Appendix 7-8: The Effect of Dry Down and Natural Fires on Mercury Methylation in the Florida Everglades

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SUMMARY

Extensive fires occurred in the Florida Everglades in May and June 1999 following a La Niña-driven dry period. Peat oxidation from burning or intense drying could potentially enhance methylation of Hg by increasing the availability of sulfate, labile carbon, and/or Hg (II) following reflooding of the dry areas. In response, the U.S. Geological Survey and the South Florida Water Management District conducted a collaborative study on the effect of sediment drying and fires on mercury (Hg) speciation and bioaccumulation at 13 sites spanning most of the north-to-south length of the remnant Everglades. The magnitude, duration, and extent of peat oxidation produced by the prolonged period of drawdown and dryout in the northern Everglades, including plant-top or peat burns in some areas, caused substantial but short-term changes in the physical, chemical, and microbiological characteristics of the peat soil and its sulfur and mercury biogeochemistries. These changes were not manifest to nearly the same degree at central Everglades sites that remained wet during this same period. These changes were followed by and likely caused a corresponding and rapid increase in MeHg production and a correspondingly rapid bioaccumulation in mosquitofish at WCA-2A-F1, a eutrophic site in the northern Everglades where foraging on benthic infauna is believed to predominate year around (Trexler et al., 1999; Rawlik et al., 2000). At the oligotrophic site, WCA-2A-U3, where autotrophic food chains eventually develop, the mosquitofish bioaccumulation response was delayed by between 90 and 120 days but was much more dramatic. Follow-up studies are planned to measure the effect of changes in sediment and pore water chemistries on methylation and demethylation rates by dosing sediment cores collected in July, August, October, and November 1999 with stable isotopes of inorganic mercury. A subsequent routine annual collection of mosquitofish, sunfish, and largemouth bass by the Florida Fish and Wildlife Conservation Commission for the District the fall of 1999 revealed an increase in the THg concentrations in young-of-the year fish over previous years at F1 and U3 in WCA-2A but not at WCA-3A-15 in (Lange et al., 2000). Whether this pulse of MeHg will persist and continue to bioaccumulate in mid- and top-predator sport fish at these sites or dissipate with growth dilution and depuration over the next several years can only be determined through continued annual monitoring. Proposed changes to the timing, routing, magnitude, duration, and frequency of water flow in the Everglades are intended to increase the average hydroperiod in the northern Everglades. This may have the collateral benefit of decreasing the extent, magnitude, duration, and frequency of extreme peat oxidation conditions that could be exacerbating the Everglades mercury problem.

INTRODUCTION

Mercury levels in several species of predator sport fish from the Everglades exceed the Florida action level of 0.5 ppm (Ware et al., 1990). The mean concentration of Hg in largemouth bass from the central Everglades exceeds 1.5 ppm, which is high in comparison to any published studies. In March 1989, the Florida Department of Health and Rehabilitative Services issued fish consumption advisories for Hg in each of the Water Conservation Areas (WCAs) and the Everglades National Park. Although advisories are given for Hg, almost all of mercury in fish tissues is methylmercury (MeHg), and thus it is necessary to understand the distribution, production mechanisms, and bioaccumulation pathways of MeHg. The ecological significance of the occurrence of high concentrations of MeHg in the aquatic environment includes threats to such endangered species as the Florida panther and fish-eating birds, such as the wood stork.

It is not yet completely understood what controls the apparent susceptibility of Everglades to methylmercury bioaccumulation: high annual inorganic mercuric ion loads; high concentrations of inorganic mercury in peat soils via historical accumulation and occasional concentration via plant or muck fires; high bioavailable fraction of Hg available for methylation; high absolute rates of Hg methylation and corresponding low rates of demethylation of methylmercury; high biotic uptake rates of produced MeHg; high biomagnification factors in the aquatic food chain; or any combinations of the above. Studies by the U.S. Geological Survey (USGS) under the Aquatic Cycling of Mercury in the Everglades (ACME) Project (Krabbenhoft, 1996) of the underlying transport, transformation, fate, and bioaccumulation processes that describe these chemical interrelationships have been underway since 1995.

Plant-top and muck fires in the Everglades are part of the natural biogeochemical cycle of the Everglades. In addition, fires may become more frequent in some areas of the Everglades under more natural hydrologic conditions that may result from implementation of the restoration plan. These extreme chemical oxidation events can change soil and water chemistries that influence inorganic mercury availability, or other chemical constituents needed for methylation. The creation of reservoirs by flooding dry soils is known to produce extended periods of MeHg production and subsequent bioaccumulation (Bodaly et al., 1984). More recent studies have demonstrated that the MeHg load in boreal catchments is strongly influenced by the area of inundated upstream natural wetlands (St. Louis et al., 1996). Increases in MeHg production and bioaccumulation have also been observed in an artificial wetland created by diking a natural river (Paterson et al., 1998). It has been hypothesized that the flooding of dry soils to create reservoirs or wetlands fosters the release of labile inorganic mercury in a highly bioavailable form or the release of one or more chemical factors that facilitate methylmercury production. *A priori*, one might expect that fires could liberate a significant fraction of otherwise unavailable mercury, sulfate, and/or labile carbon, and thus stimulate the methylation process. However, there are no known studies on how fires affect mercury cycling and bioaccumulation in wetlands.

After an extended period of drawdown and dryout in the northern Everglades following a severe, extended dry season caused by a La Niña event, plant-top and muck fires occurred at several locations over several thousand acres in May and June 1999. In some locations, the fire burned the exposed peat soil to the underlying rock. This presented a unique opportunity to quantify the effect of post-burn changes in peat soil and surface water chemistries and surface soil microbial ecology on methylmercury production and bioaccumulation on the scale of the Everglades.

The hypothesis to be tested by this study was that oxidation of peat from intense drying or burning would increase the rate of methylation of inorganic mercury, Hg(II), because of an

increase in the availability of sulfate, labile carbon, and/or Hg (II) for methylation. To test this hypothesis, the U.S. Geological Survey (USGS) and the South Florida Water Management District (District) conducted a collaborative study on the effect of sediment drying and fires on Hg speciation and bioaccumulation in the Everglades.

METHODS

The first post-burn sampling was conducted in July 1999, after allowing for a period of about five weeks of inundation from the delayed onset of the summer rainy season. Thirteen sites were sampled (**Figure A7-8-1** and **Table A7-8-1**), including ten sites previously studied by the ACME project (one of which, 3A33, was burned) and three additional sites from burned areas. The ten ACME sampling sites span almost the entire north-to-south length of the remnant Everglades, and represent many of the varied sub-ecosystem types. The sampled burn sites were focused in and around northern WCA-3A where the most widespread burns occurred. With this array of sites, data comparisons could be made on three levels: (1) 1999 data from burned versus unburned areas, (2) 1995-98 data versus post-burn data collected at site 3A33, and (3) ACME data for 1995-98 from all sites versus the post burn time period. In addition, to track the temporal effects of the burn and

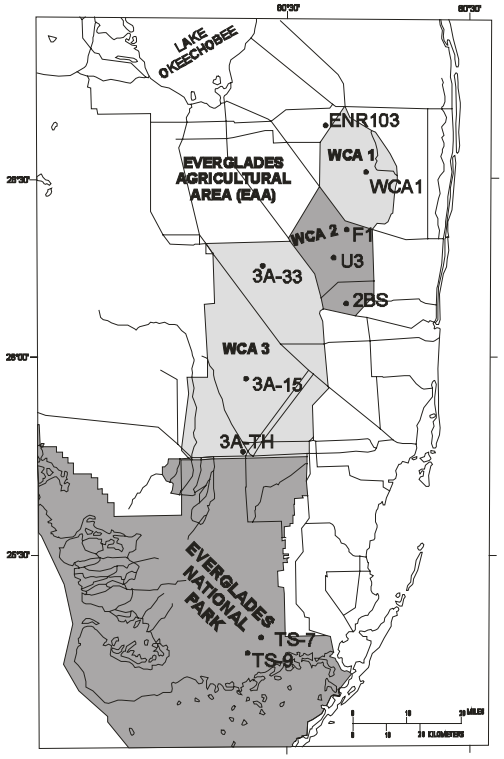

Figure A7-8-1. Post-Dry/Burn Study Sites in the Florida Everglades

dry down, follow-up sampling was conducted at six sites in August, October, and November for surface water, mosquitofish, sediment, and periphyton.

Previously established ultra-clean sampling methods by the ACME project were used to collect and analyze the samples for this study (Hurley et al., 1998; Krabbenhoft et al., 1998; Cleckner et al., 1998; Olson et al., 1997; and Olson and DeWild, 1999). Sites were accessed primarily by helicopter, but in some cases airboats were used. When helicopter transport was utilized, field crews walked several hundred feet away from the helicopter to ensure undisturbed samples were acquired. At each site, samples of surface water (mid water column, filtered [0.45 um] and unfiltered), peat porewater (from 5 cm depth), sediment (top 5 cm), floating periphyton (may not have reestablished yet at burn sites), and mosquitofish (composite analysis of 10-15 individuals) were collected for analysis of total Hg (THg) and methylmercury. In addition, aqueous samples were analyzed for temperature, pH, and dissolved (0.45 um) sulfate, chloride, sulfide, dissolved organic carbon, specific UV absorbance (SUVA) at 254 nm, and total suspended solids. Temperature was measured at two surface water depths (mid water column and 5-10 cm above the sediments) as well as at 5 cm sediment depth. Water column depth was measured at 5 locations per site to estimate average water column depth. Follow-up collections by District staff at WCA-2A-F1, WCA-2A-U3, WCA-2B-AB, WCA-3A-4, WCA-3A-15, and WCA-3A-33 omitted sediment pore water.

RESULTS

Following the onset of the first substantial wet-season rainfall event in early June 1999, the dried out and burned study sites were reinundated. The first sampling event in July 1999 was intended to capture the early physical, chemical, and microbiological responses to this reinundation, while the later collections were intended to capture the peaks in MeHg accumulations and the return of the water, sediment, periphyton, and mosquitofish to more typical THg and MeHg concentration levels. The THg and MeHg concentrations in surface water, sediment, periphyton, and mosquitofish for the July, August, October, and November 1999 campaign are depicted in **Figures A7-8-2** through **A7-8-8**. The long-term average concentrations of THg in mosquitfush at WCA-2A-F1 and U3 are depicted in **Figure A7-8-9** to put the amplitude and frequency of post-burn data variability at those sites in historical perspective. The ratios of THg in mosquitofish to the corresponding THg concentration in sediment and the MeHg concentrations in water (filtered), sediment, and periphyton are depicted for the same sites and campaigns in **Figures A7-8-10** through **A7-8-13**. The ratio of the MeHg concentration in periphyton to the corresponding concentrations in water (filtered) and sediment are displayed in **Figures A7-8-14** and **A7-8-15**. The surface and pore water concentrations of filtered THg, MeHg, and DOC, SO4, and sulfide are depicted in **Figures A7-8-16** and **A7-8-17**, and **Figures A7-8-18** and **A7-8-19** depict the ratios of the post-burn values to the long-term average values for the period 1995-1998. However, the comparison to long-term average values may not be appropriate where natural seasonal variability in biogeochemistry and trophic structure generates similar temporal variabilities. Unfortunately, too few samples were collected in each season over the last five years to define typical values of key state constituents as a benchmark for abnormal response.

At the time of the first post-burn sampling (July 1999), MeHg concentrations in surface water and sediments peaked or had nearly peaked at all study sites, with the exception of WCA-3A-15, which had not dried out. MeHg in periphyton peaked at WCA-2A-U3 in July 1999, at WCA-2A-F1 in August, at WCA-2B-AB and WCA-3A-33 in October at WCA-3A-4 and WCA-3A-15 in November, but WCA-3A again exhibited a virtually flat response across the sampling period. Pore water concentrations of sulfate and sulfide in July 1999 were much higher than historical averages (**Figure A7-8-18**). The THg concentration in mosquitofish at the eutrophic site at WCA-2A-F1 showed a maximum in June during a routine District quarterly sampling event that had to be postponed from the usual May collection date due to low water levels (**Figure A7-8-20**). The THg in mosquitofish at the oligotrophic site at WCA-2A-U3 about 8 km south of F1 peaked about 120 days later in October 1999. The unburned WCA-3A-15 site also exhibited a dramatic increase in THg in mosquitofish in October 1999 (**Figure A7-8-8**), but this was not a disproportionate response when compared with historical values (**Figure A7-8-19**).

Table A7-8-1. Sampling results for unfiltered surface water and sediment from the thirteen study sites, and comparison of historical average values (1995-98) to July 1999 conditions.

Site	Spring 1999 Flood Status	Lati-tude	Long-itude	7/99 Unfiltered Surface Water		7/99 Sediment (ng/g, dry)		Water Ratio: 1995-98 Average/7-99		Sediment Ratio: 1995-98 Average/7-99	
				THg	MeHg	THg	MeHg	THg	MeHg	THg	MeHg
EN103	Wet	26 38.24	80 25.36	0.57	0.019	105.38	0.035				
WCA1	Wet	26 30.61	80 18.63	3.24	0.260	204.92	13.143	0.72	1.00	0.82	2.76
F1	Dried	26 21.58	80 22.23	2.03	0.484	116.51	8.600	0.65	1.86	1.22	28.75
U3	Dried	26 17.25	80 24.68	4.39	1.618	257.96	7.124	0.95	2.74	2.32	7.14
2BS	Wet	26 09.82	80 22.68	2.7	0.923	249.45	1.387	0.97	1.85	1.62	1.36
2AB	Burn	26 23.48	80 27.81	3.45	2.080	99.63	19.810	new site	new site	new site	new site
3A-1	Burn	26 11.21	80 44.41	2.33	0.463	149.32	11.074	new site	new site	new site	new site
3A-4	Burn	26 19.05	80 47.83	3.16	1.142	81.02	57.582	new site	new site	new site	new site
3A-33	Burn	26 16.16	80 36.82	2.1	0.545	110.09	35.734	1.13	1.76	1.56	7.08
3A-15	Wet	25 58.45	80 40.13	1.95	0.193	350.28	0.997	1.15	0.86	0.94	2.99
3A-TH	Wet	25 46.87	80 41.12	1.85	0.644	257.05	1.708	0.89	1.37	0.69	27.42
TS-7	Wet	25 17.23	80 38.78	2.07	0.622	41.42	1.772	0.71	3.45	1.33	18.25
TS-9	Wet	25 14.85	80 40.94	1.32	0.413	77.53	4.313	0.44	1.53	2.41	0.29

Latitude and longitude in degrees, minutes and hundredths of minutes

Table A7-8-2. Results for Total Hg (Hg_T) and Methylmercury (MeHg) for filtered (F) and unfiltered (U) water samples.

July 1999 Data	Surface Water (ng/L))			Porewater (5 cm depth, ng/L)		
Site	UHg_T	FHg_T	UMeHg	FMeHg	FHg_T	FMeHg
ENR103	0.57	0.49	0.019	0.035	1.2	0.000
Lox, WCA1	3.24	2.02	0.260	0.129	5.01	1.914
F1	2.03	1.53	0.484	0.540	1.28	0.007
U3	4.39	4.44	1.618	1.624	3.94	2.750
2BS	2.7	2.4	0.923	0.906	0.64	0.011
2AB (Burn site in 2A)	3.45	3.02	2.080	1.550	5.66	4.419
3A-1	2.33	2.26	0.463	0.614	6.21	3.470
3A-4	3.16	2.91	1.142	0.528	5.3	0.831
3A-33	2.1	1.48	0.545	0.467	17.4	14.708
3A-15	1.95	1.16	0.193	0.155	0.62	0.025
3A-TH	1.85	1.73	0.644	0.660	0.49	0.103
TS-7	2.07	1.63	0.622	0.474	1.58	0.411
TS-9	1.32	1.43	0.413	0.367	1.13	0.105

Table A7-8-3. Results for Total Hg (Hg_T) and Methylmercury (MeHg) for sediments and periphyton

July 1999 Data	Sediment	(ng/g, dr wt)	(ng/g, dr wt)		Periphyton (ng/g, wet wt)		
Site	% Dry	Hg_T	MeHg	%MeHg	Hg_T	MeHg	%MeHg
ENR103	18.000	105.38	0.035	0.03%	0.94	0.000	0.00%
Lox, WCA1	6.300	204.92	13.143	6.41%	2.5	0.393	15.72%
F1	8.600	116.51	8.600	7.38%	3.27	0.036	1.10%
U3	10.300	257.96	7.124	2.76%	17.51	1.510	8.62%
2BS	15.500	249.45	1.387	0.56%	2.7	0.402	14.89%
2AB	13.500	99.63	19.810	19.88%	9.88	0.682	6.90%
3A-1	13.970	149.32	11.074	7.42%	13.07	0.778	5.95%
3A-4	11.410	81.02	57.582	71.07%	1.2	0.058	4.83%
3A-33	11.590	110.09	35.734	32.46%	4.14	0.588	14.20%
3A-15	10.500	350.28	0.997	0.28%	2.96	0.146	4.93%
3A-TH	9.500	257.05	1.708	0.66%	1.79	0.135	7.54%
TS-7	14.000	41.42	1.772	4.28%	1.91	0.376	19.69%
TS-9	9.300	77.53	4.313	5.56%	8.33	0.458	5.50%

Table A7-8-4. Results for ancillary chemical data collected at each site.

July 1999 Data	DOC	SUVA	SW pH	PW pH	SW Sulfide	PW Sulfide	SW SO4	SW Cl
Site	(mg/L)				(mg/L)	(mg/L)	(mg/L)	(mg/L)
ENR103	33.1	0.036	7.4	5.92	0.009	0.873	51.4	149.5
Lox, WCA1	24.7	0.026	8.1	6.6	0.004	0.074	0.1	17.2
F1	41.4	0.039	7.5	6.59	0.022	6.261	53.6	121.3
U3	40.4	0.038	7.98	6.36	0.009	1.166	61.2	138.8
2BS	16.4	0.03	7.72	6.34	0.004	0.19	6	45.8
2AB	29.8	0.039	7.8	6.44	0.008	0.211	12.6	128.1
3A-1	21.7	0.037	7.5	6.22	0.002	0.113	13.5	50.3
3A-4	25.4	0.043	7.6	6.12	0.005	0.073	15.5	52.1
3A-33	29.7	0.039	7.4	6.19	0.002	0.27	18.2	62.5
3A-15	13.8	0.033	7.6	6.55	0.003	0.026	2	16.0
3A-TH	17.2	0.033	7.75	6.36	0.003	0.202	13.2	50.3
TS-7	12.3	0.027	8.1	6.45	0.001	0.013	1	33.7
TS-9	11.1	0.031	7.9	6.18	0.003	1.333	0.7	23.3

Table A7-8-5. Results for the 1999 post-burn follow-up sampling for Total Hg (Hg_T) and Methylmercury (MeHg) for filtered (F) and unfiltered (U) surface water samples [ng/L].

	UF Hg-T				F Hg-T			
Site	July	August	October	November	July	August	October	November
F1	2.03	1.76	1.85	0.78	1.53	1.70	1.08	0.54
2A-B	3.45	5.00	3.76	1.79	3.02	3.07	2.81	1.53
U3	4.39	5.31	3.52	1.79	4.44	4.24	2.71	1.61
3A-4	3.16	2.36	1.23	1.33	2.91	2.41	0.91	0.93
3A-33	2.10	2.02	1.34	1.30	1.48	1.58	1.03	0.78
3A-15	1.95	1.67	1.09	1.04	1.16	1.36	0.82	0.87
	UF MeHg				F MeHg			
Site	July	August	October	November	July	August	October	November
F1	0.48	0.43	0.11	0.08	0.54	0.40	0.12	0.07
2A-B	2.08	0.44	0.28	0.39	1.55	0.38	0.19	0.36
U3	1.62	1.76	0.82	0.34	1.62	1.45	0.52	0.31
3A-4	1.14	0.29	0.14	0.37	0.53	0.29	0.07	0.30
3A-33	0.55	0.24	0.21	0.24	0.47	0.14	0.14	0.18
3A-15	0.19	0.09	0.08	0.15	0.15	0.08	0.05	0.16

Table A7-8-6. Results for the 1999 post-burn follow-up sampling for Total Hg (Hg_T) and Methylmercury (MeHg) for sediment (top 5 cm) [ng/g, dry wt] samples and periphyton [ng/g, wet wt].

	Sed-HgT				Sed-MeHg			
Site	**July**	**August**	**October**	**November**	**July**	**August**	**October**	**November**
F1	116.51	117.18	87.42	118.36	8.60	0.51	0.32	0.21
U3	257.96	199.98	262.62	167.54	7.12	9.43	1.36	0.47
2A-B	99.63	182.82	246.00	158.27	19.81	7.18	6.36	9.59
3A-4	81.02	37.52	129.29	10.16	57.58	3.87	1.14	0.13
3A-33	110.09	100.39	116.09	124.09	35.73	6.33	2.16	4.75
3A-15	350.28	131.65	203.85	181.40	1.00	0.95	0.87	1.55

	Peri-HgT				Peri-MeHg			
Site	**July**	**August**	**October**	**November**	**July**	**August**	**October**	**November**
F1	3.27	6.25	3.86	1.32	0.04	0.69	0.23	0.05
U3	17.51	4.69	5.27	3.49	1.51	0.76	0.96	0.49
2A-B	9.88	8.80	10.36	5.65	0.68	1.73	4.23	1.39
3A-4	1.20	0.92	2.06	2.19	0.06	0.25	0.17	0.62
3A-33	4.14	2.37	3.63	2.06	0.59	0.22	0.88	0.34
3A-15	2.96	5.43	1.68	1.62	0.15	0.26	0.14	0.48

Table A7-8-7. Results for the 1999 post-burn follow-up sampling Total Hg (Hg_T) and Methylmercury (MeHg) [ng/g, wet wt] in Gambusia.

Site	**July '99**		**August '99**		**October '99**		**November '99**	
	Hg_T	**MeHg**	**Hg_T**	**MeHg**	**Hg_T**	**MeHg**	**Hg_T**	**MeHg**
ENR103	12.85	1.74	NA	NA	NA	NA	NA	NA
Lox, WCA1	49.40	40.37	NA	NA	NA	NA	NA	NA
F1	10.92	2.31	4.76	NA	2.30	NA	0.55	NA
U3	74.06	77.69	44.70	NA	243.64	NA	33.80	NA
2BS	26.47	27.34	NA	NA	NA	NA	NA	NA
2AB	84.51	70.76	34.98	NA	106.77	NA	22.08	NA
3A-1	31.70	29.91	NA	NA	NA	NA	NA	NA
3A-4	28.71	26.95	NA	NA	NA	NA	NA	NA
3A-33	19.95	16.22	25.79	NA	75.94	NA	10.30	NA
3A-15	51.07	43.30	58.93	NA	143.32	NA	22.63	NA
3A-TH	27.57	22.67	NA	NA	NA	NA	NA	NA
TS-7	66.83	69.21	NA	NA	NA	NA	NA	NA
TS-9	69.33	58.89	NA	NA	NA	NA	NA	NA

NA = not available

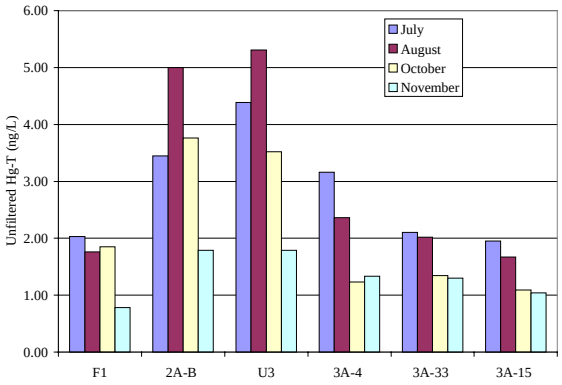

Figure A7-8-2. Unfiltered THg in Surface Water

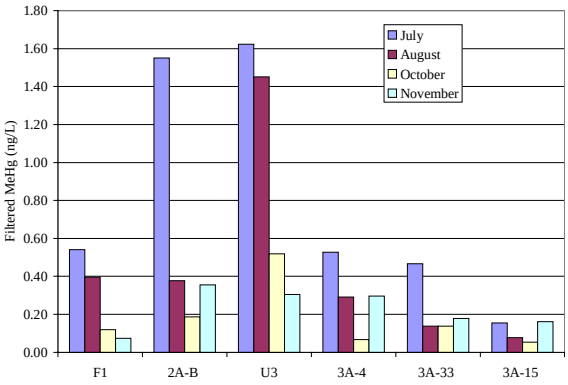

Figure A7-8-3. Filtered MeHg in Surface Water

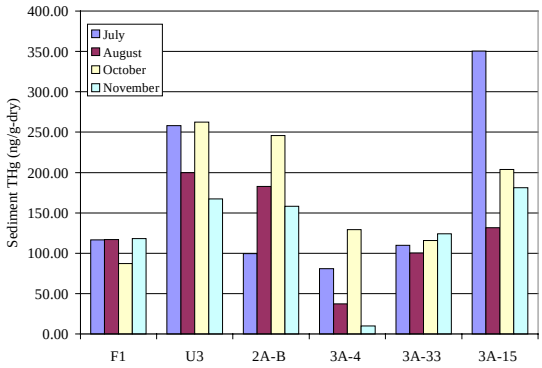

Figure A7-8-4. THg in Post-Burn Sediment

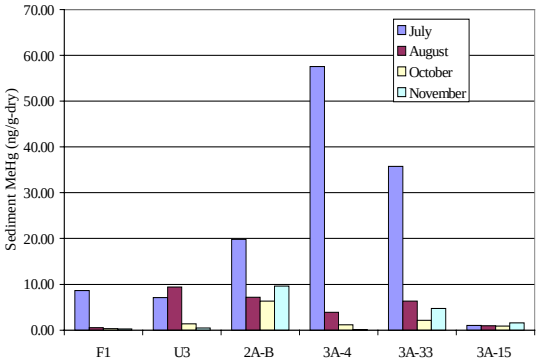

Figure A7-8-5. MeHg in Post-Burn Sediment

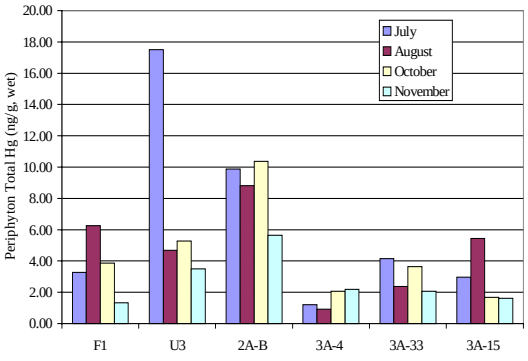

Figure A7-8-6. THg in Post-Burn Sediment

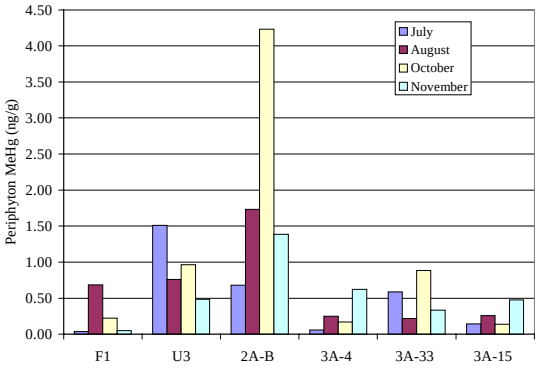

Figure A7-8-7. MeHg in Post-Burn Sediment

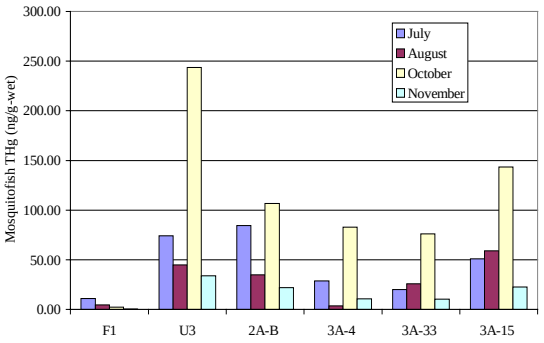

Figure A7-8-8. THg in Post-Burn Mosquitofish

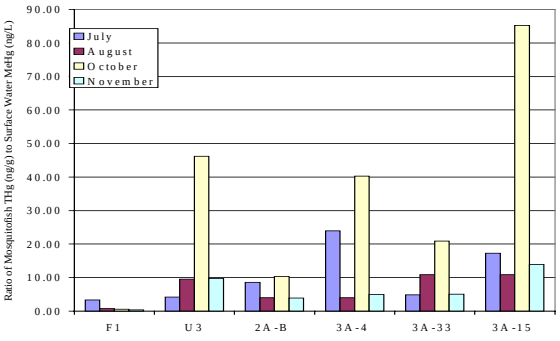

Figure A7-8-9. Ratio of Post-Burn Mosquitofish THg to Water MeHg

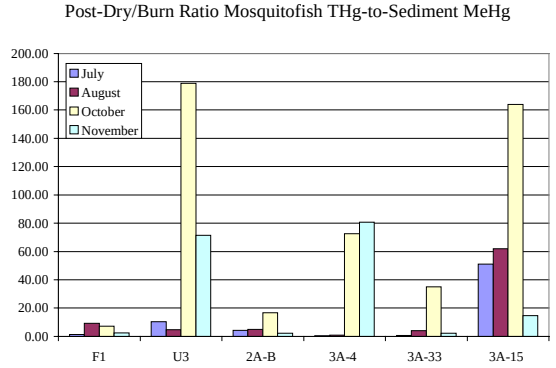

Figure A7-8-10. Ratio of Post-Burn Mosquitofish THg to Sediment MeHg

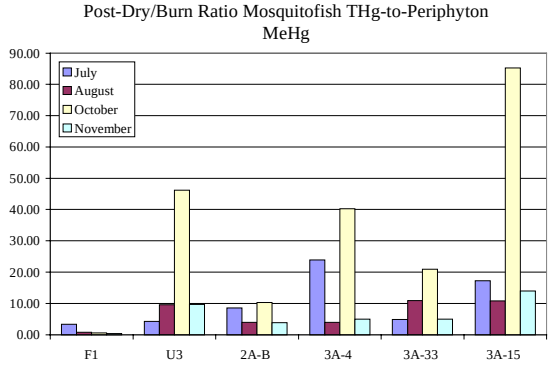

Figure A7-8-11. Ratio of Post-Burn Mosquitofish THg to Periphyton MeHg

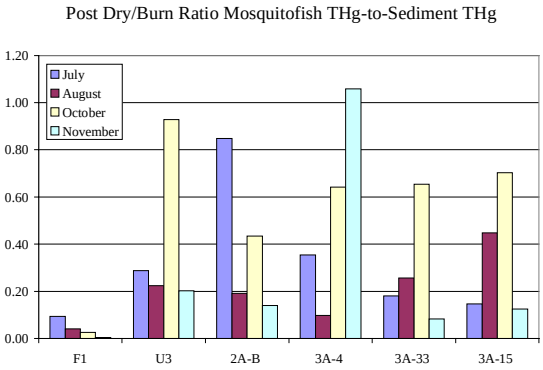

Figure A7-8-12. Ratio of Mosquitofish to Sediment THg

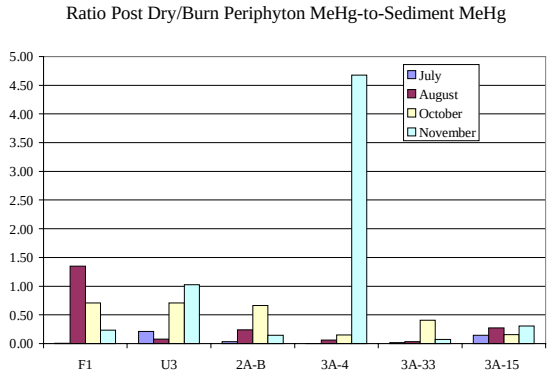

Figure A7-8-13. Ratio of Periphyton THg MeHg to Sediment MeHg

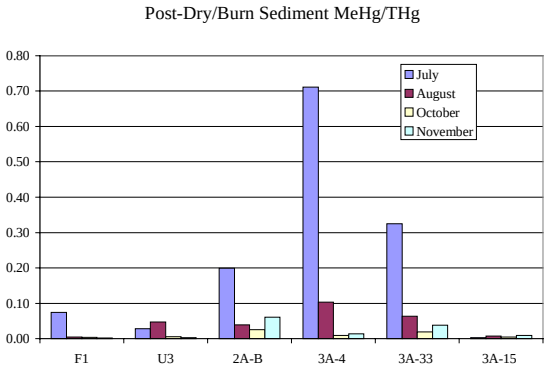

Figure A7-8-14. Post-Burn Ratio of Sediment MeHg to THg

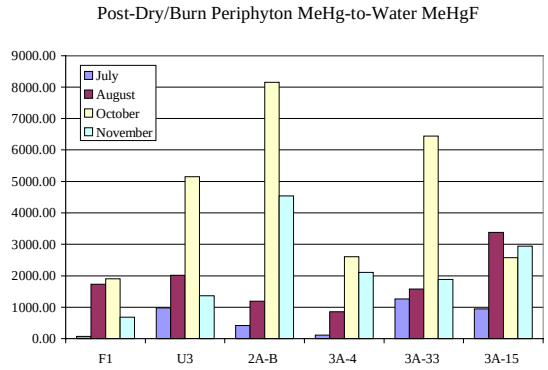

Figure A7-8-15. Post-Burn Ratio of Periphyton MeHg to Water MeHg

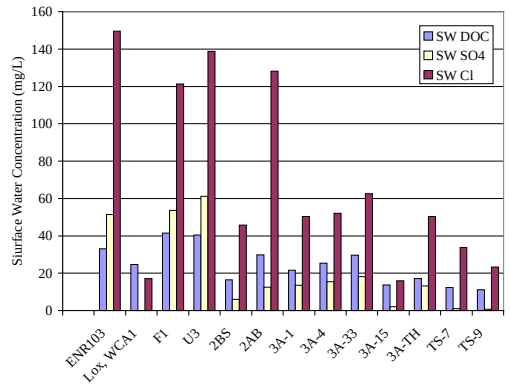

Figure A7-8-16. Post-Burn Surface Water Concs. of Influential Constituents

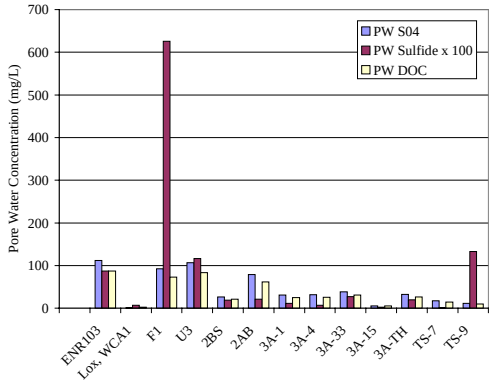

Figure A7-8-17. Post-Burn Pore Water Concs. of Influential Constituents

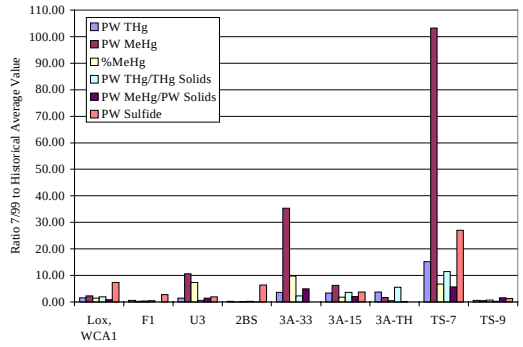

Figure A7-8-18. Ratio of 7/99 Post-Burn Pore Water Quality to Historical Values

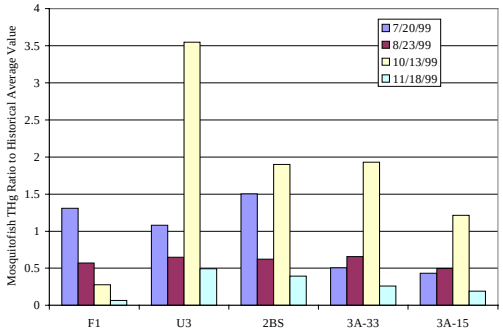

Figure A7-8-19. Ratio of 7/99 Post-Burn Mosquitofish THg to Historical Values

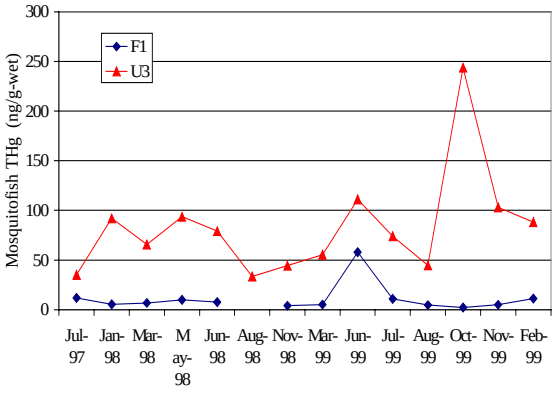

Figure A7-8-20. Long-term Variability in Mosquitofish THg Concentrations

DISCUSSION

The fact that the greatest changes were observed for porewater and sediment is not surprising because Hg methylation in the Everglades is primarily facilitated by of sulfate reducing bacteria (SRB) in the near-surface (top 5 cm) sediments (Gilmour et al., 1998), although periphyton has also been showed to methylate Hg (Cleckner et al., 1999). Maximum MeHg levels in surface water and sediment were observed in July 1999, and follow-up monitoring showed that surface water remained significantly elevated at least until November 1999 when compared to the four-years of study by the ACME project that preceded the burn. Other the other hand, sedimentary MeHg concentrations returned to "normal" levels by about October for severely dried areas, but remained high in burned areas through November. MeHg levels in biological samples showed different trends. Burdens of MeHg in mosquitofish and periphyton continued to build throughout the fall of 1999 reaching maximum observed levels in October. This observation suggests an inherent time lag on the order of 90 to 120 days between punctuated methylmercury production following reflooding of areas that experienced peat oxidation due to extended dry out , and bioaccumulation response in the food web. In addition, though most of the routine sampling sites were not burned in the spring of 1999, many of these sites incurred a prolonged period of draw down and oxidation. This may explain why, overall, we observed about 2x overall higher levels of MeHg in surface water than observed during four years of sampling from 1995 to 1998.

To efficiently carry out their anaerobic metabolic processes, SRBs require sulfate and a labile carbon substrate. To methylate Hg, they also need a bioavailable pool of inorganic Hg (Gilmour et al., 1991). This study tested the hypothesis that one or more of these three necessary ingredients (sulfate; labile, short-chain carbon, and bioavailable Hg) for Hg methylation would increase in abundance due drying and burning of peat, and yield higher levels of methylmercury. This could result from oxidation of organic or inorganic sulfide to yield sulfate; degradation of non-biodegradable carbon pools to yield labile carbon; and, liberation of mercury from unavailable pools bound to sediments. Of these three constituents, only the concentrations of sulfate in surface water and sulfide in porewater increased substantially over typical

concentrations (about 2.4x and 7.0x, respectively) in response to the drying and burning. No appreciable changes in THg were observed in water, sediment or biota, and DOC levels, and DOC quality showed no change compared to historical observations.

Based on the observation that THg and DOC quantity and quality were constant for burned sites but there was a ten-fold increase in net methylation efficiency (defined here as the percent of THg as MeHg in sediment and porewater), it can be inferred that liberation of sulfate from sediments and secondary stimulation of SRBs was a primary driving factor of excess methylmercury production in burned/dried areas. The build-up of excess sulfide in sediment pore water is also a reflection of accelerated SRB activity. Sulfide in pore water is also believed to mediate the formation of a highly bioavailable, neutrally charged complex of Hg(II) in one concentration range and an unavailable negatively charged complex at higher concentrations (Benoit et al., 1999). In the Everglades, an inverse relationship has been observed between pore water sulfide and gross Hg(II) methylation (Gilmour et al., 1998). Whether the build-up of pore water sulfide had already crossed from the stimulatory to the inhibitory concentration range by the time of the July 1999 sampling event cannot be ascertained with the data available, but it would appear likely that the maximum Hg(II) methylation rate had already been reached at several sites, because the ratio of MeHg to THg in sediment decreased thereafter. Regardless of the precise geochemical mechanism involved, data collected from this study suggests that geochemical changes induced by prolonged drying or burning of Everglades peat favor substantial Hg methylation through increased availability of important substrates such as sulfate.

CONCLUSIONS

The magnitude, duration, and extent of peat oxidation produced by the prolonged period of drawdown and dryout in the northern Everglades, including plant-top or peat burns in some areas, likely caused substantial but short-term changes in the physical, chemical, and microbiological characteristics of the peat soil and its sulfur and mercury biogeochemistries following reflooding of these areas. These changes were not detectable at central Everglades sites that remained wet during this same period. These post-oxidation changes were followed by and likely caused a corresponding and rapid increase in MeHg production and a correspondingly rapid bioaccumulation in mosquitofish at WCA-2A-F1, a eutrophic site in the northern Everglades where foraging on benthic infauna is believed to predominate. At the oligotrophic site, WCA-2A-U3, where autotrophic food webs eventually develop, the maximum mosquitofish bioaccumulation response was delayed by about 120 days but was much greater. Follow-up studies are planned to measure the effect of changes in sediment and pore water chemistries on methylation and demethylation rates by dosing sediment cores collected in July, August, October, and November 1999 with stable isotopes of inorganic mercury.

A subsequent routine annual collection of mosquitofish, sunfish, and largemouth bass by the Florida Fish and Wildlife Conservation Commission for the District in September-November 1999 revealed an increase in the THg concentrations in young-of-the year fish over previous years at F1 and U3 in WCA-2A but not at WCA-3A-15 (Lange et al., 2000). Whether this pulse of MeHg will persist and continue to bioaccumulate in mid- and top-predator sport fish at these sites or dissipate with growth dilution and depuration over the next several years can only be determined through continued annual monitoring.

Proposed changes to the timing, routing, magnitude, duration, and frequency of water flow in the Everglades are intended to increase the average hydroperiod in the northern Everglades. This

may have the collateral benefit of decreasing the extreme peat oxidation conditions that could be exacerbating the Everglades mercury problem.

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