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CARBON ISOTOPIC COMPOSITION OF METHANE IN FLORIDA EVERGLADES SOILS AND FRACTIONATION DURING ITS TRANSPORT TO THE TROPOSPHERE

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Abstract. The $\delta^{13}C$ stable carbon isotopic composition of methane collected in bubbles from the submerged soils of specific environments within the Everglades wetland in southern Florida, United States, varied from $-70°/_{oo}$ to $-63°/_{oo}$ across the system while organic carbon in the soils and dominant plants varied from $-28°/_{oo}$ to $-25°/_{oo}$. A methane isotopic budget based upon the soil bubble isotope data and published methane flux measurements predicted a flux of isotopic composition $-65°/_{oo}$, a value 5–$10°/_{oo}$ more depleted in ^{13}C than the isotopic composition of methane emanating to the atmosphere. Emergent aquatic plants, which are known to be active methane transporters between soil and atmosphere in this ecosystem, were found to transport methane of $\delta^{13}C$ content up to $12°/_{oo}$ different from the $\delta^{13}C$ content of the soil methane bubble reservoir. Methane ^{14}C content at one site was determined to be 108.6% modern ($\Delta^{14}C = 83 \pm 10°/_{oo}$).

INTRODUCTION

Considerable interest is currently focused on the atmospheric cycle of methane due to the observed increase in its tropospheric concentration [Rasmussen and Khalil, 1981; Fraser et al., 1981, 1984; Blake et al., 1982; Ehhalt et al., 1983; Pearman et al., 1986; Rinsland et al., 1985; Dickinson and Cicerone, 1986; Steele et al., 1987]. Recent models, which evaluate worldwide methane source and sink terms, postulate an important role for terrestrial tropical and subtropical wetlands in supplying methane to the atmosphere [Khalil and Rasmussen, 1983; Ehhalt and Schmidt, 1978]. The stable carbon isotopic composition of methane sources such as wetlands may help place constraints on their contribution by forcing qualitative as well as quantitative mass balance [Stevens and Rust, 1982; Stevens and Engelkemeir, 1988]. In particular, any change in the carbon isotopic composition of atmospheric methane must ultimately be linked to changes in inputs and outputs [Stevens and Rust, 1982; Tyler, 1986]. Knowledge of the characteristic isotopic composition of methane sources can be used to identify potential contributors to the increase in the atmospheric methane concentration.

The major objective of this study was to determine the stable carbon isotopic composition of methane, plants and sediments in a major continental wetland, the Florida Everglades. Samples were collected in conjunction with methane flux measurements made in distinct ecosystems which were defined by remote sensing and field data by the NASA Langley research group of Harriss et al. [this issue]. A map of the study area and environmental delineations are shown in Figure 1. These environments are wet prairie and sawgrass marsh with marl soil, wet prairie and sawgrass marsh with peat soil, flooded forest, mangrove, and impounded sawgrass prairie.

A second objective was to assess the possibility of isotopic fractionation by the processes that transport methane from submerged soils to the atmosphere. Specifically, we asked the question "In an environment dominated by emergent aquatic macrophytes, are measurements of the isotopic composition of sedimentary gas bubbles indicative of the isotopic composition of methane which is actually transported to atmosphere?"

METHODS

Sedimentary gas bubbles, surficial soils and the dominant plants were sampled from December 10 to 15, 1985, at the environments shown in Figure 1. Gas bubbles were col-

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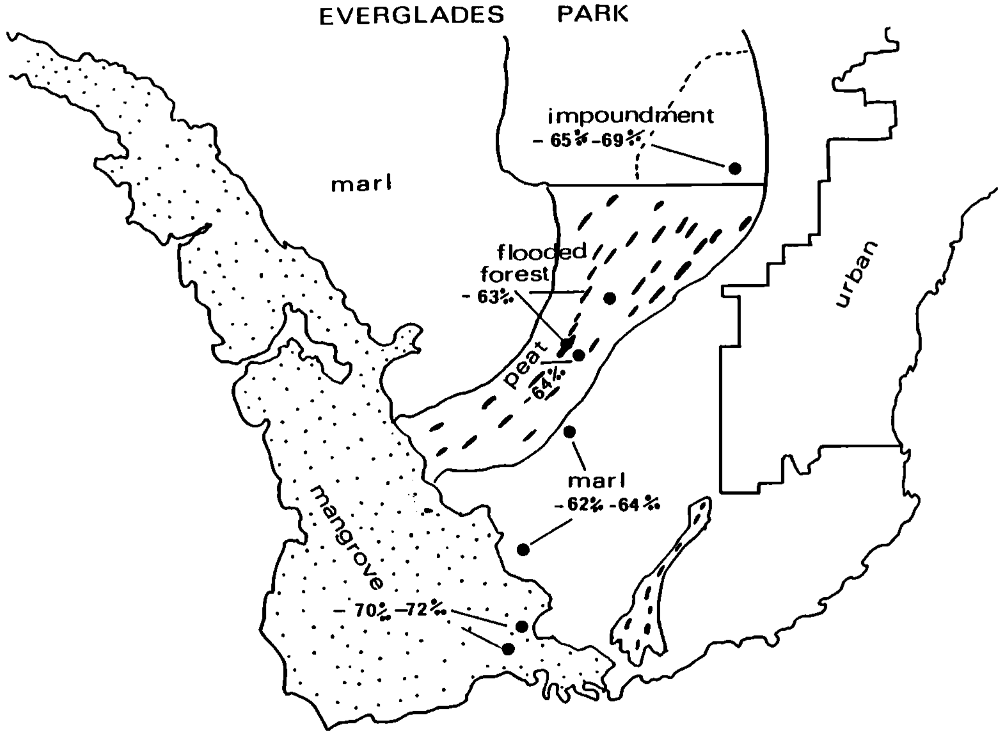

Fig. 1. Map of the Everglades study area showing the environments delineated in this study: wet prairie and sawgrass marsh with peat soil (open areas marked "peat"), wet prairie and sawgrass marsh with marl soil (open areas marked "marl"), flooded forest (oblong solid shapes in peat area), mangrove area (stippled), and impoundment (so marked). Sampling sites are indicated by the solid circles and were, starting from the north (top), impounded sawgrass prairie, P-33, Panther's Hammock, Panther Mound Grass, Mahogany Hammock, Pay Hay Okee, Hell's Bay Landing, and West Lake (see also Table 1). Methane carbon isotopic composition found in submerged soil bubbles at each environment is also shown.

lected by physically perturbing the waterlogged soils and collecting the resultant bubbles in either a 20-cm-diameter glass dome or a 1-m^2 Plexiglas pyramid. Both collectors were sealed to plastic stopcocks at their tops. Gas was transferred from the collectors to serum vials by water displacement. Vials were then sealed with 1.5-cm-thick Butyl rubber stoppers (Bellco part 2048-11800). Gas from within plant stems was collected 1-2 cm below the waterline with a needle and syringe, and transferred to serum vials as described above. A floating chamber (45 cm x 45 cm x 25 cm) was used to collect methane emitted from the plants, soils and waters of the Pay Hay Okee site. A bellows pump was used to transfer air from the chamber headspace into stainless steel flasks which were sealed until combustion of the methane fraction for isotopic analysis.

Oxygen plus argon, nitrogen, and methane analysis on gas bubbles were performed on a thermal conductivity gas chromatograph, which was equipped with a stainless steel 1/8-inch-OD column containing molecular sieve 5A and operated at 35°C with a carrier flow rate of 40 mL/min. Scott (Scott Specialty, Plumsteadville, Pennsylvania 18949) gases and dried air were used for standards. Samples containing less than 5% methane were determined on a gas chromatograph equipped with a flame ionization detector with a 6 foot by 1/8 inch stainless steel column packed with Poropak Q, and operated at a flow rate of 50 mL/min at 70°C.

Methane for isotopic analysis was carried in a helium gas stream, and combusted at 800° on a copper oxide column (efficiency, 99.99% [Carter, 1988]) as previously described [Des Marais et al., 1981; Yuen et al., 1984; Matthews and Hayes, 1978]. Isotopic analysis of the purified CO_2 which resulted from the methane combustions was performed at the North Carolina State University Stable Isotope Facility on a Finnigan MAT 251 isotope ratio mass spectrometer. Interlaboratory calibration was accomplished by the analysis of a methane standard from the NASA-Ames Stable Isotope Facility. Methane radiocarbon was quantified on one sample from Hells Bay Landing in the Everglades by Beta Analytic Incorporated, Coral Gables, Florida.

Plants and sediments were combusted on a Carlo Erba carbon-nitrogen-sulfur analyzer equipped with a cryogenic trapping system to capture CO_2 from the effluent gas stream. Prior to combustion, all samples were acid treated to remove carbonate according to the methods of Hedges and Stern [1984]. NASA-Ames glucose standards were

TABLE 1. Gas Composition of Submerged Soil Gas Bubbles

Station	% O_2 + Ar	% N_2	% CH_4	% CO_2
	Vegetated Sites			
Wet prairie and sawgrass marsh with marl sediment				
Mahogany Hammock	2.8 (0.5)	72.6 (1.4)	23.8 (3.2)	1.5
Pay Hay Okee	11.3 (0.8)	74.6 (0.1)	10.6 (0.4)	-
Wet prairie and sawgrass marsh with peat soil				
Panther Mound grass	1.5 (1.0)	59.2 (0.1)	32.9 (0.1)	1.9
P-33 sawgrass	1.8 (0.2)	70.6 (0.3)	21.4 (0.4)	1.9
P-33 spikerush	1.4 (0.0)	71.6 (0.0)	21.0 (0.0)	-
Flooded forest				
Panther's Hammock	1.3 (0.1)	64.6 (6.7)	28.3 (7.5)	-
Mangrove area				
Hell's Bay Creek border	1.1 (0.1)	56.5 (0.1)	31.0 (0.0)	4.2
Impoundment				
Sawgrass	1.9 (0.0)	82.4 (4.8)	10.3 (2.9)	-
	Unvegetated Sites			
Hell's Bay Creek channel	0.2 (0.0)	6.5 (0.1)	77.9 (0.3)	10.8(0.4)
West Lake	0.9 (0.0)	12.2 (0.1)	77.0 (0.1)	3.3

Stations are within the environments delineated in Figure 1. Oxygen content is believed to be due to air contamination during sampling. Values in parentheses represent 1/2 of the range of two samples. Samples were dried after gas loop injection so 2–3% of sample volume is water vapor.

run to insure accuracy of the sample preparation methods. Treated sediment samples were examined by X ray diffraction to verify complete removal of carbonate material.

RESULTS

Composition of Bubble Gas

Bubbles were found in all submerged waterlogged soils within the Everglades park and impoundment areas. Gas composition of the bubbles is tabulated in Table 1. Small amounts of oxygen are presumed to be contaminants derived during sampling. Methane content of bubbles collected in vegetated sites ranged from 11 to 33% methane. Unvegetated subtidal mangrove area channel and lake sediments contained bubbles relatively enriched in methane (77–78%) and depleted in nitrogen.

Presumably this difference in bubble composition between vegetated and unvegetated environments is due to aeration of the soils by plants. Plants are known to introduce air into the sediments [Armstrong, 1969;Joshi et al., 1973; Oremland and Taylor, 1977; Ando et al., 1983] and remove methane [Dacey and Klug, 1979; Dacey, 1981; Cicerone and Shetter, 1981; Sebacher et al., 1985] in the process of ventilating their roots. In anoxic unvegetated sediments, gases are transported primarily by the mechanisms of diffusion and ebullition. The latter process has been shown to strip N_2 from the sediments [Kipphut and Martens, 1982; Reeburgh, 1968, 1972; Martens and Berner, 1977]. In unvegetated sediments with low nitrate concentrations, resupply of N_2 occurs mainly via molecular diffusion from overlying waters [Kipphut and Martens, 1982].

Methane, Plant and Sedimentary Organic Carbon Isotopic Values

The isotopic composition of methane in bubbles collected at the stations shown in Figure 1 is compiled in Table 2, and is reported in the familiar "del" notation relative to Peedee belemnite (PDB) [Hoefs, 1987]. "Del" values are a measure of the stable isotopic composition or the $^{13}C/^{12}C$ ratio in a compound. Negative values indicate ^{13}C depletion; positive values indicate ^{13}C enrichment. Alternative adjectives in common use are "heavy" and "light," which indicate ^{13}C enrichment or depletion respectively.

Methane stable carbon isotopic composition (Table 2) varied from $-63^{o}/_{oo}$ to $-70^{o}/_{oo}$ across the wetland. The natural prairies and flooded forest areas contained methane enriched in ^{13}C relative to the mangrove and impoundment areas. Plant isotopic composition (Table 2) is consistent with literature values for the Cyperaceae (sedge) family, of which sawgrass *(Cladium jamaicense)* and spikerush *(Eleocharis interstincta)* are both members. Although the family contains both C3 and C4 photosynthetic pathway plants [O'Leary, 1980], as revealed by measurement of carbon isotopic ratios [Smith and Brown, 1973], these two dominant Everglades species are apparently both C3 [Smith and Brown, 1973]. *Cladium jamaicense* has been previously reported to be $-28.6^{o}/_{oo}$,

TABLE 2. Carbon Isotopic Composition ($\delta^{13}C$) of Methane, Dominant Plants, and Soil Organic Carbon in Specific Everglades Environments

Environment	CH_4, $^{o}/_{oo}$	Plants, $^{o}/_{oo}$	Soil, $^{o}/_{oo}$
Wet prairie and sawgrass marsh with marl sediment	−63.0 (4, 1.9)	−25.5 (2, 0.1)[a] −26.5 (2, 0.1)[b]	−25.7
Wet prairie and sawgrass marsh with peat sediment	−63.8 (6, 0.4)	−25.3[a] −26.1[b]	−27.8 (2, 0.4)
Flooded forest	−63.1 (3, 0.2)	-	−28.5
Mangroves	−70.1 (8, 1.8)	−27.7[c]	−27.3
Impounded sawgrass	−68.1 (2, 1.0)	−26.7[a]	−26.6 (2, 0.1)

Values in parentheses indicate number of replicates and standard deviation if $n > 2$, or 1/2 of the range if $n = 2$.

[a] Sawgrass *(Cladium jamaicense)*

[b] Spikerush *(Eleocharis interstincta)*

[c] Red mangrove *(Rhizophora mangle)*

while *Eleocharis paruula* was found to be $-21.6^{o}/_{oo}$ [Bender, 1971], somewhat heavier than our value of $-26^{o}/_{oo}$.

Additionally, methane from gas bubbles, collected by perturbing the sediments at Hell's Bay landing in the Everglades, was found to have a ^{14}C content of 108.6% modern ($\Delta^{14}C = +83 \pm 10^{o}/_{oo}$).

DISCUSSION

Methane Isotopic Variation in the Everglades Submerged Soils

Methane carbon isotopic composition varied among the various ecosystems identified by Harriss et al. [this issue]. Methane from the sawgrass prairies was enriched in $^{13}CH_4$ relative to the impoundment and mangrove areas. Overall, methane varied by $7^{o}/_{oo}$ across the entire system. Plant and sedimentary organic carbon (Table 2), however, varied by only $3^{o}/_{oo}$. The enriched methane found in the natural sawgrass peat and marl sediments may be the result of methane oxidation associated with the annual desiccation which occurs in the dry spring season. The diked impoundment areas and tidally inundated mangrove areas are exposed to desiccation to a lesser extent. Methane oxidation is a microbially mediated process which is known to consume the lighter isotope of methane preferentially [Coleman et al., 1981; Barker and Fritz, 1981]. Alternatively, the shift in methane isotopic composition may reflect shifts in the relative importance of particular methane generation pathways such as CO_2 reduction or acetate fermentation, as discussed by Whiticar et al. [1986] and Crill and Martens [1986]. Methane ^{14}C content, as reported earlier, is consistent with its production from recently photosynthesized plant matter.

Harriss et al. [this issue] have shown that the effect of diking and impounding water on the sawgrass prairie areas has been to increase the flux of methane to the atmosphere. Our isotope results (Table 2) suggest that methane collected from the impoundment areas is somewhat more depleted in ^{13}C than methane collected in the natural prairies. An additional effect of diking and impounding water on the sawgrass prairies may have been to shift the isotopic composition of methane produced there to more depleted values.

We can construct an isotopic budget for the Everglades submerged soils using the data summarized in Table 3. Following Harriss et al. [this issue], we have combined the peat and marl sawgrass prairies. In constructing this budget we have assumed (further discussion below) that methane transport processes do not fractionate isotopically. We have also assumed that the isotopic composition of methane in this subtropical environment does not vary seasonally. Burke et al. [1987b] have found only small seasonal variations in the isotopic composition of methane from subtropical south Florida environments, in contrast to seasonal variations of up to $10^{o}/_{oo}$ which have

TABLE 3. Methane Fluxes and Isotopic Composition by Environment

Environment	Annual Flux, 10^{10}g	Methane Isotopic Composition, $^{o}/_{oo}$
Wet prairie peat and marl	20.4	−63.4 (10, 1.2)
Flooded forest	2.5	−63.1 (3, 0.2)
Mangroves	0.4	−70.1 (8, 1.8)
Impounded sawgrass	12.8	−68.1 (2, 1.0)

Fluxes are from Harriss et al. [this issue]. Values in parentheses indicate the number of replicates and the standard deviation or 1/2 of the range, depending upon whether the number of replicates was greater than or equal to 2, respectively.

TABLE 4. Summary of Isotopic Differences (Δ) Between Bubble Methane and Methane Transported to the Atmosphere, From This Study and the Literature

Area	Bubble $CH_4^{\circ}/_{oo}$	CH_4 Transported to Atmosphere, $^{\circ}/_{oo}$	$\Delta^{\circ}/_{oo}$
Pay Hay Okee	-64^a	-59^a	5
Everglades	-65^b	-55^c	10
Illinois slough	-56^c	-50^c	6
Minnesota peat bogs	$-^d$	-64 to -69^d	5–15

[a] measured, this study.

[b] budget calculated, this study.

[c] Stevens and Engelkemeir [1988].

[d] Quay et al. [1987] (only transported methane and difference reported)

been reported in temperature climates [Martens et al., 1986; Chanton and Martens, this issue; Burke et al., 1988]. Based upon these assumptions, the weighted average composition of methane emitted by the Florida Everglades is $-65.1^{\circ}/_{oo}$ (±0.8, error calculated from variability in isotopic data, Table 2), a value $38^{\circ}/_{oo}$ more depleted than the bulk sedimentary organic matter (Table 2) due to isotopic fractionation occurring within the anoxic submerged soils.

Effect of Transport Processes on the Isotopic Composition of Methane

On December 14, 1985 a floating chamber experiment was conducted for 160 min in a marl sawgrass prairie (station Pay Hay Okee). The water depth was 15 cm, temperature 21.5° and the site was vegetated with sawgrass, spikerush, and floating periphyton. Sources of methane to the chamber included bubbles in the sediment, which were 10% methane with an isotopic composition of $-64^{\circ}/_{oo}$, bubbles in the periphyton which contained 0.8% methane with an isotopic composition of $-64^{\circ}/_{oo}$, and dissolved water column methane, the isotopic composition of which was not measured. The initial composition of methane in the chamber was 1.8 ppm and the final concentration at the end of 160 min was 5.5 ppm which translates to a flux of 5.6 mg $CH_4 \cdot m^{-2} \cdot d^{-1}$, a value low relative to the sawgrass prairie average [Harriss et al., this issue], but not an unreasonable value for this particular site (P. Crill, personal communication, 1985). The isotopic composition of methane in the flux box at the end of the experiment was $-53.6^{\circ}/_{oo}$. When this value is corrected for the initial atmospheric methane (1.8 ppm, $-47^{\circ}/_{oo}$ [Stevens and Rust, 1982]) and final concentration of CO (0.3 ppm, $-27^{\circ}/_{oo}$, [P. Crill, unpublished data, 1987; Stevens et al., 1972]), we calculate that the isotopic composition of methane entering the chamber was $-58.7^{\circ}/_{oo}$, or $5^{\circ}/_{oo}$ more enriched in ^{13}C than the source bubble methane at this site. Rust [Stevens and Rust, 1982; Stevens and Engelkemeir, 1988] conducted a similar experiment and reported that methane released from an Illinois slough was $6^{\circ}/_{oo}$ more enriched in $^{13}CH_4$ than the "bottom gas." Quay et al. [1987] have also observed similar effects in Minnesota wetlands, where emitted methane was $5–15^{\circ}/_{oo}$ enriched in heavy methane relative to bubble samples collected at the same sites.

Additionally, our chamber-derived value of $-58.7^{\circ}/_{oo}$ for emanating methane is in excellent agreement with the value of $-55 \pm 3^{\circ}/_{oo}$ ($n = 2$) which was determined for the Everglades methane emissions on October 31 and November 1, 1981, by Stevens and Engelkemeir [1988], who utilized the natural containment resulting from nocturnal atmospheric inversions. Their value is integrated over the whole wetland and indicates that the actual isotopic composition of emitted methane is $10^{\circ}/_{oo}$ enriched in the heavy isotope relative to the $-65.1^{\circ}/_{oo}$ value calculated in the budget based upon the methane bubble isotope and flux data (see the above section). These results and additional results from the literature are summarized in Table 4. A systematic pattern of transported methane generally being $5–15^{\circ}/_{oo}$ enriched in ^{13}C relative to bubble methane appears to emerge from the data.

Methane can be transported from the submerged soils to the atmosphere by molecular diffusion, plant advection, or bubble transport. We have begun to examine the effects of these processes by comparing the isotopic composition of methane in transit (for example, in plant stems, in natural bubbles [Chanton and Martens, this issue], and in chambers) with the isotopic composition of the methane bubble reservoir, which is representative of dissolved methane in the methane production zone [Martens et al., 1986].

Very little ebullition was observed during our December sampling trip(K. Bartlett, personal communication, 1985; J. P. Chanton and G. G. Pauly, unpublished data, 1985), so methane was being transported to the atmosphere primarily via plant advection and molecular diffusion from the water column at this time. Burke et al. [1987a] have observed ebullition to be more important during other seasons.

Table 5 shows methane concentration and isotopic data from methane removed from plant stems just below the waterline. The isotopic composition of methane bubbles collected by perturbing the sediment adjacent to the plant is also shown for comparison. These results show significant differences between sedimentary bubble and plant stem methane. Two plant types contained methane en-

TABLE 5. Carbon Isotopic Composition ($\delta^{13}C$) of Methane in Plant Stems and Adjacent Bubbles, and Methane Concentration in Gas From Plant Stems

Station	Plant	% CH_4 in Plant Stem	Plant Stem CH_4 Isotopic Composition, $^{o}/_{oo}$	Bubble CH_4 Isotopic Composition, $^{o}/_{oo}$
Panther's Hammock	*Peltandra* (arrow arum)	1.6 (4, 0.8)	−51.1 (2, 0.1)	−63.1 (3, 0.2)
Pay Hay Okee	*Sagitarria* (arrowhead)	1.5 (3, 0.6)	−59.7 (2, 0.1)	−63.8 (2, 0.1)
P-33	*Nymphaea* (white water lily)	0.7 (2, 0.1)	−74.4 (1)	−63.8 (2, 0.1)

Values in parentheses as defined in Table 2.

riched in the heavy isotope relative to the sedimentary gas bubbles, and one is depleted.

There are several possible explanations for the differences observed between plant and bubble methane. There may be a vertical gradient in the isotopic composition of methane in the soils, which could allow plants to obtain gas with a methane isotopic composition different from gas in the main zone of bubble formation. Such a gradient might be the result of a gradient in the isotopic composition of methane precursors, a shift in methane generation pathways with depth, or the result of isotopic fractionation caused by methane oxidation. Additionally, there may be methane oxidation in close association with the plant's root system. Methane-oxidizing microbes in the rhizosphere would be exposed to low oxygen partial pressures arising from root oxygen loss, and to high methane partial pressures migrating in from the soil pore water. Methane oxidation is known to consume methane containing the lighter isotope of carbon preferentially [Coleman et al., 1981; Barker and Fritz, 1981].

CONCLUSIONS

The isotopic composition of the methane being released to the atmosphere from the Everglades is more enriched in the heavy isotope of carbon relative to the submerged soil methane bubble flux budget by 5$^{o}/_{oo}$ (bubble methane versus chamber methane) to 10$^{o}/_{oo}$ (bubble budget versus the atmospheric inversion value of Stevens and Engelkemeir [1988]).

The carbon isotopic composition of methane in submerged soil gas bubbles in the Everglades varies by 7$^{o}/_{oo}$, from −70 to −63$^{o}/_{oo}$, while the dominant plant and soil organic carbon vary by only 3$^{o}/_{oo}$, from −28 to −25$^{o}/_{oo}$.

Sedimentary gas bubbles in vegetated sites are predominately composed of nitrogen while bubbles in subtidal sediment are mostly composed of methane (see also J. P. Chanton and C. S. Martens, manuscript in preparation).

Methane transported from soils to the atmosphere by emergent aquatic plants can differ from the isotopic composition of methane in the submerged soil gas bubbles by up to 12$^{o}/_{oo}$.

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