JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 104, NO. C9, PAGES 20,703–20,711, SEPTEMBER 15, 1999

# The world's most spectacular marine hydrocarbon seeps (Coal Oil Point, Santa Barbara Channel, California): Quantification of emissions

J. Scott Hornafius,[1] Derek Quigley,[2] and Bruce P. Luyendyk[2]

Institute for Crustal Studies, University of California, Santa Barbara

**Abstract.** We used 50 kHz sonar data to estimate natural hydrocarbon emission rates from the 18 km$^2$ marine seep field offshore from Coal Oil Point, Santa Barbara, California. The hydrocarbon gas emission rate is $1.7 \pm 0.3 \times 10^5$ m$^3$d$^{-1}$ (including gas captured by a subsea seep containment device) and the associated oil emission rate is $1.6 \pm 0.2 \times 10^4$ Ld$^{-1}$ (100 barrels d$^{-1}$). The nonmethane hydrocarbon emission rate from the gas seepage is $35 \pm 7$ td$^{-1}$ and a large source of air pollution in Santa Barbara County. Our estimate is equal to twice the emission rate from all the on-road vehicle traffic in the county. Our estimated methane emission rate for the Coal Oil Point seeps ($80 \pm 12$ td$^{-1}$) is 4 times higher than previous estimates. The most intense areas of seepage correspond to structural culminations along anticlinal axes. Seep locations are mostly unchanged from those documented in 1946, 1953, and 1973. An exception is the seepage field that once existed near offshore oil platform Holly. A reduction in seepage within a 1 km radius around this offshore platform is correlated with reduced reservoir pressure beneath the natural seeps due to oil production. Our findings suggest that global emissions of methane from natural marine seepage have been underestimated and may be decreasing because of oil production.

## 1. Marine Seeps in the Santa Barbara Channel

Abundant natural hydrocarbon seeps occur on the continental shelf along the northern margin of the Santa Barbara Channel. The seeps emit both liquid and gaseous hydrocarbon phases, with gas predominating at the offshore vents that are the focus of this study. The most active gas seeps form visible boils where they reach the sea surface. Literature reviews of marine hydrocarbon seepage usually conclude that the area along the northern Santa Barbara Channel is one of the most prolific hydrocarbon seepage areas in the world [*Landes*, 1973; *Wilson et al.*, 1974; *Hovland and Judd*, 1992]. Other areas of intense natural marine seepage occur in the Caspian Sea [*Guliev and Feizullayev*, 1996], and in the Gulf of Mexico [*MacDonald et al.*, 1993].

The escape of this natural gas to the atmosphere is a significant source of reactive organic gases (ROG), which are a precursor to smog-forming ozone in Santa Barbara County. Chemical analysis of air grab samples collected from airplanes over the Santa Barbara Channel suggests that geogenic sources of hydrocarbon trace gases (natural seeps) dominate over anthropogenic sources (automobile emissions) and that 86% of the nonmethane hydrocarbons in these samples originated from natural seeps [*Killus and Moore*, 1991]. The natural hydrocarbon seeps in the Santa Barbara Channel are also the principle source of dissolved methane in the California Current [*Cynar and Yayanos*, 1992].

The most intense area of natural seepage in the Santa Barbara Channel is the Coal Oil Point seep field about 15 km west of the city of Santa Barbara (Figure 1). These seeps were observed by the earliest Spanish settlers and English explorers [*Wilkinson*, 1972]. The Coal Oil Point seeps produce large oil slicks that extend for up to 10 km from their vents and have been extensively studied by remote sensing techniques [e.g., *Kraus and Estes*, 1977; *Kraus et al.*, 1977; *Estes et al.*, 1985]. The oil in the slicks evaporates as it ages on the ocean surface and is converted to isolated tar globules. These tar balls often wash ashore, resulting in the abundant tar found on southern California beaches [*Mertz*, 1959; *Welday*, 1977]. All of the tar found on Santa Barbara's beaches, as well as 55% of the tar on Los Angeles County's beaches, is derived from the Coal Oil Point seeps [*Kolpack*, 1977; *Hartman and Hammond*, 1981].

Each seep in the Coal Oil Point field is located above an anticline that contains oil in the Miocene-age Monterey Formation [*Fischer and Stevenson*, 1973; *Fischer*, 1977]. The hydrocarbons escape from the Monterey Formation through fractures in the overlying Pliocene-age Sisquoc Formation. Isotopic analysis of the oil from the natural slicks indicates that the oil is derived from the Monterey oil reservoir [*Reed and Kaplan*, 1977]. The amount of oil found in the Monterey Formation offshore from Coal Oil Point is estimated to be in excess of 1 billion barrels. Of this total, only 15% is commercially recoverable, owing to the low permeability of the formation. Platform Holly has already produced 50 million barrels of oil from an area within 2 km of the platform. An additional 100 million barrels of recoverable oil is found in the South Ellwood anticline to the southeast of Platform Holly, beneath the La Goleta seep field (Figures 2 and 3).

---

[1] Now at Mobil Oil Corporation, New Orleans.

[2] Department of Geological Sciences, University of California, Santa Barbara.

Paper number 1999JC900148.
0148-0227/99/1999JC900148$09.00

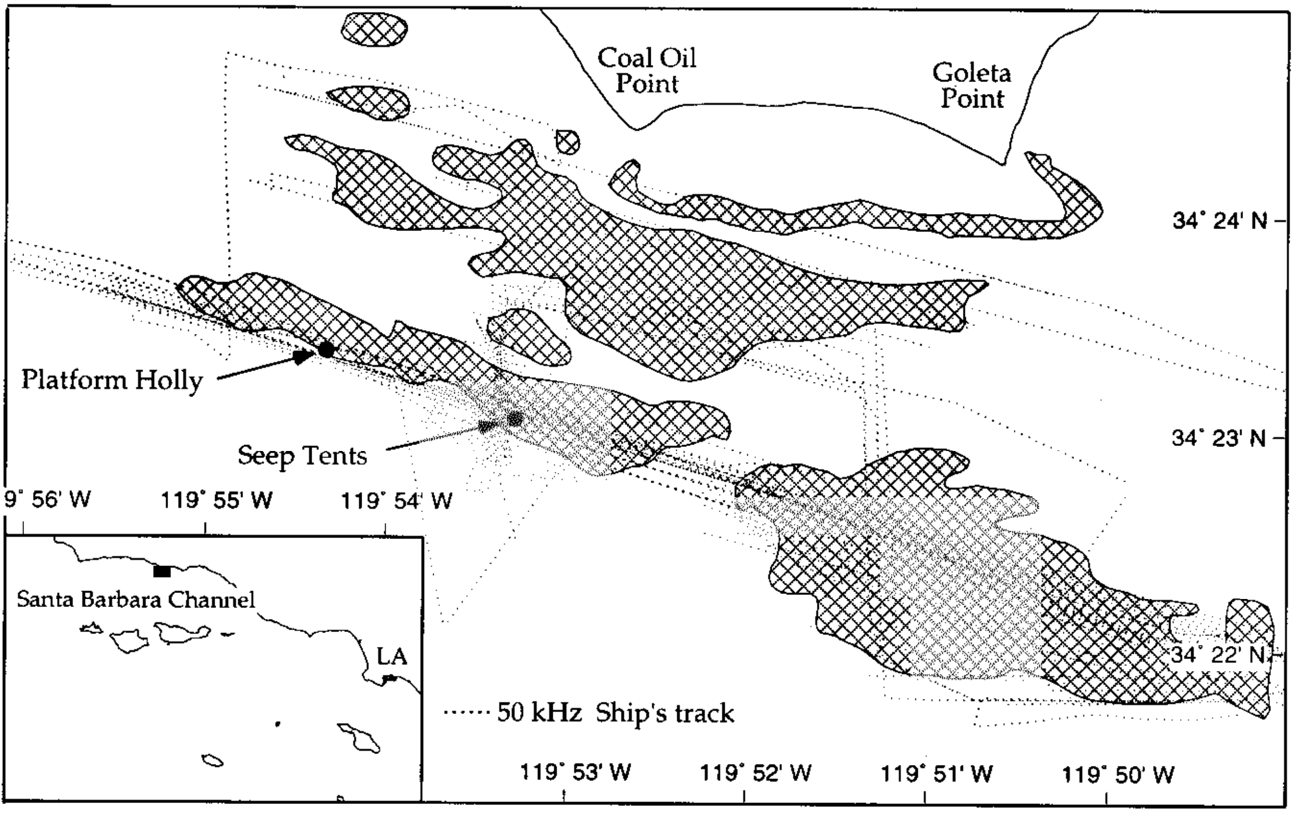

**Figure 1.** Locations of natural hydrocarbon seeps mapped between 1946 and 1973 offshore from Coal Oil Point near Santa Barbara [after *Fischer*, 1977, *Fischer and Stevens*, 1973]. Also shown are the locations of the seep containment tents, platform Holly, and the 50 kHz sonar track lines acqired in 1994 and 1995 that are discussed in this paper.

There is a well-developed community of bottom-dwelling marine organisms in the sediments associated with the seeps at Coal Oil Point [*Spies and Davis*, 1979]. Comparison of the benthic fauna at an oil seep with the fauna in an area free of seepage showed that there are higher densities of individual organisms near the seep [*Davis and Spies*, 1980]. Bacteria can metabolize the hydrocarbons, which forms the basis of a food chain [*Dando and Hovland*, 1992]. This is reflected in the lighter carbon isotope composition in the macrofauna found in the vicinity of the seeps [*Spies and Desmarais*, 1983; *Bauer et al.*, 1990].

In 1982 a seep containment device was placed on the seafloor 1.5 km east of oil platform Holly (Figure 1). This device comprises two steel pyramids or tents measuring 100 by 100 feet (30 by 30 m) that capture emissions from numerous hydrocarbon seeps [*Rintoul*, 1982]. Captured gas is sent ashore through a seafloor pipeline for commercial sale. The emission rate in 1982 was $4.2 \times 10^4$ $m^3 d^{-1}$ ($1.5 \times 10^6$ $feet^3 d^{-1}$). Rates started declining in 1989 and were down to $1.9 \times 10^4$ $m^3 d^{-1}$ ($0.65 \times 10^6$ $feet^3 d^{-1}$) by late 1994.

The goals of our study were to fully map the distribution of seepage within the Coal Oil Point field, to develop methods to estimate the volume discharge of seep gases, and to detect time variation in gas seepage. We were particularly interested in detecting any effects of oil production from offshore reservoirs on the seepage rates. Our work employed more precise navigation and greater aerial coverage than previous studies. We also calibrated our sonar surveys in order to estimate the volume discharge of gasses.

## 2. Sonar Surveys

Four 50 kHz sonar surveys were conducted aboard the R/V *Genoa* in 1994 and 1995 (tracks in Figure 1). The R/V *Genoa* was equipped with a hull-mounted 50 kHz Raytheon wide-beam transducer (model MCPT 25-05). The analog signal was recorded with a Raytheon JRC JFF-770 paper chart recorder. Chart and transceiver settings were held constant on all surveys. Navigation was by differential Global Positioning System (GPS), using a Magellan 52DX; accurate to ± 2 m) for all surveys. The cruising speed for the surveys ranged from 5.6 to 8.4 knots, (2.8 to 4.2 $ms^{-1}$) with an average of 7 knots (3.5 $ms^{-1}$). This produced paper records with a vertical exaggeration of 40:1, given the chart recorder speed.

The strength of acoustic returns from gas bubbles in water is proportional to the cross-sectional area of the bubbles [*Vagle and Farmer*, 1992]. A proportional relationship exists between scattering cross-section and bubble radius, except when the radius is equal to the resonance frequency of the source, in which case the effective cross section is about 2 orders of magnitude higher. For a 50 kHz source, the bubble resonant size is 0.1 mm radius [*Medwin*, 1977; *Vagle and Farmer*, 1992]. Measurements of bubble size distribution in photos of the ocean surface for the Coal Oil Point seep field indicate a dominant radius in the range of 1-15 mm, with a mean radius of 6 mm. We used a 50 kHz source in this study, because the seep bubble size distribution does not overlap with the resonant frequency diameter for this acoustic frequency. In a related study we also used 3.5 kHz sonar data

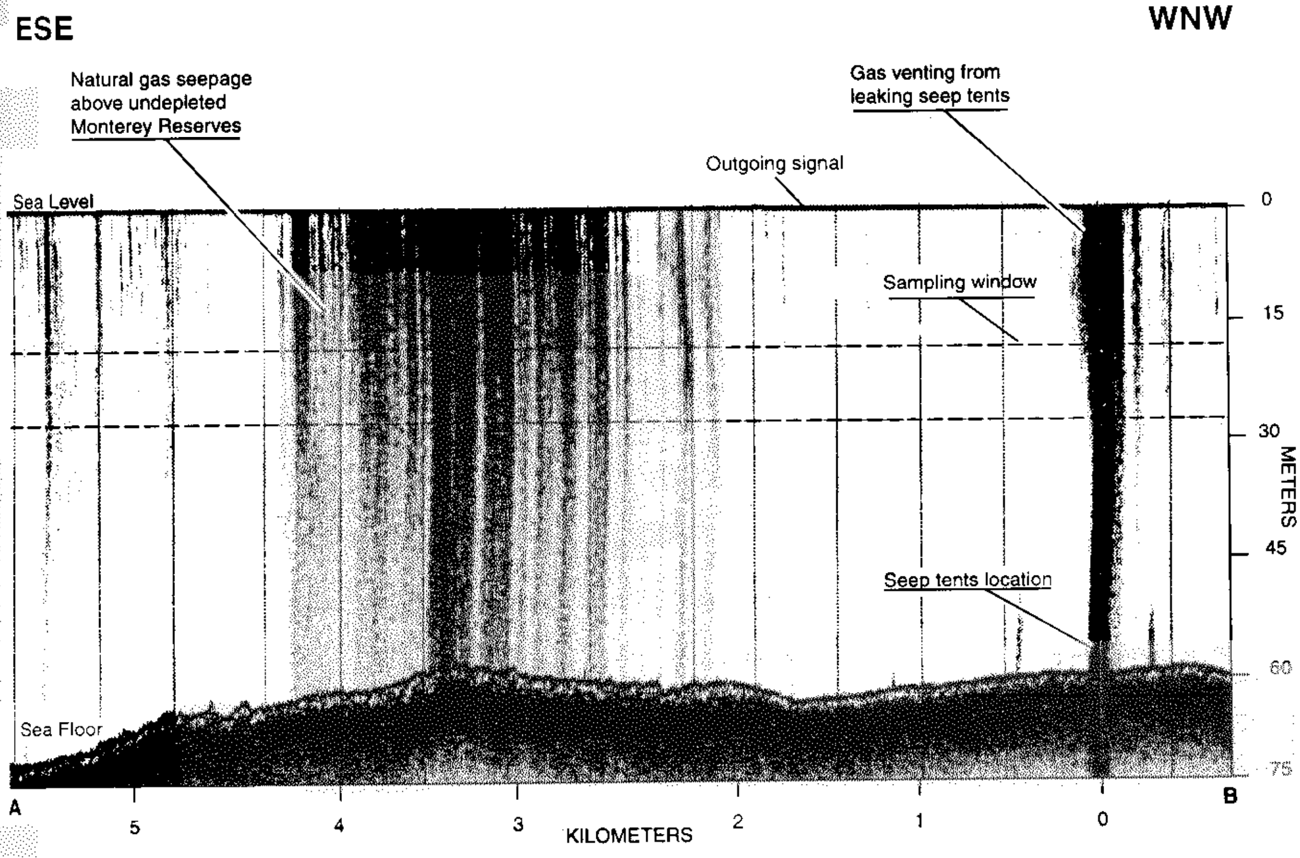

**Figure 2.** A 50 kHz sonar record along the axis of the South Ellwood anticline, offshore frm Coal Oil Point (location shown in Figure 3). Seep bubbles in the water column are shown as dark curtains. Thedashed line outlines the digital sampling window. The area of intense seepage in the east is named the La Goleta seep. Our quantitative estimateof seepage rate is 8.9 x $10^4$m$^3$ d$^{-1}$ (3.1 x $10^6$ feet$^3$ d$^{-1}$) for the La Goleta seep field and 1.3 x $10^4$m$^3$ d$^{-1}$ (4.7 x $10^5$ feet$^3$ d$^{-1}$) for the area around the seep tents. In addition to this uncontained seepage, the man-made seep tents were collecting 1.0 x 10m$^3$ d$^{-1}$) (3.5 x $10^5$ feet$^3$ d$^{-1}$) at the time this record was acquried (November 1994).

to quantify the emission rates [*Quigley*, 1997]. In the 3.5 kHz study the data were digitally recorded. However, we could not digitally record the 50 kHz data, because the digitization rate of our equipment was only 10 kHz.

Relative gas seepage volumes were quantified by digitally scanning the paper sonar records (Figure 2; 200 dots inch$^{-1}$; 256 gray scale) and then analyzing the relative darkness of the gray-scale digital images of the bubble plumes. This assumes that the seep bubble plume produces a paper sonar image that is darker for larger bubble populations (greater scattering cross section). A data window on the digital images between 25 to 37.5 ms reflection time below the transducer (which is equivalent to approximately 18 to 28 m below sea level) was extracted for quantitative evaluation. The relative signal darkness in this window was normalized to the strength of the outgoing sonar pulse (the primary signal recorded at the top of the chart; see Figure 2). The relative darkness of the image of the seep bubbles within the time window was computed from:

$$\delta = (\alpha - \beta)/(\gamma - \beta), \tag{1}$$

where $\delta$ is the fraction of the primary that returns as reflected energy, $\alpha$ is the mean gray-scale value of each vertical column of pixels within the data window, $\gamma$ is the mean gray-scale value of the primary signal, and $\beta$ is the mean gray-scale value of the background for that image. The values of $\delta$ were averaged along 30 m intervals of track, gridded with à 100 m grid spacing, and contoured (Figure 3).

Calibration of the 50 kHz sonar images to bubble plume volume was achieved by imaging bubbles leaking from compressed air bottles (scuba tanks) placed on the seafloor at 60 m. The bottles had a capacity of 2 m$^3$ (71.4 feet$^3$) of air (STP) at 2.27 x $10^7$ pascals (3300 psi). This is the size and pressure rating of commercially available scuba tanks. The *Genoa* made several profiles at 7 knots (3.5 ms$^{-1}$) over the leaking bottles in each experiment. The experiment was repeated at the end of each cruise with different leaking rates each time. The air was released through partially open regulators for a period of 30 to 40 min on the seafloor. The pressure in the bottles and time was recorded on the ship deck at the beginning and end of the deployment, and the amount of gas released was calculated from Boyle's law. The rate of leakage was assumed to be constant during the experiments.

The $\delta$ values are not linearly correlated with the release rate data (Figure 4). The 50 kHz recording system did not respond linearly, and it appears to saturate at high gas seepage rates, either because of the electronics or the chart paper or both. If high seepage rates caused saturation in our experiment, then we have underestimated the emission rates. A frequency distribution for 2700 data indicates that 90% of the sonar returns are within the linear range. Assuming that the chart recorder was responding linearly in the lower release rate experiments, the relationship between $\delta$– values and gas emission rates $E$ from the compressed air bottles is

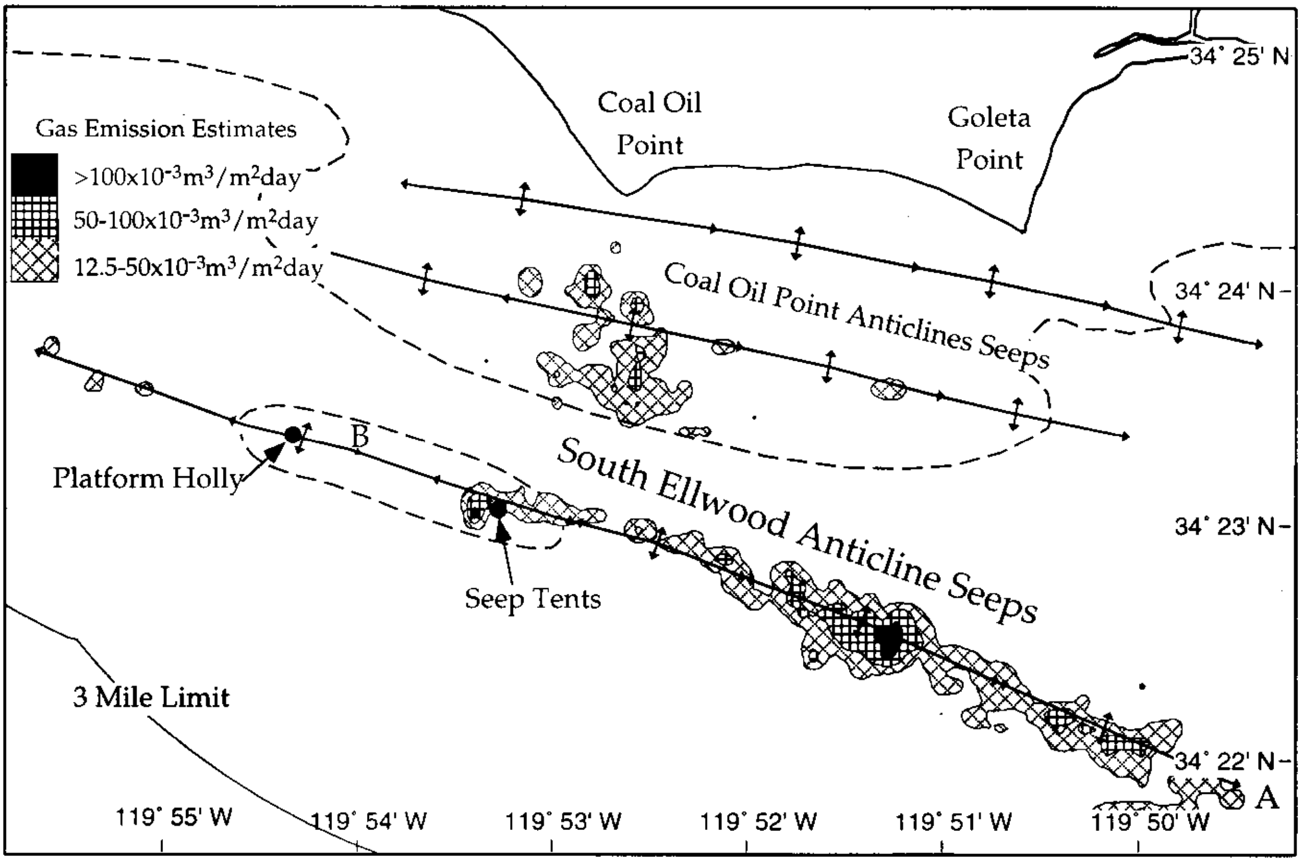

**Figure 3.** Map of seep intensity in the Coal Oil Point seep field. The seep intensity is espressed as a flux calculated from calibrated sonar data. The dashed line is the location of the formation contact between the Pliocene Sisquoc Formation and the Pleistocene Repetto Formation, where it intersects the seafloor or is uncomformably overlain by Holocene sediments. Anticlinal axes are also shown. The data in Figure 2 were taken along the anticlinal axis between points "A" and B."

$$E = c\,\delta A\,, \tag{2}$$

where $E$ is the emission rate in volume per area per day, $c$ is the calibration factor, and $A$ is the area of the sonar beam in the data window. The 50 kHz transducer has a focused beam width of 35°. At a depth of 23 m (the midpoint of the analysis window) this is equivalent to insonifying a 14 m wide swath. The area surveyed is then $A$ = track length x 14 m.

Fitting the data in the two lower release rate experiments through the origin gives $c = 0.117 \pm 0.006$ m$^3$m$^{-2}$d$^{-1}$ (error estimate is the first standard deviation). $R^2$ is 0.965 for three points. We assign a 95% uncertainty of 0.012 to $c$. This assigns about a 10% uncertainty to volume emission estimates; however, we arbitrarily use a higher uncertainty of 15% to account for other errors such as instrumental and interpretive errors.

From the value of $c$, the total gas flux to the ocean surface $J_g$ can be calculated from

$$J_g = c\,\Sigma\,(\delta_{av}\,A_{grid}), \tag{3}$$

where $\delta_{av}$ is the average value of normalized seep intensity at each grid node and $A_{grid}$ is the grid cell size used in the gridding process. The total gas flux $J_g$ was computed for all $\delta_{av} > 0$. This differs from the procedure used by *Quigley* [1997], who calculated total gas flux $J_g$ using only those grid nodes with $\delta_{av} > 0.10$ for the 50 kHz data. The procedure used by *Quigley* [1997] is inconsistent with the calibration technique described here and arbitrarily reduces the calculated emissions by 30% for the same data set (Table 1).

Our estimate of emission rates does not include the nearshore areas (north of 34°24'N), where our survey grid was inadequate to sample the shallow-water seeps (Figure 1). Three areas of visually intense seepage that are not included in our estimates are (1) the Isla Vista seep described by *Mikolaj and Ampaya* [1973], (2) the area of intense gas seepage near the Ellwood oil storage mooring, and (3) the area in shallow water immediately offshore from Coal Oil Point described by *Allen et al.* [1970].

Our estimate of seep emission rates assumes that the bubble size distribution of the seeps is the same as the size distribution of the air bubbles in the artificial release experiments. Visual estimates suggested that the air bubbles and seep bubbles were similar in size. However, we were not able to quantitatively measure the bubble sizes during the release experiments, owing to the short duration of the releases. A systematic error in the calibration method would result if the bubble size distribution in the calibration experiment is different from the size distribution of the natural seep bubbles. For example, if the mean radius of the air bubbles used in the calibration was twice as large as the mean radius of the seep bubbles, then the seep emission rates would be overestimated by approximately a factor of 2. This linear relationship assumes that the scattering cross section is proportional to the bubble radius and the bubble rise rate is the same for the two bubble sizes, which is approximately true for these size bubbles [*Vagle and Farmer*, 1992; *Wallis*, 1974].

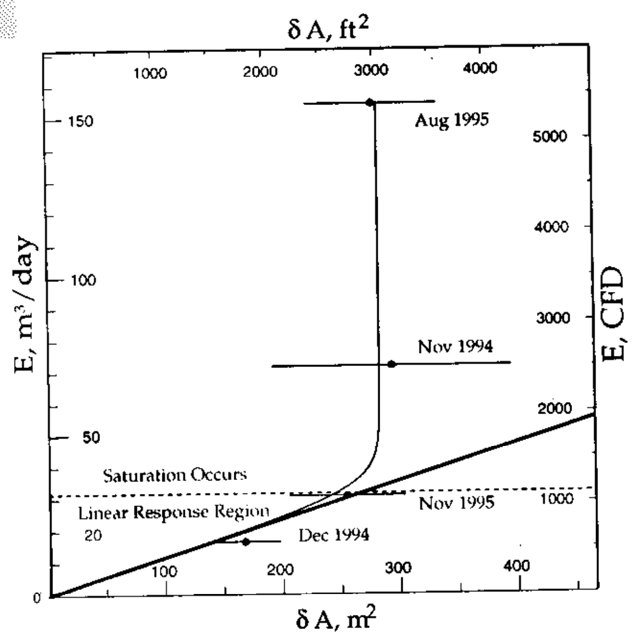

**Figure 4.** Calibration curve of emission rate $E$ (in cubic meters and feet per day) verses darkness of the sonar records in a sampled area $\delta \cdot A$ (in square meteres and feet) for 50 kHz sonar. The date of the survey during which the data was collected is given for each point on the curve. The calibration coefficient was determined by a linear fit through the origin to the two points with lowest emission rate for which the recordings did not appear to be saturating. Ninety percent of the natural seepage is within the linear range.

An alternative interpretation of the calibration data in Figure 4 is that the mean bubble size in the artificial release experiments was larger at higher release rates. If this is true, then we have best fit the calibration to the smallest bubble size distributions in the release experiments. This would result in an underestimate of the natural seepage rate, if the bubble size distribution for the natural seeps is larger than the smallest bubble sizes in the artificial releases. To investigate this possibility, we used a known seepage rate from the seep containment device to validate the calibration method. During the first survey in November 1994 there was a mechanical failure at one of the seep tents that caused 8500 m$^3$d$^{-1}$ to be released into the ocean from a depth of 50 m below sea level (Figure 2). The release rate due to this mechanical failure is well constrained, because the gases collected from the seep tents are measured daily by the Santa Barbara County Air Pollution Control District (SBCAPCD) [*Luyendyk et al.*, 1996]. The mechanical failure was repaired before the second cruise in December 1994. The computed gas flux from the vicinity of the seep tents during the first survey was 13,400 m$^3$d$^{-1}$, and during the second survey it was 7000 m$^3$d$^{-1}$ using the air bottle calibration method described above. The difference between these surveys yields a calculated emission rate of 6400 m$^3$d$^{-1}$ owing to the mechanical failure, compared with the metered emission rate of 8500 m$^3$d$^{-1}$. The emission rate from the failed seep tent was therefore underestimated by 25% (6400 versus 8500). This is equivalent to a 15% underestimate of the total emission rate from the vicinity of the seep tents in November, 1994 (i.e., the emission rate was underestimated by 2100 m$^3$d$^{-1}$ compared to a total emission rate of approximately 13400 m$^3$d$^{-1}$). This magnitude of error is consistent with the experimental errors found in our calibration experiments.

## 3. Emission Rates

The gas emission rate estimated from the 50 kHz data is 1.48 ± 0.22 x 10$^5$ m$^3$d$^{-1}$ (5.2 x 10$^6$ feet$^3$d$^{-1}$). In addition to this gas seepage, the seep containment tents located 1.5 km east of platform Holly captured 1.9 x 10$^4$ m$^3$d$^{-1}$ in late 1994. The total 1994-1995 gas emission rate from the Coal Oil Point seep field was therefore approximately 1.67 ± 0.3 x 10$^5$ m$^3$d$^{-1}$ (Table 1). The surveyed area of the nearshore Coal Oil Point seep field (between 34°23'17" and 34°24'N) composes 24% of the total seepage, whereas the seeps along the South Ellwood anticline compose 76% of the seepage (Figure 3).

We also surveyed the seep area using a 3.5 kHz sonar digitized at 10 kHz in the summers of 1995 and 1996. We ran an artificial source experiment in November 1996 to calibrate this 3.5 kHz system. This independent calibration experiment used compressed nitrogen released at different rates through diffusing nozzles deployed on the seafloor at approximately 40 m water depth. Our analysis of these sonar data suggests a seep flux of 2.03 ± 1.02 x 10$^5$ m$^3$d$^{-1}$ in July-September 1995 and 1.07 ± 0.54 x 10$^5$ m$^3$d$^{-1}$ in August 1996 for the Coal Oil Point seep field [*Quigley*, 1997] . This compares with the estimate of uncontained seepage (not including the tents) from the 50 kHz data of 1.48 ± 0.22 x 10$^5$ m$^3$d$^{-1}$, which is an average seepage rate from November 1994 to November 1995 (four surveys).

The seep gas captured by the seep containment device is composed of methane (88% by volume), nonmethane hydrocarbons (10%), and carbon dioxide and nitrogen (2%). Approximately 470 t of methane and 155 t of nonmethane hydrocarbons are contained in 1 million m$^3$ of seep gas. The methane emission rate therefore is 80 ± 12 td$^{-1}$ and the nonmethane hydrocarbon emission rate from the gas is 26 ± 4 td$^{-1}$.

**Table 1.** Calculated Emissions From Coal Oil Point Seeps

| | Total Gas, 10$^4$ m$^3$ d$^{-1}$ | |
|---|---|---|
| | This Paper [a] | *Quigley* [1997] [b] |
| 50 kHz | | |
| Total [c] | 16.8±2.5 | 11.8±5.9 |
| Holly area [c, d] | 3.6±0.5 | --- |
| 3.5 kHz, 1996 | | |
| Total [e] | --- | 11.7±5.9 |
| 3.5 kHz 1995 | | |
| Total [e] | --- | 21.3±10.7 |
| Holly area [d, e] | 3.6±0.5 | 3.30±1.7 |
| 1973 | | |
| Holly area [e] | 6.9±1.0 | 5.1±2.6 |

[a] Data were originally reported by *Luyendyk et al.* [1996]. Emissions were calculated for all $\delta > 0$ (see text).

[b] Calculated emission values are 30% lower for the 50 kHz data than reported in this paper, since *Quigley* [1997] only summed emissions for $\delta > 0.1$ (see text).

[c] Includes 1.86 x 10$^4$ m$^3$ d$^{-1}$ of natural seepage captured by the seep containment device (≅ 650,000 feet$^3$ d December 1994).

[d] Includes all seeps within a 2 km radius of the Holly oil platform.

[e] Includes 1.0 x 10$^4$ m$^3$ d$^{-1}$ captured by the seep containment device in 1995-1996 (≅ 350,000 feet$^3$ d$^{-1}$ in 1995-1996).

Oil is also emitted from the seeps and rises to the sea surface as both pure oil globules and oil on the rims of the seep gas bubbles. An oil collection experiment conducted in November 1995 established a gas-oil ratio at the seep containment tents of 94 cm$^{3}$ of oil per liter of gas [*Clester et al.*, 1996a]. Assuming that this gas-oil ratio applies for the entire Coal Oil Point seep field, the oil emission rate is 1.6x 10$^{4}$ Ld$^{-1}$ (100 barrels of oil per day). This is an underestimate, because it does not include the oil that seeps as pure oil globules closer to shore near Coal Oil Point. *Allen et al.* [1970] estimated the nearshore seepage rate at 50-70 barrels d$^{-1}$. Therefore about 150-170 barrels of oil d$^{-1}$ are leaking from the natural seeps here [*Clester et al.*, 1996b].

The seep oil that is emitted with the seep gas forms natural oil slicks on the ocean surface that rapidly evaporate and further contribute to air pollution in Santa Barbara County. Analysis of seep oil collected in the November 1995 experiment showed that 30% (by weight) is composed of aromatic compounds, 27% is saturates, and 43% is nonvolatile constituents (asphaltic and NSO compounds). This sample was collected after evaporating on the ocean surface for 3 hours, so it lost some of its volatile constituents prior to analysis. Over half (>57%) of the seep oil therefore evaporates into the atmosphere, and the other half is largely deposited on beaches as tar or enters the open ocean. The density of the seep oil is about 1.0 gm cm$^{-3}$ (10 API gravity). Consequently, we estimate that 9.1 td$^{-1}$ of nonmethane hydrocarbons are emitted into the atmosphere from the oil rims associated with the seep gas bubbles. The total amount of nonmethane hydrocarbons associated with the gas seeps that are emitted into the atmosphere (from both the seep gas and the associated bubble oil rims not including the nearshore oil seep sources) is estimated at 35 ± 7 td$^{-1}$ (= 26 + 9 td$^{-1}$). A 20% error is applied to the nonmethane hydrocarbon emission rate in order to account for the greater uncertainty in the gas/oil ratio than in the gas emission rate.

The current rates of emission of oil and gas from the natural seeps imply that large volumes of hydrocarbons have been released into the environment over the historical period that these seeps have been observed. At a rate of 150 barrels d$^{-1}$ the total oil seepage over the past 200 years would have been 11 million barrels. Assuming that there are currently 1 billion barrels of oil in place in the Monterey Formation offshore from Coal Oil Point, 1.8 x 10$^{4}$ years would be required for this subsurface reservoir to be drained at the current oil seepage rate. The gas seepage may have a shorter life span. Oil production at Platform Holly suggests that there are 9 ± 3 m$^{3}$ of gas dissolved in each barrel of oil in the subsurface. This implies a reservoir of 9 ± 3 x 10$^{9}$ m$^{3}$ of gas or a 150 ± 50 year supply at current gas seepage rates. These calculations assume that there is no recharge of the reservoir by subsurface hydrocarbon migration. The source rocks in the Monterey Formation in the basin to the south of Coal Oil Point (the Offshore Ventura Basin; see *Ogle et al.*, [1987]) are the source for the oil and gas in the Monterey reservoir. They are currently experiencing peak thermal maturity and are expelling large volumes of hydrocarbons at the present time. This has been demonstrated for the Ventura Avenue oil field, which contains over 1 billion barrels of oil [*California Division of Oil and Gas*, 1991], but formed less than 7 x 10$^{5}$ years ago [*Sarna-Wojcicki et al.*, 1991]. The Ventura Avenue field is located on the same anticlinal trend as the South Ellwood field. Continual recharge of the Monterey Formation with hydrocarbons would prolong the life of the natural gas seepage by many thousands of years.

## 4. Discussion

The areas of natural gas seepage correspond to structural highs along the anticlinal axes of three east-west trending anticlines on the shelf offshore from Coal Oil Point [*Dibblee*, 1966; Figure 3]. Well data and three-dimensional seismic reflection data indicate that there are three structural highs along the axis of the South Ellwood anticline (Figure 3): (1) at the center of the "La Goleta" seep near 119°51.4'W [*Wilkinson*, 1972], (2) at the seep tents, and (3) at the location of platform Holly. All three structural culminations were sites of active seepage in 1946-1947, 1953-1958, and 1972-1973 [*Fischer and Stevenson*, 1973; *Fischer*, 1977]. The older surveys show an apparent larger area of seepage than today (Figure 1 versus Figure 3). This could be a real effect, or it could be due to the different mapping techniques used in the older surveys, which were based on seafloor sampling (dart cores) and visual observations at the sea surface using relatively inaccurate navigation in 1946-1947 and 1953-1958. Our surveys, which were conducted in 1994 and 1995, found detectable hydrocarbon seepage over an area of 12.5 km .

Comparison of 3.5 kHz sonar profiles acquired by us in July 1995 with similar profiles collected in July 1973 by P. Fischer suggests that an 80% reduction in natural seepage rate has occurred within 1 km of platform Holly over this 22 year period [*Washburn et al.*, 1996]. Quantitative analysis of the analog sonar records, using the same technique described in this paper, suggests a decrease in seepage rate from 6.9 x 10$^{4}$ m$^{3}$d$^{-1}$ to 3.6 x 10$^{4}$ m$^{3}$d$^{-1}$ within 2 km of Platform Holly between 1973 and 1995 (Table 1). This 50% reduction in seepage rate is equivalent to about a 20 barrel d$^{-1}$ reduction in oil seepage rate and a decrease in nonmethane hydrocarbon emissions to the atmosphere of 7 td$^{-1}$. This decrease may be due to the reduction in subsurface reservoir pressure related to oil production [*Quigley*, 1997]. This possibility was originally suggested by *Fischer* [1977] and *Fischer and Stevenson* [1973]. A reduction in natural hydrocarbon seepage rates due to oil production has also been reported in Texas, Venezuela, and Iraq [*Horvitz*, 1972; *Landes*, 1973]. The large reduction in the amount of tar found on Santa Barbara beaches between 1958 and 1977 may also be due to offshore oil production [*Mertz*, 1959; *Welday*, 1977].

The nonmethane hydrocarbon emission rate from the gas seeps that we surveyed offshore from Coal Oil Point is estimated to be 35 ± 7 td$^{-1}$. These nonmethane hydrocarbons are reactive organic gases that are catalysts for the formation of tropospheric ozone, which is a health hazard if found in high concentrations (i.e., urban smog). The nonmethane hydrocarbon fraction of the seep gases include 20% by weight ethane [*Taylor and Scholle*, 1981]. Currently, the Environmental Protection Agency excludes ethane as an ROG; we include this gas in order to be consistent with earlier ROG estimates reported for Santa Barbara County. The seep field ROG emission rate we determined is about twice the predicted ROG emission rate from all the on-road vehicle traffic in Santa Barbara County of 17 td$^{-1}$ for 1990 [*SBCAPCD*, 1989]. Furthermore, our estimate of ROG emission rates from the seeps at Coal Oil Point is 3 times as large as the official Santa Barbara County Air Pollution Control District's seep

ROG emission estimate of 10 $td^{-1}$ for 1990. Our estimate of the ROG emissions associated with the gas seeps does not include the 50-70 barrels $d^{-1}$ of oil seepage from the nearshore Coal Oil Point and Isla Vista seeps described by *Allen et al.* [1970] and *Mikolaj and Ampaya* [1973]; therefore the actual ROG emission from the seep field is larger than 35 $td^{-1}$. These emission rates are large compared to the ROG emission rates from operations at platform Holly and its associated onshore oil processing facilities (0.5 metric $td^{-1}$ [*SBCAPCD*, 1994]), which are tightly regulated by Santa Barbara County.

Hydrocarbon seeps comprise the largest source of marine methane emissions [*Judd and Hovland*, 1992]. *Hovland et al.* [1993] arrived at a global flux estimate for methane from natural marine hydrocarbon seepage of 8-65 Tg $CH_4$ $yr^{-1}$ (Tg = trillion grams $yr^{-1}$; 8-65 million $tyr^{-1}$). They used an estimate of 400 gm $CH_4$ $m^{-2}$ $yr^{-1}$ and 18 $km^2$ area for the Coal Oil Point seep field to fix the upper limit of seep emission rates for an assumed lognormal probability distribution of seep sizes throughout the world. The mean emission rate for high seepage areas was calculated to be 4.7 to 38 g $CH_4$ $m^{-2}$ $yr^{-1}$ from this log normal distribution (Table 2). They then extrapolated this rate to the remainder of the world's continental shelf areas that have high seepage potential (an area of $1.7 \times 10^6$ $km^2$) to obtain a global methane emission rate of 8 to 65 Tg $yr^{-1}$. This range assumes that the Coal Oil Point seeps represent a seepage rate that is only exceeded by 0.1% and 1% of all marine seepage areas.

Our results yield a mean methane emission rate for the Coal Oil Point seep field of 1600 gm $CH_4$ $m^{-2}$ $yr^{-1}$, which is 4 times the estimate used by *Hovland et al.* [1993] to estimate the global methane marine seepage emission. We have revised the *Hovland et al.* [1993] estimate by using their methodology but with a better estimate of seepage rate at Coal Oil Point. Assuming the same minimum seepage rate (at 99.9% and 99% probability levels) as *Hovland et al.* [1993] and our estimate of 1600 gm $CH_4$ $m^{-2}$ $yr^{-1}$ (for the 0.1% and 1% probability levels) yields a mean (expected value) estimate of 15 to 208 g $CH_4$ $m^{-2}$ $yr^{-1}$ for average marine seepage rates in areas with high seepage potential (Table 2). A more likely estimate results if the lognormal distribution is truncated, so that 1600 gm $CH_4$ $m^{-2}$ $yr^{-1}$ is the maximum emission rate for natural seepage in the marine environment. Truncating the lognormal distribution at the value estimated for the Coal Oil Point seeps is consistent with the observation that this is one of the most active seepage areas in the world. The truncated distribution results in a mean methane emission rate of 10 to 28 g $CH_4$ $m^{-2}$ $yr^{-1}$ (Table 2). Extrapolating this range to the high seepage potential areas of the world's continental shelves produces a global methane flux estimate of 18 to 48 Tg $yr^{-1}$ for marine seepage.

**Table 2.** Lognormal Estimation of Global Methane Emission Rates for Marine Seepage Area.

| Probability[a] | *Hovland et al.* [1993] | This Paper | |
|---|---|---|---|
| | EV | EV [b] | EV With Truncation [b,c] |
| | *Mean Global Methane Emission* gm CH4 $m^2$ $yr^{-1}$ | | |
| *P*(1%) | 38 | 208 | 28 |
| *P*(0.1%) | 4.7 | 15 | 10 |
| | *Total Global Methane Emission* Tg CH4 $yr^{-1}$ | | |
| *P*(1%) | 65 | 353 | 48 |
| *P*(0.1%) | 8 | 26 | 18 |

[a] Probability is that the Coal Oil Point seeps have a seepage rate that is only exceeded by 0.1% and 1% of all seepage in the world's "high seepage potential areas."

[b] Values denote expected value (mean) of lognormal distribution with P(99%) or P(99.9%) probability of emission rate greater than $1.5 \times 10^4$ g CH4 $m^{-2}$ $yr^{-1}$ and *P*(1%) or *P*(0.1%) probability greater than 1600 g CH4 $m^{-2}$ $yr^{-1}$.

[c] Values denote expected value (mean) of lognormal distribution that is truncated at *P*(1%) or *P*(0.1%) probability of emission equal to 1600 g CH4 $m^{-2}$ $yr^{-1}$.

The Intergovernmental Panel on Climate Change assigns 10 Tg $yr^{-1}$ to natural seepage from all geological sources [*Houghton et al.*, 1995]. This IPCC value is far less than both the original estimates of *Hovland et al.* [1993] and our new estimate of 18 to 48 Tg $yr^{-1}$, based on emission estimates for the Coal Oil Point seep field. The total methane flux to the atmosphere is about 510 Tg $yr^{-1}$ [*Khalil and Rasmussen*, 1995]. Our estimate of methane emission from the natural seepage on the continental shelves is equivalent to 3% to 9% of global methane emissions. This estimate may only represent half of the natural methane seepage, because less than half of the world's hydrocarbon basins occur offshore. A larger estimate for global natural seepage rates would help to explain the unknown source of isotopically heavy methane in the global methane budget [*Crutzen*, 1991; *Lacroix*, 1993].

## 5. Conclusions

The ROG emission rates from the Coal Oil Point seeps are a large source of hydrocarbon pollution in Santa Barbara county (equal to twice the emission rate from all the on-road vehicle traffic in the county in 1990). Santa Barbara County has had difficulty reaching Environmental Protection Agency (EPA) air quality standards, in spite of vigilant regulation of industrial sources of ROGs and large reductions in automobile emissions over the past decade. The ROG emission rates found in our study for Coal Oil Point gas seeps (35 $td^{-1}$) are 3 times the seep ROG emission rates estimated in the official Santa Barbara County air emission inventory [*SBCAPCD*, 1994]. Furthermore, *Fischer* [1977] estimated that the Coal Oil Point seep field contains only half of the marine seeps in Santa Barbara County. The official Santa Barbara County Air Pollution Control District estimate of seep ROGs in all of that county (14.5 $td^{-1}$) is therefore too low by at least a factor of 4. Reaching EPA air quality attainment status in Santa Barbara County may require an effective means of containing or remediating the natural seeps.

The decrease in hydrocarbon seepage rate near platform Holly, possibly due to the reduction in subsurface reservoir pressure, suggests that oil production here has resulted in an unexpected benefit to the atmosphere and marine environment. Natural hydrocarbon seepage is frequently found above oil fields throughout the world [*Link*, 1952]. If the decrease in natural seepage found near Platform Holly is representative of the effect of oil production on seepage worldwide, then this has the potential to significantly alter global oil and gas seepage in the future. On a local level a reduction in seepage due to oil production can have a profound effect on the air and water quality. For example, if the 50% reduction in natural seepage rate that occurred around Platform Holly also occurred because of future oil production from the oil field beneath the La Goleta seep, this would result in a reduction in nonmethane hydrocarbon emission rates equivalent to removing half of the on-road vehicle traffic from Santa Barbara County. In addition, a 50% reduction in seepage from the La Goleta seep would remove about 25 barrels of oil per day from the sea surface, which in turn would result in a 15% reduction in the amount of tar found on Santa Barbara beaches.

Our study suggests that global estimates of natural hydrocarbon gas seepage may be too low. Using the global emission estimate of 18-48 Tg of methane per year proposed here implies that 3-9% of the global methane flux is due to natural hydrocarbon seepage on continental shelves. A large contribution from onshore natural seepage is also expected, based on the size of onshore hydrocarbon basins compared with the extent of continental shelf hydrocarbon basins. The rate of increase in global methane atmospheric concentrations has been decreasing for the past 20 years [*Houghton et al.*, 1996]. A worldwide decrease in natural hydrocarbon seepage related to onshore and offshore oil production may be causing a global reduction in natural methane emission rates.

**Acknowledgments.** This study was funded by the University of California Energy Institute. Additional support provided by the Minerals Management Service, U.S. Department of the Interior, under MMS Agreement No. 14-35-0001-30758. The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either express or implied, of the U.S. Government. We thank the captains of the *Genoa* and the *Sea Watch*, Gordon Cota, Fred Sanford, Dan Francis, Erik Bartsch, and Loren Luyendyk for their assistance. Libe Washburn and Jordan Clark provided valuable discussions throughout the project. Contribution of the Institute for Crustal Studies number 0338-94TC.

## References

Allen, A. A., R.S. Schleuter, and P.G. Mikolaj, Natural oil seepage at Coal Oil Point, Santa Barbara, California, *Science*, *170*, 974-977, 1970.

Bauer, J. E., R. B. Spies, J. S. Vogel, D. E. Nelson, and J. R. Southon, Radiocarbon evidence of fossil-carbon cycling in sediments of a nearshore hydrocarbon seep, *Nature*, *348*, 230-232, 1990.

California Division of Oil and Gas, California Oil and Gas Fields, vol. 2, Southern, Central and Offshore California, 3rd ed., *Publ. TR12*, Sacramento, 1991.

Clester, S.M., J. S. Hornafius, J. Scepan, and J. E. Estes, Quantification of the relationship between natural gas seepage rates and surface oil volume in the Santa Barbara Channel, (abstract) *Eos Trans. AGU*, *77*, (46), Fall Meet. Suppl., F419, 1996a.

Clester, S.M., J. S. Hornafius, J. Scepan, and J. E Estes, Remote sensing study of historical changes in natural oil slick volumes in the Santa Barbara Channel: Final Report 1995/1996, Calif. Energy Stud. Project, Univ. of Calif. Energy Inst., Berkeley, 1996b.

Crutzen, P. J., Methane's sinks and sources, *Nature*, *350*, 380-381, 1991.

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

Dando, P. R., and M. Hovland, Environmental effects of submarine seeping natural gas, *Cont. Shelf Res.*, *12*, 1197-1207, 1992.

Davis, P. H., and R. B. Spies, Infaunal benthos of a natural petroleum seep: study of community structure, *Mar. Biol.*, *59*, 31-41, 1980.

Dibblee, T. W., Jr., Geology of the Central Santa Ynez Mountains, Santa Barbara, California, *Bull. Calif. Div. Mines Geol.*, *186*, 84 pp., 1966.

Estes, J. E., R. E. Crippen, and J. L. Star, Natural oil seep detection in the Santa Barbara Channel, California, with Shuttle imaging radar, *Geology*, *13*, 282-284, 1985.

Fischer, P. J., Natural gas and oil seeps, Santa Barbara basin, California, in California Offshore Gas, Oil, and Tar Seeps, Staff report, pp. 1-62, State of Calif., State Lands Comm., Sacramento, 1977.

Fischer, P. J., and A. J. Stevenson, Natural hydrocarbon seeps, Santa Barbara basin, in *Santa Barbara Channel Area Revisited Field Trip Guidebook*, vol. 3, edited by P. J. Fischer, pp. 17-28, Am. Assoc. of Pet. Geol., Tulsa, Okla., 1973.

Guliev, I. S., and . A. A. Feizullayev, Geochemistry of hydrocarbon seepages, in *Hydrocarbon Migration and Its Near-Surface Expression, AAPG Mem.*, *66*, 63-70, 1996.

Hartman, B., and D. Hammond, The use of carbon and sulfur isotopes as correlation parameters for the source identification of beach tar in the southern California borderland, *Geochim. Cosmochim. Acta*, *45*, 309-319, 1981.

Horvitz, L., Vegetation and geochemical prospecting for petroleum, *AAPG Bull.*, *56*, 925-940, 1972.

Houghton, J.T., L.G. Meira Filho, J. Bruce, H. Lee, B.A. Callander, E. H., N. Harris, and K. Maskell, (Eds.), *Climate Change 1994*, Cambridge Univ. Press, New York, 1995.

Houghton, J.T., L.G. Meira Filho, J. Bruce, Hoesung Lee, B.A. Callander, N. Harris, Kattenberg, A., and K. Maskell, (Eds.), *Climate Change 1995*, Cambridge Univ. Press, New York, 1996.

Hovland, M., and A. G. Judd, The global production of methane from shallow submarine sources, *Cont. Shelf Res.*, *12*, 1231-1238, 1992.

Hovland, M., A.G. Judd, and R.A. Burke, The global flux of methane from shallow submarine sediments, *Chemosphere*, *26*, 559-578, 1993.

Judd, A. G. and M. Hovland, The evidence of shallow gas in marine sediments, *Cont. Shelf Res.*, *12*, 1081-1095, 1992.

Khalil, M. A. K., and R. A. Rasmussen, The changing composition of the Earth's atmosphere, in *Composition, Chemistry, and Climate of the Atmosphere*, edited by H. B Singh, pp. 50-87, Van Nostrand Reinhold, New York, 1995.

Killus, J. P., and G. E. Moore, Factor analysis of hydrocarbon species in the south-central coast air basin, *J. Appl. Meteorol.*, *3*, 733-743, 1991.

Kolpack, R. L., Relationship of migration of natural seep material to oceanography of Santa Barbara Channel, in California Offshore Gas, Oil, and Tar Seeps, Staff report, pp. 226-255, State Lands Comm., State of Calif., Sacramento, 1977.

Kraus, S. P., and J. E. Estes, Oil seep survey over Coal Oil Point and Santa Barbara Channel, California, October 1976, in California Offshore Gas, Oil, and Tar Seeps, Staff report, pp. 323-346, State Lands Comm., State of Calif., Sacramento, 1977.

Kraus, S. P., J. E. Estes, and Atwater, S. G., Radar detection of surface oil slicks, *Photogramm. Eng. Remote Sens.*, *43*, 1523-1531, 1977.

Lacroix, A.V., Unaccounted-for sources of fossil and isotopically-enriched methane and their contribution to the emissions inventory: A review and synthesis, *Chemosphere*, *26*, 507-557, 1993.

Landes, K. K., Mother nature as an oil polluter, *AAPG Bull.*, *57*, 637-641, 1973.

Link, W. K., Significance of oil and gas seeps in world oil exploration, *AAPG Bull.* *36*, 1505-1540, 1952.

Luyendyk, P. B., J.S. Hornafius, R. D. Quigley, and J. Francis, Geophysical investigation to determine impacts of oil production on natural hydrocarbon seepage in the Santa Barbara Channel Final Rep. 1995/1996, Calif. Energy Stud. Project, Univ. of Calif. Energy Inst., Berkeley, 1996.

MacDonald, I. R., N. L. Guinasso Jr., S. G. Ackleson, J. F. Amos, R. Duckworth, R. Sassen, and J. M. Brooks, Natural oil slicks in the Gulf of Mexico visible from space, *J. Geophys. Res.*, *98*, 16,351-16, 364, 1993.

Medwin, H., Counting bubbles acoustically: A review, *Ultrasonics*, *15*, 7-13, 1977.

Mertz, R. C., Determination of the quantity of oil substances on beaches and in nearshore waters, *Publ. 21*, 45 pp., State Water Pollut. Control Board, Scramento, 1959.

Mikolaj, P.G., and J.P. Ampaya, Tidal effects on the activity of natural submarine oil seeps, *Mar. Technol. Soc. J.*, *7*, 25-28, 1973.

Ogle, B. A., W. S. Wallis, R. G. Heck, and E. B. Edwards, Petroleum geology of the Monterey Formation in the offshore Santa Maria/Santa Barbara areas, in *Cenozoic Basin Development of Coastal California*; edited by R. V. Engersoll, and W. G. Ernst, pp. 382-406, Prentice Hall, Englewood Cliffs, N.J., 1987.

Quigley, D., Quantitative spatial and temporal variations in the distribution of natural marine hydrocarbon seeps in the Santa Barbara Channel, California, M.S. thesis, Univ. of Calif., Santa Barbara, 1997.

Reed, W. E., and I. R. Kaplan, The chemistry of marine petroleum seeps, *J. of Geochem. Explor.*, *7*, 255-293, 1977.

Rintoul, W., ARCO caps Santa Barbara Channel Seep, *Pac. Oil World, 74*, 6-9, 1982.

Santa Barbara County Air Pollution Control District (SBCAP), *The 1990 Air Quality Attainment Plan*, Appendix B, Table B-39, Santa Barbara, Calif., 1989.

Santa Barbara County Air Pollution Control District (SBCAP), *The 1994 Clean Air Plan*, Appendix D, Table 3.2, Santa Barbara, Calif., 1994.

Sarna-Wojcicki, A. M., K. R. Lajoie, C. E. Meyer, D. P. Adam, and H. J. Rieck, Tephrochronologic correlation of upper Neogene sediments along the Pacific margin, conterminous United States, in *The Geology of North America*, vol. K-2, *Quaternary Nonglacial Geology: Conterminous United States*, edited by R. B. Morrison, pp. 117-140, Geol. Soc. of Am., Boulder, Colo., 1991.

Spies, R. B., and P. H. Davis, The infaunal benthos of a natural oil seep in the Santa Barbara Channel, *Mar. Biol., 50*, 227-237, 1979.

Spies, R. B., and D. J. Desmarais, Natural isotope study of trophic enrichment of marine benthic communities by petroleum seepage, *Mar. Biol., 73*, 67-71, 1983.

Sweet, W.E., Marine acoustical hydrocarbon detection, paper presented at 5th Annual Offshore Technology Conference, Am. Inst. of Min., Metal., and Pet. Eng., Inc., Houston, Tex., April 30 to May 2, 1973.

Taylor, G. H., and C. R. Scholle, An emission measurement program at a naturally-occurring oil and gas seep off the Santa Barbara Coast, Rep. *SBAQ-81-3*, 19 pp., ARCO Oil and Gas Co., Am. Weather Consult., Salt Lake City, Utah, 1981.

Vagle, S., and Farmer, D. M., The measurement of bubble-size distributions by acoustical backscatter, *J. Oceanic Atmos. Technol., 9*, 630-644, 1992.

Wallis, G. B., The terminal speed of single drops or bubbles in an infinite medium, *Int. J. Multiphase Flow, 1*, 491-511, 1974.

Washburn, L., J.S. Hornafius, B. P. Luyendyk, J.F. Clark, D.C. Quigley, and R. D. Francis, Dispersal of hydrocarbon gas plumes from seafloor seeps in the Northern Santa Barbara Channel, Calif. (abstract), *Eos Trans., AGU, 77* (46), Fall Meet. Suppl., F419, 1996.

Welday, E. E., Oil and Tar on Santa Barbara region beaches, in California Offshore Gas, Oil, and Tar Seeps; Staff report, pp. 347-371, State Lands Comm., State of Calif., Sacramento, 1977.

Wilkinson, E. R., California Offshore Oil and Gas Seeps, *Publ. TR08*, 11 pp., Calif. Div. of Oil and Gas, Sacramento, 1972.

Wilson, R. D., P. H. Monaghan, A. Osanik, L. C. Price, and M. A. Rogers, Natural marine oil seepage, *Science, 184*, 857-865, 1974

J. S. Hornafius, Mobil Oil Corporation, 1250 Poydras St., New Orleans, LA 70113. (scott-hornafius@email.mobil.com)

B. P. Luyendyk and D. Quigley, Department of Geological Sciences, University of California, Santa Barbara, CA 93106. (luyendyk@geology.ucsb.edu)

(Received February 28, 1998; revised December 1, 1998; accepted March 8, 1999.)