

System controls on the aqueous distribution of mercury in the northern Florida Everglades

JAMES P. HURLEY^{1,2,*}, DAVID P. KRABBENHOFT³,
LISA B. CLECKNER², MARK L. OLSON³, GEORGE R. AIKEN⁴ &
PETER S. RAWLIK JR⁵

¹Bureau of Integrated Science Services, Wisconsin Department of Natural Resources, 1350 Femrite Dr., Monona, WI 53176, U.S.A.; ²Water Chemistry Program, University of Wisconsin, 660 North Park St., Madison, WI 53706, U.S.A.; ³U.S. Geological Survey, 6417 Normandy Lane, Madison, WI 53719, U.S.A.; ⁴U.S. Geological Survey, 3215 Marine St., Boulder, CO 80303, U.S.A.; ⁵South Florida Water Management District, 3301 Gun Club Rd., West Palm Beach, FL 33406, U.S.A. (* corresponding author: Phone: 608-262-3979; Fax: 608-262-0454; Email: hurley@engr.wisc.edu)

Key words: aqueous mercury species, bioaccumulation, methyl mercury, marshes, wetland systems

Abstract. The forms and partitioning of aqueous mercury species in the canals and marshes of the Northern Florida Everglades exhibit strong spatial and temporal variability. In canals feeding Water Conservation Area (WCA) 2A, unfiltered total Hg (HgT_U) is less than 3 ng L^{-1} and relatively constant. In contrast, methyl mercury (MeHg) exhibited a strong seasonal pattern, with highest levels entering WCA-2A marshes during July. Stagnation and reduced flows also lead to particle enrichment of MeHg. In the marshes of WCA-2A, 2B and 3A, HgT_U is usually $<5 \text{ ng L}^{-1}$ with no consistent north–south patterns. However, for individual dates, aqueous unfiltered MeHg (MeHg_U) levels increase from north to south with generally lowest levels in the eutrophied regions of northern WCA-2A. A strong relationship between filtered Hg species and dissolved organic carbon (DOC), evident for rivers draining wetlands in Wisconsin, was not apparent in the Everglades, suggesting either differences in the binding sites of DOC between the two regions, or non-organic Hg complexation in the Everglades.

Introduction

Mercury cycling in wetland systems has recently been the focus of several studies due to observations that production of bioaccumulative monomethyl mercury (MeHg) appears to be favored in wetlands relative to other land use/land cover patterns (St. Louis et al. 1994, 1996; Hurley et al. 1995; Krabbenhoft et al. 1995; Rudd 1995; Branfireun et al. 1996). The processes which lead to the formation of MeHg in wetlands are not fully understood (Zillioux et al. 1993), but similar formation processes, observed in lacustrine and oceanic systems (Winfrey & Rudd 1990; Gilmour et al. 1991), may be influencing MeHg formation in wetland systems.

In 1995, the U.S. Geological Survey, in cooperation with several state, federal and private agencies, initiated the project Aquatic Cycling of Mercury in the Everglades (ACME) to evaluate Hg cycling processes (Krabbenhoft 1996). Anthropogenic activities have affected hydrology, nutrient status and the quality of atmospheric deposition in the Everglades. In the late 1980s, an analysis of game fish from across Florida (Ware et al. 1990) revealed elevated levels of Hg in fish statewide, with some of the highest levels ($> 1.5 \mu\text{g g}^{-1}$) in the Everglades. In response, a fish consumption advisory was issued for almost the entire Everglades system (Lambou et al. 1991). The ACME project, in turn, was designed to evaluate the factors responsible for Hg bioaccumulation in this unique ecosystem.

The specific goals of the ACME project are to evaluate fluxes, rates and factors affecting Hg transport through the Everglades wetland system. The project has two phases which run simultaneously. The first phase evaluates seasonal distributions of Hg species in the aqueous phase at fixed canal and marsh sites in the northern Everglades. Our sampling frequency precludes a detailed analysis of seasonal cycling at a given site, however, data from water column sampling at these sites aids in identifying contrasting sites for detailed process-level studies, the second and concurrent phase of the study. More detailed discussions of process-level studies of diel cycling, sedimentary methylation and biotic transfer are given elsewhere in this volume (Krabbenhoft et al. 1997 in this issue; Gilmour et al. 1997 in this issue; Cleckner et al. 1997 in this issue). Here, we discuss the general distributional patterns of aqueous Hg at our study sites in canals and marshes during 1995. Our initial goals were to evaluate the forms and species of Hg entering Water Conservation Area 2A (WCA-2A) from canal inputs and to identify trends in Hg distribution across the eutrophication gradient in WCA-2A. We further compare the eutrophied northern canal system to a less-impacted southern canal system. Finally, we evaluate aqueous Hg dynamics in the marsh system by comparing nutrient-impacted to unimpacted sites (including sites in WCA 2B and WCA-3A). The relationship of Hg with dissolved organic carbon of this subtropical wetland to that of a northern temperate wetland system is also examined.

Site description

Sampling sites and methodologies used during 1995 evolved to answer specific research questions. Initial sampling in March 1995 was focused primarily on the canals and marshes of WCA-2A and southern canals entering the Everglades National Park. Our research further expanded during summer and winter 1995 to include sites in WCA-2B and WCA-3A (Figure 1). Stage

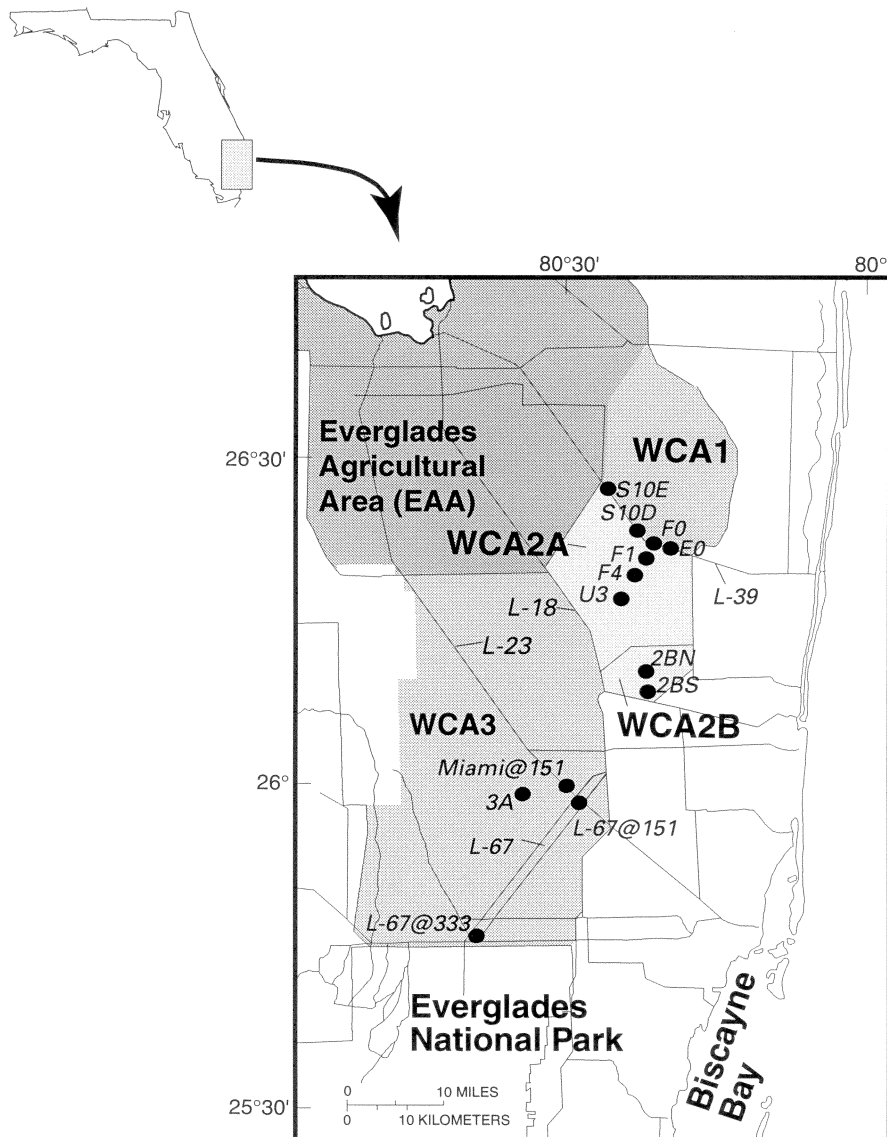


Figure 1. Site locations in the Florida Everglades. WCA 2A = Loxahatchee National Wildlife Refuge. L39 = Hillsboro Canal.

height during the study period in WCA-2A is shown in Figure 2 and indicates that March 1995 was an abnormally high water level month relative to a long-term mean.

Water Conservation Area 2A is a 547 km² diked marsh in the northern portion of the remnant Everglades. Nearly 60% of the inflow water to WCA-

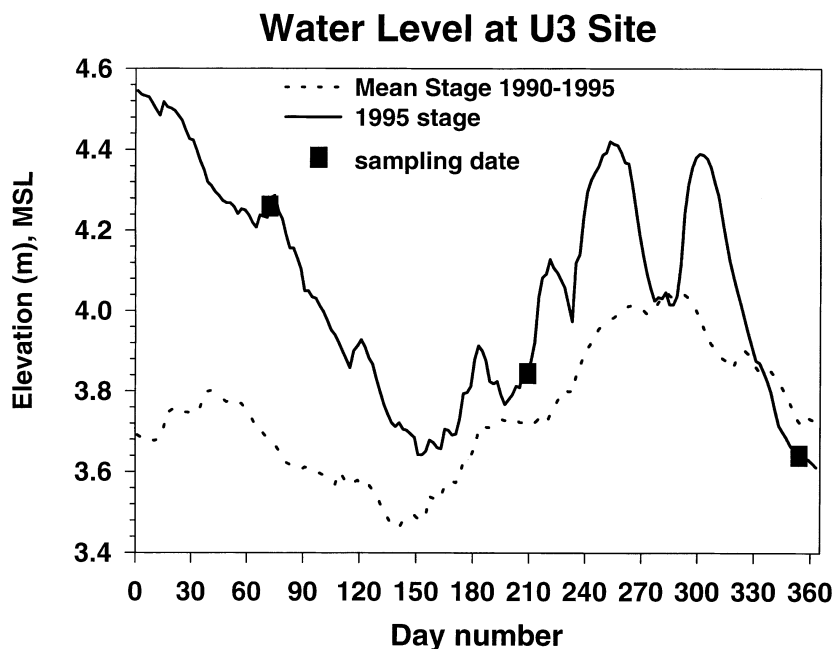


Figure 2. Water level in the WCA-2A marsh, as measured by stage at Site U3.

2A is derived from the Everglades Agricultural Area (EAA), a 2900 km² region of farmland. As a result, water in the upper Hillsboro Canal (L-39 on Figure 1) is enriched in phosphorus and other nutrients (SFWMD 1992; Table 1). Sites S10-E and S10-D are located on the Hillsboro Canal. Site S10-E is located approximately 500 m downstream of pump station S6. Flow rates at S10-D are somewhat higher due to the additional inputs of water from WCA-1, the Loxahatchee National Wildlife Refuge. Canal water is discharged into WCA-2A from a distribution canal, which receives water from the S-10 control structures located along the northern perimeter levee at the Hillsboro Canal. Site F0 is located near the western end of the distribution canal, north of site F1 in the marsh (Figure 1). Flow in the distribution canal is generally slower than in the Hillsboro Canal and is dependent upon the volume delivered through floodgates. Site E0 is located approximately 4 km downstream of F0. The E0 site was chosen to evaluate the effects of reduced flows on Hg partitioning in this nutrient-rich canal (Table 1).

Water discharged to the WCA-2A marsh creates a strong north-south water quality gradient with associated ecological changes (Belanger et al. 1989; Richardson et al. 1991; Koch & Reddy 1992; DeBusk et al. 1994). The most visible change has been the invasion and spread of cattail (*Typha domingensis* Pers.) that over the past two decades has replaced sawgrass

Table 1. Site location, water source and water chemistry characteristics of canal sites. All values mg L⁻¹ except specific conductivity ($\mu\text{S cm}^{-1}$). Data for conductivity and sulfate from ACME project database. Nutrient data for longer term from SFWMD (P. Rawlik, unpublished data).

Site	Location	Water source	ACME data		Long term data, SFWMD			
			Cond.	Filt.	Unfilt.	Filt.	(NO ₃ + NO ₂)-N	Filt. NH ₃ -N
				SO ₄	P			
S10E	26°28' N, 80°26' W	EAA	1030	74.7	0.079	0.425		0.255
S10D	26°23' N, 80°22' W	S10-E,WCA-1	1230	98.5	NA	NA		NA
F0	26°25' N, 80°22' W	S10 canal	976	64.3	0.116	0.550		0.317
E0	26°22' N, 80°21' W	S10 canal	945	NA	0.104	0.306		0.179
L67@151	26°00' N, 80°30' W	WCA-2,WCA-3	676	25.0	0.012	0.088		0.064
L67@333	25°45' N, 80°40' W	WCA-2,WCA-3	639	23.1	NA	NA		NA

(*Cladium jamaicense*) as the dominant species in the northern region of WCA-2A (Jensen et al. 1995). Table 2 summarizes the water quality characteristics of the marsh sites.

Water Conservation Area 2B is a 96 km² diked marsh situated south of WCA-2A. WCA-2B sits directly above the Hillsboro Aquifer and historically served as a recharge site of groundwater. Underlying sediments in this area are relatively conductive and, in an attempt to obtain hydrologic control, was separated from WCA-2A by the construction of the L-35B Levee in 1961. Unlike WCA-2A, rainfall provides nearly all of the external source of water for this area (SFWMD 1992). Two sites in WCA-2B were added in July, 1995 (2B-N and 2B-S; Figure 1, Table 2).

Water Conservation Area 3A is a 2,370 km² diked marsh southwest of WCA-2A. Rainfall accounts for over 59% of all water inputs into the area. Other surface water inputs include: WCA-2A through the S-11 structures, the EAA through S-8 pump and L-3 canal, stormwater runoff through S-9, drainage from Big Cypress National Preserve and other western lands, and the North New River Canal. Site 3A-15 was added as an ACME project site in December 1995, in response to recent evidence that suggests elevated Hg levels in the mosquitofish (*Gambusia* sp.) in this region relative to other regions in the Everglades (Stober & Jones 1996).

Southern canal sampling sites are located on the L-67 canal (Figure 1). These sites were incorporated to evaluate the forms of Hg entering the ENP via overland flow and serve as a comparison to the eutrophied Hillsboro-distribution system. Site L67@S151 is at the northern end of the L67 canal, at the intersection of the Miami Canal (L-23 on Figure 1). During July 1995, we also sampled in the Miami Canal at a time when water was not flowing in the Miami Canal, yet was flowing strongly in the L67 Canal. Site L67@S333 is located at the southern terminus of the L67 Canal at the Tamiami Trail. The ENP lies south of the Tamiami Trail and receives water directly from the L67 Canal.

Methodologies

Hg sampling

At each site, strict low-level trace metal clean techniques (Patterson & Settle 1976; Fitzgerald & Watras 1989; Olson et al. 1997) were used during sample collection, preservation and storage. During the initial sampling in March and July 1995, Hg samples were collected using an all-Teflon [any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government] weight that attached to Teflon

Table 2. Site location, water source and water chemistry characteristics of marsh sites. All values mg L⁻¹ except specific conductivity (μ S cm⁻¹). Data for conductivity and sulfate from ACME project database for dates discussed in text. Nutrient data for longer term from SFWMD (P. Rawlik, unpublished data).

Site	Location	Water source	Vegetation*	Calcareous periphyton types [®]	ACME data			Long term data, SFWMD		
					Cond.	Filt.	SO ₄	Unfilt.	Filt.	Filt
F1	26°22' N, 80°22' W	Canals, rainfall	Cattail (70%) Open water (25%) Sawgrass (<5%)	No	1078	53.1	0.186	0.024		0.086
F4	26°19' N, 80°23' W	Canals, rainfall	Cattail (70%) Open water (25%) Sawgrass (<5%)	No	790	48.1	0.022	0.090		0.024
U3	26°17' N, 80°25' W	Canals, rainfall	Cattail (70%) Open water (25%) Sawgrass (<5%)	Yes	973	50.9	0.009	0.064		0.029
2B-N	26°12' N, 80°22' W	Rainfall	Sawgrass Open water	Yes	711	12.0	NA	NA		NA
2B-S	26°10' N, 80°22' W	Rainfall	Sawgrass Open water	Yes	592	33.4	0.023	0.028		NA
3A	25°58' N, 80°40' W	Canals, rainfall	Sawgrass Cattail Open water	Yes	493	11.7	0.018	0.008		NA

* Data from Maio and Sklar (1997) for F1, F4, U3. Vegetation in WCA-2B and WCA-3A based on observations during December, 1995, without direct measurements.

[®] Data from McCormick et al. (1996) for F1, F4, U3. Algal composition from WCA-2B and WCA-3A determined from HPLC pigment analyses (this study).

FEP tubing and a Geotech pumping system equipped with pre-cleaned C-Flex pumphead tubing. We excluded particles by using a 0.45 μm Calyx filter capsule (particulate phase was calculated by difference from unfiltered and filtered samples). After that date, we modified our sampling approach to obtaining 5 L grab samples in the field and filtering in the laboratory under a HEPA filtered hood. We filtered samples through a 0.45 μm Millipore HAWP filter using a desiccator vacuum system (Rossman & Barres 1988). Additional particulate matter samples were collected on pre-combusted quartz fiber filters (QFF). Samples for HgT and HgR (500 ml) were preserved in the field with 10 and 1 ml of 6N HCl, respectively. Methyl Hg samples were frozen after collection.

Teflon filter holders and filters were pre-soaked in a 5% HCl solution and pre-rinsed with 0.5 L of Milli-Q water prior to filtration. Calyx filter capsules were cleaned using a two-step leaching procedure. Each capsule was soaked for at least two days in 2N HNO_3 , rinsed and soaked for several days in 4N HCl. Filters were stored in Milli-Q water until use. Samples were collected after two liters of water purged through the capsule (about 8 volumes). Filter blanks based on passing Milli-Q water through the capsules averaged $0.1 \pm 0.1 \text{ ng L}^{-1}$ of HgT.

Laboratory methods

Samples for low level (picogram) HgT (unfiltered HgT, HgT_U , and filtered HgT, HgT_F) were oxidized with BrCl , reduced with SnCl_2 and analyzed by the two-stage gold amalgamation technique using a cold vapor atomic fluorescence detection system (CVAFS) (Fitzgerald & Gill 1979; Bloom & Crecelius 1983; Bloom & Fitzgerald 1988). The instrument detection limit for HgT, based on SnCl_2 blanks was 0.03 ng L^{-1} . The method detection limit for HgT, based on filter, BrCl and bubbler blanks was 0.1 ng L^{-1} . All HgT samples were analyzed in duplicate. To meet a QA objective, the relative difference (RPD) must be within 10%. If the RPD was greater than 10%, the sample was analyzed a third time and the result reported with a relative standard deviation (RSD). Less than 10% of all Everglades samples required triplicate analysis. In cases where HgT and MeHg filtered and unfiltered concentrations were $< 0.2 \text{ ng L}^{-1}$, we measured the particulate fraction by direct analysis of QFF or HAWP filters, when available. Samples for monomethyl mercury (MeHg) were distilled prior to analysis to separate MeHg from interferences (Olson et al. 1997). Methyl Hg was determined by aqueous-phase ethylation, isothermal GC separation, followed by pyrolysis to Hg° and detection by CVAFS (Horvat et al. 1993; Liang et al. 1993). An overall detection limit for the MeHg method was 0.026 ng L^{-1} (3σ of the mean distillation blank). Mean RPD for unfiltered and filtered MeHg (MeHg_U

and MeHg_F, respectively) was 13.5% and 11.9%, respectively. Reactive Hg (Hg_R) was analyzed similarly to Hg_T, but without further oxidation than field acidification, and within 2 days of collection. The detection limit during the study was 0.03 ng L⁻¹. And the resulting RPD for duplicates was higher (20.9%) than our MeHg and Hg_T errors. This was due to the fact that samples were unfiltered and at low levels. Details of the dissolved gaseous Hg (DGM) analyses are given in Krabbenhoft et al. (this volume). Blanks were carried through all phases of Hg sampling and analysis (Olson et al. 1997).

Suspended Particulate Matter (SPM) was determined by filtering a known aliquot of water (usually 100 ml) through a pre-weighed 0.4 μm, 47 mm (diam.) polycarbonate track-etched filter (Poretics #13028). Dissolved Organic Carbon (DOC) samples were filtered through Whatman GF/F filters (nominal pore size 0.7 μm) in an all-glass filtration unit. Carbon was determined on an OI Model 700 Carbon Analyzer. Chlorophyll *a* (chl *a*) samples were collected on 0.4 μm nylon (Alltech) filter, extracted with 90% acetone and quantified using a high performance liquid chromatographic technique (Van Heukelum et al. 1994; Hurley & Watras 1991).

Results and discussion

Canals

Particle and Hg dynamics in the Hillsboro and Distribution Canals give interesting insight into processes regulating delivery of riverine Hg to the marsh of WCA-2A. During each sampling period, SPM levels were highest at the S-10E site (Figure 3) and chl *a* levels were higher in the distribution canal than in the Hillsboro Canal. These observations define a trend in particle dynamics for the system, as nutrient-rich waters from the EAA are pumped through station S6 into the Hillsboro Canal. As flows decrease and the Hillsboro Canal is opened to WCA-1, particles, presumably soil-derived, settle from the system. Water from EAA and additional water from WCA-1 flows easterly, with a portion diverted to the distribution canal and into the marsh of WCA-2A. Once this nutrient rich water allows for planktonic production in the distribution canal, biotic particles become more dominant, as seen in chl *a* distribution in Figure 2B. During this transition from soil-dominated to planktonic particles, particulate Hg_T, associated with soil-derived particles, settles from the water column (Figure 3C). As a source of water for WCA-2A, Hg_{TU} only varied by less than a factor of 2 for the three sampling events. In contrast to Hg_{TU}, MeHg_U increases along the canal flow path (Figure 3D). The increase in MeHg_U is generally associated with particulates, however, the 5-fold increase in MeHg_U in the distribution canal in July is asso-

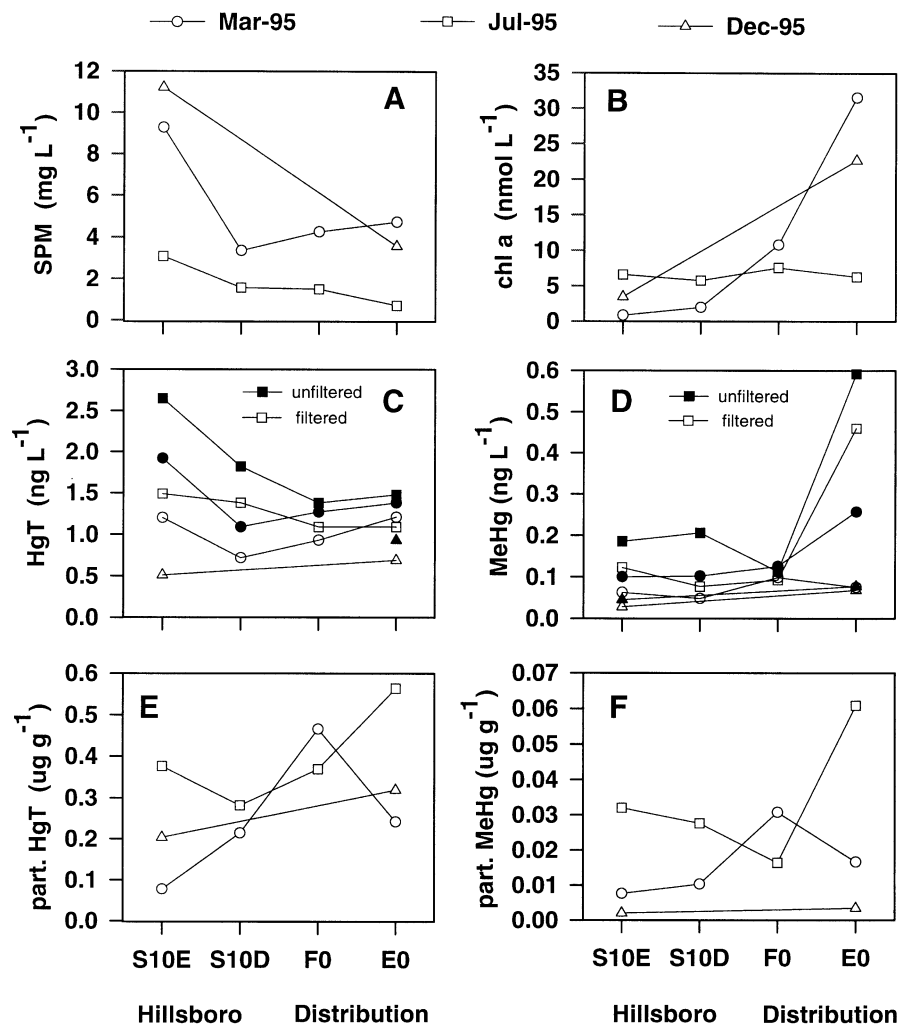


Figure 3. Suspended particulate matter (SPM), chlorophyll *a*, and aqueous Hg species in canals leading to Water Conservation Area 2A marshes.

ciated with an increase in the filtered phase. These results suggest strong seasonal differences and biotic influences on partitioning and phase distribution in the canal-derived water flowing into the marshes of WCA-2A.

Transport of water through the canal system entering the marsh of WCA-2A additionally leads to particle enrichment of Hg_T and MeHg. Particles leaving the EAA (Site S10-E) are in the range of $75\text{--}380 \text{ ng g}^{-1}$ (Figure 3E), which is of a comparable magnitude to those observed by Patrick et al. (1994) for EAA soils. Although soil particles are preferentially removed, par-

ticle Hg_T content remains high (200–600 ng g^{-1}) in the plankton-dominated particulates. With the exception of the July sample from F0, MeHg particle content increases along the flow path (Figure 3F). Log K_d (conc. on particles/conc. in water; L kg^{-1}) ranged from 4.8 to 5.7 for Hg_T and 4.7 to 5.5 for MeHg. Our results for the Hillsboro-distribution system clearly demonstrate that canal Hg dynamics exhibit strong influences on aqueous Hg levels and particle enrichment as one progresses into WCA-2A.

A further example of the effects of reduced canal flow was observed in the region of the less eutrophic L67 Canal during July, 1995. At this time, water was flowing rapidly through L67, in response to high water levels in the marshes from recent precipitation. In contrast, the Miami Canal (L23), which intersects the L67 canal, was stagnant. In addition to our routine sites, L67@S151 and L67@S333, we sampled in the Miami Canal about 500m upstream (west) of the confluence with L67. Figure 4 shows that SPM levels were comparable among the three sites, but that chlorophyll *a* levels were higher in the stagnant Miami Canal. Both unfiltered $\text{Hg}_\text{T}_\text{U}$ and MeHg_U were elevated in the Miami Canal relative to L67. Major differences in the two canals were also observed in particle Hg content. While Hg_T decreased in the Miami Canal, MeHg particle content increased about threefold in the Miami Canal over the L67 Canal. Although these particulate Hg_T and MeHg levels were generally lower and may have been of different origin than those observed in the Hillsboro-distribution system, they reveal a similar process of enrichment of MeHg in suspended particles during canal stagnation.

Marshes

A direct comparison of Hg dynamics and particle enrichment, with respect to a flowpath, cannot be assessed in marshes. Although sheetflow exists in a north to south direction across WCA-2A, sites are not directly connected, as they are in the canals leading to WCA-2A. The sites do, however, span a strong nutrient gradient (Table 2). In addition to sampling the water column at each marsh site, we also sample bottom sediments and periphyton. Periphyton is a major component of the algal biomass at most of our sites and exerts a strong influence on Hg cycling, in the marsh, and the results are given elsewhere (Cleckner et al. 1997). Sedimentary results are discussed by Gilmour et al. (1997). We restrict our discussion here to aqueous phase dynamics of open water areas of each marsh site.

Suspended particulate matter (SPM) levels ranged from 0.7–6.3 ng L^{-1} across the WCA-2A transect (F1, F4, U3) with no strong seasonal trends (Figure 5A). Chlorophyll *a* distribution in the water column (Figure 5B), however, reflects the difference in the degree of eutrophy among sites in WCA-2A as site F1 exhibits consistently higher levels than sites F4 and U3

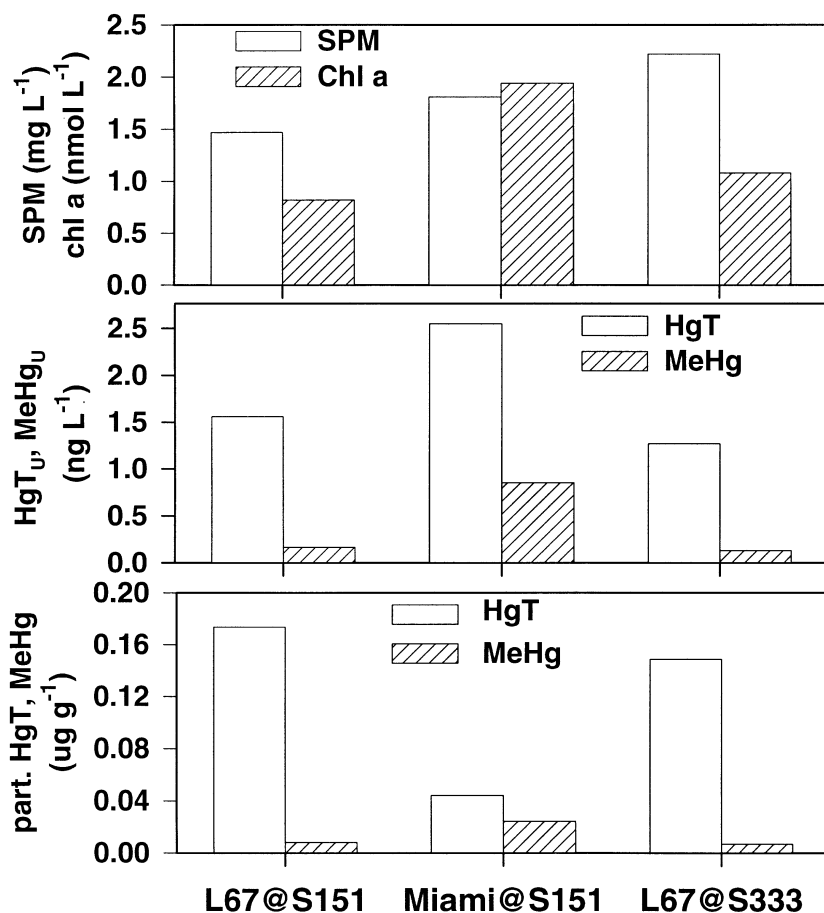


Figure 4. Suspended particulate matter (SPM), chlorophyll *a*, and aqueous Hg species in the Miami (L-23) and L-67 canals. Note that the Miami Canal flows were stagnant during this sampling period.

for a given date. The elevated level of chl *a* at WCA-3A in December was not due to eutrophic species observed at site F1 but rather the result of a diatom bloom (J.P. Hurley, unpublished pigment data). Diatoms are abundant in both the water column and on calcareous periphyton in non-eutrophied regions of the system.

Unfiltered HgT (Figure 5C) levels are slightly higher than those observed in canals, yet remain below 5 ng L⁻¹ across the marsh transect. A north to south increase is apparent for HgT_U in July, however, the pattern is not consistent during the dry period of December. For individual sites, December samples represent the lowest HgT_U levels. The HgT_U levels in March were the highest at F4 and U3. Our March 1995 sampling represented a transition

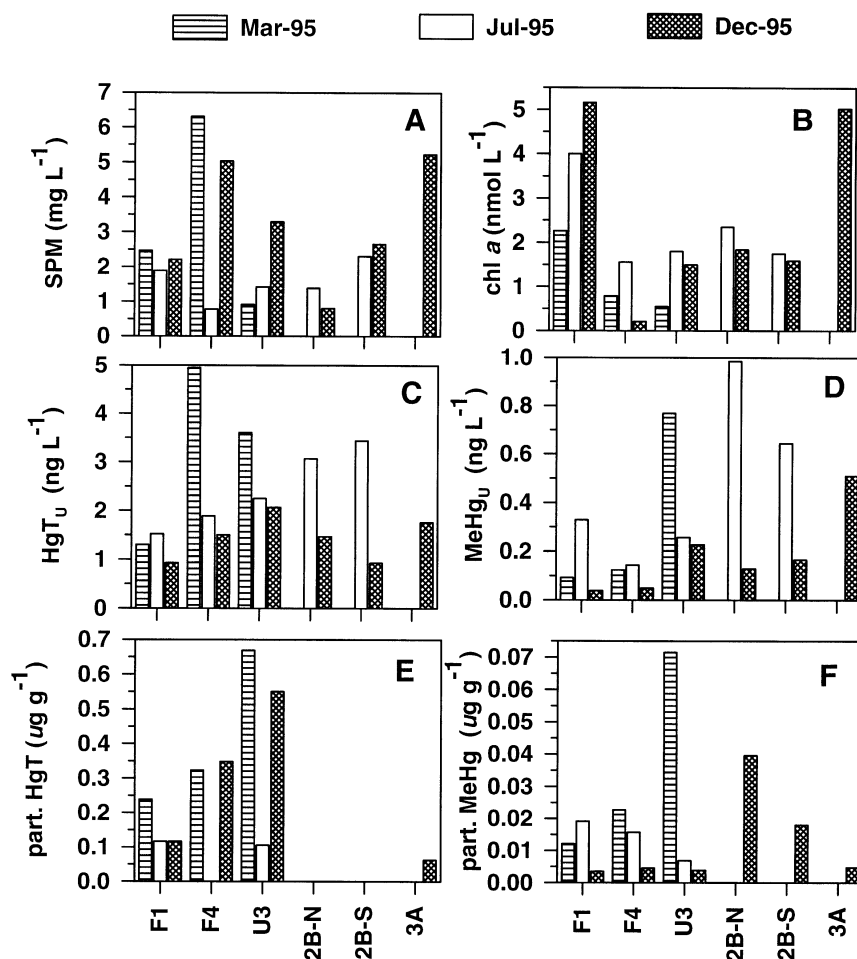


Figure 5. Suspended particulate matter (SPM), chlorophyll *a*, and aqueous Hg species in the WCA-2A marsh system.

period, rather than a typical dry period (Figure 2). Sampling occurred during a period of strong decline in water levels due to abnormally high precipitation during fall and early winter 1994. Relative to the 6-year mean, stage was about 0.7 m higher than normal. The July (wet month) and December (dry month) sampling were more typical of long-term hydrologic trends in the system.

Methyl Hg levels (Figure 5D), similar to HgT , exhibit strong seasonal variability. Similar to HgT_U , lowest levels for MeHg_U at a given site were observed in December. For a given date, there is evidence of north-south increasing trends. Unlike March and December, MeHg at site F1 in July

was higher than F4 and U3 and may suggest site-specific processes at the eutrophied F1 site. Unfiltered MeHg at sites 2BS and 2BN in July were approximately 2–5 times greater than those observed in WCA-2A. Similarly, the percent of HgT_U as MeHg_U ranged from 2.6–11.4% in WCA-2A and 19 and 32% at sites 2BN and 2BS, respectively. These observations may give insight into the role of atmospheric deposition on MeHg production. Water Conservation Area 2B receives almost all of its water from atmospheric precipitation, and aqueous HgT levels are higher than sites in WCA-2A, a marsh that receives a mix of canal and atmospheric inputs. The concurrent rise in MeHg and the percent of HgT as MeHg at WCA-2B suggest that the “reactivity” of the HgT at this site may allow for a greater degree of methylation than at sites in WCA-2A.

Suspended particulate matter in the marsh, in addition to periphyton (Cleckner et al. 1997), are likely vectors for Hg entry to the food chain (Figures 5E, 5F). Particulate HgT and MeHg content suggest a similar range as canal particles. The strong seasonal pattern, with lowest particulate MeHg content in December, is also consistent between canals and marshes. From a food chain perspective, however, marsh sites are much more periphyton-dominated than canals. Therefore, one must be cautious about inferring major food chain transport solely on the content of Hg in suspended particulate matter.

Our December 1995 sampling represented the first date that all sites from WCA-2A, 2B and 3A were sampled and that HgT , MeHg, HgR and DGM were measured (Figure 6). It appears from these data, that during December, Hg cycling was more dynamic in our non-eutrophied southern sites (U3, 2B-N, 2B-S, 3A). The percentage of unfiltered Hg[II] (Hg [II]) is calculated as $\text{HgT}_U - \text{MeHg}_U$ as HgR increased from north to south, from 3.5% in F1 to about 8% at sites in 2BS and WCA-3A. At this point, we cannot draw direct links between HgR and the formation of either DGM or MeHg, but the differences among sites will lead us to detailed studies of formation and loss processes of these important forms of Hg. Additionally, we have also observed strong diel variability in all of these species and the results of these detailed observations are discussed in Krabbenhoft et al. (1997).

High levels of DOC in the Everglades ($20\text{--}60 \text{ mg L}^{-1}$) led us to an initial hypothesis that a strong relationship might exist between Hg and DOC, similar to those observed in other regions (Andren & Harriss 1973; Mierle et al. 1991; Hurley et al. 1995; Watras et al. 1995). Since the Everglades are a wetland-dominated system, we compared Everglades Hg-DOC relationships from this study to our data set from Wisconsin rivers that drain wetland watersheds (Hurley et al. 1995). The positive relationship observed between HgT_F and DOC in the Wisconsin systems and MeHg_F and DOC was clearly not apparent

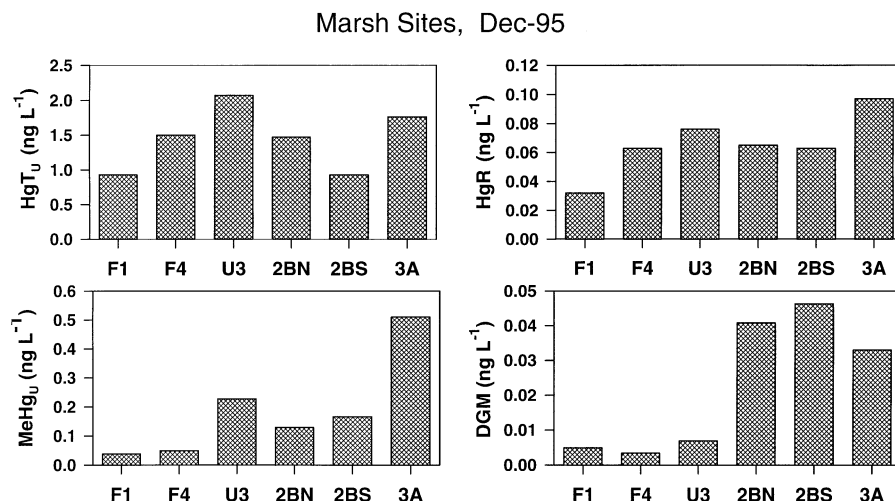


Figure 6. Hg species at marsh sites during December, 1995.

in the Everglades (Figure 7). Coefficient of correlation (r^2) values for the HgT_F and MeHg_F to DOC were <0.01 in the Everglades. Furthermore, if one were to predict Everglades HgT and MeHg concentrations using Everglades DOC and the Wisconsin rivers regression, one would expect Hg and MeHg levels to be at least 2–5 times higher than those actually observed. These observations clearly show that DOC alone relates differently with respect to Hg speciation in the two systems. Specific differences between the Wisconsin and South Florida sites may be due to differences in the quality of DOC (number of Hg-binding sites) between sites or that aqueous Hg in the Everglades may be controlled by ligands other than those in DOC. Our future efforts in this phase of research are to better characterize the composition of the DOC and to determine the influence of functional groups on Hg behavior.

Conclusions

Our observations of aqueous Hg speciation in the Northern Everglades canals and marshes reveal strong spatial and seasonal patterns. These observed trends in aqueous speciation of Hg are a result of numerous formation, degradation and bioaccumulation processes. Total Hg associated with suspended, soil-derived particles draining from EAA presumably settle out before entry into the marsh of WCA-2A. Reduced flows and stagnation of waters within canals lead to increases in both MeHg_U and particle-associated MeHg. Unfiltered HgT in surface water entering the marsh of WCA-2A ranged from about 1–1.5 ng L⁻¹ while MeHg_F exhibited a sixfold increase from winter to summer.

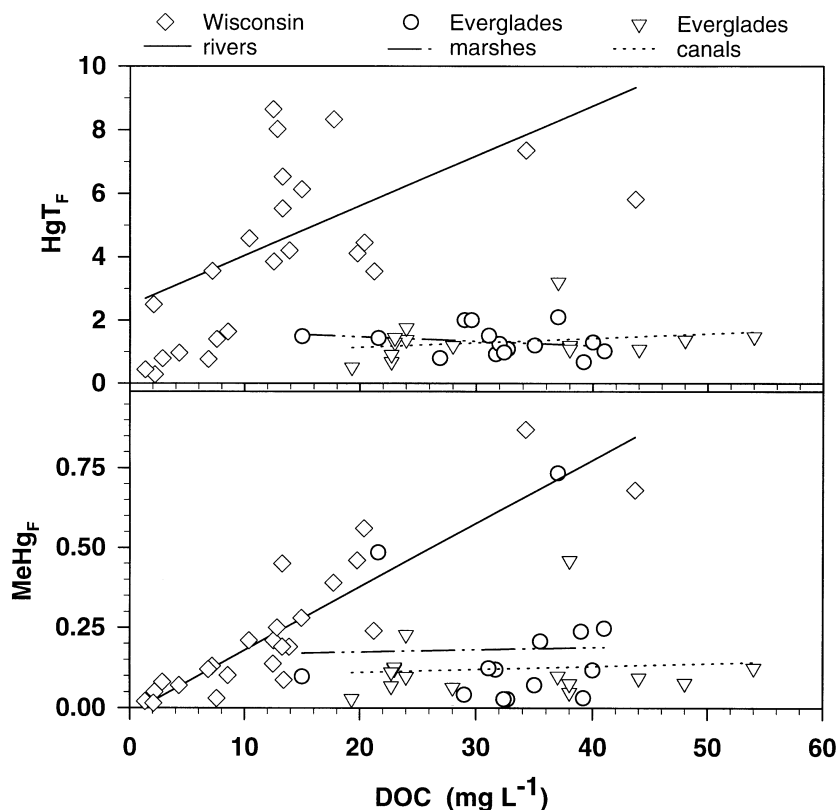


Figure 7. Relationships between filtered total and methyl mercury and dissolved organic carbon. Figure compares the data from Hurley et al. (1995) for Wisconsin rivers draining wetlands and the Everglades canal and marsh samples.

Transects across the marshes of WCA-2A, coupled with measurements in WCA-2B and WCA-3A, reveal no apparent north to south trends in HgT_U . Unfiltered MeHg , however, does appear to show enrichment at southern sites for individual sampling periods. Additional analyses of HgR and DGM across WCA-2A and additional sites in WCA-2B and WCA-3A also suggest greater reactivity of aqueous Hg at the southern sites. The strong relationship of HgT_F and MeHg_F observed in northern Wisconsin is not apparent, suggesting differences in DOC type between regions.

Acknowledgements

Funding for the ACME project is provided by the U.S.G.S. South Florida Ecosystem Program. The authors are grateful for the field and laboratory

support efforts of Paul Schuster, Jason Tregellas, Sue King, Tim Heelan, Jennifer Knepel, and Ed German. Larry Fink, Kim Jacobs, Angela Chong and many others at the South Florida Water Management District provided assistance for this study.

References

- Andren AW & Harriss RC (1975) Observations on the association between mercury and organic matter dissolved in natural waters. *Geochim. Cosmochim. Acta* 39: 1253–1257
- Belanger TV, Scheidt DJ & Platko II JR (1989) Effects of nutrient enrichment on the Florida Everglades. *Lake and Reservoir Management* 5: 101–111
- Bloom NS & Crecelius EA (1983) Determination of mercury in seawater at sub-nanogram per liter levels. *Mar. Chem.* 14: 49–59
- Bloom NS & Fitzgerald WF (1988) Determination of volatile mercury species at the picogram level by low temperature gas chromatography with cold vapor atomic fluorescence detection. *Anal. Chim. Acta* 208: 151–161
- Brianfireun BA, Heyes A & Roulet NT (1996) The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. *Water Res. Res.* 32: 1785–1794
- Cleckner LB, Garrison PJ, Hurley JP, Olson ML & Krabbenhoft DP (1997) Trophic transfer of total and methyl mercury in the Northern Everglades. *Biogeochem. This issue*
- DeBusk WF, Reddy KR, Koch MS & Wang Y (1994) Spatial distribution of soil nutrients in a Northern Everglades marsh: Water Conservation Area 2A. *Soil Sci. Am. J.* 58(2): 543–552
- Fitzgerald WF & Gill GA (1979) Subnanogram determination of mercury by two-stage gold amalgamation and gas-phase detection applied to atmospheric analysis. *Anal. Chem.* 51: 1714–1720
- Fitzgerald WF & Watras CJ (1989) Mercury in surficial waters of rural Wisconsin lakes. *Sci. Tot. Environ.* 28: 223–232
- Gilmour CC & Henry EA (1991) Mercury methylation in aquatic systems affected by acidic deposition. *Environ. Pollut.* 71: 131–169
- Gilmour CC, Gill GA, Stordal MC & Spiker E (1997) Mercury methylation and sulfur cycling in the Northern Everglades. *Biogeochem. This issue*
- Horvat M, Liang L & Bloom NS (1993) Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environment samples. *Anal. Chim. Acta* 282: 153–168
- Hurley JP & Watras CJ (1991) Identification of bacteriochlorophylls in lake waters via reverse-phase HPLC. *Limnol. Oceanogr.* 36: 307–315
- Hurley JP, Benoit JM, Babiarz CL, Shafer MM, Andren AW, Sullivan JR, Hammond R & Webb DA (1995) Influences of watershed characteristics on mercury levels in Wisconsin rivers. *Environ. Sci. Technol.* 29: 1867–1875
- Jensen JR, Rutchey K, Koch MS & Narumalani S (1995) Inland wetland change detection in the Everglades Water Conservation Area 2A using a time series of normalized remotely sensed data. *Photogrammetric Engineering & Remote Sensing* 61: 199–209
- Koch MS & Reddy KR (1992) Distribution of soil and plant nutrients along a trophic gradient in the Florida Everglades. *Soil Sci. Am. J.* 56: 1492–1499
- Krabbenhoft DP, Benoit JM, Babiarz CL, Hurley JP & Andren AW (1995) Mercury cycling in the Allequash Creek watershed, Northern Wisconsin. *Water Air Soil Pollut.* 80: 425–433
- Krabbenhoft DP (1996) Mercury Studies in the Florida Everglades. U.S. Geological Survey fact sheet, FS-166-96 (4p)
- Krabbenhoft DP, Hurley JP, Olson ML & Cleckner LB (1997) Diel variability of mercury phase and species distributions in the Florida Everglades. *Biogeochem. This issue*

- Lambou VW, Barkay T, Braman RS, Delfino JJ, Jansen JJ, Nimmo D, Parks JW, Porcella DB, Rudd J, Schultz D, Stober J, Watras C, Wiener JG, Gill G, Huckabee J & Rood B (1991) Mercury Technical Committee Interim Report, Florida State University, Tallahassee
- Liang L, Horvat M & Bloom NS (1993) An improved speciation method for mercury by GC/CVAFS after aqueous phase ethylation and room temperature precollection. *Talanta* 41: 371–379
- McCormick PV, Rawlik PS, Lurding K, Smith EP & Sklar FH (1996) Periphyton-water quality relationships along a nutrient gradient in the northern Florida Everglades. *Journal of the N. American Benthological Society* 15: 433–449.
- Miao SL & Sklar FH (1996) Everglades Vegetation studies: I. Biomass and nutrient structure of sawgrass and cattail along a nutrient gradient at several levels of organization. In press
- Mierle G & Ingram R (1991) The role of humic substances in the mobilization of mercury from watersheds. *Water Air Soil Pollut.* 56: 349–358
- Olson ML, Cleckner LB, Hurley JP & Krabbenhoft DP (1997) Resolution of matrix effects on analysis of total and methyl mercury in aqueous samples from the Florida Everglades. *Fres. Z. Anal. Chem.* 358: 392–396
- Patterson CC & Settle DM (1976) The reduction of orders of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collection, handling and analysis. In: LaFleur PD (Ed) *Accuracy in Trace Analysis: Sampling, Sample Handling, and Analysis* (pp 321–351). U.S. National Bureau of Standards Special Publication 422
- Patrick WH, Gambrell RP, Parkpain P & Tan F (1994) Mercury in soils and plants of the Florida Everglades. In: Watras CJ & Huckabee JW (Eds) *Mercury Pollution: Integration and Synthesis* (pp 609–614)
- Richardson CJ (1991) Effects of Nutrient Loadings and Hydroperiod Alterations on Control of Cattail Expansion, Community Structure and Nutrient Retention in the Water Conservation Areas of South Florida. Duke University, Durham
- Rossman R & Barres J (1988) Trace element concentrations in near-surface waters of the Great Lakes and methods of collection, storage and analysis. *J. Great Lakes Res.* 14: 199–204
- Rudd JWM (1995) Sources of methyl mercury to freshwater ecosystems: A review. *Water Air Soil Poll.* 80: 697–713
- St. Louis VL, Rudd JWM, Kelly CA, Beatty KG, Bloom NS & Flett RJ (1994) Importance of wetlands as sources of methyl mercury to boreal forest ecosystems. *Can J. Fish Aquat. Sci.* 51: 1065–1076
- South Florida Water Management District (1994) Surface Water Improvement and Management Plan for the Everglades, Supporting Information Document
- Stober QJ, Jones RD, Scheidt DJ & Thornton K (1996) Multi-media monitoring of mercury and associated parameters in the Everglades canal system: Abstract. Mercury as a Global Pollutant, Hamburg, Germany
- Swift DR (1981) Preliminary investigations of periphyton and water quality relationships in the Everglades Water Conservation Areas. SFWMD
- Swift DR & Nicholas RB (1987) Periphyton and Water Quality Relationships in the Everglades. South Florida Water Management District
- Van Huekelem L, Lewitus AJ, Kana TM & Craft NE (1994) Improved separations of phytoplankton pigments using temperature-controlled high performance liquid chromatography. *Mar. Ecol. Progr. Ser.* 114: 303–313
- Ware FJ, Royals H & Lange T (1990) Proceedings of the annual conference of the southeastern association of fish and wildlife agencies 44: 5–12
- Watras CJ, Morrison KA & Bloom NS (1995) Chemical correlates of Hg and methyl Hg in northern Wisconsin lakes under ice cover. *Water Air Soil Pollut.* 84: 253–267
- Winfrey M & Rudd JWM (1990) Environmental factors affecting the formation of methylmercury in low pH lakes: A review. *Environ. Toxicol. Chem.* 9: 853–869
- Zillioux EJ, Porcella DB & Benoit JM (1993) Mercury cycling and effects in freshwater wetland ecosystems. *Environ. Toxicol. Chem.* 12: 2245–2264