Dissolved methane distributions and air-sea flux in the plume of a massive seep field, Coal Oil Point, California

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[1]   Large quantities of natural gas are emitted from the seafloor into the stratified coastal ocean near Coal Oil Point, Santa Barbara Channel, California. Methane was quantified in the down current surface water at 79 stations in a 280 km^2 study area. The methane plume spread over an area of $\sim$70 km^2 and emitted on the order of 5×10^4 mol d^{-1} to the atmosphere. A monthly time series at 14 stations showed variable methane concentrations which were correlated with changing sub-mesoscale surface currents. Air-sea fluxes estimated from the time series indicate that the air-sea flux derived for the 280 km^2 area is representative of the daily mean flux from this area. Only 1% of the dissolved methane originating from Coal Oil Point enters the atmosphere within the study area. Most of it appears to be transported below the surface and oxidized by microbial activity. **Citation:** Mau, S., D. L. Valentine, J. F. Clark, J. Reed, R. Camilli, and L. Washburn (2007), Dissolved methane distributions and air-sea flux in the plume of a massive seep field, Coal Oil Point, California, *Geophys. Res. Lett.*, *34*, L22603, doi:10.1029/2007GL031344.

1.   Introduction

[2]   Natural marine hydrocarbon seeps are important sources of methane to the regional and global environment. Methane is a potent greenhouse gas; per unit mass, CH_4 warms the Earth 23 times more than CO_2 when averaged over 100 years [*Ramaswamy et al.*, 2001]. Quantifying methane discharge from the seabed and its flux to the atmosphere are major unsolved issues regarding the marine methane cycle. Atmospheric methane flux from seeps can proceed directly through bubble transport or indirectly from dissolved methane. The indirect or dissolved flux arising from the dissolution of bubbles during transit through the water column or from the discharge of methane-rich pore fluids from the sediment into the water column is particularly difficult to quantify [*Reeburgh*, 2007]. Dissolved methane is transferred to the atmosphere down current from seep areas via air-sea gas exchange when methane rich water is transported in the mixed layer. Physical processes such as vertical mixing and upwelling can contribute to the indirect flux [*Rehder et al.*, 2002]. Quantification of this indirect flux is critical for understanding the marine hydrocarbon contribution to the total atmospheric methane source.

[3]   One of the world's largest and best studied seep regions, the Coal Oil Point (COP) seep field, is located along the northern margin of the Santa Barbara Channel (SBC) [*Hovland et al.*, 1993]. The seep field (Figure 1a) emits gaseous, liquid (oil), and solid (tar) hydrocarbons in water 5 m to 70 m deep [e.g., *Fischer*, 1978; *Hornafius et al.*, 1999]. *Quigley* [1997] and *Hornafius et al.* [1999] used a sonar technique to estimate the total flux for the seep field to be $5.9-19.3 \times 10^4$ m^3 d^{-1}. Most seep bubbles are composed of $\sim$90% methane at the seafloor and $\sim$60–70% methane at the sea-surface [*Clark et al.*, 2003; *Leifer et al.*, 2000], thus the gaseous methane emission can be estimated to be in the range of $1.9-6.0 \times 10^6$ mol d^{-1}. *Clark et al.* [2000] investigated the flux of dissolved hydrocarbons originating from COP. They measured methane concentrations between 27–37 m water depth along four transects and extrapolated their results to the whole water column by using the bubble dissolution model of *Cline and Holmes* [1977]. They estimated 3.6×10^6 mol d^{-1} of methane are injected into the water above the seafloor vents; this flux is approximately equal to the direct emission rate (i.e., via bursting bubbles) to the atmosphere from this seep field.

[4]   Here, we estimate the methane flux to the atmosphere from the dissolved gas plume originating at COP to better understand the fate of methane injected into the ocean above seeps.

2.   Methods

[5]   Dissolved methane was sampled within a 280 km^2 region starting 7 km west of the seeps and extending another 21 km westward along shore (Figure 1a). The area between the seeps and the study region was not surveyed, because of expected intra-plume variability and the occurrence of thick oil slicks [*Kraus and Estes*, 1977a; *Kraus and Estes*, 1977b] that reduce air-sea gas exchange [*Frew*, 1997]. On 19 June 2006, water was sampled at 79 stations along 5 north-south transects and analyzed for methane. To examine plume variability, 5–14 stations along the transect defining the eastern boundary of the study area (i.e. nearest the COP seeps) were sampled once a month between May–November 2006. At three stations along most transects CTD casts were conducted over the upper 10 m of the water column.

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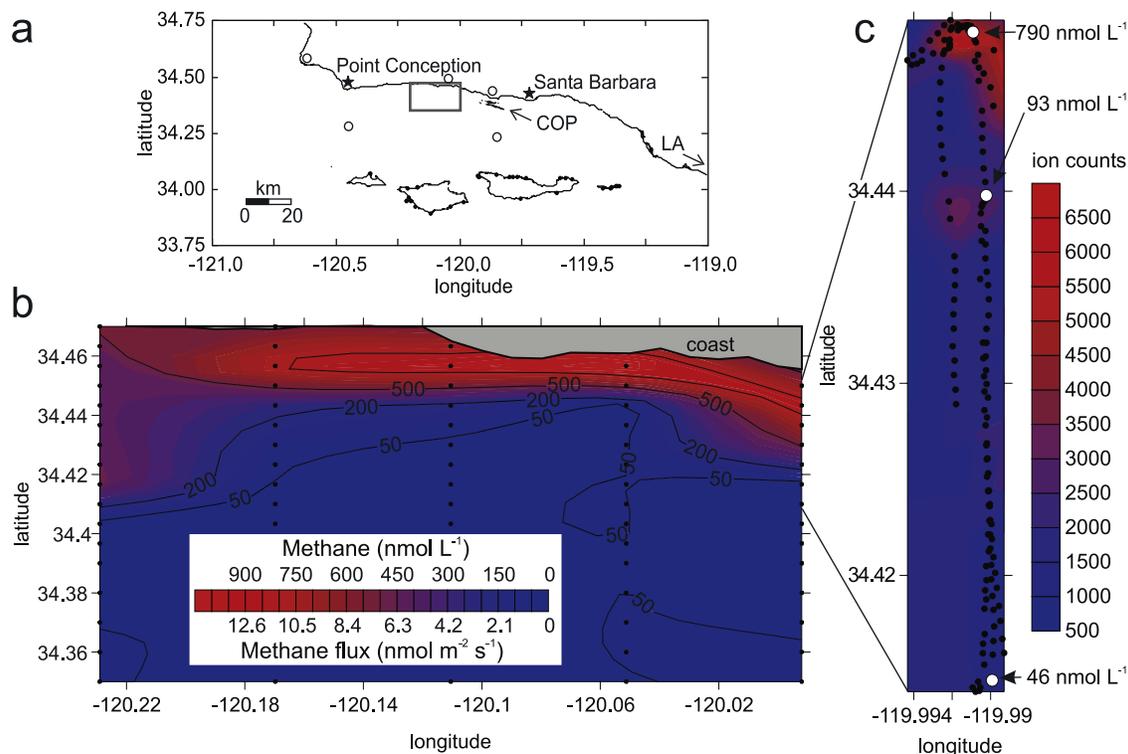
Figure 1. (a) Location of the study area off the coast of Santa Barbara County, California. The study area is indicated by the rectangle, wind recording stations are shown as circles, the gas seeps of Coal Oil Point seep field (COP) as determined by *Quigley* [1997] is illustrated as a black area. (b) Methane distribution and air-sea flux within the study area. Fluxes represent averages of calculated values which were based on different relationships between wind speed and gas transfer velocity. Labels on the contours map refer to methane concentrations and black dots show the sample grid. (c) Contour plot of methane ion counts measured by mass spectrometry along the easternmost transect in Figure 1a. Discrete methane concentrations (right of the graph) were determined for locations indicated by a white circle.

[6] Samples were collected from 0.5 m water depth with a submersible pump and stored in 125 ml crimp-top sample bottles. All sample bottles were flushed with 2 volumes of water and filled completely to eliminate bubbles. The bottles were immediately capped with butyl rubber stoppers and crimp sealed. All samples were transported to the laboratory on the day of collection, and a 10 ml headspace was introduced into each bottle as described by *Valentine et al.* [2001]. Two aliquots of the headspace were each analyzed for methane, ethane, and propane using a gas chromatograph equipped with a flame ionization detector [*Kinnaman et al.*, 2007]. Replicate analysis of samples yielded a precision of ±2% for samples with CH_4 concentration ≥ 50 nmol L^{-1} and ±5% for samples with CH_4 concentration <50 nmol L^{-1}.

[7] On 10 November 2006 a TETHYS in-situ mass spectrometer (MS) was towed behind a vessel to measure the relative abundance (i.e. not absolute concentrations) of methane and other gases on time scales of seconds to better resolve spatial variability. TETHYS is a self contained underwater mass spectrometer that uses a membrane inlet in conjunction with a linear cycloid analyzer and Faraday cup. Ionization is achieved using electron impact at 70eV. The TETHYS mass range is $1-200$ AMU with a resolution of better than 1 AMU and a minimum detection limit of typically 500 parts-per-trillion for light hydrocarbons. The MS hydrocarbon data were collected every 5 s and com-

bined with concurrent GPS and CTD data to yield latitude, longitude, and depth for each measurement. The tow speed during the survey was ~2.5 m s^{-1}, yielding an average spatial resolution of 12.5 meters between samples.

[8] The air-sea methane flux F was calculated as,

$$F = k_w(C_w - C_a) \tag{1}$$

where k_w is the gas transfer velocity, C_w the measured concentration of methane in the water, and C_a the methane concentration in atmospheric equilibrium. k_w, which depends on wind speed and the temperature-dependent Schmidt number of the gas, was estimated using parameterization developed by *Wanninkhof* [1992], *Nightingale et al.* [2000], *McGillis et al.* [2001], and *Ho et al.* [2006]. Wind data were provided by Santa Barbara County Air Pollution Control District for three stations located on-land and by the National Oceanic and Atmospheric Administration's (NOAA) Data Buoy Center for two stations offshore (Figure 1a). C_a was derived using Bunsen solubilities given by *Wiesenburg and Guinasso* [1979] and measured ocean temperatures and salinities.

3. Results

[9] A methane plume was observed within the study area (Figure 1b) with concentrations up to 1040 nmol L^{-1},
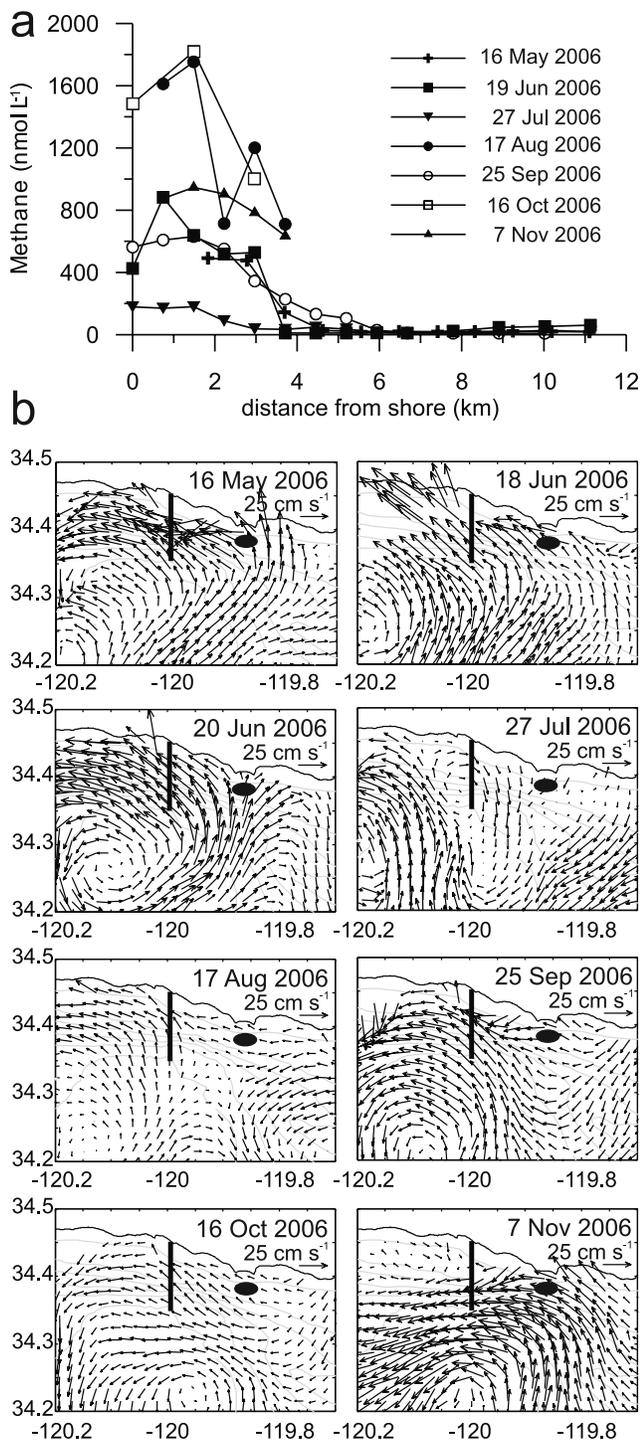
Figure 2. (a) Time series of methane concentrations along the easternmost transect in Figure 1b, the one closest to the seep field. (b) Surface ocean currents on the dates of sampling. No surface currents were recorded on 19 June 2006, but data of 18 and 20 June 2006, and visual observations made during sampling, indicate similar conditions. The currents are averages over 24 h. The black ellipse shows the location of COP seep field and the thick, black line illustrates the transect along which water samples were collected.

greater than 500 times atmospheric equilibrium but comparable to earlier measurements in the SBC near active seeps [*Clark et al.*, 2000; *Cynar and Yayanos*, 1992]. The highest methane concentrations were found close to the coast and the lowest offshore towards the center of the channel. Concentrations decrease westwards in the direction of the prevailing current. The plume widens towards the west as evidenced by the 50 and 200 nmol L^{-1} contours (Figure 1b) and reaches a maximum width at the western transect line.

[10] The methane plume was consistently located in the study area although maximum concentrations and plume width varied (Figure 2a). These variations correlate with evolving sub-mesoscale current fields as measured by a network of HF radars in the region [*Emery et al.*, 2004]. Concentrations measured on 16 May, 19 June, 25 September, and 7 November 2006 were similar (Figure 2a) when a cyclonic eddy was present. This eddy is a common feature of the SBC (Figure 2b) [*Beckenbach*, 2004; *Harms and Winant*, 1998; *Nishimoto and Washburn*, 2002]. The northern limb of this eddy transports water westwards from the COP seeps into the study area in about a day. On 27 July 2006 much lower methane concentrations were observed when a small anticyclonic eddy was present in the study area (Figure 2b). *Bassin et al.* [2005] found that these small anticyclones are common features of the area; they occur several times a year and persist over time scales of a few days. On 17 August and 16 October 2006, higher methane concentrations were observed when currents were weak along the northern SBC (Figure 2b).

[11] A spatial survey consisting of two transects was performed along the eastern edge of the study area on 10 November 2006, using the towed MS to provide enhanced spatial resolution. Ion counts from the MS (Figure 1c) are consistent with patterns of methane concentration determined for discrete samples obtained from the coarser grid survey. Three additional pumped methane samples (white circles in Figure 1c) obtained during one of the MS transects correlate with ion counts measured by the MS. For example, water samples collected close to the shore contained high concentrations of methane which match high ion counts measured by the MS.

[12] The air-sea flux of methane was estimated over the study area using measured concentrations and daily-averaged wind speed from the five land and buoy stations (Figure 1a). Daily averages were used because water sampling was conducted over 10 h and the water transit time to the western side of the study area is typically 1 day or longer. The air-sea fluxes of methane range from 0.1– 15 nmol m^{-2} s^{-1} and mirror the distribution of methane concentrations (Figure 1b). Table 1 contains the air-sea methane fluxes over the entire study area based on different k_w relationships, each of which depend strongly on wind speed.

4. Discussion

[13] For 19 June 2006 the air-sea flux of methane was estimated to be on the order of 5×10^4 mol d^{-1} over the 280 km^2 study area located west of COP seep field (Table 1). Uncertainties in this estimate arise from gas transfer (k_w) parameterization and variations in methane concentration which are discussed in detail below. Following this dis-

Table 1. Calculated Methane Air-Sea Fluxes for the Entire Study Area and Along the Easternmost Transect

Date	Wind Speed, m s^{-1}	Flux			
		W92[a]	N00[a]	M01[a]	H06[a]
Flux of 280 km^2 area (10^3 mol d^{-1})					
19 Jun 2006	4.3	54.7	50.3	54.2	46.9
Flux along easternmost transect[b] (mol d^{-1})					
19 Jun 2006	4.3	2.8	2.6	2.8	2.4
27 Jul 2006	2.8	0.3	0.4	0.5	0.3
17 Aug 2006	3.4	2.7	2.7	3.6	2.4
25 Sep 2006	3.8	2.2	2.1	2.4	1.9
16 Oct 2006	4.8	7.1	6.4	6.4	6.1
07 Nov 2006	3.8	2.6	2.4	2.8	2.2

[a]W92, *Wanninkhof* [1992]; N00, *Nightingale et al.* [2000]; M01, *McGillis et al.* [2001]; H06, *Ho et al.* [2006].
[b]Lengths of transect depend on number of stations, width assumed 1 m.

cussion, the flux is compared to the estimated amount of dissolved methane originating from COP indicating the low potential of methane transfer from the studied plume to the atmosphere.

[14] Uncertainties in methane flux from the COP plume derive from inherent uncertainties in wind speed over the 280 km^2 study area and from various relationships (for k_w) between wind speed and gas transfer velocity across the water-air boundary presented in literature. For example, a variation in wind speed from 4 m s^{-1} to 5 m s^{-1} (daily average) increases the methane-flux estimate over the whole study area from 4.3×10^4 mol d^{-1} to 6.4×10^4 mol d^{-1}, an increase of ~50% (see Figure S1 of the auxiliary material).[1] The k_w relationships of *Ho et al.* [2006], *Nightingale et al.* [2000], and *Wanninkhof* [1992] assume x- and y-axis (wind speed and k_w, respectively) intercepts at zero. But relationships not intercepting zero [e.g., *McGillis et al.*, 2001] include measurements at low wind speed and are presumably more appropriate for the study area where wind speeds are often <5 m s^{-1}. Furthermore, *Frew* [1997] showed in laboratory experiments that surface films greatly inhibit gas exchange. Oil slicks and tar floating from the seeps into the study area were observed as far west as the 4th north-south transect at $-120.17°$ W (Figure 1b). The likely damping of gas transfer by the oil suggests that lower transfer values are more realistic. For a given wind speed, use of the various k_w relationships, produces differences in methane flux of 10–40% (Table 1).

[15] The second parameter affecting flux estimates is variable methane concentrations resulting from point sources in the seep field coupled to sub-mesoscale current structures such as shown in Figure 2b. To constrain this uncertainty, a time series of methane concentration was collected between May and November 2006 along the easternmost transect at $-199.99°$ W. By evaluating the air-sea fluxes of the days sampled, we conclude that the 19 June 2006 survey represents the typical condition (Table 1). Higher methane fluxes occurred on 16 October 2006 when high concentrations of methane were associated with lower current speeds and higher wind speeds. On 27 July 2006 lower methane flux resulted from lower concentrations and lower wind speed. These low concentrations coincided with the presence of a small anticyclonic eddy. We speculate that

this eddy advected water with low methane concentrations from the mid-channel into the study area.

[16] In addition to the uncertainties of air-sea flux of methane already discussed, concentration differences within the plume not captured with our coarse grid sampling would also influence the flux estimates. Flux estimates are based on point samples that indicate a broad methane plume near-shore and a rapid drop to background concentrations farther offshore. Variable methane concentrations from the discrete samples indicate variability at a smaller spatial scale (e.g. 17 August 2006, Figure 2a). This is supported by the higher resolution in-situ MS results obtained on 10 November 2006 (Figure 1c). The three point samples taken during the towing of the MS correlate with the relative ratio measured by the MS. Calibrating the ion counts with these three point samples (ignoring that the MS measurements were collected ~0.5 m deeper than the point samples), the average methane concentration derived from the MS data (including all data points shown in Figure 1c) is 10% lower than the average of the point samples. Hence, we conclude that the discrete samples allow a reasonable estimate of the total flux.

[17] We estimated the total air-sea methane flux over the 280 km^2 survey area to be on the order of 5×10^4 mol d^{-1} for the 19 June 2006. Repeated sampling of one transect over six months and estimated air-sea fluxes based on these data indicate that the flux from 19 June is representative of the mean condition.

[18] *Clark et al.* [2000] estimated the dissolved methane flux from bubble plumes in COP seep field to be on the order of 3.6×10^6 mol d^{-1}. Approximately 1.4% of the dissolved methane is transferred to the atmosphere within the study area by air-sea exchange. Taking into account the uncertainties of the air-sea flux, at most 10% of the dissolved methane is lost to the atmosphere. Hence, most of the dissolved methane is not emitted to the atmosphere within 30 km of the plume source.

[19] The most likely fates for dissolved methane from COP are to enter the atmosphere farther away from the source, become oxidized by microbes in shallow water, or mix deeper into the water column where it is subsequently oxidized. Assuming background concentrations of 10–50 nmol L^{-1} (this study and *Cynar and Yayanos* [1992]) and the area of the entire SBC (4532 km^2) about 3×10^4–3×10^5 mol d^{-1} methane would enter the atmosphere. That is ~1–10% of the dissolved methane flux estimated by *Clark et al.* [2000] and comparable to the flux from the 70 km^2 plume directly down current of the COP seeps. Hence, most of the dissolved methane seems to be transported and oxidized below the surface water. *Clark et al.* [2000] noted that hydrocarbons were injected onto density surfaces between $\sigma = 24.5$–26.0 kg m^{-3}. Increased methane concentrations are typically found on these density surfaces at distances up to 700 km offshore [*Cynar and Yayanos*, 1992]. Thus, part of the dissolved methane plume seems to be transported below the pycnocline farther offshore. During transport and spreading of the plume, part of the methane is most likely oxidized by microbes within the shallow and deep water column. Oxidation rate measurements within the research area of this study are currently underway to investigate the extent of this sink.

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