DEP Contract Review Form

DEP Contract No.:	SP618	Original Contract:	X	Amendment No.:	
Prog Reference:	N/A	Change Order No:		Funding Increment Increase No.:	

CONTRACTOR INFORMATION	
Name (Primary):	US Geological Survey
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Phone Number:	(608) 821-3803
FEID No.:	53-0196958

OF RESOURCE ENT & MGMT.
AUG -7 2002
ENVIRONMENTAL PROTECTION

Type:	Services	X	Grant		Commodities		Concession		Other	

DMS Class/Group:	973 - 360	Procurement Method:	Other government - EXEMPT

Are Federal Funds Supporting this Contract?	no	If yes, specify federal grant and CFDA No. below.
If the answer to the above was "No", are the State funds supporting this Contract being used as match to a federal grant?	no	If yes, specify the federal grant and CFDA below.
Federal Grant:		CFDA:

Are equipment purchases authorized under this Contract?	no	Will DEP retain ownership?	
Are land purchases authorized under this Contract?	no	Will DEP/BOT retain ownership?	

Minority Business Utilization Information for the Contractor:				
	Certified Minority Business?	N/A	Category:	
	Registered Minority Business?	N/A	Category:	

Contract Period:	Begin Date:	Execution 8-7-02	End Date:	6/30/03

Subject/ Brief Description of Contract:

MESOCOSM STUDIES TO QUANTIFY HOW METHYLMERCURY IN THE EVERGLADES RESPONDS TO CHANGES IN MERCURY, SULFUR, AND NUTRIENT LOADING

Funding Information:

Ceiling Amount:		Current Funding Amt:	$100,000

Note: For projects containing an object code of 75XXXX, the CSFA must be completed. Rec Type to be completed by Procurement Section.

Specify County where work is being performed: Statewide

Journal Transfer Information (29 digit account code, if applicable):

Org Code	EO	Fund/FID	Category	YR	Obj Code	CSFA No.	Rec Type	Activ Code	Grant No.	Module	Project No.	Amount
37250201002	LA	050001	030000	02/03	132600	N/A	N/A	N/A	N/A	8567	N/A	$100,000

Contract Management Information:	Division/District:	Resource Assessment and Management	Bureau/Office:	Mercury Program		
	Contract/Project Manager:	Donald M. Axelrad, Ph.D.	Telephone No. of Manager:	(850) 414-1347	MS#:	6540

Contract Review	Approved By - Signature	Date Approved
Contract Manager:		8/2/02
Budget Representative:	Karen Willian	8/2/02
Bureau Chief:	Thos. D. Atkeson	8/2/02
Div/District Director:		8-7-02
Quality Assurance:	Gordon R. Tittle	8/7/02
Contracts Administrator:	Ruth Heggen	7/31/02
General Counsel*:		7/31/02
Division/District IRM:	N/A	
Department CIO:	N/A	

Identify Delegation of Authority for Person Executing Contract: DEP Directive 125

Reviewer Comments:

Vendor Relationship. Checklist Completed

*Review/approval by the Office of General Counsel not required for state funded activities which utilize DEP 55-205 and are not in excess of Purchasing Category Three.

IMPORTANT!!! IMPORTANT!!! IMPORTANT!!!

Separation of Duties Notice

DEP Contract No: SP618 Amendment No.
DEP Contract Manager: Don Axelrad

The attached contract/contract amendment is being routed for review and execution by the Department. Adequate separation of duty is required in the procurement of goods and services by the Department. Please be advised that the subject contract/contract amendment must be executed by a reviewing authority for the DEP Contract Manager who is authorized to execute contracts on behalf of the Department. If the DEP Contract Manager happens to have the delegated authority to execute contracts on behalf of the Department, the DEP Contract Manager ***must not execute*** the attached contract/contract amendment.

Separation of duties, which is also referred to as segregation of duties, "involves ensuring that individuals do not perform incompatible duties. Duties are considered incompatible from a control standpoint when it is possible for an individual to commit an error or irregularity and then be in a position to conceal it in the normal course of his or her duties."[1]

[1]Boynton, William C. and Kell, Walter G., *Modern Auditing*, 6th ed., New York: John Wiley & Sons, Inc.,

If you have any questions regarding this notice, please contact the Contracts Office representative identified below for assistance.

Contracts Office Rep: Ruth Heggen RH	Phone: 850/922-5942
Date: 7-31-07	SunCom: 292-5942

NOTE: This Notice is to be maintained in DEP Contract Manager's file.

Form 9-1366
(Nov. 1998)

U.S. Department of the Interior
U.S. Geological Survey
Joint Funding Agreement
FOR
WATER RESOURCES INVESTIGATIONS

FL170
DEP Contract No. SP 618

TIN #:**596001874**

THIS AGREEMENT is entered into as of the day of by the U.S. GEOLOGICAL SURVEY, UNITED STATES DEPARTMENT OF THE INTERIOR, party of the first part, and the **FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION**, party of the second part.

1. The parties hereto agree that subject to the availability of appropriations and in accordance with their respective authorities there shall be maintained in cooperation **mesocosm studiesof to quantify how methylmercury in the Everglades responds to changes in mercury, sulfur, and nutrient loading (See attachments 1, 2, and 3, attached hereto and made a part hereof)**, hereinafter called the program.
2. The following amounts shall be contributed to cover all of the cost of the necessary field and analytical work directly related to this program.

   (a) **$0.00** by the party of the first part during the period **Execution** to **June 30, 2003**

   (b) **$100,000.00** by the party of the second part during the period **Execution** to **June 30, 2003**

   (c) Additional or reduced amounts by each party during the above period or succeeding periods as may be determined by mutual agreement and set forth in an exchange of letters between the parties.
3. The costs of this program may be paid by either party in conformity with the laws and regulations respectively governing each party.
4. The field and analytical work pertaining to this program shall be under the direction of or subject to periodic review by an authorized representative of the party of the first part.
5. The areas to be included in the program shall be determined by mutual agreement between the parties hereto or their authorized representatives. The methods employed in the field and office shall be those adopted by the party of the first part to insure the required standards of accuracy subject to modification by mutual agreement.
6. During the course of this program, all field and analytical work of either party pertaining to this program shall be open to the inspection of the other party, and if the work is not being carried on in a mutually satisfactory manner, either party may terminate this agreement upon 60 days written notice to the other party.
7. The original records resulting from this program will be deposited in the office of origin of those records. Upon request, copies of the original records will be provided to the office of the other party.
8. The maps, records or reports resulting from this program shall be made available to the public as promptly as possible. The maps, records or reports normally will be published by the party of the first part. However, the party of the second part reserves the right to publish the results of this program and, if already published by the party of the first part shall, upon request, be furnished by the party of the first part, at cost, impressions suitable for purposes of reproduction similar to that for which the original copy was prepared. The maps, records or reports published by either party shall contain a statement of the cooperative relations between the parties.
9. Billing for this agreement will be rendered **quarterly**. Payments of bills are due within 60 days after the billing date. If not paid by the due date, interest will be charged at the current Treasury rate for each 30 day period, or portion thereof, that the payment is delayed beyond the due date. (31 USC 3717; Comptroller General File B-212222, August 23, 1983.).

U.S. GEOLOGICAL SURVEY
UNITED STATES
DEPARTMENT OF THE INTERIOR

By _____
(SIGNATURE & TITLE)
Warren A. Gebert, District Chief

FLORIDA DEPARTMENT OF OF ENVIRONMENTAL PROTECTION

By _____ 8-7-02
Director, Division of Resource Assessment and Management or designee

By _____

By _____

(USE REVERSE SIDE IF ADDITIONAL SIGNATURES ARE REQUIRED)

ATTACHMENT 1

DEP Contract No. SP618
USGS Joint Funding Agreement No.: FL170

Additional Agreement Terms Required by Florida Statutes and DEP

1. The party of the second part (hereinafter referred to as the "DEP") reserves the right to unilaterally cancel this Agreement for refusal by the party of the first part (hereinafter referred to as the "USGS") to allow public access to all documents, papers, letters, or other material made or received by the USGS in conjunction with this Agreement, unless the records are exempt from Section 24(a) of Article I of the State Constitution and Section 119.07(1), Florida Statutes.

2. Each invoice must be submitted in detail sufficient for preaudit and postaudit review. A final invoice must be submitted no later than June 20, 2003, to assure the availability of funds for payment.

3. All travel costs incurred by the USGS are included in the fixed price amount of this Agreement and no additional travel expenses shall be authorized.

4. Pursuant to Florida Statutes, the DEP's Contract Manager shall have five (5) working days, unless otherwise specified herein, to inspect and approve the services for payment; the Department must submit a request for payment to the Florida Department of Banking and Finance within twenty (20) days; and the Department of Banking and Finance is given ten (10) days to issue a warrant. Days are calculated from the latter date the invoice is received or services received, inspected, and approved. Invoice payment requirements do not start until a proper and correct invoice has been received. Invoices which have to be returned to a contractor for correction(s) will result in a delay in the payment. A Vendor Ombudsman has been established within the Florida Department of Banking and Finance who may be contacted if a contractor is experiencing problems in obtaining timely payment(s) from a State of Florida agency. The Vendor Ombudsman may be contacted at 850/410-9724 or 1-800-848-3792.

5. In accordance with Section 215.422, Florida Statutes, the Department shall pay the Contractor, interest at a rate as established by Section 55.03(1), Florida Statutes on the unpaid balance, if a warrant in payment of an invoice is not issued within forty (40) days after receipt of a correct invoice and receipt, inspection, and approval of the goods and services. Interest payments of less than $1 will not be enforced unless a contractor requests payment. The interest rate established pursuant to Section 55.03(1), Florida Statutes, may be obtained by calling the Department of Banking and Finance, Vendor Ombudsman at the telephone number provided above or the Department's Procurement Section at 850/922-5942.

6. The State of Florida's performance and obligation to pay under this Agreement is contingent upon an annual appropriation by the Legislature.

7. A person or affiliate who has been placed on the convicted vendor list following a conviction for a public entity crime may not perform work as a contractor, supplier, subcontractor, or consultant under an agreement with any public entity, and may not transact business with any public entity in excess of the threshold amount provided in Section 287.017, F.S., for Category Two for a period of 36 months from the date of being placed on the convicted vendor list.

8. An entity or affiliate who has been placed on the discriminatory vendor list may not submit a bid on a contract to provide goods or services to a public entity, may not submit a bid on a contract with a public entity for the construction or repair of a public building or public work, may not submit bids on leases of real property to a public entity, may not award or perform work as a contractor, supplier, subcontractor, or consultant under contract with any public entity, and may not transact business with any public entity. The Florida Department of Management Services is responsible for maintaining the discriminatory vendor list and intends to post the list on its website. Questions regarding the discriminatory vendor list may be directed to the Florida Department of Management Services, Office of Supplier Diversity at 850/487-0915.

9. The USGS shall comply with all applicable federal, state and local rules and regulations in providing services to the DEP under this Agreement. The USGS acknowledges that this requirement includes compliance with all applicable federal, state and local health and safety rules and regulations. The USGS further agrees to include this provision in all subagreements issued as a result of this Agreement.

10. In accordance with Section 216.347, Florida Statutes, the USGS is hereby prohibited from using funds provided by this Agreement for the purpose of lobbying the Legislature, the judicial branch or a state agency.

11. The USGS agrees to comply with the Quality Assurance Requirements for the work being conducted under this Agreement which are outlined in Attachment 3.

ATTACHMENT 2

SCOPE OF WORK

MESOCOSM STUDIES TO QUANTIFY HOW METHYLMERCURY IN THE EVERGLADES RESPONDS TO CHANGES IN MERCURY, SULFUR, AND NUTRIENT LOADING

Principal Investigator:

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Submitted to:

Donald M. Axelrad, Ph.D.
Mercury Program
Florida Department of Environmental Protection
2600 Blair Stone Rd. MS 6540
Tallahassee, FL 32399-2400

Date: June 12, 2002

SUMMARY of research to be conducted by USGS in FY 2002/2003

For FY 2000/2001 USGS analyzed mesocosm samples collected in year 2000, specifically, isotopic-specific mercury analysis of total mercury and methylmercury for filtered surface water, suspended particulates, pore water, and mosquito fish. These results helped to answer basic questions like how much tracer must be added to measure it effectively in all of the key matrices; what are the rates of redistribution, transformations, and fluxes of the spike compared to the ambient Hg pools; what are reasonable sampling intervals.

For FY 2001/2002, mesocosm studies were conducted at several sites within the Everglades, representing 1) eutrophic high sulfate areas, where sawgrass still predominates, 2) areas within in the MeHg maximum and 3) oligotrophic, severely sulfate-limited areas. The mesocosms were dosed using Hg stable isotopes, and the effects of mercury, sulfate and nutrient loading on accumulation of mercury and MeHg in sediment, water and biota were determined.

For Florida DEP FY 2002/03, the mesocosm-dosing research will continue, and matrices of Hg, sulfate and phosphate additions will be examined.

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BACKGROUND

In 1994, a consortium of agencies began a multi-investigator study of the factors contributing to the high levels of Hg in Everglades' biota, the Aquatic Cycling of Mercury in the Everglades (ACME) project. The overall objective has been to understand Hg cycling well enough to create management strategies that will minimize MeHg bioaccumulation in the Everglades, while fulfilling other management objectives such as nutrient reduction and hydroperiod restoration. Methylmercury production appears to be favored in wetlands and impounded wetlands, which can produce and export MeHg (e.g. St. Louis et al. 1994; Krabbenhoft et al. 1995; Branfireun et al. 1996, Gilmour et al. 1998; Heyes et al. in prep.) in quantities that may ultimately lead to elevated fish MeHg concentrations (Driscoll et al. 1994; Cleckner et al. 1998; Krabbenhoft et al. in prep). High rates of microbial MeHg production, driven by high organic matter inputs and advective flows of nutrient bearing water, are the probable cause. The ACME project has focused on the processes that lead to from Hg deposition to MeHg formation and bioaccumulation.

What drives the high levels of MeHg in fish and other biota in the Florida Everglades? Is increased loading of Hg the more important factor, or are biogeochemical controls on Hg cycling more critical? The Everglades have been subject to many stresses of which high levels of Hg deposition (Dvonich et al. 1995; Guentzel et al. 1995) is just one. Hydroperiod alterations and eutrophication are key stressors and are the foci of restoration efforts under the Restudy. Sulfur enrichment in the Everglades is a stress with specific impacts on MeHg production. The source is sulfur amendments to agricultural fields in the EAA, used to achieve soil pH reductions after burning. Soil sulfur amendments help to reduce the amount of phosphorous fertilizer required for sugar cane production, and therefore reduce phosphorous runoff (Orem et al. 2000). However, the impact of oxidized sulfur, released as sulfate, on the Everglades Hg cycle is dramatic. Sulfate-reducing bacteria mediate Hg methylation and therefore we believe that agricultural S enhances MeHg production and bioaccumulation in much of the Everglades. Conversely, the end product of sulfate respiration, sulfide, inhibits Hg uptake by methylating bacteria, and hence MeHg production. In the most eutrophic portions of the Everglades, sulfide accumulation inhibits MeHg production. The balance between sulfate load and sulfide accumulation is a crucial factor in the control of MeHg production across the Everglades.

From 1995 to 1998, the ACME team studied the biogeochemical cycling of Hg in detail at a suite of sites across the Everglades. Sites spanned the roughly north to south trophic gradient generated from agricultural runoff, from the Everglades Nutrient Removal (ENR) Area, which is a re-constructed wetland, in the north, through heavily impacted Water Conservation Area (WCA) 2A, and south through more pristine WCA 2B and WCA 3A. The southern end of the ACME transect is in Taylor Slough in Everglades National Park. A site in Loxahatchee NWR was also examined as a potential analog for the historical Everglades in terms of hydroperiod and nutrient status. ACME process studies revealed a complex and dynamic Hg cycle in the Everglades. The study identified key processes that we were then able to examine across sites and across chemical gradients in the ecosystem. By combining this targeted distributional data with a variety of experimental studies, the ACME study was able to identify the key variables that influence MeHg production and bioaccumulation in the Everglades.

KEY FINDINGS OF THE ACME PROJECT:

- MeHg bioaccumulation is driven by internal MeHg production, mainly in Everglades' surface sediments.
  - Gross Hg methylation rates (as measured using tracer ^{203}Hg injected into intact sediment cores) are strongly correlated with MeHg concentrations (Gilmour et al. 1998; Gilmour et al. in prep.).
  - Methylation rate and MeHg concentration are almost always maximal at the surface of sediments (Gilmour et al. 1998; Gilmour et al. in prep.).
  - Microbial MeHg production and destruction are both very rapid in surface sediments (Gilmour et al. 1998; Marvin-DiPasquale et al 1998; 2000). However, net MeHg production appears to easily account for MeHg accumulation in sediments and in the food web.
  - MeHg concentrations in *Gambusia* are well correlated with MeHg concentrations in surface sediments (Krabbenhoft et al. in prep.).
  - MeHg concentrations in wet deposition are not sufficient to account for MeHg pools in the Everglades.

- MeHg concentrations in all matrices (surface sediment, sediment pore water, water, biota) are maximal in the central Everglades (WCA 2B and 3). MeHg is somewhat lower in more pristine areas like ENP and LNWR, and much lower in the most eutrophic areas, WCA 2A and ENR (Hurley et al. 1998; Clecker et al. 1998; Gilmour et al. 1998; Heyes et al in prep.; Krabbenhoft et al. in prep.).

- The spatial MeHg pattern is not driven primarily by total Hg concentration, although there is weak but significant relationship between Hg and MeHg concentrations in surface sediments. The slope of the relationship between Hg and MeHg varies among sites, and is steepest in the central Everglades. Therefore, this part of the ecosystem is most sensitive to Hg deposition.

- Sulfur has a large impact on MeHg production, but the magnitude and even direction of the impact varies with the sulfate and sulfide concentration.
  - Of the parameters measured by our group, pore water sulfide best predicts MeHg concentration in surficial sediments. Sulfide and MeHg concentration are inversely correlated across the northern Everglades (Gilmour et al. 1998; Heyes et al. in prep).
  - Sulfate concentrations and sulfate reduction rates in ENR and WCA 2A are very high, similar to the oligohaline region of an estuary (Hurley et al. 1998; Gilmour et al. 1998).
  - Experimental studies show inhibition of methylation by sulfide, and stimulation by sulfate, especially in the more pristine areas of the Everglades (Benoit et al. in prep.).

- Phosphate and nitrate generally had no direct effect on MeHg production rates in sediment cores.

- Anaerobic microbial processes, including sulfate reduction, are key components

of microbial organic carbon decomposition in Everglades peats and surficial flocs.

- Microbial sulfate reduction appears to be the most important mechanism for reduced S storage in Everglades peats. Stable isotope signatures show that the majority of reduced S stored in Everglades sediments, at both eutrophic and more pristine sites, arises from dissimilatory sulfate reduction rather than assimilation by plants (Orem et al. in prep).
- Sulfate reduction was readily measured in surface sediments from all sites using isotopic tracers (Gilmour et al. 1998; Gilmour et al. in prep.).

- MeHg may leave sediments and enter food chains through solute efflux from sediment porewaters, by movement of benthic invertebrates into the water column, and by direct grazing on surface sediments and benthic invertebrates.
  - MeHg efflux from sediments has a strong diel component. Solute efflux occurs mainly at night when the sediment water interface becomes suboxic. Migration of benthic zooplankton into the water column also occurs at night.

- The mechanism of sulfide inhibition of methylation is not the expected one (precipitation of HgS).
  - Hg concentrations in Everglades sediment porewaters are controlled by sorption of Hg to the solid phase rather than precipitation of cinnabar (HgS) (Benoit et al. 1999a).
  - Dissolved Hg complexation changes across a sulfide gradient. Neutral complexes dominate at lower (low :M) sulfide concentrations, while charged Hg-S complexes dominate at higher sulfide concentrations (Benoit et al. 1999b).
  - Hg is taken up by methylating bacteria through diffusion of neutral complexes across cell membranes (Benoit et al. 2001a,b); therefore sulfide inhibits methylation through the formation of charged complexes that are not bioavailable for uptake.
  - Hg methylation rates in cell cultures, and MeHg concentrations in Everglades' surface sediments can be predicted from the modeled HgS^0 concentration in solution (Benoit et al. 1999a; 2000).

- If surface sediments in ENR and other STAs are sulfidic, methylation rates should remain low in re-constructed Everglades wetlands. The pool of sulfur accumulated within the agricultural soils used for ENR is large.

- Methylation is very rapid in certain types of periphyton (Cleckner et al. 1999). Methylation occurs only in "mats" where microbial sulfur cycling occurs, and is most common in the less-calcareous periphyton found in eutrophic areas. MeHg production in periphyton may provide a very direct entry point for MeHg into the aquatic food web. However, for most of the Everglades, methylation in surface sediments appears to be the dominant source of new MeHg.

- Photochemical redox processes are key components of the Hg and MeHg budgets for the Everglades. Photochemical Hg(II) reduction and evasion are key loss mechanisms for Hg from surface waters. Photodemethylation of MeHg is also rapid. Daytime MeHg photodemethylation must be balanced against nighttime sediment efflux to create a mass

balance for MeHg.

- Sulfur stable isotope data and the depth-based historical record suggest that sulfur concentrations in Everglades peats are elevated above historical ambient concentrations over most of the ecosystem (Orem et al. 2000).

- Drying events and fire can trigger massive new MeHg production, apparently triggered by increased sulfate supplied by reoxidation of reduced sulfur pools within sediments. These events may provide another mechanism to quantify how the sulfate/sulfide balance controls methylation - by monitoring the sequence of sulfur oxidation, sulfate reduction and the re-accumulation of sulfide, along with MeHg production.

We conclude that sulfur and Hg loading are key parameters that control MeHg production and bioaccumulation in the Everglades. Our model for control of MeHg production by sulfur in the Everglades is that 1) high concentrations of sulfide inhibit MeHg production in the northern part of the ecosystem, 2) intermediate sulfate (~50-100 :M) and low sulfide (<10:M) concentrations in the central part of the system are optimal for methylation, and 3) sulfate concentrations in the most pristine areas (<25 :M) are sub-optimal for sulfate-reduction and MeHg production. This scenario implies that the excess load of sulfur to the Everglades minimizes MeHg production in WCA 2A, but stimulates MeHg production in WCAs 2B and 3A.

Within the ACME data set, the relationships between sulfate, sulfide and MeHg in the northern (ENR to site 3A15 in WCA3) part of the system are significant. This correlative relationship is supported by experimental sulfide addition studies and by our biogeochemical models. The relationship between sulfur and methylation in the southern part of the system is less clear, mainly because of lower data density. However, data in hand show a positive relationship between sulfate and MeHg south of 3A15, and experimental studies show sulfate stimulation of methylation in surface sediments. This information supports the idea that the very low sulfate concentrations found in Taylor Slough and central LNWR limit the activity of SRB and therefore limit methylation rates. Sulfate concentrations in the freshwater marsh within ENP, and in central LNWR probably best reflect historical sulfate concentrations, which would have been derived mainly from rain.

The relationship between Hg and MeHg concentrations in sediments across the Everglades is weak but significant. Total Hg concentrations in surface sediments varied by about a factor of three across the gradient studied, while MeHg concentrations varied by more than two orders of magnitude. As noted above, the slope of the MeHg:Hg relationship varies among sites, and is steepest in the central Everglades. Therefore, this part of the ecosystem is most sensitive to changes in Hg deposition. Concentration dependence experiments to date have also shown a non-linear response of methylation rate to added Hg, with the magnitude of the response strongly affected by sediment chemistry. Because the gradient in Hg concentration across the study sites is fairly small, and because of the overriding influence of sulfur chemistry, careful quantification of the relationship between Hg loading and MeHg production using the Everglades field data set is difficult.

Nutrients (phosphate and nitrate) generally had no direct effect on MeHg production rates

in sediment cores. However, nutrients probably DO have indirect effects on MeHg production through plant growth and organic matter supply. These remain poorly understood. The organic matter supply to sediments affects microbial activity in sediments, and will control sulfate-reduction and sulfide production rates at locations where sulfate is not limiting. Further, dissolved organic carbon acts as a strong ligand for Hg (Ravichandra et al. 1999; Benoit et al. 2000) and for MeHg (Hintelmann et al. 1995) and may inhibit the uptake of MeHg into biota. Strong correlations between MeHg in surface sediments and MeHg in biota suggest that DOC does not severely impact the bioavailability of MeHg for uptake. However the impact of DOC on Hg availability for methylation bears more attention. Nutrients co-vary with sulfate in a general sense across the ecosystem, having the same agricultural source, and decreasing in concentration with distance from that source. Therefore, the effects are somewhat difficult to separate using the field data and correlative approaches. While the effects of sulfate addition are rapid, through microbial sulfate reduction, and can be tested in short-term experiments, nutrient effects on Hg cycling that are mediated through plant growth need to be examined over the longer term.

MESOCOSM EXPERIMENTS TO QUANTIFY RESPONSE TO CHANGES IN HG, S AND NUTRIENT LOADING

Everglades' restoration efforts are underway, beginning with STA construction, and including changes in flow path and rates, in water storage, and potentially including controls on Hg emissions. These changes are intended primarily to reduce nutrient loads to the Everglades, to restore more natural flow and hydroperiod, and to provide water storage and flood control to South Florida. Stormwater treatment areas are designed to reduce phosphate loading to the northern Everglades, but to date, they do not appear to have a large impact on sulfate loading (Miles and Fink 1998). However, other restoration efforts that change the timing, path and rate of flow may substantially alter delivery of nutrient, sulfur and Hg to the Everglades.

In order to model the potential effects of Everglades restoration efforts on Hg cycling, the relationships between sulfur, nutrient and Hg loading and MeHg production and bioaccumulation need to be better, and separately, quantified. In the next phase of this research, we propose to better quantify these individual relationships, and the interactions among these three key parameters, through amendments of Hg, S and nutrients, individually and in combination, to *in situ* mesocosms. Short-term addition experiments are useful in examining processes, but may not predict long-term responses, for a number of reasons. Response of plant growth to nutrients is the obvious example, but other changes, like changes in Hg speciation and bioavailability over time, or development of microbial communities, are also important. An understanding of the relationship between Hg, S or nutrient loading and MeHg production and bioaccumulation requires a long-term, large scale approach because there are many steps between the entry of inorganic Hg to the ecosystem, its conversion to the methylated form, and bioaccumulation in fish.

We propose to use stable Hg isotope amendments to examine the relationship between Hg loading and MeHg production and bioaccumulation. This new approach will allow us to track the fate of newly deposited Hg separately from the larger existing pools, and to track the bioavailability of new Hg over time. The use of individual stable Hg isotopes will allow us to follow the cycle of new Hg added to the system, from initial partitioning, accumulation in

vegetation, MeHg production and accumulation in sediments, fluxes and accumulation in the food web. We will also be able to trace burial, post-depositional reworking of Hg through sediments and plants, and Hg^0 formation. Important unknowns that stable isotopes will allow us to address are the changes in phase speciation of newly-deposited Hg over time, the relative availability of new Hg for methylation as phase speciation changes, bioavailability from decaying plant material relative to sediments for methylation, and the recycling of buried Hg to the sediment surface through plant growth and decay.

We also propose to make sulfur amendments as either a stable or radioisotope for the same reason. Sulfur isotope additions will allow us to find out how fast sulfide is turned over is sediments and made available again for sulfate reduction (through photosynthetic reoxidation of sulfide), a key variable in modeling the relationship between sulfate load, sulfate reduction rate and sulfide accumulation in the oligotrophic Everglades. Isotopes will also allow us to track what fraction of newly added sulfate is retained in sediments.

HYPOTHESES

Our working hypotheses for this study are:

- Changes in S load will have immediate effects on MeHg production and bioaccumulation. Increased S load will increase MeHg production at oligotrophic sites and decrease MeHg production at eutrophic sites.

- Changes in Hg load will have immediate effects on MeHg production and bioaccumulation. Changes in MeHg production will be roughly proportional to Hg load at mesotrophic sites, but less than proportional at eutrophic and oligotrophic sites.

- New Hg added to mesocosms will become rapidly less bioavailable for methylation and bioaccumulation over time.

- Nutrients will influence MeHg production, bioaccumulation and photodemethylation in the longer-term, mediated through plant growth and turnover and DOC production.

OBJECTIVES FOR MESOCOSM STUDIES IN 2000-2003

Using amendments to mesocosms, we will address the following objectives:

1) How will changes in Hg loading affect the magnitude and spatial distribution MeHg production and bioaccumulation in the Everglades?

2) How will changes in sulfur loading affect MeHg production and bioaccumulation in the Everglades?

3) How will changes in nutrient loading affect MeHg production and bioaccumulation in the

Everglades?

4) How do these stressors interact to affect MeHg production and bioaccumulation?

5) How do the effects of these stressors change across the trophic gradient of the Everglades?

RESULTS AND BENEFITS EXPECTED

This work will provide information needed for the management of mercury during Everglades restoration. Specifically, we will work with the developers of the Mercury Cycling Model (MCM) to incorporate new information from this study into that model. Overall, knowledge gained from the ACME study will be used to help predict how construction of the STAs, changes in hydroperiod, flow and other potential management practices, like changes in sulfur loading, will affect MeHg production.

The key management question to be addressed by this research is ***"How will changes in nutrient, sulfur and Hg load that occur as a result of restoration efforts affect the distribution and magnitude of MeHg production in the Everglades?"*** Specific management questions include:

- Do eutrophic, mesotrophic, and pristine sediments respond differently to Hg inputs? What is that magnitude of the difference in response?

- Would changes in sulfur load to the Everglades be, on balance, harmful or helpful with regard to MeHg?
    - What would happen if sulfur input to the Everglades from agriculture was reduced? Would the MeHg maximum move north? Would magnitude of the maximum increase or decrease?
    - How low would sulfate concentration have to be to in the central Everglades to significantly reduce MeHg bioaccumulation?
    - Is there enough sulfur stored in sediments now to support strong methylation for many years despite reductions in new S loading?

- Which management practice changes would have the largest benefit in reduction in MeHg production? Would changes in sulfur, Hg or nutrient loadings be most beneficial?

- How rapidly does MeHg production in the marsh respond to potential changes in phosphate, sulfate and Hg loading? Will a decrease in Hg load result in a proportional and immediate decrease in MeHg production?

- Will a decrease in the nutrient load to the northern WCAs change redox conditions and sulfide chemistry in surface sediments even if sulfate loading does not change? Changes in vegetation type and decreased growth rate resulting from reduced nutrient loads may reduce anoxia and sulfide production in sediments, which may in turn affect Hg methylation rates.

STUDY DESIGN

Mesocosm studies will be conducted at four to five sites within the Everglades, representing 1) eutrophic high sulfate areas, preferably where sawgrass still predominates, 2) areas within in the MeHg maximum and 3) oligotrophic, severely sulfate-limited areas. Sites will be chosen from the suite of sites studied intensively by ACME, based on site chemistry, background data and the logistics of access. Primary candidate sites are U3 in WCA 2A for the eutrophic site, 2BS in WCA 2A or 3A15 in WCA 3A for the intermediate sites and either Loxahatchee NWR or a site in Taylor Slough in ENP for the pristine site.

The primary endpoint variables in the mesocosm studies will be MeHg and total Hg concentrations in surface sediments and pore waters, surface water, plants and *Gambusia*. A known density of mosquito fish will be used in each ACME enclosure (when closed) as the endpoint for MeHg bioaccumulation. Additionally, processes that influence Hg fate, transport and bioavailability will be examined, for example Hg loss through evasion, Hg storage and bioavailability in various sediment pools, and photodemethylation.

At each of four mesocosm sites, the quantitative relationships between each of the three individual stressors - S, Hg and phosphate - and MeHg will be examined individually. Interactions between stressors will then be examined based on the outcome of the single stressor experiments at each site. During 2000, Hg-addition studies were conducted at 4 sites using newly installed ACME mesocosms. Also during 2000, Dr. Sue Newman of the SFWMD allowed us to sample in the District's nutrient-addition mesocosms, which let us examine the effects of PO4 on MeHg in mesocosms that were already in near-steady state with respect to nutrient loading. SFWMD operated PO4-addition mesocosms at 6 sites across the trophic gradient of the Everglades during 2000. During 2001, we will begin SO4-addition studies in ACME mesocosms. By early 2002, at least one dosing study for each stressor will have been completed at each site. If repeated dosing studies are needed to clarify patterns, they will be accomplished in late 2001 and the first half of calendar 2002. Matrices of Hg, sulfate and phosphate additions will be examined during 2002 and 2003.

Parameters to be examined in the mesocosms: In addition to the key endpoints identified above - Hg and MeHg in certain matrices - we will examine the following parameters:

- Details of surface and porewater chemistry, including sulfur chemistry, DOC amount and character;
- Water column cycling of Hg, e.g. photochemical and biological reduction and volatilization, and MeHg photodemethylation
- Stable isotopes of C, N, and S will be used to track food web structures.
- Potential Hg^0 volatilization through vegetation

Biogeochemical studies imbedded within this study design: A number of specific biogeochemical processes will be examined within the basic mesocosm study design. These studies represent continuation of work on key processes identified during the ACME study, and include:

- Solid phase Hg speciation as a measure of bioavailability and storage
- Hg(II) bioavailability to methylating bacteria.

- Distribution of SRB species across the S gradient of the marsh
- Development of methods for measurement of net and gross MeHg production and degradation using stable isotopes.

Hg-addition mesocosms

Prior to the start of this contract, Hg-addition mesocosm studies were begun in May 2000 with funding from other sources (EPA and USGS). Ten mesocosms were installed at each of four Everglades sites. Opaque polyethylene cylinders, 1m in diameter, were installed at sites F1 and U3 in WCA 2A, at site 2BS in WCA 2B and at site 3A15 in WCA 3A. Cylinders were drilled with 3" diameter holes to allow water flow, although the holes were plugged for 5-6 days after Hg spikes. The mesocosms inserted to about 20 cm depth by cutting into the peat around the edge of the cylinder with a saw. Boardwalks were constructed along the sets of mesocosms for stability, and to allow access with less disturbance of the surrounding sediments. Site vegetation was left intact. Access to study sites was by airboat or helicopter.

Enclosures were amended with Hg across a concentration range from sub-ambient (achieved using rain shields over closed enclosures) to roughly 5X ambient atmospheric Hg deposition rates in south Florida. The mesocosms were be dosed using Hg stable isotopes, pre-equilibrated with local rainwater. We chose to run these studies during the rainy season, which runs from about May until about October. The Everglades receives most of its Hg loading during summer rains and there is evidence that Hg in summer rains is more "reactive" or bioavailable, than in winter (Guentzel 1997; Landing et al. 1995, 1998). Further, Hg methylation rates and MeHg concentrations in soil pore waters are maximal during summer.

Mercury-202 spikes were made to 3 enclosures at each site in May 2000. Mercury partitioning and methylation were followed closely in a number of matrices for about a week after the spike and then checked again after 2 months. A second spike, this time of Hg-202, was made into the same three mesocosms at each site in Sept. 2000. Again, Hg partitioning and methylation were followed closely for a week after the spike and then checked again after about 2 months. A spreadsheet detailing the design of this study is attached to this SOW. This set of experiments was designed to accomplish the following:

1. First trial for timing and magnitude of pool labeling after a stable isotope Hg spike.
    a. examine detection limit for stable isotope addition in each matrix (water, sediment, pore waters, plants, periphyton)
    b. monitor time over which all matrices are labeled with isotope
    c. monitor time over which MeHg formation/accumulation occurs in all matrices

2. Obtain Hg dose/response curves for 4 sites with different trophic and S conditions.

3. Test stable isotope Hg-methylation methods
    a. Test ^{203}Hg methylation methods against stable isotope Hg methylation rate measurements in intact cores
    b. Test stable isotope methylation rate measurements against the background of another Hg isotope spiked into mesocosms

4. Deal with basic enclosure sampling issues.
    a. Can we sample cores repeatedly w/o disturbing the system too much?
        Compare repeatedly cored mesocosms to "undisturbed" mesocosms.
    b. How do we sample "undisturbed " sediment cores from within mesocosms
        Trial sediment sampling methods.
    c. How long do mesocosms mimic real world?
        Monitor basic and Hg parameters inside and outside mesocosms

These first experiments are helping to answer basic questions like how much tracer must be added to measure it effectively in all of the key matrices; what are the rates of redistribution, transformations, and fluxes of the spike compared to the ambient Hg pools; what are reasonable sampling intervals; etc. Key design questions for this mesocosm study are the whether the advantages of open systems outweigh the need for Hg and MeHg budgets; how long open and closed mesocosms can be run and still mimic the real world; and how often the enclosures should be dosed.

Analysis of about 100 HgT and 100MeHg sediment isotope samples by ICPMS was accomplished in FY 2001 under a previous contract.

Nutrient-addition mesocosms

The SFWMD has used mesocosms at six Everglades sites to study the effects of phosphate loading on production, periphyton and macrophyte growth and P storage in sediments. These 2 m diameter open –design mesocosms have been dosed with a range of phosphate concentrations over the last one to three years. Changes in emergent vegetation and periphyton communities have had significant time to develop. These mesocosms have received ambient levels of atmospheric Hg deposition during that time. Any changes in MeHg accumulation in response to changes in nutrient loading should be evident by now. Although we will not be able to examine Hg mass balances or MeHg in mobile biota in these open mesocosms, the ACME study showed that MeHg in surface flocs is extremely good predictor of MeHg in *Gambusia* across the Everglades.

During 2000, ACME and SFWMD sampled surface sediments (0-4 cm) from each of these mesocosms. Porewater and surface water samples were taken from a subset of sites. A spreadsheet detailing the design of this study is attached to this SOW. Analysis of these samples for HgT, MeHg and reduced S pools samples will allow us to estimate the influence of phosphate alone on MeHg and on S-cycling. These samples are also awaiting analysis. Analysis of about 35 HgT and 105 0MeHg sediment isotope samples will be accomplished in FY 2001 under this contract. The chance to collaborate with Dr. Newman and to build on the SFWMD's knowledge base on mesocosm work and nutrient effects adds invaluably to this study

Sulfate-addition mesocosms

Sulfate addition studies will focus on the effects of increasing SO4 loads at low SO4 sites. We are confident that sulfide inhibits MeHg production at high SO4 concentrations and want to examine stimulation of MeHg production by SO4 in the less-impacted parts of the ecosystem. Therefore, we will conduct these studies at sites in central WCA1, U3 in WCA2, 2BS in WCA 2B and 3A15 in WCA 3A. At U3 and 2BS we will use mesocosms installed in May

2000 (unamended and open to flow since that time). Fifteen new mesocosms were installed in WCA1 in January 2001, as well as 5 additional mesocosms at 3A15. The large number of mesocosms will allow us to also begin to study DOC effects (in separate mesocosms) while we are running the sulfate study.

The range of sulfate loadings to mesocosms will vary across the sites, based on ambient concentrations, and the probable sulfate concentrations at each site given restoration scenarios. For example, at site 3A15 in central WCA 3A, ambient sulfate concentrations range from < 1 μM to about 100 μM, and could either increase or decrease after restoration. Increased flow might carry sulfate farther south; while implementation of BMP for sulfur use on the cane fields could decrease overall S load. At this site, loadings might be made to achieve surface water concentrations ranging from sub-ambient to roughly 5X the ambient average, e.g. 0 to 250 μM. In WCA 2A however, it is unlikely that restoration would increase S load any further. Therefore target concentrations for this site would range down from ambient loadings, ranging from maybe 50 to 500 μM. Reductions in sulfate load will most likely be generated by maintaining closed systems and allowing sulfate depletion to occur. Sulfate additions to mesocosms above ambient concentration will need to be made frequently to prevent depletion.

ANALYTICAL METHODS

Most of the methods to be used in this work are in place in our laboratories and have been described in detail in prior proposals, publications, and in the FL DEP RQUAP for the ANSERC effort within ACME. Hg stable isotopes will be used to 1) trace Hg additions in mesocosms and 2) make instantaneous and simultaneous measurements of Hg methylation and demethylation. The QA plan developed for SP595 is applicable to this DEP FY 2002/2003 research.

Use of stable Hg isotopes. In order to follow the Hg added to our study ecosystems separately from existing pools, we make use of the many stable isotopes of Hg. The ability to use stable Hg isotopes should result in a fundamental improvement in our ability to study Hg in the environment. The use of Hg stable isotopes to trace new Hg is a novel approach in the Hg research community will require some time to develop. Development of new ICP-MS analytical methods for Hg isotopes for use in biogeochemical cycling in the environment is a fundamental component of this study. Natural mercury is a mixture of 7 stable isotopes, 6 of which occur in greater than 5 % abundance. By adding new Hg to the system as one particular isotope, the new Hg can be traced through the ecosystem by monitoring changes in the ratios of the Hg isotopes in different matrices, or essentially by measuring isotope dilution. Stable isotopes are commonly used to measure rate reactions of major nutrients (e.g. C and N), mainly as tracers. Here, however, we propose a change in overall Hg concentration in the study enclosures, with the entire addition as a single isotope. We feel this is a reasonable approach for a trace metal like Hg because the concentration of mercury *in situ* is very low (parts per billion in sediments; parts per trillion in water) and therefore the amount of isotope needed is relatively low.

Analysis of Hg stable isotopes using ICP-MS. During this project, much of our routine Hg and MeHg analysis will switch from CVAF-based detection to ICP-MS based detection. The switch will allow determination of isotope ratios pursuant to the mesocosm loading studies and the instantaneous rate measurements. The recent improvements in ICP-MS instrumentation have

lead to an explosion in technique development for Hg measurement. Techniques for GC separation followed by ICP-MS detection have been developed for the analysis of inorganic and methylated Hg species (e.g. Hintelmann et al. 1997; Falter and Ilgen 1997; Wasik et al. 1998; Tao et al. 1998; Amouroux et al. 1998). However, method development will be a large part of this research. As of 1998, only Hintelmann had developed techniques for the use of Hg stable isotopes for biogeochemical studies. During 1999, both the USGS Middleton and University of Maryland, Chesapeake Biological Laboratory began development work on these methods. Stable isotope analysis of total Hg and MeHg is now in place at both labs. Preliminary analysis of methylation rate measurements made using ^{199}Hg in May 2000 in the Everglades enclosures suggest that methylation rates are easily measurable with these methods.

For this study, analyses will be performed on an ELAN 6100 instruments at USGS Middleton, and at ANSERC. We will continue to perform intercalibrations within the Florida Hg studies program and within our other research programs, particularly METAALICUS.

When stable isotopes are used, analysis of most samples for Hg and MeHg follows the now standard low-level CVAF-based techniques (i.e. EPA method 1631 for total Hg, and distillation, ethylation and sparge and trap onto Tenax for MeHg), substituting ICP-MS for CVAFS as the detector. The HP 4500 ICP-MS has an extra gas inlet line for the introduction of a blend gas when analyzing high organic matrices, and this port is used to allow the direct connection of the isothermal GC separation system to the inlet line of the ICP-MS system. This system is comparable to the setup of others (Hintelmann et al. 1997; Falter and Ilgen 1997). Addition of a specific isotope (isotope dilution) can be used during to track analytical recoveries, a perennial problem in Hg and especially MeHg analyses, and to allow correction for these losses. We currently have isotopes 199 (91.1% pure); 201 (91.9% pure) and 202 (99.9% pure) in stock. While other isotopes can be used in addition to the ones mentioned above, use of ^{204}Hg is complicated by the potential interference from ^{204}Pb (e.g. Hintelmann et al. 1997).

Development of stable isotope methods for measurement of net and gross MeHg production. Accurate determination of instantaneous Hg methylation and demethylation rates has historically been problematic and the subject to much interpretation. The first rate measurements were made using radioisotopes added to sediment slurries (Rudd et al. 1983; Xun et al. 1987). As awareness grew, methods evolved toward the use of less disturbed samples, and much lower added concentrations of radiolabel. During the last 5 years we have made methylation rate measurements using tracer additions of ^{203}Hg to intact sediment cores, as described in Gilmour and Riedel (1995). High specific-activity $^{203}HgCl_2$ (up 47 mCi mg^{-1}) has been being produced for this work by custom synthesis from ^{202}Hg. The specific activity of the ^{203}Hg is usually sufficient to act as a tracer in natural sediments and waters. The ^{203}Hg is pre-incubated with filtered sediment porewaters before injection into cores, to allow formation of dissolved Hg complexes. However, the bioavailability of Hg spiked into sediments relative to *in situ* pools is not well understood. Most rate estimates are probably overestimates because the spike is more available than Hg in sediments. Understanding the sediment/water partitioning, and the solid phase partitioning of ambient Hg and of Hg spikes has been and continues to a focus of our methylation research.

Demethylation rate measurements have been more difficult than methylation rate estimates. To date, there has been no available separate tracer for MeHg demethylation. The

specific activity of ^{14}C is too low to use as a tracer in most sediments. However, significant new understanding of the kinetics and pathways of demethylation have recently been made (Marvin-DiPasquale and Oremland 1998). The use of carbon-labeled MeHg does allow identification of the products of demethylation, which may be an indicator of the biogeochemical pathways of degradation (Oremland 1991, 1995). Demethylation by sulfate-reducing bacteria and methanogens appears to be the major demethylation pathway in anoxic sediments, further complicating the relationships between sulfur, organic carbon and net methylation.

Because of the lack of a tracer for demethylation, concomitant methylation and demethylation measurements with trace-level spikes have not been made. The use of multiple stable Hg isotopes should provide, for the first time, a method for simultaneous measurement of Hg methylation and MeHg demethylation within the same sediment sample, without significantly increasing the total Hg and MeHg concentrations in the sample (Hintelmann and Evans 1997). By adding Hg and MeHg as two different Hg isotopes, the rates of change of both tracers can be followed simultaneously, and from the same sample. Development and testing of this technique will be accomplished in year 1 of this study. We will also determine how to use stable isotopes for instantaneous rate measurement in samples from the Hg-loading study where one of more Hg isotopes has already been altered.

Methods for making rate measurements will be essentially those described in Gilmour and Riedel (1995), with a stable Hg isotope substituted for ^{203}Hg; and an additional spike used to trace demethylation. Use of the ^{203}Hg method in other ecosystems, the Florida Everglades and a northern seepage lake, is described in Gilmour et al. (1998) and Krabbenhoft et al. (1998). Mercury methylation and MeHg demethylation will be measured simultaneously in cores removed from the sediment or soil, by injecting, for example, $^{199}Hg(II)$ and $Me^{202}Hg$, at 1 cm depth intervals into intact cores. Use of intact sediment cores is critical to rate measurements, as *in situ* gradients in microbial activity and redox chemistry must be preserved. Sediments are incubated over short time periods (hours), chosen from the linear portion of the rate curves. After incubation, sediments are extruded from core barrels and 1 to 2 cm sections frozen for later analysis of end products by ICP MS. During 2000, methylation rates measured using stable isotopes will be directly compared with rates measured using ^{203}Hg to provide an analytical control. Initial comparisons were made in May 2000 in Florida.

Division of sampling and analytical responsibilities among laboratories:

Surface water chemistry: USGS Middleton/Reston
Sediment chemistry: ANSERC
Biota sampling: UW Madison
Surface and pore water Hg, MeHg including stable Hg isotopes:
USGS Middleton/ANSERC
Sediment Hg, MeHg, including stable Hg isotopes: ANSERC
Methylation and demethylation rates: ANSERC
Major anions (SO4, Cl) by IC in surface and pore waters: USGS Reston
Nutrients (NO3, PO4, NH4): USGS Reston
Sulfide in surface and pore waters: ANSERC/USGS Reston
Sediment S chemistry: USGS Reston and ANSERC
Hg/MeHg concentrations in biota: UW Madison
Sediment microbial activity including sulfate reduction rates: ANSERC

PROJECT MANAGEMENT AND BUDGET JUSTIFICATION

The project will be supervised by David Krabbenhoft at the USGS, Middleton, WI and William Orem at the USGS Reston, and Cynthia Gilmour at the Academy of Natural Sciences Estuarine Research Center (ANSERC),. This study will be done simultaneously with a whole-watershed Hg-dosing study being conducted in a boreal ecosystem in western Ontario by Gilmour and Krabbenhoft and many others. The interaction between the studies should increase the usefulness of both. The substantial developmental work involved in using Hg stable isotopes will be shared between these projects.

Partial funding for this work is already in place. ANSERC is funded for limited Hg-addition studies in Everglades mesocosms under USEPA STAR grants "Response of methylmercury production and accumulation to changes in Hg loading: A whole-ecosystem mercury loading study" to C.C. Gilmour, A. Heyes, R.P. Mason and J.W.M. Rudd and "Understanding the role of Sulfur in the Production and Fate of Methylmercury in Watersheds" to R.P. Mason and C.C. Gilmour. Total funding for FL under the grants is about $120,000 each year for 2001 and 2002. The Gilmour STAR grant provides salary and supply support for methylation-related studies in Hg-addition mesocosms at 3 Everglades sites. The Mason grant supports associated process work on Hg bioavailability and methylation. In 2000, the USGS provided supports for ACME-related activities in south Florida at a level of $ 221,000

None of the existing funding sources provide logistic or equipment support for mesocosm work. This request to DEP includes logistic support of all proposed mesocosm studies in the Everglades, specifically, support for airboat and helicopter costs for site access, and for construction of mesocosms and associated docks. Additionally, the request would provide salary and supply support for sulfur and nutrient addition studies not funded under existing mechanisms. Some stable isotope has already been purchased, and forty mesocosms (1m diameter) have already been purchased and emplaced. These costs are not reflected in the budget below.

USGS Budget

In order to assess the role of sulfur loading in the mercury cycle of the Everglades, 20 additional mesocosms were established at the Loxahatchee National Wildlife Refuge (LNWR). This site was chosen for the sulfur loading experiments because LNWR is a low-sulfur environment, and thus the added sulfate should induce a change in the sulfur cycle of the dosed mesocosms with anticipated influences on methylmercury production and bioaccumulation response. Florida DEP funding will support the staff at the LNWR to allow them to provide assistance to USGS to conduct these experiments. Logistic support will include airboat transport of the ACME Team, assistance in sampling the mesocosms following the sulfate additions, and performing the subsequent sulfate doses and possibly some sampling after training by the ACME staff for the first dosing.

For Florida FY 2002/2003, support for about 2 months (40 days) of Dr. Krabbenhoft's time, and about 7.5 months (150 days) of technical assistance is requested. Technical assistance will be provided by Mark Olson, John DeWilde and others. Olson and DeWilde have been part

of the ACME team for five years. A supply budget of about $13,700 for the year includes laboratory and field supplies, with maintenance and operation of the ICP requiring liquid Argon ($350/tank and up to 2 tanks per week needed), platinum cones, vacuum tubes, and vinyl gloves, acids, Teflon bottles etc. are also needed. The travel budget of about $7,500 will partially support travel to the field sites and airboat costs. Four 10-day field trips to the Everglades are planned in 2002/03, each involving 4 USGS staff. The cost of these 4 field trips alone - airfare, hotel, and car rental - is estimated at $15,000. Airboat time is $500 per day and ca. 10 days are needed. USGS funds will cover most of the travel costs involved in this project.

DELIVERABLES

A comprehensive final report addressing the "**HYPOTHESES**" and "**OBJECTIVES FOR MESOCOSM STUDIES IN 2000-2003**" as outlined in this SCOPE OF WORK will be delivered to the DEP contract manager by May 31, 2003. Quarterly progress reports will be provided with quarterly invoices.

BUDGET

BUDGET	**FY 02/03**
Salaries	$44,317
Expenses	$21,303
Indirect	$34,380
Total	$100,000

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REFERENCES

Amouroux, D., Tessier, E. Pecheyran, C. and Donard, O.F.X. 1998. Sampling and probing volatile metal(oid) species in natural waters by in-situ purge and cryogenic trapping followed by gas chromatography and inductively-coupled plasma spectroscopy (P-CT-GC-ICP/MS). Analytical Chemica Acta 377:241-254.

Benoit, J.M., C.C. Gilmour and R.P. Mason. 2001. Aspects of the Bioavailability of Mercury for Methylation in Pure Cultures of *Desulfobulbous propionicus* (1pr3). Appl. Environ. Microbiol. 67:51-58.

Benoit, J.M., C.C. Gilmour and R.P. Mason. 2001. The influence of sulfide on solid-phase mercury bioavailability for methylation by pure cultures of *Desulfobulbous propionicus* (1pr3). In press. Environ. Sci. Technol. 35 : 127-132.

Benoit, J.M. 2000. Sulfide Controls on Mercury Methylation by Sulfate Reducing Bacteria. Ph.D. dissertation. Univ. Maryland. 128 pp.

Benoit, J.M., R. P. Mason and C.C. Gilmour. 1999. Estimation of mercury-sulfide speciation in sediment pore waters using octanol-water partitioning and implications for availability to methylating bacteria. Environ. Toxicol. Chem. 18:2138-2141.

Benoit, J.M., C.C. Gilmour, R. P. Mason, and A. Heyes. 1999. Sulfide Controls on Mercury Speciation and Bioavailability in Sediment Pore Waters. Environ. Sci. Technol. 33:951-957.

Branfireun, B.A., A.Heyes and N.T. Roulet. 1996. The hydrology and methylmercury dynamics of a Precambrian Shield headwater peatland. Water Resour. Res. 32:1785-1794.

Cleckner, L., C.C. Gilmour, D. Krabbenhoft, P. Garrison, and J. Hurley. 1999. Methylmercury production by periphyton in the Florida Everglades. Limnol. Oceanogr. 44:1815-1825.

Cleckner, L.B., P.J. Garrison, J.P. Hurley, M.L. Olson and D.P. Krabbenhoft. 1998. Trophic transfer of methyl mercury in the northern Everglades. Biogeochemistry. 40: 347-361.

Dvonch, J.T., A.F. Vette, G.J. Keeler, G. Evans and R. Stevens. 1995. An intensive multi-site pilot study investigating atmopsheric mercury in Broward County, Florida. Wat. Air Soil Poll. 80:169-178.

Falter, R. and G. Ilgen. 1997. Determination of trace amounts of methylmercury in sediment and biological tissue by using water vapor distillation in combination with RP C18 preconcentration and HPLC-HPF/HHPN-ICP-MS. Fresenius J. Anal. Chem. 358:401-406.

Gilmour, C.C., G.S. Riedel, M.C. Ederington, J.T. Bell, J.M. Benoit, G.A. Gill and M.C. Stordal. 1998. Methymercury concentrations and production rates across a trophic gradient in the northern Everglades. Biogeochemistry. 40: 327-345.

Gilmour, C.C. and G.S. Riedel. 1995. Measurement of Hg methylation in sediments using high specific-activity 203Hg and ambient incubation. Wat. Air Soil Poll. 80:747-756.

Guentzel, Jane L. (1997). The Atmospheric Sources, Transport, and Deposition of Mercury in Florida. Ph. D. dissertation, Department of Oceanography, Florida State University, 177p.

Guentzel, J.L., W.M. Landing, G.A. Gill, and C.D. Pollman (1995). Atmospheric deposition of mercury in Florida: The FAMS Project (1992-1994). Water, Air, and Soil Pollution, 80: 393-402.

Hintelmann, H. and R.D. Evans. 1997. Application of stable isotopes in environmental tracer studies - Measuement of monomethylmercury by isotope dilution ICP-MS and detection of species transformation. Fesenius J. Anal. Chem. 358:378-385.

Hintelmann, H., P.M. Welbourn and R.D. Evans. 1995. Binding of methylmercury compounds by humic and fulvic acids. Water Air Soil Pollut. 80:1031-1034.

Krabbenhoft, D.P., J.M. Benoit, C.L. Babiarz, J.P. Hurley and A.W. Andren. 1995. Mercury cycling in the Allequash Creek Watershed, Northern Wisconsin. Wat. Air Soil Poll. 80: 425-433.

Landing, W. M., J. L. Guentzel, J.J. Perry, jr., G. A. Gill, and C. D. Pollman (1998). Methods for measuring mercury and other trace species in rainfall and aerosols in Florida. Atmospheric Environment, 32: 909-918.

Landing, W.M., J.J. Perry, J.L. Guentzel, G.A. Gill and C.D. Pollman. 1995. Relationships between the atmopsheric deposition of trace metals, major ions and mercury in Florida. Wat. Air Soil poll. 343-352.80:

Marvin-DiPasquale, M. and R.S. Oremland. 1998. Bacterial Methylmercury Degradation in Florida Everglades Peat Sediment. Environ. Sci. Technol. 32:2556-2563.

Marvin-DiPasquale, J. Agee, C. McGowan, R.S. Oremland, M.. Thomas, D. Krabbenhoft and C.C. Gilmour. 2000. Methyl-mercury degradation pathways: A comparison among three mercury -impacted ecosystems. Environ. Sci. Technol. 34: 4908-4916.

Miles, C.J. and L.E. Fink. 1998. Monitoring and mass budget for mercury in the Everglades Nutrient Removal Project. Arch. Environ. Contam. Toxicol. 35:549-557.

Oremland, R.S., L.G. Miller, P. Dowdle, T.Connel and T.Barkay. 1995. Methylmercury oxidative degradation potentials in contaminated and pristine sediments of the Carson River, Nevada. Appl. Environ. Microbiol. 61:2745-2753.

Oremland, R. S., C.W. Culbertson, and M.R. Winfrey. 1991. Methylmercury decomposition in sediments and bacterial cultures: Involvement of methanogens and sulfate reducers in oxidative demethylation. Appl. Environ. Microbiol. 57:130-137.

Ravichandran, M., G.R. Aiken, J.N. Ryan, and M.M. Reddy. 1999b. Inhibition of precipitation and aggregation of metacinnabar (mercuric sulfide) by dissolved organic matter isolated from the Florida Everglades. Environ. Sci. Technol. 33:1418-1423.

Rudd, J.W.M., M.A. Turner, A. Furutani, A.L. Swick and B.E. Townsend. 1983. The English-Wabigoon River system: I. A synthesis of recent research with a view towards mercury amelioration. Can. J. Fish. Aquat. Sci. 40:2206-2217.

Tao, H., T. Maurkami, M Tominaga and A. Miyazaki. 1998. Mercury speciation in natural gas condensate by gas chromatography inductively-coupled mass spectrometry. J. Anal. Atomic Spectrometry 13:1085-1093.

Wasik, A., I.R. Pereiro, C. Dietz, J. Szpunar and R. Lobinski. 1998. Speciation of mercury by ICP-MS after on-line capillary cryofocusing and ambient temperature multicapillary gas chromatography. Analytical Communications. 35: 331-335.

Xun, L., N.E.R. Campbell, and J.W.M. Rudd. 1987. Measurement of specific rates of net methylmercury production in the water column and surface sediments of acidified and circumneutral lakes. Can. J. Fish. Aquat. Sci. 44:750-757.

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ATTACHMENT 3

1 All sampling and analyses performed under this Contract must conform to the requirements set forth in Chapter 62-160, Florida Administrative Code (F.A.C.) and the document "Requirements for Field and Analytical Work performed for the Department of Environmental Protection under Contract" (DEP-QA-002/02), February 2002.

2. LABORATORIES

a. The Department has determined that because of the nature of the analytical work, certification by the Department of Health Environmental Laboratory Certification Program is not necessary. However, all laboratory activities shall conform to the standards of the National Environmental Laboratory Accreditation Conference (NELAC).

b. The laboratory shall ensure that an initial demonstration of capability (IDOC) specified in Appendix C of Chapter 5 in the NELAC standards is performed for each proposed test method. The IDOC shall be performed before the test procedure is used to generate data for this contract. If requested by the Department, documentation that supports the IDOC shall be made available for review.

c. Performance test samples (where available) shall be successfully performed at least twice annually. Analysis of standard reference material (SRM), with test results within the acceptable range for the SRM may be used in lieu of performance test samples. The laboratory must provide documentation for each analytical test that, within the last 6 months, either performance test samples have been passed, or standard reference materials have been within the acceptance limits of the SRM.

d. All non-standard laboratory procedures (i.e. those that do not appear on the Department's list of recognized methods) shall be submitted for review and approval in accordance with DEP-QA-001/01, "New and Alternative Analytical Laboratory Methods", January 1, 2002. The method must be approved by the Department before use.

e. The CONTRACTOR shall ensure that the essential quality control measures, laboratory report content and documentation are consistent with Chapter 5 of the NELAC standards and DEP-QA-002/02. In addition, the selected chemistry quality controls from the attached QC Options Table shall be performed. In addition,

i. The CONTRACTOR shall ensure that at least five percent of the field-collected environmental samples associated with this project are used to prepare matrix spikes, and laboratory duplicates or matrix spike duplicates. Spike levels must be at concentrations specified in item *iv* below.

ii. The CONTRACTOR shall ensure that the laboratory is provided with sufficient sample volume to perform the matrix-related quality control indicators at a frequency of 5% per test and matrix.

iii. Laboratory Control Samples (also known as Laboratory Fortified Blanks) (LCS) must be evaluated with each analytical batch at the same concentration as the sample matrix spikes. The results must meet method-specified limits.

iv. The final concentration of any spike fortification must be at the laboratory's stated PQL or at the action level if it exceeds the PQL. If the measured sample background exceeds the specified spike level by more than a factor of two, then the spike level must be 2-5 times the measured background level in the sample that is selected for spiking. If a spiked sample is spiked at an incorrect level, then the entire batch of samples must be re-prepared, a new aliquot of the same sample must be re-spiked at the correct level for this batch, and the batch

reanalyzed. The sample to be spiked should be randomly selected, and it must be reported which sample was spiked. All spike fortification must take place prior to any necessary preparation. The results must meet the established laboratory acceptance criteria for the specific matrix. If none have been developed, the laboratory shall use the criteria for LCS until such limits are established.

v. Sample duplicates or matrix spike duplicates must be evaluated for precision.

vi. Continuing Calibration Verifications (CCV's) must be analyzed at a minimum of 5% frequency, or one for every 20 samples. In order to accept the calibration run, all CCVs must meet the method specified acceptance criteria.

vii. When an initial instrument calibration is not performed, continuing calibration Verifications (CCV's) must be analyzed daily prior to analyzing samples. A CCV must also be analyzed at the end of the sampling day or every 12 hours whichever is less.

viii. No analyses may be performed using expired reagents, calibration solutions or check solutions

ix. The concentration of each calibration standard used to generate a nonlinear calibration curve must be calculated based on the curve. All calculated calibration concentrations must be within 85% - 115% of the known concentration for that standard.

x. Linear instrument calibration curves must have a correlation coefficient of at least 0.995.

xi. If a relative response factor is used to determine the sample concentration, the continuing calibration checks must meet the method stated acceptance criteria.

xii. Analytical sensitivity must be evaluated using a check standard prepared at the practical quantitation limit for each analytical run as described above for PQLs.

xiii. The absolute value of the raw instrument value must be less than the MDL for all blanks.

xiv. If method control limits for any measurements are exceeded (including control limits for sample matrix spikes), then the analysis must be repeated if possible. All sample data that is associated with a failed quality control measure must be appropriately qualified as specified in Chapter 62-160, F.A.C. An explanatory comment must be attached to the final report for each result that has a qualifier code other than U, I, or A. Any additional qualifier codes used, but not explicitly provided for in Chapter 62-160, F.A.C., must be identified and defined in the report.

xv. If a method blank or PQL check fails, the blank and associated sample results must be reported with the appropriate qualifier from Chapter 62-160, F.A.C., unless the affected results are at least 10 times the absolute value of the observed bias.

xvi. The reported MDL and PQL for each sample must be adjusted for dilution factors, and any relevant preparation weights and volumes.

xvii. Field duplicates (not to be confused as laboratory duplicates) shall be collected and analyzed for at a frequency of 5% of each matrix/analyte combination.

xviii. All field duplicate results greater than the PQL should agree within 20% RPD for each measured analyte. In the event that field duplicate agreement is not observed, the laboratory must investigate sufficiently to determine that poor precision is not due to a laboratory error, and report the results with appropriate qualifiers and/or comments.

xix. If a field blank, equipment blank or trip blank result is greater than the MDL, the result must be confirmed by reanalyzing a new aliquot of the sample. The laboratory must investigate sufficiently to determine that positive blank results are not due to a laboratory error, and report results with appropriate qualifiers and/or comments.

3. FIELD ACTIVITIES

a. All sample collection and field activities shall be performed in accordance with the Department's "Standard Operating Procedures for Field Activities" (DEP-SOP-001/01 dated January 1, 2002).

b. Any non-standard field procedure shall be submitted for review and approval in accordance with FA 2000 of the Department's Standard Operating Procedures. The procedure must be approved by the Department before use.

c. In addition:

i. The CONTRACTOR shall ensure that at least five percent of the field-collected environmental samples associated with this project are used to prepare matrix spikes, and laboratory duplicates or matrix spike duplicates.

ii. The CONTRACTOR shall ensure that the laboratory is provided with sufficient sample volume to perform the matrix-related quality control indicators at a frequency of 5% per test and matrix.

iii. Field duplicates (not to be confused as laboratory duplicates) shall be collected and analyzed for at a frequency of 5% of each matrix/analyte combination.

iv. No analyses may be performed using expired reagents, calibration solutions or check solutions

v. All field duplicate results greater than the PQL should agree within 20% RPD for each measured analyte. In the event that field duplicate agreement is not observed, the laboratory must investigate sufficiently to determine that poor precision is not due to a laboratory error, and report the results with appropriate qualifiers and/or comments.

vi. If a field blank, equipment blank or trip blank result is greater than the MDL, the result must be confirmed by reanalyzing a new aliquot of the sample. The laboratory must investigate sufficiently to determine that positive blank results are not due to a laboratory error, and report results with appropriate qualifiers and/or comments.

4. REPORTING, DOCUMENTATION AND RECORDS RETENTION

a. All laboratory and field records as specified in Chapter 62-160, F.A.C. shall be retained for a minimum of five years after the project completion.

b. In addition to the NELAC-compliant laboratory report, the Contractor shall require that the laboratory provide additional information to satisfy the Tier 1 (basic reporting options) validation requirements as outlined in DEP-QA-002/02.

c. The data for validation purposes shall be submitted in the electronic format specified in DEP-QA-002/002.

d. All applicable data qualifier codes as mandated by Chapter 62-160, F.A.C. and included in DEP-QA-002/02 shall be used.

e. The Contractor shall adhere to the documentation and records requirements for project data contained in DEP-QA-002/02.

f. All field and laboratory records that are associated with work performed under this contract shall be organized so that any information can be quickly and easily retrieved.

5. AUDITS

a. AUDITS BY THE DEPARTMENT – Pursuant to 62-160.650, F.A.C., the Department may conduct audits of field and/or laboratory activities. In addition to allowing Department representatives to conduct onsite audits, the Contractor, upon request, must provide the Department with the requested information, including the raw analytical data for all analyses of a sample (regardless of whether the data are reported). If an audit by the Department results in a determination that the data are not usable for the proposed purpose, the Department reserves the right to terminate the contract

b. PLANNING REVIEW AUDITS –

1. Initial: Within one month after the second sampling and analysis event has been completed (including all analyses), the Contractor and all associated subcontractors shall review the planning document (see 6 below) relative to the field and laboratory activities to determine if the data quality objectives are being met, identify any improvements to be made to the process, and refine the sampling design or schedule. A summary of the review, including any corrective action plans or amendments to the planning document shall be sent to the DEP Contract Manager within one month of the review, and a copy shall be maintained with the permanent project records.

2. Ongoing: Planning reviews as described in 1 above shall occur annually.

c. QUALITY SYSTEMS AUDITS – The Contractor and all subcontractors shall ensure that the required laboratory and field quality system and management systems audits are performed, and documented in the organization's records.

d. STATEMENTS OF USABILITY - As a part of the audit process and the final report, the Contractor shall provide statements about data usability relative to the Project Data Quality Objectives and Data Quality Indicators

6. PLANNING DOCUMENTS

a. Within 30 days of contract execution, the Contractor shall submit a detailed project proposal or sampling and analysis plan that discusses the information contained in contained in the document "Requirements for Field and Analytical Work Performed for the Department of Environmental Protection Under Contract, DEP-QA-002/02" and the additional topics specified in 62-160.600, F.A.C.

b. The Contractor and affected subcontractors have three (3) opportunities to submit an acceptable sampling and analysis plan to the Department. If any plan fails the approval process three (3) times, the Department may terminate the Contract in its entirety. Failure to provide acceptable Sampling and Analysis Plans as required will result in suspension or termination of this Contract.

c. The DEP Contract Number shall appear on the title page of the submitted document. Within forty-five (45) days of receipt of properly identified documents by the Department, the Department shall review and either approve the document, or provide comments to the Contractor and affected subcontractors as to why the Plan is not approved. If further revisions are needed, the Contractor shall then have fifteen (15) days from the receipt of such comments to respond. The Department shall respond to all revisions within 30 days of receipt.

d. If Plan review is delayed, through no fault of the Contractor, beyond sixty (60) days after the Plan is received by the Department, the Contractor shall have the option, after the Plan is approved, of requesting and receiving an extension in the term of the Contract for a time period not to exceed the period that review was delayed. This option must be exercised at least sixty (60) days prior to the current termination date of the Contract.

e. Sampling and analysis may not begin until the Plan been approved.

f. Once approved, the Contractor shall follow the protocols specified in the approved Plan including, but not limited to:

1. Ensuring that all stated quality control measures are collected, analyzed and evaluated for acceptability;
2. Using only the protocols approved in the Plan; and
3. Using only the equipment approved in the Plan.

g. If any significant changes such as changes in procedures or test methods, changes in organizations, or changes in key personnel occur, the Contractor shall submit appropriate amendments to the Department Contract Manager for review and inclusion into the Sampling and Analysis Plan. Failure to submit the required amendments or to meet any of the above-stated conditions may result in the decision by the Department Contract Manager to suspend or terminate the Contract.

7. DELIVERABLES

a. The following outlines the expected schedule for the deliverables that are associated with the Quality Assurance requirements of this Contract:

1. Non-standard laboratory or field procedures – Prior written approval, or submission of the complete packet of information for review.
2. Planning review audits – As specified in 5.b.
3. Statement of Usability – As specified in 5.d.
4. Planning Document – see 6.
5. Copies of Performance Test Results – As specified in 2.c. One set of acceptable test results shall be submitted before sampling and analysis begins.

Note: All documents referenced in the Attachment are available at the following website:

http://www.dep.state.fl.us/labs/

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DEP USE ONLY		COMPTROLLER USE ONLY
DEP Contract No.: SP618	Date Prepared: 7-31-02	Received Date:
Prepared By: RUTH HEGGEN		Approved Date:
Return to:	Mail Station No.:	Approved By:
Phone No.:	Fax No.:	

COMPTROLLER CONTRACT REVIEW CHECKLIST

Indicate Original Contract or **Amendment or **Renewal: O

1. OLO: 37 Site/District:
2. DEP Contract No.: SP618 Project Number:
3. DMS No.: 973-360
4. Contractor: U.S. GEOLOGICAL SURVEY FEID/SS#: 53-0196958
5. Contract start date: EXECUTION Contract end date: 6/30/03
6. *Contract last signed date:*
7. If last date signed is after the contract start date, you must submit emergency certification [287.058(2) F.S.] or certificate of noncompliance [287.058(2) F.S.] or settlement document [CM4 (87-88) or CM11 (91-92)].
8. Total Contract amount: $ 100,000 Ceiling amount: $
9. Contract SAMAS account code:
10. Deliverable/Milestones - must be clear, detailed, concise language (i.e. tasks, % complete, time frame or milestones, goods, services): ATTACHMENT 2
11. CONTRACT DOCUMENT—Mandatory Provisions (insert page number, paragraph number, identify section or attachment from contract in space provided, as applicable):

ATTACH 1, #4/5 215.422(5)	ATTACHMENT 2 287.058(1)(d)	N/A 287.058(4)
ATTACH 1, #10 216.347	#2 287.058(1)(e)	ATTACH 1, #6 287.0582
ATTACH 1, #2 287.058(1)(a)	N/A 287.058(1)(f)	ATTACH 1, #7 287.133(2)(a)
ATTACH 1, #3 287.058(1)(b)	287.058(2)	ATTACH 1, #8 287.134(3)(a)
ATTACH 1, #1 287.058(1)(c)	N/A 287.058(3)	N/A Rule 60A-1.017

***Complete only applicable portions of checklist for renewals, amendments, etc.*

12. Method of Procurement IGA (Refer to attached list) (Provide documentation, where applicable)
13. Method of Payment LS (FR, LS, CR, CP, AD)

A. Fixed Rate (FR) - specify unit and rates (may be multiple units & rates).

Distribution: White: Contracts Section, MS#93; Yellow and Pink: Finance & Accounting-Contracts Disbursements Section, MS#78

B. Lump Sum (LS) - specify partial payment criteria and identify what constitutes completion and acceptance.
QUARTERLY PAYMENTS

C. Cost Reimbursement (CR) (216.346 F.S. must be complied with) - Provide budget:_____

D. Cost Plus (any combination of these) (CP)_____

E. Advance funded (AD) - Y (N)
If yes, compliance with 216.181(16)(b) or 215.422(14) must be documented_____

14. Amendments /renewals /extensions N/A
*Executed prior to the end of the contract and must be in compliance with 215.425 F.S.*_____
Renewals in compliance with 287.057(12) F.S._____
Extensions in compliance with 287.057(11)._____

15. Amendments/renewals/extensions are effective on last date signed. N/A

16. Method of Procurement will be required if additional services are added to existing contract. N/A

17. INFORMATION TECHNOLOGY RESOURCE acquisitions N/A
Attach approvals, if applicable [see 282.102, F.S.]_____

18. OTHER SERVICES REQUIRING SPECIAL APPROVALS (Attach, if applicable): N/A
Private Attorney Services_____
Consultant and professional services contracts entered into by agencies under the Governor and Cabinet_____

19. Purchase of communication equipment or services in excess of Threshold Category II requires approval of the DMS Division of Communications (Rule 60C). N/A

20. Management Controls -

a) All the foregoing statements are true and correct; the undersigned management represents that controls are in place to insure that goods/services are received, and payments are made in accordance with contract terms.

b) All completed work will be verified in a certified statement signed by the contract manager or higher authority prior to payment. The undersigned understands that the State Comptroller's office reserves the right to either appoint special contract monitors on contracts or to conduct periodic site post-audits of any contracts.

Management Name (please print) RUTH HEGGEN

Management Approval Signature Ruth Heggen

Management Approval Date: 7/31/02

FLORIDA SINGLE AUDIT ACT CHECKLIST FOR NON-STATE ORGANIZATIONS - RECIPIENT/SUBRECIPIENT VS. VENDOR DETERMINATION

This checklist and the standard contract audit language may be obtained electronically from the Executive Office of the Governor's website (http://www.myflorida.com/myflorida/government/governorinitiatives/fsaa/index.html).

If a Florida Single Audit Act State Project Determination Checklist has not been previously completed, please complete it now. (Applies only to State agencies)

This checklist must be used by State agencies to evaluate the applicability of the Florida Single Audit Act (FSAA) to non-state organizations[1] after a state program has been determined (using the Florida Single Audit Act State Project Determination Checklist) to provide state financial assistance (i.e. is a State Project as defined in 215.97 (2)(r), F.S.). This checklist assists in determining if the non-state organization is a vendor, recipient/subrecipient, or an exempt organization.

[1] A non-state organization is defined as a nonprofit organization, for-profit organization (including sole proprietors), or Florida local government (excluding district school boards, charter schools and community colleges), which receives State resources.

Recipients and subrecipients of state financial assistance must also use this checklist to evaluate the applicability of the FSAA to non-state organizations to which they provide State resources to assist in carrying out a State Project.

Name of Non-state Organization: U.S. GEOLOGICAL SURVEY

Type of Non-state Organization: GOVERNMENTAL ENTITY

(i.e. nonprofit, for-profit, local government; if the non-state organization is a local government, please indicate the type of local government – municipality, county commission, constitutional officer, water management district, etc.)

Awarding Agency: DEP

Title of State Project: MESOCOSM STUDIES TO QUANTIFY METHYMERCURY

Catalog of State Financial Assistance (CSFA) Number: N/A

Contract/Grant/Agreement Number: SP618

PART A

YES	NO		
X		1.	Is the non-state organization a district school board, charter school, community college, government/public university outside of Florida or a Federal agency?
	X	2.	Is the relationship with the non-state organization **only** to procure commodities (as defined in 287.012(4) F.S.)?
	X	3.	Does the relationship with the non-state organization consist of **only** Federal resources, State matching resources for Federal Programs or local matching resources for Federal Programs?
	X	4.	Does the relationship with the non-state organization consist of **only** State maintenance of effort (MOE)[2] resources that meet **all** of the following criteria?
	X		A. Do Federal Regulations specify the requirements for the use of the State MOE resources and are there no additional State requirements?
	X		B. Do contracts contain sufficient language to identify the State MOE resources and the associated Federal Program?
	X		C. Do A-133 audit requirements apply to the State MOE resources and do contracts stipulate that the State MOE resources should be tested in an A-133 audit in accordance with Federal Program requirements?

[2] MOE refers to the Federal maintenance of effort/level of effort requirements as defined by OMB Circular A-133 Compliance Requirement G (Matching, Level of Effort, Earmarking).

If **any** of 1-4 above is **yes**, the recipient/vendor relationship determination does not need to be completed because **the FSAA is not applicable to the non-state organization.**

PART B

Recipient/Vendor Relationship Determination:

The following should be analyzed for each relationship with a non-state organization where it has been determined that the state program provides state financial assistance (i.e. is a State Project) and the non-state organization is not exempt based on the questions above. This relationship may be evidenced by, but not limited to, a contract, agreement, or application.

YES	NO	
___	X	1. Does State law or legislative proviso create the non-state organization to carry out this State Project?
___	X	2. Is the non-state organization required to provide matching resources not related to a Federal Program?
___	X	3. Is the non-state organization required to meet or comply with specified State Project requirements in order to receive State resources? (State Project requirements include laws, rules, or guidelines specific to the State Project such as eligibility guidelines, specified types of jobs to be created, donation of specified assets, etc. Specified State Project requirements do not include procurement standards, general guidelines, or general laws/rules.)
___	X	4. Is the non-state organization required to make State Project decisions, which the State agency would otherwise make? (e.g. determine eligibility, provide case management, etc.)
___	X	5. Is the non-state organization's performance measured against whether State Project objectives are met? (e.g. number of jobs to be created, number of patients to be seen, number of disadvantaged citizens to be transported, etc. Performance measures may or may not be related to State performance-based budgeting.)

If **any** of the above is **yes**, there is a **recipient/subrecipient relationship** and the non-state organization **is** subject to the FSAA. Otherwise the non-state organization is a **vendor** and is **not** subject to the FSAA.

PART C

Based on your analysis of the responses above and discussions with appropriate agency personnel, state your conclusion regarding the non-state organization:

(Check one) **Recipient/Subrecipient:** ___ **Vendor:** XX **Exempt Organization:** XX

Comments:

Print Name: RUTH HEEGEN **Telephone Number:** 850-216-2507

Title: OMC MANAGER

Signature: Ruth Heegen **Date:** 7-31-02

Note it is the program personnel's responsibility to notify Finance and Accounting of which non-state organizations have been determined to be recipients and are receiving state financial assistance (i.e. disbursements must be coded as 7500 object code in FLAIR).

Note it is possible to have a contractual agreement with a non-state organization under Chapter 287, Florida Statutes, and still consider the non-state organization a recipient under the Florida Single Audit Act.

If a recipient/subrecipient relationship exists the standard contract audit language, including Exhibit 1, must be included in the document that established the State's, recipient's, or subrecipient's relationship with the non-state organization.

Questions regarding the evaluation of a non-state organization or if it has been determined that the non-state organization is a recipient and a CSFA number has not been assigned, contact your FSAA State agency liaison or the Executive Office of the Governor, Office of Policy and Budget, Budget Management Policy Unit at (850) 487-3832 or Suncom 277-3832. Reference may be made to Rule 27D-1, FAC.