Highly elevated methane in the eastern tropical North Pacific and associated isotopically enriched fluxes to the atmosphere

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Abstract. During the May - June, 2000 Eastern Pacific Redox Experiment (EPREX) we examined the dynamics of methane (CH_4) in the eastern tropical North Pacific (ETNP), a large region of high surface-ocean productivity fueled by coastal upwelling. We discovered that (1) the ETNP contains by far the largest pool of CH_4 yet discovered in the open ocean; (2) CH_4 production in the upper half of this subsurface pool is associated with the decomposition of locally produced sinking particulate matter; (3) the deeper half of this pool is from a coastal source; (4) advection and oxidation of the upper pool leads to the heavy CH_4 isotopic values seen at midwater in the North Pacific subtropical gyre; and (5) the ETNP is a source of isotopically enriched CH_4 to the atmosphere. Our results suggest that other oceanic areas of upwelling-induced anoxia may be sites of significant atmospheric input of isotopically heavy CH_4.

1. Introduction

The eastern tropical North Pacific (ETNP) is a large, well-documented region of high surface-ocean productivity fueled by coastal upwelling of nutrient-rich deep seawater [e.g., *Deuser*, 1975; *Cline and Richards*, 1972]. Decomposition of the resulting organic matter leads to the formation of a large area of the upper ocean with highly depleted levels of dissolved oxygen (O_2). The ETNP has been the site of a number of studies of suboxic and anoxic nitrogen transformations [*e.g., Cline and Richards*, 1972; *Cohen and Gordon*, 1978]; however, methane (CH_4) cycling in this region has, to our knowledge, never previously been studied. Thus, as part of the Eastern Pacific Redox Experiment (EPREX) during May - June, 2000, we conducted an investigation of the dynamics of CH_4 in the ETNP.

2. Results and Discussion

EPREX operations included sample collection at six stations across the ETNP (Fig. 1) that allowed sampling of oceanic environments ranging from the oligotrophic subtropical gyre (Station (Stn) 1) to the nearshore coastal upwelling zone (Stn 6, 110 km offshore of southern Mexico). The vertical extent and intensity of anoxia along the transect, showing the degree of O_2 consumption, can be seen in Fig. 2a. For example, the O_2 concentration at 55 m depth at Stn 6 was 10 μM, well below the air-equilibrium value of 198 μM. Anoxic conditions ($O_2 < 1$ μM) extend to beyond Stn 4, 1500 km offshore. Suboxic

conditions ($O_2 < 50$ μM) extend beyond Stn 1, where, at depths of 650 - 1200 m, they constitute the characteristic oceanic "oxygen minimum zone". The meridional extent of the ETNP anoxia was not determined during the EPREX cruise, but has been well defined during previous expeditions. As indicated by the dashed line in Fig. 1 ($O_2 < 9$ μM at a depth of 400 m), the core of the ETNP anoxic region has an area of ~5.2 x 10^6 km^2.

Dissolved CH_4 concentrations were highly elevated in the suboxic and anoxic waters of the ETNP (Fig. 2b). For example, concentrations at Stn 6 reached 28 nM, with concentrations >5 nM over depths of 30 to 650 m. CH_4 remained >4 nM over 80 - 300 m depth for a distance of 2240 km offshore (to Stn 3). This contrasts with open-ocean background concentrations of 2 - 3 nM typically observed at these depths (e.g., Stn 1) [see also *Lamontagne et al.*, 1973; *Holmes et al.*, 2000]. In addition, elevated CH_4 levels extended up through the oceanic mixed layer (~0-80 m during EPREX) at Stations 4 - 6, even though the upper ocean is characteristically near equilibrium with the atmosphere. (Air-equilibrated concentrations [*Yamamoto et al.*, 1976] were 1.8 - 1.9 nM at the EPREX stations, assuming an atmospheric gas mixing ratio of 1.7 ppm [*Quay et al.*, 1991; *Holmes et al.*, 2000]).

This is apparently the largest accumulation of open ocean CH_4 yet reported. Its relative scale can be appreciated by comparing the ETNP CH_4 pool to methane-rich hydrothermal plumes observed along the mid-ocean ridges [e.g., *Charlou and Donval*, 1993; *Mottl et al.*, 1995]. Although rare hydrothermal plumes with focused CH_4 concentration maxima of up to ~400 nM have
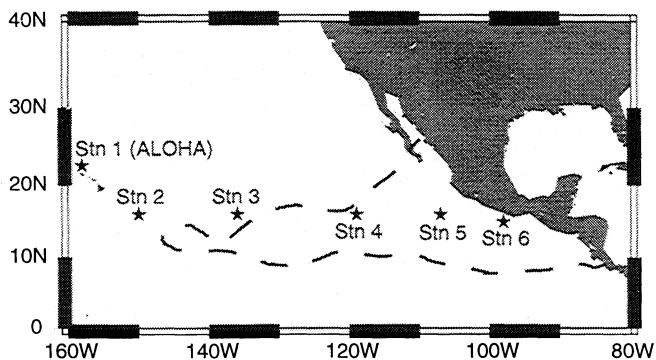
Figure 1. Location of sampling stations on the EPREX transect; Station 1 is also the site of the ongoing Station ALOHA time series experiments [*Karl*, 1999]. The dashed line indicates the location of the 9-μM dissolved O_2 isopleths at a depth of 400 m, which delineates the extent of the core of the ETNP O_2 minimum zone. Oxygen data are from the NOAA Ferret data visualization and analysis site [http://ferret.wrc.noaa.gov/Ferret/].
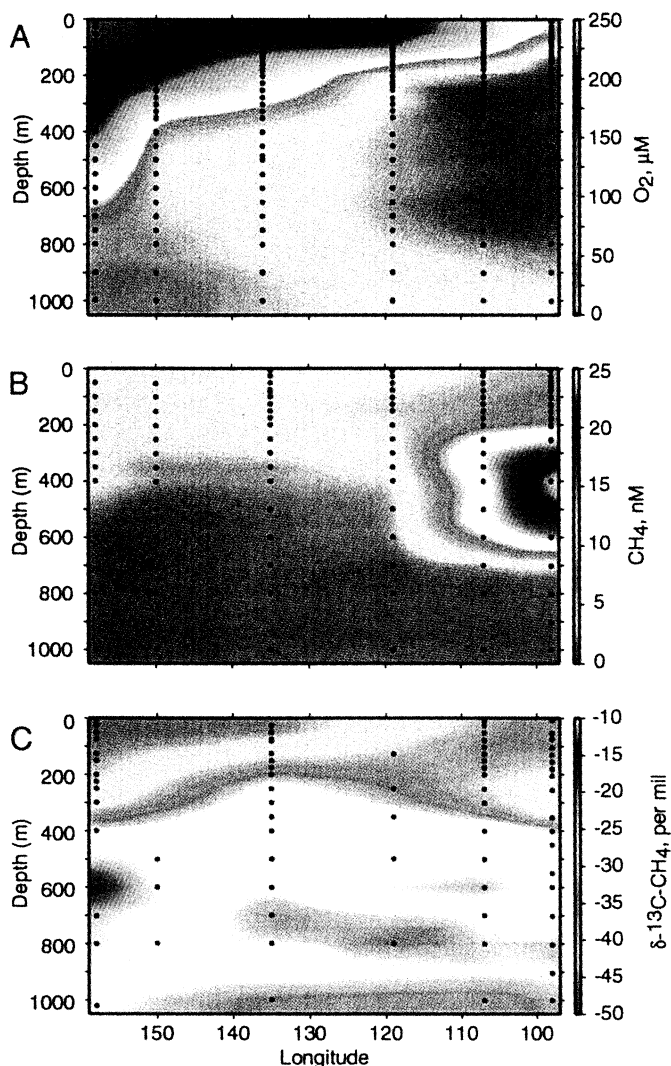
Figure 2. A) Concentration of dissolved oxygen (μM), B) concentration of dissolved methane (nM) and C) isotopic signature of dissolved methane (per mil vs. PDB) along the EPREX transect. For simplicity, the stations are plotted by longitude along the horizontal axes of the plots, although Stations 1 and 6 are not located at the same latitude as the other stations (see Fig. 1). Circles indicate the locations of samples. Plots were generated by griding and contouring the data using GMT [http://www.soest.hawaii.edu/gmt/]. Station 1 isotopic data are from April 1997 [*Holmes et al.*, 2000]. Dissolved oxygen was measured (±2 %) by Winkler titration [*Grasshoff*, 1983]. Dissolved CH_4 concentration and stable carbon isotope measurements are described by *Sansone et al.* [1997, 1999].

been observed, the plumes are generally <100 nM, similar to that in the ETNP. More importantly, these plumes have dimensions of a few hundreds of meters in height and several tens of kilometers in length, whereas the core of the ETNP CH_4 pool is over 500 m in height and extends >1000 km laterally. Using an empirical linear relationship between surface O_2 concentrations and depth-integrated CH_4 concentration over 0-600 m depth at the six EPREX stations (data not shown), and using archived data [http://www.ofps.ucar.edu/NOAAServer] to determine mean June surface O_2 concentrations for twenty-seven four-degree by four-degree regions covering the area enclosed by the dashed line in Fig. 1, we estimate that the CH_4 inventory in the ETNP was ~0.3 Tg during EPREX. In contrast, we estimate that a typical

methane-enriched hydrothermal "event" plume (*Mottl et al.* [1995], Fig. 3) had a CH_4 inventory of ~0.2 Gg.

We also used CH_4 stable carbon isotopic ratios (δ-^{13}C-CH_4) to investigate CH_4 cycling. Specifically, we hoped to determine 1) the environment and mechanism of formation of CH_4 in the ETNP, and 2) whether CH_4 produced in the ETNP is the source of the isotopically heavy CH_4 seen at midwater in the North Pacific subtropical gyre (e.g., Stn 1) [*Holmes et al.*, 2000].

At Stn 6, δ^{13}C-CH_4 values indicative of biogenic production (i.e., <-35 per mil vs. PDB [*Whiticar et al.*, 1986]) occur only in the top half of the CH_4 maximum zone (above 400 m). This production is presumably fueled by in-situ decomposition of locally produced detritus [*Bianchi et al.*, 1992; *Tilbrook and Karl*, 1995] resulting from the very high surface productivity at this site. Assuming a biogenic CH_4 source, the isotopic enrichment seen deeper in the CH_4 maximum zone suggests that the CH_4 found at these depths was produced elsewhere and had undergone partial bacterial oxidation and isotopic fractionation [*Coleman et al.*, 1981] prior to its advection to Stn 6. The likely sources of the advected CH_4 are the organic-rich sediments and/or the oxygen-depleted waters found along the western shelf of Mexico [*Hartnett*, 1998]. However, analysis of samples from stations closer to shore will be necessary to identify the source(s) of this deeper CH_4.

The band of isotopically heavy CH_4 at 500-800 m at Stn 1 (Fig. 2c) is a consistent feature that has been observed since the first measurements were made in 1996 [*Holmes et al.*, 2000]. This sub-thermocline band occurs within the depth range where CH_4 concentrations are near their minimum, suggesting that the heavy CH_4 is not from local production. Instead, it appears that the heavy CH_4 is residual CH_4 remaining from the oxidation of some upstream pool of CH_4. However, until the present work it has been unclear where this upstream pool might be located. The data presented here suggest that the sub-thermocline heavy CH_4 may be due to the biological oxidation of CH_4 advecting from CH_4 maxima occurring along the eastern margin of the Pacific. Note that in addition to the EPREX observations (e.g., 300-600 m depth at Stn 6), similar but less intense maxima have been reported along the Mexican shelf [*Burke et al.*, 1983], the California shelf [*Cynar and Yayanos*, 1992; *Tilbrook and Karl*, 1995], and the Oregon shelf [*Rehder et al.*, 2001]. Also, advection of ETNP water has been proposed for explaining observed nutrient and O_2 variability at Stn ALOHA [*Castro et al.*, 2001; *Lukas and Santiago-Mandujano*, submitted].

We tested our hypothesis by measuring the isotopic fractionation during the apparent loss of CH_4 from Stn 6 to Stn 1. If CH_4 at Station ALOHA is derived from the ETNP, then fractionation factors should fall within the range of values expected for biological CH_4 oxidation (1.004 - 1.025 [*Coleman et al.*, 1981; *Wen et al.*, 1996; *Reeburgh et al.*, 1997; *Sansone et al.*, 1999]). This is generally the case: comparing CH_4 concentration and δ^{13}C-CH_4 values from all six of the possible upstream/downstream combinations between Stations 1, 3, 5 and 6 at a specific density surface corresponding to the Stn 1 isotopic maximum (490 - 300 m depth along the transect), and using the calculation methods of *Coleman et al.* [1981], fractionation factors of 1.0060 - 1.035 (mean = 1.013) are obtained.

The flux of CH_4 from the surface ocean to the atmosphere has been estimated to be 5-50 Tg y^{-1} (2.4 - 24 μmol m^{-2} d^{-1}) for the world ocean [*Prather*, 1995], with values of 1.4 - 1.7 μmol m^{-2} d^{-1} calculated for Stn 1 [*Holmes et al.*, 2000]. In light of the highly elevated surface CH_4 concentrations present in the ETNP, we estimated the CH_4 flux to the atmosphere from this region.

Table 1. EPREX CH_4 concentrations, isotopic values, and fluxes.

	Station number					
	1	2	3	4	5	6
Mixed layer CH_4 concentration (nM)	2.84	2.26	2.72	3.11	3.96	3.51
Mixed layer δ-^{13}C-CH_4 (per mil)*	-46.43	--	-46.90	--	-41.53	-42.16
Sea-air flux (μmol m^{-2} d^{-1})†	3.0	1.3	2.1	2.5	1.2	0.77
Sea-air flux δ-^{13}C-CH_4 (per mil)*†	-46.3 to -44.6	--	-48.2 to -46.9	--	-37.5 to -37.0	-37.6 to -37.0
Subsurface eddy diffusive flux / sea-air flux (%)†‡	0.3	14	38	50	17	46

Dashes indicate data not available.

*Station 1 isotopic data are from April 1997 [*Holmes et al.*, 2000].

† Calculations were performed as in *Holmes et al.* [2000].

‡ Proportion of the sea-to-air flux derived from eddy-diffusive transport from the subsurface CH_4 maximum located immediately below 50 m depth.

Using the methods outlined in *Holmes et al.* [2000] with June monthly mean wind speeds for each station [http://www.ofps.ucar.edu/NOAAServer], we determined the characteristics of the sea-air CH_4 flux at the six EPREX stations (Table 1). The eastward decrease in the sea-air flux reflects the dominating effect of the decreasing mean wind speed going from the North Pacific subtropical gyre to the Mexican shelf, which overwhelms the opposite effect of the increasing sea-surface CH_4 concentration along this path. In addition, there is a distinct change in the isotopic signature of the CH_4 being released to the atmosphere (Table 1): at Stn 1 this CH_4 is only slightly heavier than atmospheric CH_4, whereas at Stns 5 and 6 it is approximately 10 per mil heavier.

However, our estimates of the ETNP flux are obviously limited by the fact that we have surface ocean data for only a single transect across the region. Fortunately, there appears to be approximately linear relationships between surface O_2 concentrations and depth-averaged mixed-layer (0-50 m) CH_4 concentrations and δ^{13}C-CH_4 values in the ETNP (Fig. 3). Archived data [http://www.ofps.ucar.edu/NOAAServer] were used to determine mean June surface O_2 concentrations and wind speeds for twenty-seven four-degree by four-degree regions covering the area enclosed by the dashed line in Fig. 1. Using Fig. 3, depth-averaged mixed layer CH_4 concentration and δ^{13}C-CH_4 values were computed for each region. Then, using the methods of *Holmes et al.* [2000], we estimated sea-to-air CH_4 fluxes for each region. The mean June sea-to-air CH_4 flux for the ETNP, averaged over the area delineated in Fig. 1, is estimated to be 2.3 (±0.9) μmole m^{-2} d^{-1}, with a mass-averaged stable carbon isotopic value of -40.7 (+7.1 / -10.1) per mil (both errors calculated from the 95% confidence limits of the regressions in Fig. 3, despite the non-normal distribution of δ^{13}C-CH_4 data). Thus, the areal flux of CH_4 to the atmosphere in the ETNP does not appears to be significantly different from other oceanic regions, although this CH_4 flux is distinctly enriched isotopically.

Finally, it is notable that the proportion of the sea-to-air flux derived from eddy-diffusive transport from the subsurface CH_4 maximum varies greatly across the ETNP (Table 1). Eddy-diffusive transport is negligible compared to the sea-to-air flux at Stn 1, whereas at Stns 3, 4, and 6 it is a significant source of the sea-to-air flux (assuming, as shown by *Holmes et al.* [2000] that CH_4 oxidation is small in oceanic surface waters). This

difference is due to the greatly enhanced subsurface CH_4 concentration gradient seen in the later stations. This difference also implies that at Stn 1 most of the sea-to-air flux is driven by mixed-layer methanogenesis, whereas at the other stations it is less important.

3. Conclusions

We conclude that 1) the ETNP subsurface CH_4 maximum is by far the largest pool of CH_4 yet discovered in the open ocean; 2) CH_4 production in the upper half of this pool is associated with the decomposition of locally produced sinking particulate matter; 3) the deeper half of the CH_4 pool is from a coastal source; 4) advection and oxidation of the subsurface CH_4 pool leads to the heavy CH_4 isotopic values seen at midwater in the North Pacific subtropical gyre; and 5) the ETNP is a source of
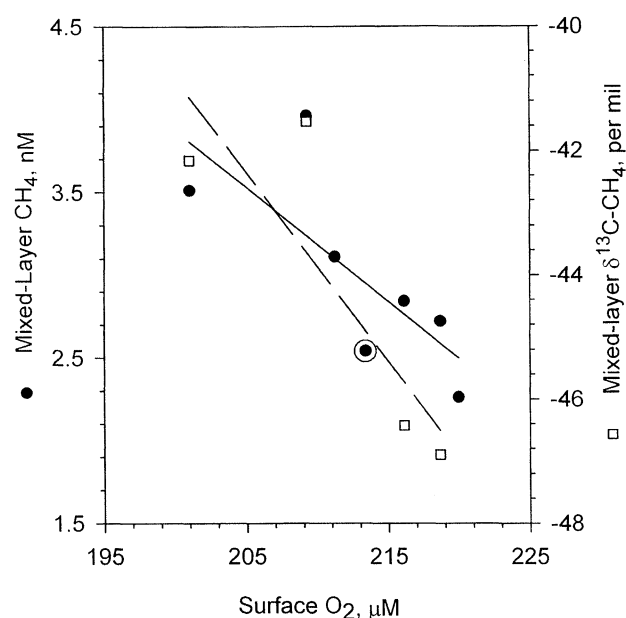
Figure 3. Relationship between surface O_2 concentrations and depth-averaged mixed-layer (0-50 m) CH_4 concentrations (solid line) and δ^{13}C-CH_4 values (dashed line) in the ETNP. Data include one point (circled) from Stn 4 of *Burke et al.* [1981].

isotopically heavy CH_4 to the atmosphere. Our results further suggest that other oceanic areas of upwelling-induced anoxia, such as the Peru margin and the Arabian Sea [*Deuser*, 1975; *Owens et al.*, 1991; *Patra et al.*, 1998], are likely to also be major sites of CH_4 accumulation and may be areas of significant atmospheric input of isotopically heavy CH_4. Field investigations of CH_4 cycling in these regions are clearly needed, and may need to be considered in global isotopic CH_4 models.

References

Bianchi, M., D. Marty, J.-L. Teyssie, and S.W. Fowler. Strickly aerobic and anaerobic bacteria associated with sinking particulate matter and zooplankton fecal pellets. *Mar. Ecol. Prog. Ser., 88,* 55-60, 1992.

Brooks, J.M., D.F. Reid, and B.B. Bernard. Methane in the upper water column of the northwestern Gulf of Mexico. *J. Geophys. Res., 86,* 11029-11040, 1981.

Burke, R.A., Jr., D.F. Reid, J.M. Brooks, and D.M. Lavoie. Upper water column methane geochemistry in the eastern tropical North Pacific. *Limnol. Oceanogr., 28,* 19-32, 1983.

Castro, C.G., F.P. Chavez, and C.A. Collins. The role of the California Undercurrent in the export of denitrified waters from the eastern tropical North Pacific. *Global Biogeochem. Cycles* (in press), 2001.

Charlou, J.-L., and J.-P. Donval. Hydrothermal methane venting between 12°N and 26°N along the Mid-Atlantic Ridge. *J. Geophys. Res., 98,* 9625-9642, 1993.

Coleman, D.D., J.B. Risatti, and M. Schoell. Fractionation of carbon and hydrogen isotopes by methane-oxidizing bacteria. *Geochim. Cosmochim. Acta,* 45, 1033-1037, 1981.

Cline, J.D., and F.A. Richards. Oxygen deficient conditions and nitrate reduction in the eastern tropical North Pacific Ocean. *Limnol. Oceanogr., 17.* 885-900, 1972.

Cohen, Y., and L.I. Gordon. Nitrous oxide in the oxygen minimum of the eastern tropical North Pacific: evidence for its consumption during denitrification and possible mechanisms for its production. *Deep-Sea Res., 25,* 509-524, 1978.

Cynar, F.J., and A.A. Yayanos. The distribution of methane in the upper waters of the Southern California Bight. *J. Geophys. Res., 97,* 11,269-11,285, 1992.

Deuser, W.G. Reducing environments, in *Chemical Oceanography, Vol. 3, 2nd Ed.,* edited by J.P. Riley and G. Skirrow, pp. 1-37, Academic, London, 1975.

Grasshoff, K. Determination of oxygen, in *Methods of Seawater Analysis, Second Ed.,* edited by K. Grasshof, M. Ehrhardt and K. Kremling, pp. 61-72, Verlag Chemie, Weinheim, 1983.

Hartnett, H.E. Organic carbon input, degradation and preservation in continental margin sediments: an assessment of the role of a strong oxygen deficient zone. Ph.D. dissertation, Univ. Washington, 1998.

Holmes, M.E., F.J. Sansone, T.M. Rust, and B.N. Popp. Methane production, consumption and air-sea exchange in the open ocean: An evaluation based on carbon isotopic ratios. *Global Biogeochem. Cycles, 14,* 1-10, 2000.

Karl, D. M. A sea of change: Biogeochemical variability in the North Pacific subtropical gyre. *Ecosystems, 2,* 181-214, 1999.

Lamontagne, R.A., J.W. Swinnerton, V.J. Linnenbom, and W.D. Smith. Methane concentrations in various marine environments, *J. Geophys. Res., 78,* 5317-5324, 1973.

Lukas, R., and F. Santiago-Mandujano. Extreme water mass anomaly observed in the Hawaiian Ocean Time-series. *Geophys. Res. Lett.* (submitted).

Mottl, M.J., F.J. Sansone, C.G. Wheat, J.A. Resing, E.T. Baker, and J.E. Lupton. Manganese and methane in hydrothermal plumes along the East Pacific Rise, 8°40' to 11°50'N. *Geochim. Cosmochim. Acta, 59,* 4147-4165, 1995.

Owens, N.J., C.S. Law, R.F. Mantoura, P.H. Burkill, and C.A. Llewellyn. Methane flux to the atmosphere from the Arabian Sea. *Nature, 354,* 293-295, 1991.

Patra, P.K., S. Lal, S. Venkataramani, M. Gauns, and V.V. Sarma. Seasonal variability in distribution and fluxes of methane in the Arabian Sea. *J. Geophys. Res., 103,* 1167-1176, 1998.

Prather, M., R. Derwent, D. Ehhalt, P. Fraser, E. Sanhueza, and X. Zhou. Other trace gases and atmospheric chemistry, in *Climate Change 1994: Relative Forcing of Climate Change and an Evaluation of the IPCC IS92 Emission Scenario,* edited by J.T. Houghton et al., Cambridge Univ. Press. pp. 73-126, 1995.

Reeburgh, W.S., A.I. Hirsch, F.J. Sansone, B.N. Popp, and T.M. Rust. Carbon isotope effect accompanying microbial oxidation of methane in boreal forest soils. *Geochim. Cosmochim. Acta, 61,* 4761-4767, 1997.

Rehder, G., R.W. Collier, K. Heeschen, P.M. Kosro, J. Barth, and E. Suess. Enhanced marine CH_4 emissions to the atmosphere off Oregon caused by coastal upwelling. *Global Biogeochem. Cycles* (submitted).

Quay, P.D., S.L. King, J.M. Landsdown, and D.O. Wilbur. Carbon isotopic composition of atmospheric CH_4: fossil and biomass burning source strengths, *Global Biogeochemical Cycles, 5,* 25-47, 1991.

Sansone, F.J., B.N. Popp, and T.M. Rust. Stable carbon isotopic analysis of low-level methane in water and gas. *Anal. Chem., 69,* 40-44, 1997

Sansone, F.J., M.E. Holmes, and B.N. Popp. Methane stable isotopic ratios and concentrations as indicators of methane dynamics in estuaries. *Global Biogeochem. Cycles, 13,* 463-474, 1999.

Tilbrook, B.D., and D.M. Karl. Methane sources, distributions and sinks from California coastal waters to the oligotrophic North Pacific gyre. *Mar. Chem., 49,* 51-64, 1995.

Wen, X, J.P. Cowen, R. Thompson, B. Popp, and F. Sansone. Methane carbon isotopic fractionation and composition at the Endeavor Segment hydrothermal system in the northeastern Pacific Ocean (abst.). *Eos, Trans. AGU, 77,* 46, suppl., F404-F405, 1996.

Whiticar, M.J., E. Faber, and M. Schoell. Biogenic methane formation in marine and freshwater environments: CO2 reduction vs. acetate fermentation - Isotope evidence, *Geochim. Cosmochim. Acta, 50,* 692-709, 1986.

Yamamoto, S., J. B. Alcauskas, and T.E. Crozier. Solubility of methane in distilled water and seawater. *J. Chem. Engin. Data, 21,* 78-80, 1976.

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