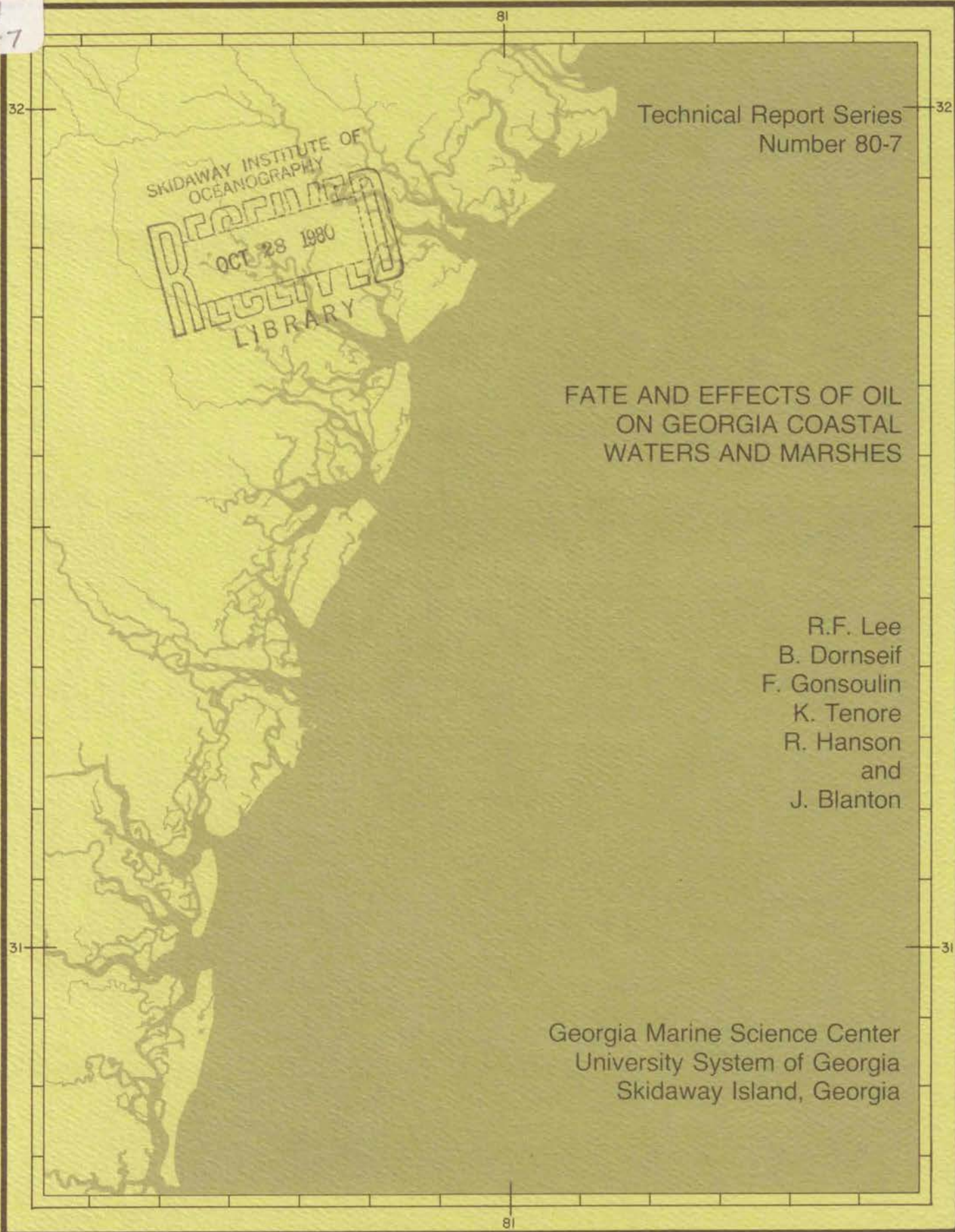


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FATE AND EFFECTS OF OIL ON GEORGIA COASTAL WATERS AND MARSHES

R.F. Lee
B. Dornseif
F. Gonsoulin
K. Tenore
R. Hanson
and
J. Blanton

Georgia Marine Science Center
University System of Georgia
Skidaway Island, Georgia

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July 3, 1980

Skidaway Institute of Oceanography
P.O. Box 13687
Savannah, Georgia 31406

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INTRODUCTION

Present sources of fossil fuel compounds in Georgia coastal waters include marine transportation, sewage outfalls and atmospheric fallout. Possible future sources include releases from offshore oil production, coastal oil refineries and new industry. This report discusses in general terms the fate of spilled oil in marine environments. This is followed by a discussion of the fate and effect of a small (40 gal) heavy fuel oil spill on an acre of salt marsh on the Wilmington River, Georgia.

CHAPTER I- FATE OF OIL

A variety of physical, chemical and biological processes affects the fate of oil in the sea (Figure 1.1). Physical and chemical processes rapidly act on oil slicks which generally results in their disappearance within a few days. Components of oil which enter the water also have short residence times with some carried to the bottom by sedimentation. Bottom sediments are the ultimate sinks for undegraded oil. For discussion purposes, this paper has separate sections on processes acting on oil slicks, oil in water and oil in sediments.

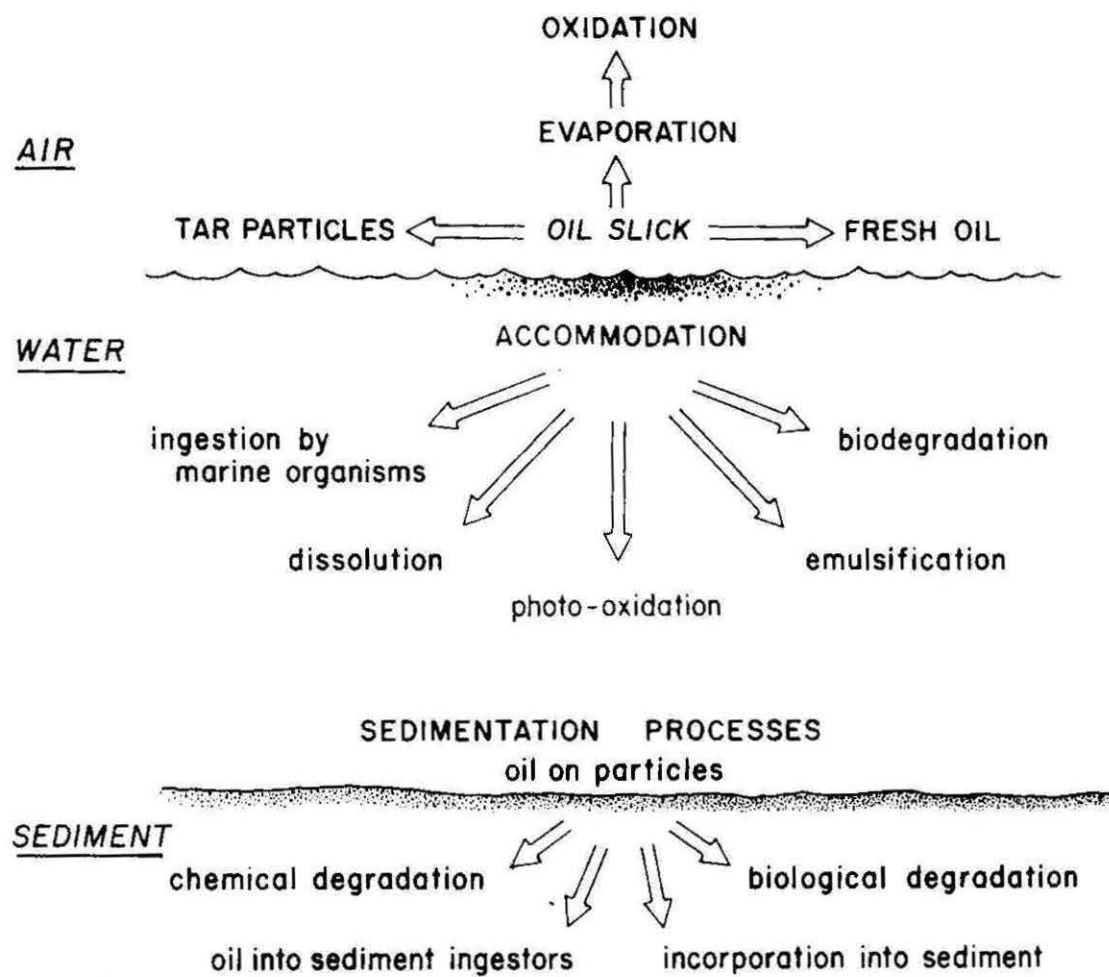


Figure 1.1. Fate of Oil at Sea

Fate of Oil in Slicks

Following discharge of oil into water, a slick forms due to the low water solubility of most components of oil. Currents, waves and winds spread the oil slick into thin films. Fallah and Stark (1976) reviewed theories and models that describe the movement of oil on water. Their models develop empirical equations which take into account the volume of oil spilled, its physical properties, elapsed time and wind speed. For example, heavy viscous oils do not spread as rapidly as less viscous types. In the open seas where wind often determines the direction and speed with which a slick moves, oil drift velocity is about 3% of the wind velocity. In nearshore areas, tidal forces also control the movement of oil. Slick-transport and slick-spreading in particular areas are best determined by carrying out experimental field spills. Jeffrey (1973) followed an experimental spill of 120 tons of light Iranian crude oil in the North Atlantic which rapidly disappeared after four days.

A first-order equation describes oil concentration changes resulting from processes of evaporation (K_V), dissolution (K_D), photochemical (K_P), emulsification (K_E) and biological decay (K_B), respectively.

$$\frac{dc}{dt} = (K_V, K_E, K_D, K_P, K_B)C$$

Approximate decay coefficients for evaporation and dissolution, the primary forces that remove slick components during the first few days, have been determined by James (cited in Harrison, 1974) for different oil fractions. The time required for and relative importance of various oil-weathering processes are summarized in Figure 1.2.

As soon as slicks form, evaporation removes volatile components. Hydrocarbons below C_{15} (which have a boiling point of less than 270°C and comprise 20 to 50% of most crude oils and 75% or more of many fuel oils) volatilize in a few days (Harrison *et al.*, 1975; McAuliffe, 1977a; Ocean Affairs Board, 1975). Hydrocarbons in the C_{15} - C_{25} range (boiling point-250 to 400°C) are volatilized from slicks only to a limited extent. The rate of evaporation is affected by temperature, wind speed, solar radiation, thickness of the slick, and composition of the oil. In an experimental 275-gallon crude oil spill in the Bahamas, all low-weight aromatics disappeared within the first 90 minutes (Harrison, 1974). The water temperature was 24°C and wind speed ranged from calm to 18 mph. It was estimated that one-third of the oil from the Torrey Canyon spill evaporated (Brunnock *et al.*, 1968).

Dissolution is the dispersal of dissolved compounds and small dispersed oil droplets into water. Following a spill of a heavy fuel oil (density of 0.97 g/ml) in Chedabucto Bay, Nova Scotia, small particles of oil (.01 to 1 mm in diameter) appeared in the upper waters along the Nova Scotia coast (Forrester, 1971). It was estimated that 107 tons of the 9500 tons spilled were dispersed into particles. Lighter

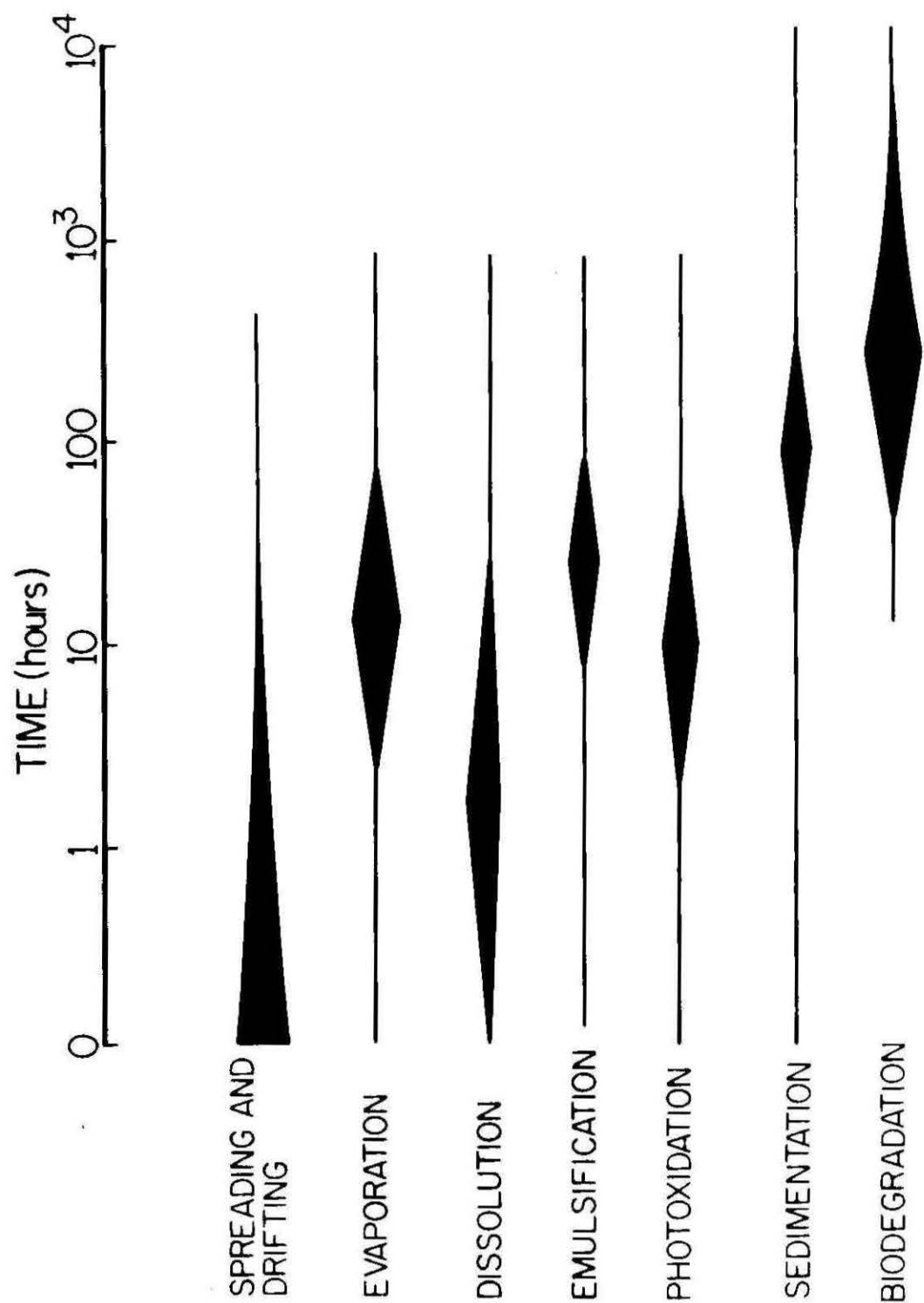


Figure 1.2. Relative Importance of Various Process Affecting Oil. Modification of a figure from Koons and Wheeler (1977). Line length is the probable time span of a process. Line width is the relative magnitude of the process.

fuel oils do not form droplets or particles of oil that remain in the water. The solubility of hydrocarbons drops exponentially as a function of their molecular volume, so that low-weight aromatics have relatively high solubility (McAuliffe, 1966). Toluene, naphthalene, phenanthrene and chrysene comprise an aromatic series with an increasing number of rings. Their solubilities in water are 515, 32, 1, and 0.002 mg/L, respectively (Mackay and Shiu, 1977). Under oil slicks, therefore, the predominant components are low-weight aromatics, such as benzene, toluene and xylenes. Under an experimental oil spill off the United States east coast, the concentration of aromatics at a depth of 1.5 m was 50 μ g/L (McAuliffe, 1977b). After a large crude oil spill in the Gulf of Mexico, less than 1% of the oil was in the water (McAuliffe *et al.*, 1975). In an experimental crude oil spill carried out in a tank, 5% of the spilled oil entered the water (Gordon *et al.*, 1976).

Evaporation and dissolution are simultaneous and competitive processes. Each hydrocarbon evaporates and enters solution at rates depending upon its vapor pressure and water solubility (McAuliffe, 1977a). In most areas, evaporation is far more important in removing oil slick components than is dissolution. Based on evaporation rate equations, Harrison *et al.* (1975) predicted that aromatic hydrocarbons would evaporate 100 times faster than the rate at which these compounds enter the water. Turbulence increases the surface-volume ratio of the spilled oil and thus enhances dissolution. Dissolution also can be promoted by naturally occurring surfactants, such as humic acids and fatty acids, which tend to concentrate in the surface microlayer (Boehm and Quinn, 1974). Certain oil components photochemically degrade by solar radiation into polar, surface-active molecules which promote dissolution of the oil.

Surface-active components in crude oil, such as porphyrins and carboxylic acids, help to form water-in-oil emulsions, sometimes referred to as "chocolate mousse" (Canevari, 1969) because of the color and consistency. This stable emulsion floats on the water and eventually can be carried ashore by winds and waves. Strong turbulent mixing can introduce emulsified oil into the water column. Fuel oil or other refined petroleum products with no surfactants do not form water-in-oil emulsions. The time required to form water-in-oil emulsions varies from a few hours to several days and depends on the nature of the oil (Ocean Affairs Board, 1975).

The processes discussed above distribute the components of oil slicks into different phases, i.e., air or water, but they do not degrade the compounds. Photooxidation and microbial degradation are the primary processes responsible for degrading the compounds in oil slicks. Energy from sunlight in the presence of oxygen can transform hydrocarbons into a number of oxygenated compounds. Because of their relatively high water solubility, the products of photooxidation which include carboxylic acids, alcohols, ketones and phenols, are detected in the water below oil slicks that have been exposed to ultra-violet irradiation (Hansen, 1975, 1977; Larson *et al.*, 1976). Aromatic

hydrocarbons are degraded by light more rapidly than aliphatics, and branched-chain aliphatics are degraded more rapidly than straight-chain aliphatics. Photooxidation products which have been isolated include fluorenone and benzoic acid (Hansen, 1975; Larson *et al.*, 1976; Figure 1.3). The ultraviolet and near-ultraviolet areas of the spectrum are responsible for degradation since exposure to light above 350 nm does not degrade oil (Hansen, 1977). Hansen (1975) calculated that three years would be required to photochemically degrade a .04 mm film of fuel oil. However, very thin oil films can be photochemically degraded in a few days (Freearde and Hatchett, 1970).

Because of the time needed to initiate microbial degradation of short-lived oil slicks, it is assumed that microbial degradation is less important than other processes discussed above in slick removal. However, once oil is dispersed into fine droplets or particles or is deposited on sediment, microbial degradation becomes of great importance.

After evaporation, dissolution, emulsification, photooxidation and biodegradation have acted on an oil slick to remove lighter weight components, a more viscous residue remains. The residual tar balls contain higher-weight hydrocarbons and oxygen and sulfur-containing compounds, asphaltenes. The percentage of crude oil which remains as a residue varies for different oils. Butler *et al.* (1976) suggested that as much as 20% of crude oils remains as a residue. The presence of tar balls in the Mediterranean and North Atlantic has been well documented (Butler *et al.*, 1970; Levy, 1977). These tar balls resist microbial degradation (Davis and Gibbs, 1975), and it has been estimated that their lifetime is on the order of several months to a year (Butler *et al.*, 1976).

Fate of Oil in Water

Oil can enter the water phase by dissolution or related processes. The concentration of oil components, whether dissolved or in particles, decreases exponentially with time due to evaporation, absorption to suspended particles, sedimentation, photochemical oxidation, uptake by zooplankton or biodegradation (Gearing *et al.*, 1979; Lee *et al.*, 1978).

Higher-weight aromatics and aliphatics in water adsorb to suspended particles because of their low water solubility. Lower-weight hydrocarbons and more polar oil components remain dissolved in the water (Herbes, 1977; Lee, 1977; Meyers and Quinn, 1973; Table 1.1). Sedimentation of particles carries hydrocarbons to the bottom. Most dissolved hydrocarbons (in estuarine areas of Georgia) adsorb to detrital particles, which are mixtures of organic matter, living bacteria, and small clay particles (Lee, 1977). Scanning electron micrographs reveal rough surfaces on these detrital particles, with bacteria fastened by mucoid pads and fibrillar appendages (Figure 1.4). Presumably, these surfaces provide hydrophobic areas for hydrocarbon adsorption.

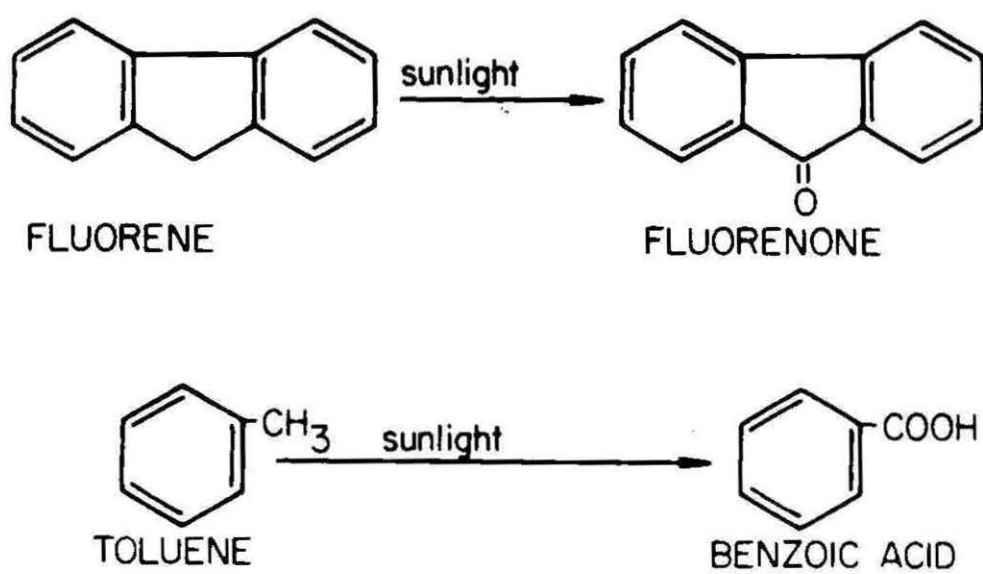


Figure 1.3. Oxidation products produced during the photooxidation of oils.

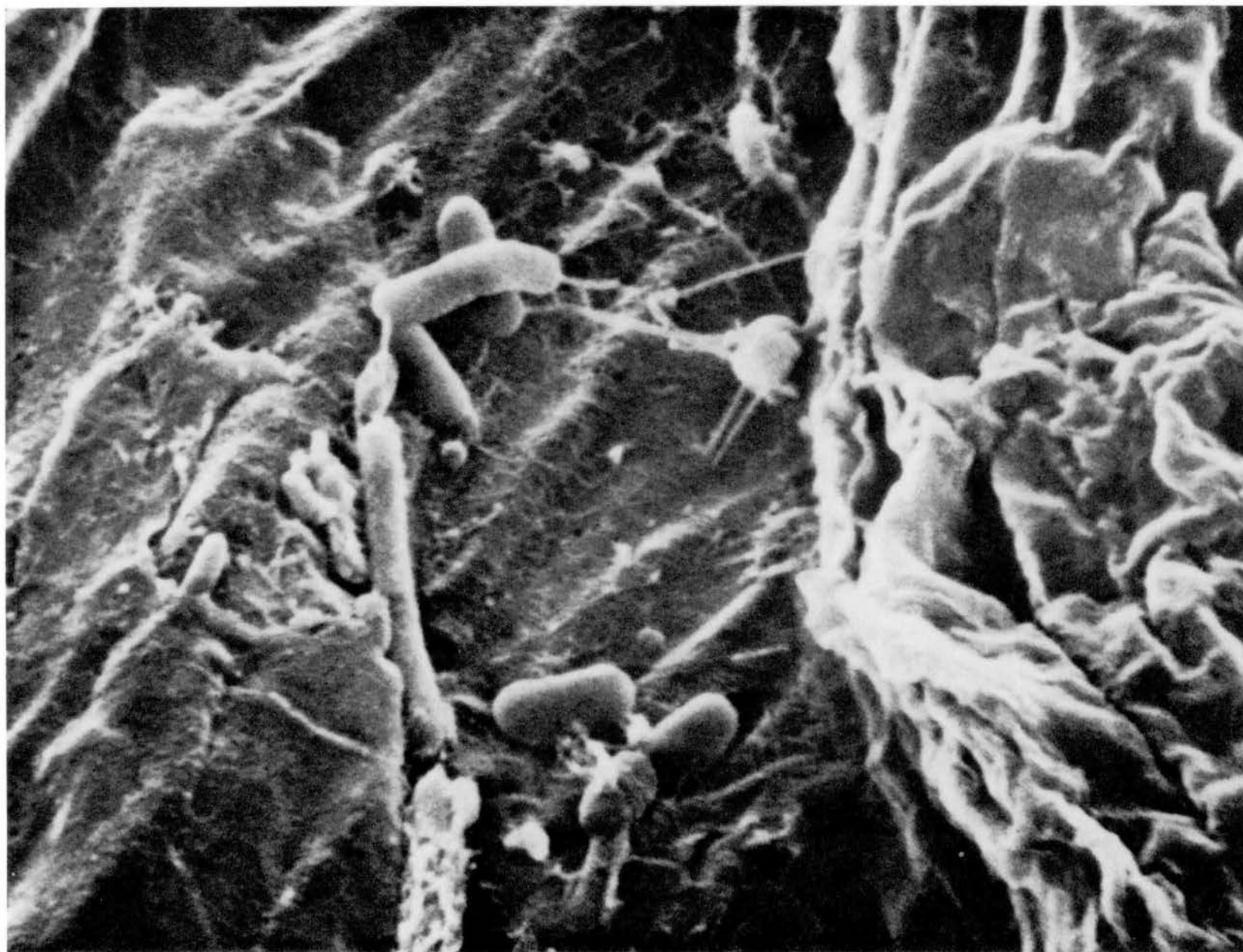


Figure 1.4. Scanning electron micrograph of detrital particle from Skidaway River, Georgia, showing attached bacteria (19,000x).

Table 1.1. Adsorption of hydrocarbons to particles in estuarine waters.

Radiolabeled hydrocarbons were added to 100 ml of water collected in the Skidaway River, Georgia. The concentration of suspended solids in this estuarine river was 40 mg/L. At the end of 3 hours, the water was filtered and the amount of hydrocarbons on particles was determined.

Hydrocarbon	Concentration of Hydrocarbon in Water ($\mu\text{g/liter}$)	Amount Adsorbed to Suspended Particles (%)
naphthalene	30	0.7
methylnaphthalene	30	6
fluorene	15	12
benz(a)anthracene	10	53
benzo(a)pyrene	3	71
hexadecane	3 10	8 19
octadecane	5	22
anthracene	4 15	6 22

Oil slicks and dispersed oil globules adsorb to clays and fine suspended sediments; and eventually these sediments, with attached oil globules or oil films, are carried to the bottom (Poirier and Thiel, 1941; Bassin and Ichiye, 1977). In open ocean areas, concentrations of suspended solids are relatively low, rarely exceeding 1 mg/L (Schubel, 1974). In estuaries and other coastal areas, the concentrations of suspended solids can be quite high. The estuaries of coastal Georgia have an average suspended solid concentration of 50 mg/L, with concentrations as high as 600 mg/L during spring tides (Oertel, 1976). After a hurricane, the concentration of suspended solids that entered one part of Chesapeake Bay rose to 10,000 mg/L. In such turbid areas, dispersed oil is soon removed by sedimentation. A practical application to accelerate sedimentation was the use of powdered chalk to sink Kuwait crude oil spilled by the Torrey Canyon (Smith, 1968).

Zooplankton, including copepods and protozoans, can consume particles of oil which are subsequently excreted, unmodified, in the feces (Andrews and Floodgate, 1974; Conover, 1971). In one oil spill, up to 20% of the particulate oil in the water was sedimented to the bottom in zooplankton feces (Conover, 1971). Copepods also take up dissolved hydrocarbons from the water. The copepods possess enzyme systems which metabolize the hydrocarbons to various hydroxylated metabolites which are later excreted (Corner et al., 1976; Lee, 1975).

Bacteria, yeasts and filamentous fungi which are capable of degrading oil have been isolated from polluted and pristine waters (Ahearn and Meyers, 1972; Floodgate, 1972; Gunkel, 1973; Miget et al., 1969; Perry and Cerniglia, 1973). Although occurring in all marine areas, hydrocarbon-degrading microbes are generally more abundant in chronically polluted water (Atlas and Bartha, 1973; Tagger et al., 1976). In the North Sea, oil-degrading bacteria were most abundant near active oil fields (Oppenheimer et al., 1977).

Rates of microbial degradation are influenced by temperature and nutrients. Atlas and Bartha (1973) found that the number of oil-degrading microbes was very low during the winter in Raritan Bay, New Jersey. Gibbs et al. (1975), using a continuous growth chamber with Irish Sea water and Kuwait crude oil, calculated that the microbial oil degradation rate was 30 mg/L/yr in the summer and 11 mg/L/yr in winter.

Photooxidation, in addition to acting on oil slicks, can also degrade components of oil in the water. Ultraviolet light does not penetrate into water, and many of the short wavelengths present in the visible region attenuate a few meters below the surface. Some high molecular weight polycyclic aromatic hydrocarbons are degraded by light longer than 300 nm (e.g., benzo(a)pyrene) and can be completely photooxidized in the seawater within a few days after exposure to sunlight (Andelman and Suess, 1970).

All of the processes discussed above act simultaneously to modify oil. An example of photochemical oxidation combined with microbial degradation is illustrated in Figure 1.5. Radiolabeled dimethylbenz(a)

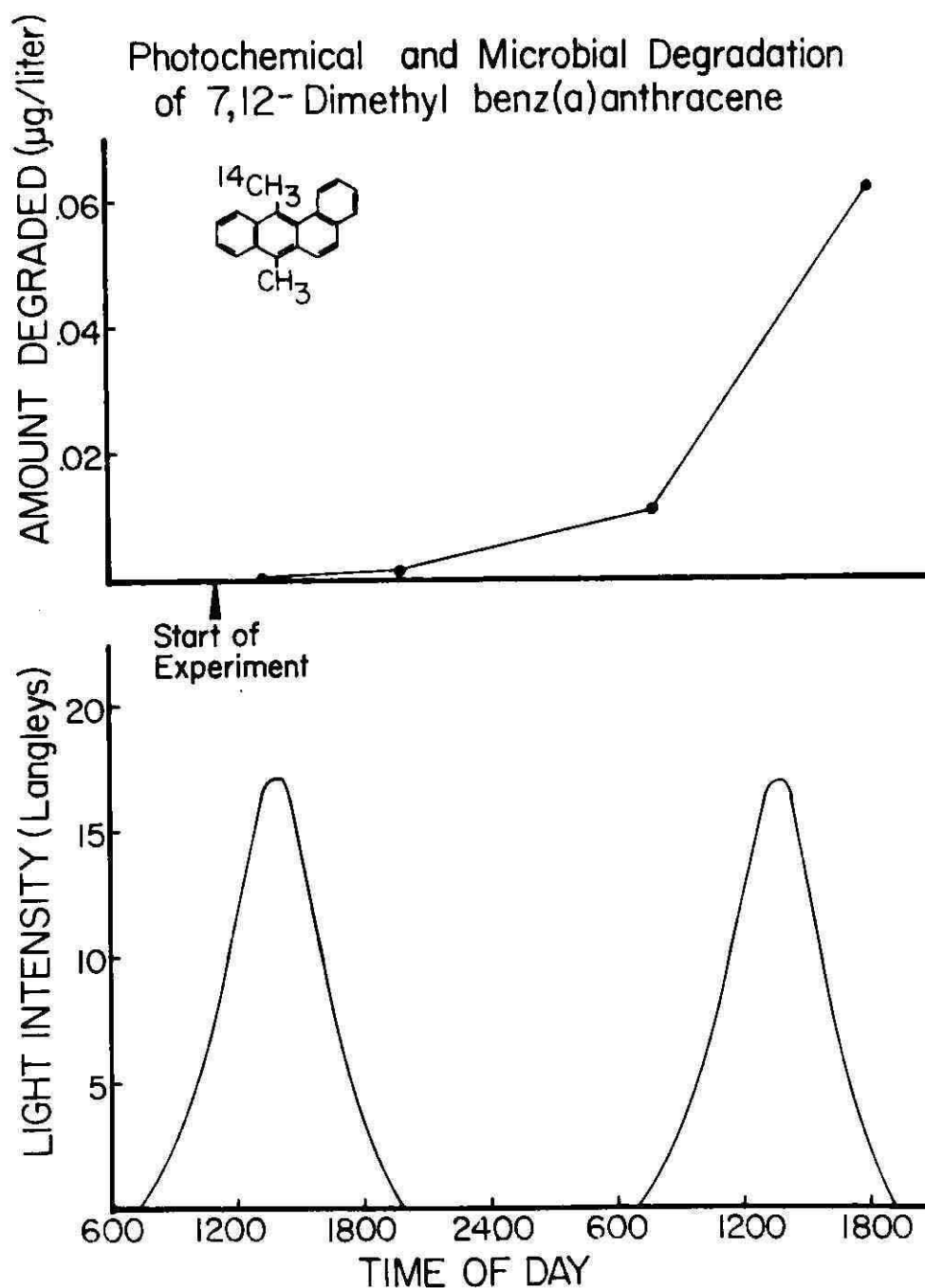


Figure 1.5. Photochemical and Microbial Degradation of 7, 12-Dimethylbenz (a)anthracene. 7, 12-Dimethyl (12-¹⁴C)benz(a)anthracene was added to an estuarine water sample (Skidaway River, Georgia) to give a final concentration of 10 µg/liter. Amount of degradation was determined by collecting ¹⁴CO₂ produced at the different time intervals. The water (100 ml) was in a quartz flask suspended in the river which allowed penetration of wavelengths longer than 200 nm. No ¹⁴CO₂ was produced when the experiment was conducted in the dark.

anthracene was not microbially degraded in the dark in Georgia estuarine waters. However, when water with dimethylbenz(a)anthracene was exposed to sunlight, rapid degradation to $^{14}\text{CO}_2$ occurred. Presumably, photooxidation products of dimethylbenz(a)anthracene were further degraded to CO_2 by microbes.

Fate of Oil in Sediments

Although difficult to quantify in the field, sedimentation processes carry significant amounts of oil to the bottom. After a drilling platform spill in the Santa Barbara channel, large quantities of oil on the bottom were believed to be due to adsorption of oil to suspended sediments derived from river runoff (Kolpack, 1971). In shallow areas, masses of oil can roll along the bottom by waves and currents and eventually wash ashore to form hard, tarry masses (Clark and Macleod, 1977). Floating tar balls or emulsions of oils can also be washed ashore by these same forces. Stranded oil undergoes various weathering processes, but the high boiling components in the larger masses of oil persist for many years (Blumer *et al.*, 1973). The sinking of supertanker Amoco Cadiz off France released 216,000 tons of crude oil, approximately 60,000 tons of which came ashore within the week (Hess, 1978).

In addition to lateral movement on the bottom, oil can penetrate deeper into the sediment, be resuspended into the overlying water, or be degraded. Tidal flow resuspends fine sediments with associated hydrocarbons. These resuspended sediments can be ingested by benthic filter feeders, such as clams, mussels and oysters. Oil in the feces of these animals can release the oil into the water. Smith and Hopkins (1972) found storm-generated transport of bottom sediments on the continental shelf in water as deep as 80 m. Strong forces generated by hurricanes can mix the top 10 cm of surface sediments in water as deep as 35 m (Hayes, 1967). Thus, Hoffman and Quinn (1978) suggested that sediment mobility was a factor explaining the low concentration of oil found in the bottom sediments after the Argo Merchant spill in the North Atlantic.

In some coastal areas, oil-derived hydrocarbons remain in the sediments for many years after the spill (Blumer and Sass, 1972; Scarratt and Zitko, 1972; Vandermeulen and Gordon, 1976). Coarser sediments allow greater penetration than fine unconsolidated sediments (Gundlach and Hayes, 1978). Highest concentrations of oil are generally associated with silt-sized sediments, possibly because these sediments have a greater area for adsorption (Meyers and Quinn, 1973; Hargrave and Phillips, 1975).

Coarser sediments, although allowing oil to penetrate to greater depth, also have high biodegradation rates relative to fine sediments, possibly because of greater aeration and nutrient flow to the subsurface. Also, coarser sediments occur on more exposed coasts so that

all other weathering forces are more effective than in low-energy areas.

The main factor affecting the persistence of oil in sediments is the rate of biodegradation which occurs there. Most rapid degradation occurs at the water-sediment interface (Gardner et al., 1979; Hughes and McKenzie, 1975; Lee, 1978; Lee et al., 1979). Microbial activity is low below the sediment surface, and oil buried a few centimeters can remain unmodified for years (Hughes and McKenzie, 1975; Gardner et al., 1979). In many estuaries, subsurface sediments are anaerobic and hydrocarbon oxidation is extremely slow.

After oil is introduced into sediment, there is a large increase in hydrocarbon-degrading microbial populations on the sediment surface (Zobell and Prokop, 1966; Walker et al., 1975). Straight-chain alkanes are rapidly degraded by a mixed community of hydrocarbon-degraded microbes. Branched-chain alkanes, cycloalkanes and aromatic hydrocarbons are attacked more slowly (Blumer, 1973; Walker et al., 1973). High boiling-point components are very resistant to microbial degradation.

Different crude and refined oils degrade at varying rates because of variations in the relative amounts of different oil components. In one experiment, hydrocarbon degrading microbes were allowed to act on two crude oils (South Louisiana and Kuwait) and two refined oils (Bunker C and No. 2 fuel oil). The South Louisiana crude oil was most susceptible to microbial degradation, and the Bunker C oil was the least degraded in the 28-day study (Walker et al., 1976). The high content of high molecular weight polycyclic aromatic hydrocarbons in Bunker C oil may explain its resistance to degradation.

In addition to microbes, marine sediments contain macrofauna and an interstitial meiofauna community, which is composed of harpacticoid copepods, nematodes, turbellarians and polychaetes (Marc, 1942). Many of these benthic species are deposit feeders and are important in oxidizing and recycling sediment organic matter (Tenore et al., 1977). In undisturbed sediment, most microbial activity is restricted to the surface, but the feeding process of benthic animals mixes the sediment to depths as great as 15 cm (Rhoads, 1967). This allows microbes to degrade organic matter from deeper sediments.

Some polychaete worms, such as Capitella capitata, occur in areas of high oil input (Reish, 1971; Sanders et al., 1972). Cell-free extracts of Capitella capitata and other polychaetes have hydrocarbon-metabolizing enzymes, while whole animals take up polycyclic aromatic hydrocarbons from the sediment and metabolize them to various hydroxylated derivatives (Lee et al., 1979). Thus, polychaetes and other benthic animals can enhance microbial degradation of subsurface oil hydrocarbons (Gardner et al., 1979; Gordon et al., 1978; Lee et al., 1979; Figure 1.6).

Hydrography and Oil Spills in Coastal Georgia

A general characterization of water masses in the nearshore

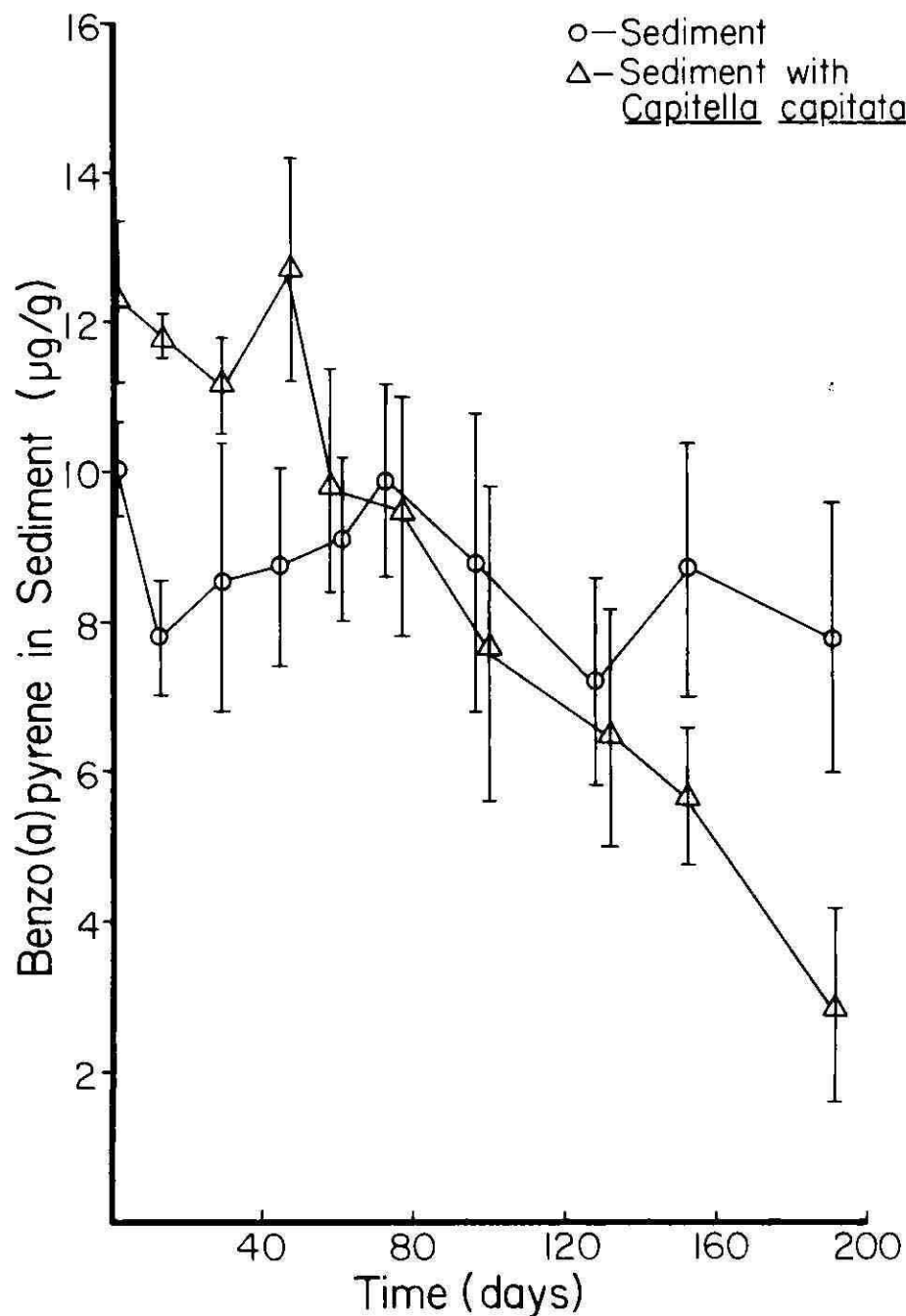


Figure 1.6. Changes in Sediment Benzo(a)pyrene Concentration With and Without the Polychaete, *Capitella capitata*.

Five ml of Kuwait crude oil, enriched with 50 mg of benzo(a)pyrene were mixed in trays containing 2000 g of estuarine sediment. Three trays were seeded with *Capitella capitata* (20 worms per tray) and at various time intervals cores were taken from each tray for the extraction of hydrocarbons. The standard deviation for the benzo(a)pyrene concentration in 3 trays is shown at each time interval. A complete description of the experiment is given in Lee *et al.* (1979).

Georgia waters is shown in Table 1.2 and Figure 1.7. Zone A contains highly turbid water (9-200 mg/L of suspended sediment) ejected from the inlets during ebb tidal flows. Wind effects in this zone are usually overwhelmed by tidal energy. Zone B is a boundary area which contains multiple surface discontinuity fronts that appear to be remnants of preceding tidal cycles. This zone contains turbid surface water mixed with clearer shelf water which overrides denser shelf water. Zone C is clear shelf water with suspended sediment concentrations less than 2.0 mg/L. Currents in this zone responded more to wind than to waters closer to shore.

The movement of oil spilled in Zone A or B is governed by tidal flow. It is predicted that oil spilled approximately 15 km from shore would require at least four tidal cycles to reach the marsh. Oil spilled within 5 km of shore would reach the marsh on the next tidal cycle. Because of tidal movement and longshore currents, oil entering one sound could subsequently flow out and into adjacent sounds.

Fate of Oil in Coastal Georgia

The fate of oil spilled in Georgia's coastal waters will depend on the composition of the oil and on external factors such as light and temperature. Photochemical oxidation, dissolution, emulsification, adsorption to particles, biodegradation and uptake by organisms interact to affect the fate of oil slicks and oil in the water. Sedimentation, as discussed earlier, causes oil in turbid inshore zones to be deposited on the bottom where it is resuspended into the water, penetrates deeper into the sediment, or is degraded. The sediment community of microbes, meiofauna and macrofauna is responsible for degrading oil in the sediment.

Table 1.2. General characteristics of nearshore water masses based on low runoff conditions, October-November 1976. A schematic diagram based on salinity is presented in Figure 1.7.

	Zone A Turbid Zone	Zone B Boundary Zone	Zone C Shelf Water
Depth, inner edge (m)	0	5-10	13-16
Depth, outer edge (m)	5-10	13-16	shelf break
Distance from shore, inner edge (km)	0	6-19	22-33
Distance from shore, outer edge (km)	6-19	22-33	shelf break
Maximum salinity gradient ($^{\circ}/_{\text{‰}}/\text{m}$)	0.5-1.0	0.2-0.5	0
Vertical density gradient (gm/cm^4)	2-10	1-2	0
Suspended sediments			
Concentration range (mg/L)	9-200	2-8	< 2.0
% organic	20-50	50-80	80-100
Dominant mineralogy*	S,K,I	S,K,I	K,I
Major size mode (μm)	8-16	64-128	16-32
Chlorophyll ($\text{mg chlor}_a/\text{m}^3$)	1.0-3.0	0.3-1.0	< 0.3
Phytoplankton cells (10^5 cells/L)	5.5-15.4	1.5-5.4	0.43-0.70
Phosphate ($\mu\text{g at P/L}$)	1.5	0.3	0.2

* From G. N. Bigham, 1973. Zone of influence - inner continental shelf of Georgia. Jour. Sed. Pet. 43(1):207-214.
(S= smectite; K=kaolinite; I= illite)

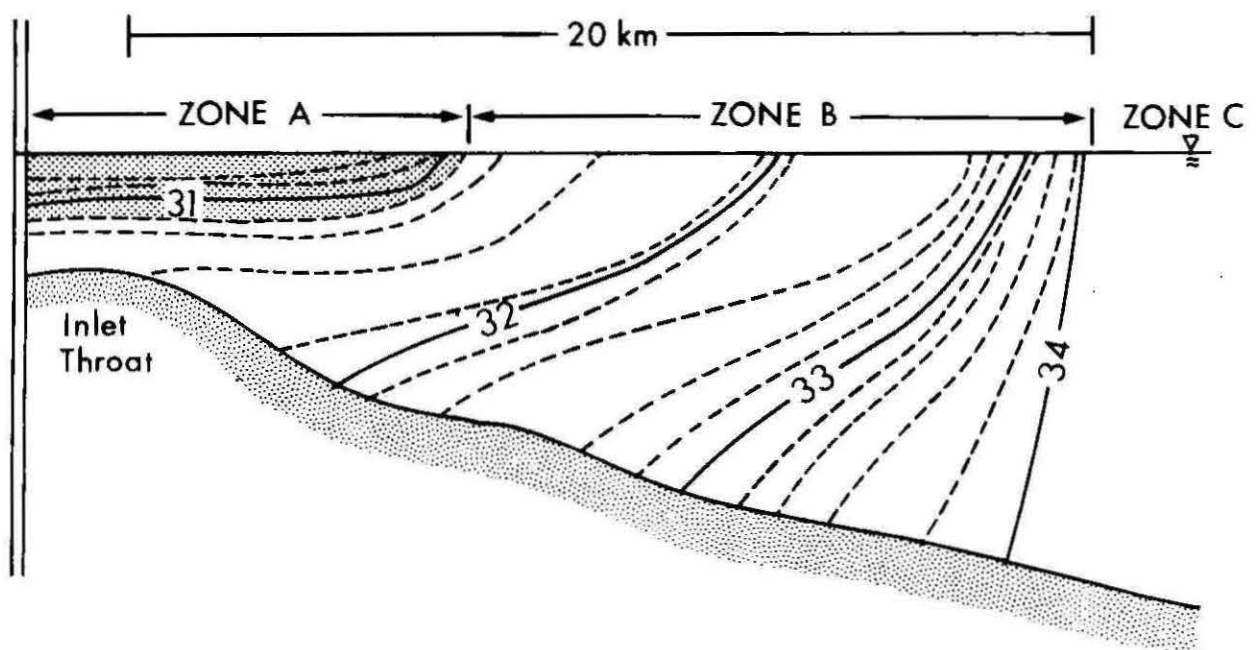


Figure 1.7. Schematic Salinity Structure Characterizing the Zonation of Nearshore Waters off Georgia.

Zone A may be very small at locations away from the inlets.

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CHAPTER II

Fate and Effects of a Heavy Fuel Oil Spill on a Georgia Salt Marsh

Heavy fuel oil was added to one acre of a Spartina alterniflora salt marsh bordering the Wilmington River, Georgia. A diagrammatic cross section of the oiled marsh showing the animals sampled is shown in Figure 2.1. The polycyclic aromatic hydrocarbons selected for study (Figure 2.2) are similar in structure to other hydrocarbons which have mutagenic and carcinogenic properties. Because of their high molecular weight, it was expected that these compounds would remain in the sediment and evaporation and dissolution would be of minor importance. Studies included: (1) analyses by high-pressure liquid chromatography of selected polycyclic aromatic hydrocarbons in sediments and animals; (2) microbial degradation of selected aromatic hydrocarbons; (3) effects of oil on benthic animals; (4) effects of oil on microbial processes important in salt marsh metabolism and productivity.

MATERIALS AND METHODS

Analytical

On November 13, 1978, 40 gal (150 L) of a No. 5 fuel oil were added to one acre (4000 m²) of a Spartina alterniflora salt marsh bordering the Wilmington River, Georgia, U.S.A. Fluoranthene (80 g), phenanthrene (80 g) and chrysene (10 g) were dissolved in the fuel oil before the oil was added to the marsh. On December 5, 1978, an additional 20 gal (75 L) of the fuel oil containing fluoranthene (10 g), phenanthrene (10 g) and chrysene (2 g) were added to a 10 m by 3 m section within the previously oiled area. The oil was sprayed on the surface of the marsh at low tide. Animals were collected at various times after the oil additions and analyzed for polycyclic aromatic hydrocarbons by high-pressure liquid chromatography. The marsh sediment consisted of 61% sand (0.062 to 2 mm particle size), 12% silt (0.002 to .062 mm particle size) and 26% clay (0.002 mm particle size). Median particle size was 0.105 mm. Cores were taken, and the top 2 cm of the cores were used for extraction and analysis of hydrocarbons.

Animal tissues were homogenized in a blender for two minutes. The sediment was mixed with an equal volume of water. Tissue or sediment slurries were saponified with 4N NaOH by heating at 95°C for two hours. The sample was mixed with 5 ml of hexane. The hexane extracts were dried under nitrogen and the residue dissolved in methanol (10 µl). The concentrate was analyzed on a high-pressure liquid chromatograph (Model 7000B-Micrometrics) with a fluorescence detector (Aminco Fluoro Monitor-American Instruments). The chromatograph was fitted with either a 4 mm x 25 cm Spherisorb ODS or a Partisil 10-ODS column. The hydrocarbons were eluted with 65% methanol in water with a flow rate of 2 ml/min at 50°C. Calibration

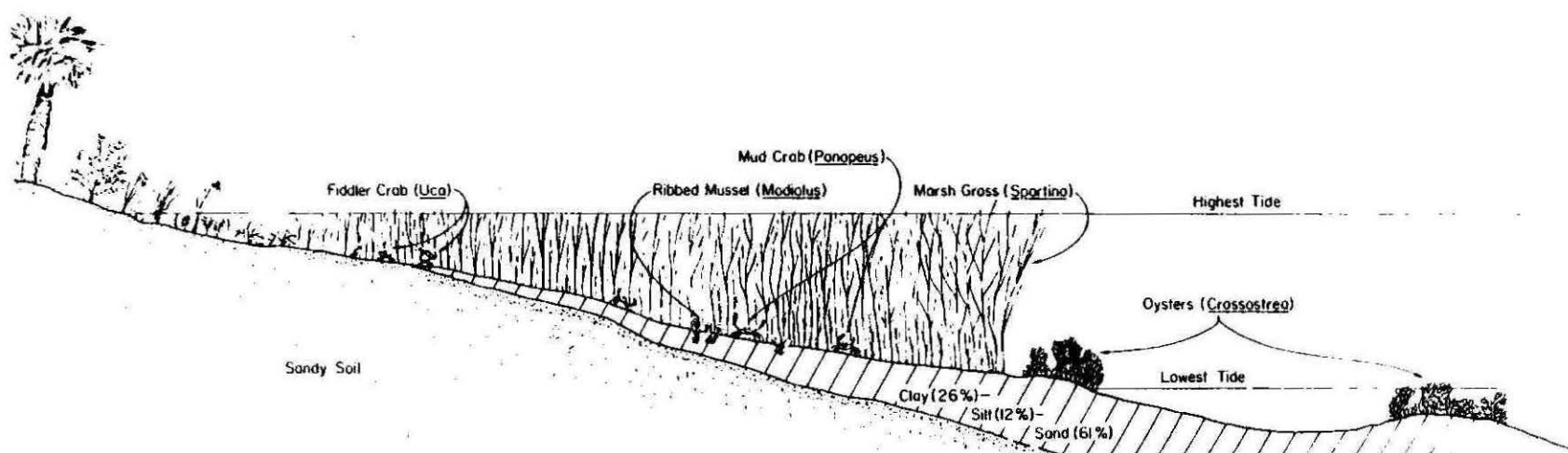
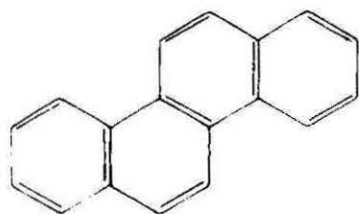
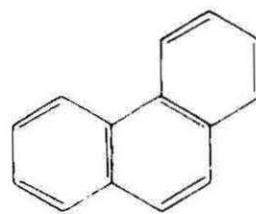


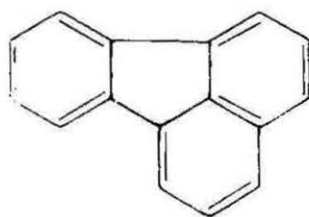
Figure 2.1. Cross Section of Salt Marsh Treated with Fuel Oil.



CHRYSENE



PHENANTHRENE



FLUORANTHENE

Figure 2.2. Polycyclic Aromatic Hydrocarbons Selected for Analysis.

curves based on peak areas were prepared daily for each compound to quantify the results.

Assays for Microbial Processes

Sediment cores (8.5 cm diameter) were taken from the control and oiled site during low tide. The control site was approximately 10 m from the oil spill site and was separated from it by a small tidal creek. Cores were processed within one hour in the laboratory. The surface layer (0-1 cm) and 5 cm layer (5-6 cm) were sliced from the core, and 1 cm³ cubes were used for microbial studies.

For total adenylate measurements, sediment (1 cm³) from the rhizosphere was squeezed through a 1 mm mesh screen and into a 5 cc disposable syringe. Duplicate samples were extracted in 15 ml of boiling (102°C) phosphate-citrate buffer (Bulleid, 1978). The extract was then treated as described by Tenore *et al.* (1979). Aliquots for each replicate were treated with appropriate enzymes to convert ADP and AMP to ATP. ATP was measured on a Chem-Glow Photometer (American Instrument Company).

Bacterial counts were determined on sediment squeezed from the rhizosphere. Samples were diluted and preserved in 0.22 µm filtered estuarine water with formaldehyde (5% v/v). After appropriate dilution, the cells were stained with acridine orange (final concentration .01%). Samples were filtered onto 0.2 µm Nuclepore filters (stained with irgalan black) and rinsed with 1 ml filtered formaldehyde-distilled water (Hobbie *et al.*, 1977). Bacterial cells that fluoresced green to red were counted with an epifluorescent Zeiss microscope.

Several metabolic processes were measured on relatively undisturbed sediment samples. Sediment samples (approximately 8-10 g net weight) from the surface and 5 cm layers were placed into replicate (4) serum bottles (volume 40 cc). Bottles with sediment samples from the 5 cm layer were flushed with helium for five minutes. Acetylene (10%) and N₂O (.01%) were added to replicates containing surface and 5 cm sediments. The other two replicates were unaltered. Samples were incubated at *in situ* temperatures, which ranged from a low of 12°C in the winter to a high of 30°C in the summer. After one hour, and again the following morning (approximately 20-22 hours later), .3 ml of the gas phase was removed with a 1 ml disposable syringe and immediately injected into an analytical gas chromatograph (Carle Instruments). Gases were separated on two columns (Porapak-40% N, 60% Q; and Molecular Sieve 13A) and detected with thermal conductivity and flame ionization detectors in series. A dual input integrator (Laboratory Data Control) computed peak area. All peak areas were normalized to detector response and nitrogen gas. Standard gases were obtained from Matheson Gas Products. Rates were calculated from the change in gas composition over the incubation period and normalized to gram dry weight (samples dried at 80°C for 24 hours). O₂ demand was computed only for surface sediments, irrespective of gas composition in the bottles (four replicates per

sample period). CO_2 production was calculated for all samples incubated with or without C_2H_2 and N_2O (four replicates to compute mean value). Ethylene production was observed only in bottles with atmosphere enriched with C_2H_2 . N_2O reduction was measured only in those bottles containing added N_2O (two replicates per depth). N_2O production was not observed in bottles with C_2H_2 . CH_4 production was calculated for samples that were not exposed to C_2H_2 and N_2O (two replicates per depth).

The signed test for paired variance was used to test whether the mean values from each site were significantly different. Student-t test was not used because normal distribution in microbial communities and bacterial populations cannot be assumed to be due to possible change in populations over time, temperature fluctuations and plant growth in each area. Paired data from a minimum of ten sample means, determined over the period from November 1978, to August 1979, were tested. In addition to comparing the means from each site, values from surface and 5 cm layers within both areas were analyzed.

Rates of microbial degradation of polycyclic aromatic hydrocarbons were determined by adding ^{14}C -labeled hydrocarbons to sediment-seawater slurries (1 g sediment; 50 ml seawater) in 125 ml incubation bottles capped with silicone stoppers. Radiolabeled hydrocarbons used were ^{14}C -12-benz(a)anthracene (4.8 mci/mm-Amersham), 3,4 - (benz, 3, 6- ^{14}C) pyrene (21 mci/mm-Amersham), ^{14}C -chrysene (6.3 mci/mm-Amersham), and ^{14}C -9-phenanthrene (11.3 mci/mm-Amersham). During the incubation the sediment was kept in suspension by shaking (Lab-Line Junior Orbit Shaker). After incubation for various time intervals at the *in situ* temperature, the respired $^{14}\text{CO}_2$ was collected on filters soaked with phenethylamine and counted with a liquid scintillation counter.

Biological Sampling

For a year prior to the oil spill, seasonal samples were taken at 13 stations randomly chosen within the marsh site. The site contained various growth forms of *Spartina*: tall *Spartina* creek bank; tall *Spartina* edge marsh; and short *Spartina* high marsh. At each station, a square frame (1 m²) was randomly positioned on the marsh, and five dominant marsh epifaunal species were collected. These included ribbed mussel, *Modiolus demissus*; the southern periwinkle, *Littorina irrorata*; the crab, *Sesarma reticulatum*; the mud crab, *Panopeus herbstii*; and the fiddler crab, *Uca pugnax*. These five species were selected because they occur in high densities and because they represent a wide spectrum of feeding types. Crabs were collected on the surface and within burrows to a depth of six inches.

After the oil spill, samples were collected every two months. Stations were chosen according to a stratified random sampling scheme. Six or seven of the total 13 stations were chosen within the oil spill area and the remainder randomly chosen within the control area.

Again, the square frame was used and the same five epifaunal species collected along with the mud snail, Nassarius obsoleta. In the laboratory, the animals were washed with tap water and frozen until analyzed. After thawing, the samples were sorted, total numbers of each species counted and individual sizes (widths for crabs and lengths for snails and mussels) recorded to construct size-class histograms. For biomass estimates, individuals of each species were dried at 80°C for 24 hours to obtain dry weight and then combusted at 475°C for 16 hours to obtain ash-free dry weight. For mussels, tissue biomass (excluding shell) was recorded. Length-tissue weight regressions for L. irrorata and N. obsoleta were used to estimate biomass.

RESULTS

Chemical and Microbiology Studies

After a heavy fuel oil was added to the marsh, high concentrations of the selected polycyclic aromatic hydrocarbons, *i.e.*, phenanthrene, chrysene and fluoranthene, were observed in sediment, oysters and mussels in the area. Extrapolation of these concentrations to whole oil indicates that the highest concentration of total oil was 120 µg/g sediment. Concentrations in the sediment remained high for 45 days, followed by a rapid decrease during the next 100 days (Figures 2.3 and 2.4). Highest concentrations were obtained on day 45 when the concentrations of phenanthrene, chrysene and fluoranthene, were 115, 105, and 76 ng/g sediment, respectively. On day 150, phenanthrene was below the detection limits (less than 0.5 ng/g), and the concentrations of fluoranthene and chrysene were 15 and 20 ng/g, respectively.

Hydrocarbons increased in mussels for 60 days following the spill and then rapidly decreased (Figure 2.5). There was a rapid decrease in the concentration of all hydrocarbons in oysters 25 days after the spill, followed by a slower decrease for the following 100 days (Figure 2.6). The times for the selected hydrocarbons to decrease to 50% of their highest values, *i.e.*, half-life, were approximately 100, 70 and 30 days for sediment, mussels and oysters, respectively. After 150 days, chrysene and fluoranthene were present at low concentrations, and phenanthrene was not detectable in either sediment or animals. The rapid release of hydrocarbons by oysters relative to mussels may be due to the position of oysters on top of the sediment, while mussels are in the sediment. Thus, mussels were continuously exposed to oiled sediment, whereas oysters obtained hydrocarbons from water or suspended particles.

A small portion of the marsh (30 m²) was heavily oiled a second time on day 30. Although sediment, mussels and oysters were collected at least 20 m from the re-oiled site, some of the oil was carried throughout the 4000 m² area. This may explain increases in the hydrocarbon concentrations of the sediment up to day 45. Oysters from

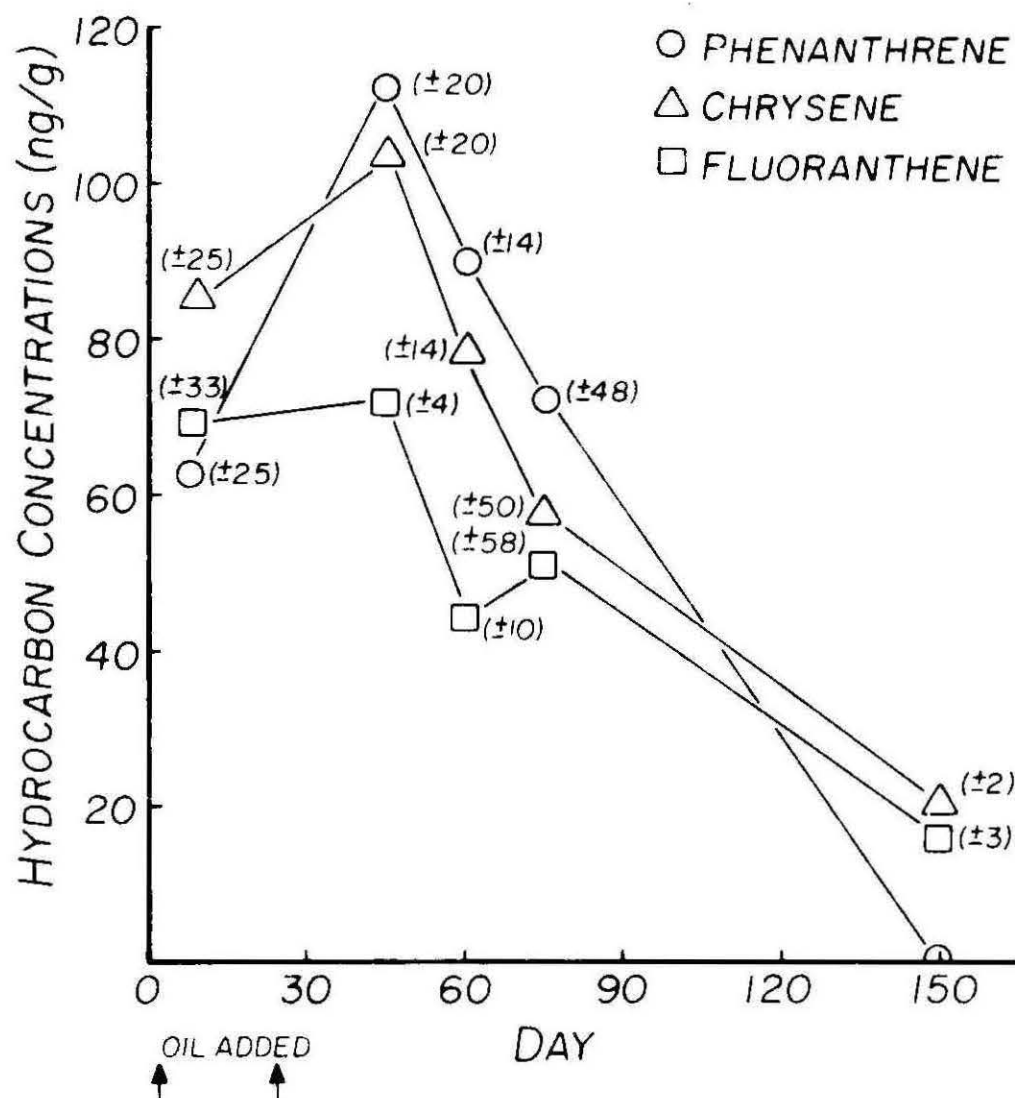


Figure 2.3. Changes in the Concentration of Polycyclic Aromatic Hydrocarbons in Sediments after Addition of Fuel Oil.

Oil was added to 4000 m² of marsh on day 0 and to a small 30 m² area within the 4000 m² area on day 23. Sediments for analysis were collected at least 20 m from the site of the second oil addition. Each point represents the average value for four samples and the standard deviation for each point is given in parentheses. The hydrocarbon concentration units are nanogram per gram of sediment (wet weight).

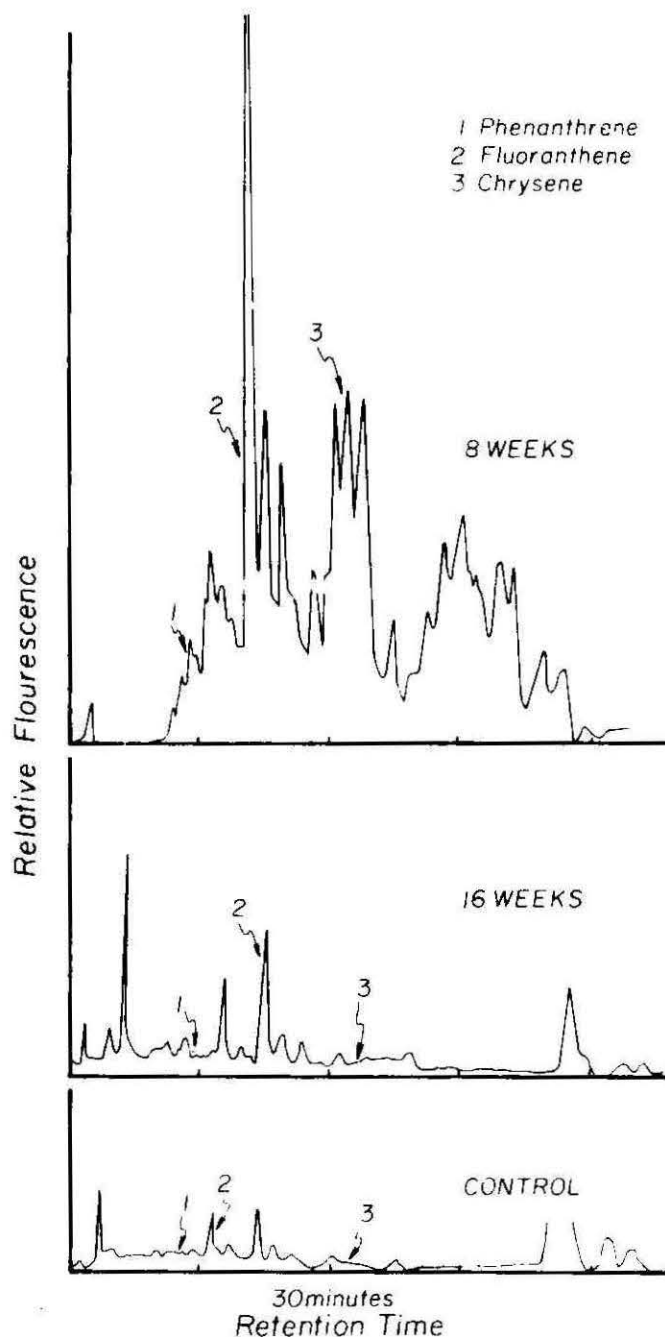


Figure 2.4. High-Pressure Liquid Chromatograms of Extracts of Sediment.

Sediments were collected from 4000 m² portion of marsh at 8 and 16 weeks after addition of fuel oil No. 5. Also included is a chromatogram of hydrocarbons from sediments of the control area. Column was a Spherisorb ODS run isocratically with 65% methanol in water with a flow rate of 2 ml/min at 50°C.

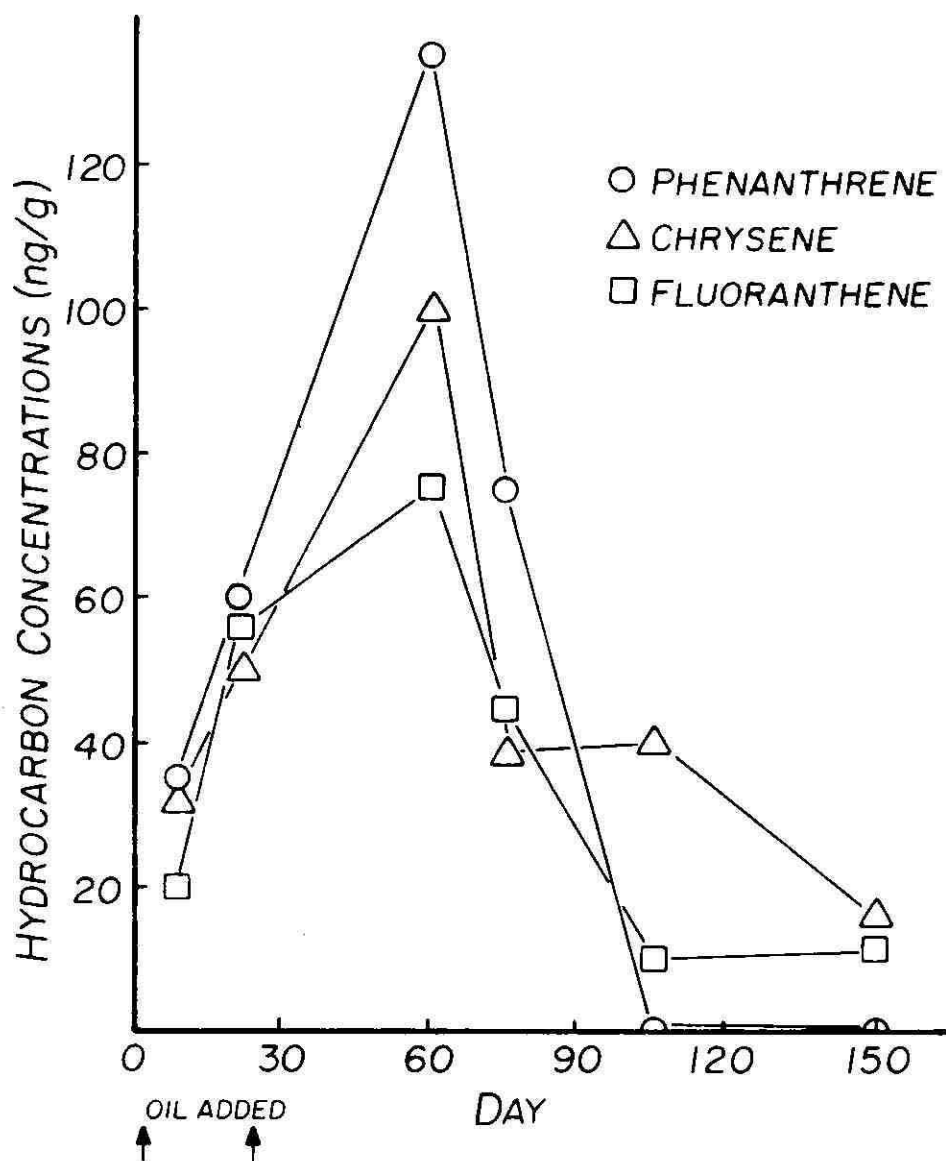


Figure 2.5. Changes in the Concentration of Polycyclic Aromatic Hydrocarbons in Ribbed Mussels (*Modiolus demissus*) after Exposure to Fuel Oil.

Oil was added to 4000 m² of marsh on day 0 and to a small 30 m² area within the 4000 m² area on day 23. Mussels were collected at least 20 m from the site of the second oil addition. Each point represents the average value for three samples. Hydrocarbon concentration units are nanogram per gram of mussel tissue (wet weight).

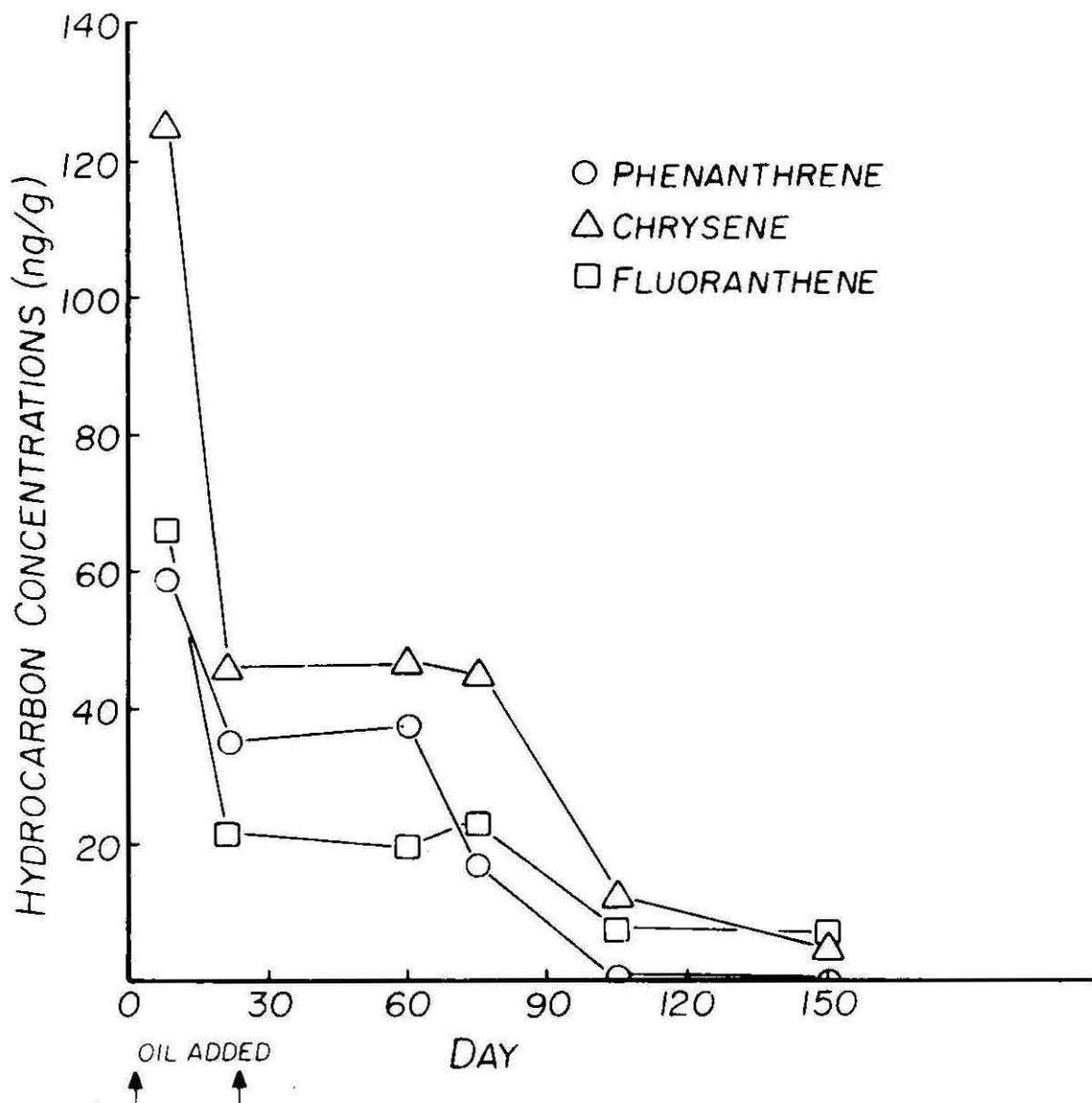


Figure 2.6. Decrease in the Concentrations of Polycyclic Aromatic Hydrocarbons in Oysters After Exposure to Low Levels of Fuel Oil.

Oil was added to 4000 m² of marsh on day 0 and to a small 30 m² area within the larger area on day 23. Oysters were collected at least 20 m from the site on the second oil addition. Each point represents the average value for three samples. Hydrocarbon concentration units are ng per gram oyster tissue (wet weight).

the re-oiled area were analyzed; and although the initial hydrocarbon concentrations were very high, rapid discharge of more than 85% of the hydrocarbons occurred during the next 120 days (Figures 2.7 and 2.8). The half-life of hydrocarbons from oysters in the heavily oiled area was 40 days.

Decreases in the concentration of the different hydrocarbons in sediment was due to weathering processes, including evaporation, biodegradation and photochemical oxidation. In addition, some of the oil was probably carried away by tidal flow. A heavy fuel oil (No. 5) was selected since it was assumed that most would remain on the sediment and would not be transported from the site. This appeared to be the case since oil was not visible in adjacent areas and there was no increase in hydrocarbons concentrations in control areas. The selected polycyclic aromatic hydrocarbons were not detected in oysters on a bar approximately 10 m from the spill. Since tides cross the bar as water enters the spill area, only resuspended oil should have been carried to these oysters.

The removal rate is believed to be due primarily to a combination of microbial and photochemical oxidation. The high molecular weight and the rate of hydrocarbon disappearance would argue that evaporation of the selected polycyclic aromatic hydrocarbons was not important. Rates of microbial degradation, determined by adding radiolabeled hydrocarbons, were much higher in sediment from the oiled area than in control sediments (Figure 2.9). The microbial degradation rate of ^{14}C -chrysene at a concentration of $2.5 \mu\text{g/g}$ sediment was $5 \text{ ng/g sediment/day}$ and $35 \text{ ng/g sediment/day}$ for control and oiled sediment, respectively. Similar differences in rates of degradation were observed when ^{14}C -phenanthrene was added to control and oiled sediment.

Microbial studies, in addition to those discussed above, included determination of total adenylates, bacterial counts, oxygen demand, carbon dioxide production, ethylene production, methane production and N_2O reduction in sediments. The mean values of these microbiological parameters for the oiled and control areas are given in Table 2.1. Comparison of all the mean values for the period after the oil spill, November 1978 to August 1979, indicates that only two processes were statistically different in oiled and control areas. The concentrations of adenylates were higher and CO_2 production lower in the surface layer of oiled areas relative to the controls. The 5 cm depth layer showed no differences between control and oil-spill areas. Microbial parameters for surface sediments were statistically different from the 5 cm layer in both oiled and control areas. In general, biomass (total adenylates and bacterial cell numbers) was higher in the surface layer, but net metabolic processes were higher in the 5 cm layer.

Macrofauna Studies

For a year prior to the oil spill, the marsh epifauna had lowest

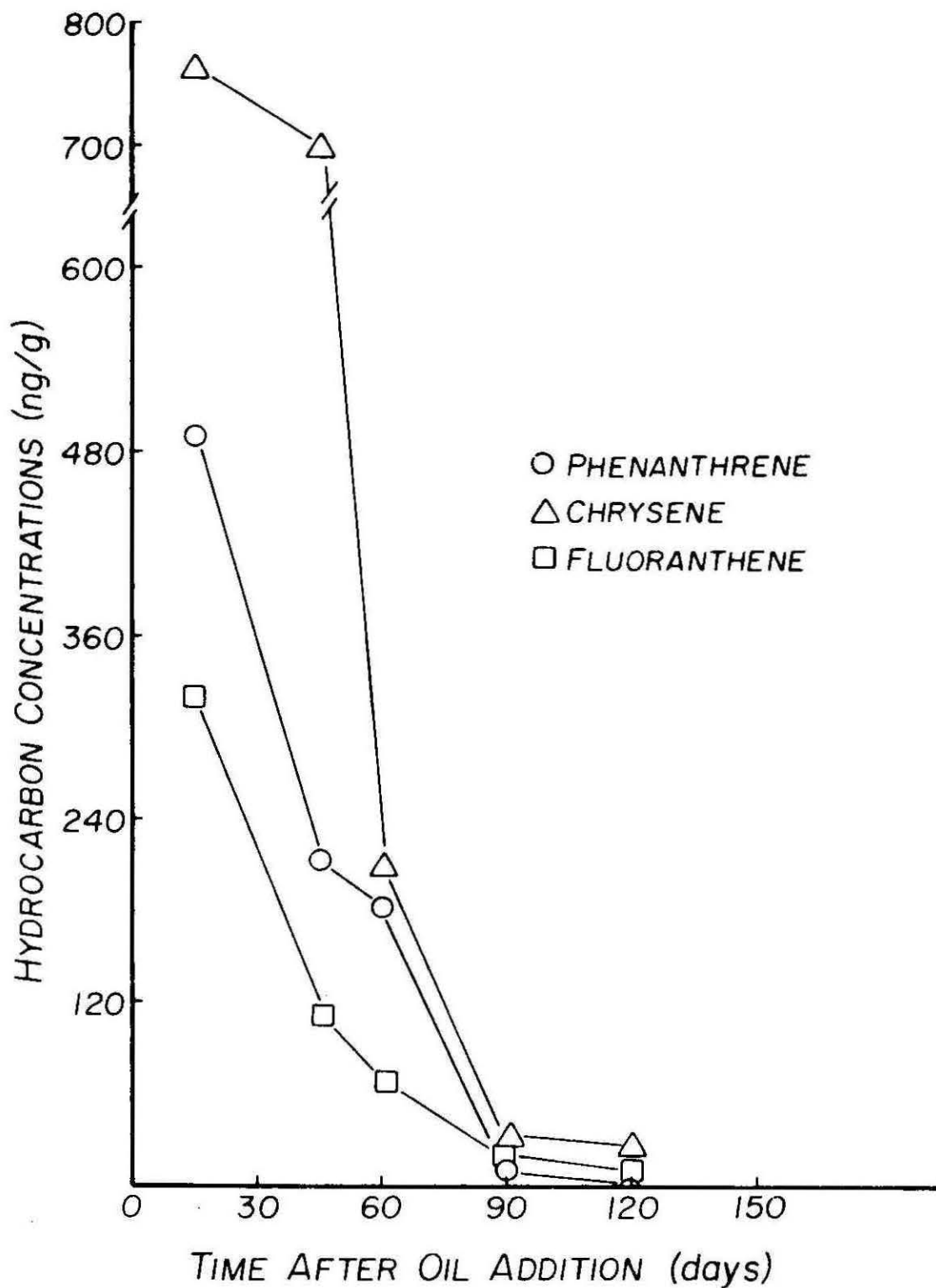


Figure 2.7. Decrease in the Concentrations of Polycyclic Aromatic Hydrocarbons in Oysters After Exposure to High Levels of Fuel Oil.

Oysters were collected from a 30 m² portion of marsh exposed to 75 liters of fuel oil No. 5. Points represent the average value for four samples. Hydrocarbon concentration units are nanogram per gram oyster tissues (wet weight).

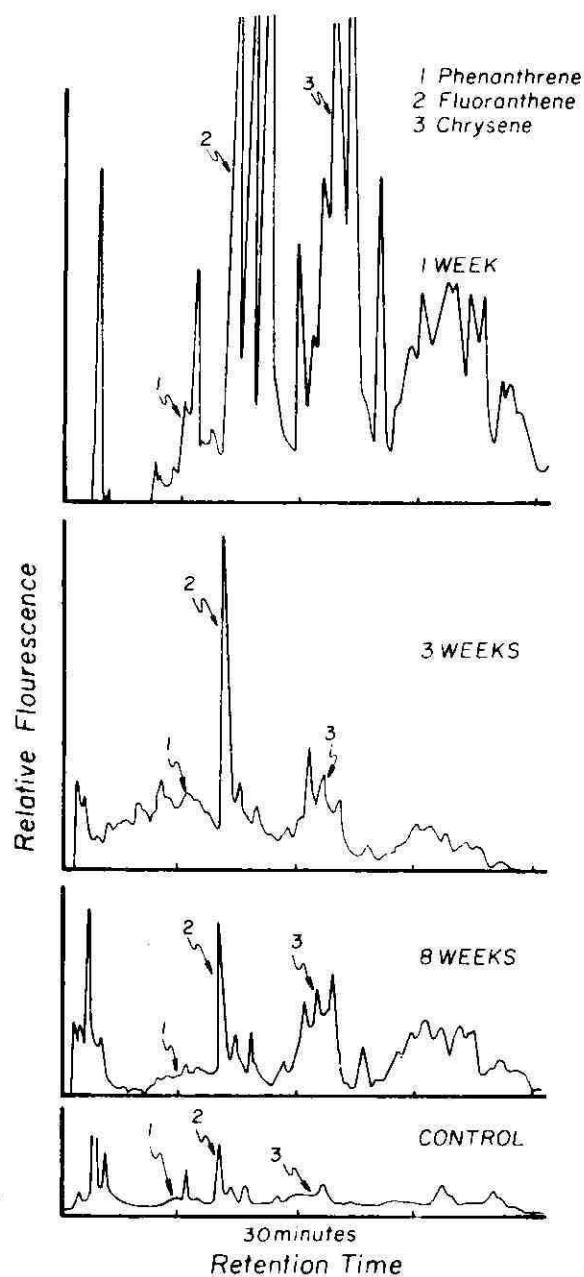


Figure 2.8. High-Pressure Liquid Chromatograms of Lipid Extracts of Oysters Exposed to High Levels of Fuel Oil

Oysters were collected from a 30 m² portion of marsh at different times after exposure to 75 liters of fuel oil No. 5. Also included is a chromatogram of oysters from the control area. Column was a Spherisorb ODS run isocratically with 65% methanol in water with a flow rate of 2 ml/min at 50°C.

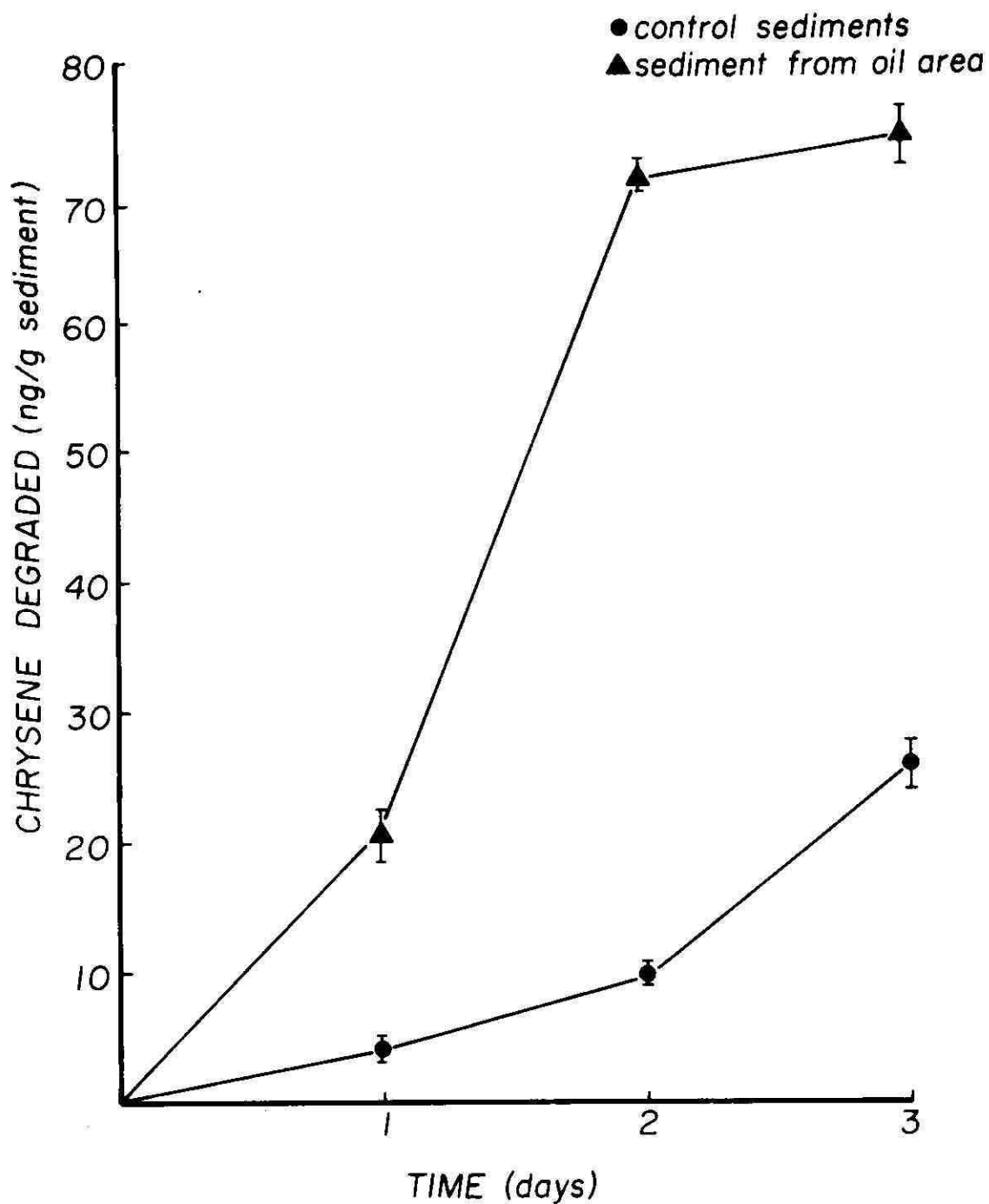


Figure 2.9. Amount of ^{14}C -Chrysene Degraded with Time in Sediment from a Fuel Oil Treated and Untreated Marsh.

^{14}C -Chrysene (6.3 mci/mm) was added to sediment-water slurries from either the control or fuel oil treated marsh sediments with a final concentration of 2.5 $\mu\text{g/g}$ sediment. Amount of degradation was determined by collecting ^{14}C - CO_2 produced at the different time intervals indicated.

Table 2.1. Summary of total adenylates, bacterial numbers and metabolic processes in an oiled salt marsh and in a non-treated control area. Significance between paired values (control vs. oil and surface vs. 5 cm in both areas) was evaluated by the signed test for paired variance. Values in parentheses are the number of samples used to compute the mean \pm S.E.

	Surface		5 cm	
	Control	Oil	Control	Oil
Total adenylates $\mu\text{g/cc}$	$^{\dagger*}2.90 \pm .65$ (10)	$^{\dagger*}4.57 \pm 1.18$ (10)	$^{\dagger*}1.56 \pm .83$ (10)	$^{\dagger*}2.56 \pm .81$ (10)
Bacteria 10^9 cells/cc	$^{\dagger}1.10 \pm .19$ (12)	$^{\dagger}0.81 \pm .13$ (12)	$^{\dagger}0.56 \pm .09$ (12)	$^{\dagger}0.53 \pm .10$ (12)
O ₂ Demand nmoles/g·h	90.5 ± 33.3 (17)	131 ± 59.9 (17)	--	--
CO ₂ Production nmoles/g·h	$^{\dagger*}136 \pm 75$ (16)	$^{\dagger*}57.6 \pm 28$ (16)	$^{\dagger}360 \pm 86$ (14)	$^{\dagger}986 \pm 353$ (16)
C ₂ H ₄ Production nmoles/g·h	$^{\dagger}1.58 \pm .46$ (13)	$^{\dagger}1.72 \pm .83$ (17)	$^{\dagger}29.5 \pm 12.2$ (12)	$^{\dagger}139 \pm 85$ (15)
CH ₄ Production nmoles/g·h	$^{\dagger}0.97 \pm .78$ (13)	$^{\dagger}0.21 \pm .09$ (17)	$^{\dagger}54.5 \pm 26.4$ (8)	$^{\dagger}15.4 \pm 6.65$ (17)
N ₂ O Reduction	$^{\dagger}5.53 \pm 4.65$ (14)	$^{\dagger}3.57 \pm 1.95$ (12)	$^{\dagger}237 \pm 118$ (16)	$^{\dagger}468 \pm 311$ (15)

† Significant difference ($p < .05$) between surface values and values obtained from 5 cm in control area and oil spill area.

*Significant difference ($p < .05$) between values from control area and oil spill area.

densities in winter followed by a spring-summer maximum and an autumn decline (Figure 2.10, Table 2.2). Few organisms were found at the marsh site in January 1977, due to an exceptionally cold winter that resulted in high mortality of the epifauna. In spring, total animal density increased to 5 organisms per m^2 with a biomass of 7.2 g AFDW per m^2 . In August, a biomass of 7.2 AFDW per m^2 was observed. In the fall, density decreased to 15 individuals per m^2 with a biomass of 3.3 g AFDW per m^2 . L. irrorata, U. pugnax and M. demissus all showed large density increases in August 1977, and very low biomass and density values in January 1976, and February 1978 (Figure 2.11).

A number of effects were observed on the marsh epibenthos as a result of the addition of oil. The early spring increase in total density and biomass was depressed in the oiled area but was quite evident in the control area (Figure 2.10). The total density for the control area in February 1979, was 17 organisms per m^2 with a biomass of .4 g AFDW per m^2 , while the oiled area had 2 organisms per m^2 and a biomass of .05 g AFDW per m^2 during the same sampling period. A large density increase occurred in the oiled area in April 1979 resulting in 28 organisms per m^2 and a biomass increase to .3 g AFDW per m^2 .

The epifauna showed three responses to the oil spill. These included an increase, a decrease or no change in macrofauna species. A initial increase occurred in N. obsoleta density (55 snails per m^2) in the oiled area one month after the spill (Figure 2.12). This increase was due to immigration of adult snails from untreated areas presumably to scavenge on animals killed by the oil. In the spring, the density in the oiled areas decreased to <1 snail per m^2 ; while in the control area, densities increased to 33 snails per m^2 . The distribution of size classes of N. obsoleta in December 1979, indicated very little difference between the oiled area and the control area (1.29 cm vs. 1.24 cm) (Figure 2.13).

There was an immediate decrease in periwinkles, L. irrorata, in the oiled area between December 1978, through February 1979 (Figure 2.12). During this period, the density decreased from 3 to 2 per m^2 in the oiled area but increased from 3 to 16 in the control area. Five months after the oil spill (April 1979), periwinkle density increased to 16 individuals per m^2 in the oiled area, with a slight biomass increase. The increased periwinkle density in the oiled area was due to recolonization of the area by juvenile forms. This can be shown by a comparison between size-class histograms for Littorina from oiled and control areas on April 1979 (Figure 2.14). A much smaller mean size-class was observed in the oiled area (.98 cm) than in the control area (1.39 cm).

A third response was that of no significant change in density or biomass after the spill, as shown by U. pugnax (Figure 2.12). Crab density values were <1 and 10 individuals per m^2 in February and April 1979, respectively, in the oiled area, and <1 and 8 individuals

Table 2.2. Seasonal variation in density and biomass (AFDW) of the five marsh macrofaunal speices at the marsh site. Values are given as means \pm 1 SD, each mean based on 13 samples.

GOOSE FIELD SAMPLING

	Oil Spill																									
	1976 Nov.			1977 Jan		April		August		Nov.	1978 Feb.		April		August		Dec.		1979 Feb.		April		June		August	
	Density(no of individuals·m ⁻²)																									
<u>Littorina</u>	4.67	±4.33	(12)	0		3.50	±5.91	(14)	13.33	±22.10	5.08±5.44	1.92±2.50	2.77±2.42	4.62±7.43	2.92± 3.30	9.54±27.55	13.62±12.50	6.31± 8.88	2.23±1.96							
<u>Modiolus</u>	2.42	±3.70	(12)	0		0.64	±1.39	(14)	1.08	± 1.78	2.08±2.56	1.46±3.86	2.23±3.19	1.85±3.02	1.08± 1.89	0.15± 0.38	0.62± 1.50	1.54± 3.15	1.31±2.14							
<u>Uca</u>	2.33	±1.21	(6)	0		4.00	±4.23	(2)	28.00	±12.24	6.17±5.08	0.31±0.63	3.77±3.35	7.92±6.02	0.62± 1.04	0.46± 0.78	8.62± 6.19	11.62±10.28	21.31±9.86							
<u>Sesarma</u>									4.5	± 5.32	0.92±2.18	0.15±0.38	0	0	0	0	0.31± 0.75	0.77± 1.42	0.46±0.78							
<u>Panopaeus</u>	0.83	±1.17	(6)	0		2.00	±2.83	(2)	0.25	± 0.45	0.15±0.55	0	0.23±0.60	0	0	0	0	0.31± 0.85	1.38±3.20							
<u>Nassarius</u>																41.08±81.69	18.08±64.58	0	14.92±41.76	0						
	Avg. Dry Wgt. (g·m ⁻²)																									
<u>Littorina</u>	1.13	±1.18	(12)	0		3.12	±6.28	(14)	11.17	±25.17	3.74±6.39	1.03±1.80	2.40±2.20	3.45±0.43	0.38± 0.43	0.47± 0.50	0.34± 0.22	0.25± 0.22	0.34±0.35							
<u>Modiolus</u>	0.93	±1.30	(12)	0		10.09	±21.26	(14)	15.20	±26.41	2.55±30.10	0.59±1.13	1.16±1.55	0.50±0.46	0.26± 0.42	0.24± 0.58	0.03± 0.20	0.41± 0.53	0.55±0.75							
<u>Uca</u>	0.68	±0.78	(4)	0					4.60	± 2.56	1.42±1.32	0.01±0.03	0.82±0.83	0.21±0.10	0.02± 0.06	0.04± 0.10	0.15± 0.05	0.23± 0.16	0.20±0.07							
<u>Sesarma</u>									0.538±	1.03	0.10±0.33	0.01±0.01	0	0	0	0	0.06± 0.19	0.21± 0.44	0.44±0.87							
<u>Panopaeus</u>	1.57	±2.72	(3)	0					0.722±	1.33	0.01±0.04	0	0.50±1.26	0.33±1.07	0	0	0	0.25± 0.71	0.05±0.09							
<u>Nassarius</u>																0.06± 0.17	0	0.06± 0.14	0							
	Biomass (g AFDW·m ⁻²)																									
<u>Littorina</u>	0.13	±0.11	(12)	0		0.45	±.04	(14)	2.93	± 6.37	0.32±0.53	0.11±0.24	0.24±0.26	0.05±0.07	0.05± 0.05	0.06± 0.07	0.05± 0.05	0.03± 0.03	0.03±0.03							
<u>Modiolus</u>	0.09	±0.13	(12)	0		1.05	±2.27	(14)	1.26	± 2.07	2.26±2.95	0.50±0.99	0.89±1.29	0.41±0.37	0.20± 0.32	0.16± 0.39	0.06± 0.14	0.26± 0.39	0.44±0.58							
<u>Uca</u>	0.37			0		0.06	±0.22	(14)	2.35	± 1.29	0.63±0.64	0.01±0.02	0.46±0.45	0.11±0.05	0.01± 0.03	0.03± 0.06	0.08± 0.03	0.14± 0.10	0.10±0.03							
<u>Sesarma</u>									0.357±	0.71	0.04±0.13	0	0	0	0	0	0.03± 0.10	0.07± 0.11	0.12±0.21							
<u>Panopaeus</u>	0.62			0		0.02	±0.10	(14)	0.278±	0.52	0	±0.02	0	0.21±0.54	0.13±0.41	0	0	0	0.10± 0.27	0.03±0.06						
<u>Nassarius</u>																0.07± 0.14	0.01± 0.01	0	0.004± 0.01	0						

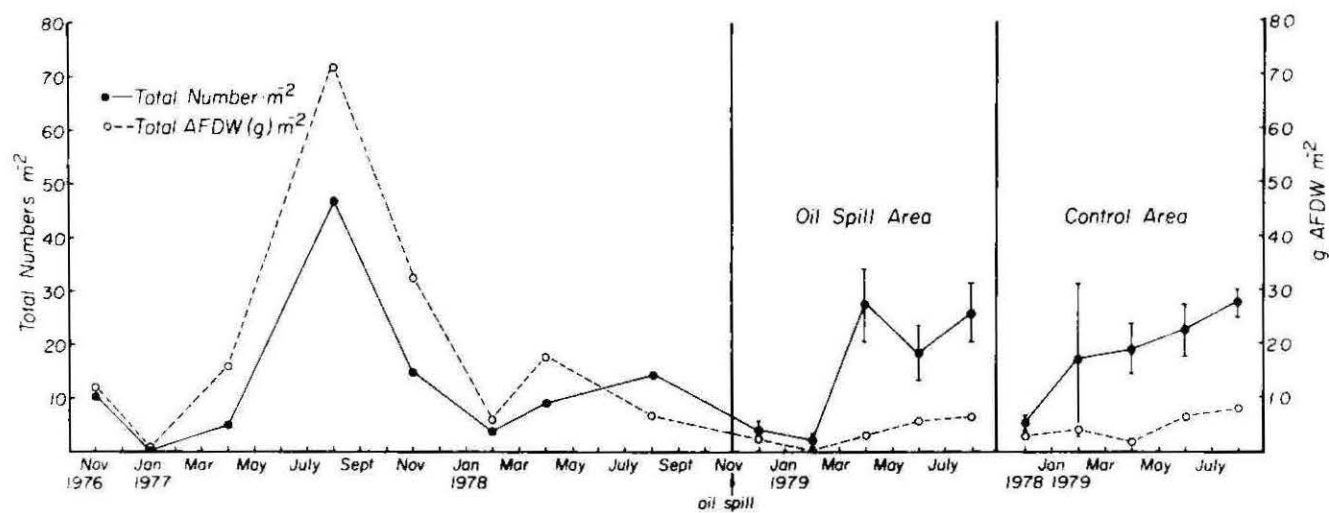


Figure 2.10. Seasonal Variation in Density and Biomass (AFDW) of Selected Marsh Macrofauna Before and After the November, 1978 Oil Spill

Values are given mean \pm the standard error based on 13 samples.

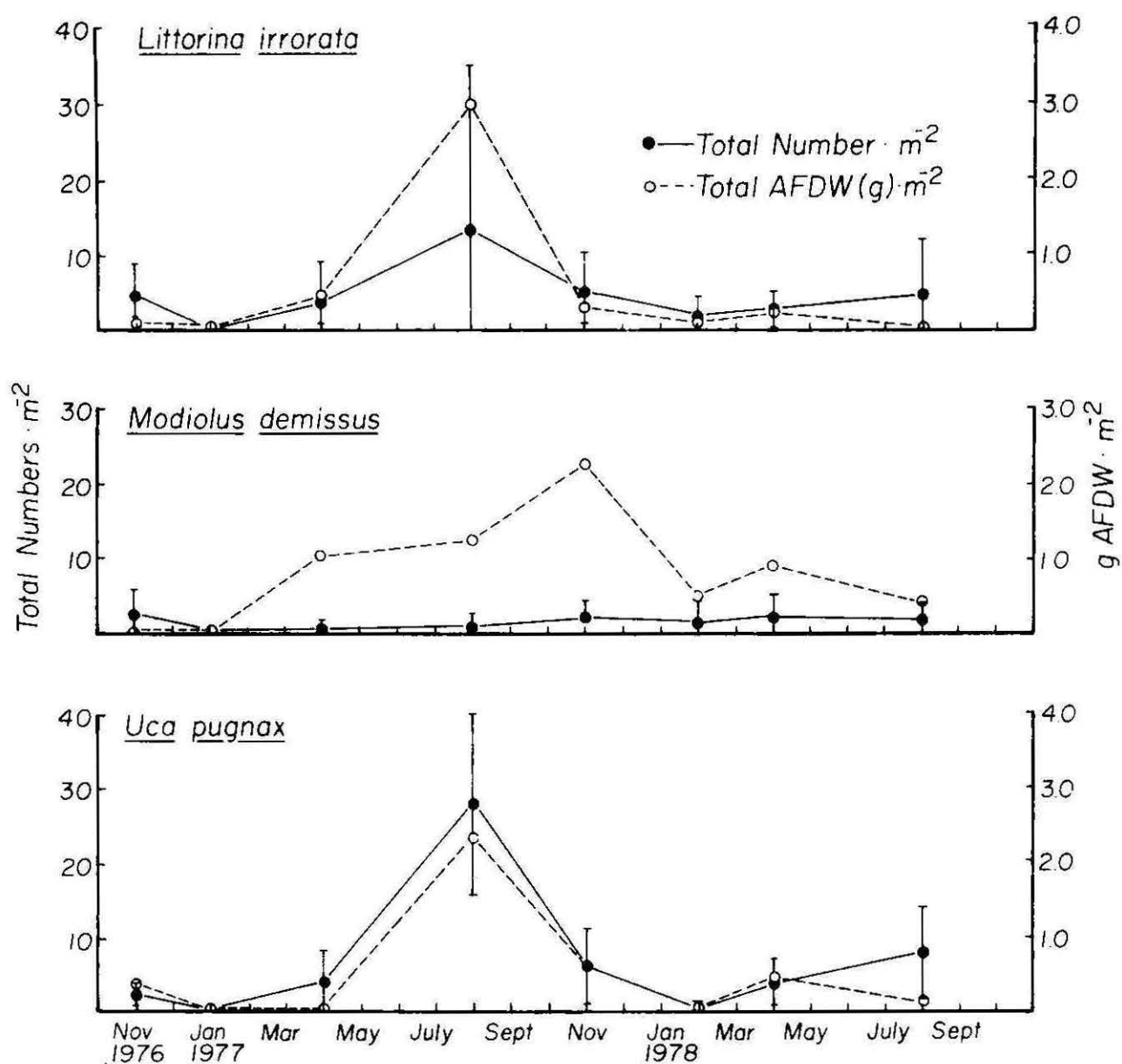


Figure 2.11. Seasonal Variation in Density and Biomass (AFDW) Of *Littorina irrorata*, *Modiolus demissus*, and *Uca pugnax* at the Marsh Site Before the Oil Spill

Values are given as mean \pm one standard deviation based on 13 samples.

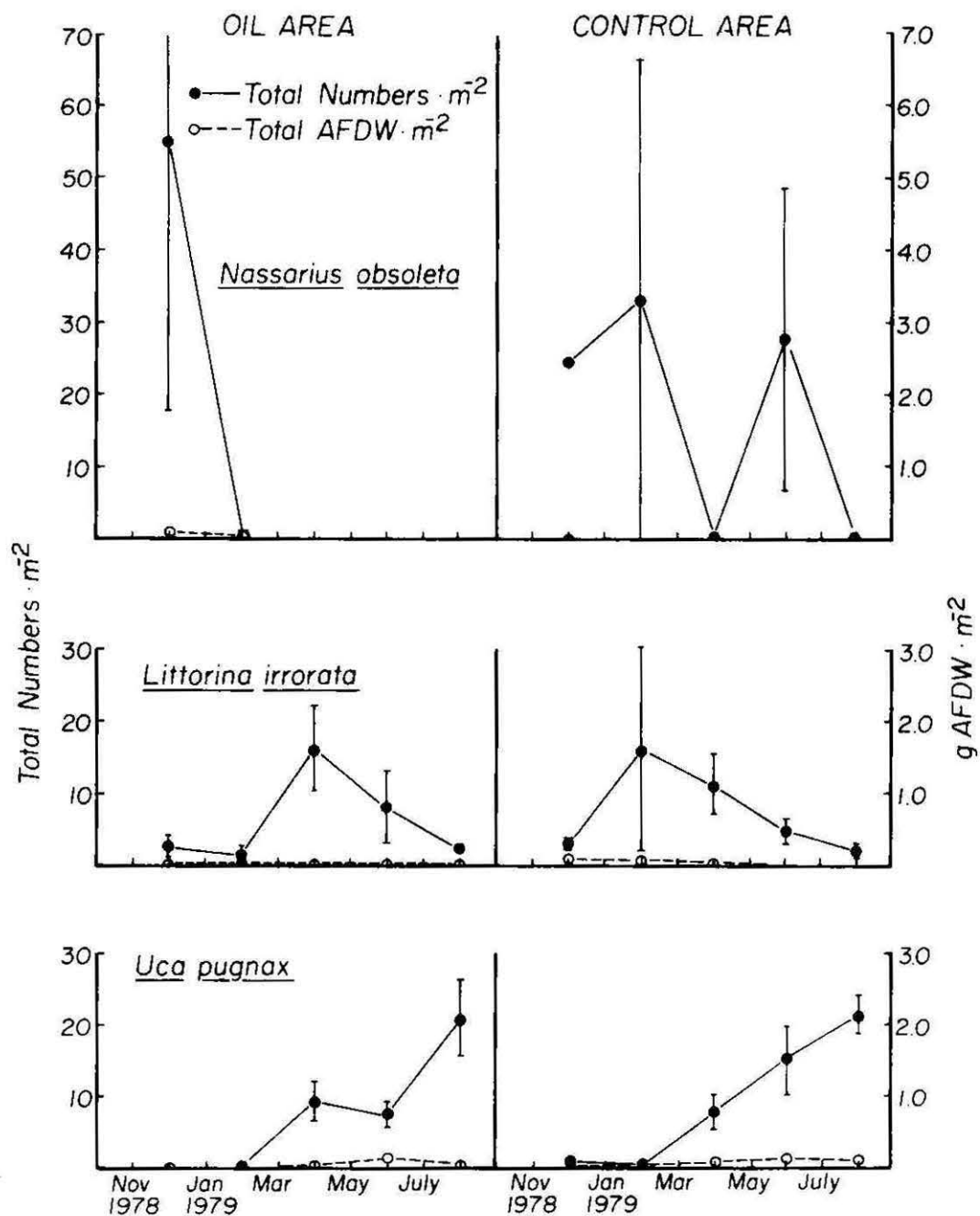


Figure 2.12. Seasonal Variation in Density of *Nassarius obsoleta*, *Littorina irrorata*, and *Uca pugnax* at the Marsh Site after November, 1978 Oil Spill

Values are given as mean \pm the standard error based on 13 samples.

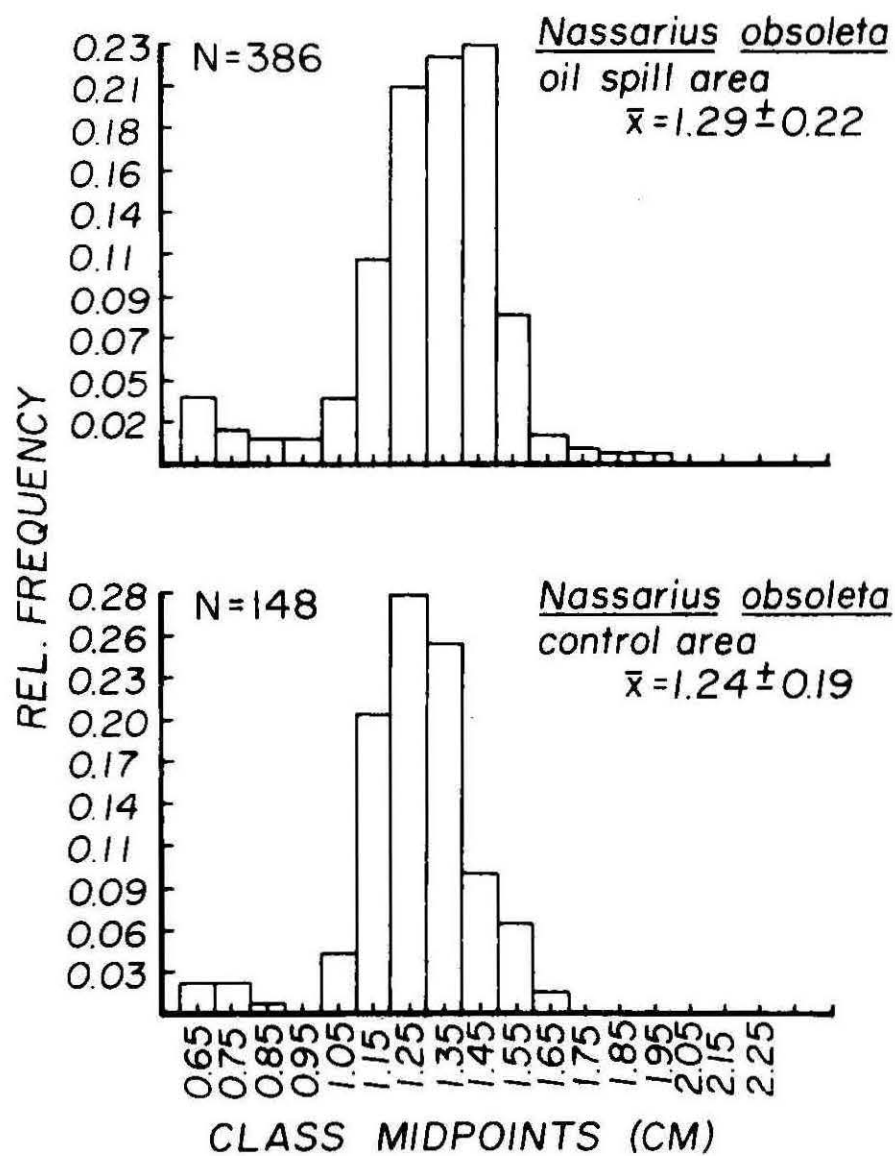


Figure 2.13. Size Class Histograms for *Nassarius obsoleta* at Oiled and Control Areas in December, 1978.

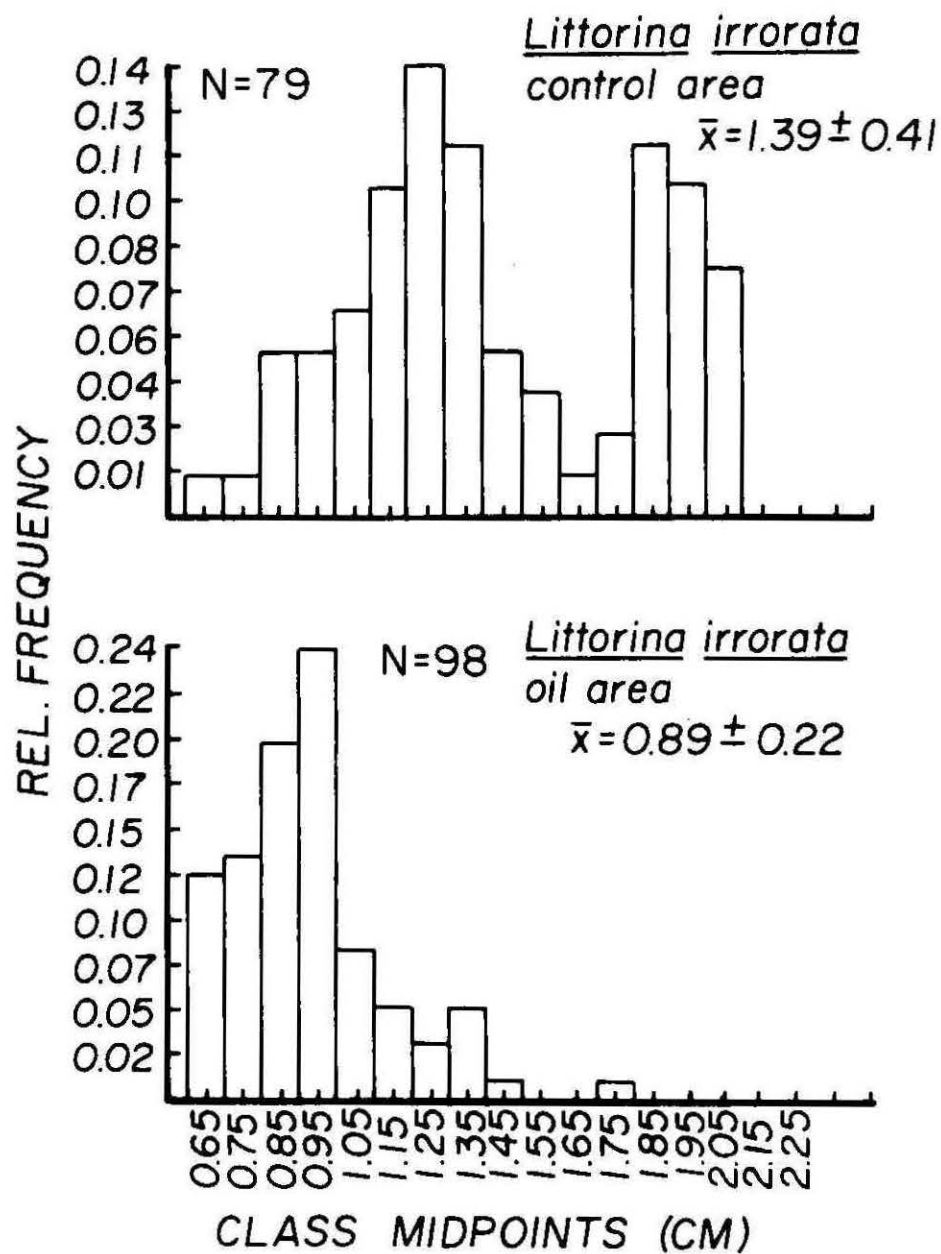


Figure 2.14. Size Class Histograms for *Littorina irrorata* at Oiled and Control Areas in April, 1979.

per m² in the control area during the same time period, respectively. The bivalves, Modiolus demissus and Crassostrea virginica, also showed no significant change in density before and after the oil treatment.

DISCUSSION

The polycyclic aromatic hydrocarbons selected for analysis are important components of heavy fuel oils. For example, the concentrations of phenanthrene, fluoranthene and chrysene in a No. 6 fuel oil are 482, 240 and 196 µg/g, respectively (Pancirov and Brown, 1975). In oil contaminated sediments from Port Angeles Harbor, Washington, the concentrations of phenanthrene, fluoranthene and pyrene averaged 190, 590 and 340 ng/g dry sediment, respectively (MacLeod *et al.*, 1977). The concentrations of phenanthrene + anthracene, fluoranthene and chrysene in sediments from Hiraka Bay, Japan, which has both industrial and domestic effluents, were 800, 800 and 400 ng/g dry sediment, respectively (Matsushima, 1979). In our oiled-marsh study, the highest concentrations observed in the sediment for phenanthrene, fluoranthene and chrysene were 115, 105, and 70 ng/g wet sediment, respectively.

A number of studies have documented the accumulation of hydrocarbons by the ribbed mussel, Modiolus demissus and oyster, Crassostrea virginica, after exposure to oil (Bieri and Stamoudis, 1977; Blumer *et al.*, 1970; Burns and Teal, 1971; Lee, 1977; Lee *et al.*, 1978; Neff *et al.*, 1976). The half-life of anthracene, fluoranthene and benz(a)anthracene in oysters exposed to a dispersion of crude oil in a controlled ecosystem in western Canada was 3, 5 and 9 days, respectively. (Lee *et al.*, 1978). The aromatic hydrocarbons in oysters collected from our oil treated marsh had half-lives of approximately 30 days. The longer half-life in our oysters was presumably due to continued input of resuspended oil from the sediment.

After an initially rapid discharge of hydrocarbon, low concentrations were retained in the tissues. Fluoranthene and chrysene were still detected in oysters and mussels 150 days after the spill. Bieri and Stamoudis (1977) studied uptake by oysters on the coast of Virginia exposed to fuel oil No. 2. The maximum concentration of three-ringed aromatics, including phenanthrene, was 1.41 µg/g after 4 days of exposure followed by a decrease to .56 µg/g after 10 days. Fuel oil hydrocarbons were still reported in oysters from an area in Buzzards Bay, Massachusetts several years after an oil spill (Blumer and Sass, 1972). The persistence of petroleum hydrocarbon in bivalves after exposure to oil depends on such factors as the size of the spill, type of oil and the amount of "clean" water circulating into the exposed area.

A number of studies have examined the effects of oil on salt marshes of the southeastern United States (Bender *et al.*, 1977; DeLaune *et al.*, 1979; Holt *et al.*, 1978; Lytle, 1975). The oil adheres to Spartina plants which results in yellowing and death of the leaves.

Plants recover by producing new growth which is usually seen within two to three weeks after the spill. Only very large oil spills or continual oiling will kill *Spartina* rhizomes. In our experiments, the *Spartina* leaves yellowed and green shoots were observed three weeks after the spill.

Our studies indicated little effect of oil on a number of microbial processes. Observed increases in hydrocarbon degradation rates presumably resulted from increases in the numbers of petroleum degrading bacteria which have been reported after oil spills on salt marshes (Kator and Herwig, 1977). The addition of oil to marsh sediment does not affect the reduction rate of nitrate, manganese, iron and sulphate on the levels of chitinolytic, cellulolytic and heterotrophic bacteria and fungi (DeLaune *et al.*, 1979; Kator and Herwig, 1977). We reported above that oil did not affect bacterial numbers, oxygen demand, ethylene production, methane production and N_2O reduction.

The mud snail, *Nassarius obsoleta*, and southern periwinkle, *Littorina irrorata*, illustrate two modes of recolonization, i.e., immigration and larval settling, which occurred in the oiled area. The large increase in *Nassarius* in the oiled area was presumably due to migration from adjacent untreated areas to feed on dead animals. Many adult *Littorina* were killed by the oil and recolonization was by larval settling. Thus, juvenile forms dominated during the spring in the oiled area. Monk *et al.*, (1978) reported a decrease in the population of *Littorina saxatilis* after a spill of diesel fuel on the coast of Norway. The hatching success of *Littorina littorea* collected from an area of Norway which was exposed to a large crude oil spill was significantly less than that of a control population (Staveland, 1979). The decrease in *Littorina* observed by us was due to direct mortality. Juvenile forms recolonized the oiled area but whether their reproductive capabilities were impaired cannot be answered. However, since concentrations of aromatic hydrocarbons in the sediment were very low by the time juvenile *Littorina* recolonized the area, we predict that their reproductive capabilities would not be affected.

As previously noted, there were no differences between *U. pugnax* population in the oiled and control areas. Both areas had low densities and biomass of crabs. This may be due to the winter behavior of the crabs, in that they then become inactive and burrow into the mud. Therefore, the effects of the oil on the crab population were coupled with the seasonal changes, and definite alterations in the population could not be determined in our short study.

Previous studies on the effects of oil and oil products on marine communities (Blumer, 1971; Scarratt and Zitko, 1972; Michael, 1977) emphasized the importance of separating the effects of oil on benthic populations from changes due to seasonal and yearly trends. Included in seasonal changes are major alterations in populations due to naturally occurring catastrophes, such as exceptionally harsh

winters or abnormally low salinities. Declines in population size or structure due to catastrophic stresses may completely mask alterations due to the effects of the oil, unless an untreated area is available for comparison.

The rate at which marsh fauna recovers from an oil spill depends on the extent and intensity of the spill. The rate of epibenthic recolonization by larval recruitment and immigration of organisms from nearby areas will depend on the size of the area affected and the remoteness of the parent populations.

SUMMARY

After the addition of a heavy fuel oil to a Spartina marsh in the fall, the highest concentrations of phenanthrene, chrysene and fluoranthene in the sediment were 112, 105 and 75 ng/g sediment, respectively. These polycyclic aromatic hydrocarbons decreased in concentration, and 150 days after the spill phenanthrene was not detectable, and the concentrations of fluoranthene and chrysene were 15 and 20 ng/g, respectively. The times for these hydrocarbons to decrease to 50% of their highest values, i.e. half-life, were approximately 100, 70 and 30 days in sediment, mussels and oysters, respectively. The rapid release of hydrocarbons by oysters relative to mussels may be due to the position of oysters on top of the sediment while mussels are in the sediment. Thus, mussels were continually exposed to oiled sediment, whereas oysters obtained hydrocarbons only from water or suspended particles.

The various microbial processes important in salt marsh metabolism and productivity, including bacteria numbers, oxygen demand, ethylene production, methane production and N_2O reduction, were not affected by the oil. Microbial hydrocarbon degradation rates were very high in the oiled marsh, presumably due to increases in the numbers of petroleum degrading bacteria.

One of the first changes in the marsh after the addition of oil was the yellowing and death of Spartina leaves. After three weeks green shoots were observed, and in the spring no differences were noted between Spartina from the oiled and control areas. The various species of benthic macrofauna responded in three ways to oil addition. These included no change, an increase, or a decrease in the population. No changes were noted in the populations for fiddler crabs, oysters and mussels. Mud snails, Nassarius obsoleta, increased in density after the spill due to immigration of adult snails from untreated areas to scavenge on animals killed by the oil. Many of the adult periwinkles, Littorina irrorata, were killed by the oil. In the spring, juvenile periwinkles recolonized the oiled areas as a result of larvae settling.

Addition of a heavy fuel oil to a Georgia salt marsh resulted in high concentrations of polycyclic aromatic hydrocarbons in the sediment and benthic animals. These initially high concentrations

rapidly decreased during the 20-week period following the spill. Initially, effects of oil were observed on the marsh macrofauna populations; but nine months after the spill, there appeared to be little or no effect on the dominant marsh epifaunal species.

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