

## Sources and flux of natural gases from Mono Lake, California

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**Abstract**—The ability to identify a formation mechanism for natural gas in a particular environment requires consideration of several geochemical factors when there are multiple sources present. Four primary sources of methane have been identified in Mono Lake. Two of these sources were associated with numerous natural gas seeps which occur at various locations in the lake and extend beyond its present boundary; the two other gas sources result from current microbiological processes. In the natural gas seeps, we observed flow rates as high as 160 moles CH<sub>4</sub> day<sup>-1</sup>, and estimate total lakewide annual seep flux to be  $2.1 \times 10^6$  moles CH<sub>4</sub>. Geochemical parameters ( $\delta^{13}\text{CH}_4$ ,  $\delta\text{DCH}_4$ ,  $\text{CH}_4/[\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8]$ ) and  $\Delta^{14}\text{CH}_4$  measurements revealed that most of the seeps originate from a paleo-biogenic ( $\delta^{13}\text{CH}_4 =$  about  $-70\%$ ) natural gas deposit of Pleistocene age which underlies the current and former lakebed. Gas seeps in the vicinity of hot springs had, in combination with the biogenic gas, a prominent thermogenic gas component resulting from hydrothermal alteration of buried organic matter.

Current microbiological processes responsible for sources of natural gas in the lake included pelagic methanogenesis and decomposition of terrestrial grasses in the littoral zone. Methanogenesis in the pelagic sediments resulted in methane saturation (2–3 mM at 50 cm;  $\delta^{13}\text{CH}_4 =$  about  $-85\%$ ). Interstitial sulfate decreased from 133 mM at the surface to 35 mM by 110 cm depth, indicating that sulfate-reduction and methanogenesis operated concurrently. Methane diffused out of the sediments resulting in concentrations of about 50  $\mu\text{M}$  in the anoxic bottom waters. Methane oxidation in the oxic/anoxic boundary lowered the concentration by  $>98\%$ , but values in surface waters (0.1–1.3  $\mu\text{M}$ ) were supersaturated with respect to the atmosphere. The  $\delta^{13}\text{CH}_4$  (range =  $-21.8$  to  $-71.8\%$ ) of this unoxidized residual methane was enriched in <sup>13</sup>C relative to methane in the bottom water and sediments. Average outward flux of this methane was  $2.77 \times 10^7$  moles yr<sup>-1</sup>. A fourth, but minor source of methane ( $\delta^{13}\text{CH}_4 = -55.2\%$ ) was associated with the decomposition of terrestrial grasses taking place in the lake's recently expanded littoral zone.

### INTRODUCTION

THE CONVERSION OF organic matter buried in sediments to natural gas takes place by two primary mechanisms: by bacterial decay under anaerobic conditions, or by thermogenic/catagenic transformations. The first process yields "biogenic" methane which generally is characterized by  $\text{CH}_4/[\text{C}_2\text{H}_6 + \text{C}_3\text{H}_8]$  (henceforth referred to as  $\text{C}_1/[\text{C}_2 + \text{C}_3]$ ) ratios  $\geq 100$  and a methane depleted in <sup>13</sup>C, giving  $\delta^{13}\text{CH}_4$  values more negative than  $-50\%$  (BERNARD *et al.*, 1978; SCHOELL, 1983). Biogenic natural gases are formed by the activities of methanogenic bacteria in anoxic sediments. A significant quantity (about 20%) of exploitable natural gas deposits are of biogenic origin (RICE and CLAYPOOL, 1981). Thermogenic natural gas deposits are formed in association with the transformation reactions that mature kerogen into petroleum products (TISSOT and WELTE, 1978; HUNT, 1979). Typical thermogenic natural gases contain more higher molecular weight gaseous alkanes than do biogenic gases, resulting in  $\text{C}_1/[\text{C}_2 + \text{C}_3]$  ratios  $< 100$ . During the generation of thermogenic gas, the methane is fractionated isotopically less with respect to the organic matter than is biogenic methane, and exhibits  $\delta^{13}\text{CH}_4$  values generally more positive than  $-50\%$  (SCHOELL, 1983).

Certain bacterial activities may alter these geochemical parameters which results in natural gas of biogenic origin taking on a more thermogenic character. One such activity is the production of non-methane gaseous

alkanes (DAVIS and SQUIRES, 1954; HUNT *et al.*, 1980; OREMLAND, 1981; VOGEL *et al.*, 1982). In some cases, production of sufficient quantities of higher alkanes by microorganisms can approach the biogenic/thermogenic transition values of  $\text{C}_1/[\text{C}_2 + \text{C}_3]$  (range = 160 to 630; VOGEL *et al.*, 1982; OREMLAND and DES MARAIS, 1983). Secondly, bacterial oxidation of methane can lower  $\text{C}_1/[\text{C}_2 + \text{C}_3]$  ratios by selective removal of methane (WHITICAR and FABER, 1986). In addition, this process results in a <sup>13</sup>C enrichment of the residual, unoxidized methane (SILVERMAN and OYAMA, 1968; BARKER and FRITZ, 1981; COLEMAN *et al.*, 1981), which can be of sufficient magnitude to alter interpretation of  $\delta^{13}\text{CH}_4$  data obtained from environmental samples (OREMLAND and DES MARAIS, 1983). Thus, a knowledge of the types of bacterial activities occurring in an environment in which natural gas is present can greatly aid in deciphering its origin. This is especially true for environments with multiple sources present, such as in meromictic lakes located in regions of active volcanism or rifting. For example, both thermogenic and biogenic methane are present in Lake Kivu (DEUSER *et al.*, 1973) and bacterial methane-oxidation occurs in the lake's water column (JANNASCH, 1975).

In this study we report our findings with respect to the sources and flux of natural gas emanating from a meromictic lake located in a region of active volcanism: Mono Lake, California. By employing standard geochemical hydrocarbon indices in conjunction with

measures of radiocarbon and bacterial activities we were able to identify four types of natural gases in the lake: 1) a deposit of biogenic gas of Pleistocene origin underlies the lakebed and outgasses to the surface; 2) seeps located in regions of hot-springs have a strong thermogenic component derived from pyrolysis of buried organic matter; 3) current methanogenic activity in the lake's anoxic pelagic sediments and 4) current activity in the littoral zone. Methane diffuses out of the pelagic sediments, but bacterial oxidation in the water column causes a  $^{13}\text{C}$ -enrichment of methane in the surface waters. Outward flux of methane from the lake to the atmosphere was dominated by degassing of this residual, unoxidized methane rather than flux associated with the seeps.

### STUDY SITE DESCRIPTION

Mono Lake is a closed basin water body located in central California (Fig. 1). Diversion of normal freshwater runoff into the lake from the Sierra, coupled with evaporation has resulted in a 14m drop in lake level and a doubling of salinity since 1941. The concentrations of major dissolved chemical constituents have varied with time as a consequence of these water management policies. MASON (1967), and WINKLER (1977) have reported the lakewaters to be hypersaline (salinity = 90‰), alkaline (pH = 9.8), and rich in carbonate + bicarbonate (0.5 M) as well as in sulfate (110 mM). Aspects of the organic geochemistry of the lake's recent sediments were reported by REED (1977). MASON (1967) noted the presence in the lake of methane gas seeps.

Normally Mono Lake is monomictic and undergoes an annual winter mixing (MASON, 1967; MELACK, 1983). However, due to unusually high precipitation during two consecutive winters (1982 and 1983),  $4.3 \times 10^8 \text{ m}^3$  of freshwater (about 10% of the lake volume) was released into the lake, causing a 2.5 m rise in lake level (Los Angeles Department of Water and Power, Briefing Document, March, 1984). This influx decreased the salinity of the surface waters (e.g., surface chloride = 21.8 g/L in 1980 vs. 18.5 g/L in 1984; L. MILLER,

unpublished data) relative to the bottom waters sufficiently to overcome the winter density increase due to cooling. Subsequently, a condition of year-round stratification (meromixis) has persisted from 1983 to date. Under these conditions the anoxic bottom waters (below 16 m) have an annual temperature of 4.5°C. During summer, surface water temperatures reach about 23°C and the thermocline is located between 9–14 m. During winter, surface waters cool to 1.5°C, and the thermocline descends to 16–19 m. The oxycline is located in close proximity to the thermocline. Annual water column primary productivity has been estimated to be 340–550 mgC  $\text{m}^{-2}$  (JELLISON and MELACK, 1987). This productivity supports populations of the brine shrimp *Artemia monica* which is the lake's only significant zooplankter (LENZ *et al.*, 1986).

The topographic features of the Mono Basin and the bathymetry of the lake were reported by SCHOLL *et al.* (1967), and the Quaternary history by LAJOIE (1968). The Mono Basin was formed about  $3 \times 10^6$  years b.p. (GILBERT *et al.*, 1968; CHRISTENSEN *et al.*, 1969). During the Pleistocene, Lake Russell (the precursor of Mono Lake) contained ~18-fold more water and covered ~5-fold more area than Mono Lake does presently (K. LAJOIE, pers. commun.). Mono Lake is located in a region of active volcanism (RUSSELL, 1889), being a northern extension of the Long Valley Caldera (BAILEY *et al.*, 1976; HILL *et al.*, 1985; SOREY, 1985). The Mono Craters, located on the lake's southern shore, had their last major eruption approximately 635 years b.p. (SIEH and BURSİK, 1986). Volcanic features extend northward from the Mono Craters into the lake. Cinder cones are present on the lake's two major islands: Paoha and Negit. In addition, hot springs are present along the southern shoreline of Paoha Island, as well as in various locations on the present shoreline of the lake. Paoha Island consists primarily of lakebed sediments which appear to have been uplifted 200–400 years b.p. (STINE 1984).

### METHODS AND MATERIALS

**Dissolved gases:** All water column and sediment samples were recovered from a station in the western basin of the lake (Fig. 1; referred to as "pelagic") near a permanently moored buoy (water depth = 26 m). No gas seeps were apparent in this region. Dissolved oxygen was measured with an *in situ* probe (CLOERN *et al.*, 1983). Water samples were recovered with a Niskin sampler (vol = 7 L). Dissolved hydrocarbons in the water column were extracted at the time of sample recovery by using a syringe gas phase equilibration procedure (RUDD *et al.*, 1974; OREMLAND and DES MARAIS, 1983). A subsample (180 ml distributed in six 60 ml syringes) was equilibrated with an equal volume of He. The extracted hydrocarbons were stored by injection of the He gas mixture into a stoppered, crimped serum bottle (vol = 160 ml) which was previously filled with distilled water. The water was entirely displaced by inverting the bottle and inserting an 18 gauge drainage needle through the stopper. This procedure allowed for recovery of the entire sample without contamination or dilution with air. Furthermore, it segregated the extracted gases from any possible post-sampling microbial alteration. Contamination by volatile organic compounds present in the black butyl rubber stoppers (Bellco Biological Glassware, Vineland, N.J.) was avoided by prior treatment (boiling in 0.1 N NaOH for 45 min followed by immersion in distilled water for ~8 hours). Blanks consisting of He-purged bottles were generated at each sampling and did not contain significant hydrocarbons. Hydrocarbons were quantified by flame ionization gas chromatography within 12 h of sample collection. Analytical procedures were those described by OREMLAND (1981) modified by use of a 1.8 m Poropak Q column (diam. = 0.64 cm.; mesh = 50–80; oven temp. = 50°C). The samples were subsequently stored at -20°C (to prevent bacterial growth) for up to 2 months before stable isotope analyses were conducted (see below). No significant changes in the quantity of extracted hydrocarbons occurred during cold storage.

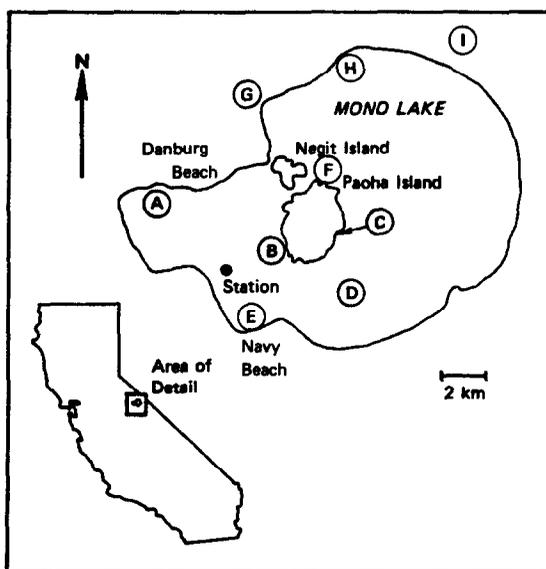


FIG. 1. A map of Mono Lake indicating the location of the water column/sediment sampling station and those of the natural gas seeps (indicated by capital letters).

**Sediments.** Sediments were sampled with either a piston core (May, 1986; OREMLAND and DES MARAIS, 1983) or a gravity core (Aug. 1986; 10 cm, i.d.) which allowed for recovery of the upper 1.6 and 1.2 m of the sediment column. Cores were extruded within 4 h of collection and all processing was done in a He-filled glove bag. Hydrocarbons were extracted by subcoring vertically with 50 ml plastic syringes (hub end severed). Two subcores (total vol = 100 ml) were recovered from each 10 cm depth interval (surface samples recovered 50 ml from the upper 5 cm). The subsamples were immediately extruded into pre-weighed mason jars (vol = 465 ml) which contained 200 ml of NaCl-saturated water, and sealed with twist-on, rubber gasket-sealed caps. The caps were fitted with a serum stopper to allow for removal of the gas samples. After core processing was completed, the sample jars were shaken on a reciprocal shaker (250 rpm) for 30 min in order to partition the gaseous hydrocarbons into the gas phase. This was arrived at empirically because no further increases in headspace methane occurred after 15 min shaking, indicating complete transfer of sediment-entrained methane should occur by 30 min. Most of the headspace (120 ml) was removed from the jars by syringe while simultaneously injecting an equal volume of water (to prevent pressure differentials). The samples were stored in crimp-sealed serum bottles as described previously. Gas chromatographic analysis of extracted hydrocarbons were performed within 2 hours of extraction.

In addition to hydrocarbons, the sediments were also sampled for interstitial sulfate. Subsamples (50 ml) from each depth interval were centrifuged ( $8,000 \times g$  for 15 min) and the pore waters were filtered ( $0.45 \mu$ ) and acidified to pH < 4 with 6 N HCl. Sulfate analyses were performed on an Waters ion chromatograph (Millipore Corp.) using a IC-PAK A 10  $\mu$  mesh polymethacrylate column. Because of the extremely high sulfate content of Mono Lake water, it was necessary to dilute the samples (1:100) with deionized water prior to injection on the chromatograph. Samples for porosity ( $\sim 10$  ml) were taken down the length of the core and reported as percent weight lost on drying ( $100^\circ\text{C}$  for 72 h). Values ranged from 0.89 at the surface to 0.69 by 1 m depth. Calculations of dissolved pore water constituents were converted from a wet weight basis to molarity.

**Experiments with sediment slurries.** To determine if the ethane detected in the pelagic sediments was of biogenic origin, sediment slurry incubations were conducted. Slurries were prepared (triplicates) by homogenizing equal volumes of bottom water with sediment, dispensing into serum bottles, and incubating under  $\text{N}_2$  as described elsewhere (KIENE *et al.*, 1986). Controls consisted of autoclaved slurries (250 kpa/ $120^\circ\text{C}$  for 45 min). Methane and ethane in the headspaces of the slurry-containing bottles were quantified over the course of the incubation.

**Gas seeps.** Numerous continuous-flow gas seeps could be observed during calm conditions at various locations on the lake. These seeps were counted and tallied; however, a complete enumeration was not feasible. Gas samples were collected by positioning a swimmer over the vents and collecting gases with a large, submerged funnel. The funnel was capped with a stopper and collected gases were transferred by syringe to distilled water-filled serum bottles as described previously. An evacuated glass (Corning #1720) gas collection bottle (vol = 50 ml) was used to collect hot-spring gases for analysis of  $^3\text{He}/^4\text{He}$  ratios (CRAIG *et al.*, 1978). To estimate the flow rates of the seeps, the funnel (area =  $0.05 \text{ m}^2$ ) was connected to a water-filled, 4 L bottle, and the time needed to fill the bottle was recorded. These large volume bottles were employed to obtain a sufficient quantity of methane for determination of radiocarbon activity (see below). Samples of gases derived from the anaerobic decomposition of terrestrial grasses occurring in the littoral zone underneath a tufa pavement ( $\sim 1\text{--}2$  cm thick) were collected by a similar procedure, only it was necessary to break through the tufa with a metal rod to release the entrapped gases. Hydrocarbons and other gases were quantified by flame ionization (see above) and thermal con-

ductivity gas chromatography (CULBERTSON *et al.*, 1981). In order to separate  $\text{O}_2$  from  $\text{N}_2$  and  $\text{H}_2$  from He, a 7.2 m Poropak Q column was employed. When these determinations were not of interest, a 3.6 m column was used.

**Measurement of dissolved methane flux to the atmosphere.** Plexiglas flux chambers constructed in either a dome (area =  $0.83 \text{ m}^2$ ) or cylindrical (area =  $0.165 \text{ m}^2$ ) configuration were deployed about 10–20 feet from the boat and kept from drifting by a tethering line. This allowed for the chambers to be agitated as a consequence of enhanced wave turbulence during windy periods. A headspace (either 1 or 2 L) of either air or He (when  $\delta^{13}\text{CH}_4$  analyses were conducted) was entrapped in the chambers prior to deployment. Ethane was usually added as an internal standard to determine headspace volumes. Addition of ethane was not done when flux measurements were made in proximity to hot-springs to allow for measurement of outward ethane fluxes. The headspaces were sampled at 20–30 min. intervals for 2–4 hr periods and methane concentrations determined as described previously. A further description of the chambers and methods used will appear elsewhere (MILLER and OREMLAND, in prep.). Measurements of wind speed (2 m elevation) were taken with a hand-held anemometer in conjunction with chamber sampling. Chambers were deployed in regions lacking gas seeps or noticeable gas ebullition. One deployment was made in proximity to a region of hot springs and gas seeps on the southern tip of Paoha Island; however, the chamber was situated in a location in which there were no seeps in the immediate vicinity.

**Determination of  $\delta^{13}\text{CH}_4$ ,  $\delta\text{DCH}_4$  and  $\Delta^{14}\text{CH}_4$ .** The amounts of methane recovered in individual samples from the different sources in the lake varied from  $<0.1 \mu\text{l}$  to over 7 ml. Despite the sample concentration procedure described herein, there was sometimes insufficient gas available in some samples for a reliable D/H measurement. The gas samples were partitioned and combusted in a natural gas preparation line similar to that described by FABER and STAHL, (1983). Modifications to the system included a Poropak-filled sample inlet loop which was cooled to  $-192^\circ\text{C}$  to quantitatively freeze the gases from the serum bottles. The individual gases were oxidized with CuO at  $900^\circ\text{C}$ , and the combustion products  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were distilled off and collected separately. The combustion  $\text{H}_2\text{O}$  was reduced with zinc to  $\text{H}_2$  using the method of COLEMAN *et al.* (1982). The detection limit was about 20  $\mu\text{l}$  for  $\delta^{13}\text{CH}_4$  and about 100  $\mu\text{l}$  for  $\delta\text{DCH}_4$ . Blanks consisting of He filled serum bottles were run at each sampling period and did not contain sufficient levels of contaminants to alter the stable isotope determinations. D/H and  $^{13}\text{C}/^{12}\text{C}$  ratios were measured by mass spectrometry and the results are reported in the usual delta notation:

$$\delta R = \left( \frac{\text{Ra/Rs sample} - \text{Ra/Rb standard}}{\text{Ra/Rb standard}} \right) \times 1000$$

where Ra/Rb are the  $^{13}\text{C}/^{12}\text{C}$  and D/H ratios relative to the PDB standard for carbon and the SMOW standard for hydrogen. The  $\delta^{13}\text{C}$  of dissolved inorganic carbon in the pore waters of the pelagic sediments was  $-0.52$  to  $-1.0\text{‰}$ , while the water column was  $-2.3$  to  $-3.2\text{‰}$ . The procedure of MCCREA (1950) was used for sample preparation. The  $\delta\text{DH}_2\text{O}$  of the lake water was  $-42$  to  $-50\text{‰}$ .

Measurement of radiocarbon activity of methane samples was achieved by oxidation to  $\text{CO}_2$ , followed by trapping in NaOH. A large quantity of methane (about 700 ml) was required for analysis, although for samples having a high  $^{14}\text{C}$  content, as little as 100 ml proved adequate (see below). In the case of gas seeps and entrapped bubbles, samples were collected as outlined previously. Carbon dioxide was removed from the sample by pumping and recirculating the gas through 4 N NaOH (vol. = 250 ml) for 8 hours by the action of a diaphragm pump. Methane was subsequently oxidized to  $\text{CO}_2$  by placing a CuO furnace ( $800^\circ\text{C}$ ) in line and recirculating the gas for 10 hours through fresh 4 N NaOH. The radiocarbon sample was subsequently processed and counted as outlined

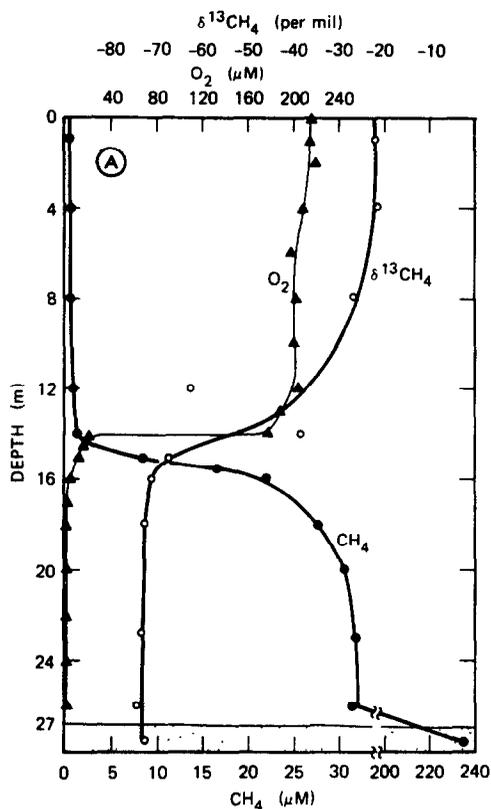


FIG. 2. Water column profile of dissolved oxygen, methane and  $\delta^{13}\text{CH}_4$  taken during October, 1984.

elsewhere (ROBINSON, 1979; KHARAKA *et al.*, 1983) and reported as  $\Delta^{14}\text{C}$  and percent modern activity (STUIVER and POLACH, 1977).

The radiocarbon activity present in the dissolved methane in the lake's anoxic bottom water was also determined. We

achieved this by stripping methane out of a flow of bottom water continuously pumped to the surface. Bottom water was pumped (peristaltic:  $1 \text{ L min}^{-1}$ ) into the top of a sealed 25 L plastic cylindrical chamber ( $1.10 \text{ m} \times 0.15 \text{ m}$ ). Siphons maintained the fluid level so that  $<10$  liters of headspace were present while degassed water was removed from the vessel's bottom. A supply of He (200 liters contained in an air mattress) was bubbled through the stripping vessel ( $14 \text{ liters min}^{-1}$  for 4 hours). Stripping efficiency was  $\sim 36\%$ . This was adequate to recover enough methane for radiocarbon analysis (fractionation was accounted for as in ROBINSON, 1979), but insufficient to fill the smallest counting chamber. To compensate for this, an equal volume of "dead"  $\text{CO}_2$  (marble) was added to the sample. This dilution was corrected for in the final calculations. No significant hydrocarbons were present in He-filled mattress blanks.

## RESULTS

*Dissolved gases in the pelagic waters and sediments.* Methane concentrations in the surface waters (above 10 m) were low, and seasonally ranged between 0.09– $1.29 \mu\text{M}$ , depending on the depth of mixing. Methane increased with depth across the oxycline (Fig. 2) reaching values of  $35 \mu\text{M}$  in the anoxic bottom waters during October, 1985. The methane concentrations of the bottom water have been increasing with time since the onset of meromixis and were  $57 \mu\text{M}$  by January, 1987. Ethane was not detected in the surface waters ( $<2 \text{ nM}$ ), but traces (about  $16 \text{ nM}$ ) were present in the bottom waters. Bottom waters also contained sulfide ( $0.8 \text{ mM}$ ) and ammonia ( $0.6 \text{ mM}$ ) (L. MILLER and R. OREMLAND, unpubl. data).

Values of  $\delta^{13}\text{CH}_4$  in the bottom waters below 16 m showed little variation with season and ranged ( $n = 20$ ) from  $-71.2$  to  $-75\text{‰}$  (Fig. 3). During the initial October, 1984 sampling a pronounced enrichment in  $^{13}\text{C}$  was evident in the methane above the oxycline (located at 14 m depth; Figs. 2 and 3) and  $\delta^{13}\text{CH}_4$  values above

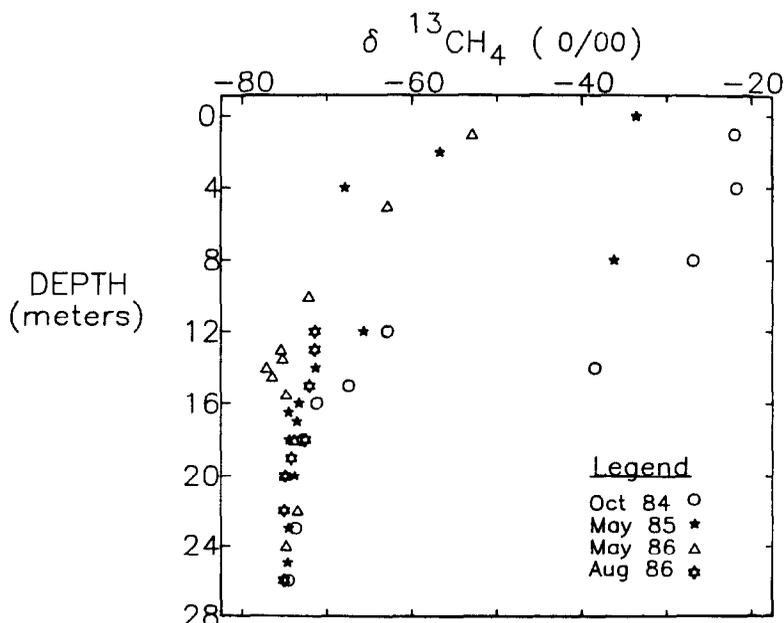


FIG. 3. Profiles of  $\delta^{13}\text{CH}_4$  in the water column of Mono Lake taken from 1984 to 1986.

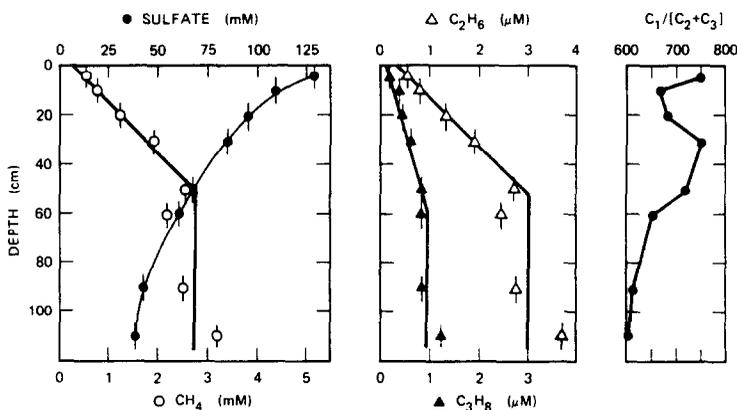


FIG. 4. Interstitial porewater profiles of A) methane and sulfate, B) ethane and propane and C)  $C_1/[C_2 + C_3]$  taken during August, 1986. Samples were taken with a gravity corer.

12 m ranged between  $-21.8$  and  $-67\%$ . The mean  $\delta^{13}\text{CH}_4$  of 12 samples collected from waters above 12 m in October, 1984 and May, 1986 and August, 1986 was  $-46.0\%$  (std. dev. =  $19.5\%$ ). Therefore,  $\delta^{13}\text{CH}_4$  values in the surface waters were consistently enriched in  $^{13}\text{C}$  and had greater variability than bottom waters (Fig. 3).

Pelagic sediment porewater concentrations of dissolved methane increased linearly from the surface (0.2–0.3 mM) and reached constant values of 2–3 mM at depths below 50 cm (Fig. 4a). Small gas pockets were evident below (but not above) 50 cm depth. In-

terstitial sulfate concentrations decreased continuously with depth; however, there was still abundant sulfate (about 35 mM) present at the 110–115 cm depth interval (Fig. 4a). Ethane and propane had porewater profiles very similar to methane (Fig. 4b). Ratios of  $C_1/[C_2 + C_3]$  ranged between 600 and 750 and had a downcore decreasing trend (Fig. 4c). No significant quantities of ethene ( $\leq 0.07 \mu\text{M}$ ) were detected.

Ratios of  $C_1/[C_2 + C_3]$  vs.  $\delta^{13}\text{CH}_4$ , and  $\delta^{13}\text{CH}_4$  vs.  $\delta\text{DCH}_4$  for the anoxic water column and two sediment cores are shown in Fig. 5 and Fig. 6, respectively. Sediment  $\delta^{13}\text{CH}_4$  values were consistently between  $-80.0$

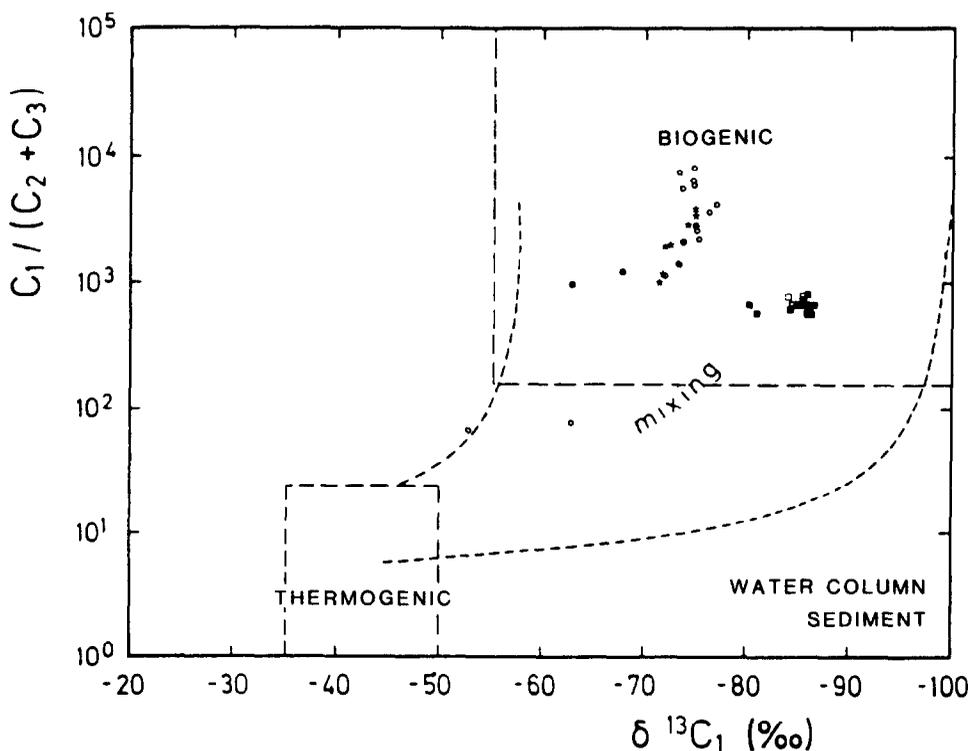


FIG. 5. Ratios of  $C_1/[C_2 + C_3]$  vs.  $\delta^{13}\text{CH}_4$  for hydrocarbons in Mono Lake. Pelagic sediments samples with a gravity corer ( $\square$ ; Aug, 1986) and a piston corer ( $\blacksquare$ ; May, 1986) and anoxic water column samples from Oct. 1984 ( $\bullet$ ), May, 1985 ( $\star$ ) and Aug. 1986 ( $\circ$ ).

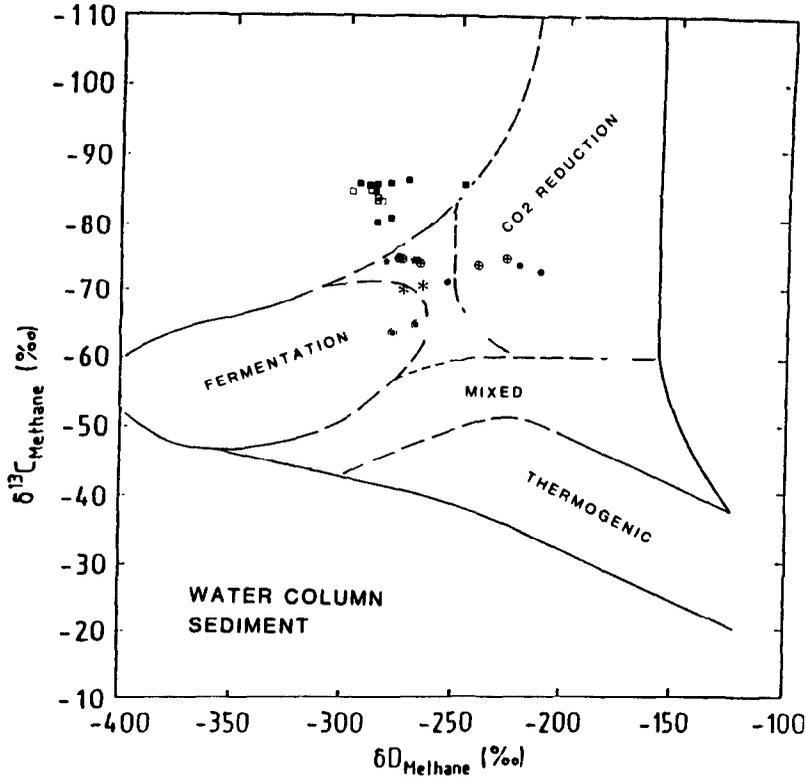


FIG. 6. Ratios of  $\delta^{13}\text{C}_{\text{Methane}}$  vs.  $\delta\text{DCH}_4$  for Mono Lake sediment ( $\square$ ,  $\blacksquare$ ) and anoxic water column samples from October, 1984 ( $\bullet$ ), May, 1985 ( $\oplus$ ), May, 1986 ( $\star$ ) and Aug. 1986 ( $\ast$ ).

to  $-86.4\text{‰}$ , while  $\delta\text{DCH}_4$  values ranged between  $-249.0$  to  $-295.0\text{‰}$ . There was no obvious downcore trend in these values (not shown). However, on average the sediments were about 12 per mil depleted in  $^{13}\text{C}$  and about 9 per mil enriched in deuterium than were the anoxic waters below 18 m. Radiocarbon activity in methane recovered from the anoxic bottom waters was about 80% of modern (Table 1), a value which was the same as that for dissolved inorganic carbon (PENG and BROECKER, 1980).

*Experiments with sediment slurries.* Sediment slurries continuously evolved ethane (as well as methane) and this activity was abolished by autoclaving (data

not shown). Mean ethane levels in the headspaces after 127 days were (nmoles/liter slurry): endogenous production = 73.4; autoclaved = 3.1. Methane levels at the end of this time period were ( $\mu\text{moles/liter slurry}$ ): endogenous production = 160; autoclaved = 0.2.

*Characteristics of natural gas seeps.* Samples were collected from nine gas seeps located at various locations on the lake, as well as on its peripheral shores (Fig. 1). We counted a total of 588 seeps which had measured flow rates ranging from 0.05 to 4 liters  $\text{min}^{-1}$  seep $^{-1}$ . The characteristics and composition of the collected gases from these nine representative locations are given in Table 2. Methane was the major component (61–93.2%) in all seep gases with the exception of the samples from Navy Beach (E), and the Dea-chambeau Ranch hot spring (G-1). Only a trace of methane (0.02%) was detected in the  $\text{CO}_2$ -rich volcanic vents along Navy Beach (E-1); however, significant quantities (13.4%) were present in the neighboring tufa-entrapped bubbles associated with the rotting grasses (E-2).

Samples from sites A and B typified most of the collected gases in that they were primarily methane, had only traces of ethane, ethane, and propane. Values of  $\delta^{13}\text{C}_{\text{CH}_4}$  and  $\delta\text{DCH}_4$  for these types of seeps ranged from  $-64.2$  to  $-69.7$  and  $-251$  and  $-283\text{‰}$ , respectively. The hot spring gases on the southern part of Paoha Island (sample C) had sufficient quantities of ethane and propane to yield a very low  $\text{C}_1/[\text{C}_2 + \text{C}_3]$

Table 1: Radiocarbon activity in methane, carbon dioxide and dissolved inorganic carbon in Mono Lake.

SOURCE	$\Delta^{14}\text{C}$	% MODERN
**		
A) Dissolved Inorganic Carbon		
Postnuclear (1978)	-140	86
Prenuclear (1950)	-187	81
B) Methane		
Bottom water, dissolved	-202	80
Littoral zone (E-2)	-482	52
Hot spring Seep (C)	-895	11
Biogenic seeps (A,B,D,F)	$-941 \pm 20$	$6 \pm 2$
C) Carbon Dioxide		
South shore seep (E-1)	-950	5

\*  $^{14}\text{C}$  precision is generally better than 5 o/oo.

\*\* Peng and Broecker (1980)

\*\*\* Mean  $\pm$  1 standard deviation

Table 2: Characteristics of gases collected in and around Mono Lake. Sites correspond to locations in Figure 1.

SITE*	N <sub>2</sub> O <sub>2</sub> CO <sub>2</sub> He H <sub>2</sub> CH <sub>4</sub>						C <sub>2</sub> H <sub>4</sub> C <sub>2</sub> H <sub>6</sub> C <sub>3</sub> H <sub>8</sub>			C <sub>1</sub> (C <sub>2</sub> + C <sub>3</sub> )	δ <sup>13</sup> CH <sub>4</sub>	δDCH <sub>4</sub>
	(percent)						(percent x 0.01)					
A	34	7	0.08	BD	0.04	62.0	0.01	0.12	0.07	32,632	-69.7	-283
B	18	5	0.08	BD	0.07	82.0	0.90	0.22	0.10	25,625	-64.2	-251
C	35	0.1	0.50	0.12	0.03	61.0	0.28	286.0	116.0	15.2	-53.3	-269
D	27	6	0.04	BD	0.01	76.0	0.02	6.3	1.7	950	-64.6	-289
*** N <sub>2</sub> + O <sub>2</sub>												
E-1	35	68.0	BD	BD	0.02	BD	0.07	BD		286	BD	BD
E-2	79	18.0	BD	BD	13.4	BD	0.01	BD		134,000	-55.2	-389
F	7	6	BD	BD	89.0	BD	0.47	0.19		13,484	-59.8	-269
G-1	ND****	ND	ND	ND	2.05	BD	7.9	4.5		16.6	-17.4	ND
G-2	ND	ND	ND	ND	67.0	BD	0.12	BD		588	-54.9	-394
H	ND	ND	ND	ND	93.2	BD	0.33	0.10		21,827	-64.7	-278
I	ND	ND	ND	ND	88.3	BD	0.10	0.02		67,923	ND	ND

\* Site characteristics: A = 2 m depth; B = 2 m depth; C = hot spring, 0.2 m depth; D = 20 m depth; E-1 = Navy Beach volcanic vent; E-2 = Navy Beach dead grass bubbles, depth = 0.2 m; F = 20 m; G-1 = Deachambeau Ranch hot spring; G-2 = Deachambeau Ranch freshwater pond; H = 8 m depth; I = onshore seep (100 m from shore)  
 \*\* BD = below detection  
 \*\*\* ND = not determined  
 \*\*\*\* column changed to one which did not resolve N<sub>2</sub> from O<sub>2</sub> (see methods)

ratio of 15.2. This was typical of gases collected in this region. Gases from this site were enriched in <sup>13</sup>C (δ<sup>13</sup>CH<sub>4</sub> range = -48.2 to -53.9‰) when compared with the other methane-rich seeps in the lake (range = -59.8 to -69.7). Plots of C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] vs. δ<sup>13</sup>CH<sub>4</sub> (Fig. 7) and δ<sup>13</sup>CH<sub>4</sub> vs. δDCH<sub>4</sub> (Fig. 8) for the gas seeps indicate that most of the seeps were of biogenic origin, while those located in the vicinity of hot springs had

a thermogenic component. Radiocarbon activity in seep methane revealed that the biogenic seeps had <8% of modern activity, while thermogenic seeps also had low values (about 10.5% of modern activity; Table 1). Methane formed from the decomposition of terrestrial grasses in the littoral zone was characterized by very high C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] ratios (Fig. 7), strong depletion in deuterium (Fig. 8), and about 52% of modern <sup>14</sup>C-ac-

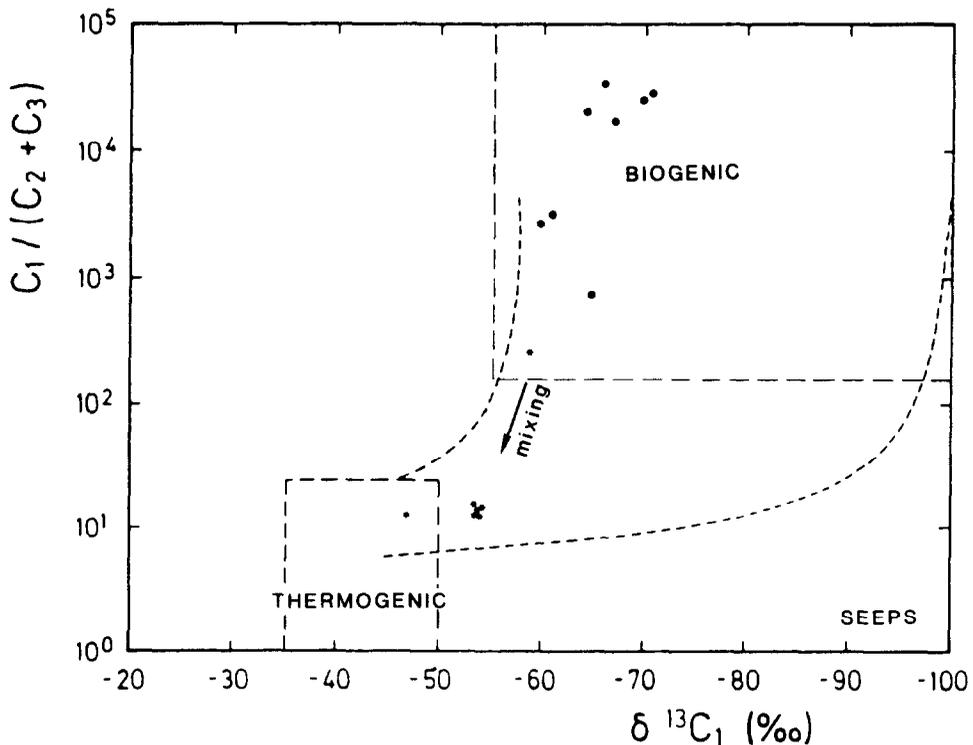


FIG. 7. Ratios of C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] vs. δ<sup>13</sup>CH<sub>4</sub> for gas seeps collected from Mono Lake biogenic seeps (●) and thermal influenced seeps (★).

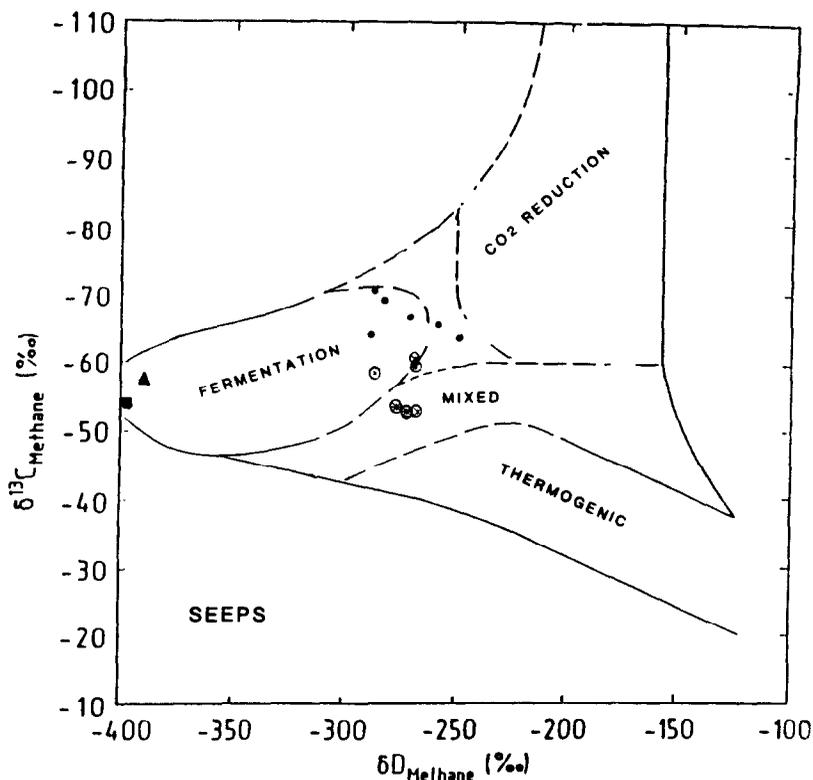


FIG. 8. Ratios of  $\delta^{13}\text{C}_{\text{CH}_4}$  vs.  $\delta\text{D}_{\text{CH}_4}$  for gas seeps collected in Mono Lake biogenic seeps (●), thermal influenced seeps (⊙), littoral zone bubbles (▲) and Deachambeau pond (■).

tivity (Table 1). Similar isotopic values were displayed by the methane taken from the Deachambeau freshwater pond sediments (Fig. 8), although it had a much lower  $\text{C}_1/[\text{C}_2 + \text{C}_3]$  (Table 2).

*Dissolved methane flux to the atmosphere.* Values of measured outward methane flux from Mono Lake surface waters are given in Table 3. Most of the measurements were conducted at the western basin station (Fig. 1), but for comparative purposes, individual

measurements were also made at three other locations. One site was located about 60 m offshore from the southern part of Paoha Island, a region containing hot springs and gas seeps having a major component of higher hydrocarbons (e.g., Table 2, site C).

Methane increases in the flux chambers occurred over the deployment periods and these increases were generally linear for intervals (2–3 hr) having comparable wind speeds (not shown). Similar flux data was

Table 3: Flux of dissolved methane to the atmosphere from Mono Lake surface waters.

DATE	METHANE ( $\mu\text{M}$ )	ETHANE ( $\mu\text{M}$ )	WIND (m/s)	TEMP. * ( $^{\circ}\text{C}$ )	$\text{CH}_4$ FLUX ** ( $\text{mmol}/\text{m}^2/\text{d}$ )	$\text{C}_2\text{H}_6$ FLUX ( $\text{mmol}/\text{m}^2/\text{d}$ )	CHAMBER
Western Basin Station:							
10/8/85	0.52	BD***	5.9	13.9	1.100	BD	DOME
10/8/85	0.52	BD	5.9	13.9	1.140	BD	CYLINDER
5/23/86	0.23	BD	0.5	13.8	0.069	BD	DOME
8/3/86	0.09	BD	0.5	22.6	0.069	BD	DOME
8/3/86	0.09	BD	2.2	22.6	0.131	BD	DOME
8/13/86	0.09	BD	0.5	22.6	0.113	BD	DOME
11/4/86	0.30	BD	0.5	9.7	0.144	BD	DOME
1/19/87	1.29	BD	8.9	1.5	0.500	BD	DOME
Paoha Island (800 m east):							
5/26/86	0.18	BD	6.7	13.8	0.319	BD	DOME
Hot Spring Cove (60 m south of Paoha Island shore):							
10/13/85	17.9	0.7	0.8	21.0	0.388	0.010	DOME
Buoy located about 3 km south of Paoha Island:							
10/13/85	3.0	BD	1.5	13.9	0.131	BD	CYLINDER

\* surface water temperature

\*\* error was less than 20 % for each determination

\*\*\*

BD = below detection

obtained for both the dome and cylindrical-shaped chambers (Table 3, 10/8/85 data set). In general, methane flux increased with wind speed, surface methane concentrations, and temperature. Flux measurements ranged from 0.07 to 1.14 mmol CH<sub>4</sub> m<sup>-2</sup> d<sup>-1</sup> (mean = 0.36) for the entire data set. Highest fluxes (1.10–1.14 mmol m<sup>-2</sup> d<sup>-1</sup>) were obtained on 10/8/85 when both wind speed (5.9 m sec<sup>-1</sup>) and dissolved methane (0.52 μM) were high, and surface water temperature had intermediate values (13.9°C). During 1/19/87, when wind-speeds (8.9 m sec<sup>-1</sup>) and surface methane levels (1.29 μM) were the highest recorded, but temperature was the lowest (1.5°C), the flux estimate was 0.5 mmol m<sup>-2</sup> d<sup>-1</sup>. Calculated piston velocities (gas transfer coefficients) from our flux measurements averaged 0.90 ± 0.57 m day<sup>-1</sup> at a mean wind speed of 2.8 m sec<sup>-1</sup> (MILLER and OREMLAND, in prep.). By comparison, WANNINKHOF (1986) obtained an average piston velocity of 0.77 ± 0.53 m day<sup>-1</sup> at a mean wind speed of 3.1 m sec<sup>-1</sup> using SF<sub>6</sub> as a tracer in Mono Lake. These comparable piston velocities for two different gases indicate the validity of our methane data.

Determination of flux chamber δ<sup>13</sup>CH<sub>4</sub> on 3 and 13 August 1986 yielded values of -60.9 and -54.9‰, respectively, when sampled after a 2 h exchange interval. The δ<sup>13</sup>CH<sub>4</sub> of dissolved methane at 1 m depth during this period was -52.9‰ (Fig. 3). No outward flux of ethane was observed from any of the sites, with the exception of Hot Spring Cove (see below).

An unusual situation was encountered at Hot Spring Cove on the southern shore of Paoha Island. When compared with other locations, the surface water in this region had elevated methane (17.9 μM), ethane (0.7 μM), and temperature (21°C). Water from a depth of 0.5 m at this site was cooler (14°C), had much less methane (1.5 μM) and no detectable ethane. Apparently, a narrow plume of hot, methane-rich spring water (salinity = 21‰; temp. = ~70°C) extended southwards from Paoha Island. Because of its lower density, this water dispersed out over the local Mono Lake water. This resulted in higher outward flux of methane and ethane (Table 3) when compared to other sites under similar wind conditions. However, this situation was not representative of the majority of Mono Lake's surface.

#### DISCUSSION

The application of commonly used geochemical hydrocarbon indices (e.g., δ<sup>13</sup>CH<sub>4</sub>, δDCH<sub>4</sub>, C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>]), measures of methane radiocarbon activity, and a consideration of bacterial activities and niches have enabled us to identify four different sources of natural gas within Mono Lake. In some cases it was necessary to employ all these factors to be able to distinguish between gases which were otherwise similar in molecular and isotopic character, or represented mixtures of two primary sources. We will now discuss the characteristics of these different gases, their mechanisms of formation and estimate their contribution to lakewide flux of methane to the atmosphere.

*Dissolved gases in the pelagic sediments.* Methane, ethane and propane had similar depth profiles in the pelagic sediments (Fig. 4). Values of δ<sup>13</sup>CH<sub>4</sub>, δDCH<sub>4</sub>, and C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] determined in these sediments (Figs. 5 and 6) clearly lie within the "envelope" assigned to natural gases produced by bacterial processes (BERNARD *et al.*, 1978; SCHOELL, 1980, 1983; WHITICAR *et al.*, 1986). In addition, methanogenic activity was previously detected in these sediments (KIENE *et al.*, 1986). Similarly, we observed the formation of traces of ethane (and methane) over the course of sediment slurry incubations. Because autoclaving blocked both methane and ethane formation, a biological source was indicated for both gases. Final C<sub>1</sub>/C<sub>2</sub> ratios in the un-amended slurries (2,179) were comparable to ratios in the pelagic sediments (600–750; Fig. 4), indicating that bacterial production of traces of ethane in slurries was consistent with the observed field data. Sediments of the Orca Basin and Big Soda Lake, both of which are anoxic and hypersaline, have similar δ<sup>13</sup>CH<sub>4</sub> and C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] ratios to those of Mono Lake (SACKETT *et al.*, 1979; OREMLAND and DES MARAIS, 1983; WIESENBERG *et al.*, 1985). Bacterial processes were thought to be responsible for C<sub>1</sub> – C<sub>3</sub> alkane formation in those environments. Bacterial formation of C<sub>1</sub> – C<sub>4</sub> alkanes has been reported previously in sediments (VOGEL *et al.*, 1982), and in the case of ethane, methanogenic bacteria were the causative agents (OREMLAND, 1981). We have recently determined that ethylated reduced sulfur compounds are the likely precursors which methanogens metabolize to ethane in sediments (R. OREMLAND, M. WHITICAR, F. STROHMAIER and R. KIENE, in prep.). Therefore, based on the similarity of profiles, stable isotopic compositions of methane, C<sub>1</sub>/[C<sub>2</sub> + C<sub>3</sub>] and slurry incubations, we conclude that all three gases in Mono Lake sediments were derived from bacterial activities.

What is not clear is the particular bacterial substrate(s) from which methane in the sediments was derived. WHITICAR *et al.*, (1986) devised a scheme which employed δDCH<sub>4</sub> and δ<sup>13</sup>CH<sub>4</sub> values to distinguish between methane formed *via* CO<sub>2</sub> reduction from that formed *via* "fermentation" (derived from methyl groups). However, based on the stable isotope data in Fig. 6, the methane in Mono Lake sediments does not fall into either category. This could be the result of a mixture of both types of substrate sources. Thus, the answer cannot be obtained from the stable isotopes alone, but at a minimum requires measurements of the turnover of methanogenic substrates.

Interpretation is further complicated by the presence of considerable quantities of sulfate (about 35 mM) at the bottom of the core (Fig. 3). Although methanogenesis can take place concurrently with sulfate-reduction by metabolism of "non-competitive" substrates like methylated amines (OREMLAND *et al.*, 1982; OREMLAND and POLCIN, 1982), conventional wisdom rules out a significant contribution of either acetate or CO<sub>2</sub> reduction until nearly all the sulfate is depleted (e.g., ~0.1 mM) (CLAYPOOL and KAPLAN, 1974;

MARTENS and BERNER, 1974; OREMLAND and POLCIN, 1982; KING, 1984; LOVLEY and KLUG, 1983). This implies that non-competitive substrates were the major precursors of methane in the Mono Lake sediments. However, a clear "fermentative" signal could not be interpreted from the stable isotope data (Fig. 6).

We have made preliminary measurements of Mono Lake sediment  $^{35}\text{S}$ -sulfate-reduction and production of  $^{14}\text{CH}_4$  from  $^{14}\text{C}$ -labeled substrates. Initial results indicate that sulfate-reduction rates ( $220 \mu\text{moles l}^{-1} \text{d}^{-1}$ ) greatly exceed methanogenesis ( $3 \mu\text{moles l}^{-1} \text{d}^{-1}$ ) in the upper 5 cm of the core, but below that depth methanogenesis ( $2\text{--}8 \mu\text{moles l}^{-1} \text{d}^{-1}$ ) and sulfate-reduction ( $\leq 6 \mu\text{moles l}^{-1} \text{d}^{-1}$ ) were equivalent. Most of the methane is derived from  $\text{CO}_2$  reduction; however, trimethylamine may account for as much as 25% of the methane formed in the upper 3 cm. (R. OREMLAND, G. KING, R. SMITH and R. KIENE, unpubl. data). These preliminary results support the stable isotope data in that they imply a mixed substrate origin for methane.

*Dissolved gases in the water column.* Diffusive flux of methane out of the sediments and into the anoxic bottom waters can be estimated by employing the equation:

$$J\text{CH}_4 = -\phi D_s dC/dx$$

where  $J$  = flux,  $D_s$  = sediment diffusion coefficient of methane,  $\phi$  = porosity (0.9),  $C$  = methane concentration and  $x$  = vertical distance. We estimate a  $D_s$  value of  $0.94 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$  by correcting the molecular diffusion coefficient (ISENOGLE, 1985) for the dynamic viscosity of Mono Lake water at  $5^\circ\text{C}$  (1.8 centipoise; MASON, 1967) and correcting for tortuosity ( $\theta^2 = 1.37$ ) using the relationship between porosity and tortuosity suggested by ULLMAN and ALLER (1982) for fine-grained sediments of high porosity. Then for a bottom water concentration of  $50 \mu\text{M}$  and an interstitial concentration of  $500 \mu\text{M}$  at 2.5 cm (Fig. 3a):

$$\begin{aligned} J\text{CH}_4 &= -(0.9)(0.94 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}) \\ &\quad \times (0.45 \mu\text{mol cm}^{-3}/2.5 \text{ cm}) \\ &= -1.52 \times 10^{-6} \mu\text{mol cm}^{-2} \text{ s}^{-1} \\ &= -1.32 \text{ mmoles m}^{-2} \text{ d}^{-1}. \end{aligned}$$

This represents a crude estimate for comparative purposes, since we did not employ close-interval methane gradients in the upper sediment in the calculation. Had we done this we probably would have found a stronger gradient near the top of the core, which would have correspondingly increased estimates of outward flux. Nonetheless, the outward diffusion of dissolved methane from the sediments into the anoxic water column was confirmed by the  $\Delta^{14}\text{CH}_4$  data. Bottom waters have a radiocarbon activity of  $\sim 80\%$  of present, which is less than that for the dissolved inorganic carbon (DIC) presently in the lake but close to the pre-nuclear DIC value (Table 1; PENG and BROECKER, 1980). Since the  $^{14}\text{C}$  activity of the seep-associated methane was much

lower than that of the dissolved methane, these sources do not contribute significantly to dissolved methane in the water column.

The  $\delta^{13}\text{CH}_4$  in the bottom waters was on average about 12‰ heavier than in the sediments (Figs. 5 and 6). Bacterial oxidation of methane occurs in anoxic environments (PANGANIBAN *et al.*, 1979; REEBURGH, 1980; IVERSEN and BLACKBURN, 1981; DEVOL, 1983) including the waters of Big Soda Lake, an environment similar to Mono Lake (IVERSEN *et al.*, 1987). It has been suggested that this process was responsible for the enrichment in  $^{13}\text{C}$  in the methane found near the surface of marine sediments (WHITICAR and WERNER, 1981) and in the anoxic waters of Big Soda Lake (OREMLAND and DES MARAIS, 1983). It also appears to have been responsible for the  $^{13}\text{C}$ -enrichment of methane in the anoxic water column of Mono Lake.

A further enrichment in  $^{13}\text{C}$  (range 3.6 to 52.3‰) was noted in all of the methane samples extracted from the surface waters of Mono Lake when compared with the mean  $\delta^{13}\text{CH}_4$  ( $-74.1\%$ ) of the bottom waters (Fig. 3). Methane as heavy as  $-21.8\%$  occurred near the surface (Figs. 2 and 3). Values of  $\delta^{13}\text{CH}_4$  for the seep gases were generally more depleted in  $^{13}\text{C}$  than the dissolved methane in the surface waters (Figs. 7 and 8) which indicates that a contribution from this source to the surface water was unlikely. The  $^{13}\text{C}$ -enrichment of water column  $\delta^{13}\text{CH}_4$  always occurred just above the oxycline and was associated with a pronounced decrease in dissolved methane (Fig. 3). Aerobic bacterial methane oxidation commonly occurs in stratified lakes (RUDD *et al.*, 1974) and rates are highest within methane gradients occurring in oxyclines (HARRITS and HANSON, 1980). It has been well-established that aerobic methane-oxidizing bacteria are capable of a sizeable stable isotope fractionation, thereby leaving residual unoxidized methane enriched in  $^{13}\text{C}$  (SILVERMAN and OYAMA, 1968; COLEMAN *et al.*, 1981; BARKER and FRITZ, 1981; WHITICAR and FABER, 1986). Therefore, aerobic bacterial methane oxidation occurring within the oxic/anoxic transition of Mono Lake's water column appears to be responsible for the  $^{13}\text{C}$  enrichment of methane in the surface waters.

Preliminary *in situ* experiments with  $^{14}\text{CH}_4$  indicate that aerobic bacterial methane oxidation occurs near the oxycline and that anaerobic oxidation takes place in the bottom waters (N. IVERSEN, unpubl. data). Thus, the combined effects of aerobic and anaerobic methane oxidation had a net maximal  $^{13}\text{C}$ -enrichment of about 64‰ when comparing the most  $^{13}\text{C}$ -enriched surface  $\delta^{13}\text{CH}_4$  value ( $-21.8\%$ ) with the most depleted sediment value ( $-85.7\%$ ). The fact that surface water  $\delta^{13}\text{CH}_4$  values were highly seasonally variable (Fig. 3) suggests that winter mixing redistributes methane trapped below the thermocline into the epilimnion. The higher concentrations of dissolved methane in the surface waters observed during winter support this explanation (Table 3).

Methane concentrations in the surface waters ranged between  $0.09\text{--}1.29 \mu\text{M}$  seasonally. These values were

about 50 to 800-fold supersaturated with respect to the partial pressure of methane in the atmosphere (LAMONTAGNE *et al.*, 1973). Therefore, an outward flux of dissolved methane from the lake's surface could be quantified (see below). Because of bacterial oxidation, methane leaving the lake was enriched in  $^{13}\text{C}$ . The values of  $\delta^{13}\text{CH}_4$  we measured in our flux chambers during August, 1986 ( $-60.9$  and  $-54.9\%$ ) reflected surface water  $\delta^{13}\text{CH}_4$  ( $-52.9\%$ ), which approached the biogenic/thermogenic transition value of  $-50\%$ . Presumably then, methane of  $\delta^{13}\text{CH}_4$  values as heavy as  $-22\%$  (Figs. 2 and 3) may also exit the lake at times. This value (when taken on its own) would falsely indicate a thermogenic origin for the gas.

*Natural gas seeps.* Methane was the major constituent of all the gas seeps occurring within the lake's present boundary (Table 2). The Navy Beach volcanic vent (sample E-1) was the only sample in which methane was present at trace levels. By contrast, carbon dioxide was the major constituent of this gas, which agrees with previous determinations (BARNES *et al.*, 1981). Carbon dioxide was also a significant component (18%) in the neighboring sample taken from tufa-entrapped decomposing grasses (E-2). However, carbon dioxide was present only in trace quantities in samples recovered within the lake (A, B, C and D). It appears, therefore, that the samples from Navy Beach (E-1 and 2) arise from a different source than do the methane-rich gases from sites A, B, C, D, F, H and I. It is also evident that the same can be said for the methane in the Deachambeau hot spring sample (G-1:  $\delta^{13}\text{CH}_4 = -17.4\%$ ) as well as the freshwater pond gases from that site (Fig. 8).

However, whereas the pelagic sediment gases were a consequence of anaerobic bacterial decomposition processes operating currently in the lake, these seep

gases derive from a much older accumulation of bacterially formed natural gas. The evidence for this conclusion consists of several facts. First, dissolved methane formed currently in the pelagic sediments diffuses out into the bottom water without bubble ebullition, while the seeps have extremely high continuous-flow bubble ebullition rates. Although bubble ebullition of methane from bacterial activity typically occurs in freshwater lakes, it is characterized by discontinuous flow rates which are about 2-4 orders of magnitude lower than what we observed emanating from the seeps (BAKER-BLOCKER *et al.*, 1977; Table 4). Second, the seeps are located in a diverse array of bottom topographies including rocky shallow regions (sites A and B), as well as onshore (site I), whereas current methanogenesis takes place in the soft, reducing pelagic sediments (*e.g.*, KIENE *et al.*, 1986). Third, the radiocarbon activity of the methane dissolved in the bottom water (which originated from the bottom sediments) was the same as that for DIC in the lakewater, whereas the seep gas had activity levels that were virtually indistinguishable from "dead" carbon (Table 1). Because the "biogenic" natural gas seeps were widely distributed over the lake (Fig. 1, sites A, B, D, F, H, I) we suggest that they emanate *via* faults and fractures from a larger deposit which underlies the lakebed. We estimate that the radiocarbon age of this gas is  $>22,000$  years b.p., which would indicate that the source material is of Pleistocene age.

Gases taken in the vicinity of the Paoha Island hot springs had significant quantities of ethane and propane (*e.g.* about 4% of sample C) as well as  $\delta^{13}\text{CH}_4$  values which were significantly enriched in  $^{13}\text{C}$  relative to those from the biogenic seeps (Table 2, Fig. 7). These samples appear to be mixtures of thermogenic gas with the biogenic gases (Figs. 7 and 8). By contrast, all the

Table 4: Flux of methane from Mono Lake in comparison with other environments.

SITE	DAILY FLUX (mmoles $\text{m}^{-2}$ )	ANNUAL SITE FLUX (moles)
-----		
Mono Lake:	**	
pelagic sediment (diffusive)	1.32	-
surface degassing	0.07 - 1.14	$2.77 \times 10^7$
seeps	$(2.52 - 305) \times 10^3$	$2.1 \times 10^6$
Cape Lookout Sediments (Martens and Klump, 1980):		
seasonal average bubble	11.8	-
seasonal average diffusive	2.3	-
Total Cape Lookout Flux	-	$4.3 \times 10^6$
Orca Brine (Wiesenburg <i>et al.</i> , 1985):		
diffusive to water column	0.01	$1.8 \times 10^6$
Big Soda Lake (Iversen <i>et al.</i> , 1987):		
surface diffusive	0.04	$2.1 \times 10^3$
Swamps and Ponds (Baker-Blocker <i>et al.</i> , 1977):		
bubbles	$5.8 \frac{\text{m}^3}{52}$	$(3.4 - 17) \times 10^4$
-----		

\* value for Big Soda Lake represents one determination during calm period

\*\* probably underestimated by a factor of 2 - 3 (see discussion)

other sites had only minor quantities of ethane and propane (Table 2). The  $^{14}\text{C}$ -activity of the methane recovered from site C was slightly higher (10.5% of modern) than that of the biogenic seeps (Table 1). This indicates that the thermogenic component of the hydrocarbons in the Paoha hot spring seeps were derived from near surface hydrothermal conversion of more recently deposited organic matter. Hydrothermal hydrocarbon generation associated with recent volcanism has also been reported in marine environments (WHITICAR *et al.*, 1985; SIMONEIT *et al.*, 1986).

Ratios of  $\text{C}_1/[\text{C}_2 + \text{C}_3]$  in Paoha Island hot spring (C) and the Deachambeau Ranch hot spring (G-1) were nearly equivalent (15.2 and 16.6, respectively). This ratio was  $\geq 950$  in all of the other methane-rich, biogenic seeps. It is possible that the Deachambeau Hot spring gases were related to the Paoha Island hot springs; however, the extremely  $^{13}\text{C}$ -enriched value of  $\delta^{13}\text{CH}_4$  for the Deachambeau Ranch ( $-17.4\%$ ) indicates that this relationship is unlikely. A small quantity of helium (0.12%) was detected only in the hot spring sample from the Paoha Island shoreline (C). The  $^3\text{He}/^4\text{He}$  ratio of this sample was 2.7 which indicates a contribution of gas from the mantle (CRAIG *et al.*, 1978). This result is consistent with  $^3\text{He}/^4\text{He}$  measurements taken from springs on the south shore of the lake (HILTON *et al.*, 1986).

The methane contained in the gases taken in the littoral region of Navy Beach (sample E-2; Table 2) represent a minor, but interesting biogenic source. These gases were located in close proximity (a few cm distant in some cases) to the carbon dioxide seeps which contained only a trace of methane (sample E-1). The origin of the methane in sample E-1 was from the anaerobic decomposition of terrestrial grasses, the rotting rhizomes of which were evident under the tufa "pavement" where the bubbles were entrapped. This setting was the result of the recent rise in lake level inundating grassy regions on the former lake margin, followed by the deposition of a tufa crust over these regions from springs along the shoreline. The methane in these gases was clearly of biogenic origin, but was isotopically distinct from other gases, due primarily to its  $\delta\text{DCH}_4$  value of  $-389\%$  (Fig. 8). A similar isotopic composition was noted for the freshwater pond gases on the Deachambeau Ranch. Therefore, these terrestrial/littoral and freshwater-derived methanes can be distinguished from the lacustrine sources in Mono Lake, whether they are "ancient" seeps or current pelagic sources. The radiocarbon activity in this littoral zone methane was considerably less ( $\sim 55\%$  of modern) than what we would have expected for the decomposition of terrestrial grass. However, because the carbon dioxide in the proximate volcanic seeps was "dead" (Table 1), this gas probably diluted the radiocarbon signal ultimately measured in the methane. This could only be achieved by biological fixation of some of the volcanic  $\text{CO}_2$  into organic matter, followed by its decomposition to methane. The fixation of volcanic  $\text{CO}_2$  into biological material was reported in hot spring biota (ROUNICK

and JAMES, 1984). The isotopic composition of the littoral zone and pond methanes indicates fermentation (methyl group origin) rather than  $\text{CO}_2$  reduction (Fig. 8) as the mechanism for methane formation (WHITICAR *et al.*, 1986); however, microbiological studies would be required to confirm this.

*Methane flux to the atmosphere.* The outward flux of methane from Mono Lake consists of seep bubbles and loss from dissolved methane in the surface waters. Individual seeps had flow rates ranging from 0.05 to 4.0 liters  $\text{CH}_4 \text{ min}^{-1}$ . To convert these observations into areal fluxes (liters  $\text{CH}_4 \text{ m}^{-2} \text{ min}^{-1}$ ), we calculated a lower limit by assuming that 1 "low flow" seep (0.05 liters  $\text{min}^{-1}$ ) occupies 1  $\text{m}^2$ . Similarly, we arrived at an upper limit by assuming that 1.5 "high flow" (4 liters  $\text{min}^{-1}$ ) seeps occupy 1  $\text{m}^2$ . When these values are corrected for pressure at this altitude (600 mm Hg) and converted to moles, we arrive at a range of 2.52–305 moles  $\text{CH}_4 \text{ m}^{-2} \text{ day}^{-1}$  (Table 4). We counted a total of 588 seeps, but unobserved seeps could increase this by a factor of 2. It is necessary that we make some assumptions concerning the average flow rates. A conservative estimate is a flow rate of 0.05 liters  $\text{min}^{-1}$  for 600 seeps. We also counted 12 seeps which had flow rates  $> 2$  liters  $\text{min}^{-1}$ . We estimate that there may be as many as 20 seeps with methane flows of 4 liters  $\text{min}^{-1}$ . These assumptions yield an annual lakewide methane seep flux of  $2.1 \times 10^6$  moles (Table 4). If we underestimated the number of "low-flow" seeps by a factor of 2, then this would increase to  $2.7 \times 10^6$  moles. If we also underestimated their flow rates by a factor of 2, this would increase to  $3.3 \times 10^6$  moles.

Surface water flux varied between 0.07 to 1.14 mmoles  $\text{m}^{-2} \text{ day}^{-1}$ , with an average value of 0.38 mmoles  $\text{m}^{-2} \text{ day}^{-1}$  (Tables 3 and 4). These values exceed the windless surface flux from Big Soda Lake as well as the flux to the upper water column from the Orca Brine (Table 4). Bubble-associated fluxes from Cape Lookout Bight or from temperate swamps and eutrophic ponds were considerably higher than the surface water degassing of Mono Lake. The surface area of Mono Lake is about 200  $\text{km}^2$  (MASON, 1967). Therefore, lakewide average annual surface water degassing flux is about  $2.77 \times 10^7$  moles  $\text{CH}_4$ . Our preliminary estimate of total flux of methane to the atmosphere from Mono Lake is  $2.98 \times 10^7$  moles  $\text{year}^{-1}$ , of which 93% is due to surface water flux and only 7% due to seep flux.

We estimate a diffusive flux of methane from the pelagic sediments to the anoxic water column to be 1.32 mmoles  $\text{m}^{-2} \text{ d}^{-1}$ , which is about half the average sediment diffusive flux for Cape Lookout Bight (Table 4). Our sediment flux is close to the upper limit of the range of the Mono Lake outward surface water flux (1.14  $\text{mmol m}^{-2} \text{ d}^{-1}$ ). This result appears to be inconsistent in that it would require essentially no loss from oxidation or storage. However, surface flux varies as a function of temperature, wind speed, and ambient methane concentration (Table 3), and is thus related to the mixing and degassing of the entire water column

above the thermocline. Thus, because of episodes of greater mixing, the surface loss can approach the rate of supply from the sediments. This is counterbalanced by periods of low exchange, when surface flux is ~20-fold lower than supply from the sediments (Table 3). Furthermore, it appears that we have underestimated the sediment flux, which indicates that outward flux to the atmosphere was always less than supply from the sediments (see below).

Assuming that the core we retrieved was characteristic of all of the sediments in Mono Lake, then annual sediment flux for the lake should be about  $9.6 \times 10^7$  moles  $\text{CH}_4$ . The average value of surface water degassing ( $2.65 \times 10^7$  moles  $\text{yr}^{-1}$ ) therefore represents a loss to the atmosphere of 28% of the methane entering the water column. This value appears to be too high in light of the lake's stratification and methane-oxidation. For example, RUDD and HAMILTON (1978) found that during periods of thermal stratification, only 6% of the methane entering the water column of a eutrophic lake was lost to the atmosphere, 12% was oxidized at the oxic/anoxic transition, while the remainder was stored in the hypolimnion. We have observed an increase in methane in the bottom waters of Mono Lake of  $22 \mu\text{moles liter}^{-1}$  in the 15 months from October, 1985 to January, 1987, which would correspond to an increase of  $176 \text{ mmoles CH}_4 \text{ m}^{-2}$  under the bottom 8 m. Sediment flux over this period would have been about  $594 \text{ mmoles m}^{-2}$ , and loss to the atmosphere about  $164 \text{ mmol m}^{-2}$ . If we assume that:

$J\text{CH}_4$  (sediment)

$$= \text{CH}_4 \text{ (stored)} + \text{CH}_4 \text{ (oxidized)} + J\text{CH}_4 \text{ (atmos)}.$$

Then  $\text{CH}_4$  (oxidized) =  $254 \text{ mmoles } 15 \text{ months}^{-1}$ , which would be equivalent to an average rate of  $47 \text{ nmoles liter}^{-1} \text{ day}^{-1}$  for the water column below 12 m. These values are somewhat less than the rates of anaerobic oxidation ( $49\text{--}85 \text{ nmoles liter}^{-1} \text{ day}^{-1}$ ) measured in Big Soda Lake (IVERSEN *et al.*, 1987) and below the range of our preliminary *in situ* estimates for Mono Lake ( $0.2\text{--}1.2 \mu\text{moles liter}^{-1} \text{ day}^{-1}$ ; N. IVERSEN, unpubl. data). Therefore, it appears that we have underestimated the sediment diffusive flux by a factor of at least 2 to 3.

## CONCLUSIONS

1. Four sources of methane were identified in Mono Lake. Stable carbon and hydrogen isotopes, radiocarbon activity, methane abundance relative to ethane and propane as well as assessments of microbial activities were required to identify these sources. Because some of these sources were nearly identical in two or three of these parameters, all of the above considerations were required to identify all sources properly. Therefore, the two most commonly used parameters ( $\delta^{13}\text{CH}_4$ ;  $C_1/[C_2 + C_3]$ ) for source identification are inadequate by themselves in complex situations such as that in Mono Lake.

2. Outward flux of methane to the atmosphere was dominated by loss of dissolved methane from the supersaturated surface waters. The source of this methane was from recent methanogenic activity in the pelagic sediments. Loss from "ancient" natural gas seeps (biogenic and thermogenic) was only about 7% of total loss, even though individual seep flows exceed areal flux estimates from various aquatic ecosystems by several orders of magnitude.

3. The biogenic methane lost to the atmosphere from the lake was enriched in  $^{13}\text{C}$  relative to its original isotopic composition because of the effects of bacterial methane oxidation occurring in the stratified water column.

4. Methane achieves saturation levels in pelagic sediments in the presence of substantial quantities of sulfate, indicating that the processes of sulfate-reduction and methanogenesis operate concurrently in this environment.

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