

UPPER OCEAN METHANE DYNAMICS -- ANNUAL REPORT

Francis J. Sansone
Oceanography Department
University of Hawaii
1000 Pope Road
Honolulu, HI 96822
email: sansone@soest.hawaii.edu
phone: (808) 956-8370
fax: (808) 956-7112

co-PI: Brian N. Popp
Oceanography Department
University of Hawaii
1000 Pope Road
Honolulu, HI 96822
email: popp@soest.hawaii.edu
phone: (808) 956-6206
fax: (808) 956-7112

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LONG TERM GOALS

1. Determine the temporal and spatial variability of the stable carbon isotopic ratios of oceanic methane (CH_4), paying particular attention to coastal regions and other areas of high productivity.
2. Elucidate the details of CH_4 production and consumption in the upper ocean.
3. Determine the importance of terrestrial sources to the oceanic CH_4 cycle.

OBJECTIVES

The objectives of this project are to provide a better understanding of the carbon cycle in the ocean and to allow estimation of the carbon isotopic composition of methane exchanging with the atmosphere from surface waters. Estimates of the oceanic component of global CH_4 models can thereby be better constrained. This work is supported by ONR Chemical Oceanography.

APPROACH

In order to achieve the above mentioned long-term goals, the isotopic signature of CH_4 produced by plankton and in particulate matter, which may be the source of the observed CH_4 supersaturation in open ocean surface waters, will be determined. The temporal and vertical spatial variability of CH_4 in the upper ocean are also investigated. In addition, the isotopic composition of CH_4 in coastal waters and nearby oligotrophic surface waters have been compared in order to elucidate the spatial and temporal importance of CH_4 production and consumption processes across this transition zone. Finally, the degree of equilibrium between the atmosphere and the surface ocean for CH_4 fugacity and isotopic are determined.

WORK COMPLETED

To achieve to the long-term goal of determining the variability of CH_4 in the ocean, water samples have been taken at an oligotrophic site in the Pacific ocean near Hawaii (Station ALOHA)¹ over a seasonal cycle (July 1995, 1997, October 1996, January and April 1997) and measured for CH_4 concentration and isotopic composition (data is soon to be available on the Hawaii Ocean Time-series website²). Samples were collected from several depths throughout the upper 1000 m and in July 1997 throughout the upper 4000 m. Additionally, water samples in a transect from the Sargasso

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Sea, across the Gulf Stream and over the mid-shelf have been analyzed. Surface water samples from several river-estuary-ocean transects (Columbia River (OR), Elkhorn Slough (CA), Parker River (MA), Merrimac River (MA), Great/Little Bay (NH), Kaneohe Bay (HI) and Everglades (FL)) have been analyzed, yielding information on production and consumption processes across this important transition zone.

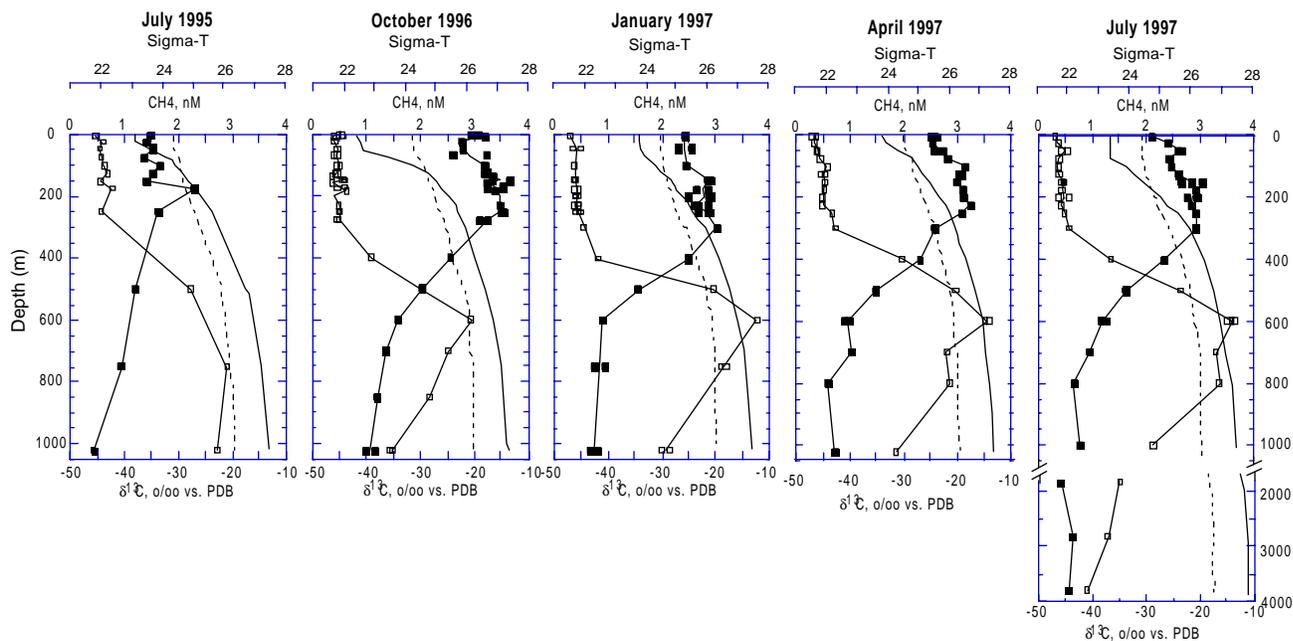
As an initial step in elucidating the details of CH₄ production and consumption in the upper ocean, particles were collected with a sediment trap and water from different depths at Station ALOHA was obtained in July 1997. These have been incubated with and without ¹³C-labelled acetate and bicarbonate in order to study potential CH₄ production in particulate matter and in water without visible particles as well as methanogenic substrate uptake.

Samples of atmospheric air have been collected simultaneously with surface water CH₄ samples to determine the degree of equilibrium between atmospheric and surface ocean CH₄ with respect to concentration and isotopic ratio. Additionally, laboratory experiments have been performed in order to measure the theoretical isotopic equilibrium values between seawater and the atmosphere at different ambient temperatures.

RESULTS

CH₄ in the upper ocean at Station ALOHA exhibited subsurface concentration maxima of 2.9 to 3.5 nM (37 to 67% supersaturated with respect to atmospheric CH₄) between 100 and 300 m during October 1996 and January, April and July 1997 (Fig. 1). On average, the ocean in this region supplied 1.2 μmol CH₄ m² d⁻¹ to the atmosphere, except in July 1995, when the ocean appeared to be a net sink for atmospheric CH₄. Isotopic values were constant throughout the year and ranged from -45 to -47‰ in the upper 300 m. The results indicate that this region is a steady source of isotopically heavy methane to the atmosphere, which had δ¹³C values of -47.0 to -47.3‰. Below 300 m, concentrations decreased and the isotopic values became heavier, exhibiting maxima at 600 m of up to -12‰. Bacterial oxidation of the methane and mixing of water masses of different ages explain variations in the methane profiles below 300 m. A similar pattern was seen in samples from the Sargasso Sea. In surface water there, CH₄ concentrations ranged from 2.4 to 3.0 nM, with isotopic ratios of -45 to -47‰ at all three sampling sites. Concentration maxima were observed at 100 to 250 m, while δ¹³C values remained similar to that measured in surface water. Below 500 m, decreasing concentrations and increasing isotopic ratios indicated net oxidation of CH₄. The correspondence of CH₄ concentration maxima with the pycnocline in both areas supports the hypothesis that methane is produced in particulate matter that accumulates at the pycnocline.

Figure 1. CH_4 concentrations (■) and $\delta^{13}\text{C}$ - CH_4 (□) of water at station ALOHA.



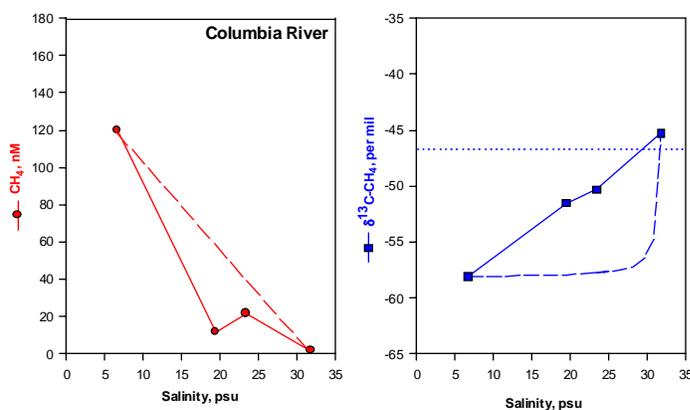
Particulate matter collected with a sediment trap from 200 m depth showed nearly a doubling in methane concentration after a two week incubation period. Although ^{13}C -labelled acetate and bicarbonate were added to some of the samples, isotopic ratios indicate these substrates were not taken up. These results suggest that the particles are similar to closed systems with respect to substrate uptake for methanogenesis. In contrast, water samples from 200 m that were incubated with ^{13}C -labelled acetate showed no significant increase in methane concentration, but the label was incorporated into CH_4 ($\delta^{13}\text{C}$ in duplicate samples was +157 and +267‰). In addition, water samples from 100 m, 250 m and 400 m were incubated with no substrate additions and showed significant methane production (0.5 to 3.0 nM) after 45 days.

Table 1. Methane concentrations and stable carbon isotopic ratios of selected rivers

River	Freshwater endmember		Mouth of estuary	
	CH ₄ (nM)	δ ¹³ C-CH ₄ (‰)	CH ₄ (nM)	δ ¹³ C-CH ₄ (‰)
Columbia	120	-58.1	12	-51.5
Parker	930	-46.2	50	-60.4
Merrimac	740	-49.3	290	-53.1
Oyster (Great Bay)	910	-36.2	32	-48.2
Picassic (Great Bay)	880	-38.1	“	“
Kaneohe	33	-56.6	4.2	-52.0

system, shows that concentrations of methane dropped below the conservative mixing line and the

Figure 2. CH₄ concentrations (●) and δ¹³C-CH₄ (■) of



tical

Transects across several river-estuary-ocean systems show the generally high concentrations and low δ¹³C values typical of river-borne CH₄ and nearly atmospheric levels and isotopic composition of the offshore endmembers (Table 1). δ¹³C values reflect the variation in the terrestrial methane sources at the different sites and the degree of oxidation of the methane. A mixing diagram of δ¹³C-CH₄ and CH₄ concentrations for the Columbia River (Fig. 2), a typical advectively dominated system, shows that concentrations of methane dropped below the conservative mixing line and the CH₄ was enriched in ¹³C relative to what would be expected based on conservative mixing. The observed trends are explained by methane oxidation, which decreases CH₄ concentrations and leaves the residual CH₄ enriched in ¹³C. The other systems studied also showed deviation from conservative behavior, with methane in some areas apparently being controlled by methane oxidation, while others were influenced by significant inputs

of methane in estuaries bordered by extensive marshes.

IMPACT

Our research this year has produced the first set of profiles of methane concentrations and isotopic compositions from the open ocean over an annual cycle. These data, in addition to the results from the Sargasso Sea and the river/estuary data will be valuable in constraining global models of methane sinks and sources. Ongoing research following up on the intriguing results obtained from the incubation of particulate matter and seawater discussed above may provide information on the source of the methane being produced in the open ocean.

RELATED PROJECTS

The research funded by this project has proven to be of great utility to other (NSF-supported) projects conducted in our laboratories on the cycling of dissolved gases in marine systems. These projects include CH₄ production in nearshore marine carbonates and in shallow volcanic seamounts.

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