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The West Falmouth Oil Spill: ~100 Kg of Oil Found to Persist Decades Later

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In order to investigate the long-term fate of petroleum hydrocarbons in salt marsh sediments in Wild Harbor (West Falmouth, MA) impacted by the *Florida* spill of 1969, 26 sediment cores were collected and analyzed for total petroleum hydrocarbons (TPH). The results from this effort indicate that the distribution of petroleum hydrocarbons is spatially heterogeneous, oil compounds are generally located at sediment depths of 4 to 20 cm in areas closest to the banks of the marsh, and ~100 kg of petroleum residues can be found to persist in intertidal sediments that were originally the most impacted.

Keywords: *Florida* spill, West Falmouth, No. 2 fuel oil, petroleum hydrocarbons, sediments

Introduction

For the past three decades, the West Falmouth oil spill has influenced and shaped our understanding of post-spill environmental impacts and developed the science of oil spill research in the marine environment (Blumer et al., 1970, 1971; Blumer and Sass, 1972a, 1972b; Burns and Teal, 1979; Frysinger et al., 2003; Hampson and Sanders, 1969; Krebs and Burns, 1977; Reddy, 2004; Reddy et al., 2002; Sanders et al., 1980; Slater et al., 2005, Teal et al., 1978, 1992; White, Reddy, et al., 2005). This spill occurred when the barge *Florida* went aground near West Falmouth, Massachusetts, and released ~700,000 l of No. 2 fuel oil into Buzzards Bay on September 16, 1969 (Figure 1). Immediately after the spill, scientists at Woods Hole Oceanographic Institution began to analyze samples from impacted sediments and biota using state-of-the-art analytical technology, mainly packed-column gas chromatography (Blumer et al., 1970). These analyses revealed that petroleum hydrocarbons could be acted upon by a series of weathering processes including evaporation, water-washing, and microbial degradation but also could persist for at least several years in salt marsh sediments (Blumer et al., 1972b).

The environmental fate of the spilled oil was intensively studied for the first seven years after the spill (Blumer et al., 1970, 1971; Blumer and Sass, 1972a, 1972b; Burns, 1975; Burns and Teal, 1979; Michael et al., 1975; Teal et al., 1978) and then some sites were revisited 20 (Teal et al., 1992) and 30 years (Frysinger et al., 2003; Reddy et al., 2002) later. All of these studies demonstrated that petroleum hydrocarbons did persist for many years in the intertidal salt marsh sediments of Wild Harbor (Figure 1), where no human intervention or cleanup was done after the spill except for water-based emulsifiers applied immediately after the spill. While investigating intertidal marsh sediments collected in 2000 at the M-1 site in Wild Harbor (Figure 1), Reddy et al. (2002) were also able to provide a highly refined inventory of existing petroleum hydrocarbons using comprehensive two-dimensional gas chromatography (GC × GC). This novel technology showed that after three decades of exposure to *in situ* degradative processes, only the *n*-alkanes were completely degraded. However, despite some degradation, all other compound classes typical of No. 2 fuel oil could still be identified in the sediments at this site (Reddy et al., 2002). Because of the potential fears associated with the long-term hazards of petroleum hydrocarbons in the marine environment, the latter results attracted attention by the mainstream media and comment by the scientific community. Owens (2003) criticized this work (Reddy et al., 2002) by stating that only one location (M-1) from the whole impacted area was investigated and that likely much of the original cargo had dissipated. Reddy et al. (2003) responded to Owens's comments by stating that their study was originally focused on only sediments at the M-1 site because it was one of the most studied and contaminated sites. Nevertheless, Owens was correct that additional sediment cores from a wider area would need to be collected and analyzed before drawing conclusions about the long-term fate of the total amount of petroleum released from this spill.
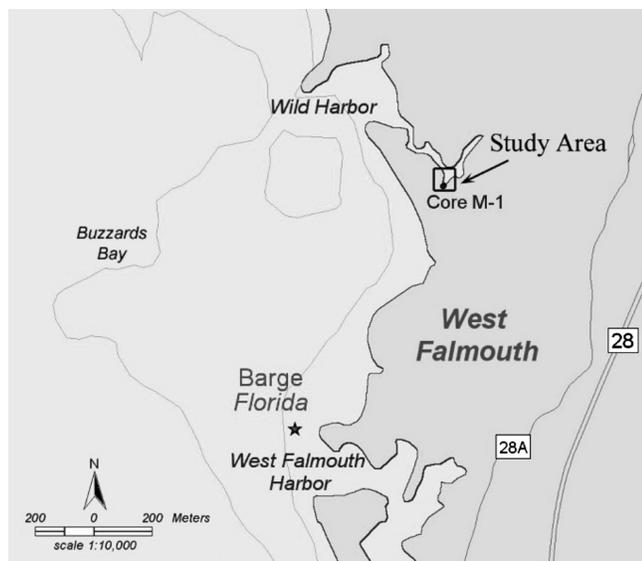
Figure 1. Map of general area near the grounding of the *Florida*.

To address Owens's comments as well as to continue to study this oil spill, we surveyed Wild Harbor marsh sediments for petroleum hydrocarbons. Twenty-six cores from intertidal marsh sediments on the west and east sides of the Wild Harbor River were collected and analyzed for petroleum hydrocarbons (Figure 2). These analytical results were evaluated horizontally and vertically in order to characterize the spatial distribution of remaining petroleum in the impacted marsh sediments. The
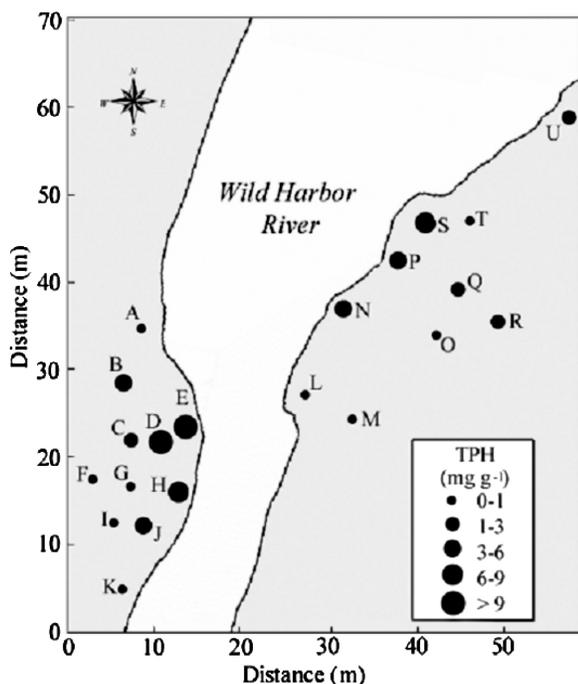

Figure 2. Map of the study area. Marker size represents the maximum TPH content (mg g^{-1}) found at each sample location, which was generally at 12–16 cm. All of the core locations are within the intertidal zone.

data were then analyzed using two independent models aimed at quantifying the volume of petroleum remaining in these sediments. Finally, these results were compared to the volume of petroleum released during the spill in order to estimate what percentage of petroleum originally released persists in these impacted sediments.

Methods

Sediment Collection

From November 2002 to March 2004, 26 sediment cores were collected from intertidal Wild Harbor marsh sediments. Methods for collecting and splitting sediment cores from this marsh have been discussed previously (Reddy et al., 2002). Briefly, a 9.5-cm diameter PVC tube was pushed into the sediments. The area around the tube was cleared with a shovel and then the tube was removed and capped. The core was returned immediately to the laboratory and frozen at $-40°$ C. After a brief thaw, the core was extruded at 4-cm intervals from 0–4 to originally 44–48 cm. (However after analyzing several of the first cores collected and finding that oil was usually limited to depths of 0 to 24 cm, we then only analyzed sections in the 0–4 to 20–24 cm horizons.) The outer one centimeter of each core was discarded in order to avoid cross-contamination. Each sample was placed in precombusted glass jars with Teflon-lined caps and frozen until analysis.

Total Petroleum Hydrocarbons (TPH) Analysis

Three to nine grams of air-dried sediment were spiked with 40 μg of hexatriacontane (n-C$_{36}$) and extracted with a 9:1 dichloromethane (DCM):methanol mixture by pressurized fluid extraction (100°C, 1000 psi). Extracts were reduced in volume, solvent exchanged into hexane, and charged onto a glass column (9 cm $\times$ 0.4 cm) packed with fully activated silica gel (100–200 mesh). The column was eluted with 12 ml of a 3:1 mixture of hexane: DCM. The extract was then treated with activated copper to remove elemental sulfur and dried with sodium sulfate. Finally, the extract was spiked with stearyl palmitate (40 μg) and analyzed on a Hewlett-Packard 6890 Series gas chromatograph with a cooled injection system (CIS) and interfaced to both a Hewlett Packard 5973 mass spectrometer and flame ionization detector (FID). A 1-μL sample was injected splitless into the CIS, which was temperature programmed from 40 (0.1-min hold) to 350°C at 720° min^{-1} (8 min hold). Compounds were separated on a glass capillary column (J&W DB-5MS, 60 m, 0.32-mm i.d., 0.25-μm film thickness) with He as the carrier gas at a constant flow of 1.5 mL min^{-1}. The GC oven temperature was programmed from 40 (1-min hold) to 80°C at 20° min^{-1} and then from 120 to 320°C at 5° min^{-1} (10-min hold). The TPH were quantified by integrating the total FID area of the unresolved complex mixture (UCM) and using response factors determined from No. 2 fuel oil standards. The carbon range of the UCM was variable but always existed between decane (n-C$_{10}$) and hexacosane (n-C$_{26}$), which excludes

most of the larger, biogenic hydrocarbons. Because a subsample of the original *Florida* cargo oil is no longer available, we used the Marine Ecosystem Research Laboratory (MERL) No. 2 fuel oil as a calibration standard (Reddy et al., 2002). We believe that the uncertainty of using a fresh oil as a calibration standard for a weathered oil is minimal, as an FID is based on the mass of carbon combusted, which should be relatively insensitive to the chemical nature of hydrocarbons (Reddy and Quinn, 1999). In addition, we assume that most, if not all, of the hydrocarbons in our operationally defined term for TPH is from the *Florida* spill. Laboratory blanks of combusted sand were free of petroleum compounds. Recoveries of No. 2 fuel oil spiked into combusted sand and analyzed were 70 to 115% with an average of 95%. Precision, based on the preparation and analysis of four duplicate pairs of samples, ranged from +0.1 to 10%. Our estimated method detection limit is 0.015 mg of TPH per gram of dry sediment (Reddy et al., 2002).

Results and Discussion

Overall of Results

To determine the extent and distribution of TPH in Wild Harbor, we chose to study the boxed area in Figure 1, which is magnified in Figure 2. All of the cores were collected in the intertidal regions of the marsh. We chose to investigate this area in Wild Harbor based on historical results (Teal et al., 1992) and unpublished work from our laboratory, which showed that only sediments from intertidal, and not subtidal, areas has detectable petroleum hydrocarbons. As the study continued over more than a year, additional core locations were selected for analysis based on our available data. It was found early in this survey that the TPH content in marsh sediments farther from the Wild Harbor River channel were minimal so more emphasis was placed on areas nearest to the shoreline. Because of the sporadic distribution of the contamination, it is possible that some contaminated pockets of the marsh were missed. However, based on 30 years of historical data and all of the new data from numerous stations that had not been previously sampled, we believe all of the hot spots have been included in this study. In total, ~150 sediment samples were analyzed from 26 sediment cores. (Please note that only data for 22 cores are shown in Figure 2. The four other cores were outside the study area shown in Figure 2 and contained very little or no TPH). In terms of TPH content, the values vary widely between locations and had a UCM eluting in the range of n-C_{10} and n-C_{26}, which is typical of partially weathered No. 2 fuel oil. Core F (Figure 2) had no detectable TPH (i.e., no detectable oil residues). Thirteen cores contained sediments with TPH concentrations greater than 1 mg per gram of dry sediment (mg g^{-1}). Of those, six sediment cores had maximum TPH values ranging from 1 to 4 mg g^{-1} and the remaining seven sediment cores had TPH values that ranged from 4.6 to 14.1 mg g^{-1}. Core H, which was collected in the same vicinity of the historical sampling site M-1, had a very similar TPH content as a core collected at M-1 in August 2000 (Reddy et al., 2002).

Spatial Trends

Spatially throughout the marsh on the west side of the river, sediments from cores in closer proximity to the water contained higher TPH concentrations than the sediments obtained from cores farther from shore (Figure 2). For example, sediments from core G contained TPH concentrations about an order of magnitude less than sediments from core H, while sediments from core F had no detectable TPH (Figure 2). This difference in TPH content at three sites occurs over a short distance of only 10 meters indicating that oil contamination has not spread laterally since the spill. The best supporting evidence for this conclusion are photographs of the marsh taken immediately after the spill. The photos reveal that a 2-wide band of oil had sorbed to the intertidal marsh sediments closest to the banks of the river. Hence, areas that were the most contaminated shortly after the spill continue to be the most impacted three decades later. On the east side of the river, a similar trend was observed. Cores N, P, Q, T, and S outline a localized hot spot with higher TPH values in sediments collected closest to the channel. In this area, which had not been previously sampled, there is a visible depression in the marsh surface. Assuming this depression existed at the time of the spill, finding elevated TPH concentrations in these sediments is consistent with the hypothesis that the horizontal distribution of sedimentary TPH concentrations is related to the original deposition of oil in this area.

Vertical Trends

Vertically, the maximum TPH value for each sediment core was consistently between 4 and 20 cm below the surface (see Figure 3 to view four down-core profiles) and most frequently observed in the 8–12 or 12–16 cm horizons. These depths are reasonably consistent with the timing of the spill (1969) and an estimated sedimentation rate of 0.35 cm yr^{-1} (White, Reddy et al., 2005). The concentrations of TPH that were found in sediments above (i.e., in surface 0 to 4 cm) and below (20–24 cm) the mid-core maximums were relatively minimal. Several of the initial cores were analyzed to a depth of 48 cm, and no oil was detected below 20 cm. The analysis of subsequent cores was then limited to a depth of 24 cm, despite the presence of oil in the 20–24 cm horizon in some samples. The maximum depth of detectable TPH varied, which could be attributed to either a difference in marsh conditions or compaction of sediments during sampling. The shape of the UCM and the presence of resolved peaks on the UCM hump (Figure 4) varied substantially with depth between cores, suggesting a depth-dependent variance in the nature of the petroleum hydrocarbons in these sediments. Preliminary GC-MS and GC $\times$ GC analysis of some samples indicate that the composition of the UCM differs as depicted by the shape of the UCM hump, thus supporting our hypothesis. Mechanistically, we believe the latter results from post-depositional movement of oil compounds based on their different abilities to partition between the pore water and sediment organic matter, a hypothesis that is evaluated and discussed elsewhere (White, Xu et al., 2005).
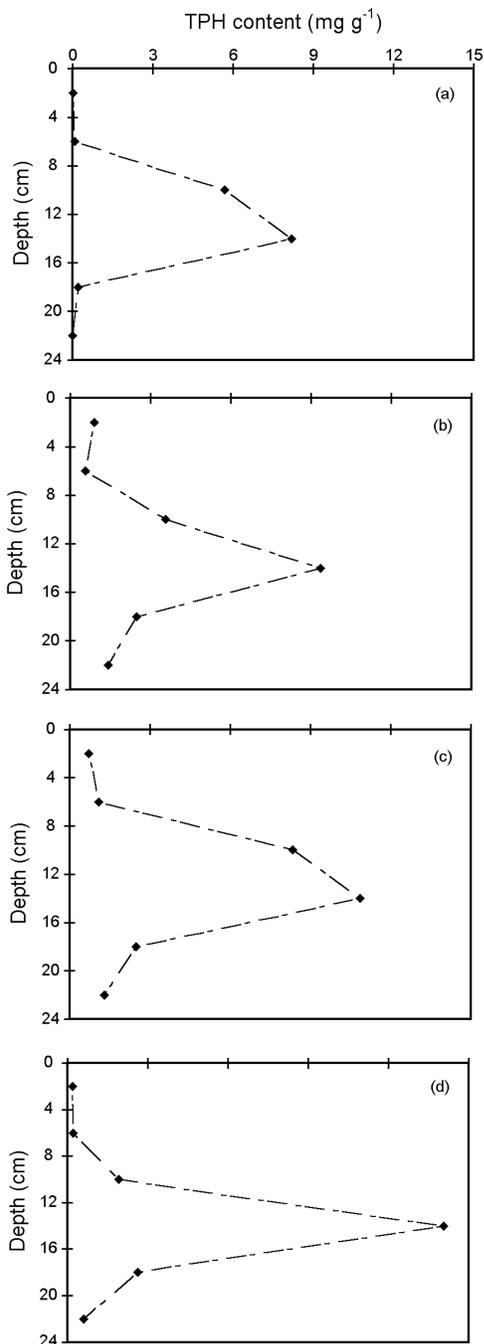
Figure 3. Typical down-core concentration profiles of TPH at Wild Harbor from locations denoted in Figure 2 as: (a) Core H, (b) Core S, (c) Core E, and (d) Core D.

Estimating the Total Oil Remaining in the Marsh

The main objective in this study was to estimate the total amount of oil remaining in the east and west sides of the marsh. To accomplish this task, the total amount of oil (identified as TPH) present in each side of the channel was volumetrically integrated. In order to account for the low statistical power caused by a less than ideal number of cores collected from the study area, two independent approaches were developed and used to estimate
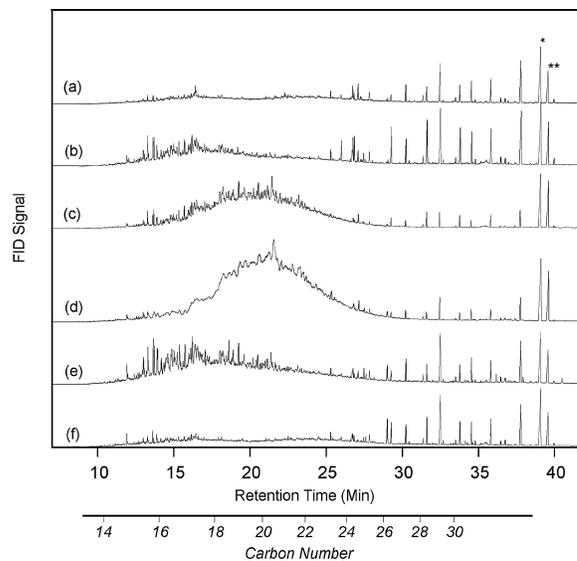

Figure 4. GC-FID chromatograms of Wild Harbor marsh sediment extracts from Core E: (a) 0–4 cm, (b) 4–8 cm, (c) 8–12 cm, (d) 12–16 cm, (e) 16–20 cm, and (f) 20–24 cm. The peaks annotated with * and ** are standards. Besides the standards, compounds eluting after n-C_{26} are biogenic hydrocarbons (see Reddy et al., 2002).

this value (Davis, 2002). Our reasoning is that by using independent lines of evidence to arrive at the same objective, if these two values are similar, we obtain a higher degree of confidence in the calculated volume of petroleum remaining in these marsh sediments.

The first approach involved the use of a grid and three-dimensional interpolation to calculate the volumes. First, all of the data from the cores were entered into a three-dimensional grid, which considered an area created by a multisided polygon of the outer perimeter of the cores. Pixel sizes in the grid were approximately 1m × 1m in the horizontal dimension and 0.02 m in the vertical. A three-dimensional, isotropic, linear interpolation algorithm (MATLAB, The Mathworks, Inc.) calculated the oil content at each point in the grid that did not have core data. These data were then integrated volumetrically to produce an estimate of 22 kg of TPH still present in the intertidal sediments on the east side and 15 kg of TPH remaining in the intertidal sediments on the west side for the areas sampled. Unfortunately, this method does not allow a means to confidently predict uncertainty.

The second approach involves a statistical method that incorporates our data set and allows for estimating the total oil remaining and the uncertainty involved. First, the TPH content throughout each sediment core was integrated over a 24-cm depth (Figure 5). We then assumed that the TPH (or oil) content in each core was homogeneous within one square meter, which we call $Y(x)$ where x is the two-dimensional location of each core. The total amount of material contained within our study region R, the boxed regions in Figure 5, is:

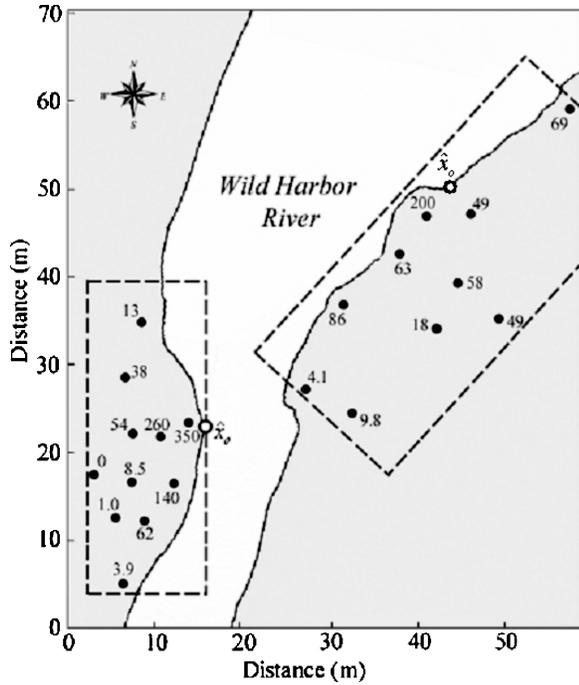$$Y_R = \int_R Y(x)\, dx \qquad (1)$$

Figure 5. Map of the study area with the TPH content (g m^{-2}) listed for each sample location. This was accomplished by integrating the total oil found in each core from 0 to 24 cm depth of each sample. Hence, Core E (see Figure 2) was estimated to have 350 g of TPH per m^2 in the top 24 cm.

Interest centers on estimating Y_R from concentrations $Y_1, Y_2, \ldots, Y_n$ measured at sample locations $x_1, x_2, \ldots, x_n$.

To estimate Y_R efficiently and particularly to give some measure of uncertainty about it, we will assume that $Y(x)$ has an ln normal distribution with parameters $\mu(x)$ and σ^2. These parameters represent the mean and variance of log $Y(x)$. The corresponding mean and variance of $Y(x)$ are:

$$\beta(x) = \exp\left(\mu(x) + \frac{\sigma^2}{2}\right) \tag{2}$$

and:

$$\tau^2(x) = (\exp \sigma^2 - 1) \exp[2\mu(x) + \sigma^2] \tag{3}$$

It follows that an estimate of Y_R is given by:

$$\hat{Y}_R = \int_R \exp\left(\hat{\mu}(x) + \frac{\hat{\sigma}^2}{2}\right) dx \tag{4}$$

where $\hat{\mu}(x)$ and $\hat{\sigma}^2$ are estimates of $\mu(x)$ and σ^2, respectively.

To estimate $\mu(x)$ and σ^2, we will assume that:

$$\mu(x) = \mu_o + \mu_1 |x - x_o| \tag{5}$$

where μ_o and μ_1 are unknown parameters and $|x - x_o|$ is the distance between location x and an unknown location x_o. Under this model, which was chosen on the basis of some preliminary analysis of the data, mean ln TPH content declines linearly—and mean TPH content declines exponentially—with distance from the location x_o (Figures 5 and 6). The model can be written as:

$$\log Y(x) = \mu_o + \mu_1 |x - x_o| + \varepsilon(x) \tag{6}$$

where $\varepsilon(x)$ is a normal error with mean 0 and unknown variance σ^2. For fixed x_o, this model can be fit by simple linear regression. Let $\hat{\mu}_o(x_o)$ and $\hat{\mu}_1(x_o)$ be the corresponding regression estimates of μ_o and μ_1, respectively, and let $RSS(x_o)$ be the corresponding residual sum of squares. The final estimate $\hat{x}_o$ is the value of x_o that minimizes $RSS(x_o)$ and the final estimates of μ_o, μ_1, and σ^2 are $\mu_o(\hat{x}_o)$, $\mu_1(\hat{x}_o)$, and $RSS(\hat{x}_o)/(n-2)$, respectively. It is possible to go beyond point estimation of Y_R to provide a measure of uncertainty. Specifically, provided the scale of any
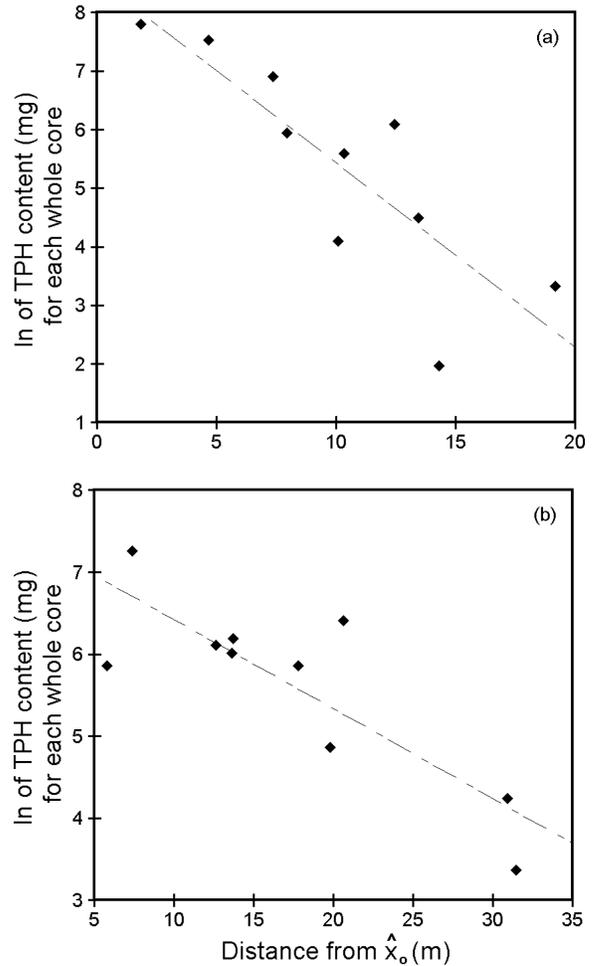

Figure 6. Plot of the ln of TPH mass (mg) in each sediment core versus distance from $\hat{x}_o$: (a) west side and (b) east side of Wild Harbor marsh. The TPH content in each core was calculated by multiplying the area of each core barrel (0.0708 m^2) by the values shown in Figure 5 and converting to mg.

spatial correlation in TPH content is small compared to the scale of R:

$$Var\ Y_R \cong \int_R \tau^2(x)\,dx \qquad (7)$$

where $\tau^2(x)$ is given in (3). An estimate $\hat{V}ar\ Y_R$ of the variance in (7) can be found by replacing μ_o, μ_1, and σ^2 in the expression for $\tau^2(x)$ by their corresponding estimates.

The statistical method described above estimated that there is 52 and 45 kg of oil (as TPH) that can be found in the sediments on the east and west sides, respectively, for the study region R. The uncertainties for the east and west sides were very good and were +2 and 6 kg, respectively. The location of $\hat{x}_o$ is depicted in Figure 5. Shown in Figure 6 is the fit of the model for the two data sets. These two independent approaches for estimating the mass of oil (as TPH) remaining in these marsh sediments give values that are within the same order of magnitude. However, the statistical model yielded estimates that were approximately three times larger than the linear interpolation approach. One factor for this discrepancy was the study region for the statistical model was ∼200% larger than the linear interpolation approach because the former required a simple rectangular study area whereas the latter used a multi-sided polygon that enclosed and only considered the area within the core locations. Hence, the linear interpolation approach assumed a zero TPH content beyond the outer perimeter of the polygon. Nevertheless, both results reveal that a small fraction of oil can be found compared to the original 595,000 kg of original product that spilled in Buzzards Bay. (This mass was calculated by using a specific gravity of 0.85 and volume of 700,000 l).

Fate of Oil in Wild Harbor Since the Spill

For further discussion, we have chosen to use the larger estimate from the statistical model because it provided an uncertainty and because some oil in the sediment may have been missed in our field sampling. Hence, less than 0.02% of the total original cargo that was spilled (∼100 kg for both sides) was found in the intertidal sediments of Wild Harbor. It is important to note that the amount of oil that initially entered Wild Harbor is not known and a significant amount of the original product likely evaporated or was transported offshore within the first few weeks of the spill (Reddy and Quinn, 2001). For example, ∼20, ∼30, and ∼50% of product evaporated days to months following spills of the *Exxon Valdez* (Wolfe et al., 1994), *Amoco Cadiz* (Gunlach et al., 1983), and *Jessica* (Kingston, 2002), respectively. In May 1970, eight months after the spill, an estimated four tons of oil still remained in Wild Harbor (Blumer et al., 1971). Although it is unclear how this value was calculated, only about 3% of that is remaining; it is difficult to accurately account for all of these losses. The majority of oil was probably lost in the subtidal sediments, which were originally heavily oiled but are now relatively free of residues from this spill. However, some of the petroleum hydrocarbons

were also removed in the intertidal sediments and evidence of this can be observed in traditional one-dimensional packed-column GC-FID chromatograms of sediment extracts from the early to mid 1970s (Burns, 1975; Burns and Teal, 1979). These chromatograms document the loss of lower molecular weight compounds, presumably from water washing/evaporation, and resolved compounds from biodegradation. By assuming that each compound in these chromatograms has a similar FID response and comparing the vintage GC chromatograms to recent GC chromatograms, we estimate that ∼20 and ∼10% of the mass of hydrocarbons in the intertidal sediments were removed due to water-washing/evaporation and biodegradation, respectively, since 1970. Despite this large estimated decrease since 1970, concentrations of petroleum hydrocarbons in leftover hot spots in intertidal sediments, such as M-1, are similar to values detected in the mid 1970s (although analytical methods may cause slight differences) and suggest that the most oiled locations have persisted the most. This is consistent with our work at M-1, where we believe that the removal of phytane and potentially other saturated, branched compounds has not significantly advanced in the last two decades (Reddy et al., 2002). Obviously, these results also need to revolve around the subjects of scale and recovery. Only a small amount of oil exists in a small area but at high concentrations. Most of Wild Harbor and Buzzards Bay does not contain any oil residues from the *Florida* spill. Blumer et al. (1971) showed that ∼8 km² of Buzzards Bay was initially oiled after the *Florida* grounding. Our recent study indicates that ∼0.001 km² of salt marsh (Figure 2) have detectable residues three decades later, which corresponds to 0.01% of the original area impacted. Visually, the marsh appears quite healthy, but studies are now underway to determine whether any plants or animals continue to be affected.

Why Do Petroleum Residues Continue to Persist in Wild Harbor?

While other types of shorelines can retain petroleum residues for several years after a particular oil spill (Hayes and Michel, 1999), numerous studies and reviews have revealed that marshes are the most capable of long-term oil preservation (Kingston, 2002; Table 1). For example, Baker (1999) compared numerous spills and different shorelines; she illustrated that sheltered salt marshes, including Wild Harbor, have the longest recovery times after an oil spill. Consider Winsor Cove marsh sediments, which are just 4 km away from Wild Harbor and were contaminated in 1974 when the *Bouchard 65* spilled an undetermined amount of No. 2 fuel oil. Recent analysis of Winsor Cove shows persistent contamination, with most of the oil residing in the top 3 cm (Reddy, 2004). Crude oil spilled by the *Amoco Cadiz* on March 16, 1978, was found in the Ile Grande salt marsh in France after 13 years. The levels there were generally low, with localized areas of higher amounts of weathered oil, also an attribute of the remaining oil in Wild Harbor (Mille et al., 1998). Long-term studies of the sheltered lagoon, Black Duck cove in Chedabucto Bay, Nova Scotia, where the tanker *Arrow* spilled

Table 1. *Examples of oil spills with petroleum residues persisting for more than 5 years*

Name of vessel	Date of spill	Location	Type of coastline	Type of oil	Size of spill	What is left
Florida	September 1969	Buzzards Bay, Massachusetts	Salt marsh	No. 2 fuel oil	700,000 l	After 30 years, TPH values are similar to values observed in mid 1970s (Reddy et al., 2002). Only *n*-alkanes completely degraded (Frysinger et al., 2003).
Arrow	February 1970	Chedabucto Bay, Nova Scotia, Canada	Beach with sand and cobbles	Bunker C	2 million l	After 22 years, *n*-alkanes were mostly lost, and target PAHs were degraded. Triterpanes and steranes remain (Wang et al., 1994).
Metula	August 1974	Straight of Magellan, Chile	Marsh and beach	Light Arabian Crude	50,000,000 l light Arabian Crude and 2,000,000 l Bunker C	After 24 years, lightly weathered oil in one marsh and heavily weathered in one marsh and one beach, with most compounds including biomarkers showing some degradation (Wang et al., 2001).
Bouchard 65	October 1974	Buzzards Bay, Massachusetts	Salt marsh	No. 2 fuel oil	42,000–140,000 l	After 30 years, partially weathered diesel fuel remains with moderate biodegradation (Reddy, 2004)
Amoco Cadiz	March 1978	Ile Grande Salt Marsh, North Coast of Brittany, France	Salt marsh, Rocky and sandy beaches	Crude, Iranian, and Arabian light	223 million l	After 13 years, hydrocarbon levels were generally low, with localized areas of highly weathered oil in the marsh. Biomarkers remain (terpanes, steranes, and diasteranes) (Mille et al., 1998).
Ruptured storage tank	April 1986	East Coast of Panama, near Galeta	Mangroves, seagrasses, and coral reefs	Medium-weight crude oil	12–16 million l	Exposed oil weathered rapidly, while oil protected under sediments retained most compounds after 5 years (Burns et al., 1994).
Exxon Valdez	March 1989	Prince William Sound, Alaska	Wide variety of beaches	Alaskan North Slope Crude oil	42 million l	Boulders and cobbles continue to protect oil in the intertidal zone, inhibiting disturbance and weathering (Hayes and Michel, 1999).

Bunker C oil in 1976, found petroleum hydrocarbons at various stages of degradation after 20 and 30 years (Lee et al., 2003; Vandermeulen and Singh, 1994). A study done 22 years after the *Arrow* spill found that biomarker compounds at this location persist while other classes of compounds are at least partially degraded (Wang et al., 1994). Weathered forms of light Arabian Crude oil spilled into the Straight of Magellan from the tanker *Metula* remain after 24 years in some protected marshes and on one beach, while much of the coastline has been cleaned by natural processes of the harsh climate (Wang et al., 2001). Mangroves have also been found to retain oil residues in a way similar to marshes with pockets of relatively high amounts of petroleum residues (Burns et al., 1994). In a recent review article assessing the *Exxon Valdez* oil spill after 14 years (Peterson et al., 2003), the authors noted that sediments, which are physically protected from wave action, disturbance, oxygenation, and photolysis, remain partially weathered oil for years. In addition to exhibiting all of these characteristics, salt marsh sediments are ideal for preserving petroleum hydrocarbons because they are in temperate regions, have a high organic carbon content, and become anoxic within the top one cm of the surface (Teal and Teal, 1969). For example, *n*-alkanes were degraded four times faster in tropical mangroves than a temperate salt marsh that experienced below freezing temperatures in the winter (Burns et al., 1994). The high organic carbon in salt marshes may aid in preserving hydrocarbon residues for two reasons. First, many other natural compounds are available and may be more labile for microbes to respire. For example, ^{14}C analysis of bacterial phospholipids in a sediment core collected at the M-1 location in Wild Harbor in 2001 have indicated that the bacteria in the contaminated sections of the core were respiring recently photosynthesized material, which has contemporary ^{14}C values and not petroleum, which has no detectable ^{14}C (Slater et al., 2005). Such a finding is consistent with the fact that the TPH in the most contaminated sites in Wild Harbor only account for ∼10% of the total organic carbon content (White, Reddy et al., 2005).

Second, the elevated organic carbon content allows for increased partitioning into the sediment and out of the porewater, which in turn reduces the bioavailibility. While evidence for anaerobic hydrocarbon degradation does now exist for select hydrocarbons in No.2 fuel oil (Widdel and Rabus, 1999), there is no "real world" data indicating that partially weathered hydrocarbon residues, which persist in Wild Harbor, can be degraded.

Summary

Wild Harbor marsh continues to store petroleum residues 30 years after the *Florida* spill. Approximately 100 kg of the original product can be found. The locations that were most heavily contaminated continue to have the most persistent residues. It is unfortunate that a more complete mass balance for the spilled oil cannot be estimated, but it is likely that evaporation and offshore transport of the fuel residing in the water column days to weeks after the spill were major removal processes. The results from this study should pave the way for future efforts that focus on the geochemical and biological factors for continued persistence of petroleum hydrocarbons in a relatively small area. Wild Harbor marsh is ideal for studies directed at gauging whether any biological effects exist and whether the ecosystem has recovered, which in turn may aid policy makers in deciding when human intervention is necessary at other impacted salt marshes.

Acknowledgements

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