

Tracking Seep Oil from Seabed to Sea Surface and Beyond at Coal Oil Point, California

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Overview

Oil slicks on the ocean surface emitted from natural marine hydrocarbon seeps offshore from Coal Oil Point (COP) in the Santa Barbara Channel, California were tracked and sampled over a period of two hours. The objectives were to characterize the seep oil and to track its composition over time using a new sampling device, a catamaran drum sampler. This paper presents design details and results from a field study.

Introduction

The fate of oil in the environment is of widespread interest. Natural oil seepage has been long used for prospecting, while mitigation and successful remediation of oil spills is also an important concern. However, studying oil in the environment is problematical due to the complexity of its interactions and unpredictability of accidental spills, the difficulty of obtaining permission for planned release experiments, and scaling difficulties for planned release experiments.

UCSB seep research primarily focuses on the COP Seep Field, a naturally leaking oil and gas reservoir (Fig. 1), and one of the largest known in the world (*Hornafius et al.*, 1999). The seeps are located above an oil sourced from the Miocene Monterey Formation with locations partly controlled by folds and faults that run sub parallel to the shoreline (*Broderick*, 2001). These perennial and continuous seeps have been known since before the arrival of Spanish explorers (*Fisher*, 1978) and provide an *ideal natural laboratory* for studying the fate of hydrocarbons in the marine environment. Total flux estimates for the field are $10^5 \text{ m}^3 \text{ day}^{-1}$ gas and $100 \text{ bbl oil day}^{-1}$ (*Hornafius et al.*, 1999), but these rates, especially for oil, are poorly constrained.

Oil coated bubbles consisting primarily of methane are commonly observed rising from the seabed at the COP seeps, while only in a few locations are oil droplets without gas observed. Due to their greater buoyancy, bubbles rise orders of magnitude faster than oil droplets. Therefore bubble-mediated oil transport is markedly more rapid than unaided oil droplet ascension. As a result, the oil transit time within the water column is reduced, causing a reduction in the size of the surfacing footprint (i.e., the droplets have less time to disperse; *MacDonald et al.*, 2002).

At the sea surface, the oil forms a slick and drifts under the effects of wind and currents. Predicting the impact of a spill, and thus the best spill response strategy (*Reed et al.*, 1995) requires understanding of the fate of the many oil components since they have different toxicities (*Riazi and Al-Enzi*, 1999). Processes during the initial phases of oil slick evolution include volatilization (evaporation), dissolution and flocculation, dispersion (diffusion), advection, and photolysis (*Mackay and McAuliffe*, 1988). Weathering can reduce oil slick volume by 70% and 40% for light crude and refined oils, respectively, primarily due to volatilization (*Fingas*, 1995).

Volatilization also shifts the peak in the n-alkane spectrum towards heavier n-alkanes (*MacDonald et al.*, 2002). Other physical and biological weathering processes, such as biodegradation, are important over longer time periods and thus were not addressed.

CATDRUMS Oil Slick Sampler

A CATamaran DRUM Sampler (CATDRUMS) was developed to sample oil slicks and was a modification for oil of a microlayer sampler developed by *Harvey* (1966). Photos at Shane Seep are shown in Fig. 2. The sampler consisted of a 20-cm diameter, 30-cm long rotating stainless steel drum with its axis maintained a fixed (but adjustable) distance above

the surface. Oil adheres to the rotating drum and is collected in a trough on the drum's downward side. The drum is motor driven with power located on the boat. Rudders off the stern aided steering. Contact between the trough and drum is maintained by a thin Teflon wiper. Solvent is sprayed into the trough and pumped out through a port at the trough base via 1/8 inch Teflon tubing and a gear head pump to the sample jar.

Collection protocol and field trip conditions

Surface water temperature during the field sampling cruise on Oct. 9, 2002 was 16.7C and the air temperature ranged from 17C at 10:00 AM to 19C at 12:20 PM. Winds were very light, 0-3 knots, and the sky was overcast. Sample locations are shown in Fig. 3. Oil slicks were sampled in, up-current and down-current of Shane Seep, and in a convergence zone at the edge of Shane Seep where very thick, brown, oil slicks are common. After each sample, the Teflon tubing was flushed with DMC, and the trough and drum were wiped clean with DMC-soaked Kimwipes. Divers also collected freshly deposited seabed tar at Shane Seep (22-m depth).

Fresh Shane Seep oil was very thin (and light) and thus the sample time was five minutes (~500 rotations), while other sample times were ~1 minute. Slick tracking was tracking was done by seeding the slick with hollow glass microspheres 30 to 70 micrometers diameter. Due to their small size the spheres truly track the oil. Eventually (#13) the oil ran into a kelp bed and sampling was terminated. Samples were analyzed by Gas Chromatography/Flame Ion detection (GC/FID) by Steve Sweet at The Geological and Environmental Research Group of Texas A&M, College Station.

Results

The initial (Fresh Shane Seep Oil) chromatogram is shown in Fig. 6A, with the n-alkane peaks clearly distinguishable down to decane (n-C10). Concentrations were very low (i.e., compared to surrogates) despite the long (5 min) sampling time. Due to the currents, oil slicks from the inshore seeps drifted towards Shane Seep.

A chromatogram from the oil slick near the IV Super Seep is shown in Fig. 4B. This sample shows some degradation including a small unresolved complex hydrocarbon mixture (UCM) "hump" peak from 18 to 24 min retention time. The increased number of non-alkane peaks also indicates degradation. Collected oil probably included a mixture of oil from the IV Super Seep and other inshore seeps. Another feature of the IV Super Seep oil is the dominance of n-C22 relative to other n-alkanes, unlike in Shane Seep oil.

The strong bubble-driven outwelling flow at Shane Seep protects the center from penetration by (and mixing with) other oil slicks, shown by the absence of the degradation characteristics observed in the up-current oil slicks (i.e., Fig. 4B). Thus the outwelling flow causes oil drifting towards Shane Seep either to diverges around Shane Seep or become trapped in a convergence zone at Shane Seep's edge. A chromatogram from this convergence zone is shown in Fig. 4C. Degradation is much greater with a dominant UCM hump and the more volatile components (lighter than n-C16) gone, although n-alkane compounds heavier than n-C16 are identifiable. This probably resulted from oil mixing in the convergence zone and weathering. Shown in Fig. 4D is a sample from a freshly deposited tarball taken at the seabed at Shane Seep. The tar is highly biodegraded, mostly UCM, although n-alkane peaks are still visible. Since it is unusual in an oil this degraded to have n-alkane peaks as light as n-C15, the tar must contain some (relatively) fresh oil (i.e., as in Fig. 4A) in addition to highly degraded oil. Tar and oil slick chromatograms are quite different, strongly supporting the conclusion that the mechanism by which oil and tar reach the seabed is dramatically different.

The Shane Seep oil slick was sampled at 15, 30, 60, 100, and 120 min. To account for varying oil recovery, n-alkane concentrations were normalized to n-C18, which varied less between samples than most other n-alkanes. The n-C12 to n-C15 concentration markedly decreased for the first 30 min, then rose for the following hour, and then dropped steeply at 120 min (Fig. 5A). Clearly, the Shane Seep oil slick changed between 30 and 60 m and between 100 and 120 minutes. Chromatograms for 15 and 30 m are similar to the initial chromatogram (Fig. 4A). The chromatogram at 60 min showed both a strong n-C22 peak and a similarly shaped UCM hump to that for IV Super Seep (Fig. 6B). Thus these chromatograms suggest strongly that the oil slick up-current of Shane Seep diverged around the seep and subsequently merged with the Shane Seep oil slick after about an hour. At 120 min the oil slick (and particles) drifted into a

kelp bed located along a Langmuir cell line, and became trapped. The 120 min and 60 min chromatograms were dramatically different. The 120 min chromatogram showed a stronger UCM than the Shane Seep convergence zone (Fig. 4C) including features similar to the tar ball. Probably the oil had adhered to the kelp and degraded over a long time relative to oil in the Shane Seep convergence zone. However, the chromatogram has easily identifiable n-alkane peaks indicating fresh oil input.

N-alkane decay rates, τ , were calculated for the first 30 min of drift by a fit of exponential to the normalized concentrations (Fig. 5B). With increasing n-alkane number (decreasing volatility), τ decreased. The half life is given by $1/\tau$, and varied from ~ 15 min. for n-C12 to ~ 90 min for n-C16. N-alkane diffusivity in seawater also increases with increasing mass, from $1.61 \times 10^{-5} \text{ cm s}^{-2}$ to $1.56 \times 10^{-5} \text{ cm}^{-2}$ for n-C12 and n-C17, respectively (Wilke and Chang, 1955). This diffusivity trend implies faster surface diffusion (dispersion) for lighter n-alkanes, although the decrease is too small to explain the dramatic increase in lifetime with n-alkane number.

Acknowledgements

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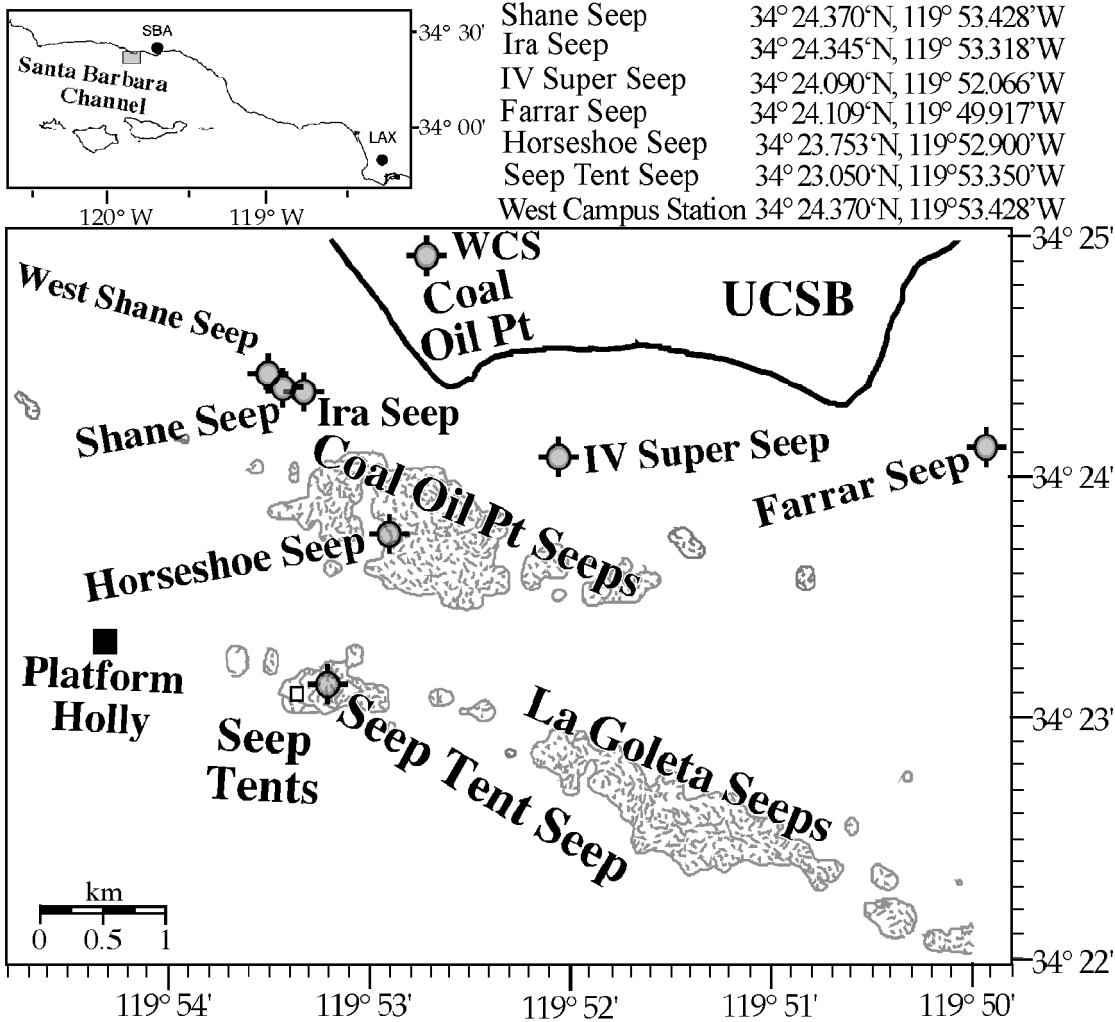


Figure 1. Coal Oil Point seep field with active gas seepage regions from 3.5 khz sonar (Quigley, 1997) indicated. WCS is West Campus Air Quality Station.

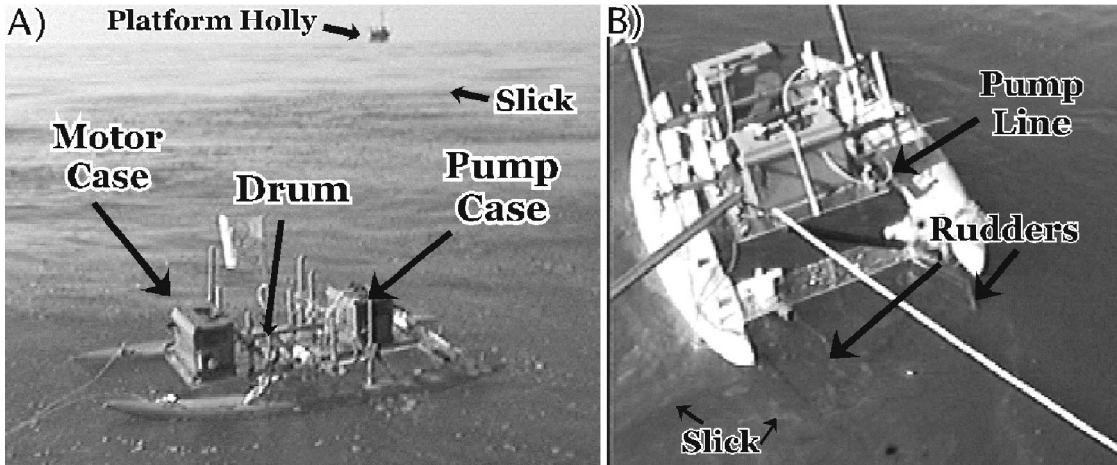


Figure 2. Photos of CATDRUMS at Shane Seep. A) CATDRUMS was in drift mode, B) was towed. An oil slick is visible beyond CATDRUMS in A).

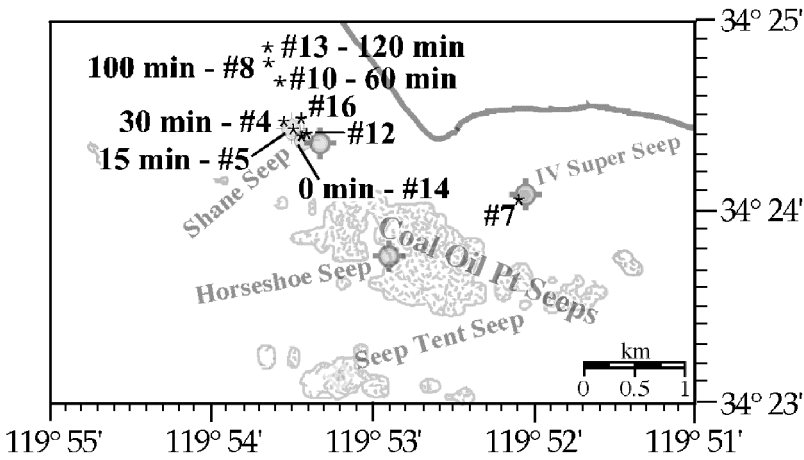


Figure 3. Map showing location of oil slick samples, and time where appropriate.

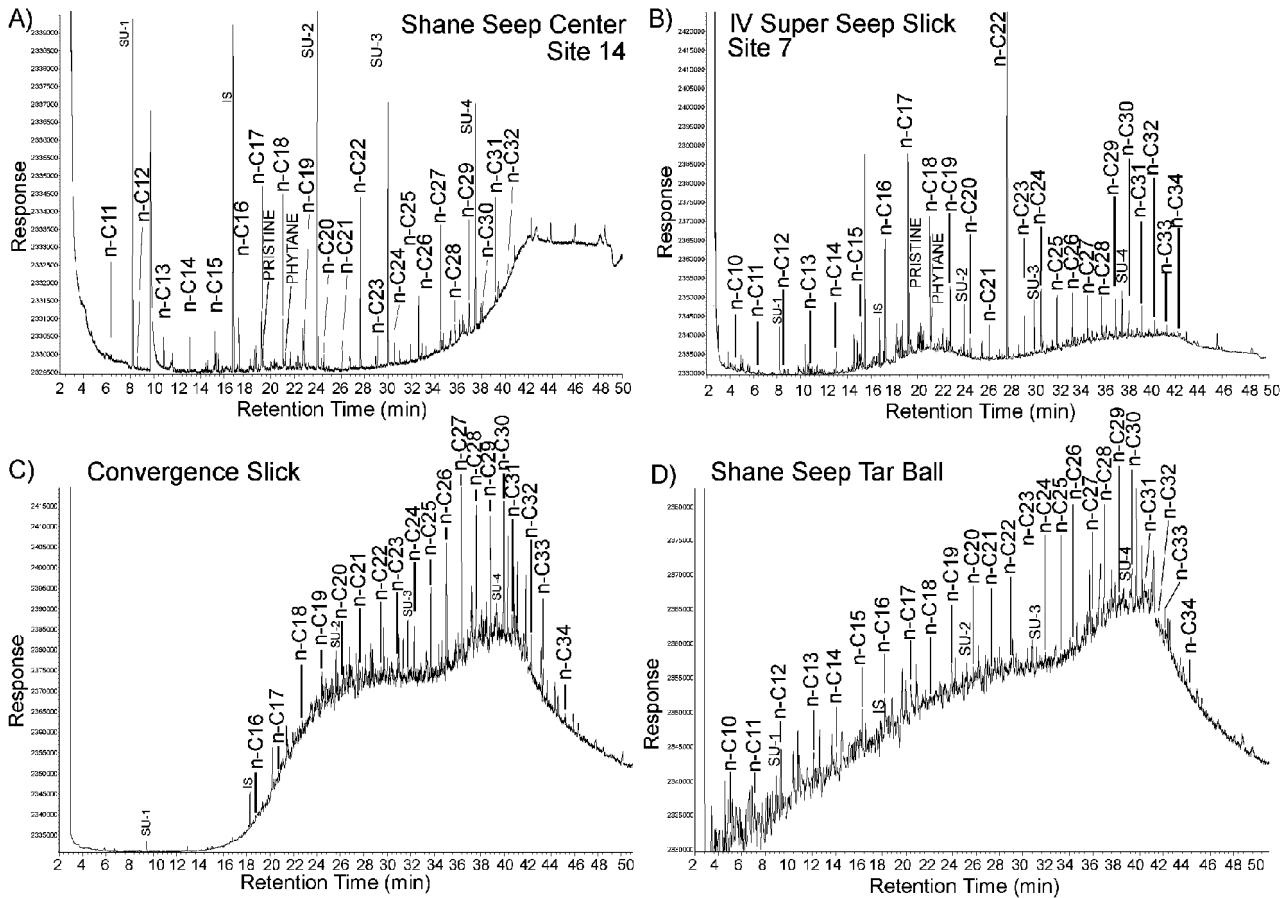


Figure 4. Chromatograms from A) Shane Seep slick, B) IV Super Seep slick, C) Shane Seep convergence slick, and D) Shane Seep tar ball. N-alkanes labeled on figure. IS is Internal Standard, SU is Surrogate compound.

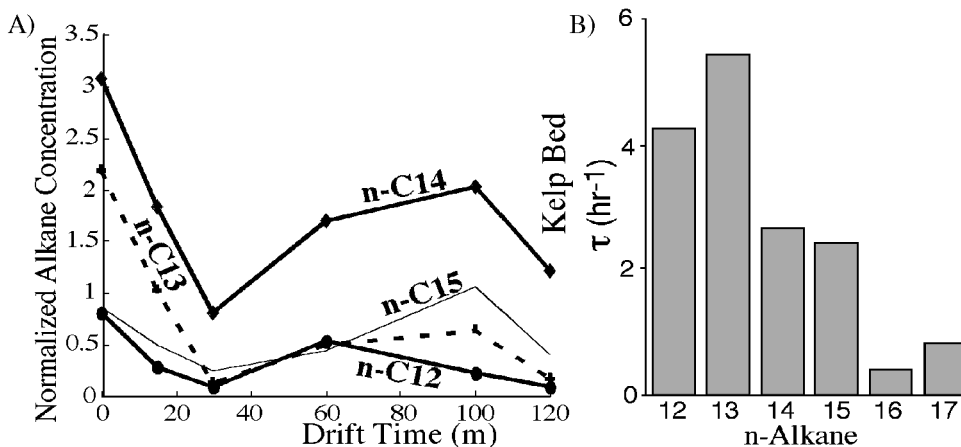


Figure 5. Variation in n-alkane concentration normalized to n-C18 with drift time from Shane Seep and B) decay rate (τ) from an exponential fit for n-C12 to n-C17 for drift time < 30 min. N-alkanes labeled on figure.