



A Review on the Factors Affecting the Deposition, Retention, and Biodegradation of Oil Stranded on Beaches and Guidelines for Designing Laboratory Experiments

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Abstract

The distribution and persistence of oil within the matrix of a beach depends on the oil and beach properties, the presence of fines in the water column, and beach hydrodynamics and biochemistry. In this review, we attempted to provide an assessment of the journey of oil from offshore oil spills until it deposits within beaches. In particular, we addressed the disparity of spatial scales between microscopic processes, such as the formation of oil particle aggregates and oil biodegradation, and large-scale forcings, such as the tide. While aerobic biodegradation can remove more than 80% of the oil mass from the environment, its rate depends on the pore water concentration of oxygen and nutrients, both of them vary across the beach and with time. For this reason, we discussed in details the methods used for measuring water properties in situ and ex situ. We also noted that existing first-order decay models for oil biodegradation are expedient, but might not capture impacts of water chemistry on oil biodegradation. We found that there is a need to treat the beach–nearshore system as one unit rather than two separate entities. Scaling down large-scale hydrodynamics requires a coarser porous medium in the laboratory. Unfortunately, this implies that microscopic-scale processes cannot be reproduced in such a setup, and one needs a separate system for simulating small-scale processes. Our findings of large spatio-temporal variability in pore-water properties suggest that major advancements in addressing oil spills on beaches require holistic approaches that combine hydrodynamics with biochemistry and oil chemistry.

Keywords Oil spills · Bioremediation · Biodegradation · Beach dynamics · Laboratory experiment · Environmental factors

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Introduction

Oil spilled on beaches can be detrimental to the ecology and economy of the impacted regions. Even after the initial efforts of cleaning up oiled shorelines, the persistence of residual oil in the beaches ([93]) could continue to have lingering effects. Therefore, it is important to understand both the chemical and physical properties of spilled oil along with the environmental factors affecting oil deposition and persistence.

Oil is made up of thousands of chemicals ([78, 137]) that can be placed into four groups: saturates, aromatics, resins, and asphaltenes (referred to as SARA). In most crude oils, saturates and aromatics make up a large portion of the entire composition on a mass basis (upward of 80%). Light oils contain more saturates and aromatics, whereas heavy oils contain more resins and asphaltenes. The physical, chemical, and

biological properties of these components dictate their overall environmental fate in an oil spill situation ([148]).

When oil is released into the environment, the chemical and physical properties begin to change immediately through a series of processes collectively known as “weathering.” Evaporation removes the light oil components, typically of $C < 14$, which includes the BTEX (benzene, toluene, ethylbenzene, and the xylenes) and saturates ([87]); depending on the type of oil, evaporation can cause the oil density to increase by upward of 20% and the oil viscosity to increase several orders of magnitude ([69]). Oil emulsification will also occur as small water droplets become entrapped within the oil, and eventually potentially form a thick mousse ([49]), whose viscosity can be more than a million times of the viscosity of the original oil ([76]); thus, such an oil would not penetrate deeply (or not at all) into the beach matrix. Photooxidation (due to exposure to sun light) ([74, 125, 169]) also can cause oil viscosity to increase. Highly viscous oils will not likely penetrate into a beach matrix unless the beach has very large void spaces or, for finer materials, the beach sediments are significantly reworked and redistributed in a storm. Viscosity is dependent on the temperature. In this regard, waxy crudes are particularly sensitive to the low temperature due to the increase of viscosity ([100]), often crystallizing even under mildly cold conditions ([153]).

The interaction of oil with sediments and other materials (organic and inorganic) in the water near the shorelines can generate oil particle aggregates (OPA) of various sizes and composition. ([1, 26, 65, 89, 120, 154, 180, 181]). It is likely that the interaction of oil with fines results in less oil depositing within the beach matrix. On very fine-grained beaches, as large (macroscopic, > 1 mm) OPA, often in the form of residue balls and patties, arrives at the beach ([75]), it may contain a large volume of sediments and highly weathered oil, but still contain a non-negligible content of bioavailable hydrocarbons to make them impactful ([116]). Regardless of beach texture, the attachment of fines on the oil is likely to reduce the adhesion between the oil and the beach matrix ([7, 37, 43, 52, 79, 85, 86, 88, 89, 113, 115, 119, 120, 154, 155, 167, 170, 178, 179]). A recent laboratory study by Zhao et al. [180] observed the penetration of clay particles into the oil, but not the surface coverage as commonly assumed. In such a case, the continual flushing of water around the oil in the pore space with the particles sticking out of the oil could cause the oil to disintegrate into smaller volumes that would be carried away by pore water. Verifying whether this mechanism occurs within the pores is a topic of investigation for the current authors.

Beside the role of fines in altering the properties of oil through the formation of OPA, the depth of penetration of oil into the beach subsurface depends to a large degree on beach hydraulics (tide, waves, and groundwater flow), beach permeability, and oil properties ([77, 93, 121]).

Beach Dynamics

Beach Hydraulics

The tidal range (vertical distance between the high and low tide levels) plays an important role in beach hydraulics. As the tide rises, the water table rises relatively fast. However, as the tide drops, the water table tends to lag behind sea level ([19, 123]). When averaged over a tidal period, the mean water table within the beach is higher than the mean sea level, causing a persistent seaward hydraulic gradient in beaches. In terms of exchange flux, most of the seawater enters the beach near the high tide line, and the majority of pore water leaves the beach near the low tide line ([95]). This contributes to slowing the drop of the water table going seaward (because pore water from the landward side is discharging at seaward location within the beach). A solute plume within the intertidal zone tends to move downward during rising tides and seaward during falling tides ([24]). These concepts are illustrated in Fig. 1. The presence of a strong groundwater flow moving seaward could sustain the height of the water table during low tides, thereby limiting the depth of oil penetration. This was indeed noticed in works related to the *Exxon Valdez* oil spill ([64, 173]).

Waves create two seaward hydraulic gradients in a beach ([96, 141]): A steep hydraulic gradient in the swash zone that is comparable to the beach slope and a mild hydraulic gradient landward of the swash zone (Fig. 2). Consequently, the pore water that is landward of the swash zone moves slowly seaward until it reaches the swash zone where it moves rapidly. Boufadel et al. [22] conducted tracer studies in a laboratory

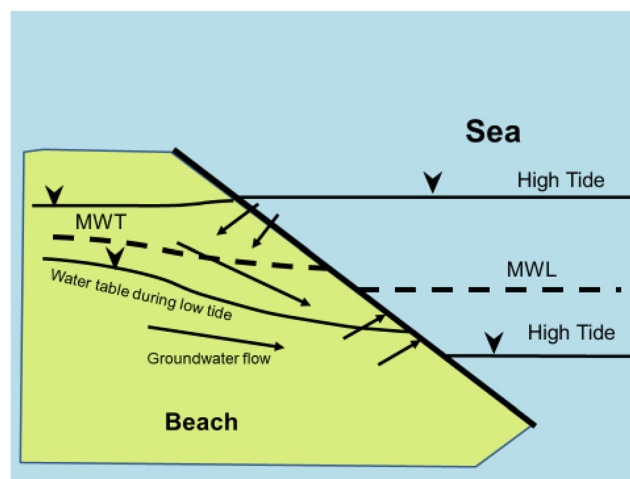


Fig. 1 Water table movement due to tidal forcing. Pore spaces within beach sediments fill with seawater to near the high tide line on the rising tide and drain during the ebb tide. Over the tidal cycles, the mean water table (MWT) within the beach is higher than the mean water level (MWL) at sea, causing a net seaward flow as a result of the tide. Influx of fresh groundwater (recharge) from the land side would maintain a higher groundwater table within the beach, especially during low tides

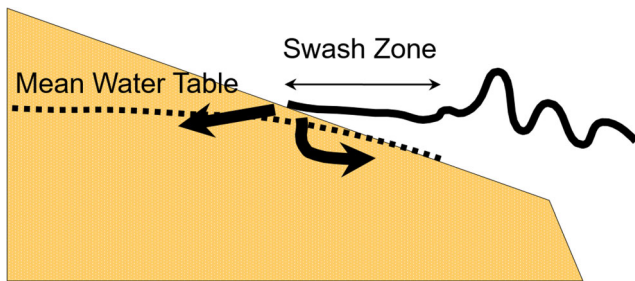


Fig. 2 Waves running up a beach. The effect of waves on the beach water table is to create two zones with two different hydraulic gradients. The gradient is steeper in the swash zone relative to the landward zone gradient

beach, and found that the superposition of waves and tides reduced the residence time of a tracer plume by about one third in comparison to the tide-only case. Detailed numerical investigations further confirmed this behavior ([58]).

The momentum of individual large waves could cause oil floating on the water to penetrate deeper into the beach. The largest depth of penetration would occur for pebble beaches, and is expected to be shallower than 10 to 20 cm deeper in comparison to the tide-only situations. In addition, the amount of penetrated oil due to waves is expected to be small due the “filtering effects” of the beach sediments. However, the major impact of moderate waves is likely that they can carry the oil into the supratidal zone, as discussed below. Nevertheless, waves can affect a major rearrangement of the beach including the displacement of large boulders ([171]). The effect of buoyancy (due to the presence of freshwater in a saltwater environment) on beach hydraulics is typically negligible in comparison with tide and waves ([93]).

Sediment Properties

Beach geomorphology (substrate texture, stratification, and slopes) plays a major role in oil distribution in surface and subsurface sediments ([121, 157]), with coarse sediments generally favoring deeper penetration of oil relative to fine sediments. Sediments that are angular and/or made up of a broad grain-size distribution tend to have smaller porosity, as they fit into each other better. Beaches can be made up of a varying combination of clay (< 4 μm), silt (4 to 60 μm), sand (60 μm to 2 mm), and larger aggregate materials. For example, beaches in the Gulf of Mexico or in New Jersey are often publicized for their fine-grained, “playground” sand, or even “sugar grain” textures. On the other hand, many beaches in glaciated regions are made up of granules (2 to 4 mm) pebbles (4 to 64 mm), cobbles (64 to 256 mm), and boulders (> 256 mm) ([67, 121]). Boufadel and co-workers ([12, 93]) noted the presence of two layers with very different permeability along some of the beaches within Prince William Sound (Alaska, USA); an upper layer with a very large permeability underlain by a layer whose permeability is 100- to

500-fold smaller. The lower layer contained more fines than the upper layer, but when efforts were made to predict the permeability in the lab based on the grain size distribution, the lab permeability of the lower layer was around 100 times that estimated from the field data (see Table 1). Bobo et al. [12] interpreted this as due to higher compaction of the lower layer, and they estimated that although the porosity of the upper layer is around 30% in the field, that of the lower layer is about 8%. See Table 2 for estimation of the permeability as a function of grain size and porosity.

There are four major approaches for measuring/estimating the intrinsic permeability (Table 1).

General formulas for obtaining the permeability of unconsolidated media in the laboratory are reported in Table 2, taken from Bobo et al. [12]. One notes that the permeability depends on the characteristic diameter, d_{10} or d_{20} raised to a power equal to or larger than 2. (The d_{10} diameter represents the sieve size that retains 90% of the sediment mass, i.e., only 10% passes through it.) Table 2 shows that the permeability depends on the porosity to the power of 2 to 3. The angularity of the sediments is addressed in the K-C formulation through the parameter F ; pores that are formed between two plates (i.e., from angular sediments) have an F value of 3, whereas those in the shape of a cylinder have an F value of 2.0. (Common practice is to use $F=2.5$.) Thus, the maximum difference due to angularity is 50%, which is a much smaller factor than that due to the characteristic grain size or porosity.

The discussion above refers to the intrinsic permeability, which is the permeability for the movement of one phase filling the whole pore space (e.g., water or oil). However, for a multiphase system, the permeability for an individual phase depends on the content of the other phase, which could act to block the flow ([42, 103]).

Beach heterogeneity (i.e., spatial variability) may be significant enough to result in distinct hydraulic properties within the beach, which can affect transport pathways ([54, 97, 177]). Heterogeneity in the vadose zone could cause water infiltrating the beach surface (due to waves and/or rising tide) to percolate in preferential pathways (fingers) toward the water table ([152]). Thus, oil reaching the shorelines could percolate preferentially through these fingers of greater permeability. Nevertheless, due to the complexity of these processes and beach heterogeneity, their modeling is commonly ignored when dealing with large-scale (meters) transient systems, such as a beach subjected to tides and waves.

Another important factor in beach hydrology is the height of the capillary fringe, which is the zone of considerable water moisture found above the water table. Researchers ([9, 19]) considered that pores with a 75% moisture content represents the top of the capillary fringe. Within this zone (Fig. 3), capillary forces cause water to rise into the sediment matrix (also known as capillary rise). The extent of the rise depends on the particle sizes. In gravel beaches the capillary rise is small (a

Table 1 Major approaches for measuring/estimating the beach intrinsic permeability

Name of the approach	Applications
Field measurements	Seepage meters ([104]), field piezometers ([145]), temperature monitoring ([39]) and inference based on the dissolution of Plaster of Paris plates in soils/sediments ([13])
Laboratory experiments	Permeameter (essentially a vertical cylinder) and using either the falling head test (for high permeability sediments) or the constant head test (for low permeability sediments) ([9])
Estimation based on sediment properties	Grain size distribution and porosity (see Table 2)
Calibration of groundwater models	Field-averaged permeability ([31]; [19])

few centimeters), whereas in fine textured sediments such as fine sand and silt the capillary fringe could be up to 1.0 m above the water table ([160]). Given that most oils are less dense than water, the moisture content within the capillary fringe will greatly limit oil penetration within this zone.

The capillary properties of sediments reflect the pore structure within the porous medium, in particular, the pore-throat connectivities and sizes ([111, 160]). Capillary properties are commonly estimated using capillary-retention experiments ([139]). Efforts to relate capillary properties to the intrinsic permeability were not successful ([108, 172]) and for this reason it is common to estimate these properties using a separate experiment known as the capillary-retention experiment ([50, 109, 110]).

Monitoring only the water table without accounting for the capillary fringe could result in an overestimation of the oil holding capacity of the beach since beaches with large capillary fringes do not allow oil to penetrate deep into them. Similarly, when the water table drops, little water is released to sea, and thus these beaches do not drain sufficiently to allow

air laden with oxygen from the atmosphere to penetrate deep into them either.

Figure 4 provides an illustration of the initial distribution of oil in a shoreline. In general, the deposition of oil is highest (on a mass of oil per mass of sediments basis) in the upper intertidal zone due to the large drop in the water table associated with that location. The mass of oil within the sediments decreases as one moves seaward (from upper to mid- to lower intertidal zones), due to the smaller water table drop as one moves seaward. Oil could also reach the supratidal zone (i.e., the zone landward of the intertidal zone) due to the action of storm waves (e.g., storm surge). Once deposited onto the supratidal zone, the oil would penetrate there as well ([67, 89, 117, 121]) and/or become covered by sediments from subsequent storm waves ([116]). However, the concentration of oil deposited into the supratidal zone tends to be lower than that deposited into the intertidal zones.

Oil Properties

The most important property of oil that affects its penetration in the beach is its viscosity. As a simplification, if one assumes that the pores are occupied only by oil, the hydraulic conductivity of oil is given by:

$$K = \frac{g}{\nu} k_o \quad (1)$$

where g is gravity acceleration (9.81 m/s^2), the term ν represents the kinematic viscosity of the fluid, which varies from $10^{-6} \text{ m}^2/\text{s}$ (1.0 centistoke) for fresh water to almost $1.0 \text{ m}^2/\text{s}$ (1 million centistoke) for weathered heavy oils and emulsions, k_o is intrinsic permeability (m^2). The hydraulic conductivity (Eq. 1) is essentially a parameter that combines information from the fluid and from the porous medium. Oil density has to be less than that of water for the oil to float above it, but in comparison with the viscosity, the density of oil varies by up to 20%, whereas oil viscosities vary by orders of magnitude.

Table 2 Formulas for obtaining the intrinsic permeability based on grain size and porosity

Name of the formula	Formula; Units are in m^2
Hazen ([68])	$k_o = 6 \times 10^{-4} [1 + 10(n - 0.26)] D_{10}^2$
Kozeny-Carmen (K-C) ([83])	$k_o = \frac{1}{F} \left(\frac{L}{L_c} \right)^2 \left[\frac{n^3}{(1-n)^2} \right] D_{10}^2$
Breyer ([11])	$k_o = 6 \times 10^{-4} \log \frac{500}{U} D_{10}^2$
Slitcher ([150])	$k_o = 10^{-2} n^{3.287} D_{10}^2$
U.S. Bureau of Reclamation (USBR) ([159])	$k_o = 4.8 \times 10^{-4} D_{20}^{2.3}$

Here, n is the porosity, D_{10} and D_{20} are the diameters (units in meter) at which 10% or 20% of the grains (by mass) pass the sieve, and U is the Uniformity Coefficient given by $U = \frac{D_{60}}{D_{10}}$. The parameter F is between 2 and 3 and typically is assigned the value of 2.5, and the term $\left(\frac{L}{L_c} \right)^2$ is known as the tortuosity and is typically assigned the value of 1/2.4



Fig. 3 The capillary fringe (dark discoloration above the water level) reflects the presence of high moisture content (more than 75% of the porosity). <http://wps.prenhall.com/wps/media/objects/5309/5437119/Figures/chapter06.htm>

Beach Holding Capacity

Free-flowing oil within the beach pore spaces may be naturally removed from a beach within days to months, leaving a residual distribution of oil within the beach that is no longer free flowing. One of the issues of importance is the beach holding capacity of oil ([63]), which is the volume of residual oil retained in pore spaces due to oil adhered to and coating grains and to oil trapped at grain-to-grain contact points ([77]). From a practical point of view, responders and scientists have considered the oil in the beach to be residual if the oil content in the beach does not change substantially after multiple tidal cycles. Some researchers refer to an acute phase versus a restoration phase for oil release off a beach (e.g., SINTEF). Other definitions could be obtained based on the capillary retention

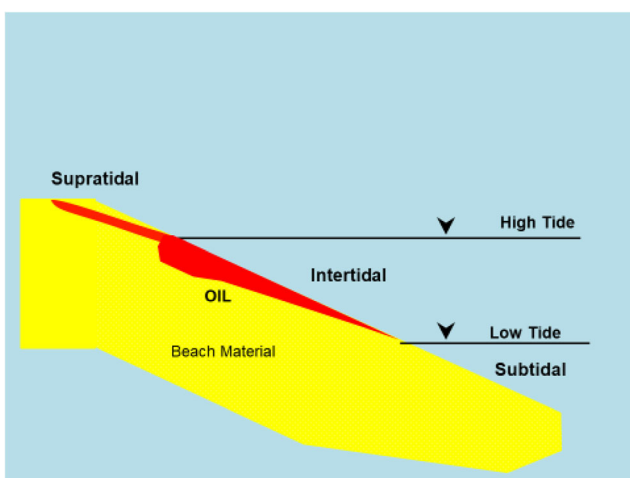


Fig. 4 Illustration of the initial oil distribution following an offshore oil spill. Oil could reach the supratidal zone during storms

curves, and they represent theoretical values ([47]) that are typically smaller than the field observation, and thus less conservative.

The initial oil deposition tends to be skewed toward the upper intertidal zone (landward portion of a shoreline) (Fig. 4). The amount of oil that is reflatated, released, or re-entrained off a beach is proportional to initial oil loading ([14, 32, 33]). But smaller amounts would exist near the lower intertidal zone. Scientists have noted the depletion of residual oil from the beach over short time scales and hypothesized that a removal process is due to the attachment of fines onto the oil ([118, 121]) as discussed earlier.

Oil Biodegradation

Oil Biodegradation in Coastal Aquifers

The principal mechanism removing oil from the environment is microbial biodegradation ([127, 135]). The very low solubility of oil ([130]) means that its degradation is limited by its surface area, either for microbial attachment or for dissolution and consumption by planktonic microbes. The classic paper by Efroymson and Alexander [46] showed that both processes are important, and clearly dependent on the intrinsic solubility of the specific hydrocarbon. It is thus no surprise that the loss and biodegradation of the most soluble hydrocarbons, benzene, toluene, ethylbenzene, and the xylenes is controlled by tidal flow. Robinson et al. [142] found tides controlled the fate of terrestrial BTEX in coastal beach aquifers, significantly enhancing subsurface BTEX degradation and reducing exit concentrations from the aquifer to the ocean. Geng et al. [59] conducted numerical simulations of a hypothetical beach polluted with benzene and toluene, and noted that these contaminants also occupied the unsaturated zone, where there was significant biodegradation. What is not yet clear is how the rate of dissolution plays into the fate of hydrocarbons in a beach—all the GC-resolvable aromatics in crude oil have non-zero solubility in seawater ([130]), yet they are routinely found in oils subjected to tidal washing for many years ([134]). Presumably, the mobility of compounds within the oil layer plays a role, and thus the size of this layer, whether attached to beach material or as a droplet is likely very important.

Tidal flow also stimulates the biodegradation of less-soluble hydrocarbons retained in the oil. Huettel et al. [71] reported that tidal pumping significantly enhanced biodegradation of oil buried in Gulf of Mexico sandy beaches. They found the falling tides drove warm oxygen-saturated air into the sand, which prompted aerobic microbial oil degradation in deeper marine sediment layers; subsequent rising tides pumped air upwards through the oil-contaminated sand, elevating moisture in sediment pores for microbial growth and

removing CO₂ from the beach. Again, the mobility of the substrates within the oil layer on the beach material likely plays an as yet undefined role, but it seems reasonable that the heavier the oil, and the lower the temperature, the slower this process will be. Microbial surfactants likely play an important role in attaching microbes to oil droplets, and perhaps in solubilizing some hydrocarbons into the aqueous phase ([6]). There is an enormous diversity of such molecules, including glycolipids, fatty acids, and much more complicated soluble and particulate polymeric structures ([6]). Although some are commercially available as purified products, none have yet been commercialized for oil spill response. Like all surfactants, they play different roles below and above their critical micellar concentration (cmc). Below the cmc, the surfactants likely attach to surfaces and lower the interfacial tension, allowing droplets to pull away from the bulk oil with less energy input. The increased surface area of the droplets would be expected to increase the rate of biodegradation. Above the cmc, the surfactants form discrete micelles that may encapsulate hydrocarbons and potentially conceal them from degrading microbes ([144]).

Oil-degrading microbes are ubiquitous, most recently being reported from the bottom of the Mariana Trench at 10,400 m below the surface ([99]). Our understanding of their taxonomic diversity continues to expand ([126]). The biochemistry of their hydrocarbon biodegradation is relatively well understood ([135]), as is the different rates of their degradation under ideal conditions ([133, 135]); in general, the rates are fastest for normal alkanes and simple aromatics, followed by branched alkanes, alkylated aromatics, and cyclic alkanes. Finally, the biomarkers such as hopane, stigmastane, and the C₂₈ 20S-triaromatic steroid are the most resistant to biodegradation, allowing them to be used as conserved biomarkers for quantifying biodegradation. This is calculated as outlined in Eq. 2, where the concentration of the compound of interest, *A*, has been normalized to the concentration of hopane, *H* ([124]). In the long run, even these biomarkers will biodegrade, leaving essentially complete biodegradation of the oil hydrocarbons ([3, 44]).

The persistence of these biomarkers allows a metric for estimating the extent of biodegradation as given by:

$$\text{percent biodegradation} = \left[1 - \frac{\left(\frac{A}{H}\right)_t}{\left(\frac{A}{H}\right)_o} \right] \times 100 \quad (2)$$

where the concentration of the compound of interest, *A*, has been normalized to the concentration of a biomarker, *H*.

Typically, 85% of the hydrocarbons are removed under optimal conditions within a month or two ([133]). Rather less is known about the biodegradation of the resins and asphaltenes, whether initially in the oil or generated by photo-oxidation ([66]), although there is evidence that at least some are biodegradable ([73, 156]). Whether significant

amounts of any partially oxidized metabolic intermediates are released by microbes remains an open question, although this is likely to be minimal since all aerobic biodegradation starts with the investment of a valuable NADH; and any organism that did not recoup this investment in subsequent metabolism would be doomed ([135]).

The differential evaporation and biodegradation of the different components of a spilled oil changes the physical and chemical properties of the residue. Most notably, the lightest components, those with less than 15 carbon atoms, evaporate readily, and the oil becomes notably more viscous as this occurs. Nevertheless, most crude oils in commerce remain liquid even after evaporation has occurred, and such oil readily permeates porous beaches. Biodegradation of the non-volatile molecules preferentially removes the hydrocarbons, almost all of which are less dense than water, and are of course the reason that most oils float. As they degrade, and leave the residue enriched in resins and asphaltenes, the density of these molecules, typically near 1.2 ([8]), overwhelms the buoyancy of the residual hydrocarbons, and the oil could become denser than seawater. Of course, the density would be much enhanced at any stage if the oil were attached to small mineral grains—most rocks have a density of > 2.5.

It must be noted that a short half-life for hydrocarbon biodegradation (1–3 weeks) is only seen with dispersed oil (that is oil in the form of small droplets in the water column) ([133, 2015, 2017; 28–30, 53, 102, 129, 140, 166]). The rate of biodegradation of floating slicks ([129]) or shoreline oil ([21, 27, 125]) is much slower than that of dispersed oil droplets. In fact, the data presented in Bragg et al. [27] show that there was essentially no biodegradation occurring on the oiled shorelines of Prince William Sound in the summer of 1990 until the responders applied fertilizer. This highlights important limitations on oil biodegradation—hydrocarbons are very energy-rich substrates, but they are unusual in two important ways; not only are they insoluble, as discussed above, so that biodegradation depends on the surface area presented to the microbes, but they lack the other essential elements of life. Dispersed droplets of oil soon dilute so that the background levels of these nutrients in the ocean are adequate for biodegradation ([92]). Floating slicks and beached oils present relatively low surface areas for microbial attachment, but more importantly the concentration of oil overwhelms the available nutrients and severely limits biodegradation. The large-scale addition of carefully chosen fertilizers to shorelines oiled following the grounding of the *Exxon Valdez* stimulated biodegradation several-fold with no detectable adverse effects ([27, 124]). A total of 48.6 t of fertilizer nitrogen was used ([128]).

While considering the importance of ancillary nutrients such as biologically available nitrogen and phosphorus, it is important to recognize that small-scale experimental spills, such as those on the Delaware Bay ([163]), the St Lawrence River ([162]), Svalbard ([125]), the San Jacinto river in Texas

([107]), and a coastal salt marsh in Nova Scotia ([51]), may not be large enough to exhaust the natural nutrients. Certainly, the “control sites” in those experiments exhibited more background degradation than the 75 km of oiled shorelines in Prince William Sound following the *Exxon Valdez* spill ([27]). Nevertheless, additional fertilizer still speeded biodegradation significantly in all the field trials mentioned.

Several models have been developed to predict hydrocarbon biodegradation. Examples include the BIOWIN EPI Suite ([2, 136]) and BIOB ([56]). In order to represent the overall attenuation rate of oil as a function of time, it is common to use a simple decay model such as:

$$\frac{C}{C_0} = \exp(-k \cdot t) \quad (3)$$

where C and C_0 are normalized concentrations of an oil component at times t and t_0 ; the term “ k ” is known as the decay constant (1/day) and is specific to the oil component being evaluated. Values of “ k ” are reported in Venosa et al. [163, 164] for different alkanes and aromatics under natural and amended nutrient concentrations. Although these values were obtained under specific conditions, and should therefore not be used indiscriminately, they provide general guidelines for estimating biodegradation times in shorelines. (As discussed above, values for dispersed oil are significantly faster, e.g., [28, 133].)

The first-order rate model could mask limiting factors impacting oil biodegradation, in particular nutrient concentration and the lag phase in oil biodegradation. More advanced models rely on using the so-called Monod kinetics to capture the impact of nutrients, for example, expressed as follows:

$$\mu = \mu_{\max} \frac{C}{K_C + C} \frac{N}{K_N + N} \quad (4)$$

where μ and μ_{\max} are the growth rate of biomass (1/day) and its maximum, N is the nutrient concentration (e.g., nitrogen), K_C is the half-saturation concentration, and K_N is the half-saturation concentration for nutrient consumption. A plethora of kinetic models have been developed based on Monod kinetics to account for various factors affecting hydrocarbon biodegradation processes ([56, 113, 114, 167]). Examples of these models include the work of Nicol et al. [114] which relied on using minimum Monod relations and the BIOB model ([56]), which relies on using multiplicative Monod relationships.

Environmental Factors

When one wishes to assess and predict natural biodegradation or the effectiveness of bioremediation, field measurements become essential tools for assessment of progress. Oil concentrations are the primary measurements, but it is advisable to

measure several additional environmental factors that influence oil biodegradation including:

- Oxygen concentration, to ensure that conditions are aerobic throughout the oiled zone. Experience suggests that biodegradation proceeds apace even at 3 ppm oxygen ([124], 2003).
- Nutrient concentrations such as nitrate, ammonium, and phosphate. Experience suggests that aiming for 100 μM bioavailable nitrogen is a safe goal ([125, 132]) with no adverse environmental impacts. Responders must remember that nitrogenous compounds leaching into the near-shore water might be toxic to fish and invertebrates, and stimulate algal blooms with their concurrent environmental impacts.
- Salinity, pH, and temperature. These are useful for understanding the local environment, but are not amenable to adjustment.
- Moisture content. This is only a problem in supratidal environments. The simplest response to potential limitations would be to redistribute the oiled sediment into the intertidal zone ([89]).
- Microbial community. This is useful for understanding the local environment, but is not amenable to adjustment—adding microbial cultures to stimulate oil biodegradation in “the real world” has not been shown to work at any significant scale for hydrocarbons.

These factors, discussed in further detail below, are measured in samples taken from the water table, pore water in the sediment, and the sediment. Furthermore, these measurements would best be conducted, when possible, at a minimum of four locations: the lower intertidal zone, the middle intertidal zone, the upper intertidal zone, and the supratidal zone of the beach (as indicated in Fig. 4). For oil located in the supratidal zone, an additional location would be landward of that zone. Also, when possible, additional measurements at un-oiled sites with similar geomorphic properties to the oiled sites should be taken to serve as controls. Similarly, samples taken before an oil impacts a beach are also desirable in order to provide baseline information.

Pressure transducers can be placed into slotted or perforated pipes installed into the beach down to depths below the low tide at that location to measure variations in the water table. Such measurements can also be used to assess the moisture in the beach and to predict the horizontal fluxes of pore water. Furthermore, the sensors used to measure water table changes provide the depth-averaged water temperature and salinity (see for example, [93]). Care should be taken, however, not to excavate the beach to install such equipment, for this will surely alter the intrinsic flow patterns in the beach. Driven hard point wells worked well in the rocky beaches of Prince William Sound ([131]).

Other parameters can also be measured through the collection of water samples from the wells. Specifically, multiport sampling wells which consist of a stainless-steel well casing with screen-covered holes drilled at several locations could be installed with care to dig holes only as large as necessary to allow depth-discrete sampling of the water. At each of these holes, separate stainless steel tubes are welded on the inside of the well casing, allowing one to take samples from each depth using a syringe attached to Luer fittings connected to the top of each tube ([23]). Alternatively, using a peristaltic pump, water could be pumped from the ground and through a sealed flow cell. Inside of the flow cell, electrochemical or optical oxygen probes can be installed. The sample container is filled from the bottom upwards to prevent the sample from being exposed and compromised by atmospheric oxygen ([23]). Colorimetric test kits are also available (e.g., <http://www.chemetrics.com/>) for rapid measurements of dissolved oxygen (1–12 ppm) using the Indigo Carmine method. Other systems, such as dialysis cells, commonly called diffusion samplers or “peepers” ([84]), could be used to sample the pore water. These cells use permeable membrane enclosures filled with deionized water prior to installation. They are then installed into wet sediments, left in place for a sufficient time (typically a week), and removed for analysis. The basic principle is that the water contained in the cells equilibrates with the pore water in the surrounding sediments; thus reflecting the concentration of constituents from those sediments at the corresponding depths. These can be used to quantify the pore water concentrations of dissolved oxygen, nutrients, salinity, and pH.

Oxygen

Although anaerobic biodegradation of petroleum hydrocarbons has been reported over the past 20 years, the rates are relatively slow compared to those commonly observed in the presence of oxygen under comparable experimental conditions ([15, 62, 174]). Certainly, hydrocarbons from marine oil spills have persisted for decades in anoxic sediments (e.g., [40, 122, 138, 168]), although they can also persist in aerobic environments (e.g., [88, 134]).

In carefully controlled laboratory studies, the dissolved oxygen (DO) concentration needed for the biodegradation of hydrocarbons in open water has been suggested to be as low as 0.1 mg/L ([10, 105]). However, results from field studies suggest that a concentration greater than 1.5 mg/L in the pore water is needed for the efficient biodegradation of oil ([16, 23, 35]). The DO in the field can be measured using various methods. The Winkler method can be very accurate for extremely low DO concentrations but requires considerable analytical skill and will most likely be difficult to conduct in the field. Electrochemical probes are commercially available and can be placed into the beach, but require good mixing or rapid flow past a membrane surface contained within the probe ([151]). Optical probes (Thermo

Scientific 2008) can be used on stagnant water and are thus more versatile. Although both of these probes are relatively easy to use in the field, their accuracy depends upon proper calibration and maintenance. Details on their usage on oil spills can be found in Boufadel et al. [23]. However, as mentioned earlier, colorimetric test kits are also available (e.g., <http://www.chemetrics.com/>) for rapid measurements of dissolved oxygen (1–12 ppm) using the Indigo Carmine method. Measurement of DO in pore water could be more straightforward in sand beaches where one could drive sensors into the beach. In gravel beaches, one could drive hardpoint wells ([131]) or could dig pits to place sensors. In the latter case, the re-placed sediment would likely be more permeable than the surroundings (the “pit effect”; [94]). To minimize this potential artifact, one should allow sufficient time for the sediments to return to their pre-digging equilibrium. In Alaskan beaches, 2 months were allowed prior to taking measurements ([23, 149]).

Coupling the biodegradation model BIOB ([56]) to the subsurface hydraulics model MARUN ([55, 60, 61]) investigated hypothetical situations of the biodegradation of Deepwater Horizon oil in Gulf of Mexico beaches. They noted a double-peaked concentration of pore-water oxygen (Fig. 5). The first peak is due to the advection of oxygen-rich seawater into the pores whereas the second peak is due to the exposure of the pores to the atmosphere.

Nutrients

Nutrients such as nitrogen and phosphorus compounds are needed for microbial activity. Nitrogen and concentrations can be measured using colorimetric test kits in the field (e.g.,

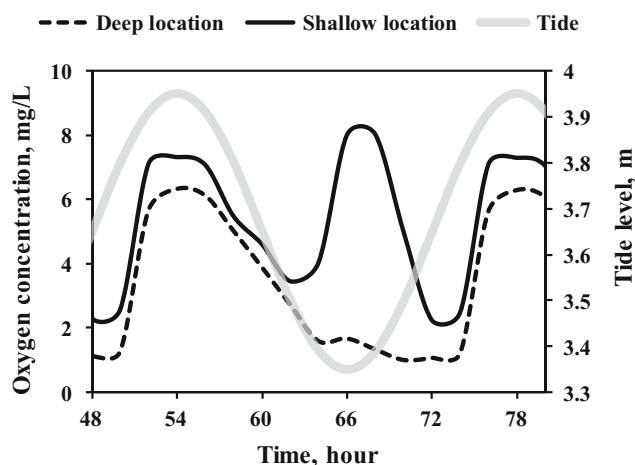


Fig. 5 Pore water oxygen concentration in the mid-intertidal zone. Note the double peaked oxygen curve within a tidal cycle, one following the rising tide and another ($t = 66$ h) at low tide. Note that the shallow and deep locations represent 1/3 and 2/3 depth of oil vertical extent in the intertidal zone of the beach, respectively.

<http://www.chemetrics.com/>) using the cadmium or zinc reduction methods. Phosphorus can be measured using the vanadomolybdophosphoric acid method or the stannous chloride method. Alternately, samples can be shipped to a laboratory and analyzed with standard ion chromatography methods ([106]).

Although hydrocarbon-degrading microbes are ubiquitous, they are usually only a small part of the indigenous microbiota of un-oiled sites; the addition of hydrocarbons dramatically increases the number of oil-degrading microbes, while decreasing the overall detectable diversity ([175, 176]). This indicates that the oil-degrading microbes must be growing and dividing, and out-competing whatever predation is occurring. Rosenberg and Ron [143] calculated that the conversion of 1.0 g of hydrocarbon to cell material requires 0.15 g of nitrogen and 0.03 g of phosphorus, and this puts a perspective on the amount of fertilizer one might add to stimulate biodegradation. An opposing concern is that excess nutrients are potentially toxic in the beach milieu, and might encourage algal blooms in nearshore water. Efforts have therefore focused on maintaining a reasonable level of nutrients in the beach pore water ([27, 124], 2003; [17, 45, 163]), variously aiming for biologically available nitrogen concentrations between 100 and 700 μM . A similar consensus has not been established for phosphorus, but N/P ratios of about 10:1 on a mass basis are close to the Redfield ratio, which represents the optimal molar ratio of nitrogen to phosphorus in marine systems ([36]).

Salinity, pH, and Temperature

Under natural conditions, changes in salinity, pH, or temperature are not expected to play significant roles in the biodegradation of oil in a beach environment unless they reach extreme value that the microorganisms are not accustomed to ([80]). Nevertheless, measurements of salinity could indicate the magnitude of fresh groundwater recharge and the washout of applied water-soluble chemicals to sea. Seawater has a pH around 8.1, and hydrocarbon biodegradation is practically unaffected between pH 6 and 9 ([4]). The optimal pH range for biodegradation is reported to be slightly alkaline water with a pH between 7 and 8.5 ([146, 182]). Microbes are also well adapted to different temperature environments, including extremely low temperatures ([41, 101, 112]). There has been a successful demonstration of bioremediation in the Arctic ([53, 125]).

In order to measure salinity (as conductivity), pH, and temperature, standard field probes are commercially available including multi-parameter instruments. Furthermore, these instruments can be deployed to collect information semi-continuously (e.g., datalogged) or at discrete times by a field team.

Moisture

Moisture content is a measure of the water-filled volume in a soil matrix. Since microorganisms and dissolved nutrients reside together within the aqueous environments of a beach, moisture content within the sediments is an important factor influencing the natural biodegradation of oil. Depending on the exchange of water and oxygen diffusion limitations in a sediment profile, a high moisture content could inhibit aerobic hydrocarbon biodegradation. Also, a low moisture content due to evaporation could cause nutrients concentration and salinity to damage soil microbes due to osmosis ([165]).

Maximum biodegradation has been shown to occur at moistures varying between 30% and 80% of the pore space ([5, 38, 98, 161]) depending on soil texture and type ([81, 165]). Fallgren et al. [48] found that the optimum value is between 30% and 50% of the pore space. In laboratory experiments, Horel and Schiewer [70] noted that a moisture saturation of 8% provided essentially the same biodegradation as that of 50% moisture saturation (100% is equal to the porosity). Tibbett et al. [158] investigated the potential of moisture content and nutrient amendments to enhance the biodegradation of crude oil in sediments from a semi-arid island. They found that the greatest levels of CO_2 respiration resulted when the percent saturation was between 50% and 70%, suggesting increased biodegradation activities within this range of moisture.

Thus, it can be concluded that oil biodegradation occurs at a broad range of soil moisture, down to 20% of the porosity, which occurs typically in the supratidal zone of beaches.

Microbial Communities

Marine sediments are usually covered with biofilms of highly diverse microbial communities ([147]), and as described above, the arrival of crude or fuel oil results in an increase in the relative proportion of hydrocarbon degraders in the microbial community ([175, 176]). In relatively oligotrophic environments, we might expect an increase in total microbial populations following the arrival of oil on a beach, and this was indeed seen on Pensacola (Florida) beaches after the Deepwater Horizon spill ([82]). Our understanding of the mechanics of biofilm evolution in response to environmental changes is still very primitive, but progress is being made ([72]). Only recently have microbiologists had reasonable tools to begin to investigate the deep biology of microbial responses to an oil spill, and the Deepwater Horizon spill led to several hundred papers. Although this work revealed the most active biodegrading organisms, their diversity, and their succession, microbiologists are not yet at a point where they can offer any new predictive information on biodegradation and bioremediation on shorelines.

Designing Laboratory Systems

Laboratory experiments are commonly used to investigate beach processes. There are two major thoughts: (1) building a system that captures the overall hydraulics of a beach as subjected to tides (with or without waves) and (2) building a setup to investigate a particular mechanism, such as the formation of oil particle aggregates (OPA) and/or oil biodegradation.

Building a Setup that Captures the Overall Hydraulics

Assuming homogeneous materials in a beach, one would use the three-dimensional equation for water flow in variably saturated media (also known as Richard’s equation) to predict the movement of water. Focusing on pore water hydraulics as subjected to tide, Boufadel et al. [25] developed a dimensionless formulation that aimed to conserve three dimensionless numbers: M , CF , and τ .

The parameter M combines the ratio of the domain dimensions and the ratio of anisotropy (Fig. 6a):

$$M = \frac{K_{x0}}{K_{z0}} \left(\frac{L_z}{L_x} \right)^2 \tag{5a}$$

The parameter CF represents the ratio of the capillary rise (vertical distance from the water table to the top of the capillary fringe) to the domain height L_z :

$$CF = \frac{h_c}{L_z} \tag{5b}$$

And the third dimensionless parameter to conserve is:

$$\tau = \frac{T \cdot k_{z0}}{L_z} \tag{5c}$$

where T is a characteristic time, such as the tidal period, and k_{z0} is the vertical permeability or simply the intrinsic permeability if the domain is assumed isotropic.

Figure 6a shows that one may even simulate an anisotropic porous domain in nature (i.e., field scale) by an isotropic domain in the laboratory provided one conserves the parameter M . Evidently, if the field-scale beach is isotropic, then one obtains the laboratory setup simply by reducing the sizes proportionally. Figure 6b addresses that when scaling down and accounting for capillarity (conserving the height of the capillary fringe h_c to the domain height, L_z), one is led to the conclusion that the height of the capillary fringe of the laboratory setup should be smaller than that of the field, which would require that the sediments of the laboratory beach be coarser than those of the natural beach. Thus, one needs to use a coarser material in laboratory setups.

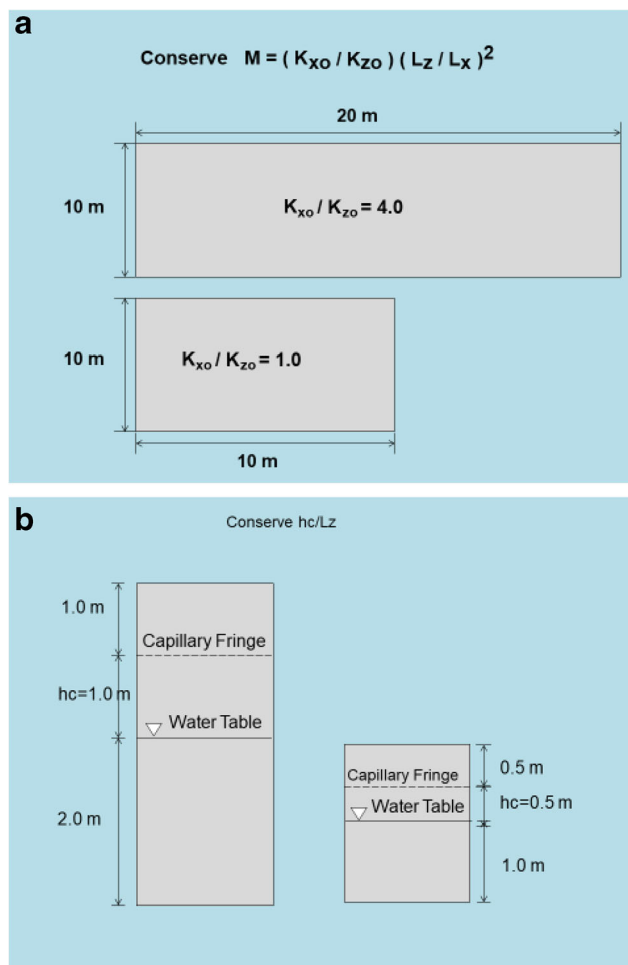


Fig. 6 Formulation to scale down beaches to the laboratory setup. (a) In the presence of natural anisotropy and (b) to account for capillarity, from ([18, 19])

After selecting a porous medium with the given capillary fringe, one measures its intrinsic permeability, which would be used to scale down the movement of the tide level in the laboratory according to the third dimensionless parameter τ (Eq. 5c).

The formulation developed above provides a good approximation for scaling down water flow in beaches in situations where the residual water content is small (say less than 10% of the porosity). In this sense, when dealing with solute transport, the formulation closely captures transport due to advection. However, the formulation has limitations in capturing solute transport where hydrodynamic dispersion is a major transport mechanism, which occurs for beaches where the sediments are poorly sorted resulting in large dispersivities. Coincidentally, these sediments tend to have a large residual saturation. The formulation could apply if one assumes that the dispersion coefficient in the porous medium is isotropic and uniform (i.e., the longitudinal and transverse dispersivities are equal) ([20]). The dimensionless formulation is not restricted to developing laboratory setups, as it can be used to generalize field

studies obtained from a specific beach, as conducted by Li et al. [95].

Scaling for Simulating a Microscopic Process

One of the main findings of the previous section is that scaling down the large-scale hydrodynamics of the beach requires a coarser porous medium in the smaller scale system. Thus, microscopic-scale processes, such as capillarity forces, the formation of oil particle aggregates (OPA), or film flow cannot be accurately reproduced in such a system. For example, a fine-textured beach could experience oxygen deficiency while its scaled-down coarse-textured laboratory setup (based on the dimensionless formulation in Eq. 5) would likely have a larger oxygen concentration. For this reason, aquifer remediation studies use the same soil and hydraulic gradient in the laboratory to mimic biochemical processes in the laboratory ([34]). Examples of scaled-down biodegradation studies include Chalneau et al. [32] who performed experiments in drill cuttings soil columns to investigate the biodegradation of fuel oil in them. Boufadel et al. [17] investigated the impact of nutrient concentration on the biodegradation of heptadecane in sand columns. Jones et al. [77] monitoring the evolution of hydrocarbon composition and generated gases during the biodegradation of hydrocarbons. Muangchinda et al. [112] conducted a microcosm experiment to study the biodegradation of high concentrations of mixed polycyclic aromatic hydrocarbons (PAH) by indigenous bacteria from river sediments. However, it is worth stressing that laboratory-scale studies on chemical processes, such as oil biodegradation are relevant to the sediments and water chemistry (namely oxygen and nutrient) conditions at which they were conducted.

The added complexity for simulating biochemical reaction herein is that the large-scale hydraulics is very dynamic due to the tide, and thus, one needs to create the appropriate conditions for reproducing those conditions on a “slice” of sediment in the laboratory (Fig. 7). The sediment type should be the same as that of the field, and preferably extracting a slice without altering it. Then, if the water level upstream (i.e., to the left) and downstream of the porous medium in the field vary in a certain way, one would need to reproduce this variation in the laboratory using water level controllers. The time series of water level could be obtained based on measurements in the field using pressure sensors or it could be simulated using a calibrated groundwater model. Boundary effects due, for example, to the formation of capillary barriers as a result of the sudden change in properties from sediments to a screen would need to be minimized through the placement of porous material behind (and below) the screens to drain the sediment column. An effort in that direction was made in Boufadel et al. [17].

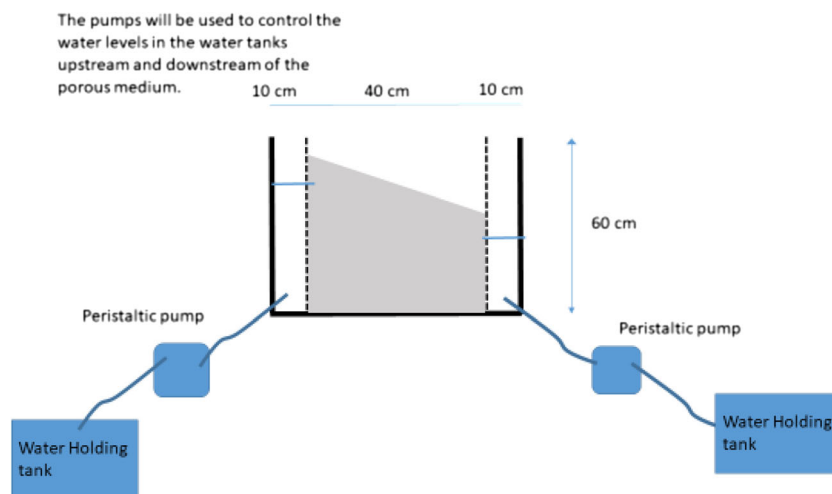
Conclusions and Recommendations

Various factors affect the distribution of oil within the matrix of beaches. These include oil properties, the presence of fines in the water column, tidal hydraulics, wave action, sediment texture, and initial oil loading. Upon release of oil into the environment, its chemical and physical properties commence to change in a process labeled as “weathering”; the oil could lose the light components by evaporation and/or dissolution, which would increase the oil density and viscosity. The latter is particularly important as it changes by up to 10- to 20-fold, which would affect the migration of oil within the pore space of the beach. However, prior to arriving at the beach, the interaction of oil with sediment results in the formation of oil particle aggregates (OPA) Zhao et al. [180] which are likely to reduce oil adherence to the sediment within the beach and/or form large OPAs ([117]). Both mechanisms result in smaller amounts of oil becoming trapped within the beach matrix in comparison to the case where no fines are present in the water column.

Tidal hydraulics (Fig. 1) plays a major role in the deposition within and the refloating of oil from beaches; as the tide drops, oil percolates in the beach, and when the tide rises, a fraction of the oil floats with the rising tide, but another fraction remains entrapped within the beach matrix due to capillary and adhesion forces ([55]). The larger depth of the water table near the high tide line ([19]) results in the highest deposition of oil there initially. However, the water flushing from that zones is relatively vigorous enhancing the rapid flushing and/or biodegradation of oil from that region relatively rapidly in comparison with the smaller amount of oil deposited at the mid-intertidal zone (and even smaller at the lower intertidal zone). Waves (Fig. 2) generate a large water exchange between the sea and the beach ([57]), which would accelerate the washout and biodegradation of oil within beaches. Within the beach, the capillary rise (or capillary fringe) is the zone of considerable moisture above the water table (Fig. 3), and its upper limit constitutes a barrier for the penetration of oil deeper into the beach. Thus, considering only the water table would overestimate the depth of oil penetration within the beach.

The initial oil distribution in the beach is illustrated in Fig. 4, which shows that, within the intertidal zone (between the high tide line and the low tide line), the largest depth of penetration occurs near the high tide line and decreases seaward, which is due to the fact that the water table and the capillary fringe riding on it drop the most near the high tide line ([121]). The oil could reach the supratidal zone due to waves, especially during storms, and could penetrate into the sediment or become buried by accretion (say during a subsequent storm). In fact, waves can completely modify the beach face through erosion and deposition (accretion).

Fig. 7 Using a laboratory setup to represent a slice of the natural beach for investigation of microscopic processes



Although the depth of oil penetration depends greatly on the tidal range (Fig. 1), it also depends on the beach permeability and oil viscosity. Table 1 provides means of estimating/measuring the beach permeability and Table 2 provides formulas that could be used to predict the permeability based on the grain size distribution, grain angularity, and beach porosity. As beach permeability (Table 2) and oil viscosity (Eq. 1) each can vary easily by 10 folds between beaches and oils, the movement of fresh oil into a pebble beach could be 100 times faster than the movement of a weathered oil (thus high viscosity oil) in a sand beach. In fact, if the oil viscosity is too large, the oil would not penetrate into the beach even as the tide drops, rather staying at the beach surface.

Oil biodegradation is the only mechanism that removes oil naturally from the environment. Although anaerobic biodegradation has been reported in some cases, it is too slow and too selective (for example, it has not yet been clearly demonstrated that alkylated three-ring polycyclic aromatic hydrocarbons biodegrade anaerobically) to be a major pathway for oil biodegradation. Aerobic oil biodegradation is more common, as it is almost certain that a beach would contain microorganisms capable of removing more than 80% of a fresh oil provided there is sufficient oxygen and nutrient within the pore space ([21, 90, 91, 126]). For this reason, the techniques for measuring oxygen and nutrients in situ and ex situ were provided herein. In particular, as one cannot usually drive sensors into large pebble beaches, one would need to excavate pits and wait a few weeks prior to taking measurements that represent the pore water deep into the beach. Otherwise, the measurements would be “contaminated” by the water from the shallower zones.

A means to assess oil biodegradation is through normalization by a biomarker (Eq. 2), and hopane is commonly used ([124]). Models for oil biodegradation within the pore space of beaches include first order decay ([163]) and Monod kinetics ([56, 114]).

When designing laboratory setups for studying oil behavior within a beach, one cannot capture both the large-scale behavior of the beach hydraulics and small-scale microscopic processes. Thus, one needs to consider one of two routes: (1) simulating the large-scale (whole beach) hydraulics or (2) simulating microscopic processes such as the formation of oil particle aggregates (OPA) ([89, 181]) or oil biodegradation. For the former, a methodology was presented in Eqs. 5 and Fig. 6, and it requires that one uses coarser sediment when scaling down the natural scale beach.

When analyzing the factors affecting the oil deposition on the beach, the following is recommended:

1. Account for the complex hydrology and geomorphology of beaches. Realize that even for homogeneous beaches, the environmental factors such as oxygen and nutrient will vary across the beach. Therefore, the locations of oil measurements are of tremendous importance. In a numerical study by Geng et al. [60], it was found that nitrogen was the limiting factor for oil biodegradation in the upper intertidal zone whereas oxygen was the limiting factor in the mid to lower intertidal zone. Thus, adding nutrient to beach would likely enhance the biodegradation in the upper intertidal zone, but might not affect oil biodegradation elsewhere within the beach.
2. Measure and/or estimate the height of the capillary fringe rather than focusing on measuring only the depth to the water table.
3. Measure pore water oxygen and nutrient content at various locations in the beach. For cobble/pebble beaches, the sediments are packed tightly, and thus one needs to wait a few weeks after excavating pits and placing sensors in them to allow the sediments to rearrange and pack again. In the works of Boufadel et al. [23] and Sharifi et al. [149], 2 months were allowed to evolve prior to sampling for oxygen and nutrient.

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