

Modifications of the Local Environment by Natural Marine Hydrocarbon Seeps

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Abstract. The bubble gas partial pressures, dissolved gas and oil, and fluid motions within the rising bubble streams of three shallow (< 70 m) natural hydrocarbon seeps in the Santa Barbara Channel were measured. Aqueous methane concentrations near the surface in the bubble plumes were substantially greater (> 10^8 times) than atmospheric equilibrium values; at two of the seeps it was slightly supersaturated with respect to the bubble's partial pressure. This indicates that the rate limiting step for methane, CH_4 , transfer into the water column was not bubble gas transfer, but rather turbulence transfer of water out of the saturated bubble stream to the bulk ocean. Strong upwelling flows were observed, as well as elevated fluorescence indicative of dissolved oils. At the bottom, bubbles are circa 90% CH_4 , but at the surface they were circa 60% CH_4 , 30% air, and 10% higher hydrocarbons.

1. Introduction

Marine seeps are significant sources of methane (CH_4) and other hydrocarbons to the ocean and atmosphere. Methane is an important greenhouse gas and energy source. Quantification of the total seep hydrocarbon flux is difficult due to the temporal and spatial variability of the global seep distribution and interactions between rising hydrocarbon plumes and the water column are complex. Nevertheless, marine seeps may be an important source of radiocarbon-free CH_4 to the atmosphere [Judd *et al.*, 1997; Hovland *et al.*, 1993] and the most important source of oil slicks and dissolved methane to some coastal areas [Estes *et al.*, 1985]. The heavier petroleum fraction of released oil includes many carcinogenic and mutagenic compounds such as benzene and other polycyclic aromatic hydrocarbons (PAH).

The extent that gas and oil enters the water column, and thus the fraction ultimately released at the surface and into the atmosphere, depends upon the immediate seep and bubble stream environment. Predicting this flux requires a detailed understanding of how bubble plumes affect dissolution and volatilization rates, and local hydrodynamics. Unfortunately, details of seep environments are generally lacking. To address this deficiency, measurements of several seeps were conducted in November 1999, with the major objective to assess the

impact of gas-oil plumes on the water column above the seafloor vent and on hydrocarbon cycling into the ocean.

Field Location

The northern margin of the Santa Barbara Channel (SBC) is one of the most active areas of natural hydrocarbon seepage in the world [Hornafius *et al.*, 1999]. The most concentrated seepage area is in moderately shallow water (20-100m) about 3 km offshore of Coal Oil Point, Seep Field, CA (Fig. 1). It is estimated that there are more than 1500 seep vents in this seep field which continually emit both oil and gas [Fischer, 1978]. Current estimates indicate that about $1.5 \times 10^5 \text{ m}^3 \text{ d}^{-1}$ ($5 \times 10^6 \text{ ft}^3 \text{ d}^{-1}$) of gas is emitted from these seeps to the atmosphere [Hornafius *et al.*, 1999] with about an equal amount injected into the coastal ocean [Clark *et al.*, [2000]. Oil discharge estimates range between 40 and 200 barrels per day [Hornafius *et al.*, 1999].

Bubble dynamics

Generally, the emitted hydrocarbons rise as gas bubbles with oil coating its surface, although oil droplets rising separately were also observed. As the bubbles rise they exchange gases with the surrounding water: they dissolve as CH_4 outflows and grow as dissolved air (nitrogen, N_2 , and oxygen, O_2) inflows. Furthermore, expansion occurs due to the decreasing hydrostatic pressure. The gas flux for a bubble, F , is

$$F = \frac{dn}{dt} = k_B 4\pi r^2 \left(C - \frac{P_B}{H} \right) \quad (1)$$

where n is the molar concentration, k_B is the bubble gas transfer rate for a specific gas, r is the bubble equivalent radius (i.e., if the bubble was a sphere), H is the Henry's Law coefficient, C is the aqueous concentration, and P_B is the bubble partial gas pressure which is the sum of the hydrostatic pressure and the pressure due to surface tension, P_{ST} . P_{ST} is small for all but the smallest bubbles ($P_{ST} = 0.1 \text{ Atm}$ for a $r = 15\text{-}\mu\text{m}$ bubble).

The flux equation is applied to each gas in the bubble individually. The gas flux is driven by the difference, $C - P_B/H$, and thus gas outflows when $C < P_B/H$, while gas inflows when $C > P_B/H$. If C is significantly elevated due to bubble dissolution, the gas outflow from the bubbles is decreased, and more gas is transported and released into the atmosphere. If the dissolved O_2 and N_2 in the bubble stream are significantly depleted, inflow will be reduced, increasing the likelihood of

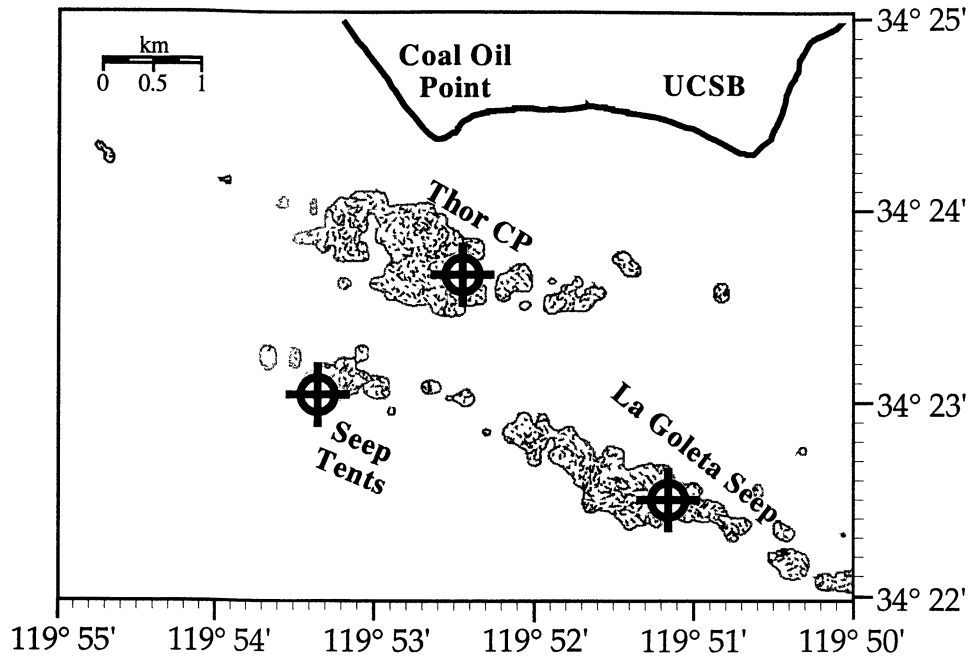


Figure 1. Map of seep field with contours of active gas seepage regions measured by 3.5 khz sonar [Quigley, 1997]. Targets show seeps visited.

dissolution, e.g., the outflowing CH_4 is not being replaced by inflowing air. The gas flux is also dependent upon r and the gas diffusivity, D , since k_B is a function of r and D (larger bubbles are significantly more efficient at gas transfer), bubble surface cleanliness, and even small scale ($\sim r$) turbulence. Finally, the total gas entering the water column depends upon the integrated flux over the bubble's lifetime. Thus, upwelling flows resulting from entrainment decrease transit time from the seafloor to the surface and decreases total flux into the water column.

Oil released from the seafloor vents undergoes many changes during its transit through the water column due to various physical, chemical, and biological processes, including dissolution, volatilization, and (bio)chemical degradation. Within the water column, oil transport can be affected by bubble gas transfer. As oily bubbles or oil droplets rise, the more volatile oil components dissolve into the water [Spies *et al.*, 1996]. Since rising bubble larger than 100 microns generate considerable turbulence and are "self ventilating" [Woolf and Thorpe, 1991], the oil dissolution rate for bubbles should be greater than for a thin film on the sea surface. And of course, oil droplets (nearly neutrally buoyant) entrained in an upwelling flow of velocity, V_{up} , will rise to the surface much faster than due solely to buoyancy.

Table 1. Details of Natural Hydrocarbon Seeps Visited.

Name	Water Depth (m)	S (m ²)	V_{up} (cm s ⁻¹)	Seep activity
Thor CP (TCS)	20	2	-	Low
La Goleta (LGS)	70	25	30	Active
Seep Tent (STS)	70	700	>100	Extreme

V_{up} is upwelling flow, S is surface area.

2. Methodology

To characterize the seep environment, dissolved gases and oils, and fluid motions were measured at three seeps of different sizes: La Goleta Seep (LGS - 34° 52.442' N, 119° 23.650' W), Thor CP Seep (TCS - 34° 51.183' N, 119° 22.500' W), and Seep Tent Seep (STS - 34° 53.350' N, 119° 23.050' W), summarized in Table 1. At each seep, two sets of water and bubble gas samples were collected by divers near the surface. Water samples were collected in 250-ml glass, septa bottles using Lab-Line water samplers. Bubble gas samples were taken by using an inverted funnel to direct bubbles into bottles. Fluid motions were studied using fluorescein dye releases. Small quantities of dye were released from a syringe through a 1 m tube into the column of rising bubbles. The velocity was determined by measuring the time to rise a distance of 1 m. Dye tracer releases were also used on the surface to determine surface divergence. Bubbles were photographed with a Nikonos underwater camera and flash.

Table 2. Summary of Gas and Dissolved Seep Observations.

Seep	z (m)	$P(O_2)$ (mbar)	$P(N_2)$ (mbar)	$P(CH_4)$ (mbar)	$[CH_4]$ (μMol l ⁻¹)	$H[CH_4]^a$ (mbar)
STS	1	85	251	691	1000	860
STS-2	2	93	274	754	-	-
LGS	2	105	339	700	1200	810
TCS	2	75	203	758	260	190
STS	1	7.69 ^c	22.8 ^c	62.8 ^c	1000	860
STS-B	90	0.14 ^c	0.79 ^c	87.5 ^c	-	-

^a H was calculated for 12 °C [Wannikhof, 1992].

^bSTS-2 is STS corrected to 2 m (hydrostatic) for comparison with other seeps.

^c Mole fraction of gas (%).

The water and gas samples were analyzed for carbon dioxide, CO₂, O₂, N₂, CH₄, and higher n-alkanes to $n = 5$ (Table 2). Gas samples were analyzed using standard gas chromatography techniques at Zymax Forensics (San Luis Obispo, Ca). Unfiltered water samples were also analyzed for dissolved organic components using excitation-emission fluorometry on a Hitachi F-4500 (Hitachi Instruments, Inc., Naperville, IL, 150W Xe lamp, 5 nm slits). Briefly, emission spectra (250 - 600 nm; 2 nm resolution) were recorded at several excitation wavelengths (200 - 450 nm; every 5 nm). Resulting 3-dimensional matrices were visualized to determine the relative composition and quantity of fluorescent molecules dissolved in seawater. Residual fluorescence was determined by removing the oil (assumed to be solvent extractable) by a solvent (dichloromethane - B & J, spectroscopic grade).

3. Seep visual observations

The STS lies near the Seep Tents (operated by Veneco, Inc.), which are two large pyramidal structures (each 30 m x 30 m at the base) that were constructed over a fraction of a very active area of natural seepage in 1982 *Rintoul* [1982]. The natural gas (transported to shore via a pipeline) is periodically analyzed and represents the seabed gas composition plus any modification that occurs during its 10 m transit through the water column. The STS-surface expression was characterized by intense upwelling flows and a few less intense areas. The rising bubbles were primarily located in a significantly smaller area within the upwelling flow (~ 10%), whose location varied rapidly within the overall upwelling flow. The upwelling flow in the center of the seep was estimated 1 - 2 m s⁻¹. Flow was so intense that divers could neither swim into the area where bubbles were surfacing nor could they submerge. Divers were towed into the collection site by boat to collect samples. Waves were observed breaking on the outer edges of the surface expression. The widest size spectrum of bubbles observed at the surface including fairly small bubbles ($r \sim 500 \mu\text{m}$) was observed at this seep.

The LGS was less active than STS with a significantly smaller surface expression. LGS comprises a series of separate bubble streams within an area of a few hundred square meters. Bubbles over a wide range were observed, with the smallest larger than at STS ($r > 1$ to 2 mm).

The smallest seep studied, TCS, had a surface expression of a few m² and was the shallowest (20 m). Bubbles near the surface were large ($r > 2$ to 3 mm diameter) and the bubble stream was very diffuse. Divers observed the bubble stream emitted from several fissures on the seafloor, and follow up. There was no evidence that rising bubbles broke up due to growth from decreasing hydrostatic pressure. Upon bursting, all bubbles left a light oil sheen which merged into the general oil slick after a few seconds. Oil droplets were not observed, although some bubbles released dark oil, and bubbles at this seep were the oiliest. Only at TCS was there surface evidence of the bubble stream separating into large and small plumes spaced by a few meters at the surface, although there was no evidence of size segregation within the plume.

4. Results and Discussion

Observations showed that the seep environment was highly different from the bulk ocean. Aqueous CH₄ concentrations were not only significantly above Santa Barbara Channel background levels (20 nmol l⁻¹ [Cynar and Yayanos, 1992;

Clark *et al.*, 2000]), but also above, by a factor of 10⁵, reported values for the methane plume that extends down current from this seep field [Clark *et al.*, 2000]. Significant upwelling flows were observed in the two large seeps, which would decrease bubble rise time by 50 - 75%. Also dissolved organic hydrocarbons concentrations were observed significantly above background at the seep edges.

Fluid motions

The rising bubble and water flow creates a complex flow system. Strong upwelling velocities were observed at the two larger seeps, while all showed surface divergence. The diverging flow decreased sharply a short (~2 m) distance from the surfacing position, at which point the surface oil slicks thickened considerably. Although the flow in the lower portion of the seep was not directly measured, continuity arguments imply convergence at the bottom, and entrainment into the rising bubble stream.

Dye clouds released at LGS were observed to rise vertically in the bubble stream, despite the presence of a horizontal current in the overall water column. This suggests that entrainment or flow separation were preventing the horizontal advection of dye from the bubble stream due to currents. At LGS, V_{up} was comparable to the rise velocity of large ($r > 500 \mu\text{m}$) bubbles. At STS, upwelling was too intense to allow dye release, and V_{up} was estimated to be 1 to 2 m s⁻¹. At the smallest seep, TCS, no clear upwelling flow was observed. Instead, as each bubble passed through the dye cloud, some dye was dragged upwards for 10 - 20 cm. After a few seconds and a few bubbles, the current advected the dye out of the bubble stream. However, the presence of surface divergence indicated the presence of a small upwelling flow.

Major gases, CH₄, O₂ and N₂

It was assumed that gas collected at the STS Bottom is representative of gas leaving the sediments. The composition of this gas is in good agreement with gas measurements from other seepage areas [Hovland *et al.*, 1993]. After rising to the surface, the bubble CH₄ mole fraction decreased from about 88% to about 63%, and the mole fraction of the sum of O₂ and N₂ increased from about 1% to about 30%, clearly demonstrating that there was gas inflow and outflow from the bubbles (Table 2).

The surface aqueous [CH₄] at STS showed the upper water column was saturated. In fact, the water is slightly above equilibrium with respect to the bubbles. Specifically, the aqueous CH₄ concentration represents equilibrium conditions at a greater depth where the hydrostatic pressure is higher. As a result, near the surface, bubbles act as a CH₄ sink not source. Supersaturation indicates that the rate limiting step for CH₄ transfer into the water column was not bubble gas transfer, but rather turbulence transfer of water out of the saturated bubble stream to the bulk ocean.

At LGS, aqueous [CH₄] is less than at STS, in agreement with the decreased seep intensity. Based on $V_{up} = 30 \text{ cm s}^{-1}$, the water is in equilibrium with bubbles at $z \sim 3$ to 4 m, implying a bubble-water column equilibration time of circa 5 s, assuming the water in the bubble plume does not mix with the bulk fluid. At TCS, the smallest seep, bubbles arrive at the surface with the highest $P(\text{CH}_4)$, despite the lowest aqueous $H[\text{CH}_4]$ (0.19 atm) and no observed upwelling. This may result from the shallowness, or the fact that bubbles at TCS were the oiliest. Surprisingly, despite the seeps small size and low

bubble density, aqueous $[\text{CH}_4]$ is still well above background. Since the water column is no longer in equilibrium with the bubbles, the time scale for transport of water out of the bubble stream must be shorter than the time scale for gas transfer from the bubbles into the bubble stream.

Dissolved oil

Fluorescence is a sensitive and versatile tool for studying oil dissolved in seawater. A wavelength independent maximum centered at 230-nm excitation and 340-nm emission dominated most spectra and can be attributed to the fluorescence of aromatic oil components. Solvent extraction of a subset of the samples and re-analysis of the residual seawater resulted in great reductions in the fluorescence of samples containing significant oil. This confirmed that the 230/340 nm peak was solvent extractable, presumably oil, and not the water soluble humic substances that dominate most marine systems. The fluorescence signal (230/340) of deionized water was subtracted from all sample measurements.

For STS, fluorescence was lower in the center than at the edge, presumably resulting from the higher upwelled flow entrainment rates of low fluorescence, deep seawater. This is in agreement with the observation that STS bubbles were the least oily. In contrast, the STS edge showed extremely high values, 35 times higher than in STS center. It is hypothesized that there is a ring of downwelling water at the edge of the surface expression where deep, cold water entrained in the bubble plume sinks below warm surrounding surface water, and significantly increases the surface slick subduction and thus dissolved oil. This is in agreement with visual observations that the slick thickened considerably at the seep edges.

LGS center fluorescence values were significantly higher than the edge (edge to center ratio of 0.76). A similarly low edge to center ratio was also observed for TCS (0.33). TCS, which contained the oiliest bubbles, also showed the highest oil fluorescence observed in the center of a plume, thus, TCS was effective at enhancing dissolved oil in its seep environment. The most interesting result was the fluorescence value 100 m from the LGS seep, which was a factor of 33 times greater than at LGS center. This sample represented an integrated value for the entire seep field as it was taken beneath a heavily slicked area. Additionally, water here was in contact with the oil slick for much longer than water in the upwelling flows in seep plume centers, suggesting that seeps in the LGS area may supply a significant amount of dissolved oil to the surface of the ocean.

5. Conclusions

Observations of upwelling flows and saturation of the water column have important implications for the transport of CH_4 to the atmosphere from marine hydrocarbon seeps. The effect of the flow was also observed in the fluorescence observations. This suggests implications to vertical fluxes (nutrient, carbon isotopes, etc.) within the ocean in the vicinity of seepage. Further investigation of the chemico-hydrodynamics of seep flows is clearly required to improve estimation of the environmental impact of seeps.

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