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PETROLEUM WEATHERING: SOME PATHWAYS, FATE, AND DISPOSITION ON MARINE WATERS

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the technical basis for setting standards to minimize undesirable
changes in living organisms in the aquatic, terrestrial and atmospheric
environments.

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PETROLEUM WEATHERING:

SOME PATHWAYS, FATE, AND DISPOSITION ON MARINE WATERS

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ABSTRACT

Three mechanisms of weathering of oil pollution on marine waters are discussed. Photolysis, interactions with trace materials, and sedimentation with particulate materials are considered as competitive to other fate of petroleum mechanisms and as having possible ecological importance.

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TABLES

SECTION I

INTRODUCTION

"Weathering" is a term used to express, qualitatively, the idea that petroleum "oils" or hydrocarbons (HC) when spread upon the sea are changed in their character with time; it is assumed that the original material, isolated within its earth strata, had been stable for long periods of time. The term weathering, involves the idea of mechanism or process, leading to ultimate disposition or, briefly: Fate.

What biological, chemical, and physical reactions occur to which may be attributed the (weathering) changes observed? Can the rates at which these competitive and cooperative possibilities occur be tabulated so that the behavior of a given petroleum in a given biogeographic/geochemical locale, and its behavior, its fractionation and disproportionation, and its biological, chemical and physical interactions, and final disposition may be quantitatively predicted?

The answer to this rather lengthy question is that at present even the possible determinants of the chemical and physical behavior of hydrocarbons disposed to the sea cannot be tested. At every level of inquiry there are significant problems of experimental methodology, mathematical and systems analysis, and even in defining the problem.

SECTION II

OBJECTIVE

The objective of this report is to discuss some of the possible
mechanisms of weathering of petroleum on marine waters.

Mikolaj (1972) lists some of the generally accepted individual
components of the generic term "weathering", evaporation, leaching of
water solubles, autooxidation, biological degradation. Presented here
are (1) <u>radiation</u> (photolysis, et seq.), (2) <u>trace material
interactions</u>, and (3) <u>particulate</u> (sedimentation) <u>interactions</u>.
Discussion of these three modes leading to weathering and ultimate
disposition of HC on the sea will of course involve other variables
(temperature, geographic location) and cannot be all inclusive, as
causes leading to ultimate fates. Thus, the importance of other
mechanisms, solubilization, emulsification, evaporation, is recognized
but they are not discussed here.

1.   Photolysis (above 3200 A°) affords an initiating mechanism, and
quite possibly a major mechanism, for:

        (a)   oxidation of larger more complex molecules (auto-catalytic
oxidation).   .
        (b)   polymerization reactions (disproportionation).
        (c)   carcinogenic hydrocarbon (CHC) compound formation and removal.
        (d)   tar ball formation.

2.   Interaction with trace materials at the surface layer involves:
        (a)   trace or heavy metals as toxicants.
        (b)   "   "   "   "   "   metabolic atoms.
        (c)   trace compounds like vitamins, amino acids, EDTA, formation
and removal of biologically significant nutrient forms of P, N.
        (d)   trace compounds that are essentially toxic or inhibitory
DDT, PCB, CHC formation and removal. Of course a, b, c, d may be the
guiding lines to what can happen and what does happen to biota at
the beginnings of the ecological pyramid or chain sequence of events
in trophic levels. This will be discussed in terms of trace materials
as ecological determinants.

3.   It is possible that geographically variable sedimentation
and particulate interaction processes are a significant factor in
predetermining the ultimate fate of HC pollutants.

The mere removal of HC by intercalation and other sedimentation phenomena
based on interaction with clays, silts, glacial flours is too simple
a view as will be developed. The reason for including this area
in a discussion of 1 and 2 above which are mechanism oriented while
3 apparently is a simple removal comparable to evaporation will be
discussed.

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SECTION III

DISCUSSION

A.   Radiation (photolysis) chemistry, (Noyes & Leighton 1966),
(Burton & Magee 1969 et seq.) is a well developed science; the lower
molecular weight HC, especially paraffins, are effectively transparent
to wave lengths occurring in sunlight, even down in the region 3200-
4400 A^0.   Thus, to photolyze methane, fluorite windows are required
for the wave lengths necessary; and while the photolysis of ethane
leads to a number of interesting products (many of them of higher
molecular weight) ethane too requires light further in the UV than
is available at the sea surface.

Nitrogen, oxygen, sulfur-containing organics do absorb in the visible,
and naphthenic acids are among the photolytically active petroleum
fractions.   The photolysis of fractions of petroleum especially
the naphthenic acids has been observed by a number of workers; ZoBell
(1963, 1971) references some of these observations.

Noyes and Leighton (1966) shows some quantitative data on anthracene, β-
methyl anthracene, transstilbene, rubrene; all respond to wave lengths
3100 A^0 and longer and are likely suspects for radiation chemical effects.
Acenaphthene, anthracene, dehydroanthracene all reacted in sunlight
(or equivalent wave lengths in glass).

Toluene and related aromatics with side chains have been photolyzed
in the presence of a variety of materials such as H_2O, H_2O_2, $H_2O+FeCl_3$;
tetrahydronaphthalene in presence of H_2O and O_2 gave polymeric materials.
Unsaturated hydrocarbons are also absorbers at the longer wave
lengths.

Hydrocarbon Photolysis as Precursor to Tar in Marine Waters.

According to the data accumulated by Morris and Butler (1973) and
shown in Table 1, the tar found in Mediterranean and in Sargasso was
more than N. Atlantic.   In the absence of quantitative data on actual ballast
oil inputs, and retention factors in various seas, and the suggested
subsequent chain of events their working hypothesis cannot easily be
tested.   Another working hypothesis might be that petroleums of comparable*
average content injected in all three oceanic areas with comparable frequency
end up as tars or tar balls in proportion to the available oil,
UV, oxygenation rates and ambient temperatures.   Quite probably the
retention times for petroleum oils (inverse of other removal processes,
currents, etc.) are just not available for firm data analysis.

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*Some, however, --e.g. Kuwait origin--as also Santa Barbara seeps,
are known to be high in the tar-genic materials.

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The kind of reactions postulated are:

(1) Oil fraction (ι) $\xrightarrow{h\nu}$ [Active intermediates]

(2) Active intermediates and products of prior steps

$\begin{cases} \xrightarrow{0^2} & \text{Auto oxidation} \\ \xrightarrow{\Delta T} & \text{Polymerization and disproportionation} \end{cases}$

(3) Active intermediates and products of prior steps $\xrightarrow{\beta}$ Degradation and/or synthesis by appropriate biota.

Reaction (2), polymerization and disproportionation involves the formation of smaller molecules plus longer chain/higher M.W. compounds. Polymeric materials are the typical outcome of initiation by irradiation and subsequent thermal reactions. [Burton and Magee 1969 et seq.]. While photochemistry is more specific in the initial chemical changes than radiation chemistry, the longer term outcome of irradiation not carried to ultimate oxidation (Armstrong et al., 1966) seems to be similar.

CARCINOGENICS FORMATION

Reaction (3), biodegradation, of course, ultimately leads to CO_2 but intermediate metabolic steps proceeding from a polycyclic aromatic base can lead to carcinogenic intermediates. The work of Boylan and Tripp (1971) shows the solubilities of various molecular forms found in kerosine (see Table 3). The review by ZoBell (1971) shows the ubiquitous nature of the carcinogenic hydrocarbons CHC and their synthetic and metabolizable properties. The discussion by Parker (1971) shows that the solubilities of petroleum in equilibrium with saline water was markedly diminished by sunlight. The formation of higher M.W. substrates and of carcinogenic materials and tar balls are interrelated phenomena involving competitive rates of radiation initiation, thermal reaction, and biosynthetic processes. They are competitive, as well, with the more usually listed physical weathering processes such as: chocolate mousse formation, emulsification, evaporation of lighter fractions.

Temperature and Tar Formation.

Allen, et al., (1970) point out how irregular is the seepage contribution to "beach tar" on the Southern California Coast. ZoBell (1963) indicates a definite temperature component in the frequency of occurrence of tar on the beaches of Southern California. Both writers indicate that the temperature or seasonal correlation is to the seepage rates. But as the temperature rises in the water off Santa Barbara, in summer, see Figure 1, it is difficult to see how the temperature of the earth volume from which seepage occurs can respond so quickly. An alternative hypothesis is that the temperature increase (as the summer season increases in sunlight occur) is reflected in increased reaction rates in the postulated series indicated previously

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on page 4, resulting then in more apparent tar availability during warm seasons and in warmer waters. The higher radiation and temperatures will result, of course, in faster agglomeration as suggested here, as well as faster evaporation as suggested by Morris and Butler (1973). Their data indicate the temperature, seasonal increase in tar ball formation. Large, fairly hard, dense pieces may not be fully accounted for by radiation initiation, followed by thermal polymerization, but evaporation alone seems quite incomplete as mechanism. Munday, (1971) finds that tar balls are significantly warmed by radiation absorption. Because of their black nature, the tar balls, once initiated, will have their energy absorption efficiency increase.

The Rate of Oxidation Removal of Oil Slicks - Photolysis Initiated.

The rate of oxidation of hydrocarbons and nitrogen, oxygen, sulfur-(NOS) compounds varies with their chemical nature (Koons 1973). For example a tertiary hydrogen is oxidized more readily than a primary or secondary hydrogen; thus, alkyl substituted naphthenes will be oxidized more rapidly than normal paraffins. Acceleration of oxidation rates may occur by photolysis initiation followed by thermal chain steps, or by catalysis caused by traces of metallic ions of variable valence, or maybe slowed by chain stopping steps due to sulfur atoms.

Experimental estimates of the actual removal rates of slicks attributable to the photolysis initiated and thermal chain reactions subsequent to the initiation have been made. Using light sources resembling the spectrum of sunlight, whose internal relative intensities are within a factor of two, the total rate of decomposition corresponds to the destruction of a 2 1/2 μm thick slick in 100 hours. (Freegarde and Hatchett 1970).

A slick of thickness 2 1/2 μm has about 2000 kg/km^2 (1300 gal/mi^2, Garrett 1969). Assuming an effective day of sunlight less than eight hours, sunlight photolysis can initiate sufficient oxidation reaction to remove the slick in a few days.

It has been noted that approximately the top 2 μm layer of a freshly laid asphalt roadway is oxidized in about one day (E. Mertens).

B. Trace Material Interactions In The Surface Layer.

Garrett (1967) has pointed out the existence and composition of a trace material rich surface layer other than petroleum on the sea. Williams (1967 has shown the existence of a variety of nutrient materials, both organic and inorganic, and probably including amino acids in the surface film. Duce and Quinn (1972) showed the significant enrichment

of this layer in trace elements (trace metals and other pollutant materials) see Table 4. Feldman (1970) has discussed the set of trace materials (TM) comprised of trace elements or metals (T.E.) and trace organic compounds (T.C.) defining, T.M. = T.E. + T.C. Guinn and coworkers (1970) have shown that the usual trace elements, nickel and vanadium, generally measured in petroleums, are by no means all that can be observed. See Table 5. For purposes of fate and mechanism it is important to note that the trace element composition of various petroleums is distinctive. Filby and Shah (1971) showed further that the various naphthenic and other fraction of petroleums can be characterized by their T.E. content. These workers were intent on a system of analysis, for government regulatory purposes, based on neutron activation analysis "fingerprinting". Lukens, et al., (1971) organized the pioneer work of Guinn and of Filby and Shah into a coherent reliable identification of petroleum system. The true utility, of the work of Filby, Shah, and Guinn, in addition to regulatory agency usage, is as a means of following the petroleum and its interactions in the surface layer with preexisting trace elements and compounds through its fate and transport processes to tar balls, carcinogenics formation, and phytoplankton, bacterial and faunal interactions.

Feldman (1970) has explained how the trace element composition of the sea is not as relatively constant as the major constituents' relative composition due to chemical processes, biological interactions, and pollutional influences. The changes in the relative quantities of trace materials, which may be essential, nutrient, or toxic, and which may be trace metals, trace compounds (vitamins, amino acids) or large molecular aggregates (humic and fulvic substances) determine the phytoplankton successions that can occur. These, in turn, determine which subsequent trophic levels and species can occur.

It is noted, therefore, that the interactions, or the pathways, of trace materials, influence the biodegradation, as well as the synthesis, of hydrocarbon materials. The succession of biota, each in its turn utilizing a particular fraction of petroleum, or an intermediate product, can be interfered with by the presence of trace compounds (herbicides and biocides of all descriptions), as well as trace materials in general which tend to concentrate in the surface layer already rich in trace materials and now also in petroleum.

Microbial degradation of oil, it is assumed, is adequate and complete. But the data do not support it. Floodgate (1972) has assembled data on this point. See Table 6. This fact is emphasized by the findings of Blumer (1972) of surprising persistence of even light fuel oil (#2) paraffinic fractions in sediments. The implication of the relations of petroleum to the active surface layer in terms of trace materials which guide and control all biotic responses is clear. The interferences with pheromone and general chemotaxic reactions is a specific instance.

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If the trace materials array can, in fact, determine not the biomass achievable (that depends on physical arrangements and total nutrient available) but the nature, i.e., the identity of the successful species, then, the trace materials at the surface is a most significant determinant of fate and mechanism and it is essentially unknown. For example, the typical petroleum analysis, in an effort to study petroleum fates and mechanisms, is by gas chromatography. Making quantitative assertions by such procedures is difficult. Apparently, no one has analyzed tar balls for trace elements though Filby and Shah (l.c.) have analyzed some weathered higher molecular weight fractions.

The concentration of other trace materials in the surface layer described by Garrett (1967), Williams (1967), Duce (1972), Hites (1972), for such obvious items as DDT, and PCB, which are known to concentrate in surface oils and are known to hinder biodegradation in accumulated oily sediments in gulf coast areas with petroleum industry pollution sources, and thought to change succession and the relative viability of algal species, [Mosser et al., 1972], seem to be inherent questions in any consideration of fates of pollutant petroleums on the sea.

An interesting and possibly very important issue for radiation and biosynthesis in weathering mechanisms is the question: "Is the oxidized, photolyzed, polymerized, and biosynthesized set of intermediate or final compounds more or less deleterious than the source materials?"

The relative rates of photochemical degradation or building versus the synthesis, uptake, or metabolism by the marine bacteria, algae, and higher plants operating in a randomly repetitive oil milieu is unknown, but to pollution discussants this ought to be a significant question. Carcinogenic materials are present in many crude petroleums. In addition they may be biosynthesized or degraded though available laboratory rates are not applicable, (ZoBell 1971). These same materials may be removed by photolysis (Suess 1972) and given the data on their formation in the internal combustion engine (ZoBell 1971), which is essentially a spark of initiation followed by chain thermal reaction steps, it is probable that sunlight initiated reactions in the oil slick can be followed by chains of reasonable length to form carcinogenic molecules. Unfortunately, no rate of formation data are available, though the marine inventory of carcinogens in sediment and biota is impressive, (ZoBell 1971). ZoBell (1971) has pointed up the ubiquitous character of the CHC and it is apparent that some of the polymeric and other photolysis resultants are of this nature. The retention and possible toxicity of some petroleum fractions has been discussed by Blumer, et al., (1970). ZoBell (1971) points out that some oxidation reactions of fossil fuels lead to CHC. See Table 7. The synthesis, bioformation, uptake, and the metabolism and removal of these potentially catastrophic materials in the case of $h\nu$, ΔT, and bacterial reactions in the surface films, where a variety of organics and inorganics is known to occur, is eminently worthy of detailed study.

C.   Sedimentation Processes As Weathering Fate Mechanism.

The intercalation of organic molecules, including petroleum fractions,
has long been the subject of inquiry. A recent definitive
review, Whitehouse (1969) discusses this subject. It has, of course,
long been known that trace elements are to be found associated with clay
layers. But in recent years the influx of large quantities of significant
metallic ions to the coastal waters has been associated with organic
particulate carriers in the river and estuary waters as the fresh waters
meet the saline waters in the zone of rapid mixing of coastal oceanic
waters. The changes in sorption and desorption of specific metals in
the region of the change of salinity as formerly defined, is now further
complicated. There are organics on the surface, as sequestrants,
coordinators, chelators, also intercalated, and in some instances
coacervated, and these are not just humic and fulvic substances,
but include vitamins, amino acids and other key substances.
The addition of petroleum at the surface where free radical and thermal
disproportionation, and possibly catalyzed reactions are occurring,
the concentration of biocidal materials, the presence of a store
of trace elements in the petroleum, makes for a unique phase of
considerable interest to students of oil pollution fates.

It is perhaps obvious to state that sinking the oil slick by application
of stearated talc or $CaCO_3$ can produce quite different ecological
impacts 200 miles at sea, or in a bay with a large nursery population
and an important marshland periphery. It is perhaps obvious to
state that the utilization of the organic and inorganic N, P in
the surface films of the Eastern Pacific (Williams 1967) may be
radically altered by the interference in this base of the trophic
pyramid or at the source of the trophic chains (Feldman, 1970) by
the presence of oil undergoing its fate processes, and interacting
at each step with the normal biologically mediated and photosynthetically
supported series.

The fate and interaction of petroleum and its fractions at the surface
during the weathering process, is competitive with other removal systems.
Thus, no assertion is made concerning solubilization, evaporation,
droplet diffusion and emulsification, and the myriad phase phenomena
whose rates are not well known, and which require research, as fate
determinants. They actually constitute another class of weathering
rates: removal to other phases or milieux where of course chemical
and biological interactions may be equally as interesting as in
the surface layer.

Thus, why discuss sedimentation which is apparently also a removal
mechanism? Particulate interactions with cellular species, on organic
aggregates of humic materials, on and with larger molecular aggregates
that have undergone at least some of the reactions of Section A all

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constitute unknown but important territory for consideration of sea surface fates. Practical considerations of course are the prime reason for pollution students to be aware of these questions: are the silt of the Southwest (Santa Barbara), the glacial flour of Alaska (Valdez), and the clays of Southeast and gulf coasts of USA, all similar in this regard? How could this be so? The sandy silicious grain may act as a nucleus for evolution of a surface polymeric system but a clay will sequester the organics in sheets and in its layers and what is more the trace element and trace compound interactions will be different in the two cases.

The practical question of the impact of petroleum industrial systems on coastlines with varying sedimentation regimes has great theoretical and practical implications for ecological impact evaluations. No rational government regulation of oil industry practices is possible without at least some investigation and understanding of these unknowns.

SECTION IV

SUMMARY

Three mechanisms, photochemical, trace material interactions, and particulate interactions, have been considered as competitive pathways for the fate of petroleum pollution on the sea surface.

Phenomena observed by a number of researchers have been related to the postulated reactions and mechanisms, and the need for research pointed out in several instances.

Knowledge and understanding of fates and pathways, and ecological and health determining interactions of petroleum pollution and trace materials is a prerequisite for rational governmental regulatory functions.

SECTION V

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TABLE 1

Estimate of Standing Stocks of Pelagic Tar in the Northwest Atlantic
Ocean and Mediterranean Sea

Region	area (units of 10^{12} m^2)	no. of samples	range of samples (mg/m^2)	mean tar conc. (mg/m^2)	probable error of mean	standing stoc (thousands of metric tons)
NW Atlantic Marginal Sea	2	8	0.0 - 2.4	0.9	0.2	2
Gulf Stream	8	16	0.1 - 9.7	2.2	2.4	18
Sargasso Sea	7	34	0.1 - 40	9.4	2.8	66
Total NW Atlantic	17	58	0.0 - 40	5.1		86
Mediterranean (Ref. 5)	2.5	41	0.0 - 540	20.0	1.3	50
Total NW Atlantic and Mediterranean	19.5	99		7.0		136

(Morris, Butler 1973)

15

TABLE 2

	Latitude	Heat Balance Due To Sunlight
Mediterranean	30°-40°N	+.014 to -.005 g cal/cm^2/min
Sargasso	30°N	+.014
N. Atlantic	40°-50°N	-.005 to -.026

TABLE 3

COMPOUND		B.PT.	PEAK #	CONC. (ug/L)
BENZENES				
1-METHYL-2-ETHYL BENZENE		161.3	2	6.68
1-METHYL-4-ETHYL BENZENE		161.99	2	
1 3.5-TRIMETHYL BENZENE		164.72	3	8.10
1-METHYL-2-ETHYL BENZENE		165.15	3	
1·2 4-TRIMETHYL BENZENE		169.35	4	20.15
1:2:3-TRIMETHYL BENZENE		176.08	5	18.07
			6	
1-METHYL-4-PROPYL BENZENE		183.30	7	5.93
1-METHYL-2-PROPYL BENZENE		184.80	7	
1·3-DIMETHYL-5-ETHYL BENZENE		183.58	7	
1·3-DIMETHYL-4-ETHYL BENZENE		188.20	8	
1:2-DIMETHYL-4-ETHYL BENZENE		189.40	8	
1:3-DIMETHYL-2-ETHYL BENZENE		190.01	8	18.17
1-METHYLINDANE		190.6	8	
2-METHYLINDANE		191.4	8	
1.3-DIMETHYL-2-ETHYL BENZENE		190.1	8	
1.2-DIMETHYL-3-ETHYL BENZENE		193.91	9	6.21
1 2:3.5-TETRAMETHYL BENZENE		198 00	10	16.57
1·2:4 5-TETRAMETHYL BENZENE		196.80	10	
4-METHYL INDANE		205.5	11	
1 2.3.4-TETRAMETHYL BENZENE		205.04	11	
1 3-DIMETHYL-4-PROPYL BENZENE		206.6	11	35.39
1 2-DIMETHYL-4-PROPYL BENZENE		208.5	11	
TETRAHYDRONAPHTHALENE		207.57	11	
NAPHTHALENES				
NAPHTHALENE		217.96	12	152.89
2-METHYL NAPHTHALENE		241.05	13	85.66
1-METHYL NAPHTHALENE		244.64	14	63 43
BIPHENYL		255 2	15	27.49
1 2-DIMETHYL NAPHTHALENE			16	32 95
1.6-DIMETHYL NAPHTHALENE			16	
2 6-DIMETHYL NAPHTHALENE		262	16	
TOTAL AROMATICS				610

Substances isolated from Seawater Extract of Kerosene

Relative Concentration of Aromatic Species in Kuwait Oil Seawater Extracts (Slow Stirring)

	µg/l.	Concentration
Benzenes and naphthalenes (Fig 1A)	657	45.2%
Polar aromatics (Fig 1B)	796	54.8%
Total amount of oil in water	1,453	
Concentration of individual compounds		
Naphthalene	32.3	(2.2%)
2-Methyl naphthalene	15.0	(1.0%)
1-Methyl naphthalene	18.0	(1.2%)

[Boylan Tripp 1971]

TABLE 4

Concentrations and enrichment factors of organic compounds and metals in surface microlayer samples from Narragansett Bay, Rhode Island.

Substance	Sample 1 Concentration (μg/liter) Surface	Sample 1 Concentration (μg/liter) Subsurface	Enrichment* factor	Sample 2 Concentration (μg/liter) Surface	Sample 2 Concentration (μg/liter) Subsurface	Enrichme, factor
Fatty acids	128 ± 26	36 ± 7	3.6 ± 1.0	94 ± 19	62 ± 12	1.5 ± 0.4
Hydrocarbons	NA†	NA†	NA†	8.5 ± 1.7	5.9 ± 1.2	1.4 ± 0.4
PCB's‡	4.2 ± 1.0	0.15 ± 0.04	28 ± 10	0.45 ± 0.11	≤ 0.05	≥ 9
Lead						
Particulate	1.4 ± 1.1	0 24 ± 0.17	5 8 ± 6.1	1.5 ± 0.2	0.28 ± 0.10	5 4 ± 2.0
Organic	1 0 ± 0 8	0 36 ± 0 06	2.7 ± 2.2	1.4 ± 0.6	0.27 ± 0.12	5.2 ± 3.1
Inorganic	1.7 ± 0 3	2.7 ± 0.5	0.6 ± 0.2	6.1 ± 1.4	3.7 ± 1.0	1.6 ± 0.6
Iron						
Particulate	320 ± 47	28 ± 4	29 ± 5	35 ± 7	8.2 ± 1.2	4.3 ± 1.1
Organic	3.7 ± 1.5	0.60 ± 0.33	6.2 ± 4.3	5.1 ± 2.3	3.8 ± 0.8	1.3 ± 0 6
Inorganic	2.8 ± 0.4	1.4 ± 0.2	2.0 ± 0.3	17 ± 8	12 ± 1	1.4 ± 0.7
Copper						
Particulate	7.2 ± 2.3	0.20 ± 0 09	36 ± 18	1.3 ± 0.4	0.26 ± 0.11	5.0 ± 2.7
Organic	5 6 ± 0.5	0.19 ± 0.11	29 ± 17	1.6 ± 1.0	0.11 ± 0.04	15 ± 11
Inorganic	3.4 ± 0.4	3.3 ± 0.3	1.0 ± 0.2	1.5 ± 0.6	1.3 ± 0.4	1.2 ± 0.6
Nickel						
Particulate	11 ± 3.0	0 2 ± 0.1	50 ± 30	13 ± 5	2.1 ± 0.3	6 2 ± 2.5
Organic	4.9 ± 2.6	0 48 ± 0.33	10 ± 8.7	5.0 ± 0.6	1.8 ± 0.7	2.8 ± 1.1
Inorganic	11 ± 4 0	14 ± 1.0	0.8 ± 0.3	21 ± 5	16 ± 2	1.3 ± 0.3

* The enrichment factor is equal to the surface concentration divided by the subsurface concentration.   † NA, hydrocarbons not detected because of limited sample.   ‡ PCB's expressed as Aroclor 1254.

[Duce, Quinn, 1972]

TABLE 5

Instrumental Neutron Activation Analysis Results
on 16 Different Marine Fuel Oils

Oil Number	ppm Concentration Found			
	V	Mn	Na	Co
1	17.5	<0.30	35	0.92
2	175	0.043	7.9	0.39
3	220	0.020	1.69	0.62
4	470	0.077	44	0.41
5	77.6	<0.37	108	1.84
6	170	0.011	2.12	<0.07
7	3.8	0.002	0.36	0.08
8	865	<0.19	38	0.13
9	91	<0.39	25.0	0.40
10	250	<0.24	19.0	0.40
11	126	<0.23	7.0	0.23
12	284	0.08	12.4	0.25
13	292	<0.28	85	0.35
14	208	0.07	6.3	0.21
15	152	0.24	32	0.57
16	57.5	0.113	13.3	<0.08

[Guinn, 1970]

TABLE 6

Oil degradation rates under varying conditions as shown by selected authors. It should be noted that seawater temperatures around the U.K. vary from about $2^\circ C$ to $16^\circ C$. The inorganic nitrogen concentration varies from <1 to around 500 μgN l^{-1}.

Bacteria involved	Kind of oil	Experimental conditions	Summary of results	Reference
Garden soil aerobes of several genera	Hydrocarbon mixtures in common use	Batch culture. Mineral salts media. Several temperatures between $20^\circ C$ and $37^\circ C$	$0.4-0.75$ g m^{-2} d^{-1} of some materials measured at $28^\circ C$	Sohngen, N. L. (1913) *Zentralbl. Bakt. Parasitkde. Ab. II:* 37, 595.
Soil aerobes	Emba crude and lubricating oils	Batch culture Nitrate or ammonia in mineral salts media. $23^\circ C$	1 2 g m^{-2} d^{-1} for crude oil (45% of added oil) 0.4 g m^{-2} d^{-1} for lubricating oil	Tausson, V. O. and Shapiro, S. L. (1934) *Mikrobiologiya,* 3: 79.
Enriched culture consisting predominantly of a marine *Pseudomonas*	Clear refined mineral oil	Probably batch culture $25^\circ C$ Aged sea water plus 0.5% KNO_3.	The oxidation of the mineral oil was indicated by O_2 uptake, CO_2 output and bacterial growth. The Q_{10} is given as about 3.0 for temperatures between 0 and $40^\circ C$. The average amount of oil degraded at $25^\circ C$ is given as 1.2×10^{-10} mg per day per bacterial cell. Hence it is calculated that if the oil is uniformly distributed in the water and the population is constant at 8×10^5 organisms ml^{-1} then the rate of oil degradation will be about 350 g m^{-3} yr^{-1} at $25^\circ C$ and about 36.5 g m^{-3} yr^{-1} at $5^\circ C$.	ZoBell, C. E. (1964) *Advances in Water Poll. Res.,* 3: 85. This paper also appears in *Air & Water Poll.,* (1960), 7: 173.
Mixed culture of oil oxidizing bacteria	American crudes	Batch culture, aerated by shaking. $25^\circ C$. Sea water medium reinforced with 0.01% (N H_4)$_2$ HPO_4. About 1 g placed in 100 ml medium. Oil dispersed on ignited asbestos.	Between 17.8% and 98.8% by weight of oil removed in 30 days. Average around 45%.	ZoBell. C. E. and Prokop, J. V. (1966). *Z. allg. Mikrobiol.* 6: 143.
Natural sea water population	Crudes and several refined products	Batch culture. $18^\circ C$. Sea water medium reinforced with NH_4Cl and phosphates.	The influence of various physical and chemical factors on oil degradation is illustrated. The presence of nitrogen and phosphate was shown to increase markedly the breakdown of diesel oil in 8 weeks. The presence of easily degraded material 'spared' the oil. The effect of temperature is also shown.	Gunkel, W. (1967) *Helgolander wiss. Meeresunters,* 15: 210
Natural marine populations	'Atmospheric residue' of Kuwait oil	Sea water percolated through columns of beach sand (median grain size 250μ) with natural meio and micro fauna. Sands were lightly or heavily oiled. $10^\circ C$.	Oxygen uptake used as indication of degradation. Using a 'B.O.D.' value of 5.0, the author calculates a loss of oil from 0 09 g oil m^{-2} d^{-1} to 0.04 g oil m^{-2} d^{-1} depending upon dosing. These rates applied for several months and accounted for 10% of the oil. Preliminary gas chromatograms suggested the main loss was of the alkane fraction. The remaining 90% decayed 'immeasurably slowly'.	Johnston, R. (1960). *J. mar. biol. Ass. UK,* 50: 925.
Selected mixed cultures of oil oxidizing organisms	Louisiana crude	Shaken flasks with sea water enriched with inorganic nitrogen, phosphates and yeast extract. Approx 70 mg oil added to 200 ml medium, $20^\circ C$ and $30^\circ C$. Also simulated field studies of large tanks (900 l). Sea water enriched with (N H_4) SO_4. 50-100 ml of crude added Temperature ambient $8-15^\circ C$. Seeded with oil oxidizing bacteria.	Initial oxidation attributed to breakdown of n-alkanes smaller than C_{12}. The initial rate was followed by a decrease and then another increase. Up to approx 50% of the crude was lost. No evidence of utilization of aromatics was found. In the large tanks the bacteria accelerated the loss of oil and changed its physical character.	Kator, H, Oppenheimer, C. H. and Miget, R. J. (1971). Prevention and control of oil spills. *American Petroleum Institute Conference, 1971,* pp. 287.

TABLE 7

Quantities of PAH Resulting From Combustion of One Gallon
of Commercial Gasoline (calculated from data published by Hoffman and Wynder [40])

PAH	mg/gal	µg/kg
1,2,5,6-Dibenzanthracene	0.007	2 6
10,11-Benzfluoranthene	0.047	17.4
3,4-Benzpyrene	0.088	32.6
1,2-Benzanthracene	0.172	63.6
1,2-Benzphenanthrene	0.175	64.7
3,4-Benzfluoranthene	0.179	66.2
1,2-Benzpyrene	1 181	426.9

· Quantities of 3,4-Benzpyrene Detected in Bottom Deposits

Material	Geographic location	BaP , µg/kg
Mud (42 stations)	Tyrrhenian Sea	1 to 3000
Mud from pyster beds	French coast	90 to 2840
Mud (17 stations)	Mediterranean coast	up to 1800
Mud (8 stations)	Villefranche Bay, France	16 to 5000
Mud (12 stations)	French coast	nil to 1700
Mud and sand	Villefranche Bay, France	nil to 1700
Calcareous deposits	Franch coast	8 to 59
Surface mud	Italian coast	nil to 2500
Mud (218 samples)	Adriatic coast	nil to 3400

Quantities of 3,4-Benzpyrene Detected in Marine Animals
(Values are expressed as µg/kg dry weight of animal tissue)

Kind of animals	Geographic location	BaP, µg/kg	
Oysters	Norfolk, Virginia	10 to 20	
"	French coast	1 to 70	
Mussels	Toulon Roads, France	2 to 30	
Holothurians	Villefranche Bay, France	up to 2000	
"	West coast of Greenland	nil	
Codfish and shellfish	" " " "	16 to 60	
Fish nad shellfish	Saint-Malo Bay, France	3 to 125	
Fish and crustaceans	Villefranche Bay, France	nil to 400	[ZoBell, 1971]
Crustaceans	Arctic Ocean	nil to 230	
Isopod crustaceans	Clipperton Lagoon	up to 530	
Various fishes	Adriatic Coast, Italy	nil to 900	
Invertebrates	" " "	nil to 2200	

FIGURE 1

Beach tar deposits compared to ocean water temperatures.

[ZoBell, 1963]

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7. Author(s) Milton H. Feldman

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16. Abstract Three mechanisms of weathering of oil pollution on marine waters are discussed. Photolysis, interactions with trace materials, and sedimentation with particulate materials are considered as competitive to other fate of petroleum mechanisms, and as having possible ecological importance. Generation of carcinogenics from close molecular precursors is considered probable.

17a. Descriptors Petroleum, photolysis, sedimentation, trace metal, ocean, degradation, trace material, oil pollution

17b. Identifiers Surface, marine, carcinogenics

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