Variability of gas composition and flux intensity in natural marine hydrocarbon seeps

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Abstract The relationship between surface bubble composition and gas flux to the atmosphere was examined at five large seeps from the Coal Oil Point seep field (Santa Barbara Channel, CA, USA). The field research was conducted using a flux buoy designed to simultaneously measure the surface bubbling gas flux and the buoy’s position with differential GPS, and to collect gas samples. Results show that the flux from the five seeps surveyed a total of 11 times ranged from 800–5,500 m³ day⁻¹. The spatial distribution of flux from the five seeps was well described by two lognormal distributions fitted to two flux ranges. The seafloor and sea surface composition of bubbles differed, with the seafloor bubbles containing significantly more CO₂ (3–25%) and less air (N₂ and O₂). At the sea surface, the mole fraction of N₂ correlated directly with O₂ (R² = 0.95) and inversely with CH₄ (R² = 0.97); the CO₂ content was reduced to the detection limit (<0.1%). These data demonstrate that the bubble composition is modified by gas exchange during ascent: dissolved air enters, and CO₂ and hydrocarbon gases leave the bubbles. The mean surface composition at the five seeps varied with water depth and gas flux, with more CH₄ and higher CH₄/N₂ ratios found in shallower seeps with higher flux. It is suggested that the CH₄/N₂ ratio is a good proxy for total or integrated gas loss from the rising bubbles, although additional study is needed before this ratio can be used quantitatively.

Introduction

Natural hydrocarbon seeps are important contributors to the global carbon cycle. They are conduits for the transfer of buried sedimentary carbon, which takes the form of methane (CH₄) and other heavy hydrocarbons including oil, to the atmosphere and ocean. How important marine seeps are to the atmospheric CH₄ cycle is debatable and depends on assumptions about the ability of the ocean to dissolve CH₄ released either as bubbles or pieces of hydrates at the seafloor. The ocean is potentially a significant barrier because it is able to absorb and oxidize these gases in situ (Reeburgh 2003, 2007).

Seafloor vents create plumes of rising bubbles, which have been observed in a variety of environments (for a summary of locations, see Judd and Hovland 2007). Large bubble plumes, such as those observed in the Santa Barbara Channel, modify the environment of the near-field water column (e.g., Leifer et al. 2000). In addition to creating large gradients in dissolved gas concentrations due to bubble–water gas transfer, the rising bubble plumes entrain ambient ocean water and generate upward vertical flows (e.g., McDougal 1978; Schladow 1992; Leifer et al. 2000, 2006; Zhang 2003; Clark et al. 2003). Thus, the upward movement of bubbles results from their own buoyancy and the rising column of plume water. Because the total amount of gas dissolving into the water column depends upon the integrated flux over the bubbles’ lifetime, the rise velocity is important. Large bubble plumes that generate strong

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vertical flows significantly decrease the transit time from the seafloor to the surface, and thus increase the flux of seep gas to the atmosphere.

The gas exchange rate and direction are determined by the concentration gradient across the bubble–water interface. Carbon dioxide (CO₂), CH₄, and other hydrocarbon gases are transferred out of rising bubbles, while nitrogen (N₂), oxygen (O₂), and other dissolved gases are transferred into the bubbles. Plume processes that affect the amount of gas exchange include plume-water saturation and the generation of upward vertical flows. Limited field observations (e.g., Leifer et al. 2000, 2006) suggest that both of these processes scale with flux. Furthermore, gas exchange rates are dependent on bubble size, and recent observations indicate that bubble size distributions differ above strong and weak seafloor vents (Leifer and Culling 2010, this issue). Strong vents emit a broader bubble spectrum, which includes large bubbles. Model calculations indicate that a smaller fraction of the initial mass dissolves from large bubbles than from small bubbles during transit through the water column (Leifer and MacDonald 2003). Modeling studies also indicate that oil on the bubble walls can slow the rate of gas exchange between the bubbles and plume water.

This paper addresses the relationship between bubbling gas flux to the atmosphere and gas composition using field measurements from the Coal Oil Point seep field. We evaluate the hypothesis that the composition of the bubbles at the sea surface can be used as a proxy for the amount of gas exchange that occurs during the bubbles’ transit through the water column. We hypothesized that, due to seep hydrodynamics, bubbles above stronger seeps would contain more hydrocarbon gases (e.g., CH₄) and less air (N₂ and O₂) than would bubbles at weaker seeps. Verification of this hypothesis would imply that (1) compared with seeps with higher flux, a greater fraction of the gas released at the seafloor from seeps with lower flux dissolves into the water column, and (2) large seeps are less efficient at transferring CH₄ and other hydrocarbon gases into the water column, and more efficient at transferring these gases to the atmosphere.

Field site

The Coal Oil Point seeps are a regional source of hydrocarbons to the atmosphere and ocean. The seeps are located in Santa Barbara County, CA, offshore of the University of California, Santa Barbara (Fig. 1), about 10 km west of the city of Santa Barbara. At various locations within this seep field, bubbles are observed to rise through the water column to the surface, creating areas of bursting bubbles at the sea surface. In addition to contributing significant amounts of tar to regional beaches (Del Sontro et al. 2007) and to the seafloor (Farwell et al. 2009), these seeps are known sources of CH₄ and other hydrocarbon gases to the regional air column (Killus and Moore 1991; Hornafius et al. 1999), and of dissolved hydrocarbons to the coastal ocean (Clark et al. 2000; Mau et al. 2007, 2010, this issue). Sonar surveys suggest that the total gas flux to the atmosphere is on the order of 1×10⁵ m³ day⁻¹ (Hornafius et al. 1999). Assuming an average composition of 60% CH₄ (see below), the CH₄ flux is approx. 30 mol s⁻¹ (1.5×10⁻⁵ Tg year⁻¹). An approximately equal amount of CH₄ dissolves above the seafloor vents (Clark et al. 2000), creating a plume that extends for 10 s to 100 s of km in the Santa Barbara Channel (Clark et al. 2000; Mau et al. 2007) and the Southern California Bight (Cynar and Yayanos 1992).

The Coal Oil Point seep field has been mapped numerous times using visual observations of surface and seafloor features (i.e., bursting bubbles, seafloor vents, etc.), remote sensing, and sonar surveys (Allen et al. 1970; Fischer 1978; Estes et al. 1985; Hornafius et al. 1999; Quigley et al. 1999; Leifer et al. 2004, 2010, this issue; Kinnaman et al. 2010, this issue). These studies have revealed that seepage occurs within an area of approx. 20 km² at water depths ranging from about 10–70 m (Fig. 1). At any given time the total area of bursting bubbles at the sea surface is much smaller, and is distributed among distinct regions determined by the seafloor geology (Hornafius et al. 1999; Leifer et al. 2010, this issue). Seep flux, defined as gas volume emitted per area of sea surface at standard pressure and temperature, is highly variable in space and time. Objective mapping of bubbling gas flux using a flux buoy (Washburn et al. 2001) showed that spatial scales over which bubbling gas flux was correlated were typically a few meters, and that areas of strong flux range from a few hundred to several thousand
that the source functions of CH4 and other gases are not constant in time (e.g., Quigley et al. 1999; Leifer et al. 2004; Leifer and Boles 2005; Kinnaman et al. 2010, this issue). Temporal variations have been associated with a number of physical processes including surface gravity waves (Leifer and Boles 2005), tides (Boles et al. 2001), and longer-term changes resulting from anthropogenic hydrocarbon production (Quigley et al. 1999). Visual observations of surface bubbles reveal changes in gas flux on time scales of seconds to minutes due to rising “curtains” of bubbles, and possibly flux variability in seafloor vents. At least one large seep, referred to as the Trilogy seep, became active sometime between 1999 and 2005 due to processes that are unclear.

Seeps within the Coal Oil Point field also exhibit a broad range of sizes. The smallest are vents from which small streams of individual bubbles with narrow bubble size distributions emanate. Also commonly found are larger vents, typically crater seeps with diameters of 1 m or less, which form bubble plumes with a broad size distribution. Bubble radii in these plumes range from <500 to >5,000 µm (Leifer et al. 2006; Leifer and Culling 2010, this issue). This type of seep has been found in SCUBA and submersible surveys to form the bubble curtains previously observed near the sea surface. In areas of the seafloor where numerous point and crater seeps are located together, bubble streams combine into single large plumes with high vertical flow velocities and elevated dissolved CH4 concentrations. The surface expressions of these combined seeps can be easily identified from surveying vessels, and are characterized by large areas of bursting bubbles with corresponding divergent surface flows.

Materials and methods

Seepage flux at the sea surface was determined with the flux buoy, a ~3 m long spar buoy and associated instrumentation that measures gas flux by capturing bubbles just below the sea surface (at ~1.5 m depth). Details of its design, operation, and calibration are given by Egland (2000), Washburn et al. (2001, 2005), and Schwager (2005). The long, narrow configuration of the flux buoy dampens motions due to small-amplitude, high-frequency surface gravity waves, a source of analytical noise. Rising bubbles are directed into a collection chamber through a circular cone ($A=0.27$ m²) at the base of the buoy. The flux, $q$, is determined from the rate of change of the pressure difference, $Δp$, between the inside of the collection chamber and the surrounding seawater. Gas accumulates in the chamber until an adjustable threshold in $Δp$ is reached. Then a microcomputer-controlled valve opens to release the accumulated gas; this starts a new measurement cycle. Data acquisition, valve operation, and data transmission are controlled by a microcomputer in the electronics pressure case. The computer records $Δp$, the chamber temperature, $T_c$, and the chamber pressure, $p_c$, from which $q$ is estimated once per second. Buoy position is logged every 2 s using a differential global positioning system (GPS) receiver mounted on the top of the spar. In field operations, the buoy is either allowed to drift freely or it is gently towed through seepage areas as the research boat moves slowly forward.

The flux buoy measures the total flux of gas at the sea surface. Compositional analyses are needed to estimate fluxes of individual gases such as CH4. To measure surface composition, we utilized two approaches. In the one, surface bubbles were collected independently of the flux buoy surveys either using swimmers or directly from the small boats with a funnel and collapsible bag, which was initially filled with seawater. After a collection period, the accumulated gas in the bag was transferred to glass septa bottles, which had previously been purged with helium, using a glass syringe. In the other approach, the flux buoy was modified so that the vented gas could be sampled for later laboratory analysis. Copper tubing (3/8” O.D. and ~2 m length) ran from the submerged collection chamber vent to sample loops, which were located above the water line near the top of the spar. The vented gas was collected in 40-cm-long, 3/8” stainless steel tubes sealed with Nupro plug valves. These tubes were bent into “U-shape” loops so that the outlet end could be placed into a small container of seawater. This created a seal, and prevented air from contaminating the seep gas samples; it also enabled field personnel to see when the accumulated seep gas had vented. After collection, these loops could be quickly replaced from the side of the boat. When operating the flux buoy in the sample collection mode, a helium gas line was attached to the base of the funnel, so that prior to collecting seep gas the funnel, collection chamber, transfer lines, and loops could be flushed. One or two helium blanks were collected during each survey to determine the efficiency of the helium flush.

At three deeper large seeps, La Goleta (65 m depth), Horseshoe (40 m depth), and Trilogy (45 m depth), which could not be sampled with SCUBA divers, seafloor vent gas was collected using the Delta submersible during September 2005 (see Fig. 1 for seep locations). Seafloor surveys revealed that these seeps are composed of hundreds of vents that ranged in size from ~0.5 m diameter craters to
small point vents. Both types of vents were sampled using an inverted funnel collection system attached to the outside of the submersible. With this system, the seep gas was collected in 3/8” stainless steel tubes that were sealed with Nupro plug values. Seep gas was transferred from these tubes to glass septa bottles, which had previously been flushed with helium gas, within a few hours after collection on board the R/V Velero IV, the support vessel.

In the laboratory, the seep gas in sample loops or septa bottles was removed using a glass syringe. Subsequently, this gas was analyzed with standard methods on an Agilent micro-gas chromatograph (GC) for CH₄, O₂, N₂, and carbon dioxide (CO₂), or a Shimadzu GC for ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀), using (respectively) a thermal conductivity detector (TCD) or flame ionization detector (FID) and helium as the carrier gas. The typical analytical uncertainty of the measurements and collection based on replicates is better than ±3%.

Field cruises

Four of the large seep areas were surveyed with the flux buoy two or more times each between 2002 and 2005 (Table 1). The largest seep area, the Seep Tents, was surveyed only once in 2002. Two additional surveys were conducted away from any visible seepage to characterize the instrument noise, which is generated by swell moving the buoy up and down. Results of these surveys are discussed by Washburn et al. (2005). The buoy was gently pulled through the seep areas usually for about 4 h during the morning before afternoon wind-driven waves developed, as typically happens in the Santa Barbara Channel. The buoy was positioned to maximize the time it remained over areas of bubbles; no predetermined grid pattern was used. As a result, the webs of survey lines were denser near areas of strongest bubbling gas flux, such as at Trilogy seep (Fig. 2). The total flux for each seep area was determined by objectively mapping q onto a 2 m×2 m grid using standard geo-statistical techniques to produce estimates of mean q in each grid square, and then summing the mean q over the survey area (Washburn et al. 2005). Surface currents caused locations of the surface expression of the seeps to change with time, but these occurred slowly over the ~4 h sampling periods, and no corrections were applied.

Composition–flux surveys at two seeps, La Goleta and Seep Tents, were conducted during two survey days (16 December 2003, and 5 October 2004). Each of these seep areas is composed of smaller regions of high flux (hereafter referred to as “sub-seeps”) surrounded by broader areas of lower flux. The different sub-seeps are visually distinct, and samples were collected from different areas by carefully positioning the flux buoy in a given sub-seep. This often required steering the boat in small circles. Because surface gas flux varied strongly, the length of time required to fill the collection chamber was as short as 10 s of seconds and as long as a half hour.

Results

Flux and area estimates of bubbling gas flux

The flux buoy surveys within the Coal Oil Point seep field indicate that the areas with measurable levels of q at the sea surface ranged from about 800–5,500 m² (16–42 m diameters; Table 1). These areas are identified in Table 1 by names and positions, which does not account for all areas with visible bursting bubbles within the field. Estimates of mean flux averaged over these areas vary from 0.4–5.1 m³ m⁻² day⁻¹ (or m day⁻¹, as given by Washburn et al. 2005).

Table 1 indicates that the distribution of flux was skewed toward higher values: typically, the highest 5–10% of q measurements for a given seep contributed more than 50% of the total flux qT (column 7, Table 1). For example, for La Goleta seep on 15 September 2005 about 6% of q samples accounted for 50% of qT. The cumulative distribution of q interpolated onto the 2 m×2 m grid is shown in Fig. 3. It is derived from 18,973 estimates of q from the five large seeps and the 20-m noise test of Table 1, along with three other smaller seeps not discussed in this paper. Seeps and days included in the cumulative distribution of Fig. 3 are indicated in Table 1. Inclusion of q estimates from the large seeps on different days produced similar results. Measurement noise due to buoy motion caused the cumulative distribution to level out for q less than ~0.03 m³ m⁻² day⁻¹. For q ≤ 1 m³ m⁻² day⁻¹, the distribution was well described by the sum of a lognormal distribution and Gaussian noise, as shown by the solid black line of Fig. 3. The lognormal portion was determined from a least square fit over the range 0.04 ≤ q < 1 m³ m⁻² day⁻¹, and parameters for this distribution and the Gaussian noise are indicated in Fig. 3. A lognormal distribution plots as a straight line for the axes of Fig. 3. For q > 1 m³ m⁻² day⁻¹, the observed distribution exceeded the modeled distribution. Another lognormal distribution was fitted over the range 1 ≤ q < 10 m³ m⁻² day⁻¹, and well described the distribution of q over this range. About 13% of q values exceeded 1 m³ m⁻² day⁻¹. For q > 10 m³ m⁻² day⁻¹, encompassing about 0.04% of values, the observed distribution departed sharply upward, indicating an excess of a few high fluxes compared to the lognormal distribution. We speculate that this resulted from sampling bias, since measurements were concentrated in areas with the highest flux. It also may have resulted from areas of strong flux at scales smaller than the 2 m×2 m averaging area used to estimate q.
Repeat surveys at the seeps with high flux showed variability in $q_T$ and $A$ from survey to survey (Table 1), such as at Trilogy seep on 19 and 20 September 2005 as shown in Fig. 2a and b, respectively. The rectangular areas of Fig. 2 are of the same size and centered on the same point (34°23.620′, 119°52.739′W). The spatial patterns of $q_T$ during the surveys were very similar, both showing a spatial trend of increasing $q_T$ toward the western and southern portions of the survey area. The eastward shift by ~20 m of the flux pattern compared with the first survey was likely due to a change in surface currents. $q_T$, $A$, maximum flux $q_{\text{max}}$, differed, by 7%, 22%, and 8%, respectively (Table 1). For other seeps, the changes between repeat surveys were larger. For example, during three surveys on 6 and 13 December 2002 and 17 January 2003 at Horseshoe seep, $A$ varied by about 200%, $q_T$ by about 50%, and $q_{\text{max}}$ by about 200%. The largest variation was found at Shane seep during surveys conducted on 15 and 23 August 2002, but this likely resulted from under-sampling. High winds and sea state on 15 August resulted in a shorter survey with few observations of $q$. This likely accounts for the lower values of mean $q$ and smaller estimated area.

Bubble gas composition

Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas composition Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas composition Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas composition Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas composition Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas composition Clark et al. (2003) reported observations of the change in bubble gas composition between the sea surface and seafloor at Shane seep where samples could be collected using SCUBA divers. During this study, seafloor samples were collected at three deeper seeps using the Delta submersible, and no mid-water column samples were collected. The $O_2$ and $N_2$ fractions of these seafloor samples were unexpectedly high, often greater than 3% and 12%, respectively. A likely source of these gases was air contamination during collection. Therefore, the compositions of the deep seafloor samples have been corrected using the $N_2/O_2$ ratio of air, and assuming the seep gas

| Seep (depth) | Location | Survey dates | $n^a$ | Mean $q^b$ (m$^3$m$^{-2}$day$^{-1}$) | $q_{\text{max}}^c$ (m$^3$m$^{-2}$day$^{-1}$) | $q_T^d$ (m$^3$day$^{-1}$) | $A^e$ (m$^2$) | % contributing to 50% of $q_T^f$ |
|-------------|----------|--------------|------|----------------------------------|----------------------------------|----------------|---------|-------------------------------|
| HS (40 m)   | 34°23.757′, 119°52.530′ | 6 Dec. 02  | 14,407 | 0.9                               | 10.9                             | 2,392          | 2,710          | 6.4 |
| HS (40 m)   | 34°23.757′, 119°52.530′ | 13 Dec. 02 | 12,933 | 0.7                               | 5.4                              | 3,653          | 5,274          | 6.5 |
| HS (40 m)   | 34°23.757′, 119°52.530′ | 17 Jan. 03 | 12,736 | 1.5                               | 11.5                             | 3,372          | 2,253          | 6.8 |
| La Gol (65 m) | 34°22.523′, 119°51.258′ | 29 Aug. 02 | 8,169  | 1.0                               | 7.1                              | 1,249          | 1,266          | 7.4 |
| La Gol (65 m) | 34°22.523′, 119°51.258′ | 20 Jun. 03 | 13,356 | 1.7                               | 8.1                              | 800            | 480            | 4.3 |
| La Gol (65 m) | 34°22.523′, 119°51.258′ | 15 Sep. 05 | 13,292 | 0.4                               | 6.2                              | 787            | 2,113          | 5.9 |
| ST (67 m)   | 34°22.523′, 119°51.258′ | 22 Nov. 02 | 15,529 | 5.1                               | 24                               | 5,732          | 1,131          | 9.4 |
| Shane (22 m) | 34°20.070′, 119°53.370′ | 15 Aug. 02 | 3,064  | 3.3                               | 12.4                             | 1,099          | 331            | 3.8 |
| Shane (22 m) | 34°24.363′, 119°53.423′ | 23 Aug. 02 | 13,216 | 3.9                               | 24                               | 2,566          | 666            | 12.1 |
| Tri (45 m)  | 34°23.620′, 119°52.739′ | 19 Sep. 05 | 16,364 | 1.0                               | 8.2                              | 5,472          | 5,380          | 9.3 |
| Tri (45 m)  | 34°23.620′, 119°52.739′ | 20 Sep. 05 | 10,056 | 0.8                               | 7.6                              | 4,159          | 5,018          | 10.1 |
| NT (20 m)   | 34°24.125′, 119°52.995′ | 19 Sep. 02 | 7,191   | 1.6                              | 35                               | –              | –              | – |
| NT (60 m)   | 34°22.950′, 119°53.076′ | 19 Sep. 02 | 6,917   | 1.2                              | 35                               | –              | –              | – |

$^a$Because the sampling rate was 1 sample s$^{-1}$, the number of samples (minus 1) is also the sampling time in seconds

$^b$Mean $q = q_T/A$

$^c$The maximum 1-s flux measured during each survey

$^d$Total flux calculated by summing the gridded mean flux (see text for details)

$^e$Upper percentile of flux measurements needed to reach 50% of $q_T$ (see text for details)

$^f$Used in cumulative distribution of Fig. 3

$^g$Difference in spatial integrals over positive and negative values of $q$ caused by buoy motion
contained a similar amount of O2 as Shane seep (0.3%). The corrected compositions of the deeper seeps are similar to the inshore shallow Shane seep, although they are more variable (Table 2). CO2 and CH4 together make up approx. 92%, non-methane hydrocarbons (NMHC) ~7%, and nitrogen less than 1%. The two major gas components correlate strongly ($R^2 = 0.94$), and show that the mole fraction of these gases varies by about 20% (Fig. 4). Each seep’s variability, however, is smaller than the variability over the entire field. The high-CO2 seeps, Horseshoe and Trilogy, occur at intermediate depths (~50 m) and tend to emit more oil. The Trilogy sample that contained ~25% carbon dioxide was from a vent with low bubbling gas flux, and may reflect local biogeochemical alteration.

Relative to the seafloor samples, the surface gas contains less CO2 and CH4, and more N2 and O2 (Table 2). The relative abundance of these gases correlated strongly (N2 vs. CH4, $R^2 = 0.97$; O2 vs. CH4, $R^2 = 0.98$; N2 vs. O2, $R^2 = 0.95$). The N2/O2 ratios of the seep gas (2.4–3.3) were between the value of air (3.7) and air-saturated water (1.8). This indicates that the bubbles were stripping gas from seawater in which 25–45% of the O2 had been consumed.

The compositions of surface samples collected with the modified flux buoy were similar to the surface samples collected by hand (Fig. 5), though they tended to contain less air and more CH4. It is likely that samples collected by hand may have been contaminated slightly with air during collection, though no correction was applied. The modified flux buoy samples were collected within areas of high $q$ from the various sub-seeps over a period of 2–4 h. The high variability of gas composition (10–15%), as quantified by the mole fractions of CH4 and N2, indicates large changes over spatial scales of a few to several meters. This variability is similar to the high variability in $q$ on...
comparable spatial scales. However, the fraction of CH$_4$ at these seeps did not correlate with $q$ (Fig. 6), indicating that the amount of gas exchange is not a simple function of bubbling gas flux within the seep area.

**Discussion and summary**

Detailed mapping of bubbling gas flux $q$ and bubble composition at large seeps from the Coal Oil Point seep field show high variability over spatial scales of a few meters. Repeat surveys separated by days to years (Table 1) show that total flux $q_T$, seep area $A$, and maximum flux $q_{\text{max}}$ were highly variable. We speculate that these differences are due to changes in gas emission rates from the seafloor, since sampling was very dense in areas of strongest seepage, which dominate estimates of $q_T$. Additionally, data could be collected only during similar, calm sea states. The magnitude of change in $q_T$ is much larger than variability caused by tides, a likely environmental parameter that could cause these differences. For example, Boles et al. (2001) analyzed time series of $q_T$ at the nearby Seep Tents (65 m depth, adjacent to the Seep Tents seep), and found that variability due to tides was less than 7%. The observed distribution for $q$ in the range $0.04 \leq q < 10$ m$^3$ m$^{-2}$ day$^{-1}$, accounting for 56% of samples, was well

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**Table 2** Bubble composition (mole fraction) from large seeps within the Coal Oil Point seep field$^a$

| Seep  | Date       | Depth     | Flux | N$_2$ | O$_2$ | CH$_4$ | CO$_2$ | NMHC | CH$_4$/N$_2$ |
|-------|------------|-----------|------|-------|-------|--------|--------|------|-------------|
| ST    | 16 Dec. 03 | Surface   | 1.1  | 17.7  | 3.3   | 71.9   | <0.1   | 7.2  | 4.07        |
| ST    | 16 Dec. 03 | Surface   | 1.9  | 22.2  | 4.0   | 67.3   | <0.1   | 6.6  | 3.04        |
| ST    | 16 Dec. 03 | Surface   | 3.1  | 23.6  | 4.4   | 65.6   | <0.1   | 6.4  | 2.79        |
| ST    | 16 Dec. 03 | Surface   | 1.0  | 24.9  | 4.6   | 64.4   | <0.1   | 6.2  | 2.59        |
| ST    | 16 Dec. 03 | Surface   | 1.2  | 25.2  | 4.6   | 64.1   | <0.1   | 6.1  | 2.54        |
| ST    | 16 Dec. 03 | Surface   | 0.1  | 18.6  | 3.4   | 70.9   | <0.1   | 7.1  | 3.81        |
| ST    | 16 Dec. 03 | Surface   | 0.2  | 16.3  | 3.1   | 73.5   | <0.1   | 7.1  | 4.50        |
| ST    | 4 Oct. 04  | Surface   | –    | 22.9  | 4.5   | 66.2   | <0.1   | 6.5  | 2.89        |
| ST    | 4 Oct. 04  | Surface   | 3.9  | 19.4  | 3.9   | 69.8   | <0.1   | 6.9  | 3.60        |
| ST    | 4 Oct. 04  | Surface   | 0.1  | 16.8  | 3.2   | 72.6   | <0.1   | 7.4  | 4.33        |
| ST    | 4 Oct. 04  | Surface   | –0.1 | 22.8  | 4.5   | 66.2   | <0.1   | 6.5  | 2.90        |
| La Gol| 4 Oct. 04  | Surface   | 1.0  | 22.8  | 4.2   | 67.4   | <0.1   | 5.6  | 2.95        |
| La Gol| 4 Oct. 04  | Surface   | 1.2  | 25.3  | 4.7   | 64.9   | <0.1   | 5.8  | 2.56        |
| La Gol| 4 Oct. 04  | Surface   | 0.2  | 19.7  | 3.7   | 71.4   | <0.1   | 5.2  | 3.63        |
| La Gol| 4 Oct. 04  | Surface   | 0.1  | 27.2  | 4.6   | 62.6   | <0.1   | 5.6  | 2.30        |
| Blank | 16 Dec. 03 | Surface   | nd   | 1.5   | 0.3   | <0.1   | <0.1   | <0.1 | <0.1        |
| Blank | 4 Oct. 04  | Surface   | nd   | 0.1   | 0.4   | 0.2    | 0.1    | <0.1 | 3.00        |
| HS    | 20 Sep. 05 | Surface   | nd   | 34.3  | 9.3   | 50.9   | <0.1   | 5.5  | 5.50        |
| HS    | 20 Sep. 05 | Surface   | nd   | 37.7  | 9.6   | 46.3   | <0.1   | 6.2  | 4.80        |
| La Gol| 20 Sep. 05 | Surface   | nd   | 41.3  | 9.6   | 45.5   | <0.1   | 3.5  | 1.10        |
| La Gol| 20 Sep. 05 | Surface   | nd   | 38.5  | 9.0   | 48.6   | <0.1   | 3.8  | 1.26        |
| La Gol| 20 Sep. 05 | Surface   | nd   | 39.8  | 9.3   | 47.3   | <0.1   | 3.7  | 1.19        |
| Tri   | 20 Sep. 05 | Surface   | nd   | 27.5  | 7.2   | 59.4   | 0.1    | 5.8  | 2.16        |
| Tri   | 20 Sep. 05 | Surface   | nd   | 33.6  | 8.3   | 52.4   | <0.1   | 5.7  | 1.56        |
| Tri   | 20 Sep. 05 | Surface   | nd   | 30.4  | 7.9   | 55.9   | <0.1   | 5.7  | 1.84        |
| HS    | 20 Sep. 05 | Seafloor  | nd   | 4.3   | 0.3   | 72.3   | 15.3   | 7.7  | 16.8        |
| HS    | 20 Sep. 05 | Seafloor  | nd   | 5.1   | 0.3   | 75.9   | 10.9   | 7.2  | 14.9        |
| HS    | 20 Sep. 05 | Seafloor  | nd   | 3.1   | 0.3   | 75.0   | 13.6   | 8.0  | 24.2        |
| HS    | 20 Sep. 05 | Seafloor  | nd   | 1.2   | 0.3   | 77.8   | 12.3   | 8.7  | 64.8        |
| La Gol| 16 Sep. 05 | Seafloor  | nd   | 3.8   | 0.3   | 76.6   | 12.8   | 6.5  | 20.2        |
| La Gol| 19 Sep. 05 | Seafloor  | nd   | 2.2   | 0.3   | 81.9   | 10.1   | 5.7  | 37.2        |
| La Gol| 16 Sep. 05 | Seafloor  | nd   | 2.1   | 0.3   | 89.7   | 3.1    | 4.9  | 42.7        |
| La Gol| 19 Sep. 05 | Seafloor  | nd   | 3.4   | 0.3   | 83.4   | 6.2    | 6.9  | 24.5        |
| Tri   | 17 Sep. 05 | Seafloor  | nd   | 2.5   | 0.3   | 64.0   | 25.5   | 7.8  | 25.6        |
| Tri   | 17 Sep. 05 | Seafloor  | nd   | 4.4   | 0.3   | 70.7   | 16.3   | 7.9  | 16.1        |

$^a$The seafloor samples were corrected for air contamination using the method described in the text. ST, Seep Tents; La Gol, La Goleta; HS, Horseshoe; Tri, Trilogy; nd, not determined.
described by two lognormal distributions fitted over two flux ranges. The distribution was not well resolved for lower \( q \) values, due to instrument noise, and for higher values due to oversampling of high-flux regions or inadequate spatial resolution of flux estimates. The total flux from the five seeps surveyed ranges between \( 15 \times 10^3 – 19 \times 10^3 \) m\(^3\) day\(^{-1}\), 15–19% of the estimated total flux from the Coal Oil Point seep field.

Comprehensive observations of the change in bubble gas composition between the sea surface and seafloor have been made at the relatively shallow but intense (mean \( q \) of \( 3–4 \) m\(^3\) m\(^{-2}\) day\(^{-1}\); Table 1) Shane seep (Clark et al. 2003). Because of its shallow depth (~22 m), the fieldwork could be conducted easily with SCUBA divers. In addition to collecting bubble samples, divers were able to map seafloor features in detail (Leifer et al. 2004, 2006). Bubbles 1 m above the seafloor vents were composed primarily of CH\(_4\) (83%), CO\(_2\) (12%), and NMHC (non-methane hydrocarbons, 2.9%); components of air, including N\(_2\) and O\(_2\), contributed less than 2% of the total volume (Clark et al. 2003). The presence of O\(_2\) indicates that some gas exchange occurred below the 1 m height of the sampling point, possibly within the sediments. Shallow circulation cells commonly form in sediments near seeps (O’Hara et al. 1995; Zimmermann et al. 1997), and could be the source of this O\(_2\). At shallower depths the CO\(_2\) mole fraction decreased to the analytical detection limit, whereas the air fraction increased. At the surface, bubbles were composed of CH\(_4\) (78%), N\(_2\) (14%), O\(_2\) (5.3%), and NMHC (2.4%). The mole fractions of CH\(_4\) and NMHC reached maxima at mid-depths due to the more rapid loss of CO\(_2\) relative to the inflow of air (Clark et al. 2003).

With the exception of Shane seep, repeat surveys of bubble composition were not conducted (Clark et al. 2003). Given the large range of compositions determined during the flux buoy surveys of the sub-seeps, which were sampled over a period of a few hours, it is likely that the temporal variability would not exceed the spatial variability. While the mole fractions of the major gases (CH\(_4\), N\(_2\), and O\(_2\)) correlated strongly \( (R^2 > 0.95) \), gas composition at the surface did not correlate with bubbling gas flux within the seeps (Fig. 6). This implies that gas exchange between the bubbles and ambient water is not a simple function of gas flux. Several factors may account for this, including (1) chaotic local circulation patterns of large bubble plumes, which may cause bubble–plume water separation and entrainment of ambient ocean water; (2) variations in the seafloor composition of vent gas; (3) variations in the bubble size distributions; and (4) variations in the gas exchange rate caused by differing amounts of surfactants (i.e., oil) coating the bubbles.
Evidence from vertical profiles of bubble composition at Shane seep shows that CO_2 is rapidly lost from the rising bubbles, presumably due to chemically enhanced gas transfer (e.g., Emerson 1975). Analyses of gas collected from the Seep Tents approx. 10 m above the seafloor and piped to shore (Clark et al. 2000) are consistent with these observations of rapid CO_2 loss. When CO_2 is excluded, the re-normalized mole fractions of the vent gas components are similar, being 89.5±4.2% and 3.3±1.5% for CH_4 and N_2, respectively. Because gas compositions are reported as mole fractions (rather than concentrations), the loss or gain of one component affects the mole fractions of the other components. This effect is seen in the vertical profile of bubble composition above Shane seep. Because of the rapid loss of CO_2, the CH_4 mole fraction is at a maximum at mid-depths (Clark et al. 2003). Therefore, the best way to assess the amount of gas exchange is to look at the relative change in gases, such as CH_4 and N_2, which are being lost and gained from the rising bubbles. As gases exchange, the CH_4/N_2 ratio will decrease from the seafloor value of about 30, to about 0 at the surface. The latter is reached when all of the CH_4 has been lost from the bubble. It is possible for a bubble plume to reach the sea surface and emit no CH_4 to the atmosphere. This would occur if all of the CH_4 had been replaced by air stripped from the water column.

Seep field trends of gas transfer can be inferred from the CH_4 and N_2 data using mean compositions. Because only five large seeps were examined, the trends are more qualitative than quantitative. The highest CH_4 and CH_4/N_2 ratios were found at the surface of Seep Tents and Shane seeps, the two most intense seeps (i.e., highest mean q and q_{max}; see Table 1). The shallower of these two seeps (Shane) contained higher values of CH_4 and CH_4/N_2 ratios. La Goleta seep, which has a similar depth as Seep Tents, contained less CH_4 and had a lower CH_4/N_2 ratio; it is a much weaker seep. Similar to the Seep Tents–La Goleta trend discussed above, Horseshoe, which has a similar depth to Trilogy but lower total flux, had less CH_4 and a lower CH_4/N_2 ratio. The amount of gas exchange, and therefore CH_4 loss, scales directly with depth and inversely with seepage intensity. Because of the small sample size (n=5), it is not possible to quantify these relationships. To establish the CH_4/N_2 ratios as a proxy for total gas exchange between the seafloor and surface, additional work is needed. Most importantly, model simulations are needed. Nevertheless, these limited field data support our hypothesis that large seeps emit a larger fraction of their CH_4 and other hydrocarbon gases to the atmosphere than do small seeps.

The detailed mapping of the surface expression of five large Coal Oil Point seeps reveals that their seepage intensity and gas composition vary over short temporal and spatial scales. Seafloor surveys indicate that some of the surface variability is inherited from below; seafloor seeps are distributed over a broad area, and consist of both point vents and larger craters that emit curtains of bubbles. The variation in bubble composition, however, suggests that bubble plume dynamics also contributes to the surface variability by influencing the bubble–water gas transfer rate. Finally, the repeat flux buoy investigations show intra-survey differences in A and q_T indicating that sedimentary processes that control the vent emission rates must also contribute to the temporal variability.

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References

Allen AA, Schlueter RS, Mikolaj PG (1970) Natural oil seepage at coal oil point, Santa Barbara, California. Science 170:974–977

Boles JR, Clark JF, Leifer I, Washburn L (2001) Temporal variation in natural methane seep rate due to tides, Coal Oil Point area, California. J Geophys Res 106:27,077–27,086

Clark JF, Washburn L, Hornafius JS, Luyendyk BP (2000) Dissolved hydrocarbon flux from natural marine seeps to the southern California Bight. J Geophys Res 105:11,509–11,522

Clark JF, Leifer I, Washburn L, Luyendyk BP (2003) Compositional changes in natural gas bubble plumes: observations from the Coal Oil Point marine hydrocarbon seep field. In: Woodside JM, Garrison RE, Moore JC, Kvenvolden KA (eds) Proc 7th Int Conf Gas in Marine Sediments, 7–12 October 2002, Baku, Azerbaijan. Geo-Mar Lett 23(3/4):187–193. doi:10.1007/s00367-003-0137-y

Cynar FJ, Yayanos AA (1992) The distribution of methane in the upper waters of the Southern California Bight. J Geophys Res 97:11,269–11,285

Del Sontro TS, Leifer I, Luyendyk BP, Broitman BR (2007) Beach tar accumulation, transport mechanisms, and sources of variability at Coal Oil Point, California. Mar Pollut Bull 54:1461–1471

Eglund ET (2000) Direct capture of gaseous emissions from natural marine hydrocarbon seeps offshore of Coal Oil Point, Santa Barbara, California. MSc Thesis, University of California, Santa Barbara, CA

Emerson S (1975) Chemically enhanced CO_2 gas exchange in a eutrophic lake: a general model. Limnol Oceanogr 20:743–753
