U.S. Department of the Interior
U.S. Geological Survey

SOUTH FLORIDA WETLANDS ECOSYSTEM: BIOGEOCHEMICAL PROCESSES IN PEAT

The South Florida wetlands ecosystem is an environment of great size and ecological diversity (figs. 1 and 2). The landscape diversity and subtropical setting of this ecosystem provide a habitat for an abundance of plants and wildlife, some of which are unique to South Florida. South Florida wetlands are currently in crisis, however, due to the combined effects of agriculture, urbanization, and nearly 100 years of water management. Serious problems facing this ecosystem include (1) phosphorus contamination producing nutrient enrichment, which is causing changes in the native vegetation, (2) methylmercury contamination of fish and other wildlife, which poses a potential threat to human health, (3) changes in the natural flow of water in the region, resulting in more frequent drying of wetlands, loss of organic soils, and a reduction in freshwater flow to Florida Bay, (4) hypersalinity, massive algal blooms, and seagrass loss in parts of Florida Bay, and (5) a decrease in wildlife populations, especially those of wading birds.

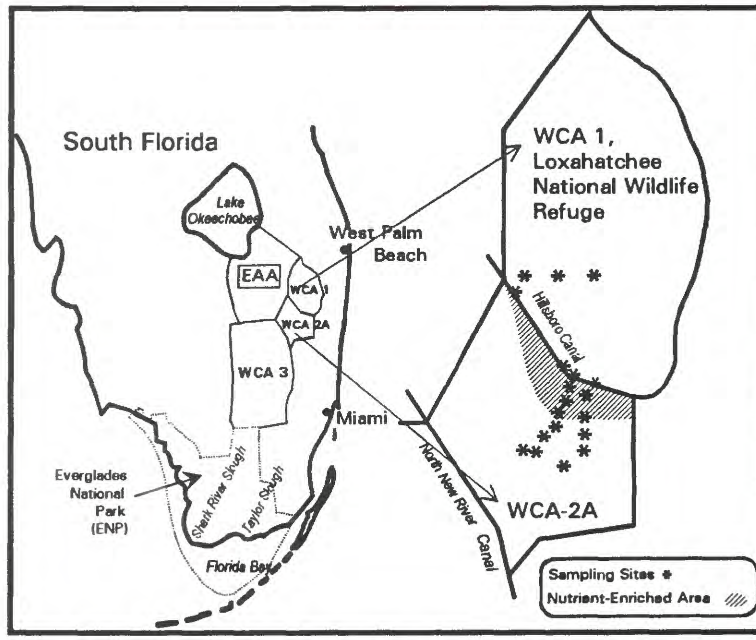

Figure 2. Major regions of the South Florida wetlands ecosystem including the Everglades Agricultural Area (EAA), the Water Conservations Areas (WCA's), and Everglades National Park (ENP). Sampling sites for the Biogeochemical Processes project are shown in Water Conservations Areas 1 and 2A and along the Hillsboro Canal.

This U.S. Geological Survey (USGS) project focuses on the role of organic-rich sediments (peat) of South Florida wetlands in regulating the concentrations and impact of important chemical species in the environment. The cycling of carbon, nitrogen, phosphorus, and sulfur in peat is an important factor in the regulation of water quality in the South Florida wetlands ecosystem. These elements are central to many of the contamination issues facing South Florida wetlands, such as nutrient enrichment, mercury toxicity, and loss of peat.

Many important chemical and biological reactions occur in peat and control the fate of chemical species in wetlands. Wetland scientists often refer to these reactions as **biogeochemical processes,** because they are chemical reactions usually mediated by microorganisms in a geological environment. An understanding of the biogeochemical processes in peat of South Florida wetlands will provide a basis for evaluating the effects on water quality of (1) constructing buffer wetlands to alleviate nutrient contamination and (2) replumbing the

Figure 1. Peat core being taken in a sawgrass marsh in the South Florida wetlands.

PROJECT GOALS:
- Examine biogeochemical processes in peats controlling nutrient and sulfur cycling in wetlands.
- Determine the rates of these biogeochemical processes for inclusion in ecosystem models.
- Examine the influence of nutrient and sulfur geochemistry in peats on mercury cycling and bioaccumulation.
- Determine the effects of differences in peat organic structure on nutrients, sulfur, and mercury.
- Develop a model of ecosystem history from studies of geochemical history and collaboration with paleoecology and geochronology groups.

ecosystem to restore natural water flow. The results may also suggest new approaches for solving problems of contamination and water quality in these wetlands.

A second focus of this project will be on the geochemical history of the South Florida ecosystem. Peat is a repository of the history of past environmental conditions in the wetland. Before effective action can be taken to correct many of the problems facing these wetlands, we must first study the biogeochemistry of the peat at depth in order to understand whether current problems are the result of recent human activity or are part of a long-term natural cycle. Coordination with other (USGS) projects for South Florida is ongoing. These projects are studying the biological history of the ecosystem by using pollen and shells buried in the peat, together with procedures for dating the peat at various depths, to develop an overall ecosystem history model, with emphasis on the last 100 years.

PEATS OF SOUTH FLORIDA WETLANDS

Large areas of South Florida wetlands (fig. 2) are underlain by peat. Peat consists of the partially decomposed remains of plants that grew in the wetlands. Waterlogged conditions in wetlands foster the accumulation of peat by excluding atmospheric oxygen from the soil and retarding the decomposition of dead vegetation. The oxygen-free or anoxic condition of most peat is a characteristic that plays an important role in the recycling of nutrient elements (carbon, nitrogen, and phosphorus) and in the transformation of mercury to its toxic methyl mercury form.

Water management practices over the last 100 years have greatly altered the natural water flow of South Florida wetlands, resulting in more frequent drying in some areas. As peats dry, they are exposed to the atmosphere, resulting in oxidation and loss of the peat. Drying can also lead to the release of nutrients and other chemical species stored in the peat when it is later rewetted. Analytical methods for determining the forms of organic compounds are being used to examine evidence of peat oxidation in areas subject to drying. Results from a study in a water impoundment area (Water Conservation Area 2A, WCA 2A) show that in some areas the surface peat is currently being oxidized. The geochemical record in peat cores is also being examined for evidence of past episodes of peat oxidation.

Other geochemical methods are being used to examine differences in peat types in various regions of the South Florida ecosystem. Significant differences have been observed in the organic structure of peats from the Water Conservation Areas (WCA's) and some parts of Everglades National Park (ENP), possibly because of differences in duration of wet periods and amount of nutrient input. These differences may indicate the capability of the peat to react with elements of environmental concern such as phosphorus, nitrogen and mercury.

BIOGEOCHEMICAL PROCESSES IN PEATS OF SOUTH FLORIDA

Sampling methods

Samples of peat and the water contained within the peat (pore water) are obtained for analysis by using a plastic coring tube, which takes a continuous cylindrical sample of peat from the peat surface down to about 1.5 meters depth (see fig. 1). The peat is extruded from the coring tube and divided into 5-centimeter sections, which are stored for later analyses. Often, only pore water is obtained by coring the peat using a plastic tube with sampling "port-holes" along its length. In these cases, water is squeezed out of the peat through the holes and into syringes using a specially designed apparatus (fig. 3) that applies piston pressure to the top and bottom ends of the peat in the coring tube.

Phosphorus and Nitrogen

Phosphorus is an element of particular concern in South Florida wetlands. High concentrations of dissolved phosphorus in canals draining the Everglades Agricultural Area (EAA) are discharged into South

Figure 3. Pore water from a peat core being squeezed into syringes.

Area (EAA) are discharged into South Florida wetlands. In the wetland marsh, phosphorus may be adsorbed by surface peat or utilized by plants and later incorporated in the peat after the plant dies or sheds leaves. Studies by this project and by others indicate that phosphorus accumulates in peats near canal discharge areas at rates of 100-1000 times greater than in peats remote from canal discharge in WCA 2A (fig. 2). High concentrations of phosphorus in surface peats near canal discharge areas may be responsible for a dramatic shift in the nature of the wetland vegetation. The native sawgrass, which is adapted to a low-phosphorus environment, is being replaced by cattails, which outcompete the sawgrass under high-phosphorus conditions.

But what is the ultimate fate of phosphorus after deposition in a wetland peat? How much is recycled within the wetland, how much is exported to other uncontaminated areas, and how much is locked away in the peat? At what rate is phosphorus recycled? These are some of the important biogeochemical questions that this project is addressing. Some of the more important biogeochemical processes governing the behavior of phosphorus are shown in figure 4. Phosphorus is deposited in the peat largely as organic phosphorus in dead plant debris. As this plant debris is transformed into peat, the phosphorus is released into water in the pore spaces of the peat. The dissolved phosphorus in the pore water is available for uptake by aquatic plants rooted in the peat, uptake by microorganisms in the peat, or diffusion or migration back into the surface water.

Concentrations of phosphorus (in the form of phosphate), and nitrogen (in the form of ammonium) dissolved in pore water (fig. 5) often greatly exceed concentrations found in the surface water. By measuring the change in concentration between surface water and pore water, and with a knowledge of peat accumulation rates, calculations can be made to estimate the rates at which these elements are recycled, and the rates at which they may diffuse or migrate back to the surface water. This kind of quantitative rate information is key to understanding the long-term effects of nutrient contamination of wetlands from agricultural or urban runoff, to predicting the long-term effectiveness of constructed buffer wetlands for protecting wetland conservation areas.

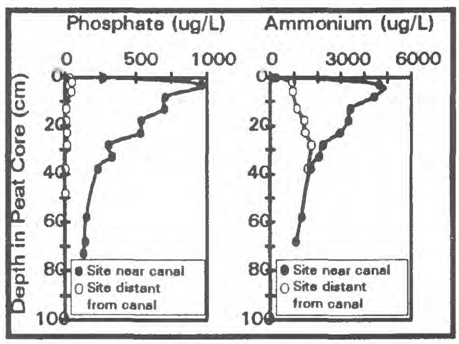

Figure 5. Dissolved phosphate and ammonium concentrations in pore water from sites in WCA 2A. Concentrations are in micrograms per liter (µg/L) and depths are in centimeters (cm).

Sulfur and Mercury

Sulfur is another element of major concern in South Florida wetlands, primarily because of its role in the cycling of mercury. Many of the important biogeochemical processes in peat involving sulfur are shown in fig. 4. In the surface water of wetlands where dissolved oxygen is present, sulfur exists primarily in its oxygenated ionic form as dissolved sulfate. Sulfate can enter the wetland from canal discharge, rainfall, or ground-water discharge.

In most freshwater wetlands, sulfate in surface water is present at low concentrations. However, areas of the South Florida wetlands ecosystem affected by phosphorus contamination also have high sulfate concentrations. The high sulfate concentration may originate from agricultural soil amendments used in the EAA. One goal of this project is to determine the source of sulfate in the wetlands by using sulfur isotope analyses. Isotopes are different forms of an element having the same number of protons in the nucleus but different numbers of neutrons. The different isotopes of an element have slightly different chemical and physical properties and can accumulate at different rates. The ratios of abundance of two isotopes of an element (expressed as $\delta^{34}S$ values in the case of sulfur) are often used in geochemistry as "fingerprints" to determine the origin of chemical species or processes affecting them. We expect sulfate originating from fertilizer to have significantly different $\delta^{34}S$ values from sulfate originating from rainwater or ground water. The

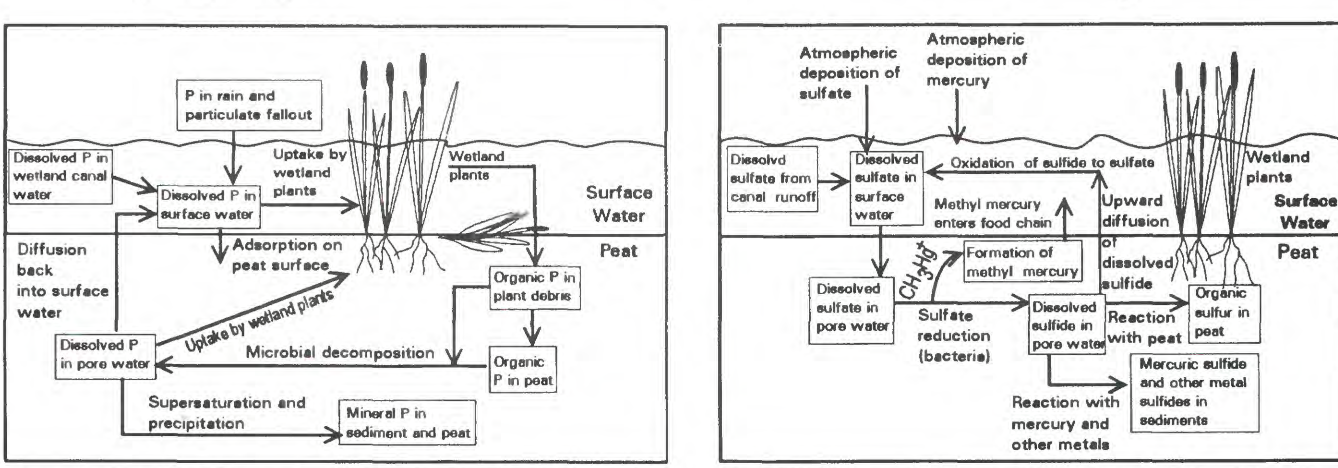

Figure 4. Simplified biogeochemical cycles for phosphorus (left) and sulfur (right) in organic-matter-rich sediments of South Florida. P, phosphorus; CH_3Hg+, methyl mercury ion.

stable isotopic ratios of the major forms of sulfur also reflect sulfate concentrations and rates of sulfate reaction to form sulfide (fig. 4).

Probably the most important biogeochemical process involving sulfur in oxygen-free sediments is sulfate "reduction, " the process by which sulfate is changed to sulfide. Under oxygen-free, "reducing" conditions in peat, certain bacteria (sulfate-reducing bacteria) use sulfate in their metabolism and produce hydrogen sulfide as a byproduct. Hydrogen sulfide is a chemical form of sulfur with a very distinctive "rotten egg" odor. It is very reactive with dissolved metals and will quickly form highly insoluble metal sulfides in the peat when present in sufficient concentrations. Mercury in peat pore water will readily react with hydrogen sulfide to form highly insoluble mercuric sulfide, which poses little health hazard buried as a solid in the peat. However, sulfate-reducing bacteria are thought to be involved in the production of toxic methylmercury (CH_3Hg+) as a byproduct of the sulfate reduction process (fig. 4).

Ongoing studies are being conducted to determine trends in sulfate concentration and $\delta^{34}S$ values in surface water from the WCA's and their adjacent canals. These trends are being related to location, season, nutrient enrichment, rates of sulfate reduction, and, ultimately, to methyl mercury production in the South Florida wetlands ecosystem.

CONTINUING STUDIES OF BIOGEOCHEMICAL PROCESSES IN PEATS OF SOUTH FLORIDA

Project work in South Florida wetlands in 1994 and 1995 primarily emphasized reconnaissance studies of peat and pore-water biogeochemistry throughout the ecosystem, with an emphasis on work along a known nutrient enrichment gradient in WCA 2A (fig. 2). In 1996, collaborative co-sampling was begun with USGS and other scientists who are focusing on the biogeochemistry of mercury. Current studies also include the effects of seasonal changes in water retention and rainfall on the exchange of nutrients and sulfur between surface water and sediments. We have recently expanded our studies into Everglades National Park, with emphasis on Taylor Slough and Shark River Slough, areas of major water transport to Florida Bay (fig. 2). Laboratory studies designed to verify interpretations of the results of field observations are planned for future years.

ANTICIPATED PROJECT SCHEDULE:

- 1994 - Reconnaissance sampling in Water Conservation Areas (WCA) and Everglades National Park (ENP); biogeochemistry of peat and pore water.
- 1995 - Focused study of peat and pore-water biogeochemistry in WCA 1 and 2.
- 1996 - Study of temporal variation in pore-water biogeochemistry in WCA 2 and 3 and buffer wetlands; Study of sediment and pore-water biogeochemistry in Taylor Slough transect (ENP).
- 1997 - Continued pore water and sediment studies in WCA 1, 2, and 3 and Taylor Slough; begining of sediment and pore-water studies in Shark River Slough; beginning of laboratory simulation studies of sulfur-mercury interactions and nutrient cycling.
- 1998 - Continued studies in Shark River Slough; completion of studies in WCA; continued laboratory simulations.
- 1999 - Completion of studies in Shark River Slough; completion of laboratory simulations; completion of synthesis and final reports.

PLANNED PRODUCTS:

- USGS open-file reports.
- Synthesis articles for publication in scientific journals.
- Data tables and rate constants for use in ecosystem models.
- Presentations at scientific meetings and at collaborating agencies.
- GIS (geographic information system) maps of sediment and pore-water geochemical parameters.

COLLABORATION AND PARTNERSHIPS

This project is closely coordinated with a number of other USGS projects in South Florida and with university projects, including projects studying mercury biogeochemistry and bioaccumulation, geochronology of peats, trace-element and mercury accumulation in peats, palynology and paleoecology, dissolved organic carbon, and hydrology. This coordination involves planning field work, co-sampling, and exchange of data, information, and ideas. Coordination and information exchange with the scientific staff and management of the South Florida Water Management District have also been key components of this project since 1994. The district provides access to Water Conservation Areas, logistical support, and information that guides the selection and timing of sampling. Information exchange and coordination of sampling activities have also been conducted with the U.S. Fish and Wildlife Service for work in WCA 1, the National Park Service for work in Everglades National Park, the Florida Department of Environmental Protection for mercury studies, and the U.S. Department of Agriculture for work in the Everglades Agricultural Area.

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