

Dissolved hydrocarbon flux from natural marine seeps to the southern California Bight

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Abstract. Natural marine seepage near Coal Oil Point, Santa Barbara Channel, California, injects large quantities of hydrocarbons into the coastal ocean. The dispersal and source strength of the injected methane, ethane, and propane from this seep field was determined using a variety of oceanographic and geochemical techniques. The results show that hydrocarbons seep into stratified coastal waters creating plumes that extend for at least 12 km. The plume structure is complex because of the large geographical distribution of seep vents and because of the chaotic nature of advection and mixing near the seeps. At the time of the survey, hydrocarbons were injected onto density surfaces between $\sigma_\theta = 24.5\text{--}26.0 \text{ kg m}^{-3}$. Earlier work has shown that subsurface methane maxima in the upper waters of the southern California Bight are typically found on these density surfaces. We estimate that the total flux of methane into the water column above the Coal Oil Point seeps is $2 \times 10^{10} \text{ g yr}^{-1}$ and is approximately equal to the total flux of dissolved methane to the atmosphere estimated for the entire southern California Bight. These observations strongly support the inference of others that coastal sources, which include some of the world's largest marine hydrocarbon seeps, maintain the methane maximum observed offshore California. Estimates of the global methane flux from coastal waters derived by extrapolating the flux from coastal California may be too large because of the anomalous amount of marine hydrocarbon seepage in these waters.

1. Introduction

Dissolved methane concentrations in the upper ocean tend to be greater than atmospheric equilibrium values [Lamontagne *et al.*, 1973; Scranton and Farrington, 1977; Brooks *et al.*, 1981; Burke *et al.*, 1983; Cynar and Yayanos, 1992, 1993; Ward and Kilpatrick, 1993; Bates *et al.*, 1996]. As a result, the ocean is a source of this important greenhouse gas to the atmosphere. The oceanic flux is relatively small compared with other atmospheric methane sources such as wetlands, rice production, and domestic animals, although it is comparable to a few sources such as wild fires and landfills [Khalil and Rasmussen, 1995]. Recent estimates suggest that the total flux from coastal waters, 4×10^{12} to $18 \times 10^{12} \text{ g yr}^{-1}$, is more than an order of magnitude greater than that of the open ocean, $0.4 \times 10^{12} \text{ g yr}^{-1}$ [Cynar and Yayanos, 1993; Kvenvolden *et al.*, 1993; Ronge *et al.*, 1994; Bates *et al.*, 1996]. Hence an understanding of methane dynamics in coastal waters is essential for refining estimates of the oceanic methane flux to the atmosphere.

Sources of methane to seawater include in situ biological processes, anoxic (organic-rich) sediments, natural seepage above hydrocarbon reservoirs, and river discharge [Brooks *et al.*, 1981; Burke *et al.*, 1983; Cynar and Yayanos, 1991, 1992; Scranton and McShane, 1991; Ward, 1992; de Angelis and

Lee, 1994]. The latter three sources have been identified mostly in coastal zones and probably contribute to the larger atmospheric flux found in these waters than in the open ocean. Natural hydrocarbon seepage can be distinguished from the other methane sources because higher hydrocarbon chains such as ethane and propane are also emitted along with methane.

Although natural marine hydrocarbon seeps are found along many continental margins, their spatial distribution and size vary considerably [Wilson *et al.*, 1974]. Thus the importance of seepage from hydrocarbon reservoirs to the distribution of methane in coastal waters should not be uniform and in many settings it is probably not important. An area where natural hydrocarbon seepage may be a strong source of methane is coastal California. The southern California coast is one of the most prolific areas of natural marine seepage in the world [Wilson *et al.*, 1974; Kvenvolden and Harbaugh, 1983]. The largest documented marine seep field, the Coal Oil Point field (Figure 1), is found along the northern margin of the Santa Barbara Channel in these waters [Hovland *et al.*, 1993].

The Coal Oil Point seep field emits both liquid and gaseous hydrocarbons from more than 250 seafloor vents and accounts for about half of the natural seepage along the northern margin of the Santa Barbara Channel [Fischer, 1978]. The seep gas is composed mostly of methane, ethane, and propane along with traces of heavier hydrocarbons such as pentane and benzene (Table 1). Liquid hydrocarbon emissions from this field have been shown to pollute the coastal environment for hundreds of kilometers [Hartman and Hammond, 1981]. The fate of the dissolved hydrocarbons resulting from the gaseous emissions into the marine environment has not been examined previously. Yet it is likely these large coastal marine seeps significantly influence regional methane concentrations in the upper waters of the southern California Bight [e.g., Cynar and Yayanos, 1992; Ward, 1992]. Thus the distribution of methane in these regional waters may be anomalous and may not be representative of other coastal regions.

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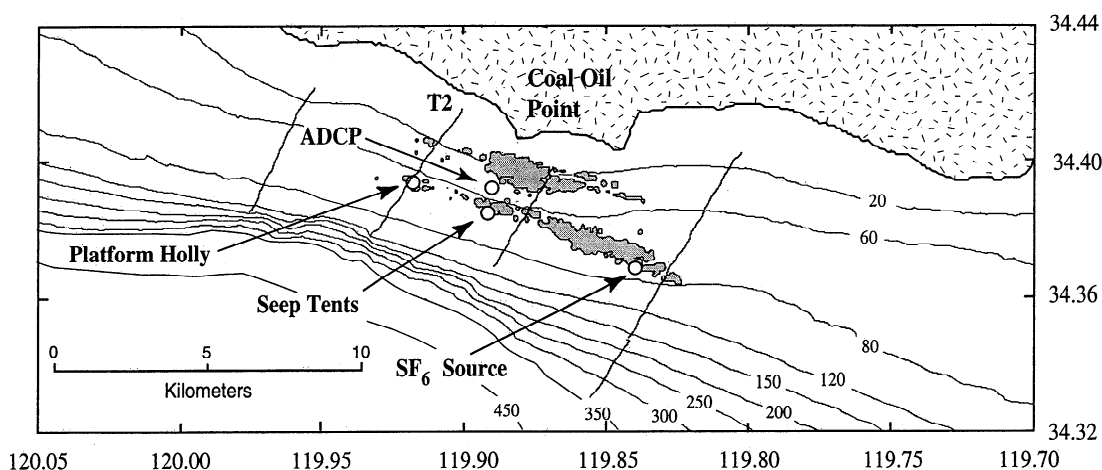


Figure 1: Map of the study site off the coast of Santa Barbara County, California. The shaded areas show the location of the Coal Oil Point gas seeps determined by *Quigley* [1997] using differential GPS and 3.5 kHz sonar in August 1996. Bathymetric contour lines (light), the towyo survey lines (dark), ADCP, SF_6 source, and hydrocarbon production facilities (Platform Holly and the Seep Tents) have been placed on the map. "T2" indicates the location of the towyo section depicted in Figure 4.

The primary objectives of this work are to characterize the oceanic source of methane, ethane, and propane from natural hydrocarbon seeps found near Coal Oil Point, and to link the near-field to regional distributions of methane in the southern California Bight. Specifically, our goals were to map the hydrocarbon plumes down current of the seeps, characterize their near-field distributions, and quantify the total flux of methane into the water column above this seep field.

Our approach was to conduct an intensive study of the dissolved methane, ethane, and propane plumes associated with the Coal Oil Point seep field. The study combined oceanographic (temperature, salinity, and local current velocities) and dissolved hydrocarbon measurements with a gas tracer release experiment. The purpose of this latter experiment was to provide additional information about the transport of dissolved gases in this dynamic coastal setting which could not be in-

ferred from the limited number of measurements of the plumes and local oceanographic conditions. Because of its success in a number of other settings [e.g., *Ledwell et al.*, 1986, 1993; *Clark et al.*, 1996; *Wanninkhof et al.*, 1997] sulfur hexafluoride (SF_6) was chosen as the gas tracer. We also hoped to use the cross-current spread of the tracer gas to estimate horizontal eddy diffusivity coefficients. However, the cross-current transport of the tracer could not be interpreted in terms of a simple diffusion model.

2. Coal Oil Point Seep Field

Surveys in California coastal waters and the southern California Bight have shown that methane is supersaturated with respect to atmospheric equilibrium values in these waters [*Cynar and Yayanos*, 1992, 1993; *Ward*, 1992; *Ward and Kilpatrick*, 1993]. A subsurface maximum extending hundreds of kilometers off the coast occurs in a narrow density band ($\sigma_\theta = 24.5\text{--}26.0 \text{ kg m}^{-3}$) at the top of the pycnocline [*Cynar and Yayanos*, 1992]. Lateral transport from coastal sources that include natural marine hydrocarbon seeps and anoxic sediments is believed to maintain the subsurface maximum [*Cynar and Yayanos*, 1992; *Ward*, 1992]. The highest methane concentrations ($>1000 \text{ nmol L}^{-1}$) in California coastal waters were found at stations in the Santa Barbara Channel [*Cynar and Yayanos*, 1992].

The most concentrated area of natural marine hydrocarbon seeps along the California coast is found near Coal Oil Point in the Santa Barbara Channel. More than half of these seeps lie above the South Elwood anticline about 3 km offshore at depths of 60 to 80 m (Figure 1). Trapped below this anticline is a significant hydrocarbon reservoir, which has been under production since the late 1960s from Platform Holly. Additional production of natural gas began in 1982 from two large gas capture devices, the "Seep Tents", which lie on the seafloor directly above an area of very intense seepage [*Rintoul*, 1982]. The Seep Tents, two concrete and steel pyramids (100 feet x 100 feet at the base), collect the natural emissions and transmit them to shore via a pipeline. The seepage rate below

Table 1. Mean Composition and Standard Deviations of 168 Seep Gas Samples Collected Between 1982 and 1996 at the Seep Tents

Gas	Mol Fraction, %	Plus or Minus
Methane	87.5	0.9
Ethane	5.1	0.3
Propane	3.1	0.3
Carbon dioxide	1.3	0.3
N-Butane	0.9	0.1
Nitrogen	0.8	0.4
Iso-Butane	0.4	0.06
Hexane+	0.3	0.22
Iso-Pentane	0.2	0.04
N-Pentane	0.2	0.05
Oxygen	0.1	0.12
Hydrogen sulfide	0.002	0.001
Methane/ethane	17	1
Methane/propane	29	3

Gas samples were collected after bubbles traveled through approximately 10 m of seawater.

the tents has been monitored since 1983, providing a record of seepage for a small area of the Coal Oil Point seep field. Initially, the tents collected about $0.4 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ of natural gas ($8 \times 10^9 \text{ g yr}^{-1}$ of methane) emanating from vents distributed over 0.2 hectare of the seafloor. By the mid-1990s the emission rate had declined by a factor of 3 to about $0.14 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ [Quigley, 1997].

Away from the Seep Tents the seep emissions form visible trains of bubbles which rise from seafloor vents to the air-water interface. Partial dissolution of the rising bubbles occurs, creating dissolved hydrocarbon plumes down current of the seeps. Above the seafloor vents the bubble trains can be imaged and mapped using acoustic methods [e.g., Sweet, 1973; Quigley, 1997; Hornafius *et al.*, 1999; Quigley *et al.*, 1999]. During the period 1994-1996, Quigley [1997] and Hornafius *et al.* [1999] estimated the total emission of natural gas to the atmosphere to be between 1×10^5 and $2 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ (2×10^{10} and $5 \times 10^{10} \text{ g yr}^{-1}$ of methane), approximately 10 times the emissions captured below the Seep Tents. Their maps of the bubble plumes indicate that approximately 3 km^2 (300 ha) of the seafloor near Coal Oil Point contain hydrocarbon seeps (Figure 1). Quigley *et al.* [1999] documented a significant decrease in the area of seepage between the mid-1990s and 1973 and suggest that this decrease was due to hydrocarbon production at Platform Holly.

3. Methods

Hydrocarbon plumes down current of natural seeps near Coal Oil Point were mapped during a 3 day cruise between August 12 and 15, 1996, on board the R/V *Seawatch*. Our study concentrated on the area between the 100 m isobath and the shore, 12 km east and west of Coal Oil Point (Figure 1). Survey lines for dissolved methane and SF_6 tracer were run in a zigzag pattern so that about half of the lines were approximately perpendicular to the mean current direction (predominately eastward during our experiment) and isobaths. Four surveys of the field area were completed at three depth intervals: survey 1 and survey 2 at 27 to 37 m, survey 3 at 10 to 16 m, and survey 4 at 45 to 60 m.

3.1. Hydrocarbon Measurements

During each survey, seawater was continuously pumped from depth using a submersible pump into a vacuum gas stripper located in the ship's laboratory. Approximately every 3 min ($\sim 200 \text{ m}$ at the mean survey speed) the gas liberated from the seawater by the stripper was collected in a gas-tight syringe and transferred immediately to a gas chromatograph (GC) equipped with a flame ionization detector for methane (CH_4), ethane (C_2H_6), and propane (C_3H_8) analysis using standard techniques. More than 700 analyses were completed during the 3 day cruise. Additionally, 179 samples of stripper gas were collected in recently evacuated glass blood serum vials (VacutainersTM) for analysis of nitrogen, oxygen, methane, carbon dioxide, and hydrogen. These gases were analyzed about 6 weeks after the cruise using standard GC techniques. The uncertainty of the gas concentration measurements were $\pm 3\%$.

The vacuum gas stripper consisted of a 10 L vertical gas-tight glass cylinder and is similar to the stripper developed by Dunlap *et al.* [1960]. Two ports were located at the top and one at the bottom of the cylinder. During the cruise, seawater was pumped from depth and sprayed into the vacuum gas stripper through one of the top ports. The water level was maintained

nearly constant by varying the pumping rate out of the bottom port such that the volumes of head space and water were approximately equal. Gases were extracted from the water by maintaining a vacuum (about 28 inches of Hg) in the head space. Samples of the stripped gas, which was composed only of gases initially dissolved in the seawater, were collected for chemical analysis downstream of the vacuum pump and a water trap.

The quantity of gas extracted per volume of seawater was measured periodically during the survey by measuring the flow rates of gas and water leaving the stripper. A comparison of this number with the total amount of dissolved gas in seawater is a direct measure of the yield or stripping efficiency. Seawater saturated with air at a temperature of 12°C and a salinity of 33.5, the mean conditions observed during the middepth surveys, contains about 17.5 mL of gas L^{-1} . During our cruise the stripper was extracting between 15 and 16 mL of gas L^{-1} from water collected at depths greater than 25 m. Assuming that nitrogen and oxygen are in solubility equilibrium with the atmosphere, the stripping efficiency was 86-91%. While nitrogen concentrations are generally a few per cent greater (0 to 5%) than the solubility equilibrium values in the upper ocean [e.g., Craig and Weiss, 1971; Emerson *et al.*, 1991], oxygen concentrations are often substantially different than the equilibrium values. Hence this mass balance approach of determining the stripping efficiency is most sensitive to the dissolved oxygen concentrations. The oxygen to nitrogen ratio, which decreased systematically with depth (Figure 2a), indicates that oxygen concentrations below 25 m were less than (50% to 75%) equilibrium values and therefore each liter of seawater contained between 15 and 16 mL of gas. The stripping efficiency must be greater than 86% (based on the water-gas mass balance), and probably close to 100% (considering that the oxygen saturation was less than 75%), for the major components of air.

Concentrations of methane, ethane, and propane in seawater (nmol L^{-1}) were calculated from their concentrations in the stripped gas (ppmv), assuming that nitrogen concentrations were in equilibrium with the atmosphere at the in situ temperature:

$$[\text{HC}]_{\text{sw}} = \frac{[\text{HC}]_{\text{gas}}}{[\text{N}_2]_{\text{gas}}} [\text{N}_2]_{\text{sw}} \quad (1)$$

where [HC] and $[\text{N}_2]$ are the concentrations of the hydrocarbons (i.e., methane, ethane, or propane) and nitrogen, respectively, and the subscripts *sw* and *gas* refer to seawater and stripper gas, respectively. $[\text{N}_2]_{\text{sw}}$ was calculated using the in situ temperature and solubility data of Weiss [1970]. Because it was only measured in a subset of samples, $[\text{N}_2]_{\text{gas}}$ was calculated from the in situ temperature using the approximately linear empirical relationship found between temperature and $[\text{N}_2]_{\text{gas}}$ in the blood serum vial samples ($R^2 = 0.84$, $n=179$; Figure 2b). Implicit in this calculation is that the stripping efficiency of nitrogen and the hydrocarbons was approximately the same. The final error in the dissolved methane concentration is derived by propagating the uncertainty of the empirical correlation between temperature and $[\text{N}_2]_{\text{gas}}$ and the analytical error of the hydrocarbon analyses, and is $\pm 15\%$. As a critical check on the stripping efficiency, we compared background methane concentrations in our study area with those of Cynar and Yayanos [1992]. Good agreement is found, indicating that our method of converting stripper gas concentrations to seawater concentrations is reasonable.

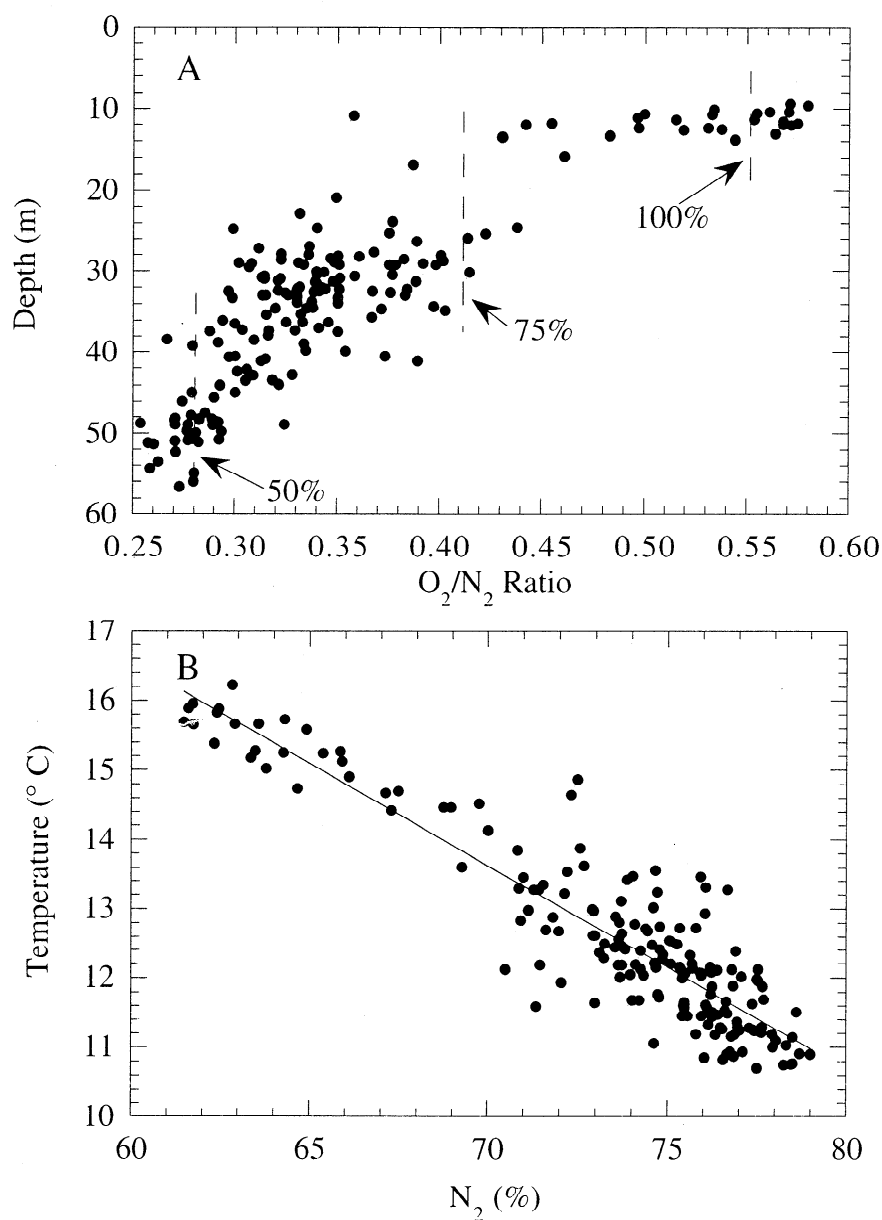


Figure 2: (a) O_2/N_2 ratios from the stripper gas plotted against pressure. The O_2/N_2 ratios of seawater in which the O_2 concentration is 100%, 75%, and 50% of the atmospheric equilibrium value are plotted as vertical dashed lines. (b) N_2 plotted as a function of the in situ temperature of the water. The empirical relationship is shown with the line.

3.2. Oceanographic Measurements

The distributions of seawater properties around the hydrocarbon seepage area were observed using standard conductivity, temperature, depth (CTD) instrumentation. Two CTDs (model 911, manufactured by SeaBird Electronics, Bellevue, Washington) were operated during the experiment in two profiling modes. First, a CTD was mounted vertically on the same platform as a submersible pump used to collect seawater samples for hydrocarbon analysis. The pump inlet was located about 0.2 m from the temperature and conductivity sensors of the CTD. The CTD/pump combination was towed at a nearly constant depth. Second, after completing the hydrocarbon and gas tracer surveys, a CTD was mounted horizontally on a sled and towed through the water along a sawtooth "towyo" path. A large vertical fin maintained the sensor orientation into the

flow to minimize wake mixing effects. During towyo profiling, the platform was winched between the sea surface and the bottom at about 0.4 m s^{-1} while the ship steamed at about 4 knots (2 m s^{-1}). The CTDs acquired time series at a sampling rate of 24 Hz. These data were filtered, corrected for differing sensor response times, and then block-averaged over 1-s intervals. The 1-s averages were used to compute salinity, density, and other derived quantities. Ship's position was obtained every 2 s using a (nondifferential) Global Positioning System (GPS) receiver.

Time series of ocean currents were measured with a bottom-mounted, upward looking Acoustic Doppler Current Profiler (ADCP) manufactured by R.D. Instruments, San Diego, California) operating at 300 kHz. The ADCP was configured with 2-m depth bins, and profiles of horizontal current velocity

were obtained every 15 min throughout the experiment. To avoid heavy trawling activity in the study region, the ADCP was placed on the 55 m isobath, inshore from the main seep area on the South Elwood anticline (Figure 1). It was necessary to place the ADCP away from areas of strong seepage rates because the seep gas bubbles strongly scatter sound and hence would degrade the current profiles. Current time series were consistently obtained between 8-50 m. A thermistor in the ADCP measured temperature changes on timescales of several minutes. The instrument was deployed approximately 1 week before the start of the hydrocarbon plume survey.

3.3. Sulfur Hexafluoride Tracer Experiment

Pure sulfur hexafluoride (99.8% SF₆), a nonreactive gas tracer, was released continuously into the ocean in the middle of the large seep area at the southeastern end of the seep field (Figure 1). The gas was injected by bubbling at a constant rate (~200 mL STP min⁻¹) from a platform at the seafloor (depth ~65 m; Figure 1). With this method a nearly vertical line of tracer was injected into the water column between the sediment and air-water interface creating a dissolved plume similar to those emanating from each hydrocarbon seep. The tracer plume was allowed to evolve for about 9 hours before starting the first survey.

Seawater was analyzed for SF₆ every 90 s (~100 m at the mean survey speed) by diverting the stripper gas flow via polyethylene tubing (~1/4 inch x 7 m in length) through a sample loop (~1 mL) contained within an inlet system similar to the one developed by Wanninkhof *et al.* [1991]. To obtain a sample, the loop was isolated, and, after the pressure in the loop had equilibrated with atmospheric pressure, the gas was injected through a Molecular Sieve 5a column into a gas chromatograph equipped with an electron capture detector. With this method we were able to run more than 1750 samples over the 48 hour survey of the tracer plume.

The detector response was calibrated on board the research vessel using a 148 ± 7 parts per trillion by volume (pptv) standard prepared by Scott-Marrin, Inc. Because the injection rate of SF₆ into the water column was higher than expected and because of the high efficiency of the stripper, maximum SF₆ concentrations in the plume were significantly greater than 148 pptv standard for many of the samples. Because of this analytical problem, the detail structure of the plume will not be examined here. Rather, only the general shape of the tracer plume and its evolution will be discussed.

4. Results

4.1. Oceanographic Conditions

Current velocities varied considerably during the 2 week period centered on the time of the field experiment. From the time the ADCP was deployed on August 6 until August 11, the current direction was primarily westward at all depths above the instrument (8-50 m) (Figure 3). Westward flow along the northern channel coast is consistent with the presence of a counterclockwise circulation commonly present in the western Santa Barbara Channel during summer [Harms and Winant, 1998; Hendershott and Winant, 1996; Brink and Muench, 1986]. On August 11, currents reversed, and eastward flow generally prevailed at all depths until August 15, although brief periods of westward flow were apparent at some depths associated with tidal currents. The period of reversed (eastward) cur-

rents encompassed most of the shipboard surveys. A temperature time series recorded at the ADCP indicates that the eastward flow coincided with lower bottom temperatures (data not shown). On August 15 the currents again reversed, and westward flow prevailed. Velocities near the bottom (50 m) were generally along isobaths, but the mid (31 m) and upper water column (13 m) often had strong cross-isobath components (data not shown). The semidiurnal (M2) tide produced current fluctuations at all depths and occasional current reversals, particularly in the northward component (Figure 3).

Sections of temperature, salinity, and density obtained from the towyo survey (tracks shown in Figure 1) indicate that the water column was well stratified near the surface. Towyo section 2 (T2) is representative and shows the highest vertical temperature and density gradients in the upper 20 m (Figure 4). No surface mixed layers were found in any of the towyo sections, although mixing in the ship's wake could obscure their presence in the upper 5 m of the water column. The buoyancy frequency in the upper 10 m of section 2 is about $N = 8$ cycles per hour. Density anomalies (σ_θ) were in the range 24.5-26.0 kg m⁻³, corresponding to temperatures in the range 10°-17°C. The spatial patterns of isopycnals and isotherms are similar, indicating thermal stratification near the surface. This probably resulted from the high solar irradiance and weak winds during the experiment.

The SF₆ tracer was easily detected downstream of the seafloor injection device at all survey depths between 10 and 60 m. For the initial 52 hours of the tracer experiment the predominant current direction was eastward (Figure. 3). Surveys 1 and 2 of the plume centered at about 32 m were collected during this period. Mid-way through the survey 3 the current direction reversed, and the plume was advected back toward the injection point. Hence the best picture of the plume dispersion can be inferred from surveys 1 and 2.

Survey 1 started west of the source 9 hours after the injection began and was completed 17.5 hours later (Figure 5). The crosscurrent width of the plume increased eastward of the point source to about 600 m and 2500 m, 2.5 km and 8.4 km down current, respectively. No SF₆ was observed west of the injection point or on the most eastern line about 10 km from the source. Thus the tracer plume was contained within the survey domain. On the basis of these data the mean current velocity during the initial 26 hours of the release was about 0.11 m s⁻¹ about due east. The mean current direction recorded by the ADCP during the same period was substantially different; at this location the current trended to the southeast with a speed of about 0.21 m s⁻¹. The strong southward component of flow may result from the bathymetry around Coal Oil Point.

4.2. Dissolved Hydrocarbon Distributions

The surveys of dissolved hydrocarbons in the coastal waters near Coal Oil Point identified methane, ethane, and propane plumes down current of the seeps. The location and the approximate structure of these plumes were identical. The plumes extended horizontally from the coastline approximately 5 km south into the channel (Figure 6). Maximum concentrations in the eastward spreading plume were 2 to 3 orders of magnitude greater than mean up current values (west of the seeps). Hydrocarbon concentrations along approximate isopycnal surfaces did not vary smoothly in either the crosscurrent or along-current directions (Figures 6 and 7). Rather, the plumes were characterized by pockets of relatively high and low concentra-

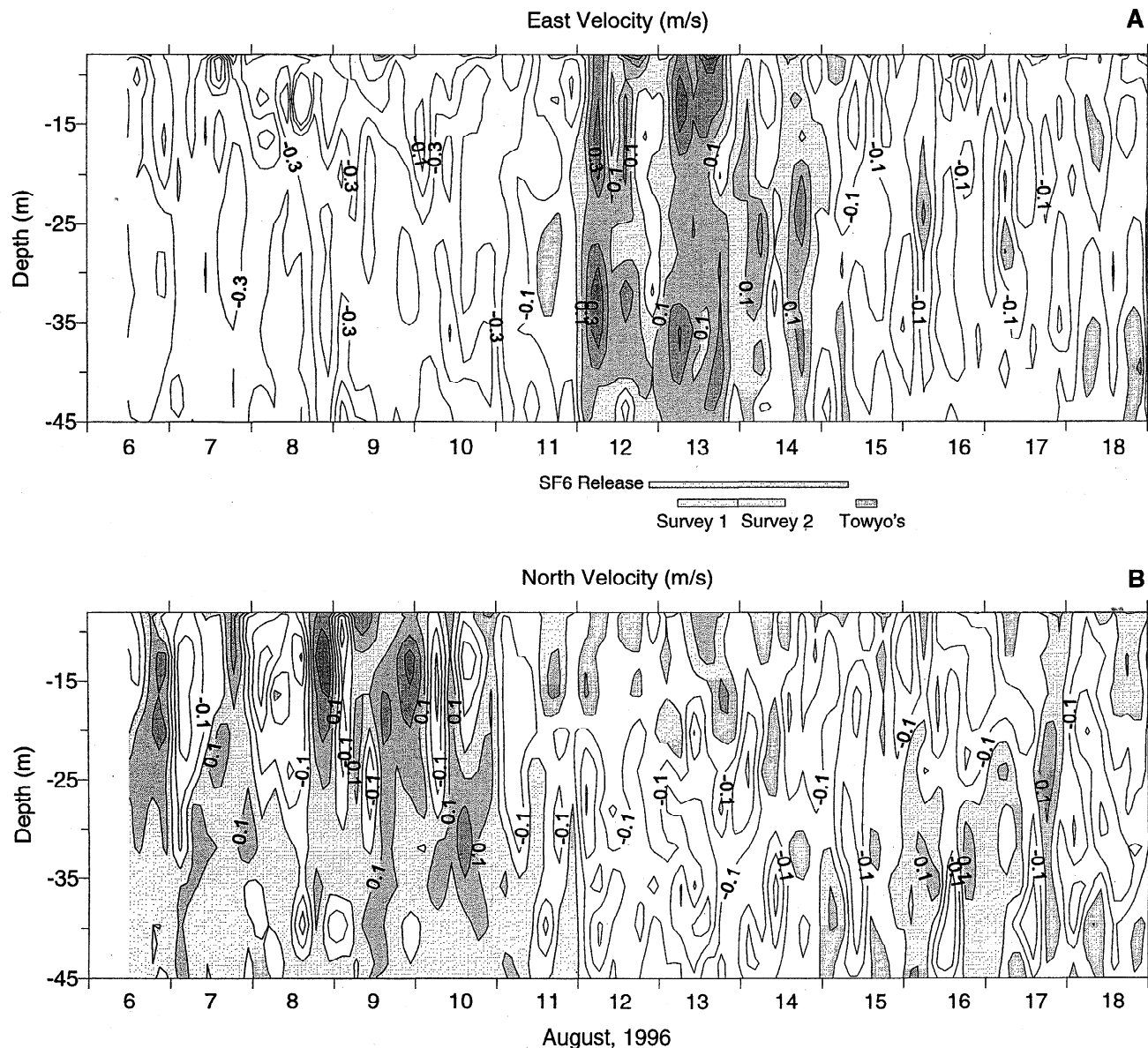


Figure 3. Contours of velocity from the 300 kHz acoustic Doppler velocity profiler (ADCP). (a) Eastward velocity component. Shaded areas indicate eastward flow. (b) Northward velocity component. Shaded areas indicate southward flow. Location of ADCP on 55 m isobath shown in Figure. 1. Bars between panels show times of survey 1, survey 2, towyo sections, and SF₆ tracer release.

tions, reflecting the complicated geometry of the seep gas source and the slow crosscurrent mixing indicated by the SF₆ tracer experiment.

Dissolved methane concentrations ranged between about 6 nmol L⁻¹ to about 5200 nmol L⁻¹, and the mean concentration in the plume was 1300 nmol L⁻¹. The lowest values, 6 to 20 nmol L⁻¹, which were found up current (west) of the seeps and south of the plume, are similar to values reported by *Cynar and Yayanos* [1992] and *Ward and Kilpatrick* [1993] for coastal California waters. The maximum methane value is about 4 times larger than the maximum value observed by *Cynar and Yayanos* [1992], who collected six stations from the Santa Barbara Channel, none of which were near Coal Oil Point. At one of their stations which was close to a large seep area near Point Conception, they report a maximum concentration of about 1400 nmol L⁻¹. In seven of the 61 samples collected up current of the seep field (west of 119.92° W), methane concentrations were significantly greater (3 to 22 times) than back-

ground values. Most likely these high samples resulted from small seeps which lie to the west of the Coal Oil Point seep field.

The methane/ethane and methane/propane ratios observed in the plumes ranged between values very close to the seep gas measured at the Seep Tents (CH₄/C₂H₆ = 17 and CH₄/C₃H₈ = 29) and values greater than 1000. Most (80%) of samples had methane/ethane ratios between 15 and 23 and methane/propane ratios between 29 and 50 (Figure 8). Some of the highest ratios in our survey area were found up current from the seeps in water that contained relatively little methane and were representative of background California coastal waters. The lowest ratios were found close to the Coal Oil Point seeps. There was a general trend for these ratios to increase slightly down current of seeps, while methane concentrations remained relatively constant, suggesting that the heavier hydrocarbons were preferentially removed (Figures 7 and 9). The increase of these ratios occurred over an area of the seafloor with no

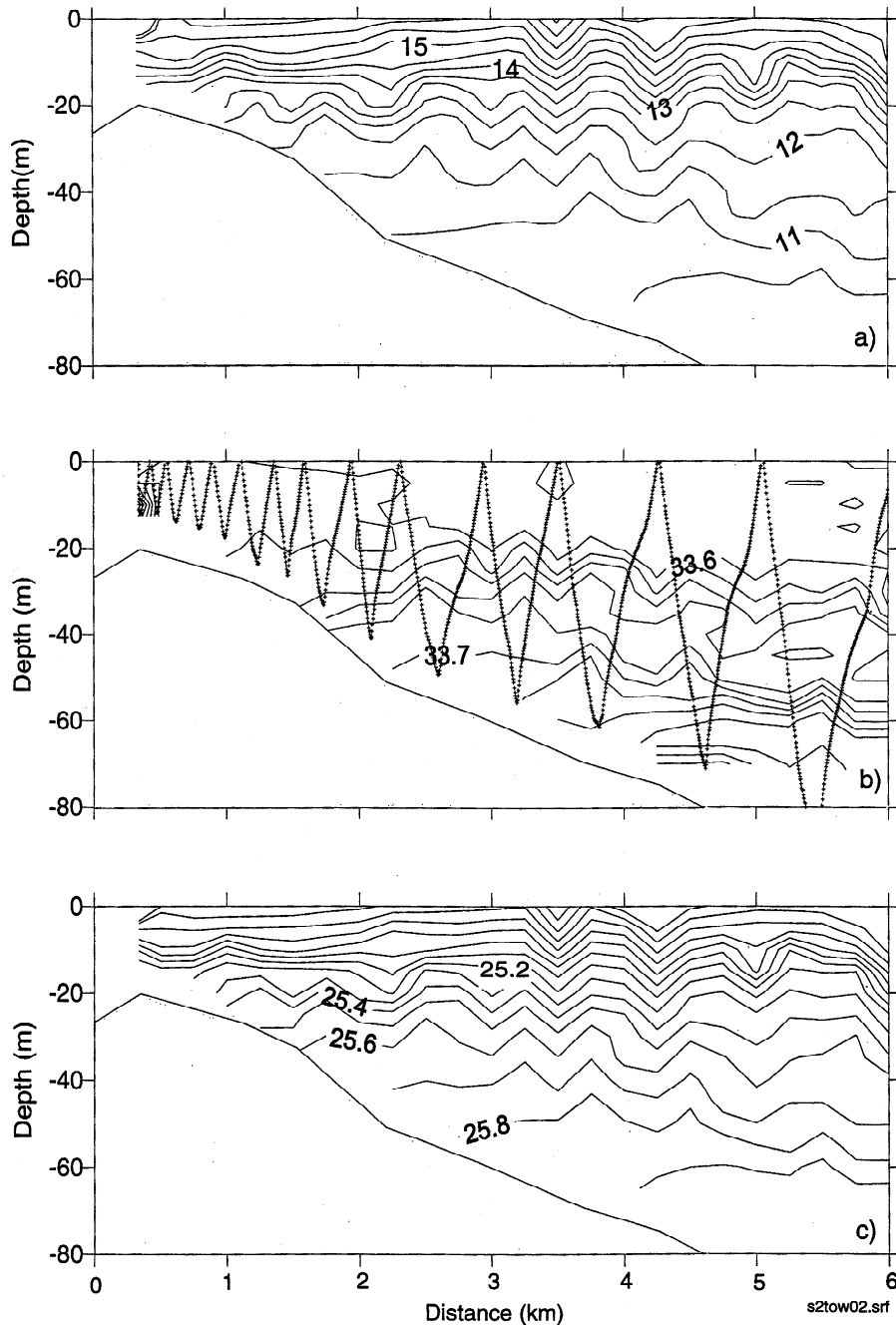


Figure 4. Contours from towyo section 2 of (a) temperature ($^{\circ}\text{C}$), (b) salinity, and (c) σ_{θ} (kg m^{-3}). Shaded areas indicate bottom. Zigzag line in Figure 4b shows path of towyo platform. Location of towyo section 2 indicated in Figure 1 as T2.

known seeps (Figure 1), so it is unlikely that the change is caused by the influx of gas with higher methane/ethane and methane/propane ratio.

5. Discussion

Along the northern boundary of the Santa Barbara Channel, currents during the summer generally flow to the west [Harms and Winant, 1998; Hendershott and Winant, 1996; Brink and Muench, 1986]. Hence the hydrocarbon plumes typically extend from the Coal Oil Point seeps west toward Point Conception. Approximately 16 hours prior to the start of our survey, currents along the northern margin of the channel reversed and

began to flow to the east. Thus our map which shows the plume extending to the east is atypical. However, most of our observations of the plume should be independent of the current direction, and our conclusions are not affected by this current reversal.

Hydrocarbons are injected into the stratified coastal water above the Coal Oil Point seep field by partial dissolution of the rising seep gas bubbles. The resulting plume can be mapped down current of the field for at least 12 km, the limit of our surveys. A simple description of the concentration distributions is not possible because of the large geographical source area and because of the complex nature of advection and mixing near the seeps. This complexity is clearly illustrated

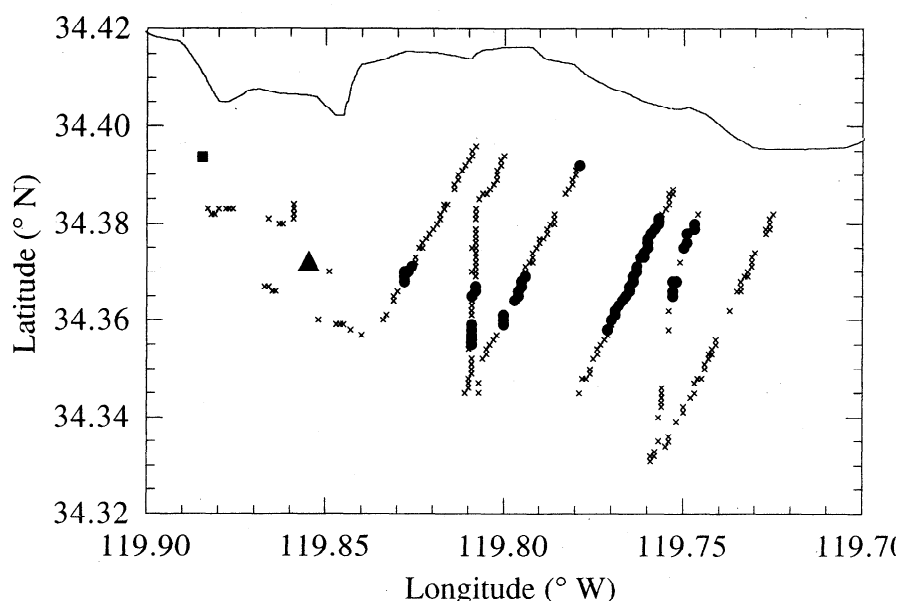


Figure 5. Survey of the SF_6 plume at depths between 27 and 37 m down current from the bottom-mounted SF_6 source on August 13 (survey 1). The map shows only the eastern half of the field area where the SF_6 plume was found, and the north-south scale has been adjusted to better show the plume. The survey was completed over a period of 17.5 hours and started 9 hours after the start of the SF_6 release. The solid circles and crosses represent samples within and outside of the SF_6 plume, respectively. The solid square and triangle represent the location of the ADCP and SF_6 source, respectively.

by the results of the SF_6 tracer experiment, in which a complex plume evolved rapidly from a point source.

At the time of our survey in August 1996, the methane emanating from the Coal Oil Point seeps was injected into density surfaces between $\sigma_\theta = 24.5\text{--}26.0 \text{ kg m}^{-3}$. *Cynar and Yayanos* [1992] mapped the regional distribution of methane in upper waters of the southern California Bight and showed that a subsurface methane maximum occurs near the 25.5 kg m^{-3} density surface which extends from the coast for hundreds of km. They also showed that this density surface deepens from about 35 m near the coast to greater than 90 m at their westernmost stations, more than 400 km offshore. From their data we infer that the injected hydrocarbons are transported away from the seep field into the regional waters along these density surfaces where they are either oxidized or diffuse through the thermocline and are lost to the atmosphere by gas exchange [*Cynar and Yayanos*, 1993; *Ward and Kilpatrick*, 1993].

Hydrocarbon concentrations observed during the initial surveys west of the field (up current) were relatively low, suggesting that the hydrocarbon plume which extended to the west prior to the current reversal was not advected back into our field area (Figure 6). (Fifty-six out of sixty-one samples collected in this area had methane concentrations less than 20 nmol L^{-1} which is typical of background values in coastal California waters [*Cynar and Yayanos*, 1992; *Ward*, 1992]. The maximum value observed was 450 nmol L^{-1} and probably resulted from a small seep west of the Coal Oil Point Seep field. Scattered seeps are found west of our survey area extending to Point Conception [*Fischer*, 1978].

The total flux of methane into the coastal ocean can be estimated with the survey and current speed data. The flux of methane through a plane perpendicular to the mean current direction

is equal to the flux of methane into the water column assuming that (1) no methane is lost between its source and the plane, (2) the flux of methane passing through this plane from seeps which are not a part of the Coal Oil Point seeps system is small, and (3) local currents do not recirculate water over the

Table 2. Inventories of Methane Determined Along Cross Sections Between 27 and 37 m

Section	Distance, ^a km	Inventory, ^b mol m^{-1}	Flux, ^c mol s^{-1}
<u>First survey</u>			
A-A'	3.2	40.8	4.49
B-B'	5.9	43.2	4.75
C-C'	8.5	35.1	3.86
D-D'	11.2	41.0	4.51
Mean		40.0 ± 3.5	4.40 ± 0.4
<u>Second survey</u>			
E-E'	3.2	38.0	4.18
F-F'	5.9	24.1	2.65
G-G'	8.5	32.0	3.52
Mean		31.4 ± 7.0	3.45 ± 0.8

Locations of the sections can be found on figure 1.

^aDistance from the eastern end of the seep field to the midpoint of the cross section.

^bInventory equals the concentration multiplied by the area of the cross section.

^cThe flux equals the inventory multiplied by the mean current speed, 0.11 m s^{-1} .

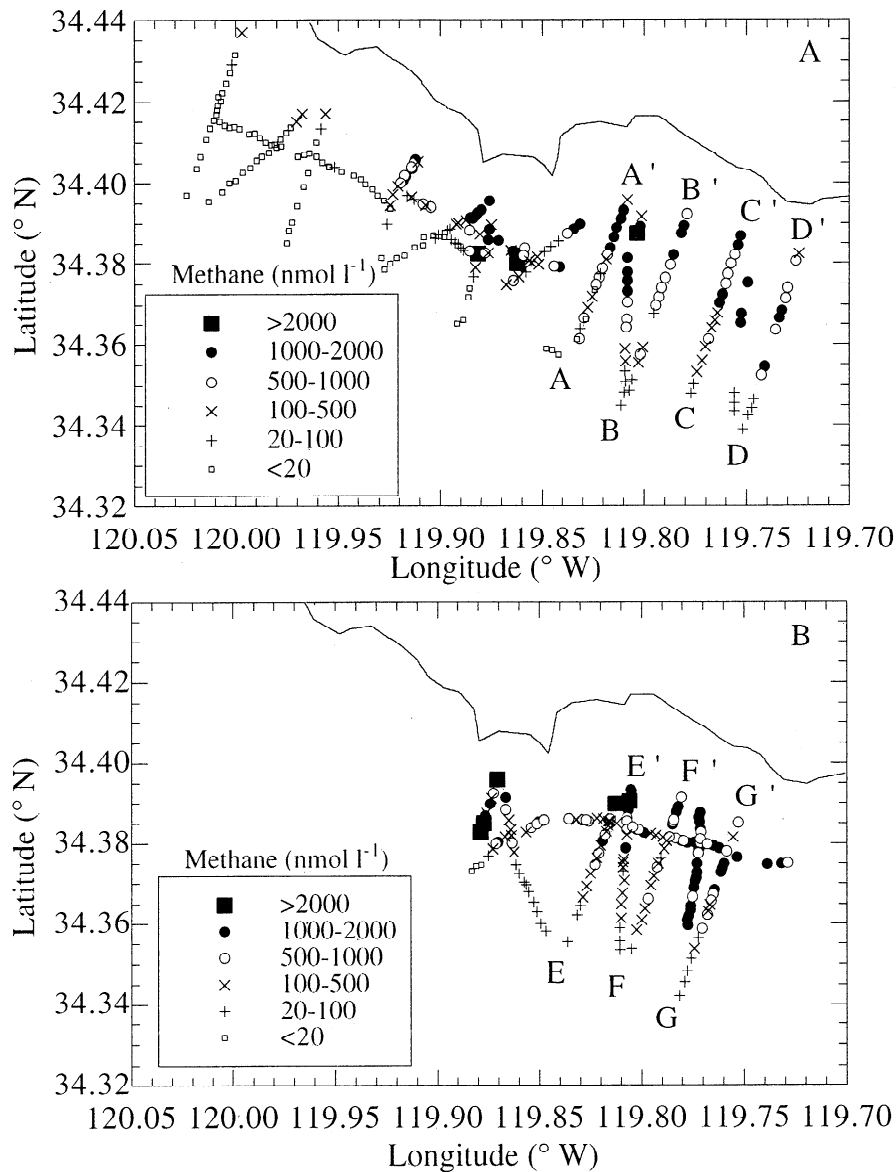


Figure 6. Distributions of methane concentrations near Coal Oil Point collected between 27 and 37 m during two time intervals: (a) August 12-13 and (b) August 13-14. At the time of these surveys the current was eastward. Methane inventories were calculated for the labeled sections (see Table 2). The northern ends of the transects approximately intersect the 30 m isobath. The north-south scale has been adjusted to better show the plume.

seep field. Conditions during the first two of the four hydrocarbon plume surveys approximately satisfy these assumptions and can be used to estimate fluxes.

During the first survey centered at 32 m, four cross sections of the plume were sampled (Figure 6 and Table 2). The mean flux of methane calculated for the cross sections over a 10 m depth window (the range of the survey depths) and a mean current speed of 0.11 m s^{-1} (determined from the advection of the SF_6 plume) was $4.4 \pm 0.4 \text{ mol s}^{-1}$. Assuming the same current speed, the mean flux during the second survey was $3.5 \pm 0.8 \text{ mol s}^{-1}$. To estimate the total flux of methane into the entire 65 m water column requires extrapolation; we do this by using the

bubble dissolution model of *Cline and Holmes* [1977]. The fractional loss (Δm) out of a rising bubble per unit time (Δt) as follows:

$$\Delta m = \frac{APM[\text{CH}_4]_{\text{sol}}k}{RT}\Delta t \quad (2)$$

where A is the bubble surface area, P is the pressure inside the bubble, T is the temperature, R is the gas constant, M is the molecular weight, k is the gas transfer rate across the bubble wall, and $[\text{CH}_4]_{\text{sol}}$ is the solubility equilibrium concentration with respect to the bubble gas [*Wiesenburg and Guinasso*,

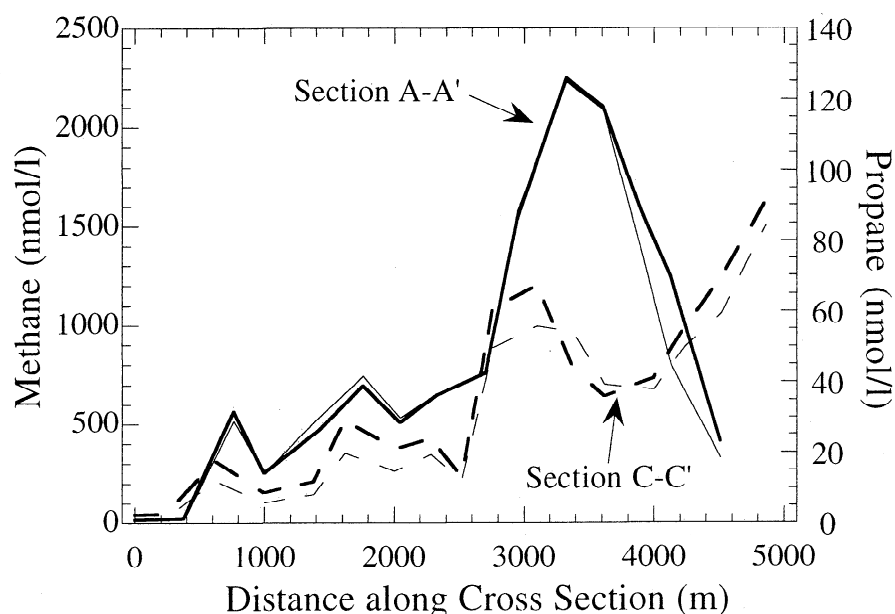


Figure 7. Methane (bold lines) and ethane (light lines) concentrations from the depth interval 27 to 37 m plotted as a function of distance along sections A-A' and C-C' (see Figure 6 for section locations). The distance is relative to the southernmost data point, and the northern end approximately intersects the 30 m isobath. The data from sections A-A' and C-C' are represented by solid and dashed lines, respectively.

1979]. The time increment was related to the distance of rise by $\Delta t = \Delta z/v_b$, where v_b is the bubble rise velocity. In the calculations it was assumed that the rising bubbles were composed of only methane and that other gases such as nitrogen were not transferred into the bubble from the seawater. The model is probably most valid for small bubble plumes where the water column through which the bubbles are rising is unlikely to become saturated with bubble gas (in our case, methane).

The critical parameters which regulate the dissolution rate of bubbles as they rise through a column of water are the bubble size and the gas transfer rate across the bubble wall into the surrounding water. Quigley [1997] reports that the mean bubble radius at the surface is 0.6 cm based on visual observations of seep gas bubbles breaking at the sea surface. This observation is the primary constraint used in the model calculations.

The initial bubble radius and gas transfer rate were allowed to vary so that the final bubble radius at the surface was 0.6 cm.

Results from a number of model calculations of bubble dissolution using various gas transfer velocities to account for the oil film surrounding the bubbles and final bubble radius are listed in Table 3 and shown in Figure 10. The ratio of the total amount dissolved in the 65 m water column calculated with the bubble dissolution model to the amount dissolved between 27 and 37 m, the depth interval into which we can estimate the hydrocarbon flux, does not vary substantially (<30%) and averages about 10. Extrapolations based on these ratios indicate that between 25 and 60 mol s⁻¹ ($2.1 \pm 0.9 \times 10^{10}$ g yr⁻¹) of methane is injected into the water column above the Coal Oil Point seeps. Using their mean ratios with methane above the Coal Oil seep field, the flux of ethane and propane into the

Table 3. Relative Flux of Mass From a Rising Bubble Through the Water Column for Different Gas Transfer Rates, k and Final Bubble Radius

k , cm h ⁻¹ (cm/hr)	Radius, mm		Percent Dissolved, ^a		Ratio, ^b
	Initial	Final	0-65 m	27-37 m	
0.3	3.1	6.0	4.3	0.5	9.1
3	3.5	6.0	31	3.3	9.5
8	4.1	6.0	60	5.8	10.3
33	7.2	6.0	92	7.3	12.6
3	0.8	1.0	74	6.9	10.8
3	3.6	6.0	31	3.3	9.5
3	5.5	10.0	18.4	1.9	9.5

See Cline and Holmes [1977] for a description of the model.

^aThe mass fraction of the bubble that dissolved within the depth interval.

^bRatio of the preceding columns.

coastal waters are estimated to be approximately 2 mol s^{-1} ($1.9 \times 10^9 \text{ g yr}^{-1}$) and 1 mol s^{-1} ($1.4 \times 10^9 \text{ g yr}^{-1}$), respectively.

The methane flux to the atmosphere from bursting bubbles at the air-water interface (2 to $5 \times 10^{10} \text{ g yr}^{-1}$) estimated by *Quigley* [1997] and *Hornafius et al.* [1999], is approximately the same as the methane flux into the coastal ocean we estimate above, and indicates that between 25% and 60% of the methane vented at the sea floor dissolves.

Cynar and Yayanos [1993] estimated that the flux of methane across the air-water interface to the atmosphere due to gas exchange was about $3 \times 10^{10} \text{ g yr}^{-1}$ in California waters between 30° to 34°N and 117° to 124°W . The majority of the gas flux occurred near the coast. On the basis of this work the flux

of dissolved methane into the water column above the Coal Oil Point seeps is approximately the same as that of *Cynar and Yayanos* [1993] and thus could support the coastal ocean flux to the atmosphere if the only loss of methane is via gas exchange. A complete mass balance of methane in these waters is not possible because the contribution of methane from other hydrocarbon seeps found along the southern California coast and the oxidation rate within the water column are not known adequately. Nevertheless, this evidence helps to close the mass balance of methane in these waters, supporting the inference that open ocean methane in the California Bight is derived largely from continental sources along the coast [*Cynar and Yayanos*, 1992; *Ward*, 1992]. It further suggests that natural

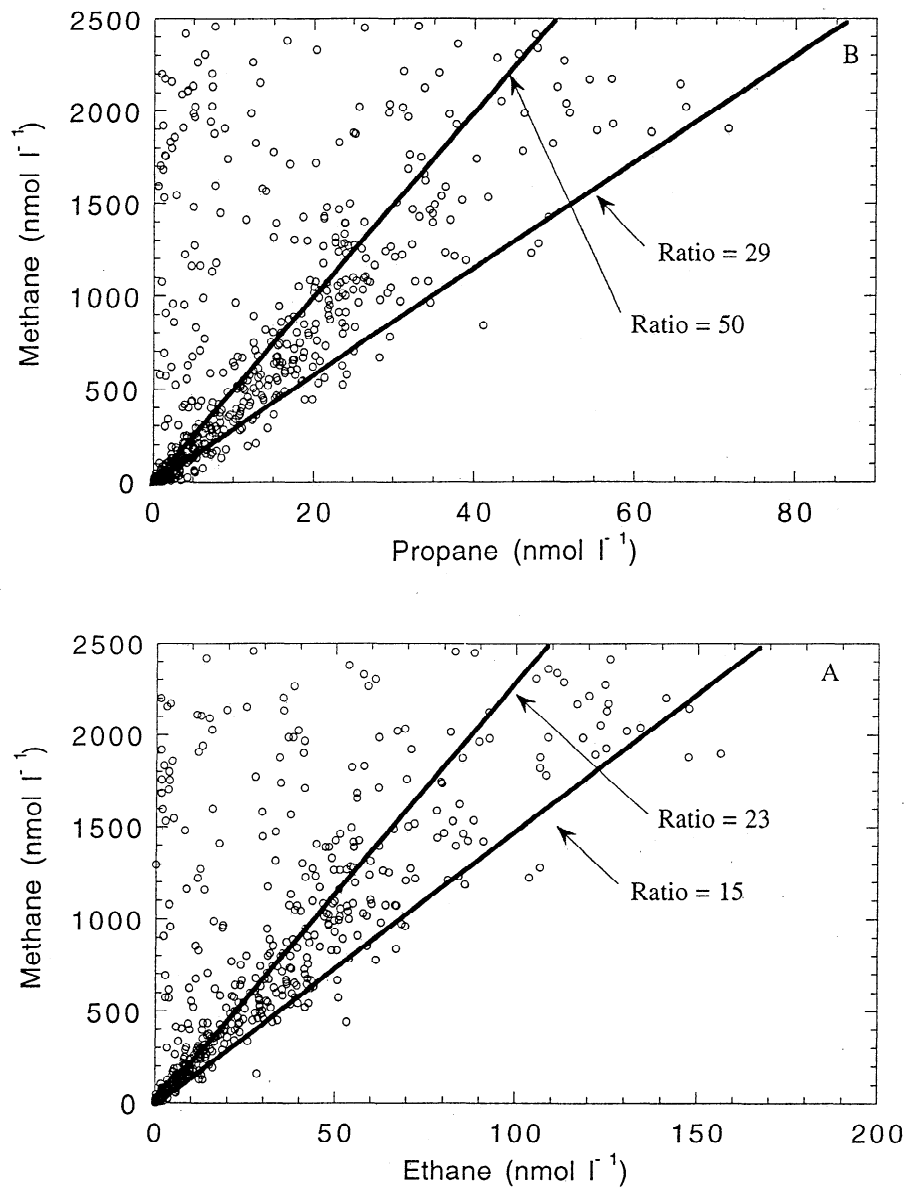


Figure 8. Scatterplots of methane versus (a) ethane and (b) propane. Samples from all depths and locations are represented on the plots. The methane/ethane and methane/propane ratios measured at the Seep Tents are 17 and 29, respectively. Spatial trends in the ratios were found in the study area (Figure 9).

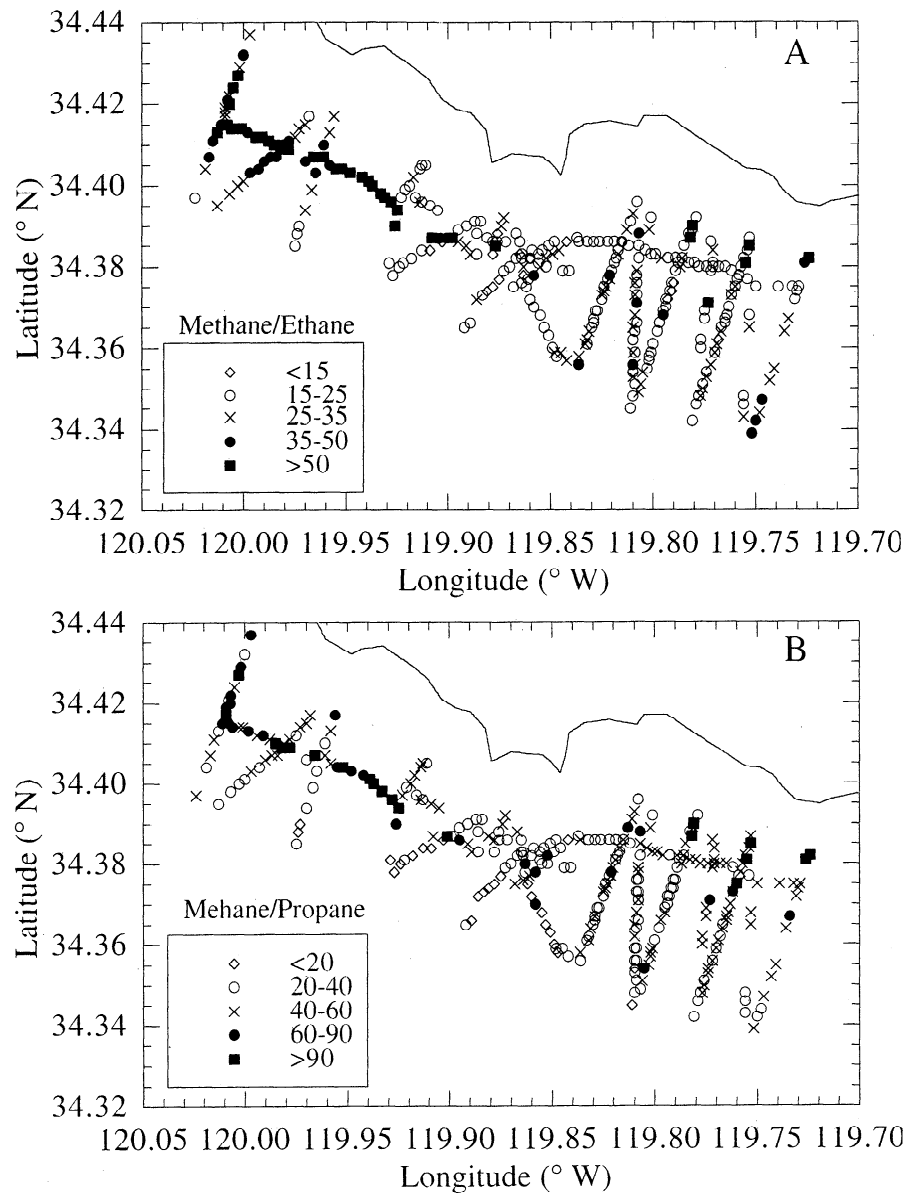


Figure 9. Distributions of (a) methane/ethane and (b) methane/propane ratios concentrations near Coal Oil Point collected in the depth window 27 and 37 m during both the first and second hydrocarbon plume surveys.

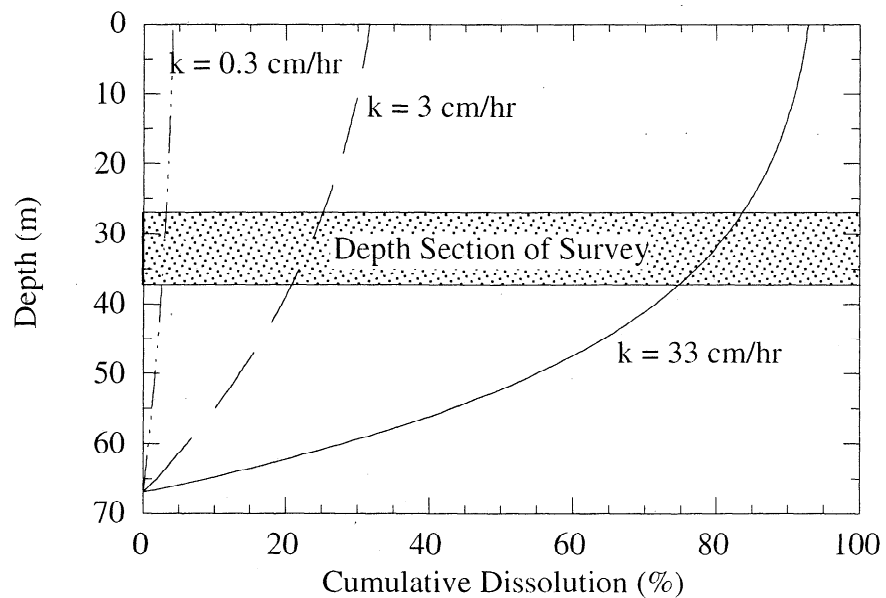


Figure 10. Results of the bubble dissolution model of *Cline and Holmes* [1977]. In all three cases the final bubble radius (at the surface) was 6.0 mm.

marine hydrocarbon seepage along the northern margin of the Santa Barbara Channel may be the dominant source of methane to the regional waters.

6. Conclusions

Surveys of dissolved hydrocarbons within 12 km the Coal Oil Point seep field identified plumes of methane, ethane, and propane which extend down current of the seeps. The maximum and mean methane concentrations within the plume were approximately 5200 nmol L⁻¹ and 1300 nmol L⁻¹, respectively. Concentration distributions were characterized by areas of high and low concentrations which resulted from the complicated geometry of the seep field as well as the complex nature of advection and mixing within the field area. Mass balance calculations indicate that approximately half of the methane (25%-60%) emitted from seafloor seep vents dissolves during transit through the water column.

Cynar and Yayanos [1992] showed that a subsurface methane maximum occurs along a narrow density horizon throughout most of the southern California Bight. They argued that this maximum was supported by coastal sources, including natural hydrocarbon seeps. At the time of our survey the density of the water receiving the influx of methane from the Coal Oil Point seeps was similar to the density of the water containing the subsurface methane maximum Cynar and Yayanos [1992] observed offshore. Furthermore, the total flux of methane into water column from the Coal Oil Point seeps, $2.1 \pm 0.9 \times 10^{10}$ g yr⁻¹, is approximately equal to the total flux of dissolved methane to the atmosphere over this broad area. These observations strongly support the inference that coastal sources maintain the excess methane observed offshore as argued by Cynar and Yayanos [1992] and Ward [1992].

An implication of this finding is that the flux of methane to the atmosphere from the southern California Bight is not typical of all coastal regions because of the anomalously large amount of hydrocarbon seepage found in the Santa Barbara Channel [Wilson et al., 1974; Kvenvolden and Harbaugh, 1983; Hovland et al., 1993]. In formulating their estimate of the total methane flux from coastal waters to the atmosphere, Cynar and Yayanos [1993] extrapolated the flux from the southern California Bight. Their estimate needs to be revised downward because of the usually higher rate of natural marine hydrocarbon seepage found along the California coast and its influence on local offshore methane concentrations.

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