimate dry weight measurements.

Water samples were collected from the South Florida region as part of an EMAP ancillary study to determine mercury concentrations in water flowing through the Florida Everglades before emerging into Florida Bay. Samples were taken in June 1995 at four sites at 2 and 4 h after deployment of a current meter at the following sites: Taylor River, Trout Creek, Shell Creek, and C-111 Canal. Near-surface (depth of 0.5 m) and near-bottom (0.5 m off-bottom) samples were collected from east and west sides of the C-111 Canal, while only surface water was taken from Shell Creek, Trout Creek, and Taylor River. Salinity, pH,

and dissolved oxygen were measured on site and water samples were filtered through a 0.45-µm cartridge filters into acid cleaned Teflon bottles. Adequate precautions were exercised to avoid contamination of water during sampling, transport, and handling.

Chemical Analysis

Total mercury in sediment and fish tissues was analyzed following the method described by Smith (1993). Sediment and fish muscle were weighed (0.5 g for sediment and 2 g for fish tissue), spiked with an enriched ^{201}Hg isotope, and digested with 5 ml of HNO_3 using a microwave digestion system. The microwave parameters were 100% power for 30 min with a maximum temperature and pressure of 160°C and 120 psi, respectively. The samples were analyzed after cold vapor reduction with an inductively coupled plasma-mass spectrometer. The isotopic ratio of $^{202}Hg/^{201}Hg$ was determined and the concentration of total mercury was calculated. Detection limits of Hg in sediment and in fish were 7 and 4 ng/g dry wt, respectively.

The determination of mercury in water was based on amalgamation onto gold-coated sand with subsequent double amalgamation and vaporization into a atomic fluorescence spectrometer. The procedure is similar to the EPA method 1631 (US EPA 1996). A 100-ml of preacidified (0.5 ml of HNO_3) sample was weighed into a reaction vessel followed by the addition of 0.5 ml of 20% $SnCl_2$. The sample was then purged with argon for 20 min at a flow rate of 350 ml/min, while the gold trap was purged with argon at a flow rate of 60 ml/min for 5 min to remove moisture. The subsequent double amalgamation process was followed by mercury detection using cold vapor atomic fluorescence spectrometer detection. The detection limit of total Hg in water was 20 pg/L.

Methyl mercury in sediment and fish tissue was analyzed following the method described by Horvat *et al.* (1993a). An aliquot of wet sediment (2 g) or homogenized, pooled fish tissue (0.2 g) was weighed into a 30-ml Teflon PTFE (polytetrafluoroethylene) vial followed by the addition of 5 ml tap water, 0.2 ml of 20% KCl, and 0.5 ml of 8 M H_2SO_4. The mixture was diluted to 10 ml with tap water. Distillation was started quickly after addition of the reagents at an argon flow rate of 60 ml/min and a heating block temperature of 145°C. The distillation rate was held at approximately 7 ml/h. The distillate was collected in a 30-ml PTFE vial kept in an ice-cooled water bath. Before distillation, 5 ml of tap water was placed in the collection vial. Water samples require a 50-ml aliquot of water in a 60-ml PTFE vial (Horvat *et al.* 1993b).

An aliquot of the distillate was added to 100 ml of tap water in a 250-ml reaction (ethylation) flask. The sample was buffered to pH 4.9 with 2 M acetic acid-sodium acetate solution (0.2 ml), followed by the addition of 50 µl of 1% aqueous sodium tetraethylborate solution. The flask was quickly closed and connected to collection trap (Tenax®) on one end and argon on the other. The mixture was allowed to react for 15 min without bubbling. The ethylation reaction results in the formation of ethylmethyl mercury from reactive methyl mercury. After the reaction period, the solution was purged for 12 min at a flow rate of 250 ml/min with Hg-free, high purity argon. The outflowing gas stream was passed through a 100-mg Tenax trap (20/35 mesh; Alltech Associates Inc., Deerfield, IL), which adsorbs the organomercury species. After the sample was purged, dry argon was flushed through the Tenax trap for 5 min to remove traces of condensed water vapor, a strong interference during chromatographic elution and atomic fluorescence detection. The mercury species on the Tenax trap was released by thermal desorption into a isothermal gas chromatography (GC) column which is a 70 cm long, U-shaped, silanized glass column filled with 15% OV-3 Chromosorb WAW, DMCS at 100°C (mesh 60/80; Supelco, Inc., Bellefonte, PA). Under a flow of argon, the eluted mercury species was converted into Hg° by thermal decomposition at 900°C and then detected by cold vapor atomic fluorescence spectrometry (Model 2500, Tekron Inc., Ontario). The output from the detector was quantified using an integrator (Model HP3394A, PA). Methyl mercury was quantified by comparing peak areas of standards (prepared in tap water) with those of samples.

Quality Assurance

Quality assurance procedures included instrument calibration using certified standards and the analyses of matrix spikes, certified reference materials, and reagent blank, according to EMAP-EPA criteria (Heitmuller and Peacher 1995). Low-level mercury determinations were performed under extremely clean conditions. PTFE vials were heated in concentrated HNO_3 and thoroughly rinsed with tap water before use. The correlation coefficient of the standard calibration run was maintained at >0.99. A continuing calibration standard, which is one of the midpoint standards, was analyzed after every 10 samples to verify that the instrument remained calibrated. Matrix spike and matrix spike duplicates were determined on 5% of the samples; actual field samples were spiked with approximately 10 times the instrument detection limit to examine the recovery of the matrix spike and to monitor matrix interference. Recoveries of total and methyl mercury spiked into sediments and fish tissues at three different levels, bracketing real sample concentrations, were between 95–110%. Analytical quality control was verified by the routine analysis of certified reference materials (BCSS-1 for mercury, 0.18 ± µg/g dry wt; PACS-1 for methyl mercury, 8.1 ± 0.46 dry wt as Hg°). Our results for methyl mercury in PACS-1 was 8.47 ± .63 ng/g as Hg° , which was similar to that reported by Horvat *et al.* (1993a). Similarly, for fish tissues, DORM-2 (4.64 ± 0.26 µg/g dry wt for total mercury and 4.6 µg/g dry wt for methyl mercury) was analyzed. Procedural blanks were run along with each batch of 15 samples.

Results and Discussion

Mercury in Sediments

Concentrations in sediments ranged from 1 to 219 ng/g (mean: 20 ng/g dry wt) for total mercury and from <1 to 490 pg/g (mean: 78 pg/g dry wt) for methyl mercury (Table 1). Sediments collected from Hillsborough Channels, Gordon River, and Caloosahatchee River had the highest total and methyl mercury concentrations. The large variation of mercury concentrations determined in this survey reflects the wide diversity of sediment characteristics and pollution intensity. Even within a given geographic area, total and methyl mercury concentrations were highly variable. For example, total and methyl mercury concentrations in sediments from Florida Bay ($n = 30$) ranged from 3 to 100 ng/g (dry wt) and from <1 to 318 pg/g (dry wt), respectively. Sediments collected within a 10-m area showed as much variability as samples collected throughout the Everglades region (Rood *et al.* 1995).

In general, the observed mercury concentrations were within ranges reported for coastal marine sediments (Kannan and Falandysz 1997). Total mercury was not correlated ($r = 0.1$; $p > 0.05$) with methyl mercury concentrations in sediments (Figure 2A) when three samples containing the highest total mercury concentrations (outliers) were excluded, which is in agreement with previous studies (Craig and Moreton 1983; Kannan and Falandysz 1997). Under anaerobic conditions Hg^{2+} has a high affinity for sulfide, resulting in the formation of insoluble HgS, which is deposited in the sediment. Once deposited as HgS, mercury is presumably not available for methylation (Andersson *et al.* 1990). Physical perturbation or

Table 1. Concentrations (dry weight basis) of total mercury and methyl mercury in sediment and fish muscle collected from the Atlantic and Gulf Coasts of Florida, USA

	Sediment			Fish[a]			
Location	n	Total Mercury (ng/g)	Methyl Mercury (pg/g)	Species	n	Total Mercury (μg/g)	Methyl Mercury (μg/g)
Biscayne Bay	5	17 (3–66)[b]	26 (<1–59)	HH catfish	1	1.58	1.96
				White grunt	2	0.87 (0.71–1.03)	0.90 (0.8–0.99)
Tampa Bay	9	8.3 (1–13)	49 (9–127)	HH catfish	3	2.09 (0.72–4.64)	1.7 (0.25–4.42)
				Ga. catfish	2	4.0 (2.62–5.4)	2.24 (2.06–2.42)
				Sand seatrout	2	2.41 (2.21–2.61)	2.04 (1.6–2.47)
				Sand perch	2	0.47 (0.4–0.54)	0.39 (0.38–0.4)
				Pinfish	1	0.32	0.20
Charlotte Harbor	3	29 (7–43)	74 (30–120)	HH catfish	2	1.31 (1.12–1.5)	1.0 (1.0)
				Ga. catfish	3	1.7 (0.86–2.16)	1.49 (0.72–2.27)
				Brown shrimp	2	0.18 (0.16–0.19)	0.13 (0.12–0.14)
Florida Bay	30	12 (3–100)	82 (<1–318)	HH catfish	7	2.64 (1.79–3.9)	1.68 (1.46–1.8)
				Ga. catfish	1	3.13	1.64
				Sand perch	1	0.49	0.49
				Pinfish	1	1.06	0.9
				White grunt	7	0.39 (0.28–0.47)	0.39 (0.32–0.53)
				Lane snapper	4	0.83 (0.3–1.2)	0.86 (0.33–1.27)
Pine Island Sound	3	6.3 (4–9)	55 (41–68)	HH catfish	2	0.4 (0.34–0.45)	0.3 (0.18–0.41)
				Ga. catfish	2	0.96 (0.76–1.16)	0.92[c] (0.92)
				Pinfish	3	0.43 (0.41–0.46)	0.37 (0.27–0.43)
				Lane snapper	2	0.36 (0.35–0.36)	0.34 (0.29–0.38)
				Spot	1	0.33	0.26
				Pigfish	1	0.38	0.31
Whitewater Bay	1	69	<1	HH catfish	1	3.39	3.54
Hillsborough Channels	1	219	490	Ga. catfish	1	4.98	4.5
Boca Ciega Bay	2	10 (4–16)	52 (42–62)	HH catfish	2	0.86 (0.44–1.28)	0.84 (0.36–1.32)
				Ga. catfish	1	1.65	1.3
				Spot	1	0.11	0.06
Sarasota Bay	2	3.5 (2–5)	63 (10–16)	Pinfish	2	0.55 (0.46–0.63)	0.43 (0.32–0.53)
				Lane snapper	2	0.28 (0.22–0.34)	0.26 (0.19–0.32)
Turtle Bay	1	3	33			NA	NA
Caloosahatchee River	1	60	35	Ga. catfish	1	1.32	1.14
Matlacha Pass	1	3	183			NA	NA
Gordon River	1	174	230	Ga. catfish	1	10.1	2.0
				Spot	1	0.43	0.4
Chokoloskee Bay	1	6	175			NA	NA
Oyster Bay	1	19	28			NA	NA
Card Sound	1	13	12	HH catfish	1	2.12	2.0
Long Sound	1	33	62			NA	NA
Barnes Sound	1	21	172			NA	NA
Tarpon Basin	1	33	19			NA	NA

Table 1. *Continued*

	Sediment			Fish[a]			
Location	n	Total Mercury (ng/g)	Methyl Mercury (pg/g)	Species	n	Total Mercury (µg/g)	Methyl Mercury (µg/g)
Torchkey Mangroves	1	10	<1			NA	NA
Cudjoe Basin	1	11	41	White grunt	1	0.44	0.31
Garrison Bight	1	38	76			NA	NA

NA = Not analyzed; HH catfish = Hardhead catfish; Ga. catfish = Gafftopsail catfish
[a] Each analysis refers to pooled sample of five to 10 individuals
[b] Values in parentheses indicate the range of concentrations
[c] Only one sample was analyzed for methyl mercury

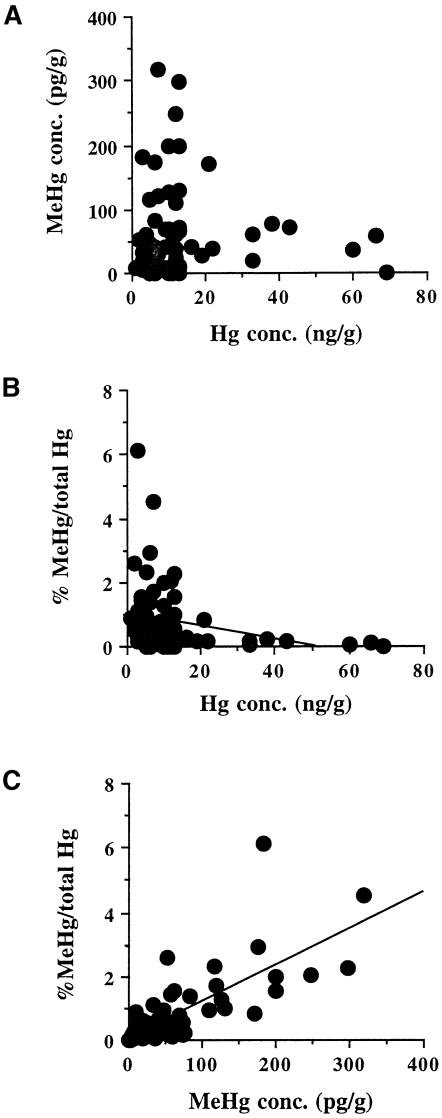

Fig. 2. Relation between the concentrations (dry wt basis) of total mercury and methyl mercury in sediments

bioturbation can oxidize HgS and thus remobilize a small percentage of HgS (Stein *et al.* 1996). The percentage of methyl mercury in total mercury concentrations in sediments varied between <0.01 and 6.1% (mean: 0.77%). Total mercury was negatively correlated ($r = -0.26$; $p = 0.05$) with percent methyl mercury (Figure 2B). In contrast, the ratio of methyl mercury to total mercury increased with its concentration in sediments ($r = 0.76$; $p < 0.05$) (Figure 2C).

Organic carbon and microbial activity in sediments play an important role in the bioavailability and methylation of inorganic mercury (Andersson *et al.* 1990). We examined the relation of mercury concentration in sediments to the corresponding organic carbon content and mud (silt + clay) content (Figure 3). While total mercury was significantly correlated with organic carbon ($r = 0.58$; $p < 0.05$) the relation of methyl mercury with organic carbon (OC) and mud content was weak. The observed correlation coefficients (''r'') were as follows: total mercury vs. OC = 0.58; total mercury vs. mud = 0.24; methyl mercury vs. OC = −0.08; methyl mercury vs. mud = −0.1; methyl mercury vs. OC = −0.22; methyl mercury vs. mud = −0.28. The proportion of methyl mercury in total mercury decreased with increasing organic carbon and mud content.

Mercury in Fish

Concentration of total mercury in fish muscle was in the range of 0.11–10.1 µg/g dry wt (mean: 1.41 µg/g) and methyl mercury ranged 0.06–4.5 µg/g dry wt (mean: 1.05 µg/g). Water content of fish muscle varied between 77% and 80%. On a wet-weight basis, total mercury and methyl mercury were 0.03–2.22 µg/g (mean: 0.31 µg/g) and 0.01–1.0 µg/g (mean: 0.23 µg/g), respectively. Total mercury concentrations in fish muscle from Florida estuaries were higher than the mean value for freshwater whole fish for the 1984–85 National Contaminant Biomonitoring Program, which was 0.1 µg/g wet wt (Schmitt and Brumbaugh 1990), but close to the national mean concentration for the whole fish of 0.26 µg/g wet wt collected in 1990 (Bahnick *et al.* 1994).

Several studies have shown that mercury concentrations in fish generally tend to increase with age, and therefore size, owing to methyl mercury accumulation with increasing exposure time (e.g., Windom and Kendall 1979; Jackson 1990). Since the samples of fish muscle analyzed in this study were from pooled samples of several individuals, these relationships were not examined. Fish size is an important factor for methyl mercury concentrations, but the distinct concentrations of mercury observed between sampling locations are probably due

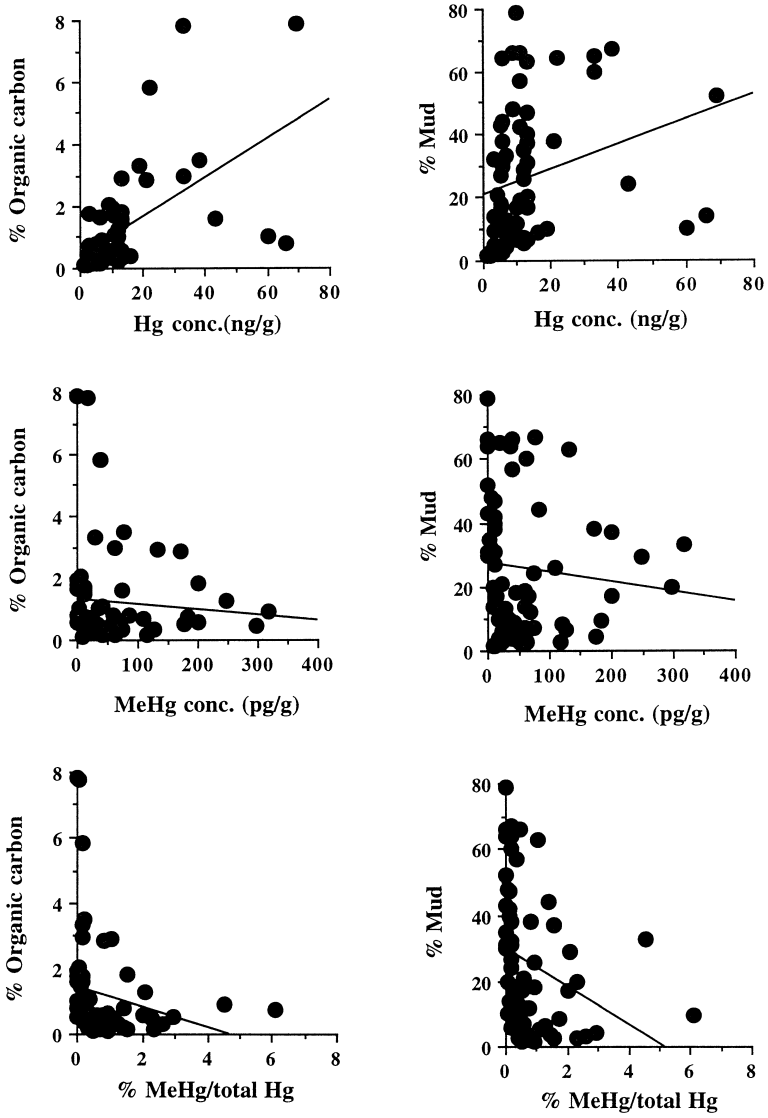

Fig. 3. Relation of sediment organic carbon (OC) and mud (silt + clay) content with the concentrations (dry wt basis) of total mercury and methyl mercury

to differing amounts of mercury inputs. Total mercury concentrations were highest in catfish collected from the Gordon River (10.1 µg/g dry wt) followed by those from Hillsborough Channels, Tampa Bay, and Florida Bay, which may suggest the presence of local inputs. These results are consistent with those observed in sediments from the same locations. Both total and methyl mercury concentrations were above 1 µg/g dry wt in catfish collected from most locations including Biscayne Bay, Charlotte Harbor, Whitewater Bay, Caloosahatchee River, and Card Sound. Among the different fishes analyzed, higher concentrations of mercury were encountered in hardhead catfish, gafftopsail catfish, and sand seatrout while brown shrimp had the lowest (Table 2). In fish, the percent of methyl mercury to total mercury varied between 45% and 124% (mean: 83%) with the exception of a catfish collected from the Gordon River that had only 20% of its mercury as methyl mercury. Reasons for unusually lower percentage of methyl mercury in Gordon River catfish is not clear. However, factors such as age, sex, and feeding habit of fish may influence such ratios. Juvenile fish that spent more time near mercury-contaminated sediments had low methyl mercury ratio (Lasorsa and Allen-Gil 1995). In contrast to sediments, total mercury concentration in fish muscle was directly proportional to methyl mercury concentrations ($r = 0.91$; $p < 0.05$) in agreement with earlier studies (Grieb *et al.* 1990; Kim 1995). Similar to sediments, total mercury concentrations in fish were negatively, but weakly correlated ($r = -0.24$; $p < 0.1$) with the percentage of methyl mercury (Figure 4B). Similar observations were made in mussels from Adriatic coastal waters (Mikac *et al.* 1985). The proportion of methyl mercury in total mercury was weakly correlated with methyl mercury concentrations in fish ($r = 0.07$; $p > 0.05$) (Figure 4C).

The relationships between mercury concentrations in fish and sediments collected from corresponding locations were examined. The concentrations of total mercury in sediments were positively correlated with those in fish ($r = 0.52$; $p < 0.05$). Similarly, total mercury in sediments were related to fish methyl mercury concentrations ($r = 0.42$; $p < 0.05$) (Figure 5A–C). Furthermore, sediment methyl mercury concentrations were correlated with those in fish ($r = 0.33$; $p < 0.05$). Mikac *et al.* (1985) showed a linear relationship between total mercury and methyl mercury concentrations in mussels and sediments from

Table 2. Concentrations of total mercury and methyl mercury (µg/g dry wt) in muscle tissue of different species of fishes collected from coastal waters of southern Florida

Species	n	Total Mercury (µg/g)	Methyl Mercury (µg/g)
Hardhead catfish	19	1.94 (0.44–4.64)	1.54 (0.18–4.42)
Gafftopsail catfish	12	3.0 (0.76–10.1)	1.86 (0.72–4.5)
Sand seatrout	2	2.41 (2.21–2.61)	2.04 (1.6–2.47)
Sand seaperch	3	0.48 (0.4–0.54)	0.42 (0.4–0.49)
Pinfish	7	0.54 (0.32–1.06)	0.44 (0.2–0.9)
White grunt	10	0.49 (0.28–1.03)	0.49 (0.31–0.99)
Lane snapper	8	0.57 (0.22–1.03)	0.58 (0.19–1.27)
Spot	3	0.29 (0.11–0.43)	0.24 (0.06–0.4)
Pigfish	1	0.38	0.31
Brown shrimp	2	0.18 (0.16–0.19)	0.13 (0.12–0.14)

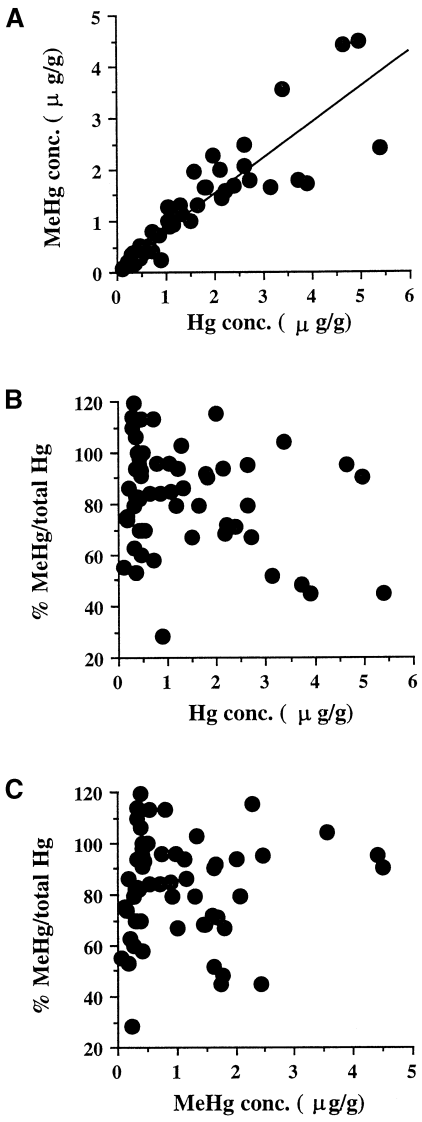

Fig. 4. Relation between the concentrations (dry wt basis) of total mercury and methyl mercury in fish muscle

the Adriatic coast. In this study, when methyl mercury concentrations in individual fish species were plotted against corresponding sediment concentrations, hardhead catfish did not exhibit a positive relationship, suggesting that several factors (such as the differences in the mobility of species) may influence such relationships (Francesconi and Lenanton 1992). The correlation between the mercury content in fish and coastal sediments, also observed in freshwater systems in Ontario (Johnson 1987), Wisconsin (Cope *et al.* 1990), Sweden (Håkanson *et al.* 1988), and Norway (Fjeld and Rognerud 1993), is not easily explained. The relationship between mercury concentrations of fish and sediments vary as a function of factors that affect sediment methylation rates and mercury bioavailability. A few studies showed that total mercury in sediments from unstratified lakes did not significantly correlate with fish mercury concentrations (Sorensen *et al.* 1990) due to the variability in methyl mercury production rates in sediments as a result of a variety of factors (such as organic carbon, amount of mercury occurring as sulfides, aerobic or anaerobic conditions, or methylation of mercury in water column). The bioavailability of sedimentary mercury in coastal sediments has been evaluated, although some studies have shown that sediments can be a sink for mercury (Rudd and Turner 1983; Sorensen *et al.* 1990). Mercury accumulation by fish depends on the combined effect of the abundance of available inorganic mercury in sediments/water column, trophic interaction and the rate at which microflora transforms mercury into methyl mercury in addition to the species-specific accumulation and seasonal variations (Jackson 1990).

Mercury in Water

The concentrations of total mercury and methyl mercury in filtered water samples collected from canals and creeks that flow into Florida Bay were 3–7.4 ng/L (mean: 4.6 ng/L) and <0.002–2.3 ng/L (mean: 0.474 ng/L), respectively (Table 3). While total mercury levels varied little in all these streams, methyl mercury levels varied considerably among locations. Shell Creek, Trout Creek, and water from the culvert that controlled the canal C111 flow had methyl mercury concentrations greater than 1 ng/L, accounting for more than 35% of the total mercury concentrations. Generally, total mercury and methyl concentrations tended to be higher in near-surface than in near-bottom waters of canal C111. Methyl mercury concentrations varied considerably for the 2- and 4-h samples collected at the same location (Table 3); these swings may be related to tidal dynamics. The catchments of these streams are intensively cultivated agricultural areas, which may result in the transport of humic substances and methyl mercury from the drainage area. Concentrations of total mercury in canals and creeks were within the range of 2 to 15 ng/L reported for coastal estuarine waters (Schroeder 1989; Stein *et al.* 1996). The mercury concentrations in Florida waters were higher than in open ocean

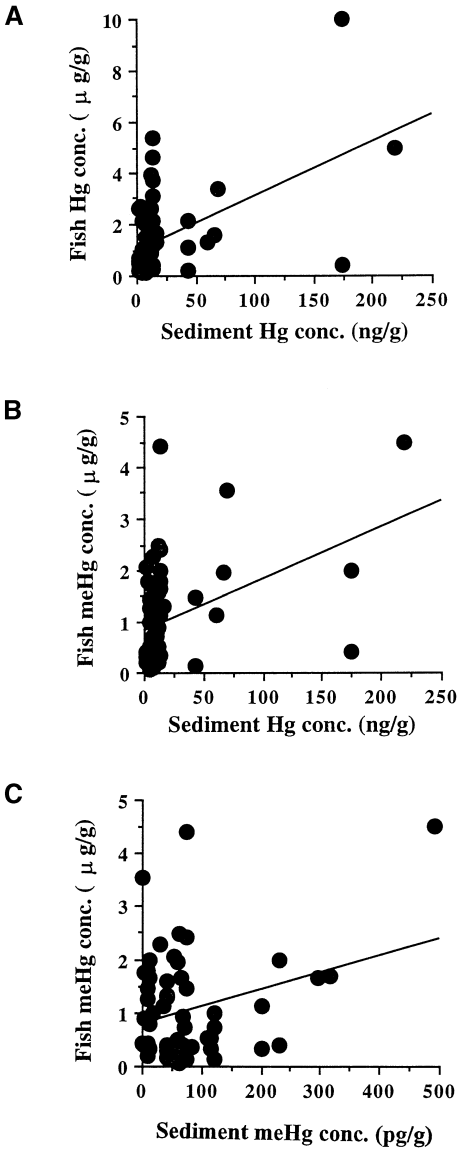

Fig. 5. Relation of sediment mercury concentrations (dry wt basis) with those of fish

waters of the North Atlantic and Pacific Oceans (Fitzgerald and Clarkson 1991; Mason *et al.* 1995), but comparable to those reported for the Baltic and North Seas (Coquery and Cossa 1995; Schmidt 1992). The U.S. EPA mercury water quality criterion for protection of freshwater is 12 ng Hg/L, and for seawater it is 100 ng/L (US EPA 1985). The water quality criterion for mercury proposed for Minnesota's freshwater is 7 ng/L while a value of 2 ng/L has been established for Wisconsin waters (Glass *et al.* 1990). The mercury concentrations found in this study were below the U.S. EPA tolerance limit, but close to or higher than those established in Minnesota and Wisconsin.

Methyl mercury accounted for <0.03–52% (mean: 10.4%) of the total mercury in estuarine waters from our study area. In coastal waters of Qatar, methyl mercury was 5% of total mercury (Al-Madfa *et al.* 1994). In freshwater areas (Gill and Bruland 1990) the proportion of methyl mercury was variable but generally higher, with an average of 25% and ranged up to 80%. Methyl mercury accounted for 6–13% of the total dissolved mercury in inland surface waters from Sweden (Lee and Hultberg 1990). In anoxic lake water, the percentage of methyl mercury was as high as 58% of the total mercury (Gilmour and Henry 1991). In open ocean surface waters (Mason and Fitzgerald 1991), reactive mercury was the dominant species (>80%) and the composition of methyl mercury was low. The wide range of methyl mercury proportions in water depends on several variables such as acidity, dissolved organic carbon, sulfate, and hydrological and geochemical factors (Gilmour and Henry 1991). It should be noted that the percentage of methyl mercury in water was higher than in Florida coast sediments.

Allowable Consumption Estimates

Presence of high concentrations of mercury in fish is of concern because the predominant exposure pathway for humans is consumption of fish. The United States Food and Drug Administration (FDA) has set the action level for mercury in fish at 1 μg/g wet wt. Some states have issued health advisories for eating mercury-contaminated fish. For example, Minnesota and Wisconsin have health advisories of 0.16 and 0.5 μg/g wet wt, respectively (Glass *et al.* 1990). The Florida Department of Health and Rehabilitative Services and the Department of Environmental Protection have advisories on the consumption of gafftopsail catfish, crevalle jack, spotted seatrout, ladyfish, spanish mackerel, and shark. The maximum consumption limits set forth were 14 g/month for adults and 3.5 g/month for pregnant women and children. In addition to the abovementioned fish species, the presence of noticeable concentrations of mercury in hardhead catfish deserves attention.

Noncarcinogenic health effects may be estimated using a reference dose value (RfD) of 3×10^{-4} mg/kg/day (US EPA 1989a). The RfD is an estimated single daily chemical intake rate that appears to be without risk if ingested over a lifetime. The estimated dose (D) can be calculated as $D = C \times I/W \times 1000$ where C = concentration of mercury in fish (μg/g wet wt), I = ingestion rate of fish (g/day), W = average body weight (70 kg). The hazard index (H) for the chemical is the ratio of the dose (D) to the upper level of daily chemical intake over a lifetime estimated to be without toxic effects (*i.e.*, RfD). If the H value is less than 1, toxic effects are not expected to occur. The H can be calculated as a function of ingestion rate and concentration of mercury in fish. Three ingestion rates were chosen to represent average consumption rates of fish by the general U.S. population (6.5 g/day), sport fisherman (30 g/day), and 95 percentile of sport fishermen (140 g/day) (US EPA 1989b). The H values were calculated for ingestion of fish containing the highest (2.22 μg/g wet wt) and mean (0.31 μg/g wet wt) mercury levels for fish from Florida coastal waters (Table 4). The results showed that steady consumption of fish at the highest mercury concentration found in this study is hazardous at the 140 and 30 g/day ingestion rates. Consumption of mercury contaminated fish containing 0.31 μg/g wet wt, the mean mercury concentration found in this study, is hazardous to human health at a consumption rate of 70 g/day, which would reach an H value of unity.

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Table 3. Concentrations of total mercury and methyl mercury in water collected from canals and creeks discharging into Florida Bay

Location	Time[a] (h)	Depth	pH	Salinity (‰)	DO (mg/L)	Methyl Mercury (ng/L)	Total Mercury (ng/L)	Methyl/Total Mercury (%)
Canal C111 east	2	s	NA	NA	NA	0.0098	5.6	0.18
Canal C111 east	4	s	NA	NA	NA	0.24	4.2	5.70
Canal C111 east	2	b	NA	NA	NA	<0.002	6.3	<0.03
Canal C111 east	4	b	NA	NA	NA	0.015	3.4	0.44
Canal C111 west	2	s	7.3	20	2.0	0.003	5.5	0.05
Canal C111 west	4	s	7.3	20	2.0	0.066	4.0	1.65
Canal C111 west	2	b	7.5	25.3	0.7	0.064	3.9	1.64
Canal C111 west	4	b	7.5	25.3	0.7	0.020	3.0	0.67
Canal C111 culvert	2	s	NA	NA	NA	1.5	4.1	37
Shell Creek	2	s	8.0	23.3	6.1	1.9	4.9	39
Shell Creek	4	s	8.0	23.3	6.1	0.017	7.4	0.23
Trout Creek	2	s	8.1	12.1	7.1	0.385	4.1	9.4
Trout Creek	4	s	8.1	12.1	7.1	2.3	4.4	52
Taylor River	2	s	7.5	10.3	3.7	0.113	3.7	3.1

s = near surface; b = near bottom; NA = data not available
[a] Time refers to samples taken at 2 and 4 h after the deployment of current meter

Table 4. Hazard index for ingestion of fish contaminated with mercury

Ingestion Rate (g/day)	Hazard Index (H) Based on Highest Hg Conc. (2.22 µg/g wet wt)	Hazard Index (H) Based on Mean Hg Conc. (0.31 µg/g wet wt)
6.5	0.69	0.10
30	3.17	0.44
140	14.8	2.07

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