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Development and Analysis of Millennial-Scale Tree Ring Records from Glacier Bay National Park and Preserve, Alaska (Glacier Bay)
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The Biogeochemistry and Environmental History of Bioluminescent Bays, Vieques, Puerto Rico
Tim Ku (Wesleyan University) Suzanne O'Connell (Wesleyan University), Anna Martini (Amherst College)
Students: Erin Algeo, Jennifer Bourdeau, Justin Clark, Margaret Selzer, Ulyanna Sorokopoud, Sarah Tracy

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Keck Geology Consortium: Projects 2007-2008
Short Contributions – Puerto Rico

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SOURCES OF ORGANIC MATTER IN MARINE SEDIMENTS OF A BIOLUMINESCENT BAY, VIEQUES PUERTO RICO.

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INTRODUCTION

Some of the most brilliant and famous bioluminescent bays are located in Vieques, Puerto Rico: the site of a 2006-2007 KECK project. The bioluminescent light is created by dinoflagellates, a type of phytoplankton, that are relatively common in oceans. However, locations that consistently maintain high concentrations of dinoflagellates (e.g. bloom level concentrations) are not common and scientists do not fully understand what specific chemical and physical conditions are required for sustaining such high concentrations of bioluminescent phytoplankton.

Organic matter (OM) and sediments deposited in the bay may record changes in sources of nutrients and depositional environments that may have impacted bioluminescence. This study investigated the coastal lagoon environment of Puerto Mosquito (PM) bay, the most luminous bay in Puerto Rico, by characterizing the inputs of OM with depth (through time) in sediment cores. Organic carbon to nitrogen ratios and stable isotopic analysis of sediments from discreet intervals were used to determine the controlling factors important for sustaining bioluminescent phytoplankton populations.

The main sources of nutrients and organic carbon in PM are phytoplankton, seagrasses and mangroves (Florentine, 2006). To distinguish between these different OM inputs through time, we used a ternary diagram, which takes advantage of the fact that mangroves, seagrasses and phytoplankton have distinct organic C/N ratios and $\delta^{13}C$ values. The ideal situation for employing a ternary diagram is that: 1) it must be possible to clearly differentiate end member sources and 2) that the end member signal is preserved after burial. Requirement 1) is easily verified by analysis of end member samples. The second requirement, on the other hand, is more difficult to confirm. It is important to note that studying the sources of OM in the sediments only reflects the preserved OM and not the OM that was originally deposited. Furthermore, very few studies have tested for post depositional alterations (e.g. diagenesis) in OM for systems with more than two end member sources.

Studies using organic C/N ratios as tracers of OM end member sources show that this ratio can be altered by chemical equilibrium and electrochemical processes such as ammonification, nitrification, and denitrification (Gonneea, 2004). In studies dealing with coastal lagoons where inputs vary in space and time, it is especially hard to distinguish end member mixing from the effects of post depositional alteration. However, it has been suggested that $\delta^{13}C$ and organic C/N ratios are not significantly altered after deposition (Meyers, 1993). An analysis of the degree of diagenesis can be accomplished by observing the isotopic ratios of sedimentary organic nitrogen. Previous studies have found that mangroves and seagrasses that have undergone diagenesis have much large $\delta^{15}N$ values (approximately 9 to 10 ‰) (Gonneea, 2004).

METHODS

Cores and water sample collection

Three different coring methods were employed to collect sediments in PM. The first two were percussion coring methods, specifically push coring and hammer coring. Longer sediment cores were taken using a method known as vibracoring. This method employs a machine powered coring device that vibrates an aluminum tube thereby driving it into the sediment.

Plants and sediments collection and preparation

Live plant samples (seagrasses and mangroves) were collected from the margins of the bays, scraped clean of carbonate material, washed with water, and then frozen within 48 hours of collection. They were kept frozen except for a 70 hour period in which they were shipped back to the laboratory for chemical analysis. The plant samples were then dried in an analytical oven at 50^{o}C, until the masses were constant.

C and N stable isotopes and elemental ratio analysis

An elemental analyzer was used to determine the total carbon and nitrogen concentrations of plant materials and sediments in the bay. We assumed that all the carbon and nitrogen in plant materials was from organic sources. In contrast, sediment samples may contain both organic and inorganic (e.g. calcite) sources of carbon. The relative concentration of inorganic carbon (C_{inorg}) in the sediment samples was determined on a carbon coulometer. The amount of organic carbon (C_{org}) present in the sediments was calculated by subtracting the inorganic carbon component from the total carbon concentration measured on the elemental analyzer ($C_{org} = C_T – C_{inorg}$). We assumed that all of the nitrogen in sediments was organic in origin.

Assuming that all C and N from the plants was derived from organic sources, plant samples were run directly on the mass spectrometer for stable isotopic ratios of C ($^{13}C/^{12}C$) and N ($^{15}N/^{14}N$). To remove inorganic carbon from the sediments, which would alter the carbon isotopic ratios, samples were acidified with sulfurous acid before being run on the mass spectrometer

Sediment dating

^{210}Pb was employed for dating of shallow sediments (<150 years old). For the deeper (and older) sediments ^{14}C of organic matter and carbonate shells were used to quantify ages of sediments. Carbon-14 is applicable to determine the age of materials up to about 50,000 years old (Clark and Fritz, 1997).

Three part mixing model

A ternary mixing model has been utilized to calculate the contribution of OM sources to the bay. In the model each OM source occupies a corner of a triangle. Samples within the limits of the triangle can be analyzed in terms of the end members, those that fall along any line connecting two end members are a mixture those two end members. Samples falling outside of the triangle must be explained.

It is important to note that anthropogenic sources of carbon and nitrogen are not considered in the ternary diagram. Puerto Mosquito is not federally protected and has been under heavy development pressures, which may contribute carbon and nitrogen to surface waters. Anthropogenic sources of pollution generally have different $\delta^{15}N$ values than natural sources of OM. Some fertilizers do have nitrate that has a $\delta^{15}N$ value near zero (Clark & Fritz, 1997). An analysis of $\delta^{15}N$ can be used to determine if organic C/N ratios and $\delta^{13}C$ values are altered by anthropogenic activities.

RESULTS

The mangrove and seagrass samples have distinct $\delta^{13}C$ values and C/N ratios, plotting as discrete end members on the ternary diagram (Table 1, Figure 1). Phytoplankton analyses are not yet complete; values for this end member in Table 1 were taken from Gonneea et al (2004). This seems to be a valid approach given that the values for mangrove and seagrass end members are very similar to those given by Gonneea et al (2004). The raw data for plant samples shows high variability C/N ratios and low variability for $\delta^{13}C$ values. This is consistent with other similar studies (Gonnee, 2004; Phlips, 1993).

end member	source	C/N	std dev	n	$\delta^{13}C$ (‰, VPDB)	std dev	n
Mangroves	this study	60.0	24.35	11	-27.60	1.54	14
Seagrasses	this study	17.5	4.44	10	-9.80	1.61	11
Phytoplankton	Gonnea et al (2004)	8.5	1.40	19	-22.31	4.15	19

Table 1. C/N ratios and carbon isotope ratios of organic matter end members used for the ternary diagram.

DISCUSSION

A general trend in the sediment data from more phytoplankton and seagrass dominated system to a mangrove dominated system with increasing depth is observed in the bay (Figure 1). Sediment dating results suggest that the within the last 50 years the organic matter deposition in PM bay has been dominated by phytoplankton and seagrass. From 50 to 100 years in the past there is significant variability in the signal, whereas older samples (more than 100 years old) tend to plot much closer to the mangrove end member. Much of the data seems to fall outside the ternary diagram to the lower right hand side of the diagrams. Nearly all of the samples that plot in this range tend to be in the first 50 cm of the sediment columns (e.g. younger in age).

avg depth (cm)	C/N	$\delta^{13}C$ (‰, VPDB)	$\delta^{15}N$ (‰, AIR)
PM 4			
3.0	9.6	-19.32	
7.5	15.8	-19.33	
12.5	11.4	-19.39	
17.5	11.5	-20.68	1.7
42.5	5.7	-18.64	
57.5	28.4	-24.41	
72.5	34.6	-23.89	
PM 12			
19	12.4	-19.87	1.9
23	16.5	-20.36	1.1
35	17.0	-19.41	0.9
45	17.5	-19.88	0.8
49	25.2	-20.58	-0.7

avg depth (cm)	C/N	$\delta^{13}C$ (‰, VPDB)	$\delta^{15}N$ (‰, AIR)
PM 14			
1.5	16.3	-18.53	0.2
25.0	18.6	-20.93	0.9
31.0	33.4	-24.14	
43.0	21.5	-23.38	
51.0	25.7	-21.76	
PM 23			
1.0	10.7	-19.58	1.2
3.0	11.1	-19.78	
7.0	11.2	-19.43	
13.0	10.7	-19.74	2.1
19.0	12.3	-19.64	2.4
27.0	10.4	-20.08	
31.0	10.7	-19.39	
35.0	9.5	-19.40	
45.5	9.8	-20.23	
60.5	9.6	-20.56	
67.0	16.3	-23.40	2.5
75.0	16.8	-22.83	1.7
81.0	29.9	-23.04	-2.2
87.0	31.3	-24.23	3.2
99.0	41.0	-24.91	-0.9

Table 2. Carbon and nitrogen isotope ratios and C/N ratios of organic matter from sediment cores collected from Puerto Mosquito bay.

Some of the outliers shown in Figure 1 may be attributed to high variability in the system (e.g. are within the range of error associated with the end members). The outliers may also be tracked to other large sources of OM that are not represented in the ternary diagram. The possibility of introducing an additional end member may need to be considered. Another possible reason for high $\delta^{13}C$ values and low C/N ratios could be diagenesis in the sediment cores. However, the $\delta^{15}N$ values in the same samples are not indicative of diagenetic alterations (e.g. are not high enough).

One more possible reason that the outlier values observed are grouped in the lower right of the diagrams is the possibility of anthropogenic influences. Manure, septic waste and fertilizers can contribute large quantities of C and N to bays, such as the one studied here. N concentrations in bays similar to PM are relatively low. Thus, an increase in N concentrations might be indicative of human sources of pollution. If manure and/or septic waste have contributed large amounts of N we should see more positive δ15N value (~10 to 20 ‰, AIR). Inputs of N derived from fertilizers would have slightly more negative $\delta^{15}N$ values (approximately -5 to +5 ‰) (Clark & Fritz, 1997). $\delta^{15}N$ values of PM sediments range from -2.2 to +3.2‰, within the range of N-fertilizers and soil organic matter. Anthropogenic sources of N coupled with a more seagrass dominated ecosystem could potentially explain the enriched 13C values and low C/N ratios. Flushing of bio-available phosphorus and nitrogen from human activity may stimulate dinoflagellate blooms in PM, as has been observed in other areas (Phlips et al., 2003).

CONCLUSION

The C/N ratios and $\delta^{13}C$ values of organic matter in plant materials and marine sediments indicate that the current depositional environment of Puerto

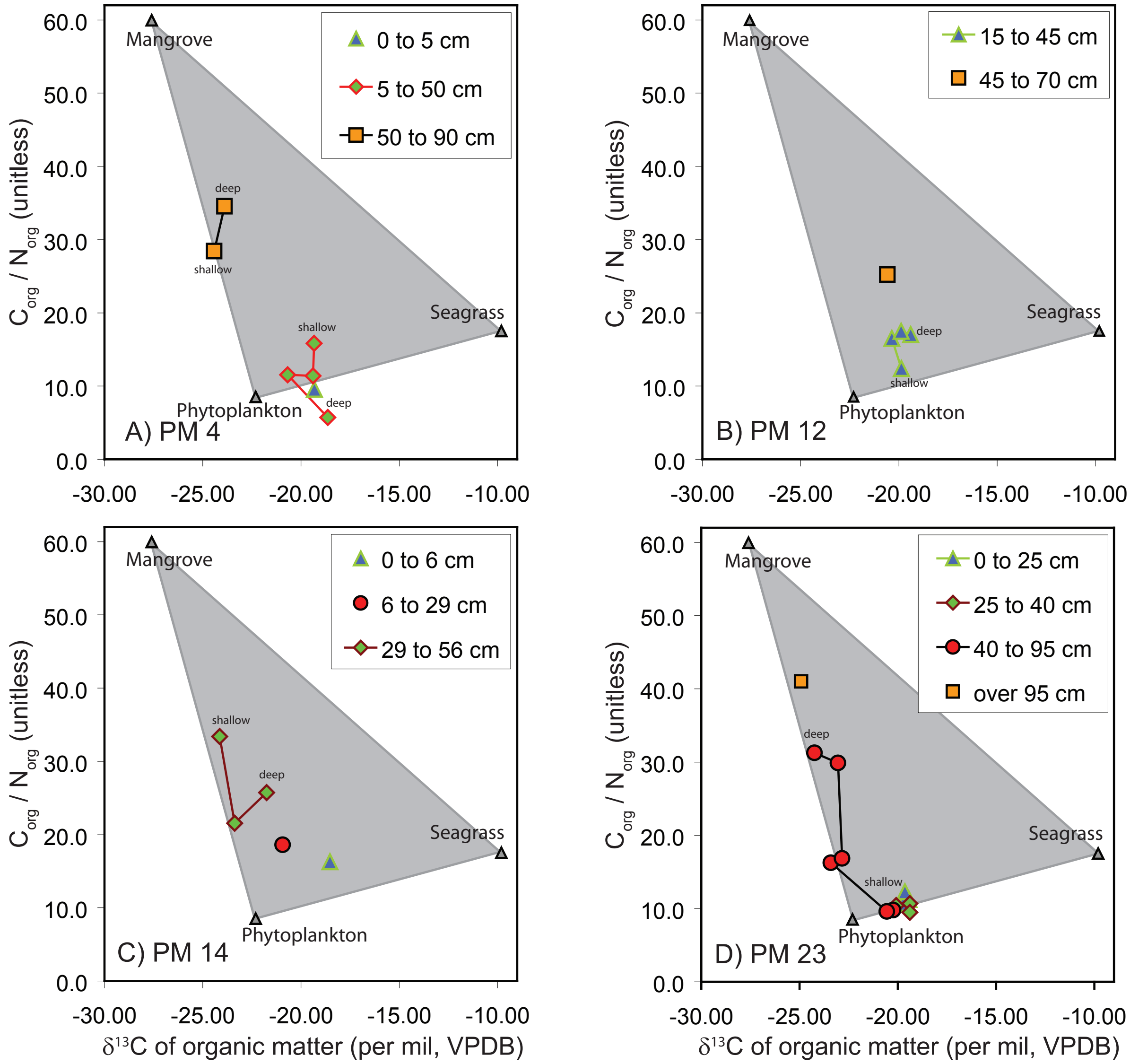

Figure 1. Ternary diagrams showing end member values for organic matter sources in Puerto Mosquito bay, and sediment samples from four cores (sampled with depth). Symbols represent major sedimentary facies that are consistent between the different cores.

Mosquito is dominated by seagrasses and phytoplankton (e.g. a more marine environment). The organic C/N ratio increase with increasing depth (and age) and $\delta^{13}C$ decreases with depth (and age). This trend indicates that, in terms of organic matter, in the past Puerto Mosquito was more dominated by mangroves (e.g. a more terrestrial environment).

Human impacts on the sources of nutrients and organic C may affect the organic matter geochemistry found in the most recent sediments. Further research would need to be done on nitrate concentrations of marine waters as well as $\delta^{18}O$ nitrate and $\delta^{15}N$ nitrate to determine if manure, septic waste and/or fertilizers may be present in the system, and if these anthropogenic inputs affect bioluminescence.

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