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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 Coal Oil Point seep field, which is located about 3 km offshore of Santa Barbara County, CA in the Santa Barbara Channel. The field research was conducted using a spar buoy designed to simultaneously measure the surface gas flux, the buoy's position with differential GPS, and collect gas samples. Results show that the gas composition varies by 10-20% at sub-seeps within seep areas. The nitrogen mole fraction correlated directly with oxygen mole fraction (R^2 = 0.94) and inversely with methane mole fraction (R^2 = 0.97). These data demonstrate that the bubble composition is modified by gas exchange during ascent from the seafloor: dissolved air enters and hydrocarbon gases leave the bubbles. While compositional differences were observed at sub-seeps, there was no relationship between flux and composition. Factors other than seep intensity controls the amount of gas transfer between the ocean water and bubbles. Therefore, when calculating the atmospheric source function of specific gases such as methane or ROGs from marine seeps, it is best to use mean compositional values determined for bubbles collected near the sea surface

Introduction

The Coal Oil Point seeps represent both a regional source of hydrocarbon contamination and an opportunity for hydrocarbon production. The seeps are located in Santa Barbara County, CA, off shore of the University of California, Santa Barbara

(Fig. 1), about 10 km west of City of Santa Barbara. Chemical signatures from these seeps can be followed for 100s of kilometers away from their source in both the ocean (*Hartman and Hammond, 1981; Cynar and Yayanos,* 1992) and atmosphere (*Killus and Moore, 1991*). In addition to contributing significant amounts of tar to regional beaches, these seeps are known sources of reactive organic gases (ROGs) and methane to the regional air (e.g., *Hornafius et al., 1999*), and dissolved hydrocarbons to the coastal ocean (*Clark et al., 2000*). ROGs are precursors to ozone-forming smog, a known health hazard, and presently, Santa Barbara County has an ozone problem (*SBAPCD, 1994*). Additionally, seafloor measurements of seep gas have shown that concentrations of benzene and other carcinogenic hydrocarbons exceed 10 ppm. This implies that these seeps are potentially a significant source of carcinogenic hydrocarbons to the local atmosphere and ocean.

Other observations from the Coal Oil Point field indicate that seepage rates vary over a broad range of time scales so the source functions for ROG's and other gasses are not constant in time (e.g., *Quigley et al., 1999; Boles et al., 2001; Leifer et al., 2004; Leifer and Boles, 2005*). Strong evidence for variability in seepage rates comes from gas flow data from two large seep containment devices ("seep tents") which cover an area of numerous, very strong seeps (*Rintoul, 1982*) and detailed surveys of seafloor vent features (*Leifer* et al., 2004).

The objective of our study was to evaluate the relationship between gas flux to the atmosphere and gas composition of the bursting bubbles so that the atmospheric source function of methane and ROGs can be better defined. Earlier investigations have shown that bubble plume processes control the amount of gas exchange that occurs between rising seep bubbles and the water column (e.g., Leifer et al, 2000; Leifer and Patro, 2002; Clark et al., 2003). The exchange rate and direction is determined by the concentration gradient across the bubble water interface. Methane and other hydrocarbon gases are transferred out of rising bubbles while nitrogen, oxygen, and

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other dissolve gases are transferred into the bubbles. Plume processes, which affect the amount of gas exchange, include plume-water saturation and the generation of upwelling flows. Limited field observations (e.g., Leifer et al 2000) suggest that both of these processes scale with flux. Furthermore, recent seafloor observations indicate that bubble size-distributions above strong and weak seafloor vents differ (Leifer, unpublished data). Strong vents emitted a broader bubble spectrum, which includes large bubbles. Model calculations indicate that a smaller fraction of the initial mass of gas dissolves from large bubbles than from small bubbles during transit through the water column.

We hypothesized that the bubbles at stronger seeps would contain more hydrocarbon gases (methane, ROGs, etc.) and less air (oxygen and nitrogen) than bubbles at weaker seeps. Therefore, a greater fraction of the gas released at the seafloor from small seeps dissolves into the water column than from large seeps. Large seeps are less efficient at transferring methane and other hydrocarbons into the water column and more efficient at transferring these gases to the atmosphere than are small seeps.

In order to test our hypothesis with field data, we proposed to:

1. Construct a gas sampling devise for the flux buoy, an existing piece of equipment, so that simultaneous measurements of gas flux and collection of gas bubbles can be conducted.
2. Deploy the modified flux buoy over Coal Oil Point seeps of varying size.
3. Analyze gas samples for oxygen, nitrogen, methane, ethane, propane, and butane.

Methods

The flux buoy is ~3 m long spar buoy which measures gas flux by capturing gas bubbles just below the sea surface. When floating in the ocean, the water line bisects the spar buoy's Styrofoam floats, about 1.3 meters from the buoy top. The long, narrow configuration of the flux buoy dampens motions due to small amplitude, high frequency surface waves. Rising bubbles are directed into a collection chamber through

a circular cone at the base of the buoy (Fig. 2). The flux is determined from the rate of change of the pressure difference, Δp, between the inside of the collection chamber and surrounding seawater. The volume flux of gas per unit area of sea surface, adjusted to standard temperature T_a and pressure p_a, is,

$$\dot{q} = (\rho g)^{-1} \frac{\partial \Delta p}{\partial t} \frac{T_a}{T_c} \frac{p_c}{p_a} \frac{A_c}{A_{co}} \qquad (1)$$

where $\partial \Delta p / \partial t$ is the time rate of change of differential pressure, T_c and p_c are temperature and pressure of the gas in the collection chamber, and A_{co} is the area of the collecting cone (0.27 m^2).

Gas accumulates in the chamber until an adjustable threshold Δp is reached. Then a microcomputer-controlled valve opens to release the accumulated gas and start a new measurement cycle. Data acquisition, valve operation, and data transmission are controlled by a microcomputer in the electronics pressure case. The computer samples Δp, T_c, and p_c once per second. Buoy position is logged every 2 seconds 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 is gently towed through seepage areas as the research boat moves slowly forward. Additional details of the flux buoy design, operation, and calibration are given by *Washburn et al.* (*2001*) and *Egland* (*2000*).

Note that equation (1) describes the total flux of gas at the sea surface. Compositional analyses are needed to estimate fluxes of individual gases like methane or ROGs. Therefore the flux buoy was modified so that the vented gas could be sampled for later laboratory analysis. The vented gas was collected in 40 cm long, 3/8" stainless steel tubes sealed with Nupro plug valves. The tubes were bent into "U-shape" loops. Copper tubing (3/8" O.D. and ~2 m in length) ran from the submerged collection chamber vent along the spar to the sample loops, which were located above the water line. After collection, these loops could be quickly replaced from the side of the boat.

In the laboratory, the sample loops were submerged in water and the seep gas was removed using a glass syringe. Subsequently this gas was analyzed on an Agilent micro-Gas Chromatograph (GC) for methane, ethane, propane, butane, oxygen, nitrogen, and carbon dioxide. The typical analytical uncertainty based on replicates is better than ±3%.

Field Cruises

Composition-flux surveys at three seeps, unofficially named Horseshoe, La Goleta, and Seep Tent, were conducted during 4 survey days (12-Aug-03, 4-Sept-03, 16-Dec-03, and 5-Oct-04). Each of these seep areas is composed of regions of high and low flux which we refer to as sub-seeps. The different sub-seep regions are visually distinct. Washburn et al. (2005) formally addressed the issue of the flux variation within a seep area by examining the spatial statistics of flux buoy data. At the Coal Oil Point seeps, they found that the spatial scales of continuity of the seeps are small, ranging from <1 to about 9 m. Samples were collected from sub-seeps of different strength by carefully positioning the flux buoy in a given area. This often required steering the boat in small circles. Surface gas flux varied strongly such that the length of time required to fill the collection chamber was as short as a few seconds and as long as a half hour.

During the surveys, the flux buoy was tied along side the survey boat so that the collect tubes could be easily changed. Our gas collection procedure included flushing the system with helium gas prior to sample collection and connecting two loops in series so that duplicate samples were obtained for each flux measurement. After connecting new sample tubes, helium was released into the funnel and the chamber was filled and vented at least five times. While seep gas was being collected, the sample loop outlet was kept submerged in a small container of water to both (1) visually confirm when gas was vented from the chamber and (2) prevent the sample from being contaminated with ambient air. After gas collection, loops were manually swapped out and capped while the flux buoy remained in the water. One or two

helium blanks were also collected during each survey to determine the efficiency of the helium flush.

To determine the weight average flux for each gas sample, we attained the least square fit to the rise of Δp with time during the last fill of the collection chamber following the procedure of Washburn et al. (2001). Three methods were used to distinguish which part of the Δp time series corresponded to gas flux for the collected gas sample.

Method one was used when the flux buoy had obviously vented collected gas at least once (Fig. 3A). Typically this approached work at the larger sub-seeps when the flux was greater than about 1 m/day. As seen in figure 3A, the buoy vented once at 255 s, and then a second time at 712 s. To determine when the seep gas sample was collected, recorded field notes of visual observations were compared with the computer time series. Consequently, start and end points for gas sample collection could be identified. In this example, gas sample collection start was at 250 s and end was at 700 s. The slope of the line between these two endpoints is proportional to the flux of the collected surface gas sample.

Method two was applied when surface bubbling gas seepage was less intense. In these cases, it took longer to fill the flux buoy chamber and consequently, increased time to vent collected gas. Often, no venting from the buoy occurred (Fig. 3B). To establish corresponding bubbling gas flux of weak seepage areas, a least square fit was determined for the entire collection time. Mean flux for the period is proportional to the slope for the entire time series.

Method three was used when a time series included varying slopes from small seeps of varying strengths (Fig. 3C). There are times when the flux buoy was outside seepage areas and thus, flux was nearly zero. There were also short periods when the buoy was over low flux areas and thus, collected gas and measured flux. The 3100 s time series (Fig. 3C) has three intervals contributing to overall flux for the collected gas sample, labeled “a”, “b”, and “c”. In between, the flux is nearly zero. Mean flux for the

gas sample was estimated from the total change in differential pressure over the three intervals divided by the total elapsed time.

Results and Discussion

We sampled 28 sub-seeps for flux and gas composition during four cruises. Unfortunately data from the first two cruises were suspect due to methodological or analytical problems. Therefore we have limited our analysis to data collected from only the 16-Dec-03 and 5-Oct-04 surveys conducted at La Goleta and Seep Tent seeps (Table 1).

The helium blanks demonstrate that our flushing procedure did a good cleaning the flux buoy collection system. Cross sample contamination was small. The helium blanks did contain oxygen, nitrogen, and occasionally methane (Table 1). The mole fractions of these components were typically less than 0.5% in the helium blanks, though occasionally the fractions were more than 1%. It is likely, that a portion of this gas was stripped from the seawater contained within the buoy's funnel.

The gas composition of the sub-seeps varied systematically. Sub-seeps high in methane were low in oxygen and nitrogen. The mole fraction of nitrogen correlated strongly with both methane and oxygen (Fig. 4), showing that bubble lost methane and gained air during their ascent from the seafloor. While the components of the gas co-varied, there was no relationship between flux and composition (Fig. 5). In fact the full range of the methane mole fraction was apparent in the weakness sub-seeps (<0.25 m/day). There is also no systematic difference in composition or flux relationship between the two seeps studied. Apparently, gas exchange with the bubble plume does not scale simply with flux within a seep. Other factors such as bubble size must be controlling the amount exchange of gases, which occurs during the bubble ascent.

Summery

During this UCEI funded study, an existing piece of equipment, the flux buoy, was modified so that the relationship between bubble composition and gas flux to the atmosphere could be examined at Coal Oil Point seep field. While compositional differences were observed at sub-seeps within seep areas, there was no relationship between flux and composition. When calculation the atmospheric source function of specific gases such as methane or ROGs, it is best to use mean values determined for bubbles collected near the sea surface.

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Table 1: Experimental results. The seep areas visited were Seep Tents (ST) and La Goleta (La Gol). The gas composition is listed as mole volumes (%) and the flux is in m/day.

Area	Latitude	Longitude	Flux	N_2	O_2	Methane	Ethane	Propane	Butane
December 16, 2003									
ST	34°23.041	119°53.409	1.1	13.9	3.41	75.0	3.86	2.69	0.94
ST	34°23.046	119°53.390	1.9	17.6	4.18	71.0	3.46	2.58	0.94
ST	34°23.070	119°53.366	3.1	20.2	4.82	68.3	3.12	2.47	0.93
ST	34°23.063	119°53.372	1.0	20.2	4.94	68.2	3.12	2.45	0.92
ST	34°23.053	119°53.410	1.2	14.5	3.51	74.4	3.84	2.65	0.89
ST	34°23.070	119°53.409	0.1	11.3	2.90	78.2	4.04	2.61	0.81
ST	34°23.074	119°53.368	0.2	19.3	4.78	69.1	3.30	2.50	0.92
Blank	34°23.079	119°53.343	-	1.57	0.26	nd	nd	nd	nd
October 4, 2004									
ST	34°23.06	119°53.382	1.2	18.3	4.72	70.0	3.38	2.55	0.95
ST	34°23.05	119°53.391	3.9	15.3	4.05	73.2	3.71	2.61	0.95
ST	34°23.04	119°53.436	0.1	13.1	3.37	75.6	4.05	2.71	0.95
ST	34°23.07	119°53.382	-0.1	18.2	4.75	70.0	3.40	2.56	0.95
La Gol	34°22.495	119°51.223	1.0	18.2	4.41	71.3	3.17	1.91	0.79
La Gol	34°22.492	119°51.225	1.2	20.3	4.97	69.2	2.74	1.86	0.81
La Gol	34°22.499	119°51.259	0.2	15.6	3.90	74.9	2.69	1.93	0.83
La Gol	34°22.501	119°51.405	0.1	21.9	4.90	66.7	2.86	2.22	0.93
Blank	34°22.476	119°51.324	-	0.07	0.43	0.21	0.14	nd	nd

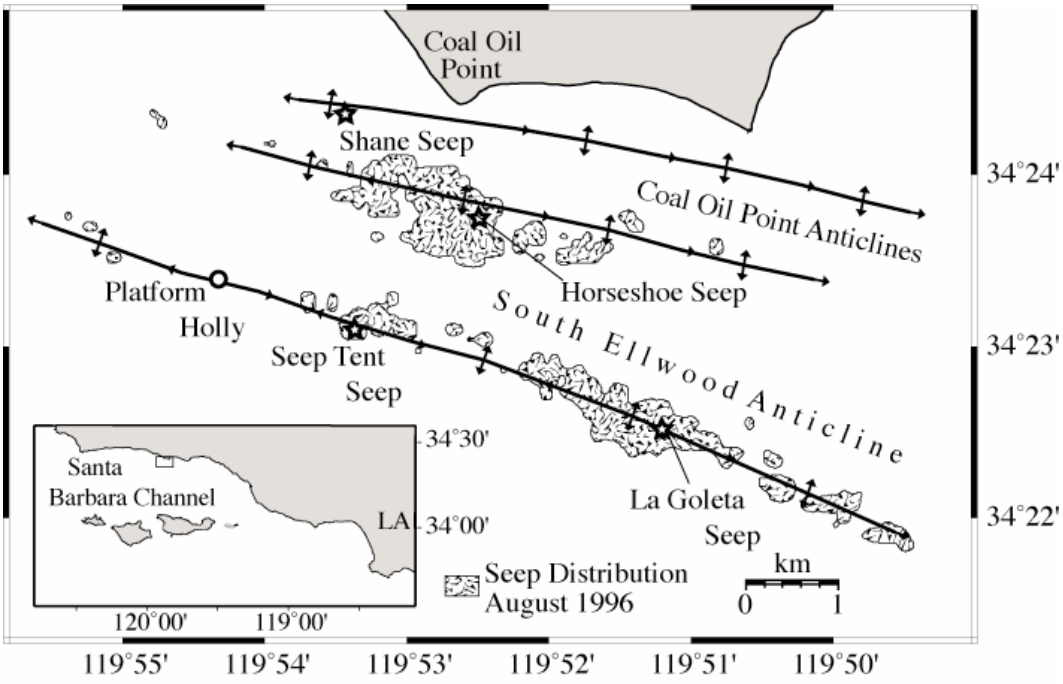


Figure 1: Coal Oil Point seep field showing the 1996 distribution determined using 3.5 khz sonar (Quigley, 1997), the primary structural features, the location of four of the largest, informally named seeps (stars), and Platform Holly (circle). Seepage along the inner anticline was too shallow for sonar surveys.

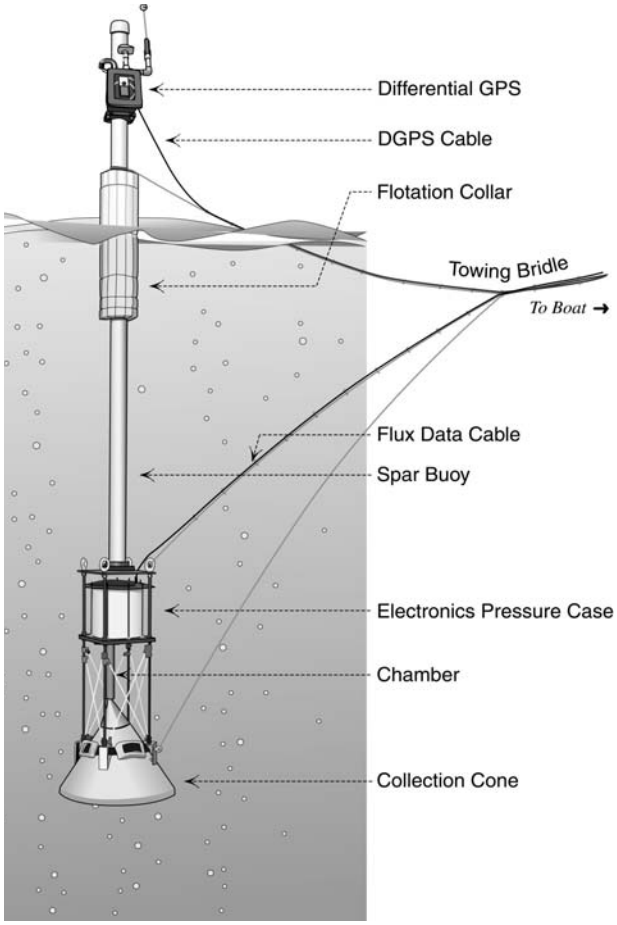
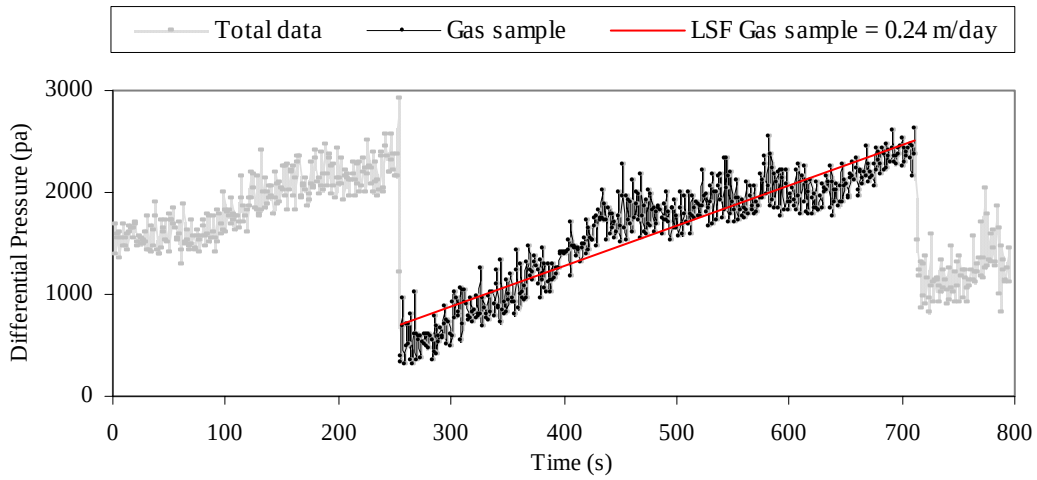
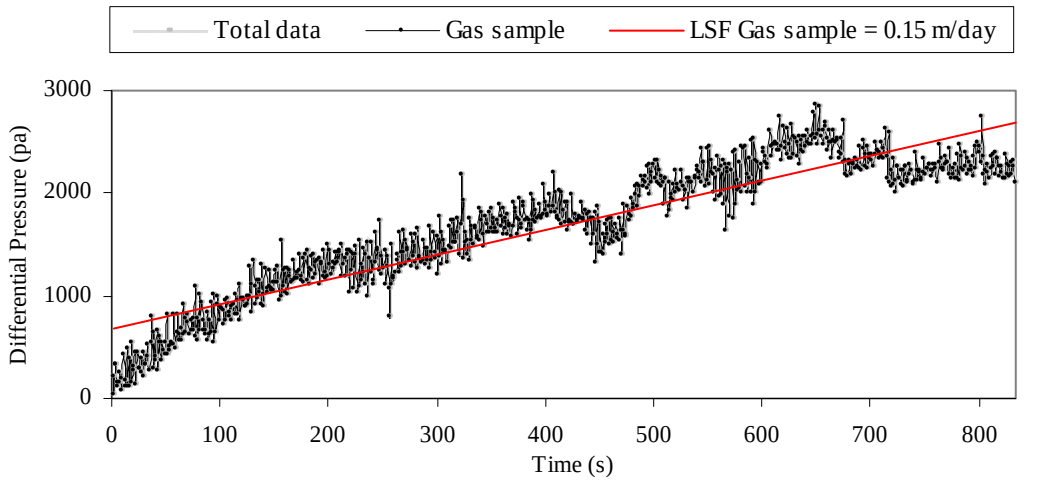


Figure 2: Diagram of flux buoy described by *Washburn et al. (2001)*.

(A)



(B)



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(C) Figure 3: Flux time series for seep surface gas samples collected at (A) LGS on 05 October 2004, (B) at STS on 16 December 2003, and (C) at STS on 05 October 2004.

c

b

a

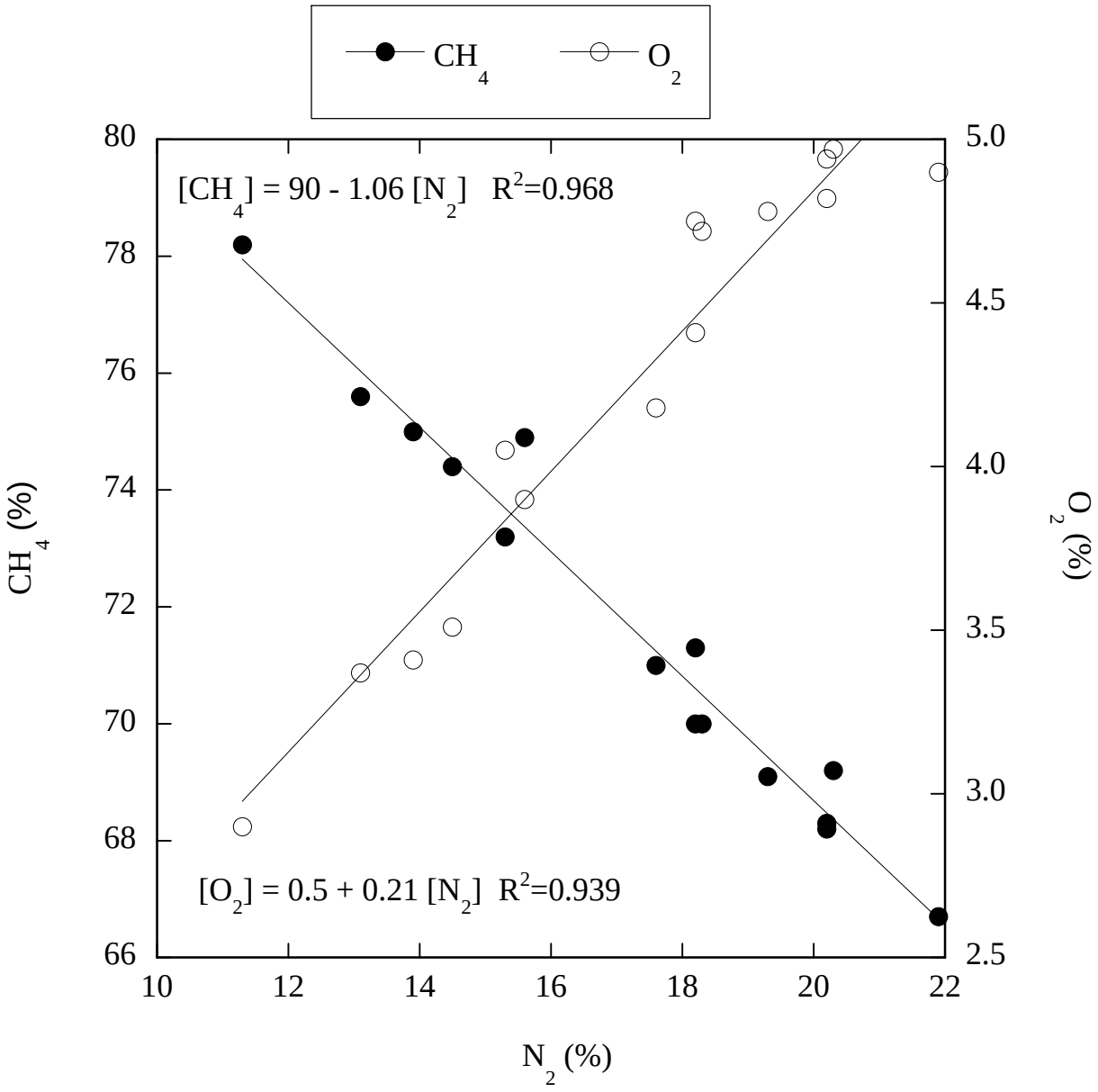

Figure 3: Gas composition (mole fraction) collected at Seep Tent and La Goleta seeps.

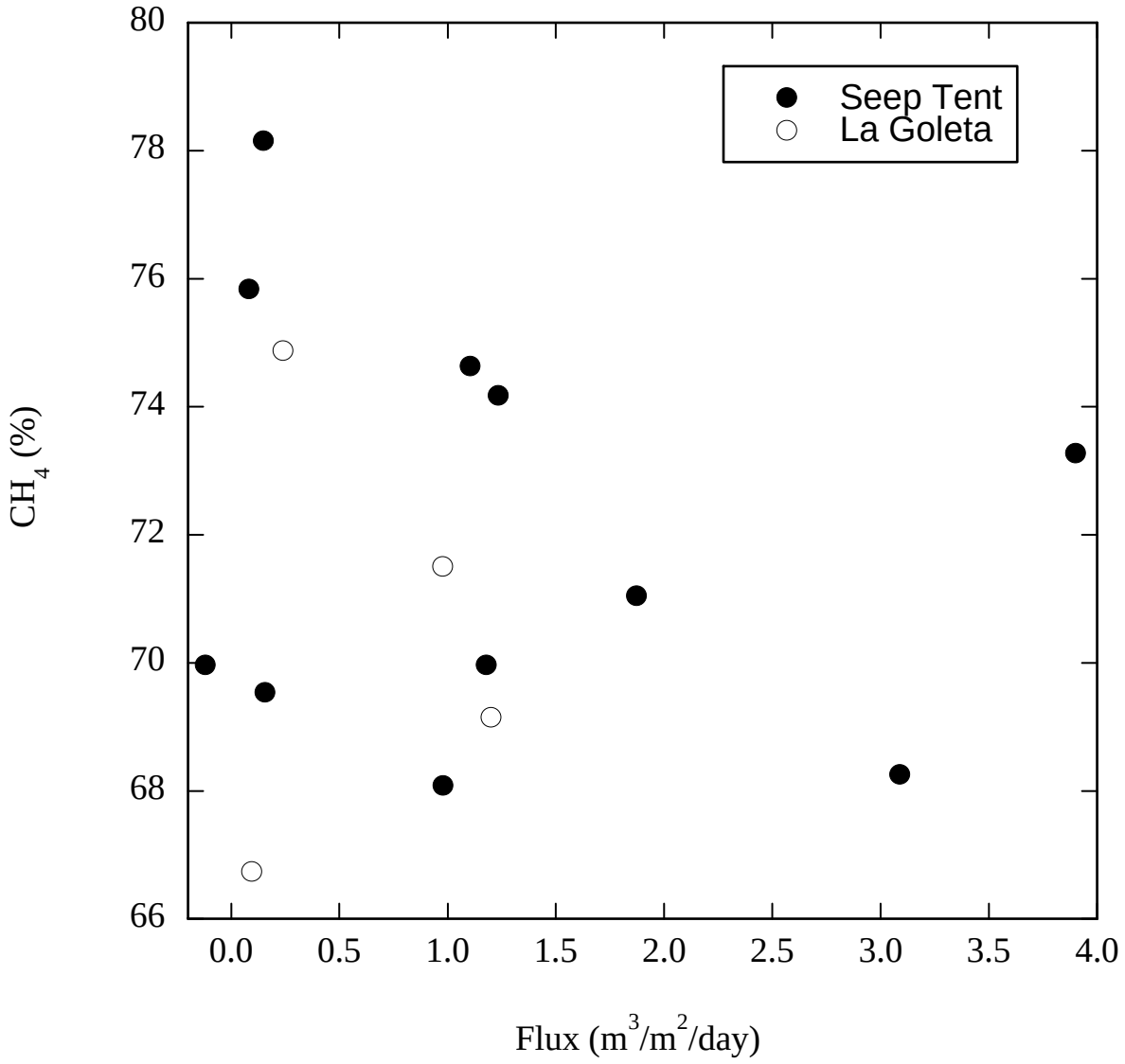

Figure 4: Methane mole fractions plotted as a function of sub-seep flux.