# A Local Oil Spill Revisited

## John M. Teal

n October 1969 George Hampson and Howard Sanders (Woods Hole Oceanographic Institution, WHOI) described a "Local Oil Spill" in *Oceanus*. The spill had occurred a month before when the barge *Florida*, loaded with no. 2 fuel oil, ran into some rocks in Buzzards Bay off West Falmouth, Massachusetts. In a more general article in that same issue of *Oceanus*, Max Blumer wrote, "The immediate, short term effects of oil pollution are obvious and well understood in kind if not in extent....In contrast, we are rather ignorant about long term and low level effects....I fear that these may well be far more serious...."

In the summer of 1989, one month shy of 20 years later, we visited the Wild Harbor marsh area that had suffered the greatest impact from the spill to see if we could find any traces of the event in the marsh ecosystem. During those 20 years, the site has been visited by graduate students in marine ecology, by reporters seeking information about current oil spills but also interested in seeing the effects of the Wild Harbor spill, and by visiting scientists curious about one of the world's best-studied oil spills.

For more than a decade after the spill, an oil sheen appeared on the surface of the water when mud from the most heavily oiled parts of the marsh was disturbed. During the second decade, the marsh's appearance returned to normal. Beginning three to five years after the spill, most of the oiled area was reinvaded by marsh grasses and occupied by marsh



An oil spill that followed the 1969 grounding of the barge Florida off West Falmouth, Massachusetts, was monitored for two decades.

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animals. An observer unfamiliar with Wild Harbor would have been unable to detect the oiled areas after 10 years.

### The Spill: Oil in Wild Harbor

The oil barge went onto the rocks off West Falmouth, Massachusetts, on a still, foggy September 1969 morning, spilling about 180,000 gallons of no. 2 fuel oil. This is the thin home-heating oil we all use, and is very similar to diesel oil. (About 60 to 65 spills of this size would be equivalent to one Exxon Valdez spill.) After the oil spilled onto the water, the wind rose and drove oil onto the Wild Harbor shore. The surf mixed oil, water, and sediments at the shoreline, making the oil-sediment mixture heavy enough to sink. This mixture contaminated several square kilometers of bottom to water depths of over 6 meters. Subsequent storms continued to extend oiled-sediment bottom contamination over the next several months. Eventually, the affected area was several times larger than it was during the first few weeks after the oil came ashore. Oil entering the quiet waters of the marsh was not mixed into the water but was carried up with the tide and deposited on the grass and surface of the sediment. As the tide ebbed, the oil ran down animal burrows and seeped into marsh sediments. The most heavily oiled places were the quiet cul-de-sacs that naturally accumulate sediments and anything else driven by the wind into the area, the Wild Harbor boat basin, and a small tidal creek in the Wild Harbor salt marsh. Some not-very-effective efforts were made to disperse the oil and to boom off the harbors and marshes-25 years ago the equipment was primitive, and there were no emergency-response



teams ready to try to contain the oil.

### **Studies Began Immediately**

Studies of the effects of the oil spill began immediately, because there were shellfishermen, nature lovers, town officials, and scientists living so close to the area that they could smell the oil as it approached the shore. George Hampson and Howard Sanders did some of the most important immediate work,

Sparse or absent marsh grass marks oiled areas of Wild Harbor one year after the spill. sampling benthic organisms right after the spill. They found that 95 percent of the benthic amphipods (small, bottom-dwelling crustacea important as fish food and in controlling bottom ecology) were killed in the heavily affected areas. They determined this by counting corpses, something that had to be done immediately, before the remains decomposed. With the resident amphipods gone, neighboring individuals moved into the area and were also killed by the oil. Fish, lobsters, crabs, annelid worms, and snails were all killed and washed up on beaches. Within days of the spill, the Falmouth shellfish warden, George Sousa, photographed shellfish beds with a striking pock-marked appearance where soft-shelled clams killed by the oil had decomposed in place. Sousa also observed that scallops in West Falmouth Harbor (where the oil slick did not enter) contacted sufficient oil in the water that they were anesthetized and became easy prey for fish.

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Shellfishing was closed over a distance of several kilometers that year, and for at least six years after the spill in Wild Harbor.

Sanders and his collaborators studied the spill's impacts for three years after it occurred. Following the death of the benthic organisms, opportunistic species of annelids (Capitellids) became the most abundant fauna. These small, red worms are animal "weeds" that can quickly

# Petroleum Chemistry

Petroleum and most of its "oil" products are composed of tens of thousands of related compounds. For purposes of discussing their fates and effects, most can be conveniently divided into four categories: alkanes, cycloalkanes, olefins (or alkenes) and cycloalkenes, and aromatics.

The simplest group are the **alkanes**, characterized by straight or branched chains of carbon atoms joined by single bonds. Chemists illustrate hydrocarbons by drawing the bonds between carbon atoms. Each carbon has four bonds, and if nothing else is shown, then all of the bonds not linked to another carbon atom have a hydrogen atom attached at that point. So, propane, an alkane with three carbon atoms, shown as

H - C = C - C - H

An **olefin** has at least one unsaturated bond, meaning that athe carbons are linked by a double or triple bond and there are fewer hydrogens in the molecule. Propene, an alkene corresponding to propane, is for HHH

H **Cycloalkanes** are alkanes that are joined to themselves to form five- and six-membered ring compounds. Cyclohexane has two hydrogens on every carbon: 
The corresponding olefin is cyclohexene:

Aromatic hydrocarbons are ring structures in which every other carbon-to-carbon bond is double. The simplest aromatic hydrocarbon is benzene with a six-carbon ring. Because of the special chemistry of aromatic rings, you cannot know just where the double bonds are, so they are usually drawn by putting a circle within the hexagon:

**Polynuclear aromatic hydrocarbons** or PAH are composed of a number of benzene rings, such as naphthalene with two benzene rings:

All of these classes of hydrocarbons can have side chains attached in place of some of the hydrogens, giving rise to compounds such as pristane, a common natural hydrocarbon found in nature:  $\downarrow \land \downarrow \land \downarrow \land \downarrow \land \downarrow \circ$  or 2,5 dimethyl naphthalene, a PAH in oil:

Alkanes are found in nature as waxes, secreted onto the surfaces of many organisms as a waterproofing. These waxes typically have an odd number of carbon atoms, usually from 21 to 31, and are common in marsh sediments. They are nontoxic, and readily degraded by microorganisms where oxygen is available. Cycloalkanes (especially large ones) are generally nontoxic, and degrade very slowly. White mineral oil that you buy at the store is composed mostly of large cycloalkanes. Olefins are not found in petroleum, although they are produced by the cracking process and occur in gasoline and light oils. Some are also made by organisms. They vary in toxicity.

Aromatic hydrocarbons are the most soluble and toxic components of oil (especially in the two- to threering sizes) and the ones that are carcinogenic and tetratogenic (especially in the four- to five-ring sizes). Aromatics are characteristic of petroleum, but are also produced by combustion in automobiles, industrial power plants, and all sorts of fires. Those produced in combustion tend to have few, if any, side chains, while those in petroleum may have many, giving one way of distinguishing the source of hydrocarbon contaminants.

Finally, there are other components of crude oil. For example, asphaltenes are very large molecules with little biological activity that are the principal component of road asphalt. There are molecules like those above that have an oxygen, nitrogen, or sulfur atom in them (therefore not strictly hydrocarbons), some of which are very toxic. The entire story is complex, and far from being completely understood.

exploit the opportunity offered by a disturbance that kills previously resident animals, such as a sewage outfall or periodic anoxia. They became extremely abundant for a few years, then declined as the local fauna gradually became more diverse and nearer to normal for the region. Further studies in 1973 and 1974 showed continuing recovery. At the fifth anniversary, the boat basin remained heavily contaminated, its fauna reduced in abundance and still dominated by opportunistic species.

It was initially easy to recognize the oil within the tissues of the marine organisms sampled, including some fish and herring gulls. But many animals are able to induce enzyme systems within their bodies, usually in their livers, that degrade the aromatic petroleum compounds. This was investigated in the mummichogs (marsh minnows) and fiddler crabs at Wild Harbor by Kathryn Burns and by John Stegeman (both at WHOI in the late 1970s; Burns is now at Bermuda Biological Station). Burns found that the fish rapidly developed an enzyme system: Fish sampled in 1974 had a much lower oil content than those sampled in 1970. The fiddler crabs, on the other hand, also induced an enzyme system, but to such a small extent that there was no reduction in oil body burden between 1970 and 1974. The level in the crabs probably represented the maximum concentration they could accumulate and still survive. Stegeman found that the Wild Harbor mummichogs continued to show high levels of these enzyme systems eight years after the spill.

The salt marsh grass, *Spartina*, was killed where it was coated with oil in 1969, along a band a few meters wide next to the tidal creeks. The oil penetrated as far as 70 centimeters into the intertidal muds, twice the depth to which oil was detected in the subtidal boat-basin sediments. The following year the oiled marsh was almost bare. Since the marsh was in a sheltered cove, the marsh mud was not washed away and recolonization by grasses and other marsh plants gradually took place.



Jack Cook/WHOI Graphics



Initial growth in the second summer was sparse but deep green in color, probably because of the high level of nutrients in the mud from the dead organisms and the lack of competition from neighboring plants. By the third summer, much of the marsh's grassy areas seemed to have recovered, although the most heavily oiled places (those containing more than 1 milligram of oil per gram of mud) were still almost bare. Eight years after the spill, a few bare areas still held 1 milligram of oil per gram of mud.

Fiddler crabs were affected in several ways besides the initial kill. Male crabs are highly territorial, so areas with lethal concentrations of oil acted as traps, killing the residents, which opened territories to neighboring individuals who moved in only to be killed in turn. The same thing happened to the subtidal benthic amphipods. In areas where there were lower-than-lethal doses of oil, the crabs were anesthetized, moved slowly, were unable to escape their predators, and were eaten. Finally, throughout the winter the crabs remain buried in the mud where, in this case, they were continually subjected to oil at the higher concentrations characteristic of the deeper sediment layers.

The West Falmouth oil degraded by losing the lighter compounds through evaporation, dissolution, decomposition, and, especially in the cases of the paraffins and olefins, by microbial decomposition. There are no resins or asphaltenes in light fuel oil. The heavier aromatic compounds are the longest lasting, especially in the deeper layers of the sediments where there is no oxygen to support microbial degradation. Analyses of the intertidal sediments in 1973 showed clearly the mixture of cycloalkane compounds in concentrations as high as 2 milligrams per gram. Analyses of the aromatic compounds in 1976 showed concentrations of 1.5 milligrams per gram still present in some surface areas, with most of the compounds having two rings and many side chains, or three rings with side chains, that is, they contained over 10 carbon atoms and were not very volatile or soluble in water. Traces of oil at some depths showed very little degradation beyond that which had occurred before the oil reached the marsh, while it was still in the slick.

All of these studies from the first few years after the spill showed that while there was considerable recovery, in heavily oiled fine sediments with deep penetration, the oil remained for years. Animals that fed on and burrowed into those sediments continued to be affected by the oil. The oil continued to degrade throughout the study period, but was still clearly recognizable—and toxic—in the anoxic sediments after seven years.

### The Spill Area 20 Years Later

We sampled the area after 20 years to see to whether the oil was still present, and if so, whether or not it had changed in composition (and therefore potential effect), and whether intertidal marsh sediments retained oil to a different extent than subtidal sediments. While there have been other oil spills in Buzzards Bay since 1969, fortunately none have entered the Wild Harbor area to confound the picture. We sampled marsh sediments in the most heavily oiled portion of the marsh (M-1—at lower right in the figure opposite), in a spot a few meters away (M-4) that was less heavily oiled than M-1, the most heavily oiled subtidal spot at the bottom of Wild Harbor (B-7), a lightly oiled subtidal site (B-5), and the original reference sites—Sippewissett Marsh and a subtidal site (B-1).

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John Farrington (left) and Bruce Tripp borrowed a nearby signpost to help retrieve a recalcitrant core during Wild Harbor sampling in 1989.

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Born and raised on the rolling plains of Nebraska, John M. Teal naturally went into oceanography as a profession. He has always maintained that the closest thing to the Nebraska landscape in general appearance is the rolling hills (swells) of the Sargasso Sea (except for the difference in wetness). He got into oil spills and their consequences by accidents too complex to describe here, and has since been able to continue to be considered an expert mostly by doing little in the field except for advising others. In keeping with his tradition in this field, almost all of the actual laboratory work on the Wild Harbor oil spill was done by those listed in the Acknowledgments.

Sediments were sampled by coring that was routine except at M-1. There, as water filled the hole once we had removed the core, we saw droplets rise to the surface, spread out, and show the rainbow sheen characteristic of an oil layer. Putting a hand into the hole and removing a bit of sediment produced the characteristic smell of fuel oil. Our laboratory analyses showed this was a remnant of the no. 2 fuel oil spilled 20 years before.

At the most heavily oiled marsh site, the oil was still present to a depth of 15 centimeters with a concentration of 1 part per million (dry weight basis) at the 15-centimeter depth from which we saw the oil droplets. At the deeper level, though the analyses showed more oil than in the control sample at that depth, we could not be sure it was oil from 1969. Our analyses showed that the oil has remained for at least 20 years in the most heavily oiled and protected intertidal sediments. A trace remains in the most heavily oiled subtidal sediments, but certainly most has gone. Subtidal mixing of sediments by weather and by animal activities, even in this protected site, must have been sufficient to release almost all of the oil into the water or oxidized sediments so it could be washed away or degraded. If the former, then it was diluted enough so that we could not detect it at the other subtidal sediment-sampling sites.

The question remained about whether the oil remaining in the marsh sediment could still be having an effect on the marsh ecosystem. Clearly there is still enough oil there that if it were released into the water en masse it would poison the resident animals. It seems not unlikely that there has been a release at some slow rate from the reservoir down in the mud, either by diffusion or by dissolution into water moving slowly through the sediments with the tides. There were crabs actively moving about on the surface of the undisturbed mud where we took the cores, and there were mussels in the mud adjacent to the hole. None were obviously being affected by oil. We sampled these animals, and fish and clams from the tidal creek about 1 meter away, to see if we could find hydrocarbons in their tissues in excess of that in animals collected from the reference marsh. We found a trace of oil in the Wild Harbor Marsh fiddler crabs, which burrow into the muds and feed on the mud surface. The mussels and fish from Wild Harbor were no more contaminated than specimens from the control marsh. The fish, however, did show an elevated level of the enzyme system that responds to oil contamination, which could be the result of contact with the remaining 1969 oil, but could also be a response to some other pollutant.

In summary, there is still some of the oil spilled in 1969 in the marsh sediments, though most of it (probably more than 99 percent) is gone, and virtually all is gone from the subtidal sediments. The marsh heavily damaged 20 years ago is now visually no different from other marshes in the area. There is still enough oil in a few local areas to kill animals that burrow into those sediments, but whether or not this happens would be very difficult to detect. Probably the only significant, although small, remaining danger would be if the still-contaminated marsh muds were to be disturbed sufficiently to release the trapped oil. Nature does clean itself up after an oil spill, though it can take a couple of decades.

We can't pretend to have all the answers, but this recent work indicates that some of our more extreme fears at the time of the spill were not well founded. The immediate catastrophe of an oil spill is worse than the long-term effects.

# Bacteria & Bioremediation of Marine Oil Spills

VIRTUALLY ALL MARINE ECOSYSTEMS harbor indigenous hydrocarbon-degrading bacteria. These hydrocarbon degraders comprise less than one percent of the bacterial community in unpolluted environments, but generally increase to one to ten percent following petroleum contamination. Various hydrocarbons are degraded by these microorganisms at different rates, so there is an evolution in the residual hydrocarbon mixture, and some hydrocarbons and asphaltic petroleum hydrocarbons remain undegraded. Fortunately, these persistent petroleum pollutants are, for the most part, insoluble or are bound to solids; hence they are not biologically available and therefore not toxic to marine organisms. Carbon dioxide, water, and cellular biomass produced by the microorganisms from the degradable hydrocarbons may be consumed by detrital feeders and comprise the end products of the natural biological degradation process.

Bioremediation attempts to accelerate the natural hydrocarbon degradation rates by overcoming factors that limit bacterial hydrocarbon degrading activities. Many commercial inocula have been developed to "seed" oil spills, in an attempt to augment the capabilities of the indigenous microorganisms. Seed inocula have yet to be proven beneficial in field applications, although laboratory testing and evaluation by the National Environmental Technology Assessment Corporation (NETAC), supported by the US Environmental Protection Agency, have identified both potentially beneficial and ineffective products.

While seeding may someday be useful, current bioremediation treatments of oil spills rely upon adding fertilizers to support the growth of indigenous hydrocarbon-degrading microorganisms. The *Exxon Valdez* oil spill formed the basis for a major bioremediation study. In the largest application of this emerging technology to date, bioremediation augmented other cleanup procedures. Application of the oleophilic fertilizer Inipol EAP 22 produced dramatic results in test plots: The surfaces of oil-blackened rocks on the shoreline turned white and were essentially oil-free within 10 days of treatment.

The striking visual results strongly supported the idea that oil degradation in Prince William Sound was limited by the amounts of available nutrients, and that fertilizer application was a useful bioremediation strategy. Both Inipol and a slow-release fertilizer were approved for shoreline treatment, and their use comprised a major part of the cleanup effort. Bioremediation became the major method for shoreline cleanup following initial physical washing, which had left oil, particularly subsurface oil, still contaminating the shorelines.

Monitoring tests demonstrated no adverse ecological effects from bioremediation, confirming toxicity testing that had established the safety of the amounts of fertilizer applied. Field monitoring also showed that fertilizer application sustained higher numbers of oil-degrading microorganisms in oiled shorelines. Rates of biodegradation were enhanced, as evidenced by the chemical changes detected in recovered oil from treated and untreated reference sites.

Proving the efficacy of bioremediation in these monitoring efforts was difficult due to the patchiness of the oil distribution. The branched hydrocarbons pristane and phytane, which are often used as internal standards, were rapidly degraded by the indigenous bacteria of Prince William Sound: these bacteria probably were adapted to the biodegradation of terpenes, which are structurally similar to pristane and phytane and occur naturally in Prince William Sound from the surrounding pine forests. It was necessary to use hopane, a compound resistant to biodegradation, as an internal standard along with multivariate statistical analyses in order to prove that biodegradation was effective. It appears that the fertilizer application enhanced the natural rate of hydrocarbon degradation by about five times.

#### -Ronald M. Atlas,

Professor of Biology at the University of Louisville, and consultant to Exxon and the US Environmental Protection Agency on bioremediation of the Alaska oil spill

# OIL SPILL MODELING...

**RECENT EVENTS HAVE LED to a new public** interest in oil spill modeling. Large spills, including Exxon Valdez, the Persian Gulf spill, the Shetland Islands spill by the oil tanker Braer, and the passage of the comprehensive Oil Pollution Act of 1990 have brought oil spill issues into mainstream thought. The Oil Pollution Act specifies that all oil-industry facilities must have oil-spill contingency plans, including fixed facilities such as refineries and transport vessels such as ships and barges. Spill models are used primarily in oil spill contingency planning, spill response, and as a basis for impact or natural-resource damage assessment following a spill. In spill contingency applications, the model is used to identify which resources are at risk if a spill should occur, and to evaluate the effectiveness of proposed response plans. The latter usually include cleanup equipment selection, positioning, and deployment strategies. For spill-response activities, the model



This model predicted the trajectory for an oil spill in upper Prince William Sound. Cleanup resources are denoted by various icons.

forecasts the transport and fate of spilled oil to provide information useful in directing and optimizing cleanup equipment use. Oil spill models, integrated with impact models or natural resource damage assessment models, are increasingly used in post-spill investigations to evaluate impacts or damages. Impact assessments vary from models of oil hitting a static resource (such as a habitat or a bird nesting area) to complex ecological and economic modeling for evaluating present and future losses of fish, birds, and wildlife, and associated economic losses.

Spill models are normally constructed by linking mathematical formulations to represent oil transport and fate processes. Fate processes of primary interest include spreading, evaporation, entrainment (oil dispersion into the water column), emulsification (incorporation of water into the surface oil), and oil-shoreline and oil-ice interactions. The transport calculation (or trajectory) determines the oil movement in space and time. The fate portion of the model estimates the oil transport between various environmental compartments; for example, evaporation is oil transport from the sea surface into the atmosphere. Most models use a mass balance approach to track the amount of oil in each compartment (sea surface, atmosphere, water column, stranded on shoreline, decayed in ice, and on the seabed). The more sophisticated models allow us to describe the oil mass balance based on subsections of the distillation or boiling-point curve, which allows accurate tracking of the oil's toxic, volatile, aromatic fraction.

Models are typically run in one of three modes: forecast/hindcast, statistical, or receptor. In the forecast/hindcast mode, the model predicts the trajectory and fate for a specified spill scenario (release location, oil discharge rate, duration, oil type, and start date). Environmental data, such as currents and winds, are included in the model data base, are user specified, or are provided by real-time observations. This information can be derived from climatology, historical observations, or data that assimilates hydrodynamic and meteorological models. Stochastic mode simulations statistically vary the current and wind data. These models provide the probability contours for oil affecting openwater areas, shorelines, or biological, socioeconomic, or other resources at risk. Receptor mode simulations are like stochastic mode simulations,

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### ... In the Field and In the Laboratory

except they run backward in time. These calculations identify spill areas from which a particular resource is vulnerable. Predictions are normally given in the form of probability contours and minimum travel times that specify how likely it is that spills at different sites will affect specific resources. The forecast/hindcast mode is typically used for spill response, spill exercises, and hindcast of specific events. Stochastic and receptor mode simulations are primarily used in spill contingency planning and risk analysis.

The most advanced spill models operate on portable computers and use a "shell-based" structure. The shell consists of the modeling software and user interface, which remains common for all applications. The user can readily switch from one operational area to another by simply selecting the appropriate location database, which includes information on the shoreline location and type, wind data, and currents. An embedded geographic information system (GIS) is usually available to organize and manipulate data. Software tools are also available to allow the user to access externally prepared GIS data, overflight information, real-time wind and current measurements or model results, biological resources at risk, cleanup equipment type, location, and status, and other relevant data. The models employ extremely user-friendly interfaces, operate quickly and effectively in a standalone mode in the field, and use clear, concise color graphics for data entry and displaying model output. Hard copy or digital output is readily available. Through the use of sophisticated data-management techniques and software design, worldwide modeling capabilities are available on personal computer platforms. Model setup, simulation, and prediction distribution can typically be completed within 30 minutes of spill notification.

Models are routinely used in responding to all major spills. They provide critical information to help the on-site coordinator direct the response equipment and personnel. Verification efforts have shown that model predictions give a good representation of spill movement and weathering, provided that accurate information is available on the oil release and the environmental conditions (winds, waves, and currents). Spill models will become increasingly sophisticated with the development of improved fate algorithms, incorporation of information from data assimilating hydrodynamic and meteorological models, and direct electronic linkages to



This input screen allows a modeller to specify wind data as input to a spill model.

real-time observing systems. Basic spill models are being extended to include atmospheric, impact-assessment, and natural-resource damageassessment components, as well as more comprehensive geographically referenced environmental data. The long-term goal is to evolve spill models into decision-support systems that employ artificial intelligence techniques to optimize spill response and minimize spill environmental impact.

Malcolm Spaulding is Professor and Chair of Ocean Engineering at the University of Rhode Island. His primary research interests are predicting the transport and fate of pollutants in estuarine and coastal environments and computational fluid dynamics. He has been actively involved in oil spill modeling for the last 20 years, and is struggling to make model forecasts as accurate as hindcasts.