BURIAL AND DECOMPOSITION OF PARTICULATE ORGANIC MATTER IN A TEMPERATE, SILICICLASTIC, SEASONAL WETLAND

A Thesis

by

LISA WILLIAMSON WELSH

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2007

Major Subject: Geology

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Approved by:

Chair of Committee,	Anne Raymond
Committee Members,	Vaughn Bryant
	Stephen Davis
	Jennifer McGuire
Head of Department,	John Spang

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ABSTRACT

Burial and Decomposition of Particulate Organic Matter in a Temperate, Siliciclastic, Seasonal Wetland. (August 2007)

Lisa Williamson Welsh, B.S., Texas A&M University

Chair of Advisory Committee: Dr. Anne Raymond

Understanding the role of freshwater wetlands in the global carbon cycle has become more important as evidence of climate change grows. In this paper, we examine the burial and decomposition of particulate organic matter (POM) in a temperate, siliciclastic, seasonal wetland. High POM abundances are found in silt layers, while sand units preserve very little POM. The POM distribution with depth is compared to the biogeochemistry of sediment porewater with depth. POM acts as a driver for reduction reactions within the wetland soil. Porewater biogeochemistry and POM decomposition are controlled by seasonal changes in the level of the water table which cause seasonal shifts in the oxic/anoxic boundary. At the oxic/anoxic boundary, reoxidation of FeS minerals in the soil cause rapid POM decomposition at the average minimum water table level in the late summer and early fall. Variation in the minimum depth of the water table from year to year may account for fluctuating POM numbers in the upper silt layers. The results from this study can be used to predict seasonal water level fluctuations in ancient wetland and to explain recurrence horizons in peat.

ACKNOWLEDGMENTS

I would like to thank my committee chair, Dr. Anne Raymond, and my committee members, Dr. Jennifer McGuire, Dr. Stephen Davis, and Dr. Vaughn Bryant, for their guidance and support throughout the course of this research.

Thanks also to Erik Smith, Scott Christensen, Susan Báez Cazull, and Tara Kneeshaw with their invaluable help with field and data collection. Additional thanks to Susan Báez Cazull for her geochemistry tutorials. Thanks also go to Dr. Stephen Hatch of the S.M. Tracy Herbarium for help identifying seeds.

I would also like to thank my family and friends, particularly my parents, Jimmie and Emie Williamson for their encouragement, and my husband, Adrian Welsh for his invaluable support and help in litter bag collection and Word formatting!

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INTRODUCTION

Wetlands cover 467 to 520 million hectares, about 3% of the Earth's land surface, and the amount of carbon stored in wetland soil ranges from 200 to 535 Gt, with much of the variation due to differing definitions of wetland, and the difficulty of obtaining accurate estimates of peat depth (Mitra et al. 2005). Estimates of the total soil carbon pool range from 1500-2300 Gt C (Amundson 2001), with wetland soil carbon constituting as little as 9% and as much as 35% of this reservoir. Although much of the carbon stored in wetland soils is peat, siliciclastic wetland soils may contain significant amounts of carbon. For example, the percentage of organic carbon in freshwater marsh sediments from the Mississippi River Delta ranged from 35-75% (Kosters 1989). Increased understanding of the processes that lead to the burial and decomposition of particulate organic matter in siliciclastic wetlands is critical to understanding how climate change will affect this reservoir, and may have implications for peat accumulating wetlands as well.

Nutrient cycling and organic matter turnover in ecosystems are directly influenced by decomposition rates. Decomposer organisms mineralize OM-associated nutrients, making them available for plant uptake. Indeed, much of the net primary productivity (NPP) of terrestrial ecosystems depends on nutrients recycled through the decomposition of plant detritus (Swift et al. 1979, Vargo et al. 1998). Thus, a better understanding of organic decomposition in wetland sediments will contribute to our understanding of wetland productivity.

This thesis follows the style of Wetlands.

Most of the particulate organic matter (POM) in wetland soils comes from plants (Mitsch and Gosselink 2000). The breakdown of POM at the sediment-water interface generally occurs in three steps: 1) initial rapid loss due to leaching; 2) microbial decomposition and conditioning; and 3) mechanical and invertebrate fragmentation. Webster and Benfield (1986) found that freshwater wetlands have the slowest POM breakdown rates, which they attributed to anoxic conditions and lower pH values. In wetlands, anoxia generally results from the presence of standing water or waterlogged soils; leading to the expectation that decomposition rates should correlate with the duration of submergence. Based on a review of POM decomposition rates, Brinson et al. (1981) suggested that hydroperiod and POM decomposition are not necessarily correlated within wetlands. Dry sites experienced faster decomposition in some cypress swamps (Duever et al. 1975, Brown 1981). Wet sites experienced faster decomposition in other cypress swamps, alluvial swamps, and freshwater marshes (Brinson 1977, Cameron 1972, Nessel 1978, Craighead 1968, Odum et al. 1978).

Brinson et al. (1981) attributed the lack of correlation between hydroperiod and POM decomposition rate to other variables including rates of water flow, low redox potentials and anoxia, temperature, and plant type. For example, under submerged conditions with no flowing water, anoxic conditions can contribute to slow decomposition. Alternating wetting and drying of soils can result in pulses of respiration and microbial density during rewetting, which can increase decomposition and nutrient availability (Sorenson 1974).

In this contribution, we present data on the distribution of POM and total organic carbon in a riverine, siliciclastic wetland from the temperate zone, the Norman Landfill Slough, in Norman, Oklahoma, USA. We analyze these data in light of the biogeochemical indicators of sediment porewater in order to better understand the role of seasonality in the decomposition and preservation of POM in slough sediments. Although the Norman Landfill Slough lies next to a contaminated landfill, the study site contains a thriving wetland community, including aquatic insects, beaver, and crayfish, that appears to be unaffected by subsurface pollution. The biogeochemistry of sediment porewaters from the slough indicates some mixing between surface waters and groundwater influenced by landfill leachate (Báez Cazull et al. in press). However, decomposition in upper slough sediments appear to be controlled primarily by seasonal fluctuations in availability of electron acceptors such as oxygen, nitrate, iron (III) minerals, and sulfate, soil mineralogy, and POM derived from slough plants (Báez Cazull et al. in press). The processes outlined in this study may be useful in understanding rates and processes of carbon cycling in all freshwater wetlands, including peat-accumulating wetlands.

STUDY SITE

The Norman Landfill Slough is an abandoned channel of the Canadian River, a large tributary of the Arkansas River that drains into the Mississippi River (Fig. 1). This channel was abandoned after a flood in 1986, when the Canadian River shifted south of the landfill, leading to the formation of the Norman Landfill Slough. Today, the slough is an elongated wetland with herbaceous vegetation, fed by groundwater discharge and precipitation (Schlottmann 2000, Báez Cazull et al. in press). Burgess (2006) described the plant communities growing in and adjacent to the slough.

The climate in Norman, OK is temperate, with an average low of -3.8°C in January and average highs of 34°C in July and August. The average yearly rainfall is 39 cm. July is the wettest month, with an average precipitation of 13 cm. The driest months, with an average rainfall of 3 to 4 cm, are February and March (Fig. 2). We used gauge height data from the USGS to determine water levels within the slough over the past 10 years (USGS site 07229053). Water levels vary seasonally and the surface of the slough can drain in the late summer and early fall (Fig. 2, Fig. 3). The timing of soil exposure (June through November, peaking in August and September) compared to average monthly rainfall, which peaks in July and August, illustrates the importance of evapotranspiration and temperature in controlling wetland hydroperiod. The soil surface is frequently exposed during July and August, which are times of high average rainfall. Table 1 reports the number of days the soil surface was subaerially exposed each year for the years 1996-2006. The average duration of exposure intervals was 59 days. The average depth of the water table below the soil surface, weighted by interval duration was -16.5 cm.

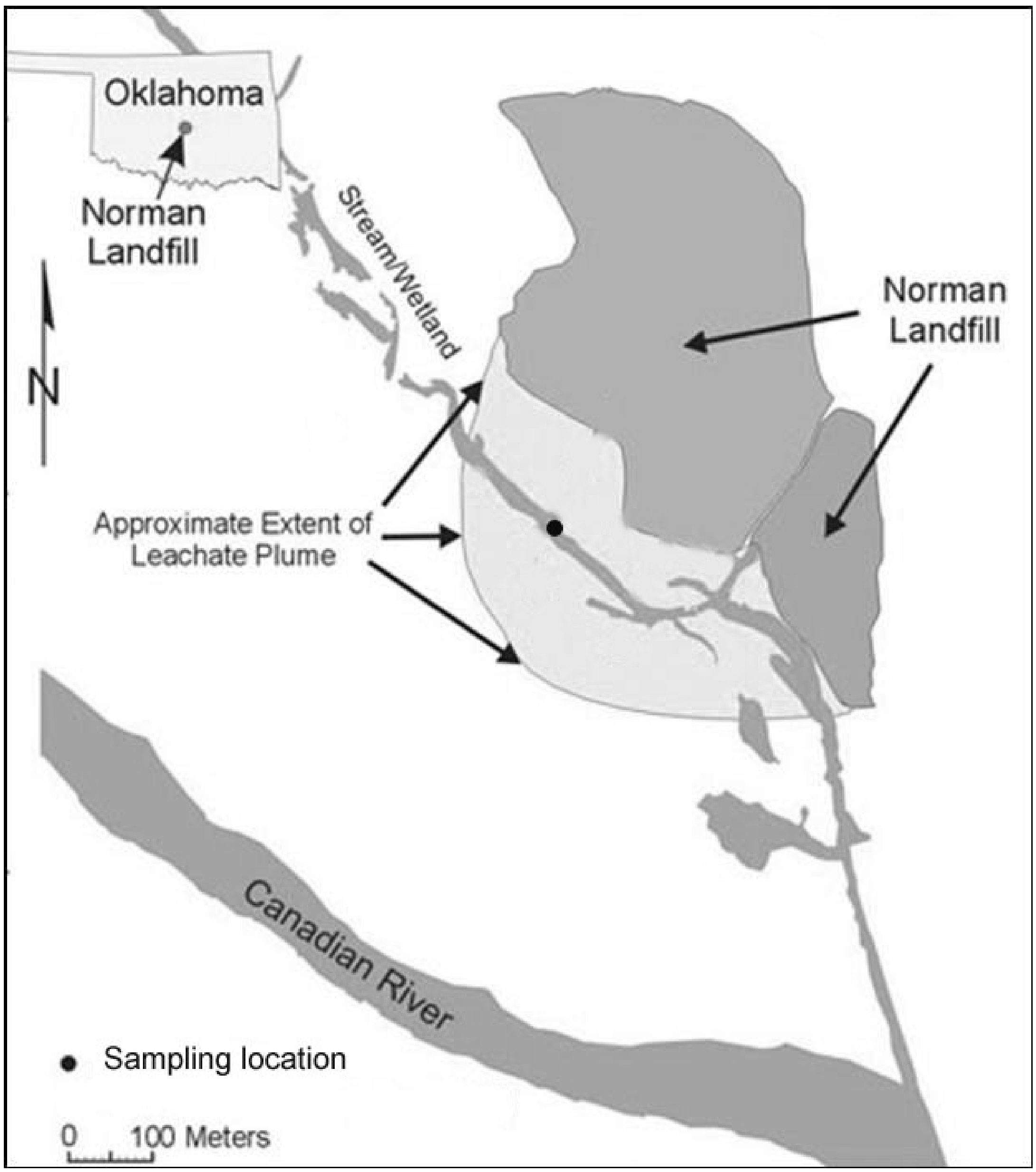

Figure 1. Norman Landfill Slough research site. The circle indicates the location of POM cores and peepers. Figure modified from http://ok.water.usgs.gov/norlan/.

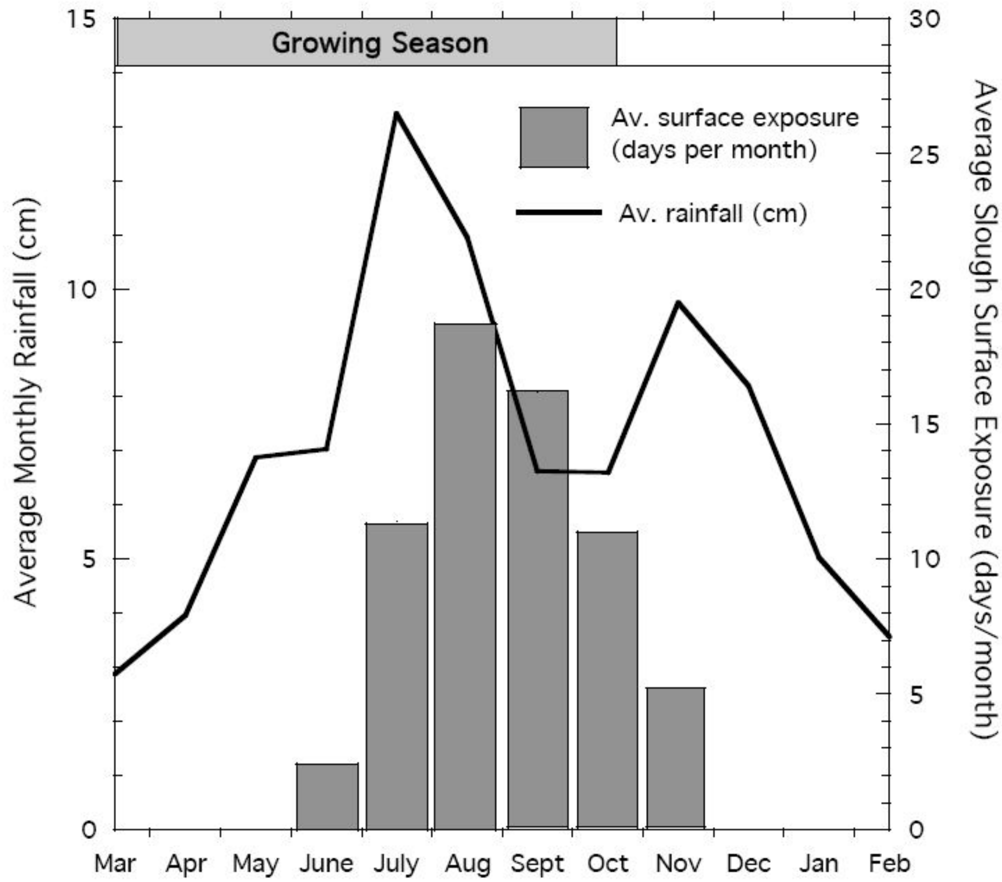

Figure 2. Average monthly rainfall compared to average days of soil surface exposure. The months with the highest average precipitation (July and August) are also the months when the soil surface is exposed due to evapotranspiration. Conversely, the soil is not exposed during the driest months in the later winter and early spring (February and March). Rainfall and water level data taken from the USGS gauge height data of site 07229053, the Canadian River Tributary at Norman, OK. http://waterdata.usgs.gov/ok/nwis/dv/?site_no=07229053&agency_cd=USGS&referred_module=sw

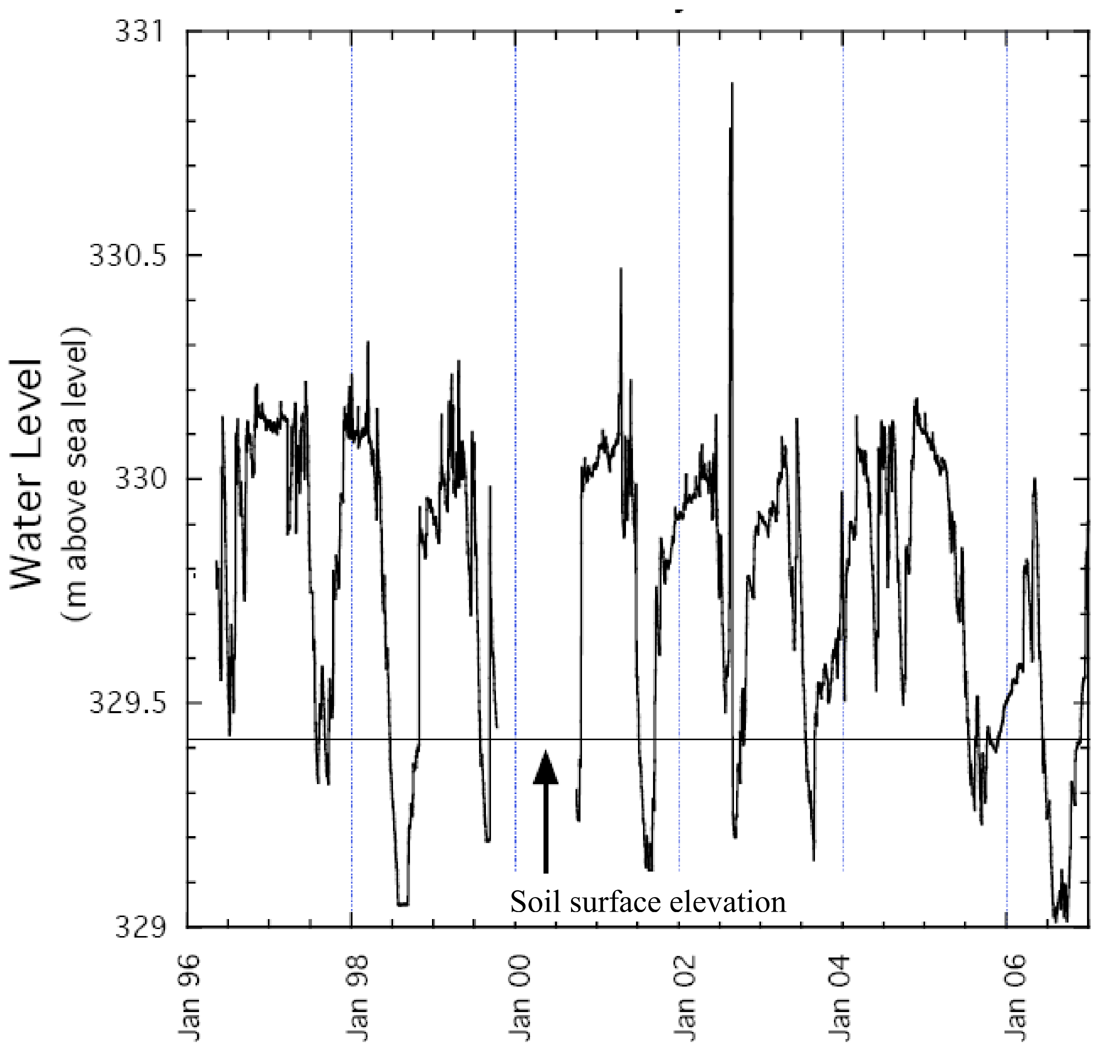

Figure 3. Norman Landfill Slough water levels from spring 1996 to fall 2006. Horizontal line indicates mean soil elevation of slough. Water levels taken from the USGS gauge height data of site 07229053, the Canadian River Tributary at Norman, OK.
http://waterdata.usgs.gov/ok/nwis/dv/?site_no=07229053&agency_cd=USGS&referred_module=sw

Table 1. The depth and duration of each exposure interval of the slough is shown from 1997 to winter 2007.

Year	Month/Day	Depth of water table below slough surface		Duration
		Average (cm)	Maximum Depth (cm)	(days)
1997	07/28 – 08/10	-5	-10	14
	09/06 – 09/22	-5	-10	17
1998	06/24 – 1-/31	-22	-37	131
1999	7/30 - 09/10	-15	-23	43
2000	10/1 - 10/21	-13	-18	21
2001	07/09 – 09/17	-19	-29	71
2002	08/29 - 10/03	-19	-22	36
	10/07 - 10/08	0	0	2
	10/16 - 10/19	-2	-1	4
2003	7/21 - 08/31	-13	-27	41
2005	7/19 – 8/17	-9	-16	30
	8/20	-2	-2	1
	09/2 - 10/6	-9	-2	35
	10/20 - 11/25	-2	-3	37
2006	06/13 – 11/27	-24	-41	109
Average	1.5 intervals/yr			59.2 days/yr
Weighted Average		-16.5	-40.6	

The Norman Landfill Slough and the adjacent Norman Landfill is a research site through the U.S. Geological Survey's (USGS) Toxic Substances Hydrology Research Program. The landfill was closed in 1985, but leachate from the unlined landfill has continued to flow in a groundwater plume underneath the slough toward the Canadian River (Scholl and Christenson 1998). Chloride concentrations can be used to trace mixing between the slough water and the landfill leachate (Röling et al. 2001). Chloride profiles suggest that upward advection/diffusion of landfill leachate from the aquifer into the wetland sediments occurs during some parts of the year (Báez Cazull et al. in press, Lorah and Cozzarelli 2004).

However, the slough ecosystem appears relatively unaffected by the presence of the contaminant plume. Beavers, crayfish, and sensitive biological indicators, such as the dragonfly nymph, have all been found thriving in the slough (unpublished field data). Burgess (2006) collected 163 different species of vascular plants from the slough. Likewise, biogeochemical processes within the upper 50 cm of the slough sediments appear to be controlled by the mineralogy of the slough soil, seasonal cycles of electron availability, and POM derived from the slough rather than the more recalcitrant DOC of the leachate plume (Báez Cazull et al. in press). Because the Norman Landfill Slough is a USGS Toxic Substances Hydrology study site, we have access to a wealth of information concerning sedimentary biogeochemistry, microbiology, water levels, and groundwater flow within the slough, enabling us to better understand the controls of POM preservation and decomposition at this site.

METHODS

POM analysis

For POM sampling, we collected two short cores (5 cm in diameter) in May 2004 near a passive diffusion sampler site, which was used for the collection of geochemical data. One core was 66 cm long, and the other core was 71 cm long. The cores were split longitudinally and photographed, described, and sampled at 1.5-centimeter intervals to determine the size distribution of POM over 150 μm. Most of the POM data reported here come from the 66 cm core. Because this core did not capture the base of the lower unit, we sampled this unit from the 71 cm core.

We wet-sieved each centimeter disk with tap water from a geology laboratory in Texas A&M University, College Station, TX through a series of three sieves: a 1-mm sieve (coarse), a 500-μm sieve (intermediate), and a 150-μm sieve (fine). Sand units yielded little or no POM, and therefore, we did not sieve all sand units from the core. We poured each sieved sample into a large Petri dish (13.5 cm diameter) with a cm grid etched into the bottom and left the samples uncovered so that the water could evaporate.

After the water had evaporated, the POM particles in each sample were counted, using the cm grid etched onto the bottom. The organ type (seed, root, leaf, twig) of the plant-derived POM was identified when possible, and the number of particles belonging to each organ type were tallied. We counted the entire Petri dish for the coarse samples; half of the Petri dish was counted for intermediate samples. The fine fraction of POM consisted primarily of plant fibers and proved difficult to count due to the high clay content of the slough sediment, which resulted in over half the samples of the fine POM fraction being coated with clay after the water evaporated. We used an elemental analyzer to determine the carbon to nitrogen (C:N) ratio based on % content of carbon and nitrogen of all fine fraction samples. We eliminated three POM samples from the upper silt of the intermediate fraction from the analysis because they were too silty to count. Recognizable taxa and organs in the coarse and intermediate POM consisted of seeds, snails, insect parts, and ostracods. We identified the most common seeds to the genus level with assistance from the S.M. Tracy Herbarium at Texas A&M University, College Station, TX.

Histograms of the number and type of POM particles in the coarse and intermediate fractions were compared to lithology and the geochemistry data.

In situ *geochemistry measurements*

Porewater samples were collected during the wet spring seasons in May 2003 and May 2005 and again during the dry, early fall season in September 2005 using passive diffusion samplers, also known as peepers (Hesslein 1976, Báez Cazull et al. in press). Peepers enable collection of discrete water samples at small spatial resolution by preventing the vertical mixing of adjacent water masses during sampling. The peeper used in this study had 37 horizontal ports: the upper 22 ports had apertures and spacing of 0.5 cm; the lower 15 ports had apertures and spacing of one cm.

Prior to deployment, peeper ports were filled with nanopure water (18 mΩ), covered with a 0.45 μm Millipore® membrane*, and deoxygenated with nitrogen for three days to remove oxygen from the water and plastic samplers. The peeper was then transported to the site in an anaerobic chamber constructed of PVC and maintained under deoxygenated conditions until insertion into the slough sediments. The peeper was positioned in the slough for 2 weeks to allow equilibration and diffusion of solutes between the nanopure water and surrounding porewater (Azcue et al. 1996, Jacobs 2002, Webster et al. 1998). In May 2003, the peeper was positioned in the center of the slough parallel to groundwater flow. The peeper was buried completely in the sediment capturing the sediment porewater down to a depth of 52 cm below the sediment-water interface (0 cm). After two weeks of equilibration, the peeper was retrieved and the water samples in the peeper were processed immediately after collection in an anaerobic glove bag filled with a N_2 atmosphere. The study cores were collected adjacent to this peeper. In subsequent years, one peeper, which sampled sediment porewater only, was deployed at the study site. The results from porewater samples collected from peepers in May 2003 and September 2005 are reported here.

Fe^{2+} and hydrogen sulfide were measured in the field using electrometric titration and colorimetric spectroscopy according to standard methods (APHA et al. 1975). Samples for cation analysis were preserved in 1% metal grade hydrochloric acid, samples for anion analysis were preserved in 0.5% formaldehyde, and samples for organic acid analysis were flash-frozen with dry ice and stored for laboratory analysis.

Before the development of peepers, the oxidation-reduction potential (Eh) of natural waters, measured with a platnum electrode, was used to identify overall reducing (low Eh) and oxidizing (high Eh) environments. For example, Pearsall (1938) found that saturated soils have low (reducing) Eh values, while terrestrial soils have higher (oxidizing) Eh values. However, electrodes often give an incomplete picture of the redox potential of natural waters because electrodes measure only the redox reactions that occur rapidly and reversibly at the surface of the platnum (Drever 1997). Processes that involve two or more redox pairs, which may not be in mutual equilibrium cannot be easily measured with electrodes (Stumm and Morgan 1996). Redox pairs that are difficult to measure using electrodes include: O_2-H_2O; SO_4^{-2}-H_2S, CO_2-CH_4, NO_3^--N_2, N_2-NH_4^+, and almost all reactions involving solid phases (Drever 1997). Because the Eh gives a single overall indication of the redox potential of the environment, individual oxidation-reduction reactions cannot be identified using Eh. The analysis of samples collected with peepers allow us to measure the importance of individual terminal electron acceptor processes (TEAPs) at different depths in the slough in light of multiple variables, such as water levels and POM abundance.

Capillary Electrophoresis analyses

An Agilent Technologies Capillary Electrophoresis* (CE) instrument with a photo diode array detector was used for the analysis of Cl^-, SO_4^{-2}, CH_4^+, and organic acids, such as acetate and proprionate). For the analysis, a 56 cm long fused silica capillary with 50 µm I.D. and an extended path length of 150 µM at the detection window was used. Tapered polypropylene vials were filled with approximately 30 uL of sample, more than sufficient volume for multiple replicate runs. The samples were injected by hydrostatic pressure followed by a two-second injection of the electrolyte chosen for each analysis (each injection consumed ~1 nL/sample). The temperature was held constant at 25ºC. Báez Cazull et al. (in press) contains a complete discussion of the use of peepers and Capillary Electrophoresis to investigate the biogeochemistry of standing water and sediment porewater in the Norman Landfill Slough.

Elemental analysis

We used a Vario EL III elemental analyzer to determine the C:N ratio based on % content in the upper silt layer of the fine POM samples that were sieved from the 66 cm core. We also analyzed the total carbon % content of bulk samples from the 71 cm core at a one-cm scale. The bulk samples were acidified to remove carbonate before analysis. The elemental analyzer uses a form of gravimetric analysis where organic compounds are burned in the presence of excess oxygen and the contents are then analyzed. We weighed out 40 mg of each sample into tin capsules and added tungsten oxide powder. The capsules were combusted in a high temperature (1800° C) furnace with oxygen. The combustion products were then carried through oxidation and reduction agents and quantified for carbon and nitrogen by the Thermal Conductivity Detector.

RESULTS

Core description

The surficial sediments of the slough adjacent to the Norman Landfill consist of alternating units of fluvial silt and sand. The following description is based on the sequence of layers in shallow cores collected near the deep peeper (Fig. 4).

Upper Silt Unit (0-40 cm). The upper 40 cm of the slough sediment consists of organic-rich silt, referred to as the upper silt unit. The uppermost 10 cm of this unit contain abundant particulate organic matter, including plant fibers, seeds, insect parts and snail shells. When exposed to light, *Najas guadalupensis* (Spreng.) Magnus (southern nymph, common water nymph) seeds in the upper 18 cm of this unit sprouted. *Najas guadalupensis* seeds occurring below 18 cm in the core did not sprout. The upper silt unit is laterally extensive and appears in all cores collected from the slough (unpublished field data).

Upper Sand Unit (40-44 cm). A layer of tan, medium to coarse grained sand, 3-4 cm thick, referred to as the upper sand unit, underlies the upper silt unit. The contact between these two units is heavily burrowed. The upper sand unit is laterally extensive and occurs in all cores collected from the slough (unpublished field data).

Middle Silt Unit (44-46 cm). A thin, organic-rich muddy silt unit, 2 cm thick, referred to as the middle silt unit, underlies the upper sand unit. The contact between the upper sand and middle silt units is erosional. Báez Cazull et al. (in press) treated the upper sand and middle silt units as a single unit, which they referred to as the transition zone. The middle silt unit is not as laterally extensive as the over- and underlying sand

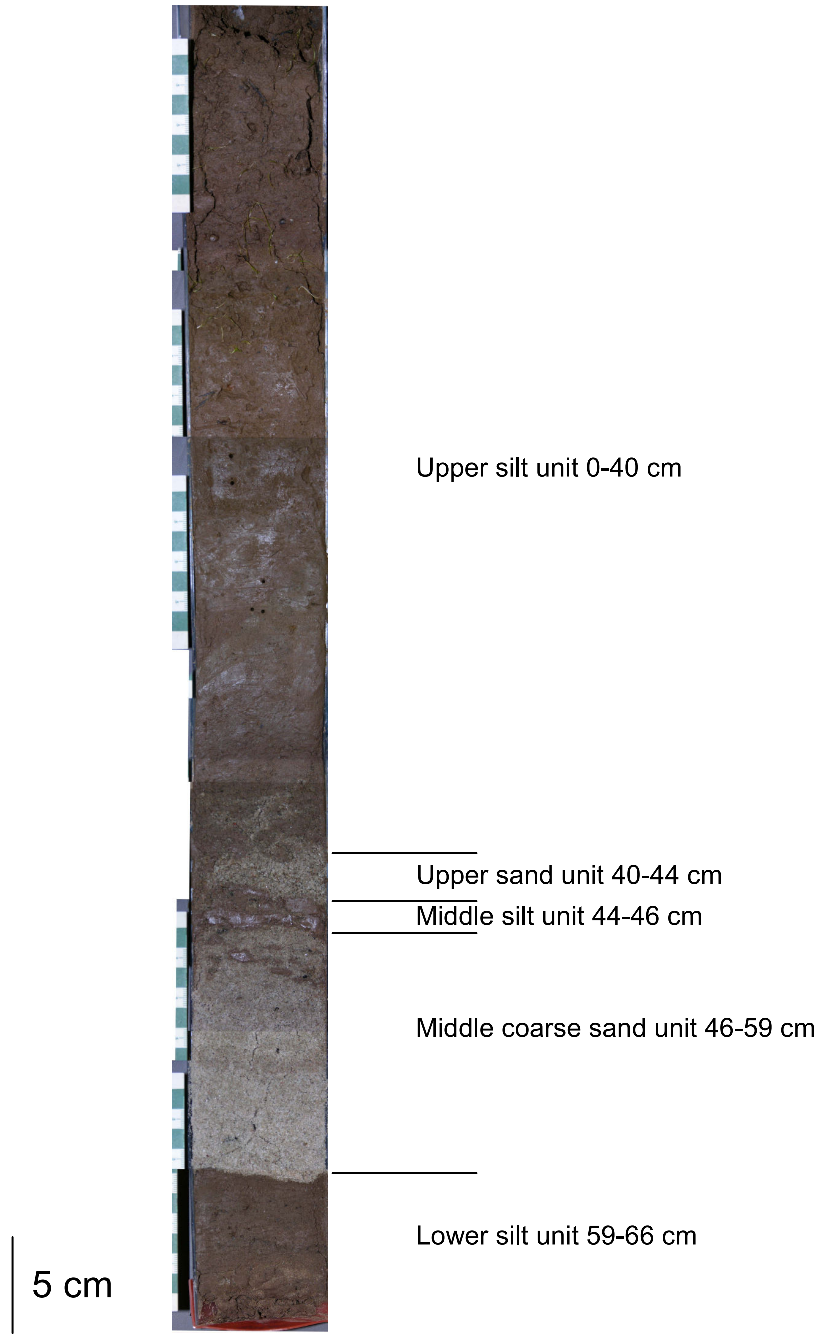

Figure 4. Core description from Norman Landfill Slough. Photograph and description of the 66 cm core that was collected near peeper 2 for POM analysis.

units, and did not occur in the 71 cm core.

Middle Coarse Sand Unit (46-59 cm). The middle silt unit overlies a clean, grey, coarse-grained sand unit, 13 cm thick, referred to as the middle coarse sand unit. The combination of coarse grain size and light grey color enable easy identification of the coarse sand unit in all cores collected from the slough. The contact between the middle silt unit and the middle coarse sand unit is burrowed. No peeper data were collected below 52 cm in the middle coarse sand unit.

This sand layer is laterally extensive and occurs in all cores collected from the slough. When the middle silt layer is absent, upper sand and middle sand units can be distinguished based on grain size and color (unpublished field data).

Lower Silt Unit (59-66 cm). Although no peeper data were collected below 52 cm, the middle coarse sand unit overlies an organic-rich silt layer, 7 cm thick, referred to as the lower silt unit. Like the coarse sand unit, the lower silt unit is laterally extensive and occurs in other cores collected from the slough (unpublished field data). The contact between the middle coarse sand layer and the lower silt unit is erosional.

Lower Sand Unit. The 66 cm core ends in the lower silt unit. In the 71 cm core, the lower silt unit overlies a fine-grained sand layer, which is at least 7 cm thick, referred to as the Lower Sand Unit. The contact between the lower silt unit and the lower sand unit is gradational.

The silt/sand couplets in these cores record three depositional sequences. We interpret the coarse sand layers as flood deposits and the overlying organic-rich silts as marsh or slough soils. One implication of this depositional interpretation is that sand units reflect rapid deposition during floods, whereas silt layers may have accumulated slowly over a series of years. Because the active river channel that became the slough was abandoned in 1986 (Schlottmann 2000), the upper silt layer probably represents no more than 21 years of accumulation. The contacts between the sand units and the underlying organic-rich silt units are erosional; the contacts between the sand units and the overlying organic-rich silt units are frequently burrowed, indicating the presence of aquatic invertebrates (probably crayfish) in the slough.

Nature of POM

On the upper soil surface, there is a 5 to 12 cm thick layer of surficial organic matter that was not recovered in the core. This surficial layer has a patchy distribution across the slough and appears thickest at the edges of the slough near rooted plants. The largest pieces of POM found in this layer were reed and grass stems, 5 mm in diameter and longer than 25 cm, which had to be cut so that we could collect the surficial debris sample; the smallest pieces were < 0.5 mm in their largest dimension. The most common types of plant debris in the surficial layer were: reed and grass stems, rootlet mats, plant fibers, sheets of plant matter, seeds, wood, and skeletonized leaf fragments. The most common animal remains were snails, insect parts, and ostracods. In addition, we recovered bivalves, a portion of a crayfish carapace, fish scales and live oligochaetes from the surficial debris layer. Occasionally, plant-derived POM in this surficial layer had mineral crusts of $CaCO_3$.

Within the soil, in the coarse (>1mm) and intermediate (500 µm – 1 mm) fractions, POM includes: plant fibers, leaf fragments, small pieces of wood, seeds, shells, and insect parts. We also noticed POM with mineral crusts and flakes of carbonate crusts with depth in the core. However, these carbonate crusts were neither quantified nor included in the POM analysis. The fine POM fraction (150 µm – 500 µm) consists mostly of plant fibers.

POM distribution with depth and lithology

The abundance of POM in the coarse and intermediate fractions changes with depth and lithology in slough sediments (Figs. 5 and 6). In general, silt units have more POM than sand units. However, in the upper sand unit, POM counts are as high as POM counts in silt layers above the unit. This is most likely due to silt-filled burrows, which increases POM in the sand layers. We did not analyze the POM of burrows separately in the upper sand unit.

Within the upper silt unit, the abundance of both coarse and intermediate POM is variable and high at the top of the unit and decreases below 16 cm depth in the core. Although both coarse and intermediate POM show the same pattern, the decrease in abundance of coarse POM below 16 cm is more pronounced than the decrease in abundance of intermediate POM. This pattern of variable but high POM abundance in the top of the unit, decreasing with depth also occurs in the lower silt unit. The middle silt unit, which is only 2 cm thick and is included in only one sieved-sample, does not show this pattern. Instead, the abundance of coarse and intermediate POM in this unit is low, similar to the POM abundance observed in sand samples and in basal samples from the upper and lower silt units.

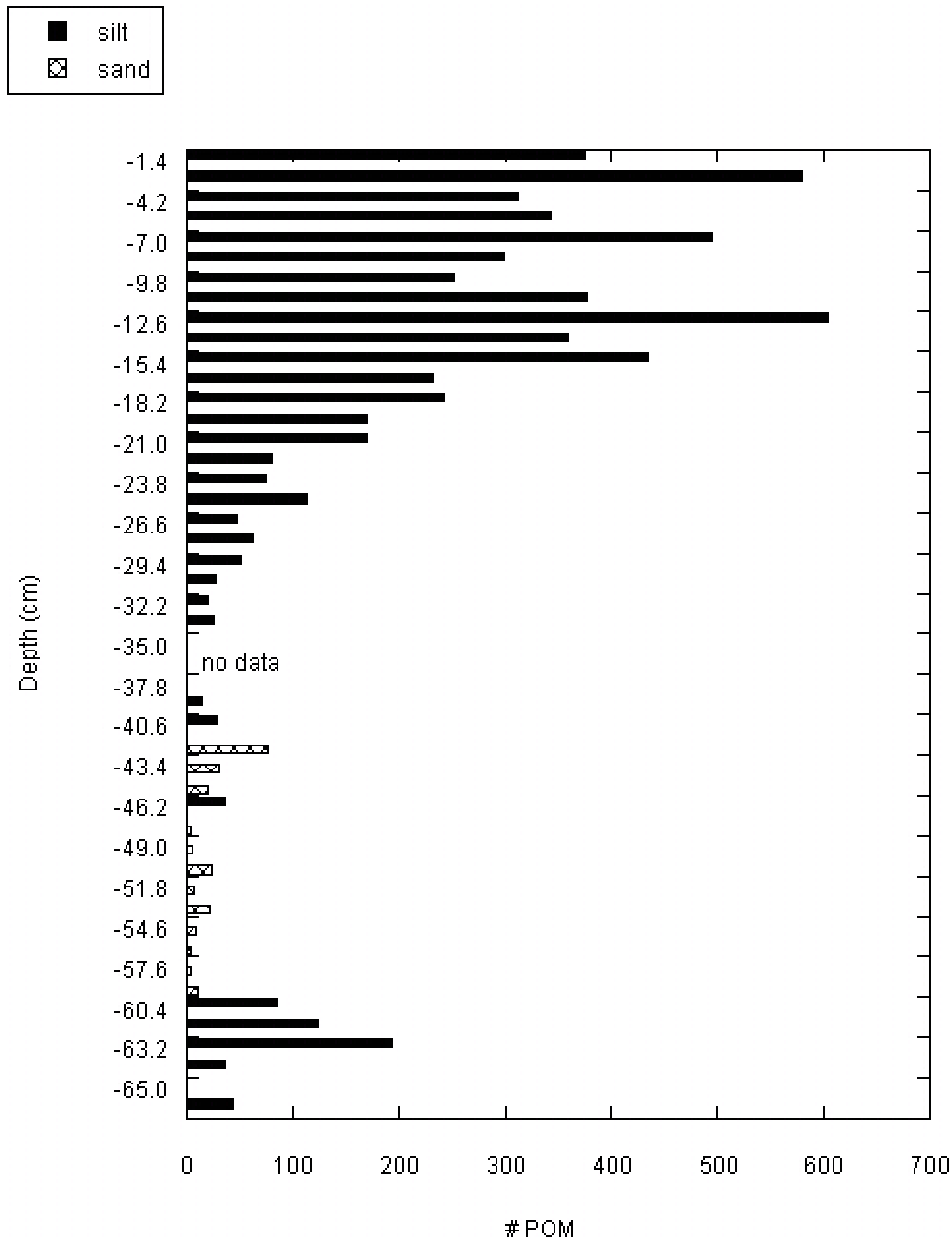

Figure 5. The distribution of the number of coarse POM particles with depth. Coarse samples include POM larger than 1 mm. Silt layers have high POM abundance; sand units have small amounts of POM, except where silt-filled burrows are present. The POM abundance drops dramatically below 16 cm in the upper silt. Fluctuating POM numbers are found throughout the silt layers. No samples were processed between -35 and -37 cm.

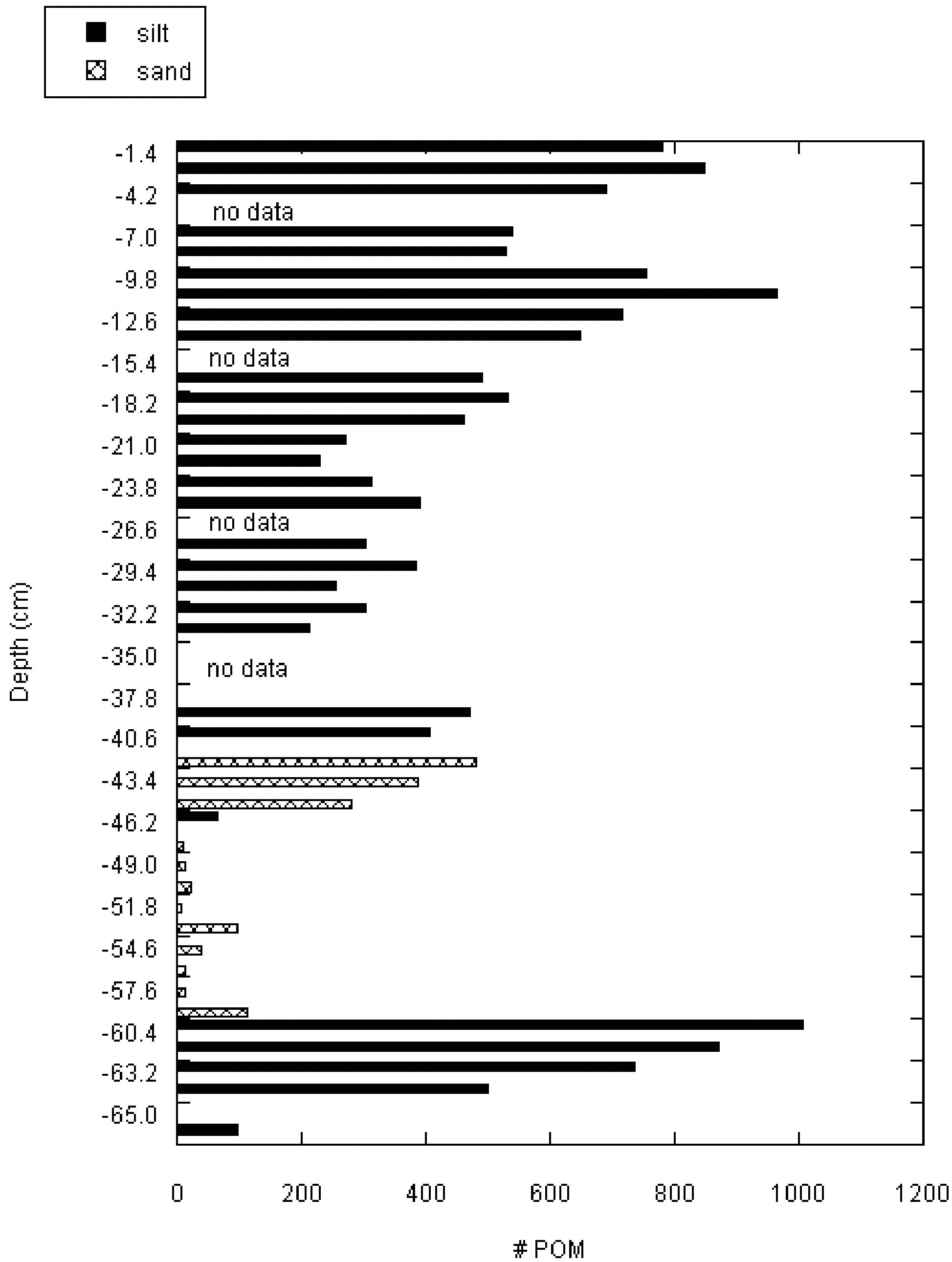

Figure 6. The distribution of the number of intermediate POM particles with depth. Intermediate samples include POM between 1 mm and 500 µm. Silt layers have high POM abundance; sand units have small amounts of POM, except where silt-filled burrows are present. The POM abundance drops dramatically below 16 cm in the upper silt. Fluctuating POM numbers are found throughout the silt layers. No samples were processed between -35 and -37 cm. Three additional samples were not counted in the upper silt, because they were too clay-rich to count.

The total carbon results from the acidified, bulk samples of the 71 cm core show a distribution pattern similar to that of POM in the 66 cm core, particularly for the upper silt and the combined upper and middle sand unit (Fig. 7). In the 71 cm core, variable, high carbon content in the upper silt layer decreases with depth below 16-18 cm. Carbon is almost absent in the combined sand units. In the 71 cm core, total carbon rises in the lower silt unit, as does POM in the 66 cm core. However, total carbon in the lower silt never reaches the high values observed at the top of the upper silt unit, and total carbon does not drop at the base of the lower silt unit. Total carbon remains relatively high in the lower sand unit of the 71 cm core as well. It is possible that dissolved organic carbon from the leachate plume could contribute to the total carbon content of the base of the lower silt unit and the lower sand in the 71 cm core.

POM type

The distribution of POM by type and depth appears in Figs. 8 and 9. Plant fibers compose the majority of the POM in slough sediments. Leaf fragments and wood also occur throughout the core in high numbers. Although seeds appear in low numbers throughout the core, the majority of seeds occur in the upper 21 cm. Animal parts (insect parts, snails, bivalves, and ostracods) occur throughout the core in very low numbers.

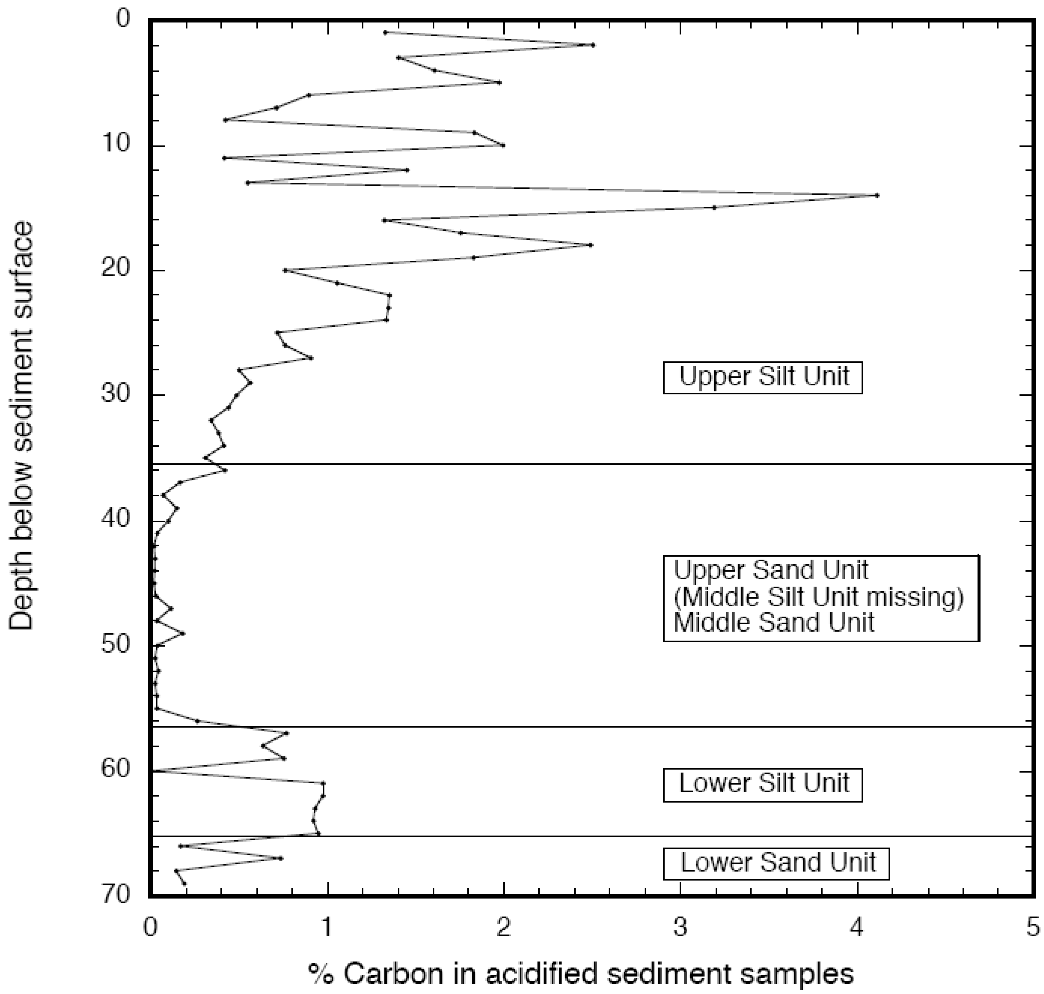

Figure 7. Total carbon from bulk samples of the 71 cm core. The samples were acidified to remove all carbonate before analysis. High carbon content is found in the silt layers, while carbon is absent in the sand units. The total carbon distribution reflects the POM abundance distributions.

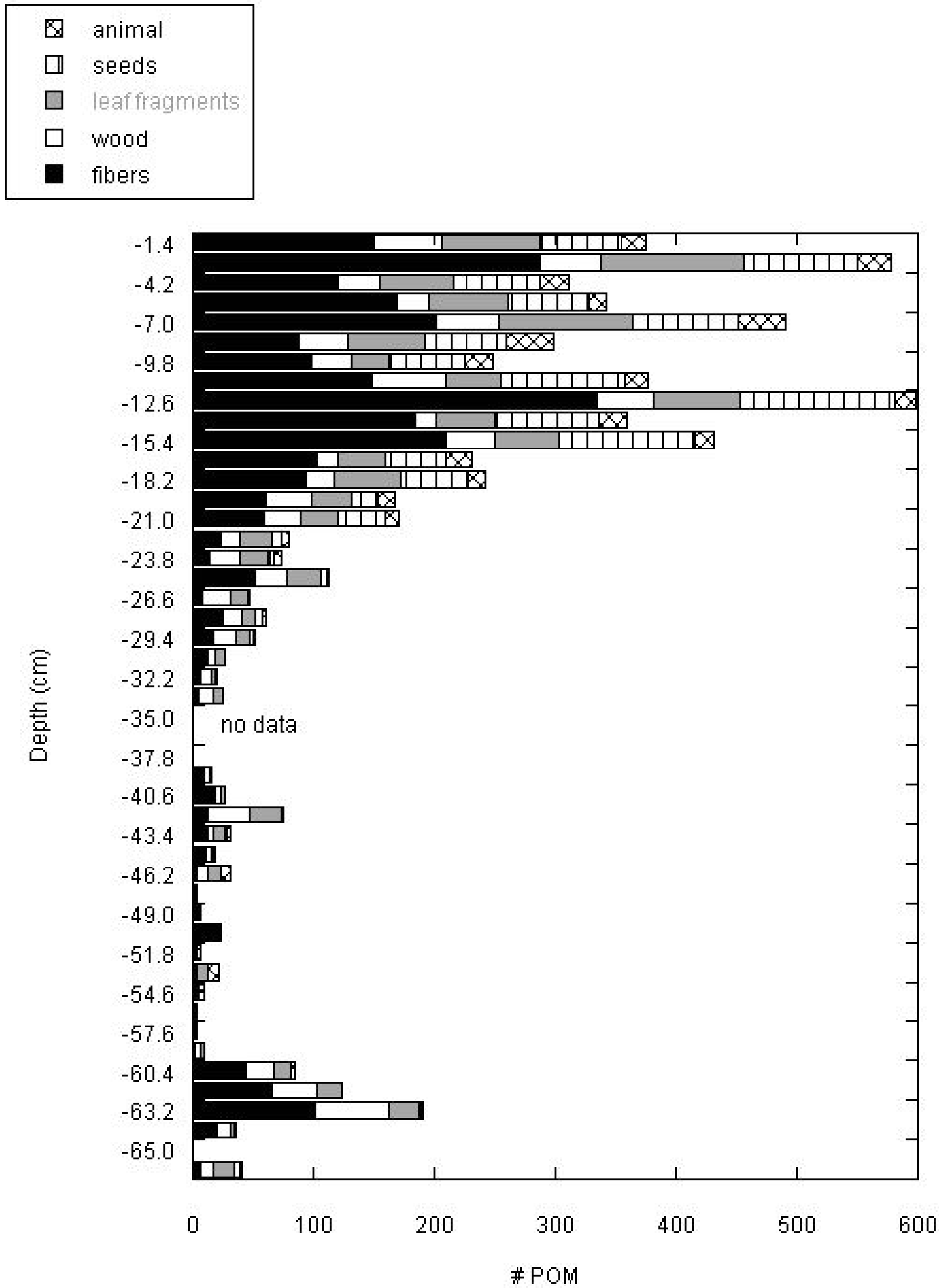

Figure 8. Distribution of coarse POM particles by type with depth. Plant fibers compose the majority of POM in slough sediments. No samples were processed between -35 and -37 cm.

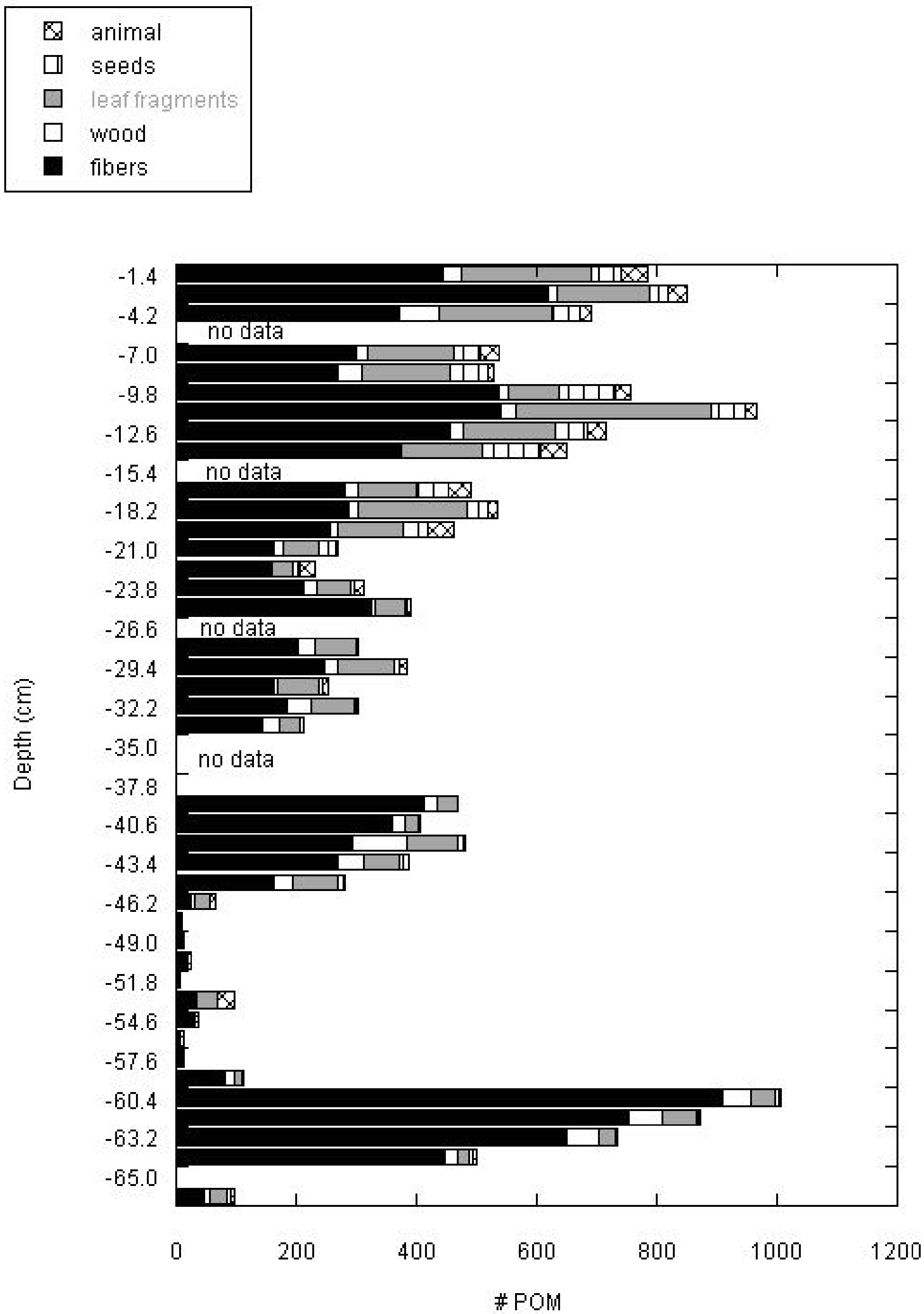

Figure 9. Distribution of intermediate POM particles by type with depth. Plant fibers compose the majority of POM in slough sediments. No samples were processed between -35 and -37 cm. Three additional samples were not counted in the upper silt, because the samples were too clay-rich to count.

Distribution of seeds

The majority of seeds appear in the upper 21 cm but seeds are still preserved at low numbers below this depth (Figs. 10 and 11). The three main types of seeds found were southern nymph (*Najas guadalupensis* (Spreng.) Magnus), barnyard grass or cockspur (*Echinochloa crus-galli* (L.) Beauv.), and rough cocklebur (*Xanthium strumarium* L.). These three seeds make up the majority of all seeds found in the core. However, it is possible that some seeds counted as *Echinochloa crus-galli* could actually be a different species of grass. *Xanthium strumarium* seeds were the most common seed within the surficial debris layer, and contributed the largest seed biomass to this layer. Nonetheless, only one nearly complete *Xanthium strumarium* seed was recovered from the core, and the most common *Xanthium strumarium* part found in the core were spines. Although a single *Xanthium strumarium* seed has up to 50 spines, each spine found in the sediment was counted as an occurrence of *Xanthium strumarium*. The seed walls of *Xanthium strumarium* contain sheets of plant tissue similar to those found as POM in the sediment. Although *Xanthium strumarium* is the probable source of at least some of these tissue sheets, we categorized them as plant fibers in this study.

In the upper third of the 66 cm core, *Najas guadalupensis* dominates the seed flora. However, *Najas guadalupensis* rarely occurs in the bottom two thirds of this core; and was not found in the lower silt unit of the 71 cm core. The only sprouting seeds recovered in POM samples from the sediment were *Najas guadalupensis* seeds, and the sprouting seeds observed before processing the core were almost certainly *Najas guadalupensis* seeds. Sprouting seeds recovered in POM samples and observed in the

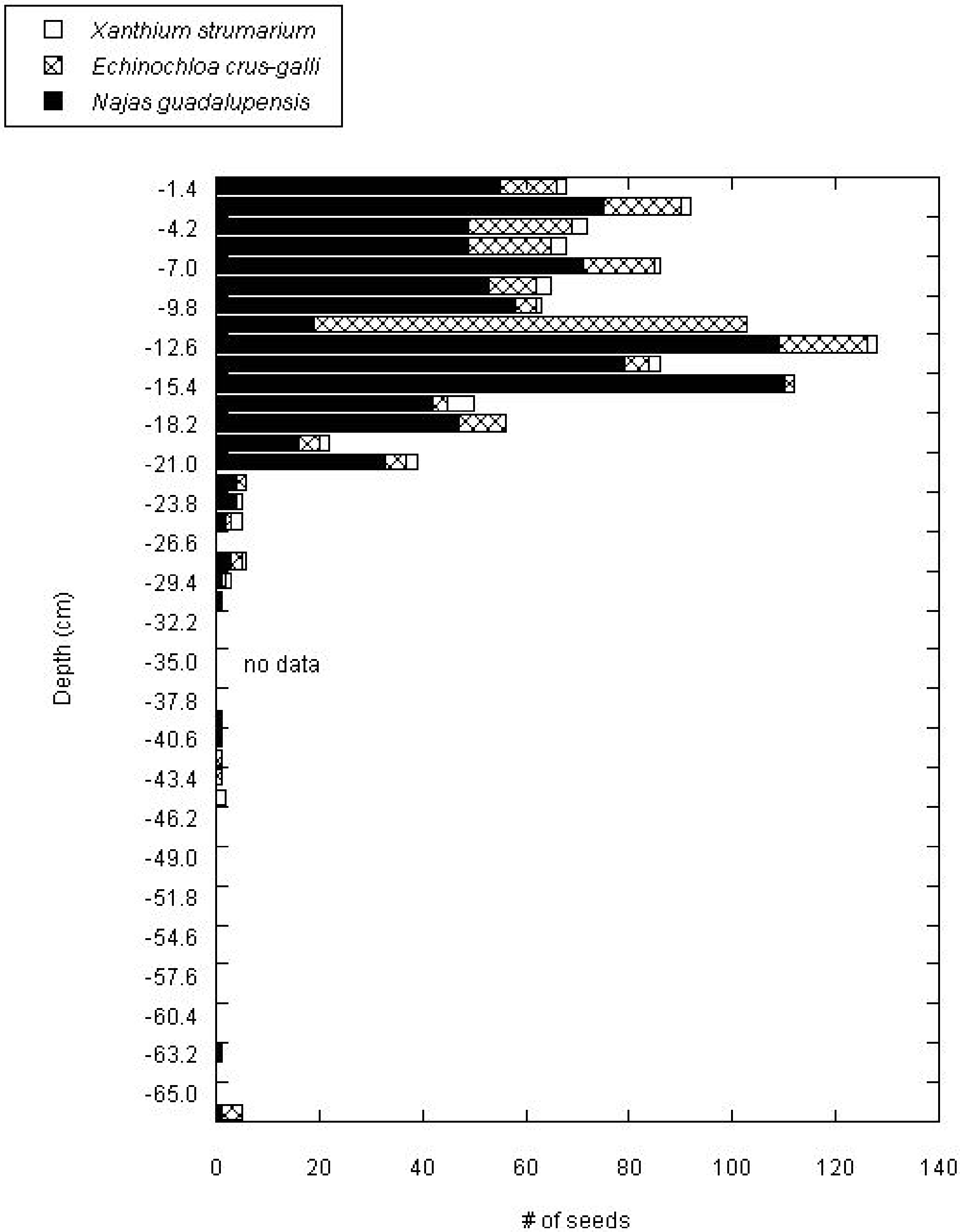

Figure 10. Distribution of seeds in coarse samples. The majority of seeds appear in the upper 21 cm. *Najas guadalupensis* dominates the seed flora in the upper third of the core. No samples were processed between -35 and -37 cm.

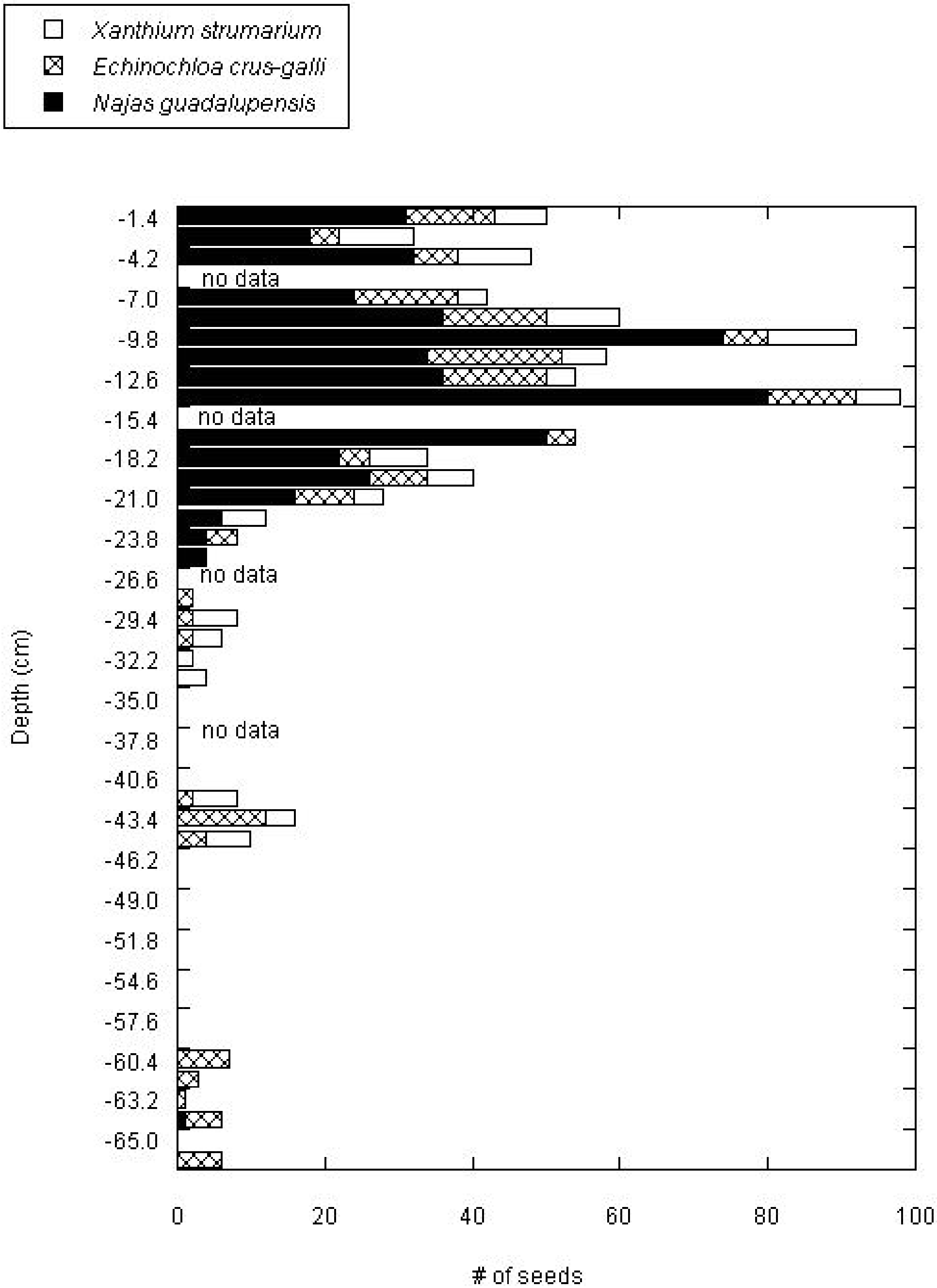

Figure 11. Distribution of seeds in intermediate samples. The majority of seeds appear in the upper 21 cm. *Najas guadalupensis* dominates the seed flora in the upper third of the core. No samples were processed between -35 and -37 cm. Three additional samples were not counted in the upper silt, because the samples were too clay-rich to count.

core were confined to the upper 18 cm of the core. The drop in the abundance of *Najas guadalupensis* seeds below 18 cm in the core may account for lack of sprouting seeds below this depth. While seeds were found in the upper sand unit, no seeds were preserved in the middle sand unit. Seeds were found once again in the lower silt unit.

C:N ratios

For the coarse POM fraction, we used the wood to fiber ratio as a proxy for the carbon to nitrogen ratio (C:N ratio), because wood has a high C:N ratio compared to other plant material and is more resistant to breakdown (Webster and Benfield 1986). The wood to fiber ratio in the upper silt layer of the coarse POM shows a slight increase of wood at depth, implying an increase in the C:N ratio with depth in the coarse POM fraction (Fig. 12). C:N ratios of the smallest POM fraction, measured with an elemental analyzer, oscillate around 20 and seem to increase with depth, suggesting that the quality of fine and coarse POM may become slightly more recalcitrant with depth (Fig. 13). However, this increase is not statistically significant. The fine POM samples were not acidified prior to analysis. Thus, C:N ratio values reported here may be artificially high due to the inclusion of calcium carbonate, either as small shell fragments or as carbonate encrusted microorganisms. However, the general trend of the C:N ratio with depth is shown with these samples.

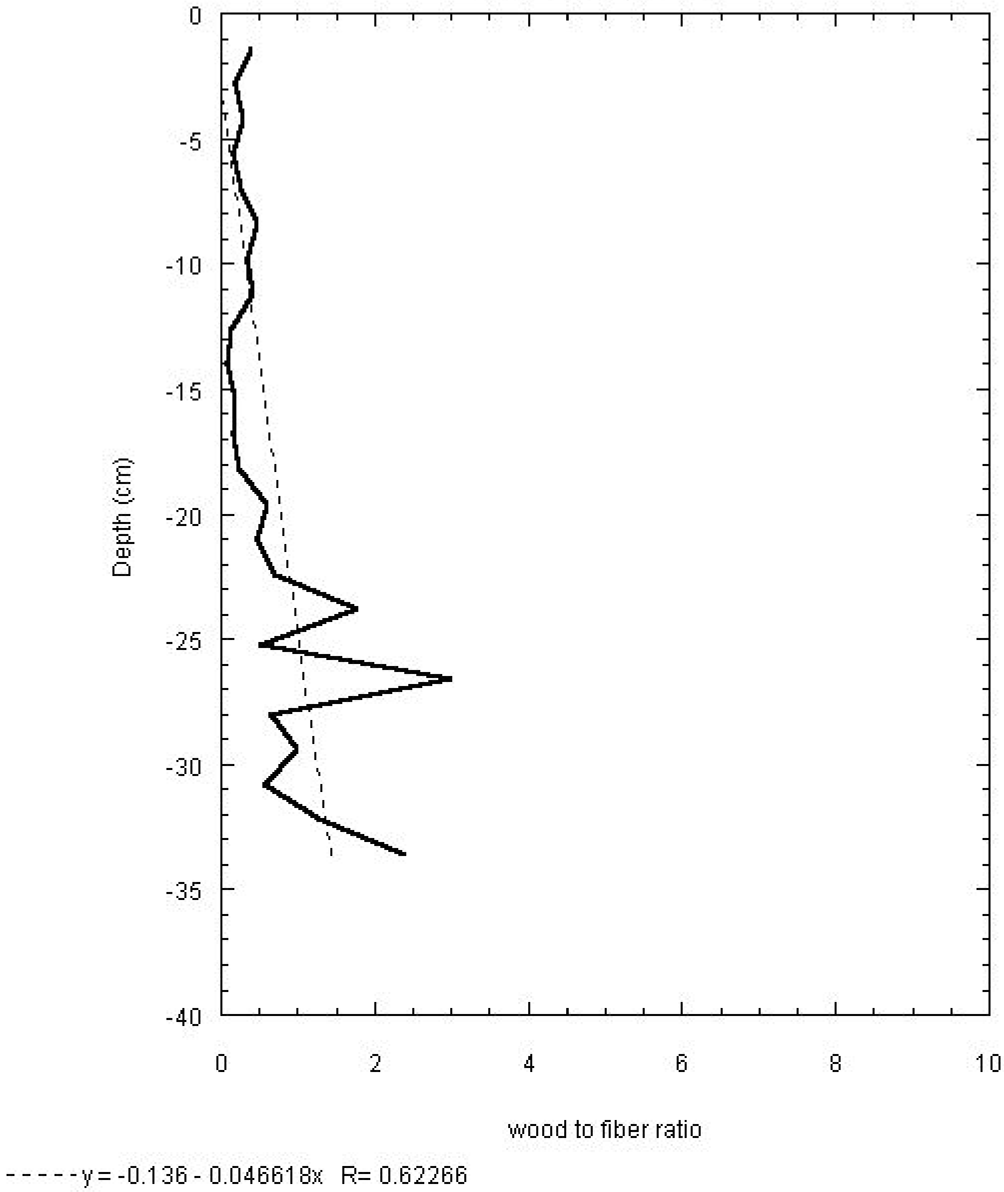

Figure 12. The wood to fiber ratio of coarse POM samples in the upper silt. The wood to fiber ratio was used as a proxy for C:N ratios. A linear regression with R = 0.62 is shown with the dashed line.

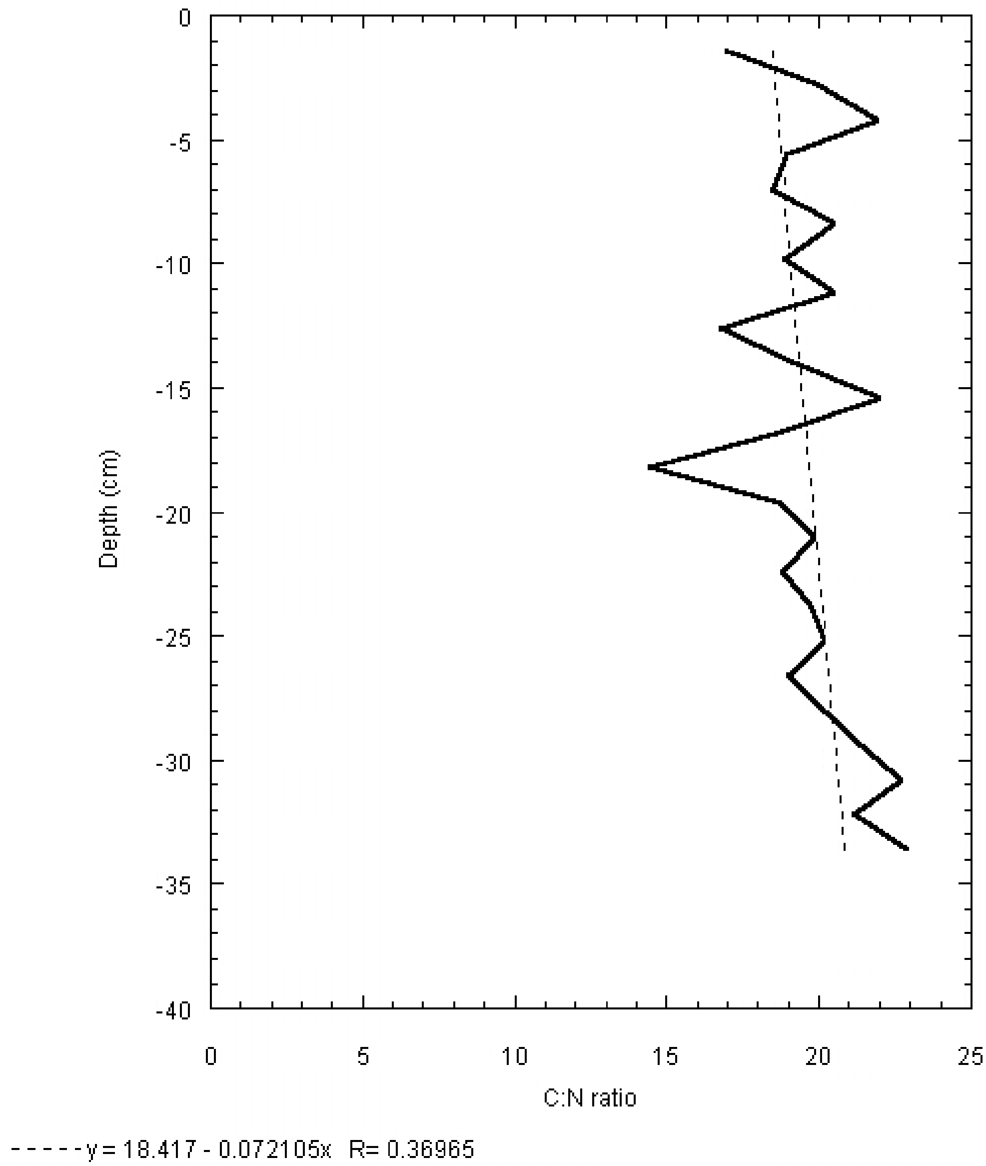

Figure 13. C:N ratio of fine POM samples. A linear regression with R = 0.37 is shown with the dashed line. Although the linear regression line suggests that fibers become more carbon rich with depth, the R value of 0.39 is not significant.

Biogeochemistry data

When the slough was completely submerged in May 2005, sulfate reduction, iron reduction, and methanogenesis occurred immediately below the sediment-water interface (Fig. 14). This is shown by high levels of Fe^{2+} concentrations throughout the slough sediments; increasing levels of CH_4^+ concentrations within the upper 15 cm of the soil; and rapidly decreasing levels of SO_4^{2-} correlated with increasing H_2S concentrations. In fact during these wet periods, sulfate was primarily observed in the surface waters where oxygen was available – not in the sediment layers. Concentrations of organic acids, such as acetate, were high at the sediment-water interface during the wet season, indicating the presence of fermenting bacteria and POM decomposition (Fig. 15). In May 2005, the acetate profile indicates that decomposition occurred at the sediment-water interface.

When the water table fell below the slough surface in September 2005, the upper sediment layers showed different geochemical processes. Products of fermentation, such as acetate, were displaced 10 cm below the sediment surface in September, coincident with the mean water level in the slough during September 2005. Much lower concentrations of small organic acids were observed at the oxic/anoxic boundary during this dry interval as compared to May 2005 (Fig. 16). Likewise, iron reduction, shown by high Fe^{2+} concentrations, was displaced 10 cm below the sediment surface (Fig. 17). The reoxidation of FeS minerals in the soil during this dry season increased sulfate concentrations two orders of magnitude greater than sulfate concentrations observed in the wet season (Fig. 18).

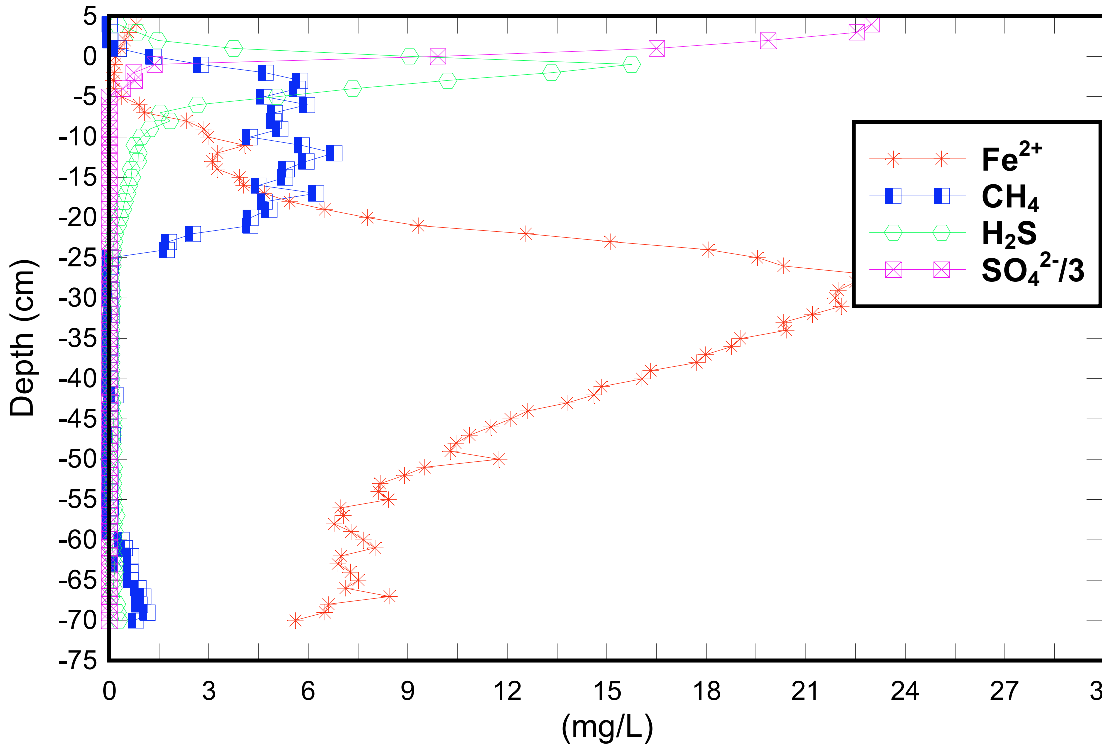

Figure 14. Reduction reactions in May 2005. Fe-reduction, SO_4^{-2}-reduction, and methanogenesis occur during the wet season. These reactions occur simultaneously at the sediment-water interface (0 cm) during the "wet" period in May 2005. However, peak levels of Fe^{2+} in sediments are displaced 20 cm below the sediment-water interface. Methanogenesis correlates approximately with the abundance of coarse and intermediate POM. SO_4^{-2} concentration values are divided by three in this graph.

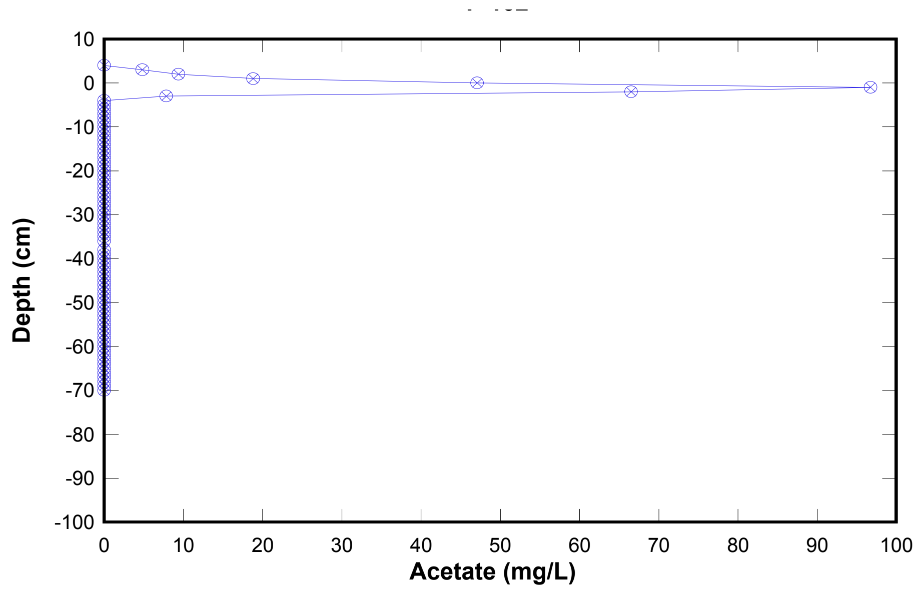

Figure 15. Acetate profile in May 2005. The acetate profile from May 2005 shows high values of acetate at the sediment-water interface. This indicates the presence of fermenting bacteria at the sediment-water interface.

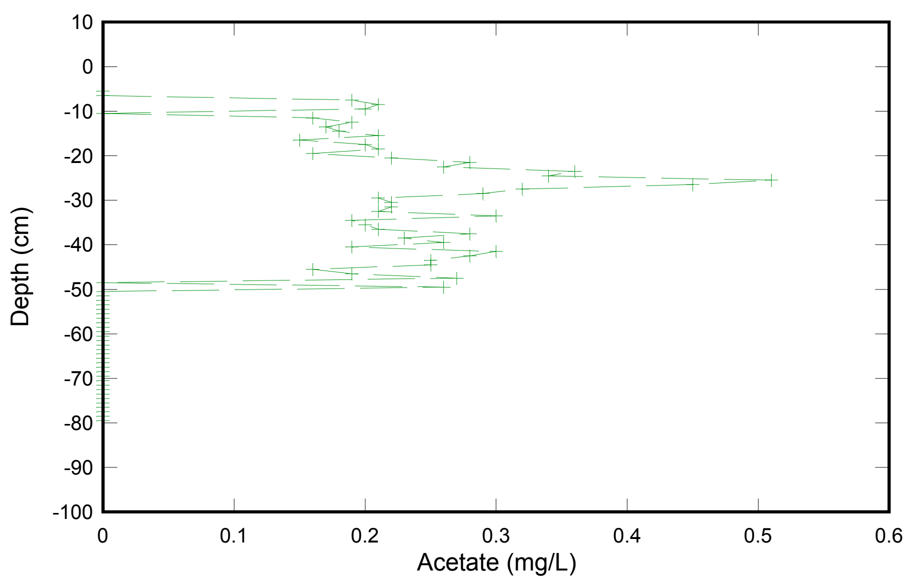

Figure 16. Acetate profile in September 2005. The acetate profile from September 2005 shows that a 10 cm lag of fermentation products occurred during the dry interval. Lower concentrations of small organic acids were observed at the oxic/anoxic boundary during this dry interval as compared to a wet interval.

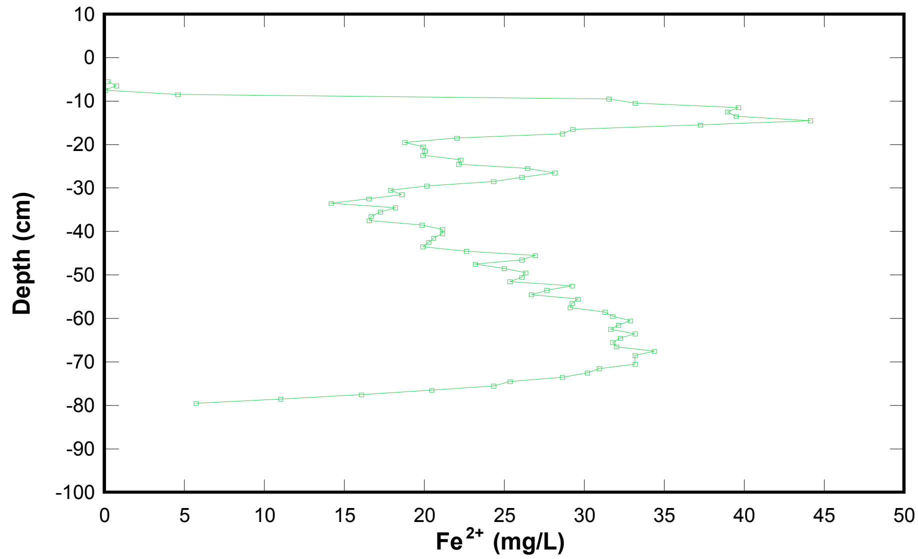

Figure 17. Dissolved iron profile in September 2005. Iron reduction did not occur until approximately 10 cm below the sediment surface in September 2005. Fe^{2+} builds up immediately below this level, and the peak concentration is approximately twice that observed in the wet season (Fig. 14).

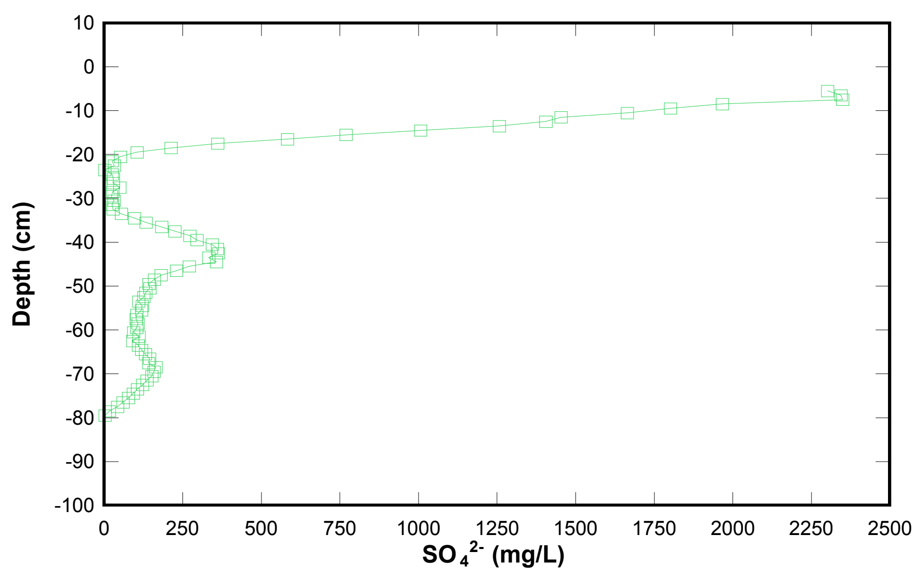

Figure 18. Sulfate profile in September 2005. The sulfate profile in September 2005 shows that sulfate-reduction does not occur until 10 cm below the sediment surface. Sulfate concentrations in sediment porewater were two orders of magnitude higher in the dry interval compared to the peak values observed in a wet interval (Fig. 14).

DISCUSSION

Seasonal biogeochemistry cycles

The porewater biogeochemistry in the slough is dominated by the seasonal cycles of vegetative growth and decay, hydrological recharge and drawdown, electron acceptor availability, and soil mineralogy. In the slough system, the dominant terminal electron acceptor processes (TEAPs) coupled to the oxidation of organic matter are Fe-reduction, SO_4^{-2} reduction, and methanogenesis (Báez Cazull et al. in press). These reactions can be traced using Fe^{2+}, sulfate, hydrogen sulfide, and small organic acid concentrations in sediment porewaters. Fe^{2+} concentrations are high throughout the saturated slough sediments during wet and dry periods indicating that sediment porewater remain anoxic throughout the year. Fe^{2+} concentrations are low in areas with active sulfate reduction as Fe^{2+} reacts with H_2S to form pyrite. The depth at which these processes occur is controlled in part by the depth of the water table in the slough (Table 1).

When the slough sediments are submerged in winter and spring, the sediment-water interface and the oxygenated middle sand layer provide the source of electron acceptors, primarily Fe (III) oxides and SO_4^{-2}. In the summer and early fall, water levels drop, revealing exposed anoxic sediments that are rich in reduced FeS minerals. Processes during the dry period, including reoxidation of FeS minerals, washing of SO_4^{-2} precipitates, and leaching of SO_4^{-2} from newly deposited leaves in the surficial detritus layer, produce Fe (III) oxide minerals and SO_4^{-2}. Although the duration and timing of the slough's hydroperiod varies every year, this pattern of alternating oxic and anoxic conditions in the upper layers of the slough sediment is repeated year to year, except in very wet years. The minimum level of the water table in the late summer and early fall also varies year to year (Table 1, Fig. 2). However, the maximum rooting depth of plants in the slough in May 2006 was 18 cm (unpublished field data), which is close to the average minimum level of the water table over the past 10 years, 16.5 cm. Because roots cannot survive in continuously anoxic waters (Mitsch and Gosselink 2000), the maximum rooting depth may be tied to the average depth at which oxic conditions occur in the dry season (late summer – early fall).

The total carbon and POM distribution data indicate that the amount of POM available controls biogeochemical reactions in slough sediments. In the upper silt unit, high amounts of organic carbon act as electron donors to drive redox reactions. Reduction processes do not occur in the upper and middle sand units where there are low amounts of organic carbon. In the lower silt unit, which has high amounts of POM, reduction reactions also occur. Within the upper silt unit, both the wood:fiber ratio of coarse POM and the C:N ratio of fine POM gradually increase with depth, although only the coarse POM shows a statistically significant decrease in quality. Based on C:N ratios, the quality of the POM decreases only slightly and does not seem to limit reduction reactions in the slough with depth.

Distribution of POM in the slough and slough sediments

The surficial layer of POM in the slough contains a wealth of plant and animal taxa and provides the best sedimentary record of the slough ecosystem. Some taxa found in the surficial layer either do not occur or are extremely rare at depth in the core (e.g. fish scales, bivalves, crayfish). On average, the size of plant debris and animal remains from this layer is much larger than the size of animal- and plant-derived sedimentary POM. Unfortunately, layers of surficial debris are seldom preserved *in situ* in fluvial depositional systems. High-energy flooding events leading to the deposition of sand layers generally erode the coarse surficial debris before it can be buried. As expected, sand units, which were deposited in high-energy conditions relative to silt unit events, contain relatively small amounts of plant-derived POM relative to silt layers.

Both the upper and lower silt units show a similar pattern of POM abundance: variable but high abundance of POM in the upper part of the unit, dropping to lower abundances at the base of the unit. The middle silt unit, with only one sieved sample, is too thin to reveal this pattern. This pattern was most clearly expressed in the upper silt unit, for which we also have peeper data, allowing us to trace terminal electron accepting processes in the upper silt unit.

Within the upper silt unit, the drop in POM and seed abundance and the loss of seed viability are relatively abrupt, even though there is no obvious lithological transition at this level. This boundary coincides approximately with the average depth of the water table below the slough surface in the late summer and early fall (Table 1). Previous studies attributed rapid POM decomposition during dry intervals to the role of oxygen in increasing the rate of decomposition (Brinson et al. 1981, Corstanje and Reddy 2004). Although the upper 16-18 cm of slough sediments become oxygenated in the late summer and early fall, the pattern of fluctuating but abundant POM in the upper 16-18 cm of the sediment and less POM below 18 cm suggests that decomposition in the late summer and early fall is concentrated at the boundary between anoxic and oxic conditions. In the Norman Landfill Slough, maximum biogeochemical cycling occurs at interface mixing zones between oxic and anoxic conditions. As water tables drop below the soil surface, a reoxidation front moves downward through the slough sediments, reoxidizing FeS and Fe-oxyhydroxide minerals and releasing SO_4^{-2} for terminal electron acceptor processes. Under these circumstances, decomposition is most rapid in the newly oxic substrates at the oxic/anoxic boundary. Debris above the boundary is sheltered from rapid decomposition, although the highly variable abundance of POM in the upper 16-18 cm of the slough suggests that this POM is vulnerable to decomposition whenever water tables drop below the slough surface. The lower boundary of the high but variable POM abundance zone marks the average depth of the minimum water table below the slough surface in dry months and the average depth of the oxic/anoxic boundary where rapid decomposition of POM occurs.

The seasonal introduction of oxygen in the upper part of the sedimentary column during dry periods has a much greater impact on POM decomposition due to the presence of reduced FeS minerals. The solubility of oxygen in water is extremely low, and in the absence of reduced FeS minerals and other dry season sources of sulfate, one expectation of lowered water tables would be to simply displace the patterns observed at the sediment-water interface during wet intervals to the new unsaturated – saturated zone interface below the sediment surface. In this situation, lowering the water table would deliver oxygen deeper in the sediments but would not increase the supply of TEAPs. Instead, the abundance of TEAPs, especially SO_4^{-2}, in slough sediments during the dry season is much higher than in the wet season (Figs. 14 and 18). The super abundance of

TEAPs in the slough sediments during the dry season results from the presence of iron minerals in the sediment. In wetland sediments with abundant FeS minerals, such as the Norman Landfill Slough, oxidation of FeS minerals as the water table drops creates a reservoir of sulfate available for POM decomposition as the water table rises.

The pattern in the upper silt unit repeats in the lower silt unit: variable but high amounts of POM at the top of the lower silt unit, and low amounts in the bottom part of the unit. This repeated pattern suggests that rapid burial of silt units in flooding events can protect POM from further decomposition over decadal and perhaps longer time intervals. We do not see this pattern in the thin middle silt unit, possibly because the upper POM rich layers were lost to erosion during the deposition of the upper sand unit, leaving only 2 cm of the middle silt unit to observe. When corrected for compaction, the pattern of POM abundance in sand/silt couplets deposited in freshwater fluvial settings could be used to predict seasonal fluctuations in the height of the water table. This depth would be a minimum depth because a portion of the zone of variable but high POM abundance would likely be eroded during flood events which deposit these sand layers.

The total carbon in bulk sediment samples shows a similar distribution pattern as POM. It is possible that elemental analysis can be used to approximate POM abundances in siliciclastic sediments.

Decomposer communities and pathways

Three important components of the decomposer community in wetland ecosystems include bacteria, fungi, and aquatic invertebrates (primarily insects and oligochaetes), which shred detritus making it more susceptible to fungal and microbial decomposition (Swift et al. 1979, Fazi and Rossi 2000). The role of aquatic invertebrates in POM decomposition within the Norman Landfill Slough is the subject of ongoing research. Because fungal decomposition requires oxygen, fungal decomposition within the slough is likely confined to the coarse surficial debris layer on the sediment surface, which is oxic most of the year. Fungal decomposition can also occur in the upper sediment layers, which become oxic when the water table drops below the surface of the slough, about 17% (59 days) of the year (Table 1). Fungal remains were not an important component of sedimentary POM recovered from the Norman Landfill Slough; however, loosely attached fungal hyphae may have been rinsed from POM in the process of wet sieving. Microbially mediated redox reactions occurring in sediments appears to be the most important mechanism of POM degradation in Norman Landfill Slough sediments. Previous work by Báez Cazull et al. (in press) and Kneeshaw et al. (in press) utilized geochemical analyses to infer microbial redox processes in these sediments and ongoing research to characterize the native microbial communities is underway.

Applications to peat decomposition studies and peat accumulation models

While the rate of organic decomposition is considerably slower in peat, peat-accumulating systems and the Norman Slough system are both electron acceptor limited and both have oxic/anoxic interfaces. The role of terminal electron acceptor processes and the reoxidation of soil minerals in POM decomposition in wetlands may help to explain the observed positive correlation between the amount of mineral matter in peat and the decomposition state. In peat-accumulating wetlands, flow rates, the abundance of minerals, nutrient availability, neutral pH, and enhanced rates of decomposition tend to be correlated (Taylor et al. 1998, Turetsky and Ripley 2005). Low rates of water flow lead to the build-up of organic acids, low pH, and low rates of decomposition (Taylor et al. 1998). In some cases, low pH can inhibit sediment influx. For example, the high humic acid content (and low pH) of coastal freshwater swamps in South Carolina caused flocculation and accumulation of clay minerals at the edge of the swamp during flooding events (Staub and Cohen 1979). Conversely, high flow rates transport sediment into the wetland and prevent the concentration of organic acids in peat porewater, leading to neutral pH.

A variety of explanations have been proposed for the correlation between rapid decomposition and high amounts of mineral matter in peat. Taylor et al. (1998) attributed slow rates of decomposition in nutrient poor bog peat to low pH, which suppressed microbial activity. Turetsky and Ripley (2005) attributed rapid decomposition of nutrient-rich, fen peat to increased nutrient availability for microbial decomposition. Enhanced decomposition of organic matter driven by the reoxidation of iron minerals under conditions of fluctuating water tables could contribute to rapid decomposition in fen peats with high percentages of mineral matter compared to bog peats.

The reoxidation of soil minerals may also influence decomposition in peat layers that lie above the permanent water table (i.e. the acrotelm). Laiho (2006) reported increased rates of peat decomposition at the base of the acrotelm, which he attributed in part to slow rates of decomposition in exposed peats caused by decreased moisture availability. However, Laiho also suggested that, as water levels drop in peat, increased aeration and recent drainage would maximize aerobic decomposition between the dry surface and the new water level. Likewise, Clymo (1991) reported more rapid decomposition at depth within the acrotelm, rather than at the acrotelm surface.

For simplicity, most peat models assume a uniform rate of decomposition throughout the acrotelm (Clymo 1984, Bauer 2004). Yet these models cannot easily explain the existence of highly humified peat layers overlying less humified peat layers, known as recurrence horizons; even though recurrence horizons are relatively common in northern peats (Clymo 1991). Recurrence horizons often occur associated with changes in the peat accumulating community and changes in climate and drainage may cause recurrence horizons as well. Our observations in the Norman Landfill Slough suggest a mechanism for recurrence horizons unrelated to changes in the plant community. If terminal electron acceptors become concentrated immediately above the fluctuating water table in peat as they are in the siliciclastic sediments of the Norman Landfill Slough, fluctuating water tables would be expected to produce recurrence horizons in peat. A series of relatively wet years or changes in drainage causing higher permanent water tables would displace the zone of rapid decomposition closer to the surface. As a result, relatively undecomposed peat could be incorporated into the peat layers below the permanent water table (i.e. the catotelm). Conversely, a series of relatively dry years would displace the zone of rapid decomposition deep in the peat body, and would expose material previously incorporated into the catotelm, to rapid decomposition, producing a layer of highly humified peat.

There are limits to this process. Peat which has already passed into the catotelm will not decompose as rapidly as peat that has not yet reached the catotelm (Laiho 2006). Nearly all freshwater peat-accumulating systems have dramatically lower concentrations of key terminal electron acceptors such as Fe^{2+} and sulfate than siliciclastic wetland sediments. Novak et al. (1994) reported the accumulation and biogeochemical cycling of sulfur in sphagnum peat from the temperate zone. Although most sulfur (85%, from 1,741 - 5,653 μg/g dry wt of peat) was organic sulfur, they found both iron sulfides (12%, from 126 to 723 μg/g dry wt of peat) and sulfate (3%, from 53 to 126 μg/g dry wt of peat). For comparison, elemental analysis of slough sediment from the 71 cm core yielded an average total sulfur content of 156,000 μg/g dry wt of sediment (range 37,000 - 639,000 mg/g dry wt of sediment). In these peats, the decomposition of organic matter at the catotelm/acrotelm boundary fuels sulfate reduction. Peak sulfate and sulfur concentrations occurred at the catotelm/acrotelm boundary. Sulfur is mobile in the unsaturated upper layers of the peat (i.e. the acrotelm) and becomes permanently incorporated into the peat at the acrotelm/catotelm boundary.

It is also important to remember that peat accumulates very slowly compared to the accumulation rate of fluvial silts. Thus, the zone of abundant POM in Norman Landfill Slough sediments could respond quickly to changes in slough hydrology or climate, while recurrence zones in peat require long periods of time to develop.

CONCLUSIONS

POM acts as an important electron donor in terminal electron acceptor processes in the slough. Fe-reduction, sulfate-reduction, and methanogenesis occur where high amounts of POM and total carbon are found. Seasonal changes in slough water levels are responsible for the shifting oxic/anoxic boundary within the slough sediments. At this oxic/anoxic boundary, rapid decomposition of POM occurred at the average depth of the minimum water table level in the late summer and early fall, because the reoxidation of FeS minerals releases incredibly high amounts of SO_4^{-2} enabling TEAPs within the slough sediment at the oxic/anoxic boundary. Varying water table levels throughout the years are responsible for the fluctuating POM numbers in the upper silt unit as the depth of oxic/anoxic boundary changes.

High amounts of POM and high percentages of total carbon are found in the silt layers, while the sand units have small amounts of POM and low percentages of total carbon. The high energy depositional environment of the sand units does not allow POM to be buried in these units, except for silt-filled burrows that may be found at the top of the sand units in some areas. The rapid deposition of the sand units above the lower silt unit protected the POM in the lower silt unit from further decomposition on a decadal time scale. Total carbon results mirror POM distribution patterns, and total carbon could act as a proxy for POM abundance in siliciclastic wetlands.

The results of this study highlight the importance of seasonal recharge and drawdown in a wetland on POM decomposition. POM distributions in ancient freshwater siliciclastic environments could be used to predict the occurrence of seasonal fluctuations in water table height. Furthermore, long term fluctuations in the height of the water table may help explain recurrence horizons in peat. As climate change proceeds, seasonal and long-term fluctuations in the water table may have a major effect on the wetland soil carbon pool.

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