VSCS Report:

Benthic Oiling from the 19 May 2015 Line 901 Rupture at Refugio: A Compilation of Evidence

Submitted to California Department of Fish and Wildlife by

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Summary:

Following the rupture of Line 901 near Refugio Beach on 19 May 2015, oil flowed along a circuitous overland route and into the surf zone, where longshore drift transported it Eastward, oiling several miles of the coastline. The overland transport of the oil provided an opportunity for loss of volatile compounds purportedly including diluent, and a decrease in temperature, which are known to synergistically change the physical properties of oil. By the time the oil entered the surf zone its viscosity, and by proxy its adhesion, would have increased significantly. The initial discharge of oil to the Ocean occurred during high tide and the subsequent oiling of the shoreline occurred on a receding tide, providing for a prolonged residence of highly-adhesive petroleum residues in the surf zone and ample opportunity for aggregation with algal and mineral materials. In this report, we analyze evidence for submerged Line 901 oil in the subtidal zone, at depths from 14-27 feet deep, that is expected to result from shoreline aggregation processes – for which we use the term submerged oil aggregates (SOAs). We find that oil from Line 901 was rapidly transported into the subtidal zone taking the form of negatively buoyant oil droplets, entrained oil droplets of circumneutral buoyancy, and as large aggregates with algae, dubbed tumble-tar. Rapid submergence of discharged Line 901 oil is indicated by the high relative abundance of volatile hydrocarbons in forensically identified samples, compounds that would normally volatilize with prolonged atmospheric exposure. The combination of a viscous and adhesive oil with discharge into the surf zone provided for a mechanism of delivery to the subtidal zone, with compounds of relevance including naphthalene, and the alkylated congeners of naphthalene, benzothiophene and benzene, and other aromatic hydrocarbons. Observations from the vicinity of Refugio Beach further suggest that submerged oil from Line 901 was most abundant at or on the sea floor in kelp beds, during the first ~7 days post discharge, and was largely diluted by transport processes by 11 days post discharge, presumably through a combination of flushing to the continental shelf, surfacing to form slicks, and incorporation into sediment. Oils from natural seeps, likely from Coal Oil Point, were also identified in the subtidal zone on 2 June, and were distinct from Line 901 oils by both their forensic profiles and by the greater depletion of volatile compounds. These findings clearly demonstrate rapid transport of Line 901 crude oil to the subtidal zone, leading to exposure including for naphthalenes and benzothiophenes, and further suggests exposure to deeper waters as SOAs departed the nearshore environment and were transported deeper onto the continental shelf.

1. Introduction.

The rupture of Line 901 on 19 May 2015 discharged heavy crude oil with an as-yet undefined volume reaching the Pacific Ocean. The crude oil being transported in Line 901 at the time of discharge on 19 May 2015 represents an uneven and undefined mixture from multiple oil platforms, representing numerous wells, all producing crude oil from the Monterey Formation. The crude oils produced from a subset of the wells were highly viscous and two measures were taken to reduce viscosity to an acceptable level to facilitate pipeline transport: 1) the oil was purportedly treated with a diluent, so-called natural gas liquids, though detailed chemical analysis of the diluent is thus-far unavailable; and 2) the oil was heated to 135 degrees Fahrenheit and the pipeline insulated to retain the heat during transport. Following the rupture of Line 901 on 19 May 2015, the oil flowed first through topsoil where it pooled until overflowing into a drainage culvert, travelled through a series of drainage pipes and culverts underneath California Highway 101 – pooling and overflowing again, flowed over soil through an uncovered drainage, and finally flowed down a steep bluff and into the surf zone. The discharge to the Ocean occurred around high tide (12:04PM at +4 feet) with much of the beach oiling occurring during the receding tide that immediately followed. The total distance of overland flow was approximately 200m, with a net vertical descent of approximately 39m.

Following discharge, Line 901 oil began to cool and underwent weathering through volatile loss beginning with its most volatile components – i.e., the natural gas liquids. Commensurate changes in physical properties are thus expected. Relevant viscosities are provided in Table 1, demonstrating the importance of temperature for maintaining low viscosity. During overland transport the oil cooled at an undefined and potentially variable rate, certainly reaching ambient water temperature (~60^{o}F) upon entering the Pacific Ocean. Simultaneously, volatile components of the oil were also lost to the atmosphere. The impact of weathering on key physical parameters, through volatile loss, is also shown in Table 1, for a heavy offshore Monterey crude oil (Sockeye Sour), with physical properties similar to the oils transported in Line 901.

Table 1. Physical properties of discharged oils (Holly and Las Flores) and for a weathering progression of Sockeye Sour, an offshore Monterey heavy crude oil.

	Platform Holly		**Las Flores**		**0% Weathered**	**10% Weathered**	**19% Weathered**
		(100^{o}F)		(100^{o}F)	-----------------	**-- Sockeye --**	---------------
Density (g cm^{-3}	0.91	NA	0.94	NA	0.94	0.97	0.98
Viscosity (mPa·s)	159	49	1694	263	820	8,700	475,000
Adhesion (g m^{-2})	NA	NA	NA	NA	75	98	605

NA = Data is not Available
Data for Holly and Las Flores is from Exponent's Line 901 Investigation Report (Stantech, 2017)
Data for Sockeye from Hollebone, 2015.
Measurements referenced to 60^{o}F unless otherwise noted.

These data reveal that, like cooling, volatile loss has a profound effect on the viscosity of oil. These data further illustrate that another relevant property of crude oil, adhesion, increases concurrently with viscosity (Hollebone 2015). Adhesion is a measure of the oil mass that adheres to a surface under controlled laboratory conditions and is not regularly measured for crude oils, as it tends to track viscosity, but is perhaps the more relevant property for considering the formation of SOAs. The cooling and volatile loss during oil transport to the Ocean is thus expected to have caused a substantial increase in both viscosity and adhesion of the crude oil residue, which in-turn are expected to have impacted the its behavior, notably leading to adhesion with mineral and algal materials present in the surf zone. In this report we compile observations pertaining to submerged oil that is expected to have formed aggregates in this fashion, and further provide context as to the timing, transport, and possible fates of these submerged oils.

2. Benthic Oil Observations.

Observations of benthic oils in the subtidal zone from the immediate vicinity of the Refugio Beach Oil Spill were reported by scientific personnel from the University of California at Santa Barbara, between 22 May 2015 and 2 June 2015. Here we provide a description of the field observations made by UCSB scientists and then focus on select sample splits made available for this study. A summary of visual observations recorded by UCSB scientists is provided in Table 2, and details about samples analyzed for this report are provided in Table 3.

First we consider the descriptions provided by scientists in the field, responding to the spill. These observations, summarized in Table 2, provide a useful context for understanding exposure that occurred in the subtidal zone.

Table 2. Summary of Relevant Field Observations made by UCSB Scientists

Date (2015)	Lat / Lon	Pertinent Observations
21 May	34.4599/ 120.0721	Benthic oiling observed and photographed at 24 feet deep (see Figure 1).
21 May	34.461/ 120.066	Benthic oiling observed and photographed 22-23 feet water depth (See Figure 1).
22 May	34.46058/ 120.0488	Multiple tar globs collected at 20 feet water depth.
22 May	34.45972/ 120.07137	Core collected that contained an oil glob; Benthic oil globs observed and collected (~20 feet water depth). Sampling supplies became coated in oil.
26 May	34.45861/ 120.08453	Little oil at this location. Oiled *Ulva* collected at 27-feet water depth; Oiled spaghetti Algae collected at 18 feet water depth.
26 May	34.45985/ 120.05770	Boat anchored at 14-feet water depth. Pea-sized tarballs located all over the dive site; understory algae almost completely coated at base; tarballs at the seafloor but slightly up-suspended off the bottom; tarballs mixed with spaghetti algae dubbed tumble-tar; tumble tar was football sized, but largest estimated at 8”× 8”× 24” (but not solid); numerous samples collected; tumble tar located between kelp areas in sandy bottom depressions between reefs – caught in low energy sand channels between ridges. Oil distribution was assessed to be: much higher concentration at bottom compared to shallower depth; oil was abundant within bottom few feet; clear evidence for resuspension and deposition; oil present higher in water column, but less abundant; blotches of sheen at surface, mainly trapped among the kelp. Negatively buoyant oil samples were documented at or near the sea floor, collected and analyzed.
2 June	34.4604/ 120.04498	Dive ranged from 27 to 17 feet water depth, observed sparse oiling as follows: oiled Phyllospadix sp; oiling was primarily in kelpy areas. Various samples were collected. Large red abalone was observed.
2 June	34.4595/ 120.0577	Dive ranged from 14-18 feet; observed oiled seagrass; penny sized oil was observed every ~9” to 2’ in the calm low-energy spots between kelp; red stringy algae is oiled but objects in contact with it are not covered; oiled seagrass collected; oiled crab shell collected; oil globs collected (RS-121 – inconsistent with Line 901); no tumble tar observed. Surface sheens were variable at the site, as observed from the boat.

A subset of the samples collected on 22 May, 26 May and 2 June (2015) were analyzed by chemical forensics (forensic reports submitted under separate cover), with pertinent details and results provided in Table 3. The sample collected 22 May and the samples collected from two locations on 26 May were all found to be consistent with Line 901 oil (and inconsistent with seep oils from Coal Oil Point), and to contain abundant volatile hydrocarbons. In contrast, samples of small tar globs collected from two locations on 2 June were found to be inconsistent with Line 901 oil, but consistent with oils from Coal Oil Point.

Table 3. Tabulation of Samples Analyzed in this Effort, Including Forensic Results.

Sample	Lat(N)/ Lon (W)	Water Depth	Date	Note	Line 901	COP Seeps	VSCS Report
RS-042a	34.459717/ 120.071367	20 feet	5/22/15	Oil Globs sampled by scuba at ~20 feet water depth	Consistent	Inconsistent	F3
RS-058	34.45861/ 120.08453	18 feet	5/26/15	Spaghetti algae - with oil; mostly sand	Consistent	Inconsistent	F4
RS-062	34.45985/ 120.0577	14 feet	5/26/15	Oil at sea floor, half-inch diameter droplet, negatively buoyant	Consistent	Inconsistent	F5
RS-063	34.45985/ 120.0577	14 feet	5/26/15	Spherical, sinking oil, 5mm diameter, sand attached	Consistent	Inconsistent	F6
RS-068	34.45985/ 120.0577	14 feet	5/26/15	Proto tumble tar, 2 small spaghetti algae with fresh gooey oil	Consistent	Inconsistent	F7
RS-104	34.4604/ 120.044983	17-24 feet	6/2/15	One oil glob, ~ 2cm, sandy	Inconsistent	Consistent	F8
RS-121	34.4595/ 120.057767	14-18 feet	6/2/15	Four submerged oil blobs collected at depth, 0.5-2cm each.	Inconsistent	Consistent	F9

COP = Coal Oil Point Seep Field; Alpha/New Fields analyzed four of these samples and compared them to Line 901 oil with results as follows: RS-063 (Match), RS-068 (Match), RS-104 (Non-Match), RS-121 (Non-Match).

In addition to the observations recorded by UCSB scientists (Table 2) and the forensic analysis of samples (Table 3), various images and videos also contribute to understanding the processes and occurrence of submerged oil. Figure 1 displays submerged oils, situated on the seafloor near Refugio Cove, from 21 May 2015. Figure 2 displays surf zone processes (Panel A) as well as the adhesion of oil to intertidal algae (Panels B and C), from images taken on 19 May 2015. Video A1 expands on the still image in Figure 1A, providing a dynamic perspective of aggregation processes occurring in the surf zone. Figure 3 displays negatively buoyant oil (Panel A) and a (slightly) positively buoyant oil (Panel B) which has aggregated with plant or algal material. Videos A2 and A3 further demonstrate the negative buoyancy of submerged oil samples collected at the sea floor in the subtidal zone, proximal to Refugio Beach, on 26 May, 2015. Video A4 provides a dynamic perspective on the image in Figure 3B, of a stable oil aggregate of near-neutral (but slightly positive) buoyancy collected 20 May 2015.

The majority of the observations presented here were from 21 May 2015, 22 May 2015, 26 May 2015 and 2 June 2015. Extensive observations are also available for a two-day period starting 30 May 2015, when the Response conducted a dedicated survey to assess whether submerged oil was likely to serve as a source for continued beach re-oiling (Michel 2015). The observations of 22 May 2015 and 26 May 2015 indicate abundant oil present in the subtidal zone (Table 2) at the sampling locations, to water depths of at-least 20 feet. In contrast, the observations of 30 May indicate no visible oil at all-but-one surveyed location. The survey of 2 June located and collected benthic oil samples, though the quantity of oil was noted to be substantially less than on 22 May or 26 May. Of the five oil samples collected at or near the seafloor two (RS-104 and RS-121) were found to be inconsistent with Line 901 oil (and consistent with seeps from Coal Oil Point) while a third (RS-112) was found to be a match (Newfields and VSCS, 2018). Although observations come from different individuals, involved different platforms, occurred with different water conditions, and were conducted for different purposes, the results are consistent with oiling of the subtidal zone in the vicinity of Refugio Beach, with oil persisting at or near the seafloor in the local area, for more than a week. Following this period, Line 901 oil was present in the subtidal, but the distribution was patchy, included seep oils from Coal Oil Point, and was at lower abundance than during the first week post spill.

The first observation of SOAs on 21 May (Table 1; Figure 1) provides only loose constraints on the timing by which oil initially submerged, insomuch as oil must have sunk to the seafloor and been transported to these locations prior to the observations. However, the chemical composition provides additional constraints. SOAs collected on 22 May and 26 May contain abundant volatile hydrocarbons, including e.g., nC_{10}. The volatile content of samples collected on these dates strongly suggests they did not experience significant atmospheric exposure, which in turn suggests they submerged rapidly, likely on 19 May, and remained submerged until the time of sampling. In contrast, samples RS-104 and RS-121, which were consistent with a seep source at Coal Oil Point, but not with Line 901 Oil, exhibited substantially greater loss of volatile hydrocarbons.

3. Processes Affecting the Fate of Submerged Line 901 Oil.

In this section, we briefly consider key factors that facilitated oil transport to the sea floor in the subtidal zone. First, it is important to note that oil discharged from Line 901 is significantly less dense than seawater (Table 1), and is not expected to submerge or sink to the benthos in the absence of other factors or forces. We consider the interplay of factors that likely contributed to the presence of oil at the sea floor. Note that this issue has been considered recently in the context of pipeline spills of diluted bitumen, as reported by the National Academy of Sciences (National Academy of Sciences, 2016), a report for which Dr. Valentine was an author.

Several processes are capable of causing oil to submerge beneath the ocean surface. These include dispersion, wherein oil is broken into small droplets which are readily suspended within the water, adhesion to minerals such as in the formation of oil-mineral-aggregates, and through flocculation with marine snow. The context of Line 901 discharge to the Ocean placed oil in prolonged (~12 hours) contact with the surf zone, and the various algal and mineral components present there. Figure 2 displays images of freshly oiled beaches, taken on 19 May 2015, approximately 250 m from the discharge point to the ocean. This image reveals the adhesion of Line 901 oil to intertidal seagrass beds, as well as the coating of rock surfaces. Video A1 included with this report provides a dynamical context of Line 901 oil interacting with beach sand through wave action. These observations provide a basis for understanding the occurrence of fresh Line 901 oil at the shoreline, and of the ballasting mechanisms that modulated the density of the oils, facilitating entrainment and sinking. The specific processes inferred from observations are considered in the paragraphs below.

i. **Mineral Ballasting.** The incorporation of dense mineral phases into oil droplets increases density and can enhance entrainment and can further lead to benthic deposition. This phenomenon has been proposed to account for the emplacement of ancient submarine asphalt volcanoes in the Santa Barbara Channel (Valentine et al., 2010), and was also active in Enbridge's 2010 Kalamazoo spill of diluted bitumen (Dollhopf et al., 2014). Two oil droplets analyzed for this study (RS-062 and RS-063) were described as being negatively buoyancy at the time of collection – suspended just above the sea floor at 14-feet depth. Videos A2 and A3 clearly display the negative buoyancy of sample RS-063, which was collected on 26 May, 2015. The presence of volatile hydrocarbons in both these samples (see VSCS Reports F5 and F6) indicates only limited atmospheric exposure, and points to mineral incorporation as the default ballasting mechanism that led to their negative buoyancy.

ii. **Entrainment of oil with circumneutral buoyancy.** The ballasting of oil by mineral and algal material could result in a range of bulk densities that span the range of negative to positive buoyancy, relative to seawater. Aggregate size is also an important consideration as small aggregates become entrained in water more easily than large aggregates. Observations support a range of size and buoyancy including the negatively buoyant oil described above, and positively buoyant oil such as in the form of floating oil aggregates (FOAs). In contrast to the expectations that negatively buoyant aggregates will sink (i.e., samples RS-062 and RS-063) and that buoyant aggregates will float (i.e., RS-035 and RS-036), the behavior of oil aggregates with circumneutral buoyancy is unclear. Observations indicate that oil droplets with circumneutral, but slightly positive, buoyancy became entrained in the water column and were transported to the sea floor in the subtidal zone. For example, sample RS-065 which was collected on 26 May 2015 but not analyzed forensically for this study, was collected at the seafloor in 14 feet of water, but was found to have a slight positive buoyancy once sealed inside of sampling jar. This observation indicates that droplet oil with circumneutral buoyancy submerged and became suspended in the water column. Without chemical analysis of this sample, we are unable to provide further insight as to the timing of submergence. Larger aggregates of submerged oil were also observed, as exemplified by the aggregate shown in Video A4, which has a slight positive buoyancy and was collected from immediately beneath the sea surface.

iii. **Adhesive co-transport.** In addition to observations of submerged oil droplets, samples were also collected as bundles of algae, adhered together by Line 901 petroleum residues. These heavily-oiled aggregates were dubbed 'tumble tar' because of the manner in which they moved at the sea floor of the subtidal zone. Splits of two such samples were analyzed chemically for this study, RS-058 (collected on 26 May, 2016 from 18 feet water depth) and RS-068 (collected on 26 May, 2016 from 14 feet water depth), and both were found to be consistent with the Line 901 oil. Both samples revealed a high content of volatile hydrocarbons, suggesting limited atmospheric exposure, and in-turn suggesting formation on e.g., 19 May 2015. Images taken on 19 May 2015 (Figure 2) reveal intertidal beds of sea grass, fully coated in oil. And other algae including Macrocycstis are common beach wrack in this area, consistent with aggregation in the intertidal zone followed by offshore benthic transport.

iv. **Sediment trapping.** When in contact with the sediment, oil or oily material can be buried and thereby incorporated into the sediment. Various occurrences of oil on or in the sediments were noted by UCSB personnel in the context of Line 901 discharge. For this study, oiled sediments were not analyzed, but sample RS-042(a), which was found to be consistent with Line 901 oil, was collected in parallel with an oil-containing sediment core (RS-042-SC1, not analyzed in this study), indicating that oil in the associated sediment likely too was from Line 901. No data is available to constrain the behavior of Line 901 oil when incorporated into benthic sediment, but given the transport cycles of sandy sediments in the region, re-exposure seems likely.

4. Contextual Considerations for Benthic Oil Exposure.

Results from this study indicate several modes by which the subtidal zone was exposed to Line 901 oil including benthic transport of negatively buoyant oil droplets, water-column transport of suspended oil droplets of circumneutral buoyancy, and benthic transport of heavily oiled materials such as algae. The patterns of volatile loss indicate that submergence occurred rapidly upon Line 901 oil reaching the ocean, insomuch as the submerged oil samples retained significant quantities of their volatile hydrocarbons. These observations are consistent with a mechanism that flushed significant quantities of submerged oil into the subtidal zone during the first tidal cycles of the spill, at which time few response personnel were on scene to observe the active processes. A possible timeline for relevant processes is overlaid on the tidal cycle and displayed as Figure 4. By this timeline, SOA formation began immediately upon discharge to surf zone, as wave action mixed the discharged crude oil with both mineral and organic material. The receding tide stranded oil on the shoreline, although Video A1, taken during low tide ~250m from the point of discharge on 19 May 2015 clearly demonstrates that sufficient wave energy was present to mix discharged crude oil with other material present in the surf zone. The high tide that occurred around 11PM on 19 May 2015, was +6 feet (compared to +4 feet for the high tide at the time of discharge) and is expected to have re-exposed all the stranded (and more weathered of its volatiles) shoreline oil to wave action, leading to significant additional SOA formation. The transport of SOAs into the subtidal zone is likely to have started immediately following discharge, but notably, the tidal swing that occurred overnight on 19 May 2015 saw high tide at +6 feet and low tide at -1 feet, and is likely to have drawn significant amounts of SOAs into the subtidal zone during the receding tide. All of the aforementioned processes would have occurred prior to ~6AM on 20 May and would have thus been easily missed by Response personnel.

The patterns of volatile loss from the submerged samples from this study are especially notable because the lack of volatile loss translates to a source of naphthalenes and benzothiophenes to the subtidal zone. Under other spill conditions for which spilled product remains exposed to the atmosphere, naphthalenes and benzothiophenes undergo significant evaporation. Interestingly, the behavior of these samples contrasts to Coal Oil point seep oils, which surface far offshore and for which volatilization (e.g., from a thin surface film) is expected to progress significantly prior to oil reaching the shoreline – where it could accumulate ballast and submerge to the subtidal. A clear example of this distinction comes from comparison of the SORCOP-1 sample (seep oil reference, collected at the sea surface in the seep field) to the submerged oil samples presented here. SORCOP-1 displays indications of evaporation that suggest substantial loss of naphthalenes and benzothiophenes, relative to the submerged oil samples. The two samples collected on 2 June 2015, which are consistent with seep oil from Coal Oil Point, support differential volatile loss as described.

Observations of submerged oil in the subtidal zone were limited by logistical constraints during the early response phase, but are bracketed by observations made at different times and for different purposes. A reasonable interpretation of the observations presented here has the bulk of the submerged oil load entering the subtidal zone in the first ~18 hours following discharge, based on the retention of volatiles and the tidal phases. Once entering the subtidal zone oil was either transported to the open continental shelf, incorporated into the sediment, or surfaced to form slicks. The transport of oil to the open shelf, which is the most likely fate for negatively buoyant aggregates, would be slowed in the kelp forests, wherein current velocities are reduced and bottom topography includes low-energy zones where benthic debris can accumulate. Oil aggregates of circumneutral density could have surfaced to form slicks or adhered to material that trapped them in the benthos. The occurrence of oil slicks within the kelp at Refugio is consistent with resurfacing of benthic oils – as occurred following the 2010 Enbridge spill. Oil droplets and visible aggregates were largely absent from the kelp beds by 30 May, when Response officials began their benthic oil survey, suggesting that flushing of the kelp beds was largely complete by this time.

6. References.

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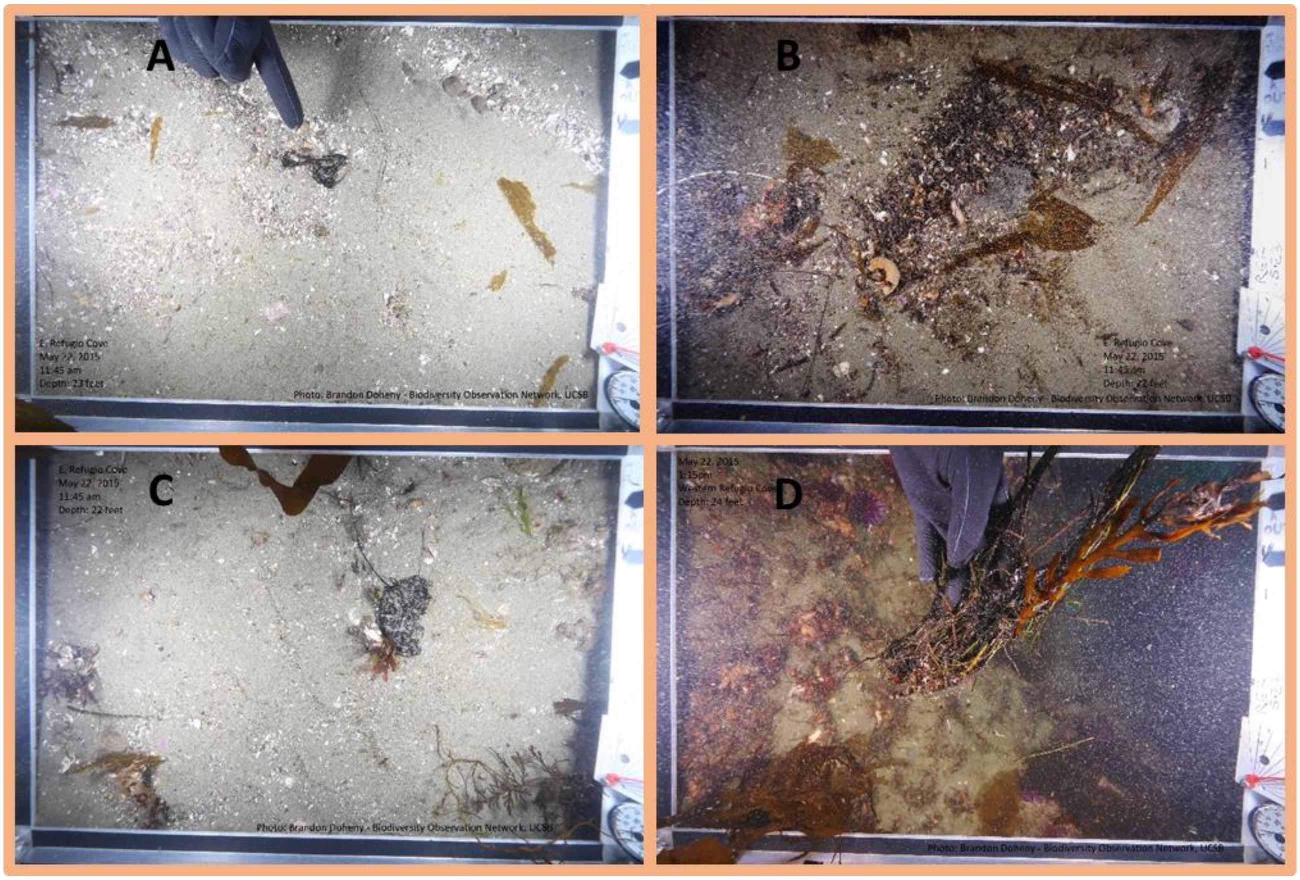

Figure 1. Images of submerged oil from 22 May 2015, from the subtidal zone in Refugio Cove. Image credit: Brandon Doheny.

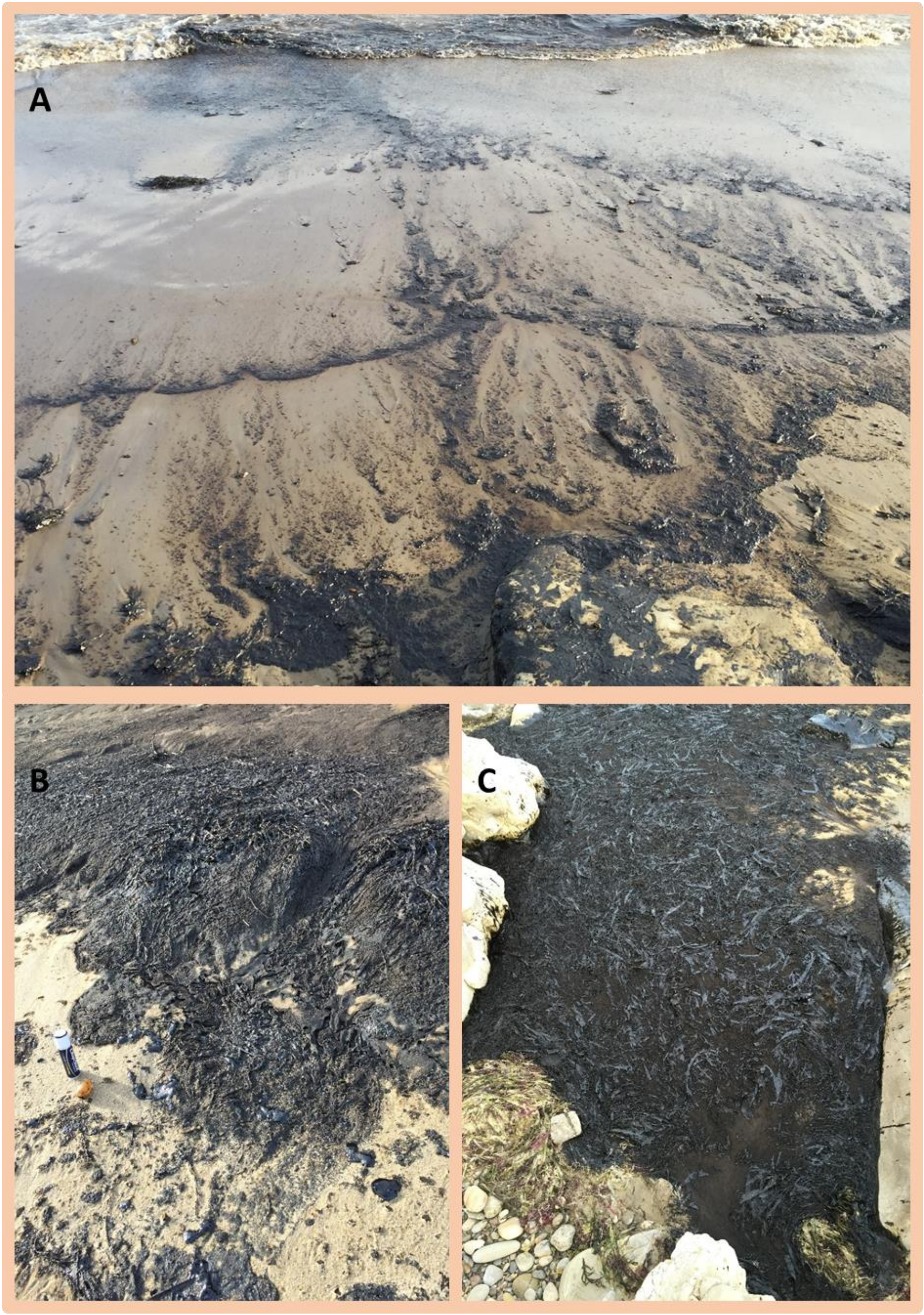

Figure 2. Images of shoreline oiling taken on 19 May 2015, from ~250m East of the Ocean discharge point, at low tide. A) Oil aggregates in the surf zone. B and C) Oiled seagrass beds and other oiling in the intertidal zone. Image credit: David L. Valentine.

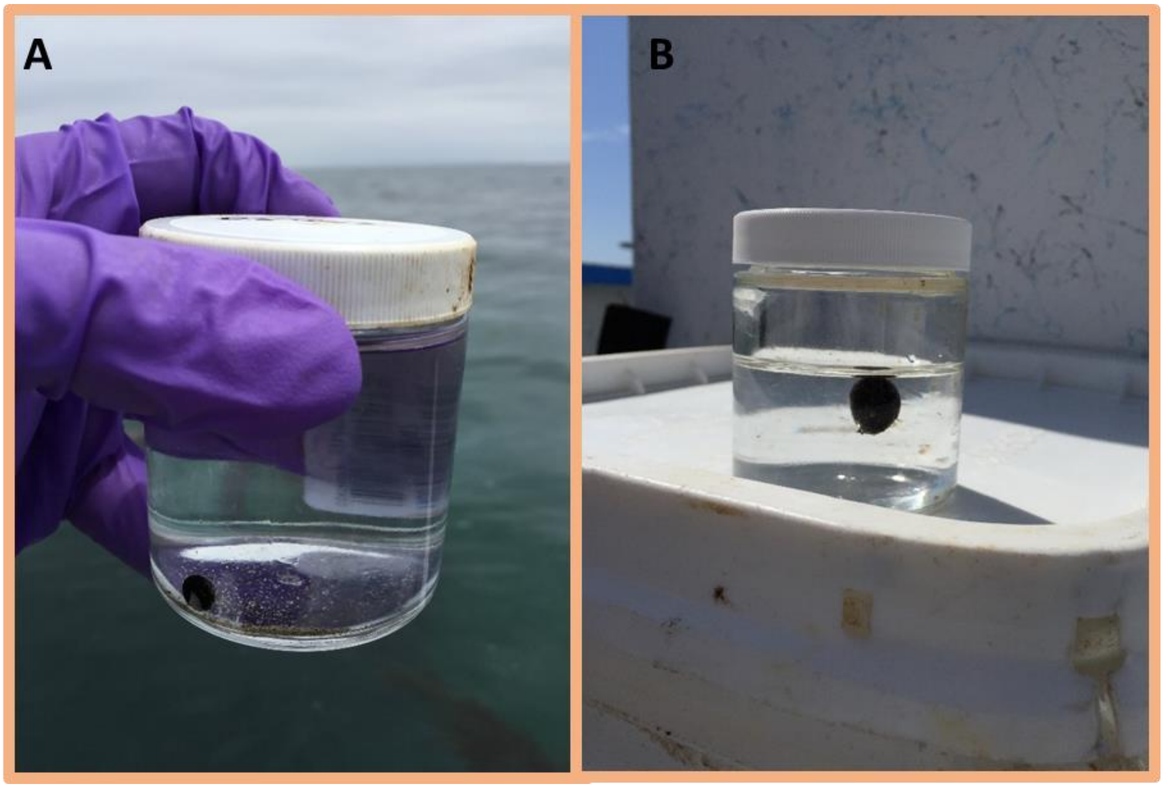

Figure 3. Images collected 20 and 26 May 2015, of submerged oil samples. A) Sample RS0-63 was negatively buoyant (See Videos A2 and A3). B) An oil aggregate/droplet (RS-022) with slight positive (but near neutral) buoyancy, collected immediately beneath the sea surface on 20 May 2015 (See Video A4). Seawater density is ~1.035 g cm^{-3}. Image credit: David L. Valentine.

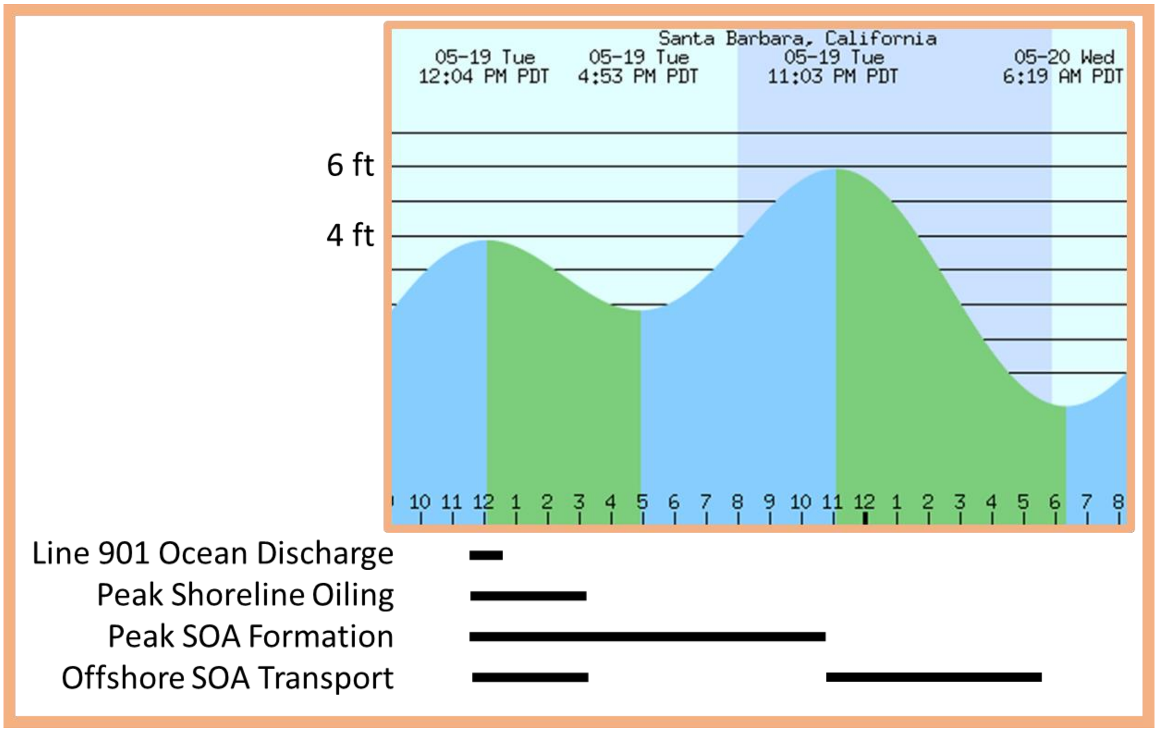

Figure 4. Tides for 19 May and 20 May, 2015 for Santa Barbara, California. From http://tides.mobilegeographics.com/locations/5608.html?y=2015&m=5&d=19. Also included is a potential timeline for key processes.