

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

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. The sampler was designed and developed at UCSB. Oil slicks were collected near COP and analyzed. Chromatograms show that oil originating from Shane Seep evolved due to weathering for about an hour before mixing with a second oil slick. Before the oil slicks merged, the volatile n-alkane components decreased with a half life that increased with increasing n-alkane number (i.e., decreasing volatility). Chromatograms of freshly surfaced oil slick and freshly deposited seabed tar were markedly different and supported the conclusion that the mechanisms by which tar and oil reach the seabed have dramatically different time scales. Future work will include further field studies, calibration experiments, and sampler improvements to allow continuous oil slick sampling and improved volume estimation.

1 Introduction

The fate of oil in the environment is of interest to scientists, regulatory agencies, and industry. Natural oil seepage has been long used for prospecting, while mitigation and successfully remediation of oil spills is also an important concern. Plans regarding potential resource exploitation and shipping lanes require informed decisions by resource planners from federal, state, and local agencies. However, studying oil in the environment is problematical due to the complexity of its interactions and unpredictability of accidental spills as well as the difficulty of obtaining permission for planned release experiments. Furthermore, planned releases are by their nature short term, while oil spills from an undersea pipeline or leaking tanker persist for significantly longer time scales and thus interact with environmental processes of longer and larger time scales than achievable in a typical release experiment.

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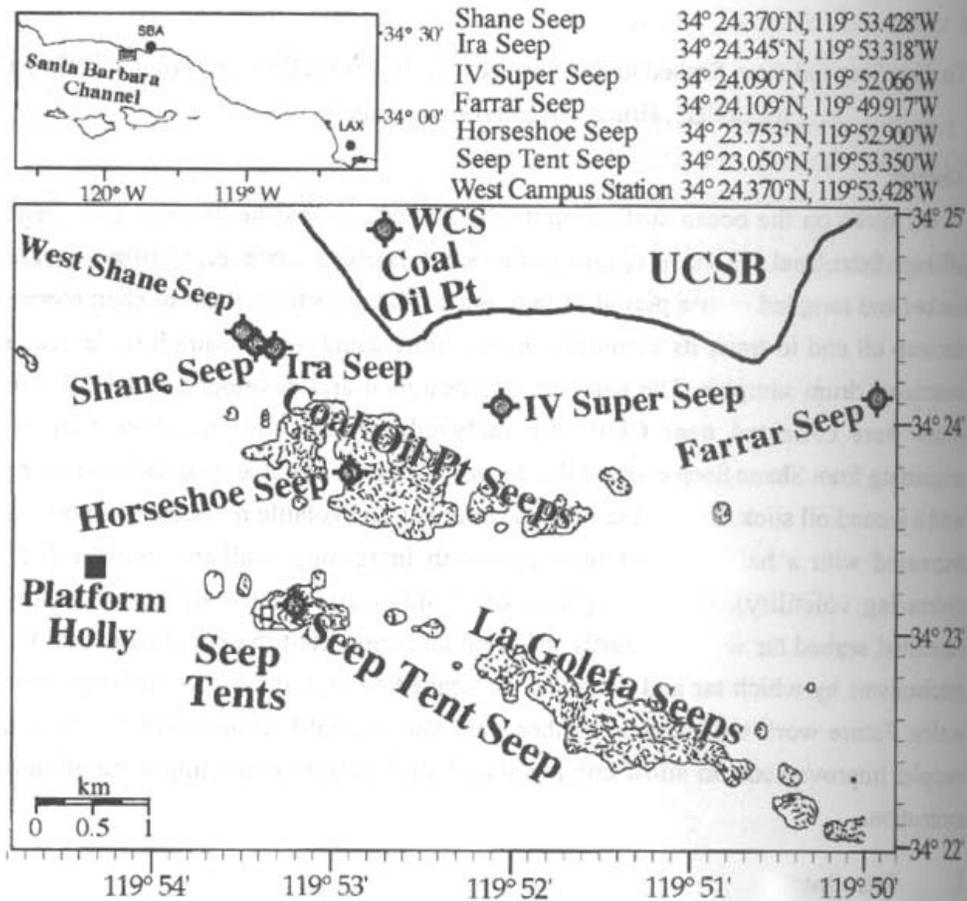


Figure 1. Map of Coal Oil Point seep field with contours of active gas seepage regions as measured by 3.5 khz sonar (Quigley, 1997). Named seeps are indicated by targets with Latitude and Longitude listed in table above map. WCS is West Campus meteorological Station where air quality is monitored.

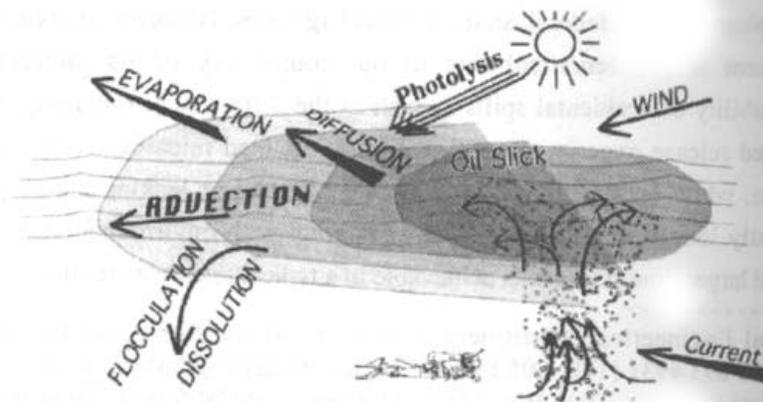


Figure 2. Schematic of major oil spill weathering processes.

Seep research at the University of California, Santa Barbara (UCSB) is addressing shortcomings in our understanding of the fate of oil in the marine environment by studying the Coal Oil Point (COP) seep field, a naturally leaking oil and gas reservoir (Fig. 1). The COP field is one of the largest known in the world, located a few kilometers from the UCSB campus. The seeps are located above an oil sourced from the Miocene Monterey Formation. Seeps locations are controlled in part by the location of folds and faults that run sub parallel to the shoreline (Broderick, 2001). The fields are produced by Venoco Oil Company from Platform Holly a few kilometers offshore. 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. Estimates of total flux for the field are 10^5 m³/day gas and 100 bbl oil per day (Hornafius et al., 1999), but these rates, especially for oil, are poorly constrained at present. Although it is popularly assumed that oil on Santa Barbara Channel beaches results from production, natural hydrocarbon seeps are an important (Quigley et al., 1999) and possibly dominant (Wellday, 1976; Elliot, 1999) source; however, irrefutable data linking oil on beaches to natural seeps are lacking.

Oils from the COP seeps and Platform Holly have been characterized (Jokuty et al., 1999). There are major differences in chemical composition and physical properties between the two oil types. For example, the flashpoint for fresh Platform Holly oil is 10°C while it is >95°C for COP oil. The flashpoint is important to assessing the accidental ignition hazard to clean-up workers. However, evaporation alters this, and after ~24% evaporation, Platform Holly oil's flash point increases to >95°C. Sulfur contained in an oil slick represents a pollution hazard if the spill ignites. COP sulfur content is 2.51%. While the sulfur content for fresh Platform Holly oil is 1.43%, it increases to 2.23% as the evaporated weight increases to 78%. Dynamic viscosity is important to oil dispersion or spreading with a higher viscosity resulting in slower spreading. COP oil dynamic viscosity is high, 165,750 mPa at 15°C; the dynamic viscosity for platform Holly oil is 3,314 mPa at 15°C, increasing to 304,550 mPa as evaporated weight increases to 78%. Thus fresh (low viscosity) oil spreads much more rapidly than oil that has undergone significant evaporative volatilization.

Bubbles consisting primarily of methane gas and coated with oil are commonly observed rising from the seabed at the COP seeps. 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 due to turbulence and currents; *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 an understanding of the fate of the many components of oil since they have different toxicities (*Labelle and Danenberger*, 1997; *Riazi and Al-Enzi*, 1999). Several processes occur during the initial phases of oil slick evolution, and are illustrated schematically in Fig. 2. These include volatilization of the lighter oil components (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). Additionally, many components have varying toxicities with the more volatile organic hydrocarbons (VOH) being more hazardous (*Engelhardt*, 1987). Very low VOH concentrations have been shown to cause nervous system effects if inhaled (a danger to marine mammals) and gill damage to fish for VOH exposure at the ppb level has been documented (*Spies et al.*, 1996). Other physical and biological weathering processes, such as biodegradation, become important over longer time periods and are not addressed here.

In this paper we present a description of a new oil slick sampling device, including results from a field test to track changes in multiple oil slicks from different sources.

II. Methodology

IIA. CATDRUMS Oil Slick Sampler

A CATamaran DRUM Sampler (CATDRUMS) was developed at UCSB to sample and characterize oil slicks as they change with time and is shown schematically in Fig. 3. The design is a modification for oil of a microlayer sampler developed by *Harvey* (1966). Another goal was to measure oil slick volume by determining the oil slick thickness. The sampler consists of a 20-cm diameter, 30-cm long rotating stainless steel drum with its axis maintained at a fixed distance above the sea surface. Oil adheres to the rotating drum and is collected in a trough on the drum's downward moving side. The drum penetration depth into the water can be adjusted by moving the entire platform vertically via threaded rods connecting the platform and pontoons. Adjusting the threaded rods also helps level CATDRUMS' platform and drum. The drum usually penetrates between ~0.7 and 1 cm below the surface. Excessively deep penetration lifts too much water with the oil, while too shallow may

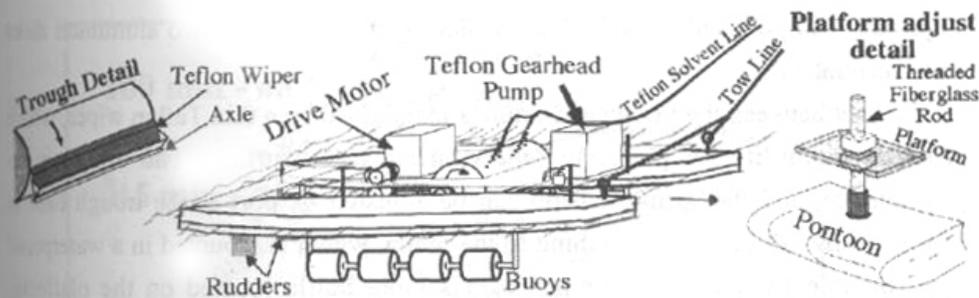


Figure 3. Schematic of the CATDRUMS rotating drum sampler shown oriented for towing. Also shown is the trough and wiper assembly and platform height adjust.

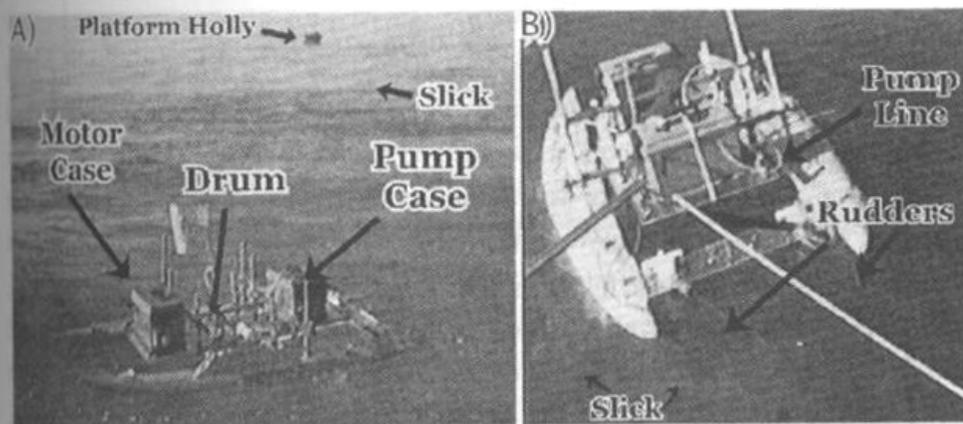


Figure 4. Photos of CATDRUMS during a field test at Shane Seep. A) CATDRUMS was in drift mode, B) was towed. An oil slick is visible beyond CATDRUMS in A).

cause the drum to rise out of the water due to waves. The threaded vertical rods between the platform and pontoons fit into plastic pipes that are siliconed into the pontoons. This provides flexibility to the entire assembly, improving CATDRUMS ability to follow the wave surface. Additional buoyancy is provided by several buoys mounted on two aluminum tubes running from bow to stern and submerged ~50 cm below the pontoons. Two rudders are mounted off a second platform at the stern and are adjustable in increments of 15 degrees.

The rotating drum is suspended below the main platform, while the sample pump and drive motor cases are mounted above. Both motor speed and pump speed can be controlled by a cable from the boat; however, the pump is generally run at full speed. The motor is mounted in a sealed waterproof container and is magnetically coupled to a drive belt that rotates the motor. A small, stainless steel trough is mounted below the platform and presses against the drum surface via springs and an axle. To minimize weight, the drum was made from 1/32 inch thick stainless steel, welded into

a cylinder and polished smooth. The cylinder is mounted over two aluminum disks with a central axle.

Contact between the trough and drum is maintained by a thin Teflon wiper, which provides flexibility for precisely following the drum surface. The trough is repositionable, and the spring tension can be adjusted. A port at the trough base is connected by 1/8 inch Teflon tubing to the pump, which is mounted in a waterproof case. Sample fluid is then pumped to a sample bottle located on the platform. Methylene chloride solvent (DMC) is sprayed on the drum from the boat through Teflon tubing to dissolve the often viscous oil and or tar collected for pumping into a sample jar.

Two lines are attached to the pontoons at the bow by a bridle for towing. The lines pass through a boom mounted pulley to maintain CATDRUMS at least several meters from the boat. The boom is mounted on the boat's forward gunwales. Power for the pump and drum motor is transmitted by cables that are attached to the towrope. To minimize oil slick disturbance by the deployment boat, Marine Science Institute Boston Whalers (7-m length) are used. For ease of transport, the pontoons, motor case, and pump case are all easily disconnected from the platform. A photo of CATDRUMS is shown in Fig. 4 during a field test at Shane Seep. Seep bubbles are visible in the photos as are oil slicks. Upon bursting each bubble leaves a very fine, light oily sheen. In Fig. 4A CATDRUMS was allowed to drift away from the boat, while in Fig. 4B, CATDRUMS was towed.

II.B. Collection Protocol and Field Trip Conditions

Surface water temperature during the field sampling cruise on Oct. 9, 2002 was 16.7°C and the air temperature ranged from 17°C at 10:00 AM to 19°C at 12:20 PM. Winds were very light, 0-3 knots, and the sky was overcast. Sample locations are shown in Fig. 5. Oil slicks were sampled up-current of Shane Seep, in Shane Seep, and down-current, and in a convergence zone at the edge of Shane Seep where very thick, brown, oil slicks are common. Samples were also collected at the Seep Tent Seep. After each sample, the Teflon tubing was flushed with DMC, and the trough and drum were wiped clean with DMC-soaked Kimwipes wipes. A new pair of disposable gloves was used for each cleaning and after each sample. Divers also collected freshly deposited tar from the seabed at Shane Seep (22-m depth).

For a comparative sampling method, a glass sheet (25 cm by 50 cm) was dipped into the oil slick and smoothly raised at $\sim 25 \text{ cm s}^{-1}$. Oil adheres to the glass surface,

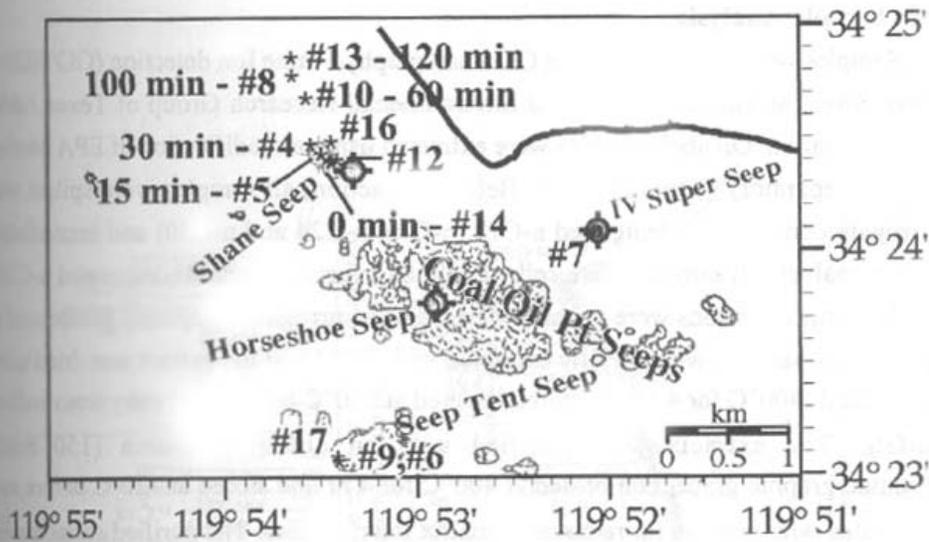


Figure 5. Map showing location of oil slick samples, and time where appropriate.

which is then rinsed with DMC into a stainless steel funnel over a sample bottle. The funnel and glass were washed after each sample with DMC-soaked Kimwipes.

IIC. Oil Slick Tracking

Oil rising in Shane Seep creates a very thin oil slick, and thus CATDRUMS was allowed to run for five minutes (~500 rotations). Other oil samples took about a minute to collect sufficient oil. After sample collection at Shane Seep, hollow glass microspheres (3M Performance Materials Division, Minnesota), 30 to 70- μm diameter were released in a patch onto the oil slick for tracking. Due to their small size and the strong affinity of oil to glass, the microsphere tracking method has several advantages over drift buoys. Specifically, since oil slick thickness is generally sub-millimeter, they are truly at the air-sea interface, while drift buoys extend much deeper into the ocean and atmosphere, and thus "feel" the stronger drag from wind and currents. The main drawback of the microsphere tracking method is that the patch must be maintained in view between sample times, since once lost it is difficult to relocate. For each sample, the boat motored towards the microsphere patch and power to the engine was cut so the boat drifted to ~10 m distant from the patch. Then CATDRUMS was started and a sample collected. Finally the boat was backed to ~50 m from the patch. At 95 minutes (#13) the oil ran into a kelp bed located in a Langmuir cell convergence zone. Oil in the kelp beds was very thick and after the particles were trapped for half an hour, oil slick tracking and sampling was terminated.

IID. Sample Analysis

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. Oil slick samples were extracted using a modification of EPA Method 3510C (separatory funnel method). Before extraction, all samples were spiked with surrogate compounds (deuterated n-C12, n-C20, n-C24 and n-C30) and immediately before analysis all samples were spiked with an internal standard (deuterated n-C16). Analyte concentrations were quantified based on a surrogate compound (deuterated n-C20). Slick samples were serially extracted with DCM and the extract was dried using combusted (400°C for 4 hours, stored covered at 130°C before use) anhydrous sodium sulfate. The extracts were purified with an alumina column (150 mesh, chromatographic grade, combusted at 400°C for 4 hr and stored at 120°C before use) and eluted with pentane for removal of matrix interferences. The purified extracts were concentrated to a final volume of 1.0 ml using the Kuderna-Danish technique. Gas chromatography (GC) of the extracts was performed on a Hewlett-Packard 5890 gas chromatograph fitted with a split/splitless injector (300°C) and a flame ionization detector (FID). The carrier gas was Helium and chromatography was carried out on a fused silica column (30-m long by 0.32-mm I.D.) coated with DB-5 bonded phase (5%-Phenyl 95% methylpolysiloxane, 0.25- μ m film thickness). The GC was temperature programmed and operated in the splitless mode with an initial oven temperature of 60°C, held for 1 minute, then ramped at 6°C min⁻¹ to 300°C, and held 10 minutes (total run time of 51 minutes).

III. Results and Discussion

IIIA. Petroleum Sources

Samples were collected to track changes in the chemical composition of the hexane fraction from the Shane Seep oil slick. The initial (time zero) chromatogram is shown in Fig. 6A, and shows no evidence of degradation, with the n-alkane compounds clearly visible and the more volatile components identifiable, even to decane (n-C10). Concentrations were very low (i.e., compared to surrogates) despite the long (5 min) sampling time. However previous attempts with other methods, e.g., dipping plate, had all failed to secure a measurable quantity of oil. Ocean currents were along the shore towards the Northwest (i.e., note boat trajectory in Fig. 5), which is typical for offshore in the channel near UCSB (Kolpack, 1976). As a result, oil slicks from the eastern inshore seeps including the IV Super Seep and Farrar Seep drifted towards Shane Seep. The most easterly of these seeps is Farrar seep. A chromatogram from

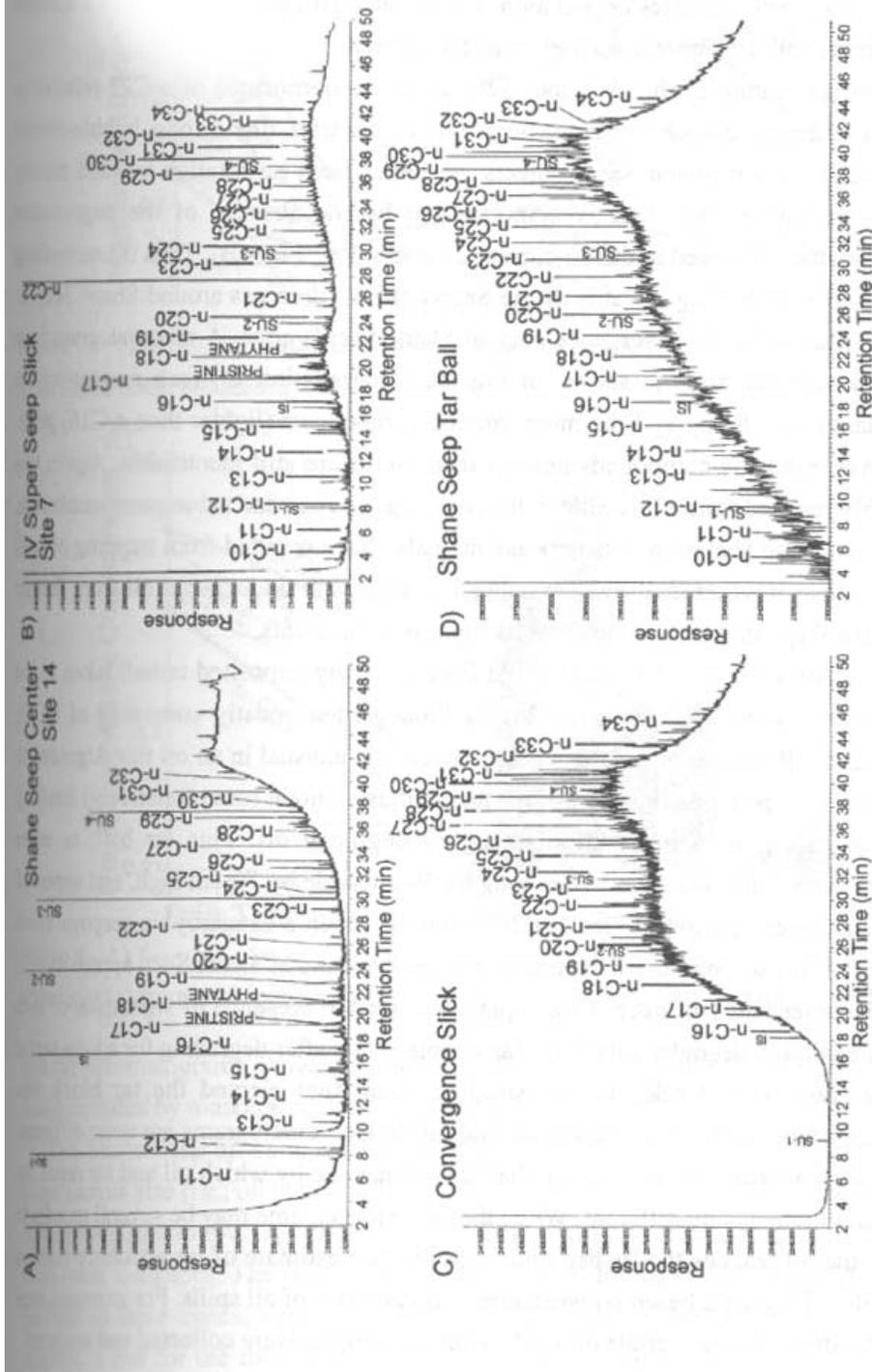


Figure 6. Chromatograms from A) Shane Seep Slick, B) IV Super Seep Slick, C) Shane Seep Convergence Slick, and D) Shane Seep Tar Ball. Alkanes labelled on figure. IS is Internal Standard, SU is Surrogate compound.

the oil slick near the IV Super Seep is shown in Fig. 6B. This sample shows some degradation including a small unresolved complex hydrocarbon mixture (UCM) "hump" peak from 18 to 24 minutes retention time. The increased number of non-alkane peaks also indicates degradation. The collected oil probably included a mixture of oil from both IV Super Seep and seeps further east.

Another feature of the IV Super Seep oil is the dominance of n-C22 relative to other n-alkanes, unlike in Shane Seep oil. In contrast, the strong bubble-driven outwelling flow at Shane Seep protects the center from penetration by (and mixing with) other oil slicks. This is demonstrated by the absence of the degradation characteristics observed in the up-current oil slicks (i.e., Fig. 6B). Thus the outwelling flow causes oil drifting towards Shane Seep either to diverge 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. 6C. Degradation is much greater with a dominant UCM hump and the more volatile components (lighter than n-C16) gone. However, n-alkane compounds heavier than n-C16 are still identifiable. Again, this probably resulted from oil mixing in the convergence zone and subsequent weathering. However, these heavier n-alkane peaks may also have resulted from trapping of both oils that had weathered elsewhere as well as relatively undegraded oil from further eastward seeps that had already lost its lightest components.

Also shown in Fig. 6D is a sample from a freshly deposited tarball taken at the seabed at Shane Seep. The tar is highly biodegraded, mostly consisting of 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. 6A) in addition to highly degraded oil. This tar ball, or more appropriately, tar block, was ~ 1-m long by 50-cm wide by 70-cm high, and appeared during a 2 week period in October 2001 during which a catastrophic seepage event occurred. This seepage event created a new mud volcano at Shane Seep approximately 4-m diameter and 1-m deep. One explanation for the presence of signatures of both fresh and highly degraded oils in the tar sample is that after degrading for a long period in the fracture network, the catastrophic event that ejected the tar block also contaminated it with fresh oil. The 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. While the tar residence time may be several months to years, the oil reaches the seabed quite rapidly. The estimate of tar residence time on the order of a year is based on weathering observations of oil spills. For example, nine months after a Kuwaiti crude oil spill, sediment samples were collected and analyzed

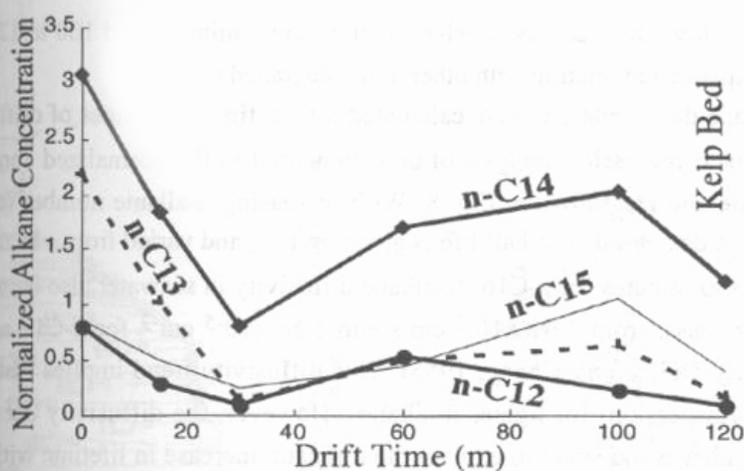


Figure 7. Variation in n-alkane concentration normalized to n-C18 with drift time from Shane Seep. N-alkanes labeled on figure.

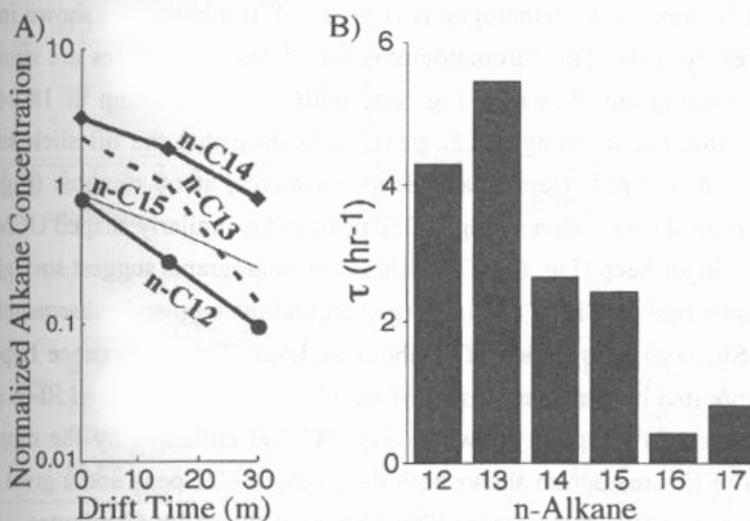


Figure 8. A) Semilog plot of normalized n-alkane concentrations in figure 7, and B) decay rate (τ) from an exponential fit for n-C12 to n-C17. N-alkanes labeled on figure.

and the chromatograms showed a similarly shaped UCM, while the reference crude was dominated by n-alkane peaks (Barakat *et al.*, 2002).

The Shane Seep oil slick was sampled at 15, 30, 60, 100, and 120 minutes age. Since sample size (i.e., oil recovered) varied between samples, n-alkane concentrations were normalized to n-C18, which was chosen as it varied less between samples than most other n-alkanes. The time variation of n-C12 to n-C15 is shown in Fig. 7. The data shows three trends, a marked decrease in n-alkane concentration for the first 30 minutes, a rise for the following hour, followed by a steep drop at 120 minutes. As

discussed below, the changes in behavior at 30 to 60 minutes and 100 to 120 minutes are best explained by mixing with other, more degraded oil slicks.

N-alkane decay rates, τ , were calculated for the first 30 minutes of drift by a least squares linear regression analysis of an exponential to the normalized concentration versus time and are shown in Fig. 8. With increasing n-alkane number (decreasing volatility), τ decreased. The half life is given by τ^{-1} , and varied from ~15 minutes for n-C12 to ~90 minutes 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. However, the diffusivity decrease with alkane number is too small to explain the dramatic increase in lifetime with n-alkane number (i.e., the decrease in τ).

Clearly, the Shane Seep oil slick changed between 30 and 60 minutes and between 100 and 120 minutes. Chromatograms at 60 and 120 minutes are shown in Figs. 9A and 9B, respectively. The chromatograms for 15 and 30 minutes are similar to the initial chromatogram shown in Fig. 6A, with no UCM hump at 18-24 minutes retention time, nor a strong n-C22 peak, indicating that the oil slick source was dominantly or entirely from Shane Seep. However, at 60 minutes (Fig. 6A) the chromatogram shows 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. This divergence hypothesis is further supported by a chromatogram of an oil slick sample from ~150-m shoreward of Shane Seep (see Fig. 5) shown in Fig. 9C and collected by the dipping plate method. The chromatogram shows both the strong n-C22 peak and a great similarity in the shapes of UCM hump for the Shane Seep oil slick after 60 minutes.

At 2 hours the oil slick (and particles) drifted into a kelp bed located along a Langmuir cell line, and became trapped. The chromatogram for the kelp bed oil is shown in Fig. 9B and is dramatically different from the oil slick at 1 hour. The chromatogram shows a stronger unresolved mass than the Shane Seep convergence zone (Fig. 6C) including some features similar to the tar ball. It is likely that 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 an input of fresh oil.

An attempt was made to compare CATDRUMS with the dipping plate method at the Seep Tent Seeps. Unfortunately, the two dipping plate samples both showed

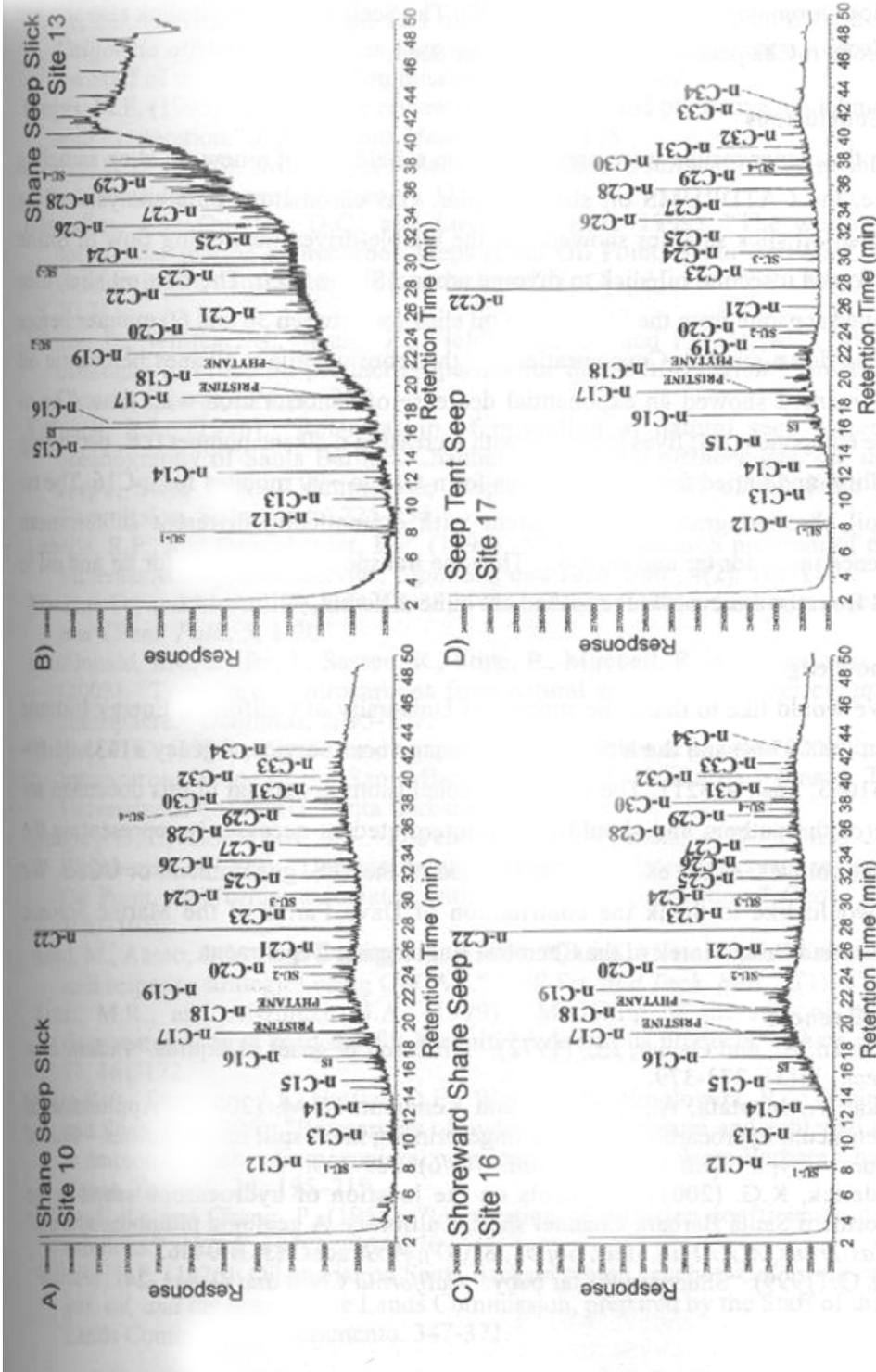


Figure 9. Chromatograms from A) Shane Seep Slick (60 min), B) Shane Seep Slick (120 min), C) 150 m Shoreward of Shane Seep, and D) Seep Tent Seep. N-alkanes labelled on figure. IS is Internal Standard, SU is Surrogate compound.

strong Pristine and Phytane peaks, an indication of biological contamination (Steve Sweet, personal communication, 2002). The CATDRUMS-collected Seep Tent Seep oil slick chromatogram is shown in Fig. 9D. The Seep Tent Seep oil slick also showed the strong n-C22 peak seen for the IV Super Seep.

IV. Conclusions

In this paper results were presented from a field test of a new oil slick sampling device, the CATDRUMS oil slick sampler. Gas chromatographic analysis of the collected oil slick samples showed that the bubble-driven outwelling flow of Shane Seep forced a second oil slick to diverge around Shane Seep. The first oil slick then remained separate from the Shane Seep oil slick for between 30 and 60 minutes before merging down-current. Concentrations of the more volatile n-alkanes before the oil slicks merged showed an exponential decrease of concentration with time. The n-alkane component half lives increased with increasing n-alkane number (i.e., decreasing volatility) and varied from ~15 minutes for n-C12 to ~90 minutes for n-C16. The tar and oil chromatograms are consistent with dramatically different subterranean residence times for tar and slick oil. Thus the transport mechanisms for tar and oil to travel from the reservoir to the seabed are quite different.

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