Photochemical processes and the environmental impact of petroleum spills

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Abstract. A review of the photochemical processes involved in the degradation of petroleum, its products, and some model compounds found in petroleum. Emphasis is given to processes which affect emulsification, water solubility, and toxicity. Water phase photodegradation is also treated. The interaction of these processes with biodegradation is discussed. Areas requiring further work are indicated. 96 references.

Introduction

The contamination of the world's water by petroleum and petroleum derivatives has been estimated to be 3.2×10^6 Metric tons per year (Clark 1989), of which 92% is directly related to human activities and one eighth of this is due to tanker accidents. The short and long term effects of this input have been the object of serious concern and much research (NAS 1985). The extent of long term contamination depends on the rate of continuous input of petroleum residues into the environment and the rate at which the environment can clean itself. Although the overall environmental recovery from large scale oil spills can be slow, the rate of recovery is different for sediments, oiled beaches and the open sea, with sediments maintaining oil for the longest time (Boehm et al. 1987) and sea water the shortest. Even after extremely large scale oil spills such as the "gulf war" spill in 1991 in which between five hundred thousand and one million tons of oil were released (Struck et al. 1993), the quantity of dissolved organic matter (DOM) in the Persian Gulf had returned to the prewar background level one year after the spill (Ehrhardt & Burns 1993). Decades of open ocean monitoring have not shown any progressive increase in oil residues; it is thus postulated that efficient processes for oil oxidation and removal must exist.

Three mechanisms have been proposed to operate in hydrocarbon removal from the sea. For low molecular weight volatile components, evaporation or

desorption from sea water followed by photooxidation in the air (Cox et al. 1981) is thought to be the dominant process (Mantoura et al. 1982). For the remaining nonvolatile components, microbiological consumption and photochemical degradation were invoked (Bongiovanni et al. 1989). For many years the role of photochemical processes was not considered and the photochemical degradation of petroleum has been much less studied than have biological processes. This may be a serious oversight as it has been suggested that in tropical waters, which receive a high solar flux and are nutrient depleted, reducing microbiological productivity, photochemical processes may be as important as biological degradation (Ehrhardt et al. 1992).

Photochemical transformations may also affect biological productivity in a number of ways and this area has received little attention. It is the intention of this short review to indicate these deficiencies and to stimulate more interdisciplinary research between environmental photochemists and microbiologists.

Surface oil weathering

Our knowledge of crude oil transformations is due in considerable part to research in response to major oil spills beginning with the 1967 Torrey Canyon tanker spill off the coast of Cornwall, G.B. which spilled 119,000 tons of crude oil. Attempts at clean-up using toxic detergents proved to be the major factor in environmental degradation (Clark 1989) and demonstrated the lack of knowledge of the impact, and fate of oil in the environment, and ignorance of results of attempted clean up. Later spills were then studied in greater detail. Table 1 gives a list of major spills. In addition to these, there have been numerous smaller accidents and some small scale controlled research spills designed to study environmental effects and clean up measures. In these spills, except the Ixtoc-1 blowout, the majority of the studies involve beach and sediment deposits, and marine organism contamination. The fate of oil in the sea is much less studied or understood.

The oil slick dislocation, due to wind and current, and spreading, due to gravity, increase the oil-water and oil-air interfaces resulting in enhanced evaporation and dissolution. Although the rate of loss will depend on the film thickness, viscosity, temperature, wind speed and surface conditions, the lower molecular weight components are quickly lost (Lee 1991). As a result, the oil viscosity and density will increase and water in oil emulsions will be stabilized (Berridge et al. 1968). It has been noted, however, that oil incorporation into sediments can considerably slow evaporation and dissolution under both arctic (Boehm et al. 1987) and tropical (Struck et al. 1993) conditions.

Table 1.

Source (S = ship)	Year	Spill place	Oil spilled $\times 10^3$ (ton)
Torrey Canyon (S)	1967	United Kingdom	119
Wafra (S)	1971	South Africa	65
Metula (S)	1974	Chile	53
Jakdo Maersk (S)	1975	Portugal	80
Urquiola (S)	1976	Spain	108
Hawaiian Patriot (S)	1977	Honolulu	99
Amoco Cadiz (S)	1978	France	227
Atlantic Empress (S)	1978	Trinidad Tobago	280
Independent (S)	1979	Turkey	93
Castillo de Bellver (S)	1983	Africa	257
Assinla (S)	1983	Oman	53
Nova (S)	1985	Persian Gulf	70
Odyssey (S)	1988	Canada	132
Exxon Valdez (S)	1989	Alaska	37
ABT Summer (S)	1991	Angola	260
Haven (S)	1991	Italy	140
Asgean Sea (S)	1992	Spain	72
Katina (S)	1992	Mozambique	72
Braer (S)	1993	United Kingdom	85
Ixtoc (Well)	1979	Gulf of Mexico	290
Gulf War	1991	Persian Gulf	1400

The linear alkanes are lost faster than branched alkanes (Hostettler & Kvenvolden 1994). Increased oxygenation of the samples is also seen by infrared analysis (Mansur et al. 1989; Young & Sethi 1975). The loss of the prominent linear alkanes coupled with a possible increase in the complexity of the aliphatic hydrocarbon fraction as analyzed by gas chromatography (GC) leads to the appearance of a continuous unresolved complex mixture or UCM (Boehm et al. 1987; Hostettler & Kvenvolden 1994).

A series of experimental parameters based on GC and GC-MS analysis has been developed to aid in the evaluation of petroleum residue weathering (Boehm et al. 1987). Two indices, the Saturated Hydrocarbon Weathering Ratio and the Aromatic Weathering Ratio (Boehm et al. 1984), measure the extent of evaporation. Another two indices measure the extent of admixture or contamination of the oil residue with biogenic hydrocarbons. These are the Pristane/Phytane Ratio (NAS 1985) and the Carbon Preference Index (Farrington & Tripp 1970). The Biodegradation Potential (Atlas et al. 1981) and the n-c_{18}/Phytane Ratio (NAS 1985) are designed to measure the extent of

biodegradation. It should be noted that photochemical processes could affect these last two ratios (Ehrhardt et al. 1992) and reduce the perceived extent of biological alteration. There is at present no index that can be used to measure the extent of abiotic (mainly photochemical) degradation.

The results of petroleum weathering are reasonably well known as a result of environmental analyses but the processes which produce the alterations are not as well understood. Initially, evaporation increases the viscosity and density of the altered oil and aids in the formation of water in oil emulsions called Chocolate Mousse (treated below). This heavier oil is further transformed by biological and photochemical processes. Biological transformations are expected to depend on the nature of the oil (which is constantly changing), on temperature, and on nutrient availability (bound nitrogen, sulfur, phosphorus, etc) as well as the initial populations of microflora and fauna. Depending on the latitude and season, photochemical processes could also be important since thinning of the oil slick constantly increases the area exposed to sunlight and most crude petroleums absorb strongly in the ultraviolet and visible regions of the solar spectrum. To exemplify, the solar spectrum and the absorption spectrum of a Brazilian intermediate petroleum are shown in Figure 1. The biological processes have been studied extensively (NAS 1985), partly in support of bioremediation programs (LeBlanc & Fitzgerald 1990) but these processes will not be treated here.

Photochemical processes have been shown to affect physical properties, oil composition, mousse formation, and solubility. Increased solubility affects biological toxicity and biodegradation and permits water column photodegradation. These topics are treated individually.

Oil composition

The composition of crude petroleum is extremely complex and varies with the petroleum sample (NAS 1985). The composition can even change over a period of time as samples of petroleum are taken from a single well. It is therefore usual to indicate the composition only in general terms. Crude petroleum contains aliphatic and aromatic hydrocarbons, some nitrogen and sulfur heterocyclics, and very low concentrations of alkenes and oxygen containing components. This general composition is reflected in the elemental analysis which gives the percent composition of C, H, N, and S. Another common way of analyzing petroleum utilizes solubility and absorption chromatography. The high molecular weight fraction insoluble in pentane or heptane is called the asphaltene fraction. The remainder is separated into aliphatic, aromatic, and polar fractions by elution from silica gel (Daling et al. 1990).
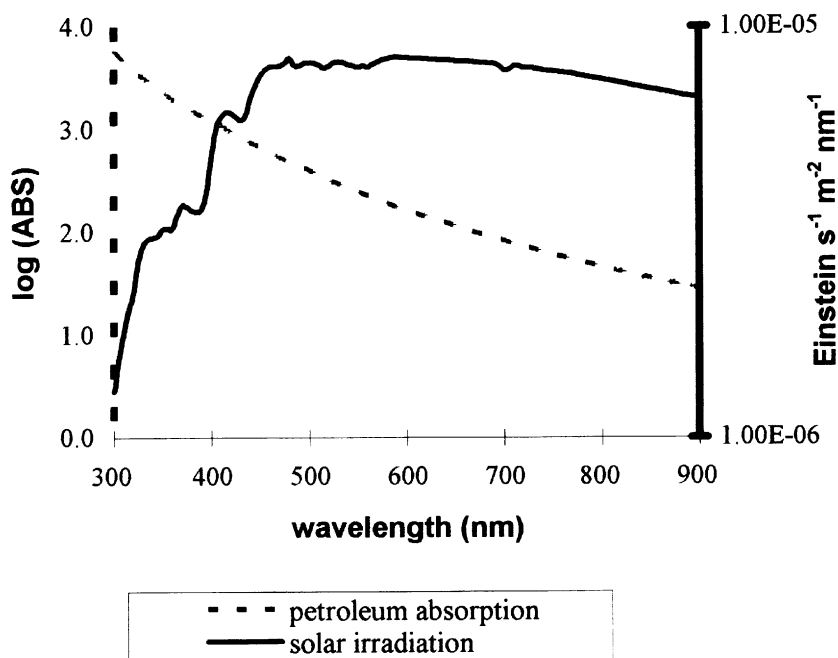
Figure 1. Solar spectrum and absorbance of a typical crude petroleum.

Aged beach deposits invariably show increased oxygenation when analyzed by elemental analysis, while studies of oil films over sea water have given mixed results. A controlled study of a film of Prudhoe Bay crude petroleum over sea water in a large tank did not show an increase in polar components in the oil surface film after 4 months of exposure to solar irradiation (Jordan 1991). In another controlled experiment detergent dispersed Ekofish crude was irradiated with sunlight for 20 days. The undispersed surface film did not accumulate polar components (Tjessem et al. 1984). However, in this case the presence of detergent could facilitate transfer of polar components into the water column. On the other hand analysis of aged mousse from the Ixtoc 1 oil spill showed increased oxygenation (Patton et al. 1981) as have several controlled experiments (Sydnes et al. 1985a; Ducreux et al. 1986; Daling et al. 1990). As expected, the polar fraction of these petroleum films increased while the aromatic fraction decreased (Ducreux et al. 1986; Daling et al. 1990). The loss of aromatics can also be seen using fluorimetry (Gordon et al. 1976). Since the aromatic components are the most toxic, their loss reduces oil toxicity. Infra-red analysis reveals the formation of ethers (Young & Sethi 1975), carbonyl containing derivatives (Thominette & Verdu 1984b; Watkinson & Griffiths 1987), alcohols (Thominette & Verdu 1984b),

and possibly sulfone groups (Young & Sethi 1975). There are, however, significant differences in rate for samples of different petroleums receiving the same UV light dose (Thominette & Verdu 1984b).

Aliphatic components are also found to be consumed with branched aliphatics being more reactive (Hansen 1975), but the loss of these compounds does not mean that they are completely degraded. In a study using carbon 14 spiked petroleum (^{14}C hexadecane and phenanthrene) it was found that the majority of the label became "chemically bound" in the high molecular weight fraction (Tjessem et al. 1983). Polymerization has been reported to occur when petroleum is irradiated (Thominette & Verdu 1984a), but decreases in the mean molecular weight were also reported (Bongiovanni et al. 1989); this aspect deserves further research.

The sulphur containing components are readily photooxidized to the corresponding oxides. Both aliphatic sulfides (Burwood & Speers 1974) and aromatic thiophanes are converted in nature and in laboratory tests (Overton et al. 1979; Patel et al. 1979). Several studies have found that carboxylic acids were formed (Freegarde et al. 1971; Hansen 1975; Lamathe 1982), and it has been suggested that these are responsible for the formation and stabilization of water in oil emulsions.

Mechanisms

Although compositional changes upon weathering have been observed, and those reported here are attributed to photochemical processes, the majority of these studies were performed under conditions in which both biological and photochemical processes may be occurring simultaneously so that the relative contribution of each process can not be ascertained reliably. The number of studies is very small, the samples studied vary enormously in characteristics from distilled fractions to heavy crude oils, and the experimental conditions are quite diverse. It is not, therefore, surprising that results can be different or even contradictory. It is clear, however, that photochemical transformations are important in oil weathering and mechanisms have been proposed (Tjessem & Aaberg 1983; Payne & Phillips 1985; Bongiovanni et al. 1989). Basically two processes have been considered.

In the first, energy transfer from electronic excited states (usually triplet) of the aromatic and polar components to molecular oxygen generates singlet oxygen (Gorman 1992) which can then react with aromatic and heterocyclic sulfur compounds by addition. It has been found that diluted petroleum fractions (maltene) generate singlet oxygen (Lichtenthaler et al. 1989) and that β-carotene, a good singlet oxygen quencher, retards the photooxidation of a fuel oil (Larson & Hunt 1978). In a study on the oxidation of dimethylnaph-

thalenes sensitized by petroleum, the authors (Sydnes et al. 1985b) conclude that the reaction occurs via singlet oxygen. On the other hand, photooxidation of a crude oil was not affected by β-carotene or other singlet oxygen quenchers and the authors (Thominette & Verdu 1984a) concluded that in this case singlet oxygen was not involved.

Free radical induced autoxidation has also been proposed to explain the products, and it was found that a free radical quencher inhibited photooxidation in one case (Thominette & Verdu 1984a). Although free radical processes readily explain the observed products, and there are numerous photochemical reactions which lead directly to free radicals through hydrogen atom abstraction of homolytic bond cleavages, it is difficult to imagine a reasonable photochemical process involving known petroleum constituents that undergo this type of reaction. One possibility around this problem could involve a combination of singlet oxygen and free radical mechanisms. In this case singlet oxygen mediated oxidation would generate compounds such as ketones and quinones (Dowty et al. 1974; Rontani & Giral 1990), which could then initiate photochemically induced free radical processes (Wagner & Park 1991). Thiophene oxides generated via singlet oxygen (Overton et al. 1979; Patel et al. 1979) are another possibility. It is known that photolysis of thiophene oxides regenerates the thiophene and eliminates atomic oxygen (Wan & Jenks 1995). Atomic oxygen would then abstract hydrogen and form free radicals.

The possibility of photooxidation via free radicals has been suggested in model studies using several free radical generating sensitizers as films over seawater. Naphthalene derivatives sensitize the oxidation of alkyl benzenes and purified mineral oil (Sanniez & Pilpel 1978) and xanthone has been used to oxidize hexadecane (Gesser et al. 1977). Anthraquinone has been used in several studies utilizing alkyl benzenes (Ehrhardt & Petrick 1984), pentadecane (Ehrhardt & Petrick 1985), nonlinear hydrocarbons (Rontani & Giusti 1987; Rontani & Giusti 1988), and cycloalkanes (Ehrhardt & Weber 1995).

A third possibility which has not previously been proposed, involves electron transfer initiated oxygenations (Lopez 1990). It is possible that in a thin film of petroleum over sea water, photochemical reactions could occur at the interface and that in the presence of water, electron transfer could generate cation radicals and anion radicals which could then initiate free radical oxygenations. The surprising formation of hexadecanoic acid upon sunlight irradiation of a thin film of hexadecane (in the presence of anthraquinone) over seawater (Rontani 1991) is explainable if the reaction occurs preferentially at the interface and the hexadecane is oriented to reduce hydrophobic interactions. It was also reported that the reaction of 1-naphthol with a number

of substrates as a thin film over water give simplified kinetics and product distributions (Klein & Pilpel 1973; Klein & Pipel 1974a). The hydrocarbon – water interface may then be important for photochemical transformations and allow processes which generate polar intermediates.

Physical properties

The most important physical changes affecting environmental impact are evaporation, spreading, emulsification, and dissolution; chemical alterations affect all these processes. These processes have been (Berridge et al. 1968) and continue to be studied (Lee 1991) due to their importance in mathematical models of spill dynamics (Mackey & McAuliffe 1988; Seymour & Geyer 1992). However, none of the models include photochemical parameters. Emulsification and dissolution have been studied in more detail and are discussed separately below.

There is little data on the formation of low molecular weight volatile components as a result of photooxidation (Ehrhardt & Weber 1991), or on the alteration of viscosity (Klein & Pilpel 1974b). These processes require study. Considering that photochemical processes can quickly alter the physical characteristics of petroleum films and that these properties affect the dislocation of oil, this interface merits more research.

Mousse formation

When oil is spilled on the water surface, the action of wind and waves churns the mixture and disperses some oil into the water column. Perhaps more importantly, it also forms water-in-oil emulsions which can contain up to 90% water (Thingstad & Pengerud 1983); they can be extremely stable and difficult to break. This emulsion, called chocolate mousse because of its appearance, increases the volume and viscosity of the spilled oil and makes mechanical oil removal from the water surface more difficult. The mousse sticks more readily to beach material and therefore abets beach oiling and increases the resulting impact on beach and intertidal flora and fauna. Its high viscosity impedes microbiological degradation but also makes sediment penetration more difficult (Seymour & Geyer 1992).

It has been noted that mousse formation is dependent on the type of oil and often only begins to form some time after a spill occurs as a result of weathering (Payne et al. 1987). Photolysis, however, has only recently been recognized as an important slick weathering process involved in mousse formation (Mackay & McAuliffe 1988).

The ability of unweathered crude oils to form water-in-oil emulsions depends on the asphaltene concentration (Mackay et al. 1973), and the high molecular weight asphaltene fraction increases upon irradiation (Daling et al. 1990; Ducreux et al. 1986; Thominette & Verdu 1984a). It has been suggested that the formation of high molecular weight polar material is responsible for mousse formation (Thominette & Verdu 1984a). The formation of surfactants has also been shown (Lamathe 1982), and these could also be responsible for the formation of water-in-oil emulsions. Laboratory tests show that interfacial tension rapidly drops, and that chocolate mousse forms when crude oil films are exposed to sunlight (Thingstad & Pengerud 1983; Ducreux et al. 1986; Daling et al. 1990); water-in-oil emulsions are stabilized after even short irradiation times (Fernandes 1994) in which changes in the oil composition can not be measured. Although the increase in the asphaltenic fraction may not be necessary for initial mousse formation, it has been suggested that structural organization of the asphaltenes causes the observed increase in emulsion viscosity (Desmaison et al. 1984). Since the asphaltenic fraction increases with irradiation, photochemical processes may also be involved.

The formation of mousse can be inhibited by β-carotene, a good singlet oxygen quencher, and it has been proposed that the formation of surfactant molecules involves singlet oxygen (Thingstad & Pengerud 1983). Free radical processes can also generate carboxylic acids (Sanniez & Pilpel 1978) implicated as surface active components (Hansen 1975; Desmaison et al. 1984); at present the relative importance of these two processes is not known.

Even with the limited results available it is obvious that photochemical processes are important for the formation and stabilization of chocolate mousse. The mechanisms involved are however very poorly understood. This area merits more detailed study, especially considering the importance of this process on the environmental impact of floating oil.

Water solubility

Petroleum has very limited solubility in sea water and this certainly is not a principal source of oil film loss (EXXON 1985). For example, a film of Prudhoe Bay crude under which was pumped seawater, lost only 2% of the oil by dissolution in the water even with exhaustive extraction (Payne et al. 1983). For crude petroleums having a small low boiling fraction and high viscosity an even smaller fraction will dissolve in water (Klein & Pilpel 1974b) than will refined petroleum products such as gasoline, diesel fuel, and fuel oil (Zürcher & Thuer 1978). This is true because the lower weight components, such as the monocyclic aromatic fraction, are the most soluble. These same components have high volatility and are rapidly lost to the atmosphere so that

they are not usually found in sea water and can have only transient effects on the environment.

Irradiation of oil films by either solar or artificial illumination has been shown to increase the "oil solubility" in water (Scheier & Gominger 1976; Ducreux et al. 1986). This increase can be from 32 to 295 ppm for a #2 fuel oil (Griffin & Calder 1977), in the range of 4 to 30–40 ppm for light crudes (Gordon et al. 1976; Sydnes et al. 1985a), but much lower for highly viscous crudes (Klein & Pilpel 1974b). As a very general rule a tenfold increase in solubility is observed.

The increased solubility is due to the formation of polar derivatives of all petroleum fractions including ketones (Jordan 1991), alcohols (Sydnes et al. 1985c), hydroperoxides (Sydnes et al. 1985b; Larson et al. 1977, 1979), sulfoxides (Burwood & Speers 1974), phenols (Larson et al. 1977, 1979) and carboxylic acids (Larson et al. 1977, 1979; Sydnes et al. 1985a). These polar compounds can be aliphatic or aromatic, and the aromatic fraction increases the water fluorescence (Ducreux et al. 1986).

Analysis of oil pollution in sea water by GC-MS and fluorimetry shows the presence of petroleum derived components (Ehrhardt & Knap 1989). However, most of the fluorescent material in sea water is more polar than petroleum (Theobald 1989) and may or may not be derived from petroleum. Further, the majority of the petroleum derived organic material is less fluorescent than the hydrocarbon precursors (Ehrhardt & Burns 1993). As an example, phenanthroic acids were formed from alkyl phenanthrenes and found in analyses of the IXTOC-1 well blow-out (Atwood & Ferguson 1982). Even when the components are apparently unaltered components of petroleum, the relative concentrations of similar compounds can be altered. For example, in alkyl substituted naphthalenes, fluorenes, and phenanthrenes, the more alkylated components are depleted relative to their abundance in petroleum; this has been attributed to preferential photochemical degradation of the more substituted members of each series (Ehrhardt & Petrick 1993).

These studies show that photochemical oxidation of petroleum and petroleum derived products is an important process in transferring organic material from the oil phase into the water column. The photochemical mechanisms responsible for these processes are poorly understood and more work is needed. Consequences of this transfer on water toxicity are discussed in the next section.

Oil toxicity

The toxicity of oil and of the water soluble fraction of oil has been studied extensively (NAS 1985) and will not be commented on here. Solar irradia-

tion is known to affect oil toxicity (Larson & Berenbaum 1988; Bongiovanni et al. 1989). Surface films become less toxic due to the loss of polycyclic aromatic hydrocarbons but the water soluble fraction becomes more toxic. Since bacterial degradation occurs at the oil water interface or in the aqueous phase, the increased toxicity could have important repercussions on the biological impact of an oil spill.

It has been shown that increased toxicity is due to polar components formed when #2 fuel oil (Scheier & Gominger 1976) or crude oil (Ostgaard et al. 1987) is irradiated. In a general way the elevated toxic effects are due to the increased concentration of petroleum derived organic material, but the acid fraction (Larson et al. 1977) and especially the hydroperoxides (Larson et al. 1979) are the most toxic. The hydroperoxides are probably responsible for the observed increase in toxicity to cod eggs when these were exposed to water in close contact with an irradiated petroleum film (Sydnes et al. 1985a).

When water samples are used some time after equilibration with irradiated oil films (so that hydroperoxides will have decomposed), the increased toxic effect appears to be due to the increased concentration of organic material in the water. The specific toxicities were the same (Sydnes et al. 1985b) or lower (Griffin & Calder 1977) than those of non-irradiated samples. It should also be noted that the concentration of dissolved organic matter used in most biological tests (in the range of 10–30 ppm) was considerably greater than that actually found under oil slicks (Freegarde et al. 1971; Atwood & Ferguson 1982) which is in the range of 1–300 ppb.

At lower concentrations where acute toxic effects would be less important, this organic material may actually support bacterial growth and aid biodegradation. There are indications that the formation of polar compounds may increase the rate of biodegradation of petroleum. In a study of lake water containing humic acid, it was found that irradiation of non-petroleum derived, biologically refractory, dissolved organic material renders this material more biodegradable (Lindell et al. 1995). Also, in a study of dispersed petroleum in seawater, it was found that biological and photo-degradation operated differently, and that a combination of both photo and bio-oxidation was capable of greater degradation, that in fact there was synergy (Literathy 1989).

In a study of model systems related to petroleum, it was found that the photooxidation of n-nonylbenzene accelerated biological utilization (Rontani et al. 1987), and that biological metabolites could be further photooxidized (Rontani et al. 1988). The photooxidation of anthracene also aids in its biological degradation since anthraquinone is more readily biodegraded than is anthracene (Rontani et al. 1985).

It could be that photooxidation of petroleum to polar water soluble components, followed by biological metabolism of these products provides a major

pathway for the removal of petroleum derived DOM from the sea, but in the absence of supporting studies this possibility can not be properly evaluated. More work in this area is definitely required.

Water column photodegradation

It is well known that photochemical processes are an important part of the chemistry of aquatic systems (Cooper & Herr 1987), with various mechanisms in operation (Zafiriou et al. 1984) including singlet oxygen formation (Zepp et al. 1977; Zepp et al. 1984). It would be surprising, then, if petroleum derivatives which dissolve in seawater did not undergo further photodegradation in the aqueous phase. This aspect has not been specifically researched, but related work with unweathered petroleum, petroleum components, and model compounds, indicates that rapid photodegradation would be expected.

It was found that the water soluble fraction of a Nigerian Crude oil was photodegraded by sunlight with preferential loss of the more alkyl substituted components (Ehrhardt et al. 1992). The authors concluded that photochemical processes could be as important as biological pathways for hydrocarbon degradation in tropical waters.

Anthraquinone, which has been found in sea water (Ehrhardt et al. 1982), has been used as a sensitizer in several studies. It was found that the water soluble fraction of gasoline was readily photodegraded giving alcohols, aldehydes and ketones (Ehrhardt 1987). Irradiation of an aqueous solution of n-tetradecane gave volatile aldehydes and ketones such as formaldehyde, acetaldehyde and acetone, and the same products were observed when petroleum samples were used instead of tetradecane (Ehrhardt & Weber 1991). Anthraquinone has also been used to sensitize the photodegradation of n-nonylbenzene (Rontani et al. 1987), and monoalkylated benzenes (Ehrhardt & Petrick 1984). In all these cases it was suggested that anthraquinone absorbs light, generates its excited triplet state and initiates free radical mediated autoxidation by abstraction of hydrogen.

The direct aqueous phase photooxidation of dimethyl biphenyls (El Anba-Lurot et al. 1995) and dialkylnaphthalenes (Sydnes et al. 1985b) also gives products expected from free radical initiated oxidation even though no sensitizer was used. On the other hand photooxidation of anthracene was postulated to involve initial electron transfer as well as singlet oxygen (Sigman et al. 1991).

Polycyclic aromatic hydrocarbons were destroyed when dilute aqueous solutions were irradiated by sunlight (Paalme et al. 1990; Kirso et al. 1993); the relative rates of loss implicate the involvement of singlet oxygen. In other
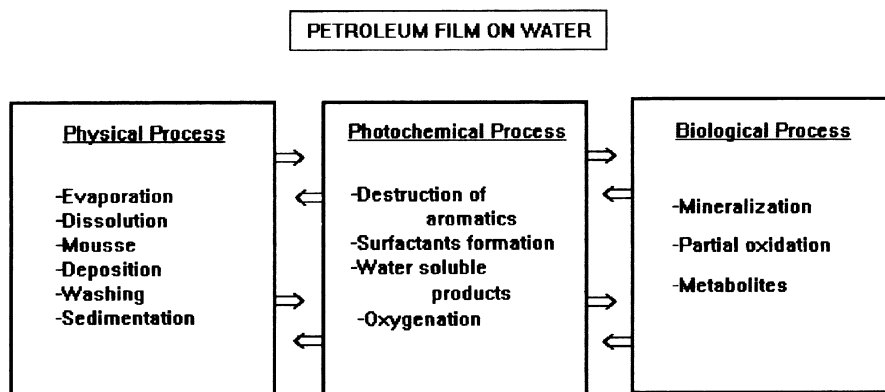
PETROLEUM FILM ON WATER

Physical Process

-Evaporation
-Dissolution
-Mousse
-Deposition
-Washing
-Sedimentation

Photochemical Process

-Destruction of
    aromatics
-Surfactants formation
-Water soluble
    products
-Oxygenation

Biological Process

-Mineralization

-Partial oxidation

-Metabolites

Figure 2. Interaction between processes which lead to petroleum removal from the sea.

studies 1-naphthol (Larson & Rounds 1987) and benzothiophene (Andersson & Bobinger 1992) have been found to photodegrade in water.

Considering what is now known, it would be very useful to study the photochemistry of aqueous extracts of photochemically weathered petroleum in order to analyze the importance of this process on petroleum removal from the environment.

Conclusions

Petroleum weathering occurs by physical, chemical (photochemical), and biological processes which are interconnected. Although the rate of photochemical transformation can be slow, the oxidized products affect the viscosity and the formation of mousse and alter the weathered petroleum's physical properties. This in turn affects biological degradation.

Photochemical transformations also directly affect biological properties to the extent that toxic components are destroyed, new toxic components may be generated, and water soluble products are formed. The interaction between these processes is indicated in Figure 2.

Unfortunately there has been very little research on the relationship between photochemical ageing and the physical characteristics of weathered oil. The interaction between photooxidation and biodegradation is even less well understood. This may be understandable in light of our still fragmentary understanding of the photochemical processes involved and the factors which control these processes. It is hoped that this review will stimulate research in this interface, and that the questions brought up will be answered in the near future.

Acknowledgements

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