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Oil pollution of beaches

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Oil contamination of beaches causes significant damage as these ecosystems are unique habitats that provide foraging and nesting grounds for a variety of animals including endangered species, and play pivotal roles in shore line protection and coastal economies. Even small oil spills in the ocean result in sizable slicks that currents transport to sandy beaches that line a third of the global shoreline. Weathering during transit reduces the degradability, viscosity and density of the oil, influencing its fate at the shore. While photolysis, biodegradation, tidal pumping, and seasonal sediment movement facilitate relatively rapid removal of stranded oil from sandy beaches of temperate and warm climes, thick buried oil layers persist for decades in armored gravel beaches of cold shores, emphasizing the controls of beach morphodynamics, biodegradation, and climate in the recovery from beach oil pollution.

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The signaling function of oiled beaches

Oil spills in the oceans may receive most attention through the pollution of beaches, where the environmental impact of the crude becomes intensely apparent through the killing of shore birds, stinking slicks on the water, and black oiling of the white sands. The dramatic images prompt extensive media coverage and swift public responses that push research and legislation addressing the effects of the oil on human health, the environment, and coastal economies. The pollution of beaches thus has a signaling function that strongly influences our perception of crude oil and its impacts. This article summarizes processes that govern the oil pollution of beaches and the fate of the stranded petroleum hydrocarbons.

Marine oil spills likely end up at beaches

Even small remote spills are likely to pollute large segments of beaches owing to the physicochemical characteristics of crude oil, its interactions with the marine environment, and the morphology of the global coastline. Liquid crude released to the sea accumulates at the surface, where the hydrophobic effect and high internal energy of water cause that the nonpolar drops quickly self-associate [1]. The ensuing cohesive layer rapidly expands due to inertia, gravity, and the pull by the greater surface tension of water [2], and the spill that started as point source rapidly morphs from a compact volume into a quasi 2-dimensional slick [3]. Oil released from natural seeps may spread out to 0.1 μm thick sheens [4], and within days, 1 L of seeped oil can coat a sea surface of 10 000 m^2. The surface slick smoothens the ocean's waves, counteracting oil dispersion and altering its path as the relative influence of wind is reduced [5]. Currents can transport the slick over hundreds of kilometers [6], and stretch it into elongated shapes that eventually may split as currents separate. The dramatic size increase and added travel directions enhance the spill's reach and amplify the likelihood that it will contaminate one of the sandy beaches that occupy one third of the worlds coastline [7].

Oil type and path define its degradability after stranding

Behavior and degradability of the petroleum hydrocarbons eventually reaching the shore hinge on the type and composition of the oil. The majority of marine oil platforms produces light crude but the demand for heavy oils and their shipping over the oceans is growing, increasing the chance of beach contamination with oils of lower degradability [8]. Even spills of lighter crudes result in deposition of less-degradable hydrocarbons because of the weathering during transit to the coast [9]. In the first few days, light oils may lose nearly half of their mass through releasing gases, dissolution of water-soluble hydrocarbons, and evaporation of volatile compounds [10,11]. At the surface, exposure to UV-light decomposes large hydrocarbon molecules making them more accessible to biodegradation [12], and bacteria colonize the oil surface initiating degradation [13]. Waves fold the slicks, infusing them with water, generating colorful emulsions or 'mousse' with increased viscosity and density [14]. When the slick approaches the shallow nearshore environment, adhesion of resuspended mineral and detritus particles further increase its density and 'new' organic matter content, and some oil sinks. Crude that finally contacts the shore is stripped from its more degradable, light weight hydrocarbons but enriched in water, minerals, nutrients, new organic matter, and hydrocarbon-degrading microbes, all of which benefit its biodegradation.

Controls and characteristics of oil stranding

Mechanisms and effectiveness of the deposition of oil onto beaches are mainly governed by prevailing winds and currents, wave action, tidal range, beach profile and oil type. Onshore winds push slicks toward the coast where breaking waves and high tides dump them onto the beach. The wide gentle slope of dissipative beaches [15] leads to oil contamination of large beach faces as observed after the Prestige tanker accident on the Galician coast [16] or recently on the Peruvian shore. Here large waves caused by the explosion of the submarine volcano in Tonga moved thick heavy fuel oil slicks onto the beach, forming massive coast-parallel oil bands. Here waves moved thick heavy fuel oil slicks onto the beach, forming massive coast-parallel coherent oil bands (Figure 1a). Light crude from the Deepwater Horizon accident that was washed onto roughly 1000 km of sandy Gulf of Mexico beaches [17,18], was deposited in distinct forms causing different impacts: deposition of thin oil sheens coated the sand grains of the upper sand layer of the beach face with a brown hydrocarbon film (Figure 1b) [19]. Multiple films accumulated to an oil-sand-mesh at the beach surface that eventually ripped, resulting in sand-oil-agglomerates that were pushed up the beach or back into the water where they amassed into submerged oil mats [20]. Oil dumped landward of the beach berm melted together under hot Florida temperatures to accumulations that expanded over large areas of the supralittoral (Figure 1c) [19,21]. Incorporation of wrack mixed the liquified recalcitrant fossil hydrocarbons with degradable algae, seagrass debris, and detritus. Large floats with high-viscosity oil mousse disintegrated in the surf and were moved as oil lumps up the beach face where they fused, forming large sand-oil-agglomerates up to wheel barrel size (Figure 1d).

Burial in beaches

State of the beach, sediment characteristics, magnitude of waves, tidal cycle and season define whether oil is buried and how long it remains in the beach. Burial of large oil lumps (Figure 1d) is accelerated by their interaction with the swash [22]. In dissipative beaches, as those on the Peruvian coast, high wave energy promotes spreading and mechanical fragmentation of oil deposits, which can promote burial as well as their removal [23]. However, even a low-energy accreting summer beach may quickly bury surface oil under thick sediment layers, locking the petroleum hydrocarbons in the beach as reported from Florida shores impacted by the Deepwater Horizon spill [19,21]. In such settings, alternating oil and sand deposition can build stratified layers exceeding 50 cm thickness in the lower beach (Figure 1e). Ghost crabs that excavate vertical burrows, sea turtles digging their nests [24], and human cleanup activities produce conduits for oil to deeper sediment layers or mix oil into the surface layer of the beach. In gravel or coble beaches, even viscous crude can seep deep into the beach, where it can form thick coherent subsurface oil layers that may float on the groundwater (Figure 1f) [25].

Degradation of oil deposited on beaches

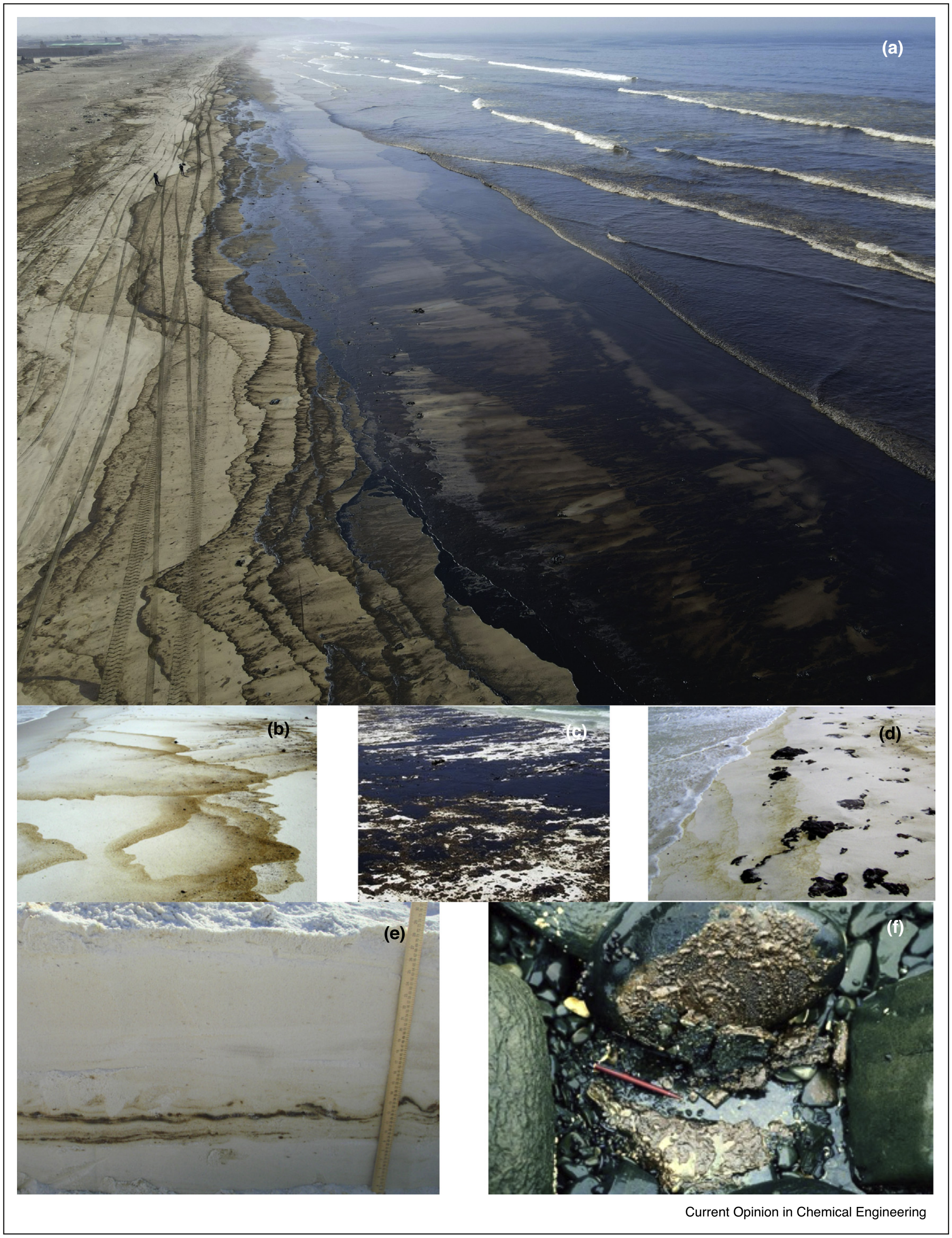
Physicochemical decomposition

Stranded oil decomposition hinges on its exposure and the dynamics of the beach environment. At the beach surface oil degrades faster than after burial because photolysis, mechanical disintegration, oxygen availability, and increased temperature boost physical, chemical, and biological decomposition process [27,28]. Photooxidation degrades aromatic compounds, converting them into polar species that are more soluble and susceptible to biodegradation [12,29]. The photochemical oxidation affects larger molecules and alkyl substitutions more strongly, which again is beneficial for the microbial decomposition process as smaller and less substituted compounds are more accessible to biodegradation [30]. Notably, photooxidation facilitates decomposition of large polycyclic aromatic hydrocarbons (PAHs) that stand out through their toxicity and resistance to biodegradation, for example, up to 90% of larger PAHs were lost after 12 hour in an experiment with simulated solar irradiation [12,31•]. Mechanical energy, enhancing abrasion, fragmentation, oil dispersion, and sediment reworking, is considered a dominant factor accelerating crude oil burial and attenuation in high-energy shoreline environments [32,33]. The breakup of large oil aggregates into small particles is pivotal as it accelerates burial and defines the surface to volume ratio in a degradation process that predominantly takes place at the surface of the oil [34]. In the exposed Galician shore, thick layers of oil-coated sand grains were found under more than 3 m of beach sand after the Prestige accident [35] but beach morphodynamics drove a sequence of physicochemical processes that allowed substantial weathering despite the deep burial [36].

Microbial oil degradation

Next to photooxidation, biodegration is the major pathway for the decomposition of oil in the beach, and dominates hydrocarbon degradation in the subsurface layers. Since hydrocarbons are natural products also generated by modern plankton organisms [37•,38••], a microbial food web evolved that can metabolize hydrocarbons including those contained in crude oil [39–41]. The main actors decomposing petroleum hydrocarbons are organisms belonging to the bacteria, cyanobacteria, archaea, molds, yeasts, and green algae [42•,43,44] but bacteria and fungi may be the dominant oil degraders in sandy beaches [45,46]. The abundance of hydrocarbon-oxidizing bacteria in Florida beach sands increased immediately after Deepwater Horizon oil contamination by two to four

Figure 1



Oil pollution of beaches. A: Pollution of a wide high-energy dissipative sand beach at Ventanilla, Peru, on January 18, 2022, after high waves attributed to the eruption of an undersea volcano in Tonga caused an oil spill (Photo: Martin Mejia). B–E: Deposition of light crude on sandy Florida beaches after the Deepwater Horizon explosion. B: deposition of oil sheen; overlay of multiple layers results in the formation of sand-oil-agglomerates visible as dark particles. C: deposition of a thick oil slick onto the supralittoral at Pensacola, USA, on June 23, 2010. Warm temperatures melted the slick resulting in oil puddles with embedded wrack D: Burial of oil mousse lumps. Only the upper surface of the lumps is visible. E: Layers of oil buried below ~ 50 cm of sand (Photos: Huettel or public domain (c)) F: Oil mousse from the Exxon Valdez accident remaining after a decade within an armored gravel beach in Prince William Sound/Alaska [26].

orders of magnitude [19,46]. This is remarkable as the degradation of the hydrophobic oil particles requires special adaptations, restricting the spectrum of microbes that can decompose petroleum hydrocarbons. Oil-degrading microbes have evolved mechanisms that permit cell adhesion to the hydrophobic hydrocarbons and enzymatic attack. Through the production of biosurfactants and emulsifiers, they mobilize water-insoluble compounds and modify the hydrophobic surface, facilitating cell attachment [47]. Using exopolysaccharide excretion, the attached microbes generate biofilms that stabilize moisture and adhesion to the oil-coated grains [48,49].

Main players

Analyses of Deepwater Horizon polluted Gulf of Mexico beach sands revealed bacteria primarily belonging to the Gammaproteobacteria, including representatives of genera with known hydrocarbon degraders, such as *Alcanivorax*, *Halomonas*, *Marinobacter*, *Pseudomonas*, and *Acinetobacter* [50–53]. Kostka *et al.* [46] isolated 24 bacterial strains from 14 genera from four classes within the phyla Proteobacteria, Firmicutes, and Actinobacteria from the oiled beach sands that were confirmed as oil-degrading microorganisms. The majority of the isolates belonged to the orders Oceanospirilalles, Alteromonadales, Vibrionales, and Pseudomonadales within the class Gammaproteobacteria and one isolate was identified within the Alphaproteobacteria. About one third of the total microbial community was comprises the novel Gammaproteobacterium *Macondimonas diazotrophica*, a nitrogen fixing hydrocarbon degrader [54]. The ability of this bacterium to produce biosurfactants and utilize dinitrogen make it highly competitive in nitrogen-limited oiled environments explaining its dominance in the beach and other oil-contaminated sites globally [54]. Nonetheless, beach oil biodegradation progresses through a sequence of microbial consortia with a variety of catabolic genes, and the synergistic effects of these genes allow degradation of a multitude of different oil compounds [46,51]. Microbial communities in Florida beaches initially degraded mostly aliphatic hydrocarbons and were replaced after three months by communities capable of decomposing aromatics. Microbial taxonomic diversity dropped owing to oil toxicity affecting sensitive taxa, while functional diversity increased driven by the bloom of microbes capable of hydrocarbon degradation [55]. The disturbance thus favored generalists, supporting the specialization-disturbance hypothesis [56]. Besides bacteria, fungi contributed to the oil decomposition in the Gulf sandy beaches. Simister *et al.* [45] identified three Ascomycota (*Fusarium*, *Scopulariopsis* and *Aspergillus*) that degraded structurally diverse oil compounds including short and long chain n-alkanes. Through their metabolic plasticity, fungi can assimilate hydrocarbons in the beach even at low nutrient concentrations and relatively low pH [57,58•]. The ability of their filamentous hyphae to extend in length through apical growth allows fungi to penetrate into oil-sand aggregates [42•]. Fungi thereby may act as biocatalysts that can effectively accelerate oil decomposition by increasing the oil surface area for microbial colonization and access to oxygen.

Aerobic and anaerobic pathways of oil biodegradation in the beach

Macondo well oil spilled after the Deepwater Horizon explosion contains more than 13 000 non-volatile components [59], evidencing that its decomposition in the beach is a complex process with numerous different catabolic pathways progressing at different rates. Access to air facilitates aerobic metabolisms in the dry layer of the beach. Initial step in the aerobic hydrocarbon biodegradation is the introduction of oxygen into the molecules by cell membrane-bound oxygenases, which requires direct contact of the microbes with the oil [60]. This activation, producing alcohols that may be further oxidized to fatty acids [61], increases the hydrocarbons' solubility in water, enhancing their dispersion within the beach. Oxygenases also catalyze oxidation of aromatic compounds, resulting in ring cleavage that unlocks a variety of degradation pathways [62]. In thick layers of concentrated oil, as found for example, in the gravel beaches of Prince William sound after the Exxon Valdez accident, only the surface of the oil layer may have access to oxygen. Hydrocarbon degradation here may progress mostly anaerobically, mediated by denitrifying, sulfate-reducing and iron (III)-reducing microbes [63•,64]. These bacteria use fumarate addition, oxygen-independent hydroxylation, or carboxylation to activate hydrocarbons [65]. The anaerobic degradation rates typically are orders of magnitude lower than their aerobic counterparts, and buried oil can endure under such conditions nearly unchanged over decades [26,66].

Controls of biodegradation in the beach

Factors boosting microbial activity also enhance beach oil decomposition, with temperature, moisture, access to oxygen and availability of nutrients being central rate-limiting constraints [28,67,68]. Degradation rates of n-alkanes as well as aromatic hydrocarbons increases with rising temperature [69,70], and Rowland *et al.* [71] reported a Q_{10} value of approximately three for buried oil decomposition in beach sand. Heat and wind remove moisture from the permeable beach sand, which impedes biodegradation through restricting microbial access to water [72] and by generating hypersaline conditions [73•]. Cycles of ocean spray deposition and evaporation may elevate salt concentrations to salinities exceeding 100, suppressing degradation rates up to 90% [74]. Precipitation can relieve these moisture and salinity restrictions as revealed by a doubling of CO_2 release from oil-contaminated beach sands after heavy rain [71]. On the other hand, rain storms or beach overwash that water-saturate the surface sediment layer can create a gas lock that slows the sedimentary oil degradation [71]. Sparging with air therefore is used to support oil biodegradation in oxygen-limited soil subsurface layers [75]. The low nutrient content of crude oils and the supralittoral sands it is embedded in hampers microbial oil degradation in the dry beach [76,77]. Wrack, detritus and plankton washed onto the beach can accelerate the oil decomposition through co-catabolism facilitated by the microbial release of enzymes or cofactors during degradation of the fresh organic matter [78]. Although natural nitrogen and phosphorus contents of beach sands suggest some availability of nutrients [79,80], these nutrients in the dry beach are bound to mineral surfaces or detritus particles and may not be accessible to microbial oil decomposition. Rainwater, groundwater or seawater can mobilize these nutrients and transport them to buried oil, stimulating its degradation. Therefore fertilizer application is central in beach oil bioremediation efforts [44,81,82], and nutrient amendments at a C:N:P ratio of 100:10:3 ratio were shown to accelerate light crude decomposition in sand 10-fold [83]. Since oil forms coatings on sediment particles, grain size influences the specific surface area of oil exposed to degradation, favoring decomposition in sand over degradation in gravel. However, in fine-grained silty beaches, sediment pores may be completely locked by oil, and the mineral grains can effectively shield the hydrocarbons from oxygen, nutrients and microbial attack limiting their degradation [28]. In contrast, the relatively high permeability of sand and gravel beaches enhances the coupling of oiled subsurface layers to the environmental settings at the surface and the water-saturated deep layers of the beach. The tidal water table oscillations within the beach force air in and out of the beach similar to the action of a piston pump, enhancing gas movement through the pore space and microbial activity: Air drawn into the beach during ebb carries heat and oxygen into the sand, while air pushed upwards during flood moves moisture and CO_2 from deep sediment layers towards the dry surface layers (Figure 2a). This is similar to a breathing process, with the beach inhaling oxygen during ebb and exhaling CO_2 during flood. The associated increased oxygen, heat and moisture supply to the buried oil and removal of CO_2 generated during its decomposition, increases the microbial biodegradation process [19]. Oil embedded deep in the beach may become submerged when the tidal water level changes, rinsing it with oxygen and nutrient containing-water thereby supporting biodegradation [84]. Tidal vertical oscillation of liquid oil layers floating on the ground water table of gravel beaches may enhance oil dispersion and emulsification promoting its breakdown, or even push oil out of the sediment (Figure 2c).

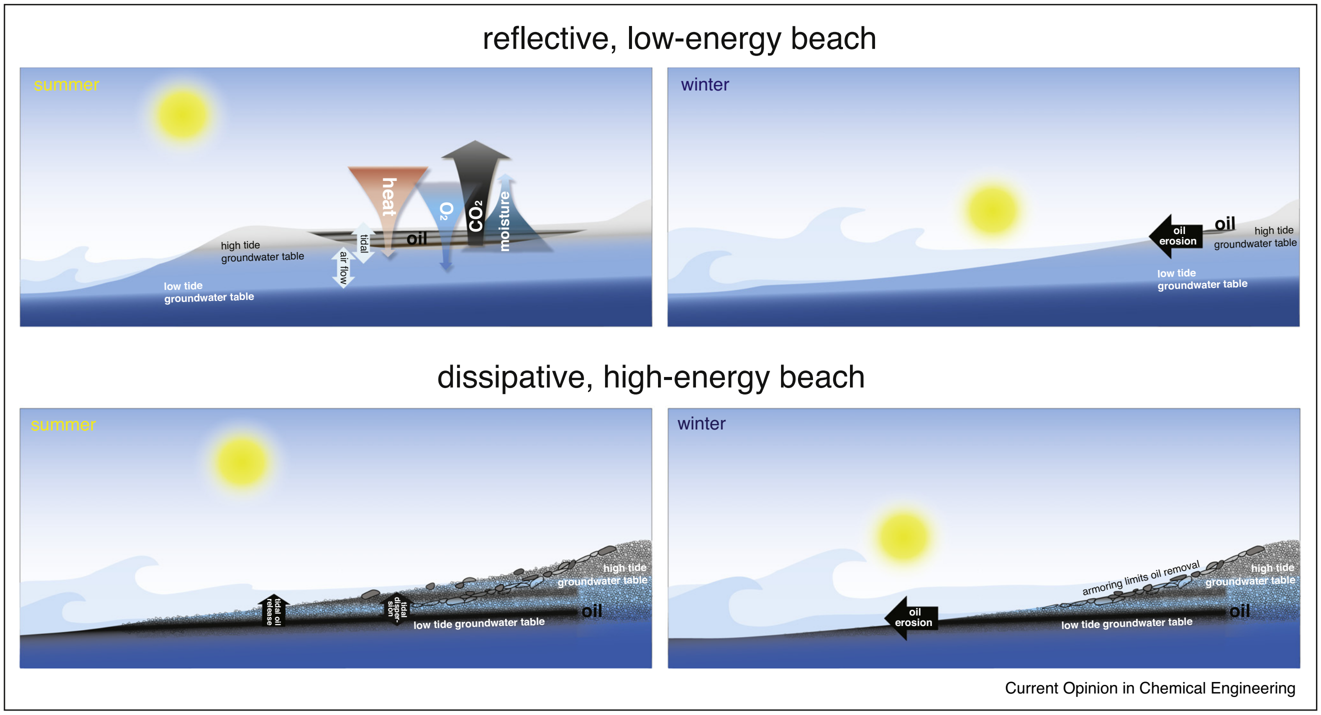
The broad range of oil degradation rates in beaches

Degradation rates of crude oils deposited in beaches range from a few months to decades depending on the oil characteristics, climate zone, beach type, and shoreline energy [99]. In sheltered beaches, buried oil can persist for decades even in a warm climes as observed in the Mediterranean after the massive Gulf war spill [85]. Thin oil coatings of sand grains as observed in the upper tens of centimeters in Florida beaches after the Deepwater Horizon spill were largely degraded within half a year [19]. The average half-life ranged from 20 to 70 days, similar to the rates reported from oil-contaminated Delaware (~30 d) [100], and Louisiana beaches [72]. PAHs in the surf zone of Pensacola Beach/Florida had half-lives of 53 d–67 d [86]. Conversely, complete decomposition of golf-ball size sand-oil-agglomerates produced by the same oil spill and buried in the dry upper 50 cm of the same Florida beach was estimated to take at least 30 years [27], emphasizing that oil degradation is a surface phenomenon and a function of surface to volume ratio. Isolating sand-oil-agglomerates from sediment contact reduced their decomposition rates by factor 3, corroborating a key role of the beach subsurface environment in the degradation process. On the other hand, biodegradation contributes to accumulation of oxygen in oil residues, which can convert them into more recalcitrant oxyhydrocarbons with longer half-lives [87,88]. In many cases, the slow decomposition process of large, buried sand-oil-aggregates is cut short by seasonal events. In contrast to inland soils, the non-cohesive beach sands are subject to substantial-episodic, frequent, and seasonal sediment transport that redistributes, disperses and removes stranded oil. Eroding winter beaches may re-expose buried oil, and seasonal storms converting reflective into dissipative beach profiles return sand and embedded oil to the sea as observed at Pensacola Beach/Florida (Figure 2b). This constitutes a cyclical mechanism that can remove buried oil from beaches [19]. Exception to this may be coarse gravel beaches, where cobles armor the surface, protecting buried oil from removal during storms [26,89]. This process, cold temperatures, and limited access to oxygen may be responsible for Exxon Valdez oil persisting at 25–50 cm depth within beaches of Prince William Sound that were polluted in 1989 [90]. Nevertheless, tidal pumping also can move oil layers embedded in gravel beaches, resulting in dispersal and partial removal (Figure 2d).

Remediation of oiled beaches

Regardless of the effects of beach morphodynamics, the highly visible pollution of beaches and their substantial socio-economical value usually trigger rapid responses to oil contamination. Clean-up activities typically start with the removal of stranded oil from the beach surface, followed by bioremediation activities designed to accelerate the degradation of buried petroleum hydrocarbons. The cleaning strategies intend balancing the benefits of the oil removal and potential environmental harm caused by the cleanup effort. High-pressure cleaning with hot sea-water of oiled surfaces as applied after the Exxon Valdez accident can increase damage to the beach ecosystem and slow the recovery process [91]. Likewise,

Figure 2



Environmental factors influencing oil deposited in reflective and dissipative beaches. **(a)** Macondo well light crude oil from the Deepwater Horizon accident was buried in several layers in the dry supralittoral reflective sandy beach at Pensacola/Florida during spring 2010. Tidal pumping transported heat, oxygen and moisture to the embedded oil and removed carbon dioxide, thereby enhancing biodegradation of the petroleum hydrocarbons during summer months [19]. **(b)** Winter storms moved sand and a large fraction of the remaining embedded oil back to the sea. **(c)** North Slope heavy crude oil could seep deep into the high-energy, dissipative gravel beaches of Prince William Sound after the Exxon Valdez accident in spring 1989. The oil formed thick subsurface layers that were moved and dispersed by tidal pumping. **(d)** Winter storms caused seasonal erosion that could eat away some stranded oil but the armoring of the beach protects embedded oil layers from removal [26].

removal of algal wrack and supratidal macrofauna together with oiled surface sand may harm beach ecosystems [92]. More recently, soybean lecithin was proposed as an effective and environmentally sustainable alternative to synthetic surfactants in washing treatments of hydrocarbon-contaminated sands and gravel [93]. On smaller scales, use of ultrasound may help accelerating oil removal from sands [94]. Elimination of petroleum hydrocarbons buried in deeper layers can be accomplished most effectively through biostimulation via fertilizer addition and bioaugmentation utilizing inoculation of pre-stimulated indigenous hydrocarbon-degrading microorganisms. Various injection mechanisms were proposed for subsurface biostimulation [81,95], which may be critical in gravel beaches where oil persists under nearly anoxic conditions [96]. However, even microorganisms and nutrients added to the beach surface may reach the buried oil [97]. For the selection of bioremediation strategies and prediction of oil persistence in beaches, models were developed that may allow reducing negative environmental impacts while improving effectiveness of the bioremediation [98]. As seasonal changes in beach morphology can be substantial, such modeling approaches should take beach morphodynamics into account [16].

Conclusions

Exposed beaches are exceptionally dynamic sedimentary environments, where high levels of kinetic and radiation energy effectively accelerate decomposition of stranded oil. Wave kinetic energy drives substantial sediment transport that fragments and disperses the oil. When waves grind a golf-ball size oil agglomerate into sand-size particles, the attachment area for microbes and exposure of hydrocarbons to irradiation increases hundred-fold. Such smaller oil particles rapidly become buried and integrated in the sedimentary biodegradation process. Microbial densities exceeding those of seawater by orders of magnitude, combined with aeration through tidal pumping and co-catabolism of new organic matter, facilitate relatively rapid decomposition of old fossil petroleum hydrocarbons as long as the oil particles are small, temperatures are moderate, and aerobic biodegradation dominates. Wave-erosion of oil-contaminated sand layers during storms and subsequent export of oil particles to deeper waters, allow re-deposition of clean sands onto the beach, providing a mechanism for seasonal removal of highly refractory oil compounds (resins, asphaltenes, oxyhydrocarbons). Exposed sandy beaches in temperate or warm climates thus may recover relatively quickly from oil pollution as observed in Gulf of Mexico beaches after the Deepwater Horizon spill. This scenario differs dramatically where crude oil is washed onto cold-climate gravel beaches. Even heavy oils here can seep rapidly deep into the coarse sediment, forming thick, coherent subsurface oil layers with limited access of light, microbes, oxygen, and nutrients to the hydrocarbons. Cold temperatures paired with anaerobic conditions effectively slow biodegradation, and beach armoring by larger stones prevent natural oil removal during major storms. Coarse-grained beaches of boreal and arctic shores thus may be the most vulnerable to oil pollution, which must be taken into account when considering oil exploration in these environments.

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Conflict of interest statement

Nothing declared.

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- •• of outstanding interest

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