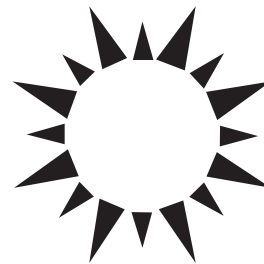# Crude Oil Releases to the Environment: Natural Fate and Remediation Options

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Glossary

API (American Petroleum Institute) gravity A scale describing the density of an oil. Oils with gravities >40° are known as light oils, and those with gravities <17° are said to be heavy.

asphaltenes Large complex molecules in crude oils and heavy fuels, often with molecular weights in the many thousands, composed of carbon, hydrogen, oxygen, and other heteroatoms. They are responsible for most of the color of crude and heavy oils and typically are not "oily" to the touch.

bioremediation Stimulating the natural process of oil biodegradation. To date, this has been restricted to the addition of fertilizers to alleviate nutrient limitations for these organisms. Adding bacteria has not been shown to be necessary.

booms Floating devices for corralling, or sometimes absorbing, oil on water. There are many different designs for different situations, including stationary booms in rivers, towed booms for collecting oil, and fireproof booms for holding oil for combustion.

Bunker C Fuel oil used to power ships' engines. It is a very heavy, viscous fuel derived from the heaviest hydrocarbon compounds that remain after processing whole crude oil.

crude oil Natural product that is the remains of biomass that was typically alive 100 million years ago. It is a complex mixture of hydrocarbons, resins, and asphaltenes.

dispersants Concentrated solutions of surfactants that can be sprayed on floating oil to cause it to disperse into the water column, where it is naturally biodegraded.

hydrocarbons Compounds composed of only carbon and hydrocarbon; these are the most abundant molecules in most crude oils and refined fuels. They are a diverse mixture of linear, branched, and cyclic saturated compounds with 1–80 carbon atoms, together with aromatic compounds, most commonly with more than one ring and with multiple alkyl substituents.

natural attenuation The natural processes that eventually remove hydrocarbons from the atmosphere.

resins Moderately large complex molecules in crude oils and heavy fuels, often with molecular weights in the thousands, composed of carbon, hydrogen, oxygen, and other heteroatoms.

skimmers Mechanical devices to remove floating oil from water. There are many designs, including moving belts, weirs, mops, and vacuum pumps.

Crude oils and other hydrocarbons have been a part of the biosphere for millennia, so it is no surprise that a ubiquitous, diverse population of hydrocarbon-consuming microorganisms are able to exploit this resource. These organisms can be recruited to help respond to human-associated oil spills, although sometimes only after physical treatments to remove bulk oil, such as mechanical pick-up or combustion:

- If oil is floating at sea, the addition of dispersants to dramatically increase the surface area available for microbial attack will stimulate biodegradation

and also inhibit the formation of troublesome tar balls and minimize the amount of oil that reaches the shore.

- If oil is on a shoreline, the addition of fertilizers to provide necessary ancillary nutrients for the degrading microorganisms will stimulate oil biodegradation.
- If oil is in surface soil, adding fertilizers and tilling the soil will provide both the nutrients and the air needed to stimulate biodegradation.
- If soluble hydrocarbons are in an underground water plume, adding a source of oxygen, whether as a gas or a soluble or slow-release peroxides, will stimulate aerobic biodegradation.

Together, these approaches exemplify modern environmentally responsible remediation activities: working with natural processes to stimulate them without causing any additional adverse environmental impact.

1. INTRODUCTION

Crude oils have been a part of the biosphere for millennia, and human use extends back thousands of years. Early uses included hafting stone axes to handles, use as an embalming agent, and use as a medical nostrum. In the Bible, Genesis implies that bitumen was used as the mortar for the Tower of Babel. It also seems likely that several religions started near natural gas seeps, either as eternal flames or as sources of hallucinogenic vapors. However, these were very minor uses, and it is only in the past century and a half that oil has come to play a truly central role in our lives. Terrestrial seeps were the first locations to be drilled when oil production began in earnest in the 19th century, such as the 1859 Drake well in Pennsylvania. Today, oil is recovered from all over the world, except the Antarctic, and from great depths, including coastal margins such as offshore West Africa and South America. The scale of oil production is staggering; global use is on the order of 10^{12} U.S. gallons per year (3.25×10^9 tonnes or 3.8×10^{12} liters/year), and much of it is transported thousands of miles before it is used. For example, the United States imported 350,000 tonnes of oil per day from the Middle East alone in 1999. Unfortunately, despite the best efforts of the oil industry, some (a relatively small fraction) of this material has been spilled at production and refinery facilities and from pipelines and vessels. Such spills generate enormous public pressure for speedy clean-up, but the obvious approach of simply sucking up the oil from the environment is rarely simple or complete. This article addresses the natural fate of oil in the environment and how understanding the underlying processes allows intervention to safely stimulate them and thereby minimize the environmental impact of spills.

2. COMPOSITION OF CRUDE OILS AND REFINED PRODUCTS

2.1 Origins

Crude oils are natural products, the result of the burial and alteration of biomass from the distant past. The alteration processes are known as diagenesis and catagenesis. The initial process of diagenesis typically occurs at temperatures at which microbes partially degrade the biomass and results in dehydration, condensation, cyclization, and polymerization of the biomass. Subsequent burial under more sediments, and thus at higher temperatures and pressures, allows catagenesis to complete the transformation of the biomass to fossil fuel by thermal cracking and decarboxylation.

It is generally accepted that most petroleum reserves are derived from aquatic algae, albeit sometimes with some terrestrial material, whereas the great coal reserves of the world arose from deposits of higher plants, typically in nonmarine environments. The generation of oil and gas invariably occurs at significant depth and under great pressure, which forcibly expels the oil and gas from the initial source rock. Commercially valuable reservoirs are formed if the migrating oil becomes trapped in a geological structure so that the oil and gas can accumulate. Most petroleum reservoirs are found in sandstones, siltstones, and carbonates with porosities of 5–30%. The traps are never completely full of oil, and there is always some water, usually containing substantial amounts of inorganic salts (brine), underlying the oil. Typical commercial oils originated from biomass that was produced on the order of 100 million years ago, although the oldest commercially valuable oils are from Ordovician biomass (486 million years ago), whereas others are as young as the late Tertiary (a few million years ago).

2.2 Hydrocarbons

Crude oils and refined products are very complex mixtures of molecules, both hydrocarbons and

compounds containing other elements, such as sulfur, oxygen, and nitrogen. The hydrocarbons, containing only hydrogen and carbon, are the best studied and understood, and they can be divided into broad classes based on their overall chemical properties. The hydrogen to carbon ratio of crude oils is between 1.5 and 2.0; the organic molecules are thus principally saturated molecules (i.e., the predominant form of carbon is -CH_2-). The convention in the oil industry is to call linear alkanes paraffins and cyclic alkanes naphthenes. There are also significant amounts of aromatic carbon in all crude oils and polar molecules containing the heteroatoms oxygen, nitrogen, and sulfur. These latter molecules can be fractionated by column chromatography, and the fractions have a variety of names, including resins and asphaltenes. In their classic 1984 book "Petroleum Formation and Occurrence," Tissot and Welte state that the average composition of 527 crude oils is 58.2% saturates, 28.6% aromatics, and 14.2% polar compounds, although the absolute values vary widely in different oils. On average, there is rough parity between paraffins, naphthenes, and aromatics.

The paraffins include the linear alkanes from methane to waxes with up to 80 carbons. Linear alkanes typically make up 10–20% of a crude oil, although their content can range from essentially undetectable to as high as 35% depending on source and reservoir conditions. There are also branched alkanes, usually most abundant in the C_6–C_8 range. Two branched alkanes found in almost all crude oils, pristane ($C_{19}H_{40}$) and phytane ($C_{20}H_{42}$), are molecular relics of the phytol chains of chlorophylls and perhaps other biomolecules in the original biomass that gave rise to the oil.

The naphthenes include simple compounds such as cyclopentane, cyclohexane, and decalin, together with their alkylated congeners. Tissot and Welte state that the average composition of the naphthene fraction of 299 crude oils is 54.9% one- and two-ring naphthenes, 20.4% tricyclic naphthenes, and 24.0% tetra- and pentacyclic naphthenes. These latter molecules are molecular relics of membrane components of the original biomass, and they are very useful fingerprints of individual oils.

The aromatic molecules in crude oils range from benzene to three- and four-ring structures, with traces of even larger ring systems. Because of the separation procedures used in the characterization of crude oils, any molecule containing at least one aromatic ring is included in the "aromatic" fraction, regardless of the presence of saturated rings and alkyl substituents. Crude oils typically contain aromatic molecules with up to four aromatic rings; one series contains just six-membered rings and their alkylated derivatives—benzene (one ring), naphthalene (two rings), phenanthrene (three rings), chrysene (four rings), etc. Another series includes one five-membered ring in addition to the six-membered ones—fluorene (three rings), fluoranthene (four rings), etc. Because of the operational definition based on chromatography, sulfur aromatic heterocycles, such as thiophenes, benzothiophenes, and dibenzothiophenes, are included in the aromatic category. Indoles and carbazoles, usually the most abundant nitrogen-containing species, and the less abundant basic nitrogen species such as quinolines are also included in the aromatic category. Alkylated aromatic species are usually more abundant than their parent compounds, with mono-, di-, and trimethyl derivatives usually being most abundant. Nevertheless, the median aromatic structure probably has one or two methyl substituents together with a long-chain alkyl substituent.

2.3 Nonhydrocarbons

The polar molecules of crude oils are the most difficult to characterize because they are often unamenable to gas chromatography, the usual method of choice for the molecular characterization of petroleum. All are thought to contain heteroatoms, such as nitrogen, oxygen, and/or sulfur, and the category includes the porphyrins (usually nickel or vanadium species) and naphthenic acids. Some of these molecules have molecular weights in the thousands or higher, and many are suspended in the oil rather than dissolved in it. The polar fraction of the oil contains the majority of the color centers in crude oil, and in isolation these materials are difficult to distinguish from recent biological residues, such as humic and fulvic acids.

2.4 Oil Classification

Oils are classified by several criteria, but among the most important is the specific gravity. The oil industry uses a unit known as API (American Petroleum Institute) gravity, which is defined as [141.5/(specific gravity)]−131.5 and expressed in degrees. Thus, water has an API gravity of 10°, and denser fluids have lower API gravities. Less dense fluids (e.g., most hydrocarbons) have API gravities >10°. For convenience, oils with API gravities >40° are said to be light oils, whereas those with API gravities <17° are said to be heavy (Table I). Light

TABLE I

Conversion Table for a Medium Crude Oil

1 tonne	308 U.S. gallons
	7.33 barrels
	858 liters

oils have higher proportions of small molecules; heavy oils are rich in larger molecules. Viscosity is inversely proportional to API gravity, but it is also dependent on the physical state of the polar compounds and longer alkanes in the oil, and it is highly dependent on temperature.

2.5 Refined Products

Crude oil is transported in the largest volumes, both in pipelines and in tankers, but refined products are also transported long distances, particularly in pipelines. Refining starts with distillation, and the simplest distinction of the various refined products can be related to this process. The most volatile liquid product is aviation gasoline, followed by automobile gasoline, jet fuels, diesel and heating oils, and the heavy oils that are used for fueling ships and some electrical generation. All ships contain large volumes of heavy fuel oil, often called Bunker C, that is barely liquid at ambient temperatures and must be kept warm to be pumped into engines.

Most of the molecules in gasoline have 4–10 carbons (Table II), most in diesel fuel have 9–20, and heavy fuel oils typically have very few molecules with less than 15 carbon atoms except for some added as a diluent to achieve the appropriate viscosity. It is important to recognize that fuels are not sold by their composition but by their properties, such as octane, cetane, or viscosity, and there are many chemical mixtures that meet these requirements. The chemical composition of fuels with the same name can thus be very different, even though all meet their specifications. The lightest products (i.e., those with the lowest boiling points, such as gasolines and diesels) are almost entirely hydrocarbons, whereas the heavy fuel oils are enriched in the polar constituents such as asphaltenes; this is reflected in the color of the products.

3. RELEASES TO THE ENVIRONMENT

Crude oil has been released to the natural environment from seeps for millennia and, as mentioned

TABLE II

Number of Carbon Atoms in the Majority of Compounds in Refined Products

Product	Approximate carbon range
Aviation gasoline	C_4–C_8
Regular gasoline	C_4–C_{10}
JP4 jet fuel	C_5–C_{11}
JP8 jet fuel	C_8–C_{15}
Kerosene	C_9–C_{16}
Diesel No. 1	C_9–C_{17}
Diesel No. 2	C_9–C_{20}
Bunker C	C_8–C_{10}, C_{15}–C_{50}
Hydraulic oil	C_{18}–C_{36}
Automatic transmission fluid	C_{19}–C_{36}

TABLE III

National Research Council's Estimates of Annual Input of Oil to the Sea

Source	North America, tonnes	World, tonnes
Seeps	160,000	600,000
Consumers	90,000	480,000
Spills	12,100	160,000
Extraction	3,000	38,000
Total	260,000	1,300,000

previously, these have proved useful sources for humankind. Some seeps are relatively small, and the oil affects only a very small area. This was true for the seeps that gave rise to "perpetual flames" in Iraq and bitumen reserves in eastern North America. However, some are vast and have given rise to huge asphalt lakes and tarpits. The La Brea tarpits in Los Angeles are well-known, not least for the impressive bones from tigers that unwittingly became entrapped, and the large asphalt lakes in Trinidad (140 acres) were once exploited to deliver asphalt for paving in Newark, New Jersey. Clearly, a major determinant of the environmental impact is the scale of the release. Table III shows 2002 estimates of the scale of oil releases into the sea both in the United States and throughout the world.

3.1 Natural Seeps

Natural seeps are found all over the world, and the scale of their releases is quite large. In 2002, the National Research Council estimated that the total annual input of petroleum into the sea from all

sources is approximately 1.3 million tonnes, with almost 50% coming from natural seeps. For example, natural seeps in the Gulf of Mexico release an estimated 140,000 tonnes of oil per year into the sea, those offshore Southern California release 20,000 tonnes per year, and those offshore Alaska release 40,000 tonnes.

3.2 Municipal Runoff

The National Research Council estimates that releases due to the consumption of crude oil, principally municipal runoff but also including spills from nontanker ships, recreational uses, and atmospheric deposition, are the second largest input of oil into the world's oceans, far dwarfing that from catastrophic tanker spills. Again, the sheer scale of oil use is staggering; it is estimated that just the input of lubricating oil from two-stroke engine use in the U.S. coastal seas is 5300 tonnes per year.

3.3 Tanker Spills

Almost half of all oil moves by seagoing tanker at some stage between production and use, and spills from these vessels attract by far the largest amount of attention from the media. As discussed previously, their total input is relatively small compared to other inputs, and a recent estimate is that more than 99.98% of the oil in transit reaches its destination safely. The issue, of course, is that when they do occur, tanker spills are very localized, and they can have substantial localized environmental impacts that call for a cleanup response. The industry has responded to public concerns, and tanker spills are fortunately becoming rarer; for the period 1990–1999, spillage from vessels in U.S. waters was less than one-third that released in 1980–1989. Similar improvements have occurred worldwide, although there is always need for improvement.

3.4 Pipeline Spills

The Minerals Management Service estimates that there are 21,000 miles of undersea oil pipelines installed on the U.S. continental shelf delivering oil from wellheads to collection points and refineries. Spills are rare but are estimated to be approximately 1,700 tonnes per year, mainly in the Gulf of Mexico. To put this in perspective, the largest spill in the Gulf occurred in 1979, when the IXTOC-1 well "blew out" approximately 80 km off Ciudad del Carmen on the Mexican coast. The blowout lasted 9 months and

spilled 476,000 tonnes of crude oil before it could be controlled.

Total U.S. liquid petroleum pipelines include a total of 114,000 miles of crude oil pipelines and 86,500 miles of pipeline for refined products, which together transport two-thirds of all U.S. petroleum. Pipeline leaks, often caused by excavation errors, lead to annual spills of approximately 19,500 tonnes, and again there has been a substantial improvement in safety during the past few decades. Because of the physical barriers around most pipeline spills, they are usually contained, and most spilled oil is collected with pumps. Unfortunately, this is not always the case; in 1997, an underwater pipeline released 940 tonnes of south Louisiana crude oil into Lake Barre in Louisiana. The spill affected 1750 ha with a light sheen, but only 0.1 ha of marsh died back. Much of the oil evaporated, some pooled oil at the edges of some marshes was recovered, and the lightly oiled areas appeared to be clean within 2 months.

3.5 Wars, Environmental Terrorism, and Vandalism

The past decade has seen a resurgence of oil spills associated with warfare, terrorism, and vandalism. Many ships were sunk in World War II, and some still contain substantial amounts of oil; an example is the USS Mississinewa, which was sunk in Ulithi Lagoon in Micronesia in 1944 and recently located. It is estimated to contain 3300–10,000 tonnes of heavy fuel oil, and this is beginning to leak from the decaying vessel. By far the largest oils spills in history were those deliberately released by Iraqi forces retreating from Kuwait in 1991. At least 10 million barrels of oil were deliberately poured into the Arabian Gulf, and 700 oil wells were ignited or otherwise destroyed. Vast lakes of oil covering approximately $49\,km^2$ were formed, and most remain after a decade. The volumes are so huge that the totals remain unknown.

Smaller wars also cause the release of substantial volumes of oil, although again the totals are difficult to estimate. Colombia's 780-km Cano Limon pipeline, which ships 110,000 barrels of oil per day, was bombed at least 170 times in 2001, and estimates of total oil spilled are far higher than those of well-known tanker spills. The French supertanker Limberg was apparently attacked by terrorists offshore Yemen in 2002. Even the Trans Alaska Pipeline is not immune to vandalism; 925 tonnes were spilled when a high-velocity rifle slug penetrated the pipeline in 2001.

4. NATURAL FATE OF OIL IN THE ENVIRONMENT

The description of the various inputs of oil into our environment, mainly from natural seeps and municipal runoff, makes it clear that oil has been part of the biosphere for millennia. However, we are not overwhelmed by it. This is because a variety of natural processes contribute to its removal, the most important of which is biodegradation. Crude oils and refined products provide an excellent source of carbon and energy to organisms, principally micro-organisms, able to exploit it. These organisms are responsible for the consumption of most of the hydrocarbons that get into the biosphere and that are not collected or burnt. Nevertheless, this process is relatively slow, and several physical processes typically act on spilled oil before it is eventually biodegraded.

4.1 Flotation and Spreading

Almost all oils in commerce float; thus, they spread rapidly if the spill is on water. This has the effect of providing a dramatically larger surface area for evaporation and dissolution, and eventually the floating layer becomes subject to physical disruption by waves. A few very heavy oils, such as that spilled in the Delaware River from the Presidente Rivera in 1989, are sufficiently dense that they form almost solid lumps that submerge in fresh water. They do not usually sink, however, and can be collected by subsurface nets.

4.2 Evaporation

Small hydrocarbons are very volatile, and molecules smaller than those with approximately 15 carbons typically evaporate quite readily if a spill is on the surface. This can be effectively complete in a matter of days, although underground spills do not typically evaporate very rapidly. Spills are not the only source of volatile hydrocarbons in the atmosphere; trees liberate vast quantities of isoprene and other terpenes. Whatever the source, some interact with reactive nitrogen oxides in the presence of light and in high enough concentrations can contribute to photochemical smogs, The Blue Mountains got their name from this natural phenomenon long before the onset of the petroleum era. Eventually, most volatile compounds, and the reaction products of photochemical oxidations, are "rained out" and deposited on the ground, where they are biodegraded. Some biodegradation may even take place on water droplets in the atmosphere because there are many bacteria in the air.

4.3 Dissolution

A few hydrocarbons are sufficiently soluble in water that they "wash out" of floating surface or underground spills into the water phase. This phenomenon is usually only significant for the BTEX compounds (benzene, toluene, ethylbenzene, and the xylenes) and oxygenated compounds such as methyl-tertiarybutylether. Such compounds have the tendency to wash out from floating spills, whether on surface water or on the water table underground. This phenomenon is of particular concern underground because the soluble compounds have the potential to migrate and contaminate wells and surface water. Fortunately, they are biodegradable under both aerobic and anaerobic conditions.

4.4 Dispersion

Although oils do not dissolve in water, they can disperse. Wave action breaks up floating slicks and may disperse the oil so finely that it is readily biodegraded. This is what happened to most of the 85,000 tonnes of oil lost in the 1993 spill off the Shetland Islands from the Braer. Adding chemical dispersants to encourage this process is an important oil-spill response tool. If the oil is merely broken into large globs, however, these can coalesce and form tar balls that can drift for thousands of miles before eventually beaching. It is not unusual for tar balls to accumulate other debris during their travels or even to be colonized by barnacles.

4.5 Emulsification

Many oils will form very stable water-in-oil emulsions, particularly after they have weathered sufficiently to form a critical concentration of asphaltenes that can stabilize such emulsions. This can multiply the mass of the original oil by up to five times, increasing the recovery and disposal burden. Water-in-oil emulsions can achieve extremely high viscosities, making relatively light oils behave more like heavy fuel oils. This can slow the evaporative and dissolution processes so that if the emulsions are broken, the released oil's properties are more similar to those of the original material than if emulsification had not occurred.

4.6 Physical Interactions with Sediments

The formation of long-lived "pavements" is a poorly understood phenomenon that can have a significant effect on the persistence of oil in the environment. At high enough concentrations, crude oils and heavy refined products such as bunker fuels interact with sand and gravel so that the oil becomes completely saturated with sediment and vice versa. Even quite liquid oils and fine sediments can form pavements that mimic commercial asphalt, and when this occurs the inner oil is essentially entombed and protected from biodegradation. It can then last for years without significant weathering, as happened in Tierra del Fuego following the 1974 spill of 50,000 tonnes of oil and fuel from the Metula. Spill response efforts aim to minimize and prevent the formation of these pavements.

At the microscale, however, the interaction of oil with fine sediments is proving to be an important natural process that removes oil from oiled shorelines. Fine particles become associated with droplets of oil and effectively disperse into the water column, where biodegradation occurs quite rapidly. The scale and importance of this phenomenon have only been recognized during approximately the past decade.

4.7 Photooxidation

Photooxidation by sunlight is very effective at oxidizing three-, four-, and five-ring aromatics in floating slicks and stranded oil. The molecules are not completely destroyed, but they seem to be polymerized and incorporated into the resin and polar fractions of the oil, where they are probably no longer bioavailable. Photooxidation of the surface of pavements and tar balls may contribute to their longevity. Photooxidation seems to have far less of an effect on the saturated components of oil.

Photooxidation is an important phenomenon not because it removes large volumes of oil from the environment but because it removes the molecules of most toxicological concern. Crude oils and heavy fuels contain trace amounts of potentially carcinogenic polycyclic aromatic hydrocarbons such as benzo[a]pyrene. Fortunately, these are among the most susceptible to photooxidation, and they are readily destroyed if an oil is exposed to sunlight.

4.8 Combustion

The natural ignition of gaseous seeps is still a source of wonder whenever it occurs. All hydrocarbons are combustible, and sometimes shipwrecks catch on fire (e.g., the 144,000-tonne spill from the Haven near Genoa in 1991) or are deliberately ignited (e.g., the 1360 tonnes of fuel oil on board the New Carissa offshore Oregon in 1999). A major problem is that the oil has to maintain a high temperature to continue burning, and heat transfer to water underneath a slick usually extinguishes any fire as the slick thins. Burning spilled oil thus usually requires containment within fireproof booms, but if successful it can be very effective; combustion of $>90\%$ has been reported in several trials. Burning may be particularly useful in ice-infested waters, in which skimming is very difficult and the ice can act as an effective boom. The residue, although viscous, is not very different from oil that weathers without heat, and there is only a small increase in pyrogenic compounds in the residue. Burning oil, however, can generate a large amount of black smoke. The smoke is very low in residual hydrocarbon, but may, in certain circumstances, present a potential health concern due to fine particulate matter. If burning occurs away from population centers, the potential for environmental and health impacts of the smoke is minimal.

4.9 Biodegradation

4.1.1 Aerobic

Biodegradation is the ultimate fate of hydrocarbons released into the environment, although it is sometimes a slow process. Biodegradation under aerobic conditions has been studied for at least a century, and the variety of organisms able to consume hydrocarbons and the diverse pathways and enzymes used in the process are well understood. More than 60 genera of bacteria and 95 genera of fungi have been described that catalyze this process, along with a few species of archaea and algae. These organisms share the ability to insert one or two of the oxygen atoms of diatomic O_2 into a hydrocarbon molecule, thereby activating it and making it accessible to the central metabolism of the organism. The oxygenated hydrocarbon then serves as a source of reductant for the growth of the organism, and much more oxygen is required as the terminal oxidant.

Almost all hydrocarbons that have been studied have been shown to be biodegraded in the presence of oxygen. The small aromatics (benzene and the substituted benzenes) and alkanes are most readily consumed, followed by the larger alkanes and the two- and three-ring aromatics and their alkylated

derivatives. The branched alkanes are slightly more resistant, but they are still readily degraded. The biodegradation of alkylated three- and four-ring aromatics is slower, and some of the four- and five-ring saturated compounds, the hopanes and steranes, are among the most resistant. Indeed, they are so resistant that they can serve as conserved internal markers in the oil, and their concentration in the residual oil increases as biodegradation proceeds. They remain as "fingerprints" of the initial composition of the oil until the very last stages of biodegradation.

Estimates for the total biodegradability of the hydrocarbon fraction of different crude oils range from 70 to 97%. Less is known about the biodegradability of the resins, asphaltenes, and other polar species in crude oils, and the larger ones are not thought to be very susceptible to the process. Fortunately, these compounds lack "oiliness," are friable in small quantities, and are essentially biologically inert. Indeed, they are essentially indistinguishable from other relatively inert biomass in the environment, such as the humic and fulvic acids that make up the organic fraction of soils and sediments and are so essential for plant growth.

Aerobic oil-degrading microorganisms are ubiquitous, having been found in all natural environments in which they have been diligently pursued. Indeed, aerobic hydrocarbon-degrading organisms are the foundations of the extensive ecosystems that exploit marine oil seeps, which often include large multicellular organisms that feed on the hydrocarbon-oxidizing microbes. Oil seeps may even serve as the primary food sources for some fisheries, such as those of Atlantic Canada.

4.1.2 Anaerobic

For some time, it has been known that hydrocarbons are also biodegraded under anaerobic conditions. The hydrocarbon still acts as a reductant, and in the absence of oxygen something else must serve as a terminal electron acceptor. Sulfate (reduced to sulfide), nitrate (reduced to nitrogen), chlorate (reduced to chloride), ferric and manganic ions (reduced to ferrous and manganous ions), and carbon dioxide (reduced to methane) have all been shown to be effective oxidants for hydrocarbon degradation, at least in mixed cultures of organisms. Only a few genera of anaerobic bacteria that can catalyze these reactions have been identified, but this undoubtedly is just the tip of the iceberg and probably more an indication of the difficulty of isolating these organisms than of their scarcity in

anaerobic environments. In the absence of oxygen, something else must be added to the hydrocarbon to initiate its metabolism, and at least two pathways have been identified. One adds a molecule of fumarate to the hydrocarbon, whereas the other seems to add a molecule of carbon dioxide. The anaerobic biodegradation of small hydrocarbons, especially the BTEXs, which are of most concern if they leak from storage tanks, is becoming quite well understood.

An important feature of crude oils and refined products is that although they are a rich source of carbon and energy for microbes able to consume them, they are almost uniquely unbalanced foods. Microbes typically have a carbon:nitrogen:phosphorus ratio of approximately 100:10:1, but oil contains no significant amounts of either nitrogen or phosphorus. Oil-degrading microbes must therefore obtain these elements in useful forms from elsewhere in the environment, and if there is a significant amount of hydrocarbon it is likely that the growth of the degrading organisms will be limited by the supply of these nutrients.

5. RESPONSES TO SPILLS

The first response to a spill is to stop any further release and to contain and pick up as much as possible. On land, this is relatively simple, albeit time-consuming and expensive. Indeed, most of the "oil lakes" left in Kuwait from the Gulf War are still awaiting treatment. At sea and on lakes and rivers, however, any collection requires corralling the oil with booms to stop it from spreading.

5.1 Booms, Skimming, and Combustion

Many different types of boom are available; some are inflatable, and others are rigid. Some are designed to withstand ocean waves, and others are designed to work in sheltered harbors. Often, booms are used to keep oil out of particularly sensitive areas, such as fish hatcheries and marshes. Others are designed to be towed to "sweep up" oil, and still others are fire resistant and designed to allow the oil within the boom to be ignited.

Once the oil has been corralled, it has to be collected. This is done with skimmers, which remove oil while accumulating as little water as possible. There are many different designs; mops, moving belts, and floating suction devices are all used. Each is best suited for a particular type of oil and may be

ineffective against other oils, but all attempt to collect the oil without collecting much water or debris.

Igniting oil in fireproof booms is not a trivial matter, and special igniters are usually required.

5.2 Physical Removal

If oil reaches a sandy shoreline, it can often be collected with scrapers and bulldozers. This was very effective following the 1996 spill of 72,000 tonnes of crude oil from the Sea Empress off the south coast of Wales. Sometimes, manual removal by teams of workers with shovels is appropriate, as in the case of the 2002 spill from the Prestige off the coast of Spain. If the shoreline is inappropriate for heavy equipment—such as the shorelines of Prince William Sound, Alaska, affected by the spill from the Exxon Valdez—the oil can be flushed back into the water, corralled within booms, and collected with skimmers. Recent developments include special surfactant products that help lift oil from the shoreline while allowing its retention within booms for subsequent skimming, thus allowing more oil to be released with cooler flushing. In the United Kingdom, it is permissible to use dispersants for this purpose in certain circumstances, provided that they have passed the required approval protocols. In North America, use of dispersants on shores is not permitted, and so a new generation of products have been developed that loosen the oils for removal by water stream without the unwanted effect of oil being dispersed into the near-shore water column. These products are specially formulated with amounts of surfactants sufficient to wet the surface but insufficient to foster dispersion. Some of these products have been successfully used on spills in Canada and the United States. Their main objective is to allow weathered oils to be removed by washing without having to use heated water, which could have detrimental side effects on biological communities.

5.3 Bioremediation

Although the physical removal of small near-shore spills can usually be carried out quite effectively and completely, this is rarely possible with large spills at sea. Even when physical collection or combustion are fairly effective, there is almost always some oil that escapes capture. As discussed previously, the ultimate fate of this residual oil is biodegradation, and there are several environmentally responsible ways of stimulating this process. Colloquially known as bioremediation, these can be divided into two complementary strategies. While oil is afloat at sea, the surface area available for microbial attack limits its biodegradation. Adding dispersants to disperse the oil into the water, and dramatically increase the surface area for microbial colonization, is an important option. In contrast, the biodegradation of oil remaining on a shoreline is likely limited by the supply of other necessary microbial nutrients, such as biologically available nitrogen and phosphorus, and carefully adding fertilizers is a very useful option.

5.3.1 Dispersants

Dispersants are concentrated solutions of surfactants that can be applied from the air or from ships equipped with spray booms or fire hoses. Typical application rates are approximately 5% of the oil volume, so quite large stockpiles are required, and indeed are available, in central depots. The dispersants need to be added fairly soon after a spill, but there is usually a window of several days during which they are effective. Even mild wave energy disperses the oil very effectively into the water column, and it has been demonstrated that this substantially increases the rate of biodegradation. Some dispersants also include molecules that actively stimulate oil biodegradation either by providing limiting nutrients or by adding preferred substrates. Dispersion also minimizes the beaching of spilled oils. Dispersants were used very effectively following the 1996 spill of 72,000 tonnes of a relatively light crude oil from the Sea Empress off the south coast of Wales.

5.3.2 Fertilizers

Heavily oiled sites that have been washed or otherwise physically treated to remove the bulk of the oil always retain some residual oil, and this is an ideal target for bioremediation through the addition of fertilizers. Lightly oiled beaches may also provide excellent opportunities for use of this technology without pretreatment. Aerobic oil-degrading microbes are ubiquitous, but their abundance is usually limited by the availability of oil. An oil spill removes this limitation, and there is invariably a "bloom" of oil-degrading microbes, both in terrestrial and in aquatic environments. Their growth becomes limited by the availability of something else. In marine environments, this is usually nitrogen, and although a few oil-degrading microorganisms are able to fix atmospheric nitrogen, most have to await the arrival of low levels of nitrogen with every tide. Carefully applying fertilizers to partially

overcome this limitation can substantially increase the rate of biodegradation with no adverse environmental impact. Slow-release and oleophilic fertilizers (designed to adhere to the oil) seem most effective, and they were used with significant success following the 1989 spill from the Exxon Valdez in Alaska. The oleophilic fertilizer was applied with airless sprayers, and the granular slow-release fertilizer was applied with agricultural "whirligigs." Careful monitoring revealed no adverse environmental impacts from this approach and a stimulation of the rate of oil biodegradation of between two- and fivefold. In other words, although the technique did not make the oil disappear overnight, it sufficiently stimulated a process predicted to take a decade so that it occurred in a couple of years.

Since then, bioremediation has been used on a limited site as part of the cleanup of the 1996 Sea Empress spill and has been demonstrated on experimental spills in marine or brackish environments on the Delaware Bay, a Texas wetland, a fine-sand beach in England, mangroves in Australia, and an Arctic shoreline in Spitsbergen. Experience suggests that fertilizer should be added to maintain soluble nitrogen at approximately $100 \mu M$ in the interstitial water of the oiled sediment, and this may require reapplication every few weeks. Such a level of fertilizer nutrients does not seem to cause any adverse environmental impact but stimulates the rate of oil biodegradation severalfold.

Fertilizers have also been used with success at many terrestrial spill sites after the bulk of the spilled oil has been collected. Often, biodegradation at terrestrial sites is also limited by the availability of oxygen, and this can be ameliorated by tilling of surface soils or by the addition of oxygen as air or dissolved or slow-release peroxides for subsurface plumes. One approach suspends slow-release peroxides in a series of wells that intercept flowing groundwater plumes; others sparge air into similar wells.

5.3.3 Natural Attenuation

Biodegradation is such an effective environmental process that in some cases it can be relied on to clean an oil spill without further human intervention. Sometimes this is necessary because human interven-tion may cause more environmental impact than the spill, such as attempts to remove small amounts of oil from marshes. Other situations in which such an approach can be appropriate include underground spills, in which soluble hydrocarbons enter the groundwater. Usually, these are degraded *in situ*, and if the source is plugged the contaminants may be degraded before the plume intercepts any sensitive receptor. In such a case, it may be best to rely on the natural biodegradation process rather than attempt to stimulate it. Clearly, it is important to have a realistic understanding of the natural processes that will remediate the spill before natural attenuation is accepted as the appropriate response.

Together, these approaches exemplify modern environmentally responsible remediation activities—working with natural processes to stimulate them without causing any additional adverse environmental impact.

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