Environ. Sci. Technol. **1998**, *32,* 3719−3723

Photooxidation of Crude Oils

ROBERT M. GARRETT,*,† INGRID J. PICKERING,‡ COPPER E. HAITH,† AND ROGER C. PRINCE†

Exxon Research and Engineering Company, Route 22 East Annandale, New Jersey 08801, and Stanford Synchrotron Radiation Laboratory, Stanford University, SLAC, P.O. Box 4349, MS 69 Stanford, California 94309

Photooxidation is a potentially significant process in the degradation of crude oil spilled at sea. Moreover, a fundamental understanding of the effect of photochemical degradation on crude oil is a prerequisite for providing an accurate description of the recent history and potential fate of oil spilled in a marine environment. In this report we examine the effect of ultraviolet illumination on crude oil using a variety of techniques including gas chromatography/mass spectroscopy and X-ray absorption spectroscopy. The saturated compounds are resistant, but the aromatic compounds are particularly sensitive to photooxidation. Greater size and increasing alkyl substitution increase the sensitivity of aromatic compounds to photochemical oxidation. The photooxidized products appear in the resin and polar fractions as determined by thin-layer chromatography. Thus, the effect of photooxidation is distinctly different from that of biodegradation, where larger and more substituted compounds are more resistant to degradation. Perhaps surprisingly, X-ray absorption spectroscopy indicates that the aliphatic sulfur compounds are more readily oxidized than the thiophenic compounds with the sulfur being oxidized to sulfoxides, sulfones, sulfonates, and sulfates in approximately equal amounts.

Introduction

Significant amounts of petroleum enter the marine environment each year from municipal and industrial sources, transportation, natural oil seeps, and oil spills (*1*). The environmental impact of oil contamination in marine environments is potentially serious, and thus much attention has recently been focused on the fate of oil in the environment and the natural mechanisms by which oil is degraded. A fundamental understanding of the many processes affecting crude oil spilled in marine environments is required for elucidating the recent history and predicting the future fate of the oil and should prove to be a valuable resource in the effort to develop innovative remediation technologies.

Most crude oils spilled at sea spread rapidly to form slicks with greatly increased surface area. This oil is immediately subject to a variety of abiotic and biotic processes including evaporation, dispersion, photooxidation, and microbial degradation. The formation of slicks promotes the evaporation of those compounds with a significant vapor pressure, the dissolution of those compounds with appreciable aqueous solubility, and likely the photooxidation of susceptible compounds. The subsequent dispersion of oil into the water column further increases its surface area, thereby promoting microbial degradation which occurs at the oil−water interface.

The microbial degradation of crude oil is a well understood phenomenon which has been reviewed in detail (*2*). Microbes readily degrade the alkanes and unsubstituted aromatic compounds. Alkyl substituted aromatic compounds are degraded less readily than the parent molecules, with decreasing rates of degradation associated with greater alkyl substitution.

The phenomenon of photooxidation of crude oil via natural sunlight is less well understood but may provide an opportunity for the introduction of novel procedures for the remediation of marine oil spills. In fact, the use of catalyst-coated microbeads to enhance crude oil photooxidation has been proposed as one potential strategy (*3, 4*). Wise and Sancier have reported evidence that beaches may undergo a photocatalytic self-cleaning oxidation of crude oil contaminants (*5*). There is recent evidence that methyl substituted aromatic molecules photochemically oxidize at a faster rate than the parent compounds (*6, 7*). The products of photooxidation of aromatic hydrocarbons are the corresponding alcohols, aldehydes, ketones, and acids (*8*−*13*).

The above reports, however, have focused primarily on single compounds and simple mixtures of hydrocarbons and, while informative, offer little information regarding the effect of UV irradiation on unrefined products. In fact, a major difficulty in understanding the fate of oil in the environment is its complexity. Crude oils are mixtures of hundreds of different hydrocarbons and other organic molecules containing heteroatoms. Some hydrocarbons are individually quite abundant and are ideally analyzed by very specific techniques such as gas chromatography coupled with mass spectrometry. Conversely, many individual species are present at too low abundance for this technique, or they are nonvolatile and cannot be analyzed by gas chromatography. Such molecules can be detected by more generic properties such as solubility. For example, petroleum components can be classified into four general categories, the saturates, aromatics, resins, and asphaltenes, by thin-layer chromatography. The saturates include the straight and branched chain alkanes and cycloalkanes. The aromatic fraction consists of aromatic mono- or polycyclic compounds, often with alkyl or cycloalkane substituents. The resins and asphaltenes, which are nonvolatile, contain heteroatoms such as oxygen, nitrogen, and sulfur but differ in their size and solubility. X-ray absorption spectroscopy, particularly at the sulfur K-edge, is another tool for characterizing oils. We have used all three techniques to address the changes that occur in weathered crude oil when it is subjected to UV light in the presence of air. The data presented here afford a greater understanding of the effect of photochemical oxidation on crude oil and should prove useful in efforts to determine the recent history and potential fate of crude oil spilled in marine environments.

Materials and Methods

Crude Oils. We have used Alaska North Slope, Forties, and Gullfaks crude oils. These have API (American Petroleum Institute) gravities (defined as [142.5/(specific gravity)] − 131.5, and expressed as degrees) of 29.0, 40.7, and 35.6 and sulfur contents of 1.06, 0.29, and 0.28%. The majority of the experiments used an artificially weathered Alaska North Slope crude oil that had been heated to 272 °C under a partial

* Corresponding author phone: (973)730-2656; fax: (973)730-3301; e-mail: rmgarre@erenj.com.
† Exxon Research and Engineering Company.
‡ Stanford University.

10.1021/es980201r CCC: $15.00
Published on Web 10/02/1998

vacuum so as to have lost 30% of its initial weight by evaporation. This approximates the extent of weathering this oil is likely to undergo while floating as an oil slick (*14*) and also minimizes evaporative losses during experimental manipulations. Qualitatively similar results were obtained with whole Forties and Gullfaks crudes, both from the North Sea. We have chosen these oils because all have been spilled at sea in recent years: Alaska North Slope from the *Exxon Valdez* (*15*), Gullfaks from the *Braer* (*16*), and Forties from the *Sea Empress* (*17*).

UV Irradiation. Dry films of crude oil were prepared by dissolution of 50 mg of crude oil in 5 mL of methylene chloride in a 75 mm glass crystallization dish and allowed to evaporate. Artificial oil slicks were created by floating 50 mg of crude oil on artificial seawater (Sigma S-9883) containing 0.2% sodium azide in a 75 mm glass crystallization dish. Thickness of the crude oil phase was estimated to average 15 μm. The samples were irradiated for 48 h via a 55 W UV transilluminator (VWR Scientific model LM 20E) operated in the 302 nm mode at a distance of approximately 15 cm. Control samples were prepared as above and maintained under ambient light conditions. Samples were extracted with methylene chloride and concentrated to 15 mg/mL for analysis.

Gas Chromatography/Mass Spectroscopy. Analysis of the oil by gas chromatography/mass spectroscopy (GC/MS) essentially followed published procedures (*18*). Separation was performed on a Hewlett-Packard HP 5890 gas chromatograph fitted with a 30 m × 0.25 mm fused silica capillary column with 5% cross-linked phenyl methyl silicone as the stationary phase. Helium was used as the carrier gas at a flow rate of 1 mL/min. Samples of 1 μL were injected automatically by a HP 6890 Injector. The column temperature was set to 45 °C for the first 4 min, increased 8 °C/min to a temperature of 270 °C, then increased 5 °C/min to 310 °C, and maintained at 310 °C for 5 min. Mass spectral data were obtained with a Hewlett-Packard 5972 mass selective detector at an electron energy of 70 eV over a mass range of 35−500 atomic mass units in the total ion mode. Spectral tuning with perfluorotributylamine followed USEPA method 8270C.

X-ray Absorption Spectroscopy. X-ray absorption spectra at the sulfur K-edge were recorded on beamline 6-2 at the Stanford Synchrotron Radiation Laboratory using a Si(111) double crystal monochromator and a downstream nickel-coated harmonic rejection mirror. Data were collected at room temperature, and incident intensity was measured using a helium-filled ion chamber. Spectra were recorded in fluorescence using a nitrogen-filled Stern−Heald−Lytle detector (*19*, *20*). Data were energy-calibrated with respect to a sodium thiosulfate powder standard, where the first maximum was assumed to be 2469.2 eV (*21*).

Thin-Layer Chromatography. Analysis of samples by thin-layer chromatography was conducted using 0.9 mm Chromarod quartz rods sintered with silica gel (Iatron Laboratories, Tokyo) (*22*). Samples of 1 μL were applied and chromatographed in *n*-hexane for 35 min, toluene for 15 min, and 95% methylene chloride, 5% methanol for 2 min. Chromatographs were analyzed on an Iatroscan MK-5 flame ionization detector (Iatron Laboratories).

Results and Discussion

Crude oil was irradiated with ultraviolet light and analyzed by gas chromatography/mass spectroscopy, X-ray absorption spectroscopy, and thin-layer chromatography to identify which components of the crude oil are most susceptible to photooxidation. Our desire was to generate an easily measurable effect on the oil, thus, conditions were designed to yield a high degree of photooxidation. Crude oil was floated on the surface of artificial seawater to simulate a marine oil slick with an estimated average thickness of 15 μm. After 48 h of irradiation the oil was extracted and concentrated for analysis. The data presented here are the average of two experiments using Alaska North Slope crude oil. Other experiments with Alaska North Slope, Forties, and Gullfaks crude oils as artificial oil slicks on seawater and as thin films on glass yielded similar results.

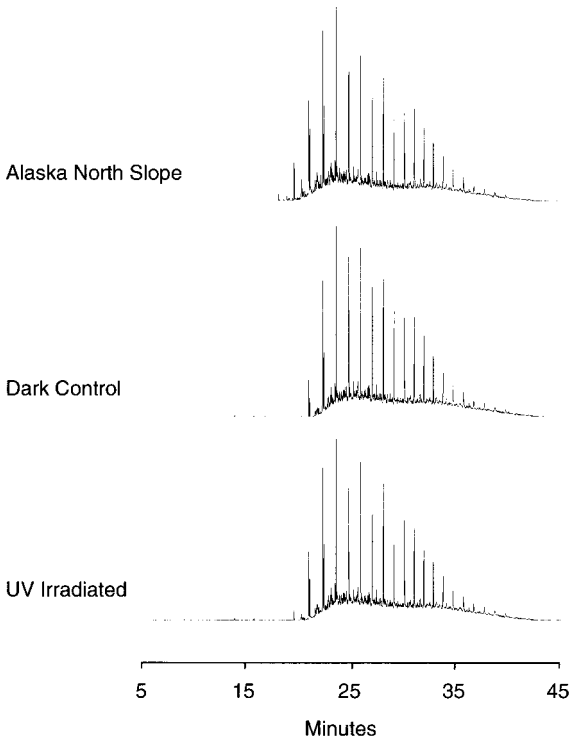

FIGURE 1. Total ion chromatograms of initial, control, and irradiated oils. The resolved peaks are mainly the *n*-alkanes, present at 1000−3000 ppm in the initial oil.

Gas chromatography/mass spectroscopy was used to examine the initial oil, a dark control, and a UV irradiated sample. The mass spectrometer was operated in both total ion mode to characterize as much of the oil as possible and in selected ion mode to examine the degree of photooxidation of selected polynuclear aromatic hydrocarbons including phenanthrene, dibenzothiophene, chrysene, and their alkylated homologues. The methyl substituted aromatic compounds were analyzed together in this study without regard to the position of the methyl group. Likewise, the dimethyl and ethyl substituted compounds are grouped as the C2 compounds, and the trimethyl, methyl ethyl, and propyl compounds are grouped together as C3 compounds. The total ion chromatograms of the three samples are dominated by the straight chain saturates and appear quite similar with the exception of the loss of the lightest compounds in the two experimental samples, suggesting that the linear alkanes are resistant to photooxidation under these conditions (Figure 1). Figure 2 shows the single ion chromatogram for ions of $m/z = 191$, which detects the triterpanes including the hopanes (*23*). Quantitation of the GC/MS peaks in this study was by integration of total peak area normalized to hopane, and thus it is important to note that the hopane distribution was unaffected by UV irradiation under these conditions. Hopane is quite resistant to many biological and chemical processes, and the use of hopane as an internal GC/MS standard is well established (*24*−*27*).

Figure 3 shows the degree of photooxidation of some selected alkanes and aromatic compounds in the irradiated and control sample relative to the initial oil. The dark control samples exhibited a loss of approximately 10% of the alkanes

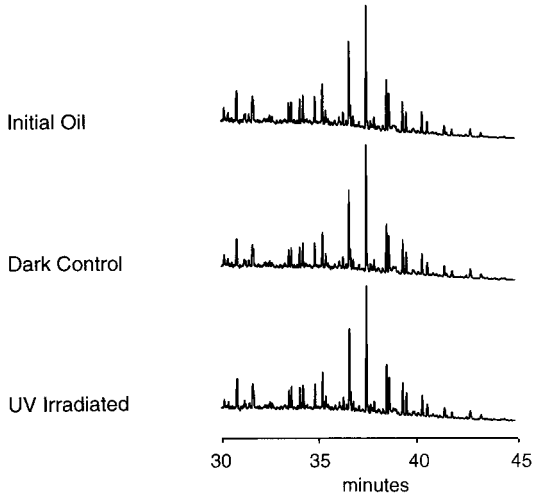

FIGURE 2. Hopane distribution in the initial, control, and irradiated oil. The largest peak, at approximately 37.4 min, is 17α(*H*),21β(*H*)-hopane, present at approximately 300 ppm in the initial oil.

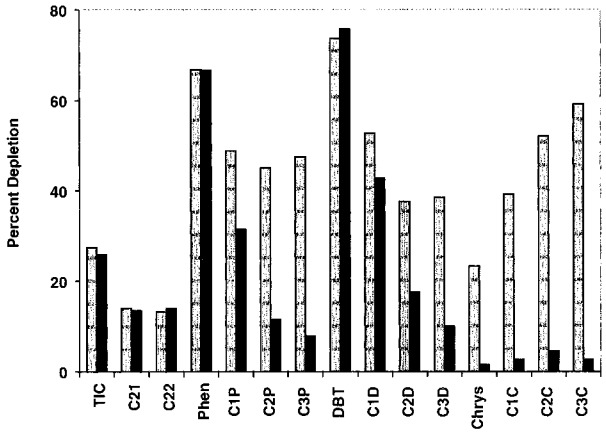

FIGURE 3. Depletion of selected alkanes and polycyclic aromatic hydrocarbons in irradiated crude oil. Percent depletion in the dark control (black) and UV irradiated (gray) samples is calculated relative to the initial oil and normalized to hopane. TIC is the total ion count. C21 and C22 refer to heneicosane and docosane, respectively. Phen, DBT, and Chrys refer to phenanthrene, dibenzothiophene, and chrysene respectively, and the prefixes C1, C2, and C3 refer to the methyl; dimethyl and ethyl; and trimethyl, methyl ethyl, and propyl species of phenanthrene (P), dibenzothiophene (D), and chrysene (C), respectively.

in the C20 range; this was due to evaporation and was expected since the oil film used in the study was quite thin, and the reaction vessels were maintained at room temperature. The UV light had no significant effect on the alkanes. The aromatics showed, as expected, a decreasing degree of evaporation with increasing alkyl substitution, a reflection of the decrease in vapor pressure due to greater molecular mass. The parent phenanthrene and dibenzothiophene were evaporated to the extent that any effect of the UV light was difficult to detect. Unlike the saturates, the alkyl substituted aromatic molecules exhibited remarkable sensitivity to UV radiation. Increasing alkyl substitution of the aromatic molecules resulted in a dramatic increase in the sensitivity to UV light, with the C3 compounds being approximately 50% degraded. This is more clearly seen in Figure 4, which shows the degree of photooxidation of the same compounds corrected by subtraction of that loss due only to evaporation. The three aromatic compounds shown here all exhibit increasing sensitivity to photooxidation with increasing alkyl substitution. Surprisingly, the parent phenanthrene and

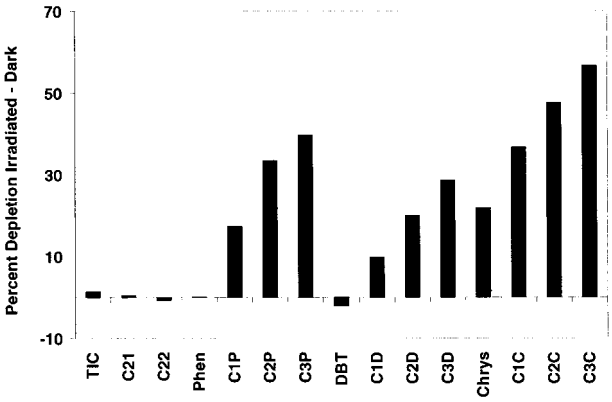

FIGURE 4. Photooxidation of selected polycyclic aromatic hydrocarbons in crude oil. Calculated depletion is derived by subtracting the percent depletion in the absence of UV irradiation from that observed in the presence of UV irradiation. Abbreviations are as for Figure 3.

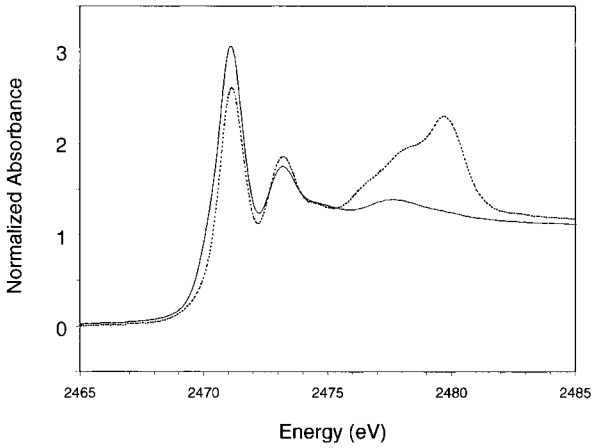

FIGURE 5. X-ray absorption spectra of irradiated (dashed line) and control (solid line) crude oil.

TABLE 1. Results of Curve Fitting Linear Combinations of Model Compounds to the Spectra of Figure 5[a]

sulfur type	model compd	dark control, %	UV irradiated, %
aliphatic sulfide	benzyl sulfide	21	5
thiophenic sulfur	dibenzothiophene	74	65
sulfoxide	dimethyl sulfoxide	5	9
sulfone	dibenzothiophene sulfone	0	6
sulfonate	anthraquinone sulfonate	0	6
sulfate	potassium sulfate	0	8

[a] Small shifts in spectral position (<0.2 eV) were allowed in the fitting procedure (*28*, *30*).

dibenzothiophene appear to be quite resistant to photooxidation. We attribute this phenomenon to the fact that the majority of those compounds evaporated leaving only a small amount available for photooxidation.

Figure 5 shows the sulfur K-edge X-ray absorption edges of irradiated and control oils. Sulfur K-edge spectra have a large chemical shift range (some 14.5 eV) and relatively sharp line widths, which combine to make sulfur K-edge spectroscopy a powerful probe for the quantitatve and qualitative speciation of sulfur in complex mixtures (*28*−*31*). Figure 5 shows that there was a substantial oxidation of sulfur species

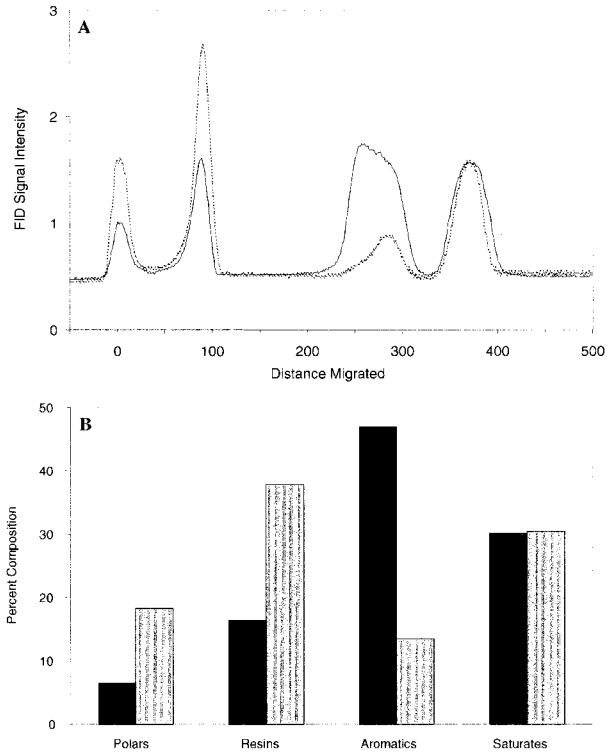

FIGURE 6. Thin-layer chromatography of irradiated (dotted line) and control (solid line) crude oil (panel A). The peaks represent, from left to right, the polars, resins, aromatics, and saturates. The data in panel A are normalized to the saturate peak height; panel B shows the percent composition of irradiated (gray) and control (black) oils.

during the UV irradiation; we have fit the spectra of Figure 5 to linear combinations of aliphatic sulfide, thiophenic sulfur, sulfoxide, sulfone, sulfonate, and sulfate (*28*, *30*) using the model compounds listed in Table 1.

The results of the spectral fitting are shown in Table 1. Sulfur in the initial oil was mainly thiophenic, but there was a significant amount of aliphatic sulfide and a trace of oxidized sulfur in the form of sulfone. The aliphatic sulfur was more sensitive than the thiophenic sulfur to photooxidation; more than 76% disappeared during the illumination, compared to only about 12% disappearance of thiophenic forms. The sulfur was oxidized to sulfoxides, sulfones, sulfonates, and sulfates in approximately equal amounts.

Thin-layer chromatography was used to examine the changes in the relative amounts of saturate, aromatic, resin, and polar compounds in irradiated crude oils. Figure 6 shows an example of our data; the UV irradiated sample exhibits a significant decrease in the aromatic fraction concomitant with a substantial increase in the resin and polar fractions. These data suggest that the aromatic compounds are preferentially oxidized in the presence of UV light which is consistent with the conclusions from the GC/MS data. The increase in the peak representing the polar fraction suggests that the oxidation of aromatic compounds produces polar compounds and is consistent with both the X-ray absorption data and previous reports concluding that photooxidation of aromatic hydrocarbons produces the corresponding acids and other oxidized products (*8*, *9*). The only minimal changes in the saturate fraction are consistent with the fact that the aliphatic sulfur compounds that showed the most marked oxidation in Figure 5 comprise only a tiny portion of the saturate fraction of the oil.

Our data indicate that photooxidation and biodegradation have opposite effects on aromatic hydrocarbons in crude oils. Whereas microbial degradation and evaporation result in the depletion of unsubstituted aromatic compounds relative to their alkylated homologues, photooxidation selectively degrades the alkylated aromatic compounds. It is thus conceivable that a photooxidized and biodegraded oil might show a very similar polycyclic aromatic hydrocarbon "fingerprint" to a fresh oil. Nevertheless, since neither photochemistry or biodegradation affect the levels of hopanes and other biomarkers to a significant extent, referencing the polycyclic aromatic hydrocarbons to hopane or a similar conserved marker will reveal the extent of degradation. This also applies to the use of ratios of alkylated polycyclic aromatic hydrocarbons as "fingerprints" of oil origin and extent of degradation (*32*). Alkylated phenanthrenes and dibenzothiophenes, for example the C-3 series, are biodegraded at very similar rates, so their ratio remains quite constant as biodegradation proceeds. Both series are biodegraded more rapidly than the equivalent chrysenes, which have four aromatic rings, and so the ratio of, for example, C3-phenanthrene to C3-chrysene is a useful indicator of the extent of biodegradation. It is clear from the data presented here that photochemical oxidation might lead to an underestimate of the extent of biodegradation, although it should not interfere with the use of the alkylated phenanthrene-to-dibenzothiophene ratio as a "fingerprint". Referencing the polycyclic aromatic hydrocarbons to a conserved marker such as hopane would indicate whether photooxidation has been a significant process in the recent history of a sample of oil.

Acknowledgments

Stanford Synchrotron Radiation Laboratory is funded by the Department of Energy, Office of Basic Energy Sciences, Divisions of Chemicals and Materials Science. The Biotechnology Program is supported by the National Institutes of Health, National Center for Research Resources, Biomedical Technology Program. Further support is provided by the Department of Energy, Office of Biological and Environmental Research. We are grateful to Dr. Graham George of SSRL for his participation in the collection of the sulfur K-edge data and for the use of his EXAFSPAK and DATFIT software.

Literature Cited

(1) Etkin, D. S.; Wells, P.; Nauke, M.; Campbell, J.; Grey, C.; Koefoed, J.; Meyer, T.; Reddy, S. *Proceedings of the Twenty-First Arctic and Marine Oilspill Program Technical Seminar*; Environment Canada: Edmonton, Alberta, **1998**; pp 903−910.
(2) Prince, R. C. Crude Oil Biodegradation. In *Encyclopedia of Environmental Analysis and Remediation*; Wiley: New York, 1988; Vol. 2, pp 1327−1342.
(3) Ollis, D. *Nature* **1992**, *358*, 453−454.
(4) Rosenberg, I.; Brock, J. R.; Heller, A. *J. Phys. Chem.* **1992**, *96*, 3423−3428.
(5) Wise, H.; Sancier, K. M. *Catal. Lett.* **1991**, *11*, 277−284.
(6) Ehrhardt, M. G.; Burns, K. A.; Bicego, M. C. *Mar. Chem.* **1992**, *37*, 53−64.
(7) Moza, P. N.; Hustert, K.; Leoff, S. *Toxicol. Environ. Chem.* **1991**, *31*−*32*, 103−106.
(8) Sanniez, W. H.; Pinckney, J. L. *J. Chem. Soc., Faraday Trans.* **1978**, *74*, 123−130.
(9) Larson, R. A.; Bott, T. L.; Hunt, L. L.; Rogenmuser, K. *Environ. Sci. Technol.* **1979**, *13*, 965−969.
(10) Ehrhardt, M. G.; Weber, R. R. *J. Anal. Chem.* **1995**, *352*, 357−363.
(11) Ehrhardt, M. G.; Bicego, M. C.; Weber, R. R. *J. Photochem. Photobiol.* **1997**, *108*, 253−259.
(12) Ehrhardt, M. G. *Mar. Chem.* **1987**, *22*, 85−94.
(13) Hansen, H. P. *Mar. Chem.* **1975**, *3*, 183−195.
(14) Payne, J. R.; Clayton, J. R.; Mcnabb, G. D.; Kirstein, B. E. *Proceedings of the 1991 International Oil Spill Conference*; American Petroleum Institute: Washington, D.C., 1997; pp 641−654.
(15) Harrison, O. R. *Proceedings of the 1991 International Oil Spill Conference*; American Petroleum Institute: Washington, D.C., 1991; pp 313−320.

(16) Thomas, D. *Petrol. Rev.* **1993**, *47*, 263−265.
(17) Harris, C. *Proceedings of the 1997 International Oil Spill Conference*; American Peroleum Institute: Washington, D.C., 1997; pp 177−184.
(18) Douglas, G. S.; McCarthy, K. J.; Dahlen, D. T.; Seavey, J. A.; Steinhauer, W. G.; Prince, R. C.; Elmendorf, D. L. *J. Soil. Contam.* **1992**, *1*, 197−216.
(19) Stern, E.; Heald, S. C. *Rev. Sci. Instrum.* **1979**, *50*, 1579−1581.
(20) Lytle, F. W.; Greegor, R. B.; Sandstrom, D. R.; Marques, E. C.; Wong, J.; Spiro, C. L.; Huffman, G. P.; Huggins, F. E. *Nucl. Instrum. Methods Phys. Res.* **1997**, *226*, 542−548.
(21) Sekiyama, H.; Kosugi, N.; Ohta, T. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 575−579.
(22) Ackman, R. G.; McLeod, C. A.; Banerjee, A. K. *J. Planar Chromatogr.* **1990**, *3*, 450−462.
(23) Peters, K. E.; Moldowan, J. M. *The Biomarker Guide; Interpreting molecular fossils in petroleum and ancient sediments*; Prentice-Hall: Englewood Cliffs, NJ, 1993.
(24) Butler, E. L.; Douglas, G. S.; Steinhauer, W. G.; Prince, R. C.; Aczel, T.; Hsu, C. S.; Bronson, M. T.; Clark, J. R.; Lindstrom, J. E. Hopane, a new chemical tool for measuring oil biodegradation. In *On-site Reclamation. Processes for xenobiotic and hydrocarbon treatment*; Hinchee, R. E., Olfenbuttel, R. F. Eds; Butterworth-Heinemann: Boston, 1991; pp 515−521.
(25) Prince, R. C.; Elmendorf, D. L.; Lute, J. R.; Hsu, C. S.; Haith, C. E.; Senius, J. D.; Dechart, G. J.; Douglas, G. S.; Butler, E. L. *Environ. Sci. Technol.* **1994**, *28*, 142−145.
(26) Douglas, G. S.; Prince, R. C.; Butler, E. L.; Steinhauer, W. G. The use of internal chemical indicators in petroleum and refined products to evaluate the extent of biodegradation. In *Hydrocarbon Remediation*; Hinchee, R. E., Alleman, B. C., Hoeppel, R. E., Miller, R. N., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 219−236.
(27) Venosa, A. D.; Suidan, M. T.; King, D.; Wrenn, B. A. *J. Indust. Microbiol. Biotech.* **1997**, *18*, 131−139.
(28) George, G. N.; Gorbaty, M. L. *J. Am. Chem. Soc.* **1989**, *111*, 3182−3186.
(29) Shadle, S. E.; Penner-Hahn, J. E.; Schugar, H. J.; Hedman, B.; Hodgson, K. O.; Soloman, E. I. *J. Am. Chem. Soc.* **1993**, *115*, 767−776.
(30) George, G. N.; Garrett, R. M.; Prince, R. C.; Rajagopalan, K. V. *J. Am. Chem. Soc.* **1996**, *118*, 8588−8592.
(31) Williams, K. R.; Gamelin, D. R.; LaCroix, L. B.; Houser, R. P.; Tolman, W. B.; Mulder, T. C.; deVries, S.; Hedman, B.; Hodgson, K. O.; Soloman, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 613−614.
(32) Douglas, G. S.; Bence, A. E.; Prince, R. C.; McMillen, S. J.; Butler, E. L. *Environ. Sci. Technol.* **1996**, *30*, 2332−2339.

Received for review March 2, 1998. Revised manuscript received June 19, 1998. Accepted August 19, 1998.

ES980201R