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THE RISK OF TAINTING IN FLATFISH STOCKS DURING OFFSHORE OIL SPILLS

S.L. Ross Environmental Research Limited
717 Belfast Road, Suite 200
Ottawa, Ontario
K1G 0Z4

and

Ledrew, Fudge and Associates
607 Torbay Road
P.O. Box 9370, Station B
St. John's, Newfoundland
A1A 2Y3

Scientific Advisor: Dr. Jerry Payne

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EXECUTIVE SUMMARY

A review of major historical spills shows that tanker spills and oil well blowouts commonly cause oil contamination of the seabed and in some cases this contamination is linked to deleterious effects on benthic species, including flatfish. Oil exploration/production activities and oil tanker traffic in Canadian waters carry with them the risk of spills and a potential threat to both flatfish stocks and the fisheries that they support. The potential risks to flatfish from major oil spills in shallower, nearshore areas is well recognized, but the potential for damage from major spills in deeper, offshore waters is less well understood. The objective of the present study was to review the knowledge-base concerning the potential for organoleptic tainting of flatfish stocks caused by marine oil spills in Canada's deeper offshore waters.

Three important subject areas were reviewed: i) sedimentation of oil and oil contamination of seabed sediments during spills; ii) hydrocarbon exposure conditions causing tainting in flatfish; and iii) the ability of flatfish to detect and avoid oil-contaminated sediments. The results of literature reviews and mail surveys are summarized below.

Seabed Contamination During Historical Spills. During larger historical spills, measurements have been made of oil sedimentation and seabed contamination with oil. These studies demonstrate that some hydrocarbons settle through the water-column and reach the seabed. In larger spills, very large areas of seabed have been contaminated. Unfortunately, too few spills have been studied to permit us to generalize a relationship between spill conditions and seabed contamination. However, information suggests that in offshore spills, initial levels of contamination in the seabed range from 10 ppm to several hundred parts per million, with concentrations as high as 1000 ppm being observed occasionally. For major spills, the area of measurable seabed contamination may be as large as several thousand km^2.

The Sedimentation Rate of Oil. The level, areal extent and pattern of seabed contamination resulting from offshore spills are determined by a number of processes and variables, one of the more important of which is the rate of sinking of oil-contaminated particles. Studies conducted during actual spills have demonstrated that overall mass transfer coefficients for oil sedimentation are low, in the range of 0.01 to 0.05 m day^{-1}. At these low sinking rates oiled particles would require months to reach the seabed. During this time ocean currents would disperse oil particles broadly over a large area and the contamination in any single location would be very, very low. Other data suggest that some oiled particles settle much more rapidly. The data suggests that the larger (>45 μ dia.) oiled particles settle as quickly as 1 to 2 m day^{-1}. Oil associated with these rapidly sinking particles might reach the seabed quickly and cause significant contamination near the spill site. The data show, however, that the proportion of the oil entering the water-column adhering to these larger rapidly sinking particles is very small. These data

suggest that the potential for heavy contamination of the seabed at a deep water spill site is quite limited.

Chemical Composition of Sedimented Oil. The available data suggests that the oil reaching the seabed in offshore waters probably differs greatly in composition from the oil that was spilled. Oil reaching the seabed via sedimentation in deeper waters would be depleted in the lighter (<C15) alkanes and lower molecules weight (LMW) aromatic compounds (one- and two-ring compounds) that are associated with petroleum tainting of fishes. The remaining, higher molecular weight (HMW) alkanes and aromatics have not been implicated in tainting in the past and do not appear to pose a threat of tainting. However, certain of the HMW aromatic compounds have been shown to be carcinogenic and may pose a human health threat.

The fate of two other important groups of crude oil constituents, resins and asphaltenes, appear to be poorly understood. Few of these compounds have been associated with tainting in the past, except for certain sulphur-bearing compounds, such as dibenzothiophenes (DBT). DBTs have been associated with tainting in fish; they are common in sedimented oil; and they are persistent in sediments. The tainting potential of benzothiophenes might be worthy of further study.

Tainting of Flatfish by Hydrocarbons from Sediments. Flatfish have been shown to suffer tainting and other sublethal effects after exposure to oiled sediments. The present review has found no evidence of tainting of flatfish resulting from spills in deeper, offshore waters. Neither has there been experimental work on the oil tainting in flatfish when oil exposure conditions are similar to those in offshore waters as described above. There are conflicting arguments concerning the potential for oil tainting in flatfish during offshore spills. On the one hand, the heavily weathered oil that reaches the seabed in offshore spills is likely to be depleted in the LMW hydrocarbons traditionally linked to tainting. In addition, sediments in deeper waters are unlikely to become heavily contaminated with hydrocarbons (maximum concentration <1000 ppm) regardless of its composition. These arguments suggest that tainting of flatfish in deeper, offshore spills is unlikely. On the other hand, sulphur-bearing compounds that have been implicated in tainting have been observed in offshore oil-contaminated sediments suggesting that there may be some justification for concern over flatfish tainting from spills in deeper, offshore waters.

Tainting of flatfish by nearshore oil spills or by drill cuttings have received some study. Flatfish have become tainted during nearshore spills and available data suggest that oil concentrations in sediments of 2000 ppm (fresh oil) are sufficient to cause tainting. The minimum exposure threshold is not known, and should be identified.

Tainting of flatfish by oil-contaminated drill cuttings has been observed in the North Sea, but the evidence is not conclusive. Although oil-based drilling muds contain potentially tainting compounds, the risk to fisheries appears to be minimal for three reasons: i) cuttings would be stripped of tainting compounds while settling through the

water-column; ii) contamination of seabed would be short-lived; and iii) the area contaminated by cuttings would be very small.

Avoidance of Oil-Contaminated Sediments by Flatfish. Some pelagic fish appear to avoid elevated concentrations of hydrocarbons in the water-column, and certain benthic species may avoid hydrocarbons in sediments. Although the results are fragmentary, the data suggest that flatfish are indifferent to the presence of oil in seabed sediments and apparently do not avoid high concentrations of hydrocarbons in sediments.

Recommendations for Research. A number of recommendations for further study have been made; including:

i) studies of oil sedimentation and seabed contamination should be made during spills of opportunity to verify sedimentation models;

ii) studies of the tainting of flatfish by oil-contaminated sediments containing fresh oil should be made to define the threshold exposure conditions for causing tainting in flatfish; and

iii) monitoring of flatfish near deep-water drilling operations are needed to confirm conclusions of earlier studies that the risk of tainting of flatfish from spent drill cuttings is slight.

RÉSUMÉ À L'INTENTION DE LA DIRECTION

Un examen des déversements historiques d'envergure révèle que les produits déversés par les pétroliers et l'éruption des puits de pétrole sont des causes courantes de contamination des fonds marins par le pétrole et que, dans certains cas, cette contamination provoque des effets nocifs sur les espèces benthiques, dont les poissons plats. Les activités d'exploration et de production et la présence de pétroliers dans les eaux canadiennes comportent des risques de déversement et constituent une menace potentielle pour les populations de poissons plats et l'industrie des pêches qui y est associée. Les risques que représentent pour les poissons plats les déversements pétroliers d'envergure dans les zones littorales peu profondes constituent un danger bien connu, mais les dommages que peuvent causer de tels déversements au large en eau profonde sont moins bien connus. L'objectif de cette étude était de revoir l'ensemble des connaissances sur le risque d'altération des qualités organoleptiques de la chair des poissons plats par du pétrole déversé au large en eau profonde.

Voici les domaines importants qui ont été examinés: i) sédimentation du pétrole et contamination par le pétrole des sédiments de fond à la suite d'un déversement; ii) conditions d'exposition aux hydrocarbures responsables de l'altération des qualités organoleptiques de la chair des poissons plats; et iii) capacité des poissons plats à déceler et à éviter les sédiments contaminés par du pétrole. On résume ci-après les résultats d'études de la documentation et de sondages postaux.

Contamination de fonds marins au cours de déversements historiques. On a mesuré, au cours de déversements historiques d'importance, la sédimentation du pétrole et la contamination des fonds marins par le pétrole. Ces études montrent que certains hydrocarbures traversent la colonne d'eau et se déposent sur le fond marin. De grandes zones de fond marin ont été contaminées à la suite d'importants déversements. Malheureusement, on ne peut établir une relation générale entre les conditions de déversement et la contamination des fonds marins, en raison du faible nombre de déversements qui ont fait l'objet d'études. Toutefois, selon les informations obtenues, dans le cas de déversements au large, les concentrations initiales de pétrole dans le fond marin varient d'une dizaine à plusieurs centaines de ppm et peuvent à l'occasion atteindre 1000 ppm. Dans le cas de déversements d'envergure, l'aire contaminée mesurable peut s'élever à plusieurs milliers de km^2.

Vitesse de sédimentation du pétrole. L'importance, l'étendue et la distribution de la contamination résultant de déversements au large dépendent d'un certain nombre de processus et de variables, dont l'un des plus importants est la vitesse de sédimentation des particules contaminées par du pétrole. Des études réalisées au cours de déversements réels ont montré que dans l'ensemble les coefficients de transfert de matière pour la sédimentation du pétrole sont faibles, soit dans l'intervalle de 0,01- 0,05 $m.d^{-1}$. Animées de ces faibles vitesses de sédimentation, les particules chargées de pétrole mettraient des mois pour atteindre le fond marin. Pendant ce temps, les courants océaniques disperseraient les particules de pétrole sur une très grande surface et la contamination en un point quelconque serait très très faible. Selon d'autres

données, certaines particules chargées de pétrole se déposent beaucoup plus rapidement; en effet, la vitesse de sédimentation des grosses particules (> 45 μ de diamètre) serait aussi élevée que 1 - 2 $m.d^{-1}$. Le pétrole associé à ces particules se déposant rapidement pourrait atteindre rapidement le fond marin et entraîner une importante contamination à proximité du site de déversement. Toutefois, les données révèlent que la proportion du pétrole qui pénètre dans l'eau avec ces grosses particules se déposant rapidement est très faible. Selon ces données, le risque qu'un déversement en eau profonde provoque une importante contamination du fond marin est très limité.

Composition chimique du pétrole sédimenté. Selon les données disponibles, le pétrole qui atteint le fond marin après un déversement au large possède probablement une composition très différente du pétrole déversé. Le pétrole déposé en eau profonde ne contiendrait à peu près plus d'alcanes légers (< C_{15}) et de composés aromatiques de faible masse moléculaire (monocycliques et bicycliques) qui sont responsables de l'altération des qualités organoleptiques de la chair des poissons. Les autres alcanes et composés aromatiques plus lourds n'ont jamais été tenus responsables de l'altération des qualités organoleptiques et ne semblent pas constituer une menace à cet égard. Toutefois, certains des composés aromatiques lourds sont cancérogènes et peuvent constituer une menace pour la santé humaine.

On ignore à peu près tout, semble-t-il, du devenir des deux autres importants groupes de constituants du pétrole brut, soit les résines et les asphaltènes. Exception faite de certains composés soufrés comme les dibenzothiophènes (DBT), seuls quelques-uns de ces composés ont été associés à l'altération des qualités organoleptiques. Les DBT ont été associés à l'altération des qualités organoleptiques de la chair des poissons, et on les trouve fréquemment dans le pétrole contaminé; ce sont des espèces persistantes dans les sédiments. Il y aurait peut-être lieu d'étudier dans quelle mesure les benzothiophènes risquent d'altérer les qualités organoleptiques.

Altération par les hydrocarbures des qualités organoleptiques de la chair des poissons plats. L'exposition à des sédiments chargés de pétrole provoque, chez les poissons plats, une altération des qualités organoleptiques ainsi que d'autres effets sublétaux. Cette étude n'a révélé aucune altération de la chair des poissons plats à la suite de déversements au large en eau profonde. De même, aucune étude expérimentale n'a été effectuée sur l'altération de la chair des poissons plats par le pétrole dans des conditions d'exposition semblables à celles observées au large en eau profonde, comme celles décrites ci-dessus. Des thèses contradictoires ont été avancées sur les risques d'altération de la chair des poissons plats au cours d'opérations de forage off-shore. D'autre part, le pétrole fortement altéré qui se dépose sur le fond marin à la suite d'un déversement au large contient probablement très peu des hydrocarbures de faible masse moléculaire qui interviennent normalement dans le processus d'altération des qualités organoleptiques. De plus, les sédiments en eau profonde risquent moins de devenir fortement contaminés par des hydrocarbures (concentration maximum < 1000 ppm) et ce, quelle que soit la composition du pétrole. Selon ces données, les risques d'altération des qualités organoleptiques de la chair des poissons plats au large en eau profonde sont faibles. Par contre, on a décelé des composés soufrés associés à l'altération des qualités organoleptiques dans les sédiments au large contaminés par du pétrole, ce qui laisse supposer que l'inquiétude que suscite

le risque d'altération de la chair des poissons plats par des déversements au large en eau profonde est peut-être justifiée.

L'altération des qualités organoleptiques de la chair des poissons plats par des déblais de forage ou du pétrole déversé à proximité du littoral a été quelque peu étudiée. Les qualités organoleptiques de la chair des poissons plats ont été altérées au cours de déversements à proximité du littoral et, selon les données disponibles, des concentrations de pétrole de 2000 ppm dans les sédiments (pétrole non modifié) sont suffisantes pour causer une altération. On ne sait pas quel est le seuil d'exposition, mais il y aurait lieu d'en déterminer la valeur.

On a observé des cas d'altération de la chair des poissons plats par des déblais de forage contaminés par du pétrole dans la mer du Nord, mais les données ne sont pas concluantes. Les boues de forage à base de pétrole contiennent des composés susceptibles d'altérer les qualités organoleptiques du poisson. Néanmoins, les risques que représentent ces boues pour l'industrie de la pêche sont minimes, semble-t-il, pour les trois raisons que voici: i) au fur et à mesure qu'ils se déposent dans la colonne d'eau, les déblais de forage perdraient leurs composés responsables de l'altération; ii) la contamination du fond marin serait de courte durée; et iii) la zone contaminée par les déblais serait très petite.

Évitement, par les poissons plats, des sédiments contaminés par du pétrole. Certains poissons pélagiques semblent éviter les zones où l'eau possède une concentration élevée d'hydrocarbures, et certaines espèces benthiques peuvent éviter les hydrocarbures dans les sédiments. Les résultats sont fragmentaires, mais les données laissent supposer que les poissons plats ne réagissent pas à la présence de pétrole dans les sédiments de fond et ne semblent pas éviter les sédiments dont la concentration d'hydrocarbures est élevée.

Recommandations relatives à la recherche. Un certain nombre de recommandations relatives aux études qu'il y aurait lieu d'effectuer ont été formulées, dont les suivantes:

i) il y aurait lieu d'étudier la sédimentation du pétrole et la contamination du fond marin au cours de déversements réels, en vue de vérifier les modèles de sédimentation;

ii) il y aurait lieu d'étudier l'altération des poissons plats par des sédiments contaminés contenant du pétrole non modifié, en vue de définir les conditions d'exposition minimales provoquant l'altération chez ces poissons; et

iii) il faudrait procéder à un contrôle des poissons plats à proximité des zones de forage en eau profonde, en vue de confirmer les conclusions tirées d'études antérieures et selon lesquelles le risque d'altération des qualités organoleptiques de la chair des poissons plats par les déblais de forage est faible.

INTRODUCTION

Petroleum exploration/production activities in Canadian coastal and shelf areas and oil tanker traffic through Canada's coastal waters, carry with them the risk of petroleum spills. These spills pose risks of hydrocarbon contamination to a variety of marine habitats including the seabed sediments. The flatfish inhabiting the seabed would be in intimate contact with these oil-contaminated seabed sediments and might suffer adverse effects as they have done in the past during major oil spills (Elmgren et al. 1983, Haensley et al. 1982). Risks to flatfishes from spills in shallow nearshore areas are well recognized, but the potential risks from spills in deeper offshore areas are almost completely unstudied. The objectives of this study are to:

i) review the state of knowledge concerning the tainting of flatfish by petroleum hydrocarbons accumulated from sediments,
ii) review the state of knowledge concerning the ability of flatfish to detect and avoid oil-contaminated sediments; and
iii) review knowledge concerning the processes controlling the transport of spilled hydrocarbons from surface oil slicks to seabed sediments.

Although flatfish inhabit both shallow, nearshore and deeper, offshore habitats, and suffer a variety of effects from exposure to petroleum hydrocarbons, particular emphasis in this study has been limited largely to the risks of tainting of flatfish from spills in deeper, offshore habitats such as the Newfoundland Grand Banks.

Contamination of seabed sediment with petroleum hydrocarbons has been documented during a number of historical spills including coastal zone spills (e.g., Amoco Cadiz spill, Marchand and Caprais 1981; Florida barge spill, Sanders et al. 1980) and offshore spills (e.g., Main Pass Blocks 41 spill, McAuliffe et al. 1975; Ixtoc-1 spill, Boehm and Fiest 1980, Payne et al. 1980). Flatfishes exposed to hydrocarbons in these as well as other spills have been shown to suffer a variety of effects ranging from simple hydrocarbon contamination of tissues (Elmgren et al. 1983) and organoleptic tainting (Simpson 1968; Palmork & Wilhelmsen 1974) to extensive tissue necrosis (Haensley et al. 1982) and reproductive failure (Desaunay 1981). The possibility that oil spills on the Grand Banks might have similar effects on local flatfish stocks is of considerable interest in Canada because of the importance of the flatfish fishery in this area. American plaice and yellowtail flounder together make up a significant proportion of the annual yield to Canadian fishermen on the Grand Banks.

Risks to flatfish from spills in shallow, nearshore areas are well recognized, but risks from offshore spills represent unique problems and are less well understood. In nearshore spills, flatfish in shallow nearshore waters might be exposed to greatly elevated concentrations of fresh oil both in the water-column or in sediments. In offshore spills, flatfish in deeper waters are unlikely to be exposed to elevated hydrocarbon concentrations in the water-column, but might suffer prolonged exposure to the oil that

accumulates over time in the seabed sediments. In shallow nearshore areas the oil mixed into the sediments might be relatively fresh, while oil reaching the sediments in offshore spills might be somewhat weathered. In the present study emphasis has been placed on the offshore spills where fishes might be exposed only to weathered oil in sediments.

In both nearshore and offshore cases, flatfish might experience a variety of effects. These effects would range from simple contamination and tainting to severe sublethal effects and even mortality. In the present work we are concerned with only tainting.

In assessing the risk of tainting to offshore fisheries from spills on the Grand Banks, a number of questions might be addressed.

i) What amounts or concentrations of petroleum in sediments are necessary to cause adverse effects (such as tainting) in flatfish?
ii) What amounts or concentrations of hydrocarbons might accumulate in seabed sediments as a result of an oil spill in deeper, offshore waters?
iii) How large an area might be contaminated?
iv) To what degree would sedimented oil be depleted/altered in composition?
v) If significant levels of seabed contamination did result from a spill, how much time would be required for degradation to reduce hydrocarbon concentrations in sediments to innocuous levels?

An extensive review of the literature and a mail survey of workers in the field have been used to address these questions.

APPROACH

In order to address the above questions information from a variety of sources has been examined. In particular we have analyzed the following.

i) Information concerning the transport of oil from oil slicks to seabed sediments was examined by reviewing experimental studies and studies of historical spills. The aims of this analysis were to determine the nature of hydrocarbon exposure conditions that flatfish might experience as a result of spills in deeper, offshore waters, and to assess the state of knowledge concerning the processes involved in the sedimentation of oil.

ii) An exhaustive review of the literature was conducted into hydrocarbon tainting of flatfish with particular emphasis on hydrocarbons accumulated from sediments.

iii) A detailed review of the literature was conducted into the behaviour of flatfish in order to determine assess the potential for flatfish to detect and avoid hydrocarbon-contaminated sediments and thereby avoid exposure to dangerously high concentrations of hydrocarbon in sediments.

iv) Preliminary work had indicated that very little published information was available concerning the tainting of flatfish or flatfish behaviour and hence an extensive international mail and telephone survey of workers in the field was conducted in order to identify any additional information available. (A copy of the names and addresses of the workers contacted are given in the Appendix to this report.)

The results of these reviews and surveys are included in this report.

LIMITATIONS

This study could conceivably deal with the broad subject of the potential for adverse effects on benthic species from oil-contaminated sediments. However, as far as possible, the following limitations have been applied.

i) The study focuses on offshore spills in deeper waters where shoreline impingement of oil slicks and the redistribution of stranded oil to subtidal benthic sediments is not an issue. In these offshore environments contamination of sediments would result from sedimentation of hydrocarbon through the water-column rather than from the direct mixing of fresh oil into sediments or from seaward migration of oil stranded in the intertidal zone.

ii) As much as possible we have limited this study to effects of hydrocarbon-contaminated sediments on flatfishes rather than other benthic or demersal species.

iii) Although a wide variety of effects have been demonstrated in flatfish resulting from exposure to hydrocarbon-contaminated sediments (including contamination, pathologies, necroses, and tumors), this study will be limited as much as possible to organoleptically detectible tainting, that is tainting or "off-flavours" that are detectible to taste testers.

SEABED CONTAMINATION FROM OIL SPILLS

INTRODUCTION

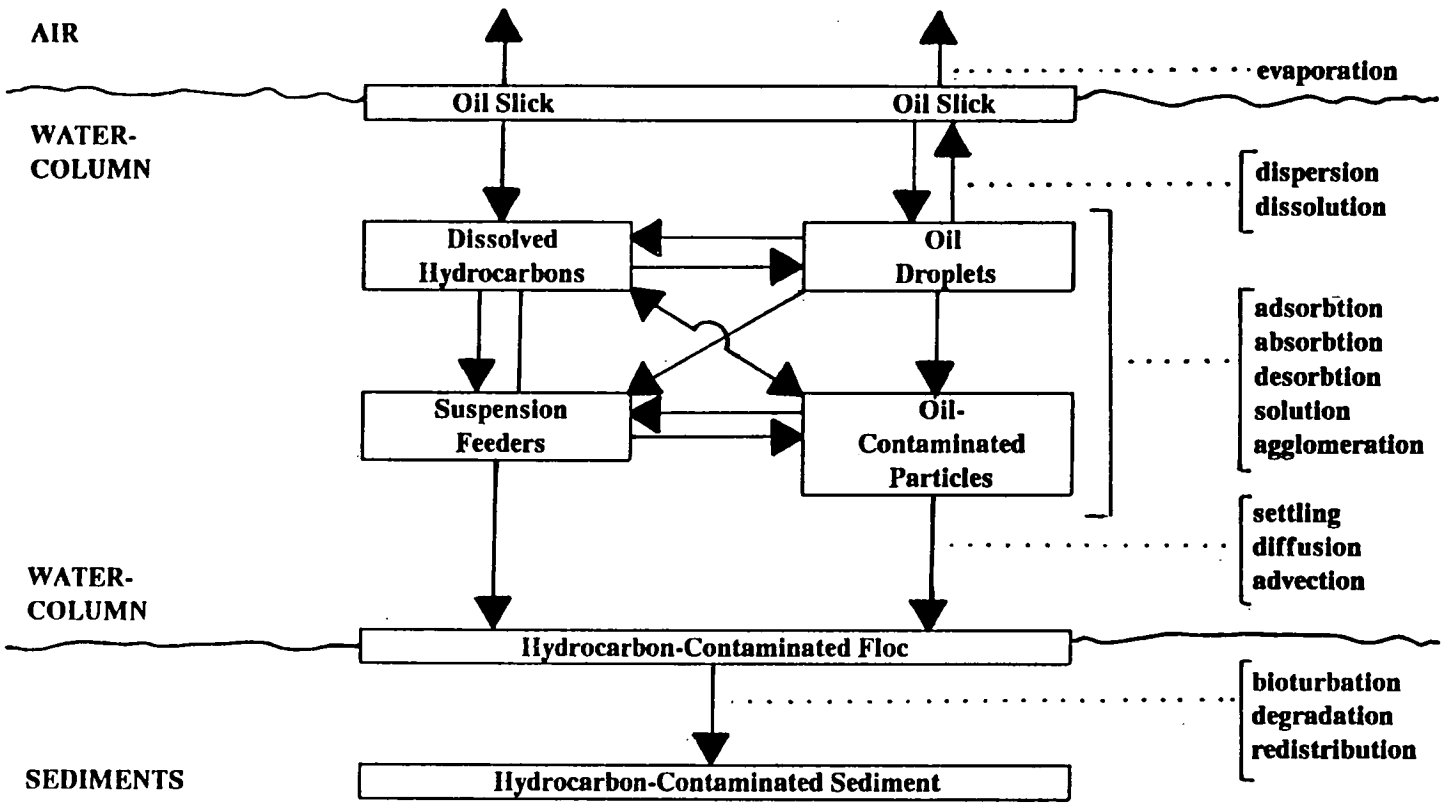
A variety of field studies have demonstrated that during oil spills some of the discharged hydrocarbons have reached the seabed sediments. The level of seabed contamination, the areal extent of contamination, the chemical composition of contaminants, and the persistence of hydrocarbons in the sediments are important in determining the possible effects of a spill on fisheries through tainting. This section is devoted to a brief review of information concerning these factors and the processes that control them. This review is important in several regards. First it is essential to understand the hydrocarbon exposure conditions (chemical composition, physical form) in order to be able to adequately interpret the results of experimental studies of tainting. It is also important to understand the processes by which seabed sediments become contaminated in order to be able to begin to predict the level of seabed contamination and the spatial pattern of contamination. The following is a brief description of the transport of hydrocarbons from the surface oil slick to the seabed. Much of this is taken from several reviews of the subject (Jordan and Payne 1980, Lee 1980, Mackay 1984, National Research Council (U.S.) 1985).

During oil spills hydrocarbons find their way from the surface oil slick into the sea bed in a number of ways. In shallow, near-shore, high-energy environments hydrocarbon droplets may be mixed directly into the seabed sediments by wave action and turbulence. Also in these shallow, near-shore areas, oil that has been stranded on the beach in the intertidal tidal zone may be redistributed to the subtidal zone. In both shallow, nearshore waters and deeper offshore waters some hydrocarbons from oil slicks become entrained into the water-column in the form of particles or oil droplets, become associated with particulate matter in the water-column, and settle to the sea floor. In this review we will concentrate on processes controlling seabed contamination during offshore spills of the type that might occur on the Newfoundland Grand Banks. In spills at this location oil would reach the bed sediments almost exclusively by being entrained into the water-column, becoming associated with suspended particulate matter and then settling through the water-column toward the seabed.

Oil reaching the seabed during spills in offshore waters has undergone a variety of processes as it moves from the sea surface to the seafloor. These processes are summarized in Figure 2.1. The lighter, more volatile hydrocarbons are lost by evaporation from the oil slick on the sea surface. Part of the remaining mass of oil becomes entrained into the water-column through dispersion of oil droplets into the surface waters by turbulence and breaking waves. The size of the droplets entering the water-column is important from the perspective of i) sedimentation, ii) stability of the oil-water dispersion, iii) interactions with marine life, and iv) interactions with non-living suspended sediments. The larger droplets rise to the sea surface and rejoin the slick, but the smaller droplets, though buoyant, appear to be held in suspension through turbulence. In the water-column, the water-soluble, low-molecular-weight molecules such

FIGURE 2.1

Movement of Oil from the Surface Oil Slick to the Sea Bed Sediments



as the lighter aromatics (benzenes, naphthalenes) dissolve from the oil droplets into the water phase while the less soluble, higher-molecular-weight hydrocarbons remain in the oil droplets. The larger of these droplets agglomerate with suspended material while the smaller particles adsorb onto particles as well. The larger and more dense of the resultant oil-contaminated particles sediment rapidly. The smaller and less dense of the contaminated particles settle very slowly and may themselves be kept in suspension through turbulence.

Contaminated particles that fall into the appropriate size ranges are ingested by suspension-feeding organisms and some of this ingested hydrocarbon material is subsequently egested as fecal pellets. The larger fecal pellets sink rapidly toward seabed.

Except in areas containing large quantities of large, dense particles, gross sedimentation rates of oil appear to be very low. While the oil-contaminated suspended matter is settling to the seabed, it is no doubt advected by sub-surface currents and diffuses outward by turbulent diffusion. Hence the cloud of sedimenting particulate material is carried down-current away from the spill site and spreads as the oiled particles diffuse through the water-column.

As particles settle through the water-column certain hydrocarbons may undergo degradation by either microbial or chemical means.

Hydrocarbon-contaminated particles arrive at the seabed in the form of light flocculent material that settles on the surface of the seabed. This material is very light and hence can be resuspended and redistributed by seabed ocean currents. The hydrocarbon-bearing floc may settle on the surface of the seabed or it may penetrate into the interstices of the coarser sediments. Initially hydrocarbons form a thin layer only a few mm thick on the surface of the seabed. This material may become mixed into the seabed to a depth of several centimetres through activities of benthic infauna. Hydrocarbons occurring in well-oxygenated surface sediments become degraded with time, but hydrocarbons that become buried deeply into the anoxic sediment layers may remain unchanged for years.

In the following sections information concerning sediment contamination from spills and sedimentation of oil are reviewed from the perspective of predicting the hydrocarbon exposure conditions likely to be experienced by flatfish following offshore spills. Historical spills are examined to determine the level of contamination and areal extent of contamination that has occurred in the past during offshore spills. Sedimentation of oil from the water-column is considered. Finally the persistence of oil in sediment is considered because this determines the longevity of any tainting problems that might occur.

SEABED CONTAMINATION DURING HISTORICAL SPILLS

The level and areal extent of seabed contamination are important when estimating potential damage to benthos from spills. The level (concentration) of spill-derived hydrocarbons in the sediments is a measure of the hydrocarbon exposure conditions that flatfish experience and hence determines the potential risk of deleterious effects. The areal extent of sediment contamination taken in conjunction with the spatial distributions of benthic fish stocks determine the proportion of the stocks and fisheries that might be adversely affected by the spill. In this section historical spills are re-examined to determine the levels of seabed contamination and the approximate areal extent of contamination that were observed.

When interpreting observational data concerning hydrocarbon-contaminated sediments it is important to recognize two considerations. First, the mere presence of hydrocarbons in sediments does not prove spill-related contamination. Sediments contain hydrocarbons of natural origin, as well as hydrocarbon contaminants from diffuse man-made sources such as the burning of fossil fuels. Spill-related contamination is recognizable in some cases as consistently elevated levels of contamination (higher than background) or in other cases as the presence of petroleum having a chemical composition (fingerprint) similar to the oil that had been spilled. Second, it is important to bear in mind the form of the seabed contamination and how it is sampled. Spill-related hydrocarbons arrive at the seabed associated with light flocculent material that forms a thin layer (several mm thick) of hydrocarbon-rich material on the surface of the seabed sediments. Conventional sampling devices are usually ineffective in sampling this floc because the "bow waves" of the sampling gear blow the floc aside when sampling or the samplers allow the floc-material to spill out with drainage as the sampler is hauled aboard the sampling vessel. In addition, even if the floc is adequately sampled, the results must be considered to be a composite of both the floc containing high concentrations of hydrocarbons plus the upper 3-4 cm of sediment containing background concentrations of hydrocarbons.

Background levels of hydrocarbons in marine sediments in subtidal and shelf areas of North America are shown in Table 2.1. These data suggest that background levels of hydrocarbons in sediments from various locations are largely lower than 10 ppm total hydrocarbon on a dry weight basis. The levels of seabed contamination and areal extent of contamination for several historical spills are summarized in Tables 2.2 and 2.3. The circumstances of the spills and the resultant seabed contamination are summarized below.

The Ixtoc-1 spill was a subsea blowout in the Bay of Campeche, Gulf of Mexico in which oil was released at a rate of approximately 2000 m^3 per day for 9 months, for a total discharge of approximately 600,000 tonnes of crude oil. The spill began on 3 June 1979 and ended on 20 March 1980. A limited sampling program was undertaken in September 1979 in which samples were taken of seabed sediment and suspended sediments (Boehm and Fiest 1980). Hydrocarbons of spill origin were identifiable in benthic samples as far as 46 km from the spill site, but not at a station 96 km away.

Hydrocarbon concentrations in sediment samples taken at stations 31 km and 46 km away from the spill site ranged from 30 to 143 ppm dry weight. There were too few samples to determine whether any clear concentration gradient existed, although the authors suggested that higher concentrations might have existed closer to the spill site.

Concentrations of hydrocarbons on particles collected in sediment traps within the upper 15 m of the water-column were estimated by authors to range from 1000 to 25000 ppm. The dramatic difference between hydrocarbon concentrations on particles collected in sediment traps and seabed samples reflects the fact that the sediment trap samples consist largely of heavily contaminated floc material while seabed samples consists of a relatively small amount of heavily contaminated floc combined with large amounts of bed sediment which contain only background concentrations of hydrocarbons.

Based on this rather limited data set the authors suggested that detectible seabed contamination might have extended to as far as 30 to 50 km from the blowout site for a total area of contamination of 2800 to 8800 km^2. This was consistent with observations that clearly elevated water-column concentrations of hydrocarbons could be detected up to 40 km from the spill site (Boehm and Fiest, 1980). The authors suggested that approximately 1 to 2 % of the hydrocarbons discharged up to that time had found their way to the seabed sediments.

The Main Pass Block 41 (MP41) spill was an above-sea blowout in which an estimated 10,000 m^3 of oil was released during a 3-week period in February and March of 1970, near the mouth of the Mississippi River in the Gulf of Mexico. A very extensive benthic sampling program was undertaken (McAuliffe et al. 1975) in which 75 bed sediment samples were collected and analyzed from areas adjacent to the rig to distances as great as 75 km from the rig. All oil identifiably of MP41 origin occurred in samples taken within eight km of the spill site, a far shorter distance than in the Ixtoc-1 spill. Significantly, all samples containing MP41 hydrocarbons occurred within the area that was frequently slick-covered while the well was discharging oil.

Hydrocarbon concentrations in the sediments were highly variable within and eight-km radius with no clear evidence of a concentration gradient. The most heavily contaminated sediments contained oil concentrations slightly greater than 1000 ppm, but most sediments samples were in the 100 to 1000 ppm range. (Table 2.2). In this spill, seabed contamination might have been expected to be greater than average in terms of oil concentrations in the sediments concentrations and lower than average in spatial extent for several reasons.

i) Chemical dispersing agents were used for fire suppression during the early phases of the spill putting large quantities of oil into the water-column near the spill site.
ii) A high suspended sediment load from the Mississippi outfall might have helped precipitate the hydrocarbons quickly near the spill site and not allow them time to spread away from the well.

TABLE 2.1
Background Levels of Hydrocarbons in Coastal and Shelf Sediments in North America

	Range of Hydrocarbon Concentrations in Sediments	
Location	ppm, dry weight	Reference
Grand Banks	<7.3	Levy 1983
Scotian Shelf	0.01 to 2.3	Kaiser et al. 1978
Northeastern Gulf of Mexico	1.5 to 11.7	Lytle and Lytle 1977
Eastern Arctic	<7.5	Boehm 1981

TABLE 2.2

Level of Seabed Contamination Resulting from Historical Spills

Spill	Total Hydrocarbon Concentration in Sediments (ppm, dry wt.)					
	<10	10-100	100-1000	1000+	Greatest Concentration Measured	Reference
Main Pass Block 41[1,2]	18	18(2)	19(9)	(2)	1250	McAuliffe et al. 1977
Amoco Cadiz[3]		3	7	1	1230	Law 1978
Amoco Cadiz	3	18	1	1	1117	Marchand & Caprais 1981
Amoco Cadiz	1	29	4	0	219	Marchand & Caprais 1981
Ixtoc-1[2]	0	5	(5)	0	143	Boehm et al. 1982
Ekofisk[2]	4	0	0	0	0.9	Law 1978
Tsesis	no data					Boehm et al. 1982

1. Main Pass Block 41 results reflect concentrations of C_{12} to C_{33} hydrocarbons measured by GC. Values are reported in McAuliffe et al. (1977) were in terms of wet weight of sediments and have been converted to dry weight by assuming 90% moisture content by weight.
2. Values in parenthesis for these studies represent samples in which hydrocarbons in sediments are clearly derived from the spilled oil.
3. Amoco Cadiz sediment samples reported in wet weight terms, converted to dry weight assuming 90% moisture.

TABLE 2.3

Areal Extent of Seabed Contamination During Historical Spills

Spill	Volume of Oil Spilled m^3	Distance Offshore km	Water Depth m	Area of Seabed Oiled km^2	Percent Reaching Seabed	Reference
Blowouts						
Ixtoc-1	600,000	80	51	3000 to 8000	1-2[4]	Boehm and Fiest 1980
Ekofisk (Bravo)	25,000	300	45	?[1]	?	Law 1978
Main Pass Block 41	10,300	17	15	200	1[4]	McAuliffe et al. 1977
Tanker Spills						
Amoco Cadiz[2]	223,000	1.5	0-50	6000	?	Marchand & Caprais 1981
Tsesis	1100	<10	20+	no data[3]	10-15[5]	Boehm et al. 1982

1. Seabed samples may have been taken too early in the spill before sedimentary hydrocarbons arrived at the seabed.
2. Amoco Cadiz spill impinged in shorelines.
3. Authors hypothesized that sediment sampling equipment failed to sample the oil-contaminated floc on the seabed surface.
4. Based on sampling of seabed sediments.
5. Based on oil recovered from sediments traps.

iii) Water depths were shallow (~ 15 m at the spill site) allowing sediments to reach the seabed quickly and not allowing them to spread.

In short, the authors suggest that significant levels of seabed contamination were measurable only within 8 km of the spill site for an area of contamination of approximately 200 km^2. Levels of contamination were mostly in the 10 to 100 and 100 to 1000 ppm range with only a few samples measuring over 1000 ppm. Only approximately 1% of the spilled oil appears to have reached the seabed sediments.

The Ekofisk/Bravo blowout was an above-sea blowout in which oil was released at a rate of approximately 2500 to 4000 m^3 per day for 7.5 days for a total of 20,000 to 30,000 m^3. The spill occurred in approximately 45 m of water in April 1977 in the Ekofisk field in the North Sea. Seabed sediment samples taken only days after the blowout was capped showed no evidence of oil contamination, while material collected in sediment traps showed that oil-contaminated particulate matter was settling through the water-column at distances as great as 46 km down-current from the blowout site.

There are at least two explanations for the failure to find oil contamination in the sediments in this spill.

i) The sediment sampling methods used may have failed to retain the oil-contaminated floc layer adequately.
ii) The samples may have been taken before appreciable amounts of hydrocarbon-contaminated floc accumulated on the seabed.

Few offshore tanker spills have received detailed scientific study. To my knowledge no offshore tanker spill has been studied even to the limited extent of the above blowouts. However, two nearshore tanker spills have been thoroughly studied and results of these studies are considered here.

The Tsesis tanker spill was a relatively small spill involving the release of approximately 1000 tonnes of medium fuel oil (No. 5 fuel oil plus some bunker oil) among the islands of an archipelago in the Baltic Sea. As in the Ekofisk spill, sediment samples failed to show any significant oil contamination of sediments. This was possibly due to the ineffectiveness of traditional sampling equipment for adequately sampling the oil-contaminated floc layer (Boehm et al. 1982). However, significant amounts of hydrocarbon-contaminated particles were collected in sediment traps within several km of the spill site, demonstrating that some of the spilled oil was indeed settling through the water-column. Based on an extensive series of sediment trap samples, the authors concluded that 30 to 60 tonnes of oil or 10 to 15% of the unrecovered oil[1] had sedimented through the water-column within several km of the spill site. Oiled particulate material was found sedimenting through the water-column at least 6 km downwind and

1 A major proportion of the spilled oil was recovered during shoreline cleanup operations.

2.5 km upwind, but no information is available concerning the area of seabed contaminated.

The Amoco Cadiz tanker spill was a large, nearshore discharge involving more than 200,000 m^3 of crude oil, 2.8 km off the coast of Brittany in which an extensive stretch of shoreline was heavily oiled. An extensive benthic sampling program was undertaken in both coastal and offshore areas (Marchand and Caprais 1981). The latter authors found that significant contamination was restricted to an area of shelf approximately 100 km in length extending from the subtidal area seaward to the 50 m isobath. This area corresponded to an area to the east of the spill site where oil slicks had been evident during the first month of the spill. The size of the area involved was approximately 6000 km^2. Oil concentrations in sediments were as high as 1000 ppm, but most concentrations were far lower, in the 10 to 100 ppm range (Table 2.2) . Hydrocarbon concentrations were greatest in the shallow, nearshore areas and declined with increasing depth. No studies of oil sedimentation through the water-column during this spill have been found.

Our understanding of seabed contamination from offshore spills is limited due to the small numbers of spills that have been studied and by difficulties in sampling newly settled, oil-contaminated sediment. However, these few spills have provided us with certain information. In all of these spills, workers have estimated that from 1 to 15% of the spilled oil has reached the seabed sediments near the spill site. Hydrocarbon-contaminated particulate material settling to the seabed may contain from 1000 to 25000 ppm (dry weight) hydrocarbons. When this material arrives at the seabed forming a thin layer (a few mm in thickness) over the bed sediments the mean concentration of hydrocarbons in the upper 4 cm of bed sediment range from a few tens to a few hundreds of parts per million, with occasional samples registering as high as 1000 ppm. In the major spills that have been studied, measurable amounts of spill-derived hydrocarbons have been detected in seabed sediments or in suspended particulate matter as far as 46 km from the spill site. Areas of seabed contaminated in the larger of those spills have been less than 10,000 km^2. In most studies, however, the number of samples taken have been too small to reliably estimate the size of the area affected or to identify a concentration gradient of oil in the sediments. The number of spills studied is too small to show quantitative relationships between spill conditions and the concentration of hydrocarbons in sediments or the size of the area affected.

HYDROCARBON SEDIMENTATION THROUGH THE WATER-COLUMN

The key to predicting the pattern of seabed contamination from spills lies in our understanding of the sedimentation process. This process has been studied during several actual spills and in a number mesoscale experiments. These studies have focused on a variety of subjects including the partitioning of hydrocarbons between particulate and aqueous phases, the sinking rate of oil-contaminated particles and the chemical changes undergone by oils during sedimentation. Sedimentation of oil through the water-column is very important in the present context because the competing process of settling and lateral diffusion determine whether enough oil-contaminated particles settle to the seabed

near the spill site to cause high concentrations of oil in seabed sediments. In this section information concerning the sedimentation of oil has been summarized based on historical spills and mesoscale studies.

Historical Spills

During the Tsesis[2] spill Johansson et al. (1980) and Boehm et al. (1982) collected sedimenting oil in traps placed a few metres above the sea floor at various locations near the spill site. These authors found that measurable amounts of oil settled through the water-column from the oil slick in the days immediately following the spill. The authors found that initial oil sedimentation rates were high ranging from 28 to 62 mg oil m^{-2}. They also found that the oil that reached the sediments in the vicinity of the spill site settled to the seabed quickly, within 14 days or less of the spill date, with little oil sedimenting after this time (Table 2.4). Since water depths in this area ranged from 15 to 25 m this oil settled to the seabed at an average rate of at least 1 to 2 metres per day. Unfortunately no values for oil concentrations in the water-column were reported in this study and hence no mass transfer coefficients could be calculated. The authors hypothesized that sedimentation of oil in this case was facilitated by high levels of seston in the water-column caused by wind-induced resuspension of bottom sediments. They found that significant amounts of oil settled to the bottom not only in slick-covered areas downwind of the spill site, but also at a location several km upwind from the spill where no slick had been evident (Table 2.4., Station #4). They concluded that once oil had entered the water-column from the slick it would be redistributed by the sub-surface water currents to nearby areas not covered by the slick.

2 Tsesis spill was a spill of 1100 metric tonnes of No. 5 fuel oil from a tanker in the Baltic Sea in October 1977.

TABLE 2.4
Petroleum Sedimentation During Historical Spills

Spill	Station	Water Depth at Sample Site m	Time Interval	Total Sedimented Material g $m^{-2}d^{-1}$	Concentration of Oil in Suspended Sediments ug g^{-1}	Rate of Sedimentation mg $m^{-2}d^{-1}$	Reference
Tsesis	#2, 6.1 km from spill	20	Nov. 2-9	--	4779	38.0[2]	Johansson et al. 1980
			Nov. 9-12	6.6	2816	18.6	
			Nov. 17-Dec. 21	2.9	186	0.5	
Tsesis	#5, 4.5 km from spill	25	Nov. 1-9	8.6	7265	62.5	Johansson et al. 1980
			Nov. 9-17	5.7	2073	11.8	
			Nov. 17-Dec. 14	3.9	843	3.3	
Tsesis	#4, 2.5 km from spill	15	Nov. 2-9	7.3	3939	28.7	Johansson et al. 1980
			Nov. 9-17	9.1	63	0.6	
			Nov. 17-Dec. 21	2.0	104	0.2	
Ekofisk	#2, 46 km NE downwind	12	May 2-6	.028	21,800	0.61	Mackie et al. 1978
		22		.024	10,400	0.25	
		32		.069	4,200	0.29	
		42		.365	1,000	0.37	
Ixtoc-1	3 stations 16-40 km down current from spill site	2.5, 5, 15m	Sept. 11-27	2-10	1,000-25,000	10-50	Boehm and Fiest 1981

1. All sediment measurements expressed as dry weight.
2. No measurement of total sedimented matter available. Rate of sedimentation based on average of #4 and #5.

Johansson et al. (1980) concluded that in the case of the Tsesis spill, sedimentation of oil to the seabed was rapid and constituted a quantitatively important pathway for determining the environmental distribution of oil since from 10 to 15% of the unrecovered oil reached the sediments near the spill site quickly, within 14 days of the spill. The Ekofisk blowout[3], an above-sea blowout resulted in an oil slick of approximately 4000 km^2 in area extending downwind in a NE direction from the platform site. Gale force winds and chemical oil spill dispersants applied to the oil slick near the platform served to maximize the proportion of the oil that entered the water-column near the spill site. Mackie et al. (1978) collected samples of sedimenting oil within 3 to 7 days of the end of the blowout at a range of depths 46 km downwind from the blowout within the area that had been covered by slicks. Oil concentrations in the water-column were low, but at 10 to 15 ppm were well above background. The oil sedimentation rates, 0.3 to 0.6 mg oil $m^{-1}d^{-1}$, were much lower than were observed in the Tsesis spill (Table 2.4 and 2.5). The authors themselves make no comment on these findings, but it would appear that the low sedimentation rates might have been due to the distance away from the spill site at which samples were taken or to the fact that the overall rate of sedimentation of sestonic particles was much lower in the offshore North Sea than in the nearshore Baltic Sea. The mass transfer coefficients given in Table 2.5 range from .016 to .05 m d^{-1} estimated at intermediate depths show that the net downward movement of oil was very slow[4]. At this rate oil would require more than 2.5 years to settle from the sea surface to the seabed at a depth of 45 m.

During the Ixtoc-1 blowout[5] in Campeche Bay, Gulf of Mexico, Boehm and Fiest (1980) collected sedimenting oil at depths of 2.5 to 15 m from the sea surface at a number of stations 16 to 40 km down-current from the spill site during the period when oil was being actively discharged. The authors pooled their samples, but estimated that oil sedimentation rates might have ranged from 10 to 50 mg oil m^{-2} day^{-1} (Table 2.5). These sedimentation rates were much higher than the rates measured during the Ekofisk blowout, but were consistent with those in the Tsesis tanker spill. Higher than usual sedimentation rates might have been expected during the Ixtoc-1 study because: i) the Ixtoc-1 spill was a seabed blowout that actually entrained seabed sediments into the plume of gas and oil as it rose from the sea floor; and ii) the suspended sediment load in waters of Campeche Bay was higher than usual at the time of the study due to the

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3 The Ekofisk blowout was an above-sea blowout in which between 20,000 and 30,000 tonnes were released from a platform in the Ekofisk field in the North Sea in a 7½ day period from April 22-30, 1977.

4 The mass transfer coefficient in the average distance hydrocarbons in a given m^3 of water column sink per unit time.

5 The Ixtoc-1 blowout was a seabed blowout in which approximately 600,000 tonnes of oil were discharged from June 3, 1979 to March 20, 1980.

TABLE 2.5

Sedimentation Rates for Oil During Historical Spills

Spill	Depth	Period	Rate of Oil Sedimentation	Oil Concentration in Water-Column	Mass Transfer Coefficients	References
			mg $m^{-2}d^{-1}$	mg m^{-3}	m d^{-1}	
Ekofisk	1	May 2-61	---	10.3	---	Mackie et al. 1978
	5		---	13.0	---	
	10-15		0.61	13.5	.045	
	20-25		0.25	15.2	.016	
	30-35		0.29	13.4	.022	
	40-45		0.37	2.0	.185	
Ixtoc-1[1]	2.5-15	Sept. 11-27	10-50	20-2100	.02-.50	Boehm and Fiest 1981, Fiest and Boehm 1981

1. Samples were pooled and ranges estimated by authors Boehm and Fiest (1981)

recent passage of a tropical storm which had stirred seabed sediments into the water-column. Precise estimates of mass transfer coefficients cannot be made in this study because of the pooling of samples, but available data yield estimates ranging from as low as 0.02 m d^{-1} which are consistent with those of the Ekofisk spill to as high as 0.50 m d^{-1}. Little additional information could be gleaned from the Ixtoc-1 study other than that, unlike the Tsesis spill, sedimentary oil in the Ixtoc-1 spill showed little evidence of microbial degradation, potentially due to nutrient limitation of microbial growth.

The results of these studies suggest that during spills measurable amounts of oil settle through the water-column and under certain circumstances measurable amounts of oil accumulate on the sea floor during spills. The results from the Tsesis spill demonstrated that hydrocarbon flux rates near the spill site are greatest within the first few days after the spill and that some of the oil in the water-column may reach the seabed quickly. In the Tsesis spill sinking rates for oil could be estimated to be 1 to 2 m d^{-1}. This appears to be inconsistent with results from other studies in which the mass transfer coefficients for oil settling through the water-column are very low, 0.01 to 0.1 m d^{-1} suggesting that oil would require a very, very long time to reach the seabed. One possible explanation for this apparent inconsistency is that in all spills a portion of the spilled oil is associated with particles that settle quickly to the seafloor, while the majority of the oil is associated with particles that settle more slowly, and hence the overall mass transfer coefficient for all of the oil in the water-column is very, very slow. The lack of measured oil concentrations in the water-column in some of the studies make it impossible to resolve the problem based on available data. The mesoscale studies proved useful in resolving certain questions.

Mesoscale Experiments

Several mesoscale experimental studies of oil sedimentation are worthy of note. In the late 1970's and early 1980's a series of studies using closed systems were undertaken at the University of Rhode Island. In these studies oil-water dispersions of No. 2 fuel oil were added chronically to enclosed ecosystems over many months. Wade and Quinn (1980) studied the distribution of hydrocarbons among seston particles of different sizes. The authors found that in water samples 20% or less of the hydrocarbons were either in solution or were associated with particles that could pass through a 0.3 um filter. Approximately 80% of the oil could be removed by filtration on a 0.3 um filter, but no detectable oil could be retained by a 45 um filter. On the other hand if particulate material captured in a sediment trap were examined, approximately 78% of the oil associated with sedimented particulate matter could be retained in a 45 um filter, while the balance was retained on a 0.3 um filter. These results suggest that the majority (78%) of the rapidly sedimenting material is in the form of large (45 um) particles that would sediment quickly. This large-sized fraction, however, contains only a very, very minor proportion of the total oil in the water-column. The smaller-sized particles which contain much of the oil sink only very slowly. Hence even though a portion of the oiled particles may settle quickly, the overall average settling rate is very slow.

The results of a later experiment conducted in an artificial ecosystem by Laake et al. (1984) are also consistent with Wade and Quinn (1980). In this experiment Laake et al. layered Ekofisk crude oil on the water-surface in a 1 m diameter x 13 hr m deep marine enclosure. The authors monitored oil concentrations in the water-column, oil partitioning between particles and solution, and oil sedimentation through the water-column for 14 days. The authors found that at all depths throughout the 14-day experiment the distribution of oil in the water-column amongst particles of different sizes was as follows: i) particles 0.4 um to 5 um = 60%; ii) particles 5 to 30 um = 14%; iii) particles 30 to 180 um = 13%; and iv) particles >180 um = 13%. Hence only a small proportion of the total oil in the water-column was associated with very large particles. In addition the authors reported settling rates some of the larger particle groups to be of the order of 1.2 to 3.6 m d^{-1} throughout the 14 day experiment. These results are consistent with the observed sedimentation of oil during the Tsesis spill and would explain the apparent rapid sedimentation of some of the oil during that spill. However, the data of Laake et al. are somewhat suspect because the oil concentrations in the upper segment of the water-column are very high 2-3 ppm, and the hydrocarbon flux rate through the water-column is also very high 4.2 g oil $m^{-2}d^{-1}$ when compared to flux rates observed in actual spills. It also appears that oil concentrations in the upper water-column were high enough to kill or damage the phytoplankton (diatom) community and as a result the high hydrocarbon flux rates and sinking rates may simply reflect the unnaturally rapid sinking of the dead, oil-contaminated diatoms.

Summary

In summary, it appears that in historical spills only a small proportion, perhaps a few percent, of the total oil discharged during a spill would settle quickly to the seabed, contaminating the sediments near the spill site. The available data suggest that some oil-contaminated particles may settle through the water-column at a rapid rate, of the order of 1 to 2 m day^{-1} or faster, and as a result might reach the seabed relatively near the spill site. There is empirical evidence of both rapid settling rates for oil and significant seabed contamination near the spill site in certain spills. The limited available evidence suggests, however, that the overall settling rate of oil through the water-column is much, much slower, of the order of 0.01 to 0.1 m day^{-1}. It must follow therefore that although a very small portion of the oil in the water-column is settling quickly, the vast majority settles much more slowly. For the latter the settling rates are so slow that particles could be transported great distances from the spill site and would disperse over very large areas before they actually reach the seabed. Thus the potential for heavy contamination of the seabed near the spill site is very limited in spills in deep, offshore waters.

But what determines the proportion of hydrocarbons that become associated with rapidly sinking segment of the seston? Do suspension-feeding plankton organisms generally play a significant roll in the sedimentation of oil? The answers to these questions do not appear to be available in the literature and hence the ability to credibly predict the pattern of seabed contamination resulting from offshore spills in deep water is questionable.

CHEMICAL COMPOSITION OF HYDROCARBONS CONTAMINATING THE SEABED

Crude oil is a complex mixture composed of dozens of different hydrocarbon compounds. Since certain of these compounds are far more potent than others at causing adverse effects (including tainting), it is important to recognize that the chemical composition of spilled oil changes dramatically from the time it is discharged into the sea to the time it arrives at the sea floor. The potential for tainting of flatfish (or for that matter the potential for causing adverse effects of any kind) depends upon not only the amount of oil present in the sediments, but also its chemical composition. The chemical composition of oil reaching the seabed depends on the original composition of the oil and the physical and chemical processes that affect it on the sea surface, in the water-column, and in the seabed sediments.

As described elsewhere in this report, petroleum is composed of dozens of compounds that can be grouped into four families namely: alkanes (paraffins unsaturates), aromatics, polar compounds and asphaltenes. The relative contributions of each of these to the composition of several crude oils are listed in Table 2.6. Among the compounds that make up these crude oils are certain of the hydrocarbons that have been associated with tainting in past studies (Table 2.7). As the oil moves from the surface to the seabed, processes such as evaporation, solution, and degradation alter its composition with certain major constituents being greatly depleted. These changes have been observed during the course of several historical spills (Table 2.8).

Studies of historical spills have demonstrated that as oil weathers on the sea surface the more volatile compounds are lost quickly. As the oil is entrained into the water-column and hydrocarbons partition between the particulate and dissolved phases. Finally compounds are degraded either microbially or chemically either on the surface, in the water-column or in the sediments. Where fresh or slightly weathered oil is entrained into the water-column, hydrocarbons partition between the aqueous and particulate phases based on aqueous solubility. Gearing et al. (1979) noted that low molecular weight (m.w.) aromatic compounds partitioned preferentially into the aqueous phase, while aliphatics and higher m.w. aromatics partitioned to the particulate phase. During the Ixtoc-1 spill, Payne et al. (1980) and Fiest and Boehm (1980) analyzed the hydrocarbons in filtered water samples, on suspended particles and in settling, oil-contaminated particles collected in sediment traps. They found that low m.w. aromatics(benzene, toluene, xylene and ethylbenzene) were present mostly in the aqueous phase despite the fact that very high concentrations of suspended solids in the water-column near the blowout site scavenged most of the remainder of the hydrocarbons from solution. Alkanes were more abundant in the particulate phase than aromatics since, on a per-carbon atom basis, alkanes are less water- soluble than aromatics. At greater distances from the spill site the more soluble, lower m.w. alkanes became less common in the particulate phase and, at 16 km from the spill site, the particulate matter collected in sediment traps was largely depleted in alkanes smaller than n-C_{15}. This trend was also reflected in the hydrocarbons

TABLE 2.6
Chemical Composition (%) of Certain Crude and Refined Oils (From National Research Council 1985)

Constituents	Prudhoe Bay Crude Oil	South Louisiana Crude Oil	Kuwait Crude Oil	No. 2 Fuel Oil	Bunker C
SATURATES (Alkanes)					
n-paraffins					
C11 to C15	1.7	1.8	1.7	5.2	0.3
C16 to C20	2.3	2.2	1.8	2.8	0.7
C21 to C25	1.1	0.8	0.7	0.1	0.5
C26 to C30	0.5	0.3	0.3	0.0	0.1
C31 plus	0.2	0.0	0.1	0.0	0.1
Total n-paraffins	5.8	5.2	4.7	8.1	1.8
Total isoparaffins	---	14.0	13.2	22.3	5.0
ring paraffins					
1-ring	9.9	12.4	6.2	17.5	3.9
2-ring	7.7	9.4	4.5	9.4	3.4
3-ring	5.5	6.8	3.3	4.5	2.9
4-ring	5.4	4.8	1.8	0.0	2.7
5-ring	---	3.2	0.4	0.0	2.7
6-ring	---	1.1	---	0.0	0.4
Total ring paraffins	28.5	37.7	16.2	31.4	15.2
Total Saturates	34.3	56.3	34.0	61.8	22.0
AROMATICS (Aromatics)					
benzenes	7.0	3.9	4.8	10.3	1.9
indans & tetralins	---	2.4	2.2	7.3	2.1
Naphthenobenzenes	---	2.9	2.0	4.6	2.0
Naphthalenes	9.9	1.3	0.7	5.9	2.6
Acenaphthenes	---	1.4	0.9	3.8	3.1
Phenanthene	3.1	0.9	0.3	0.0	11.6
Acenaphthalenes	---	2.8	1.5	5.4	7.0
Pyrenes	1.5	---	---	0.0	1.7
Chrysenes	---	---	0.2	0.0	0.0
Benzothiophenes	1.7	0.5	5.4	0.9	1.5
Dibenzothiophenes	1.3	0.4	3.3	0.0	0.7
Indanothiophenes	---	---	0.6	0.0	0.0
Total Aromatics	25.0	16.5	21.9	38.2	34.2
POLAR COMPOUNDS	2.9	8.4	17.9	0.0	30.2
INSOLUBLES (Asphaltenes)	1.2	0.2	3.5	0.0	14.4

TABLE 2.7

Some Petroleum Compounds Associated with Tainting in Past Studies (GESAMP 1977)

Hydrocarbons	Group
Tetradecans	Paraffins
Napthenic acids	Paraffins
Phenols	Aromatic
Toluene	Aromatic
Alkylated Napththalenes	Aromatic
Mercaptans	Resins
Dibenzothiophenes	Aromatic/Resin

TABLE 2.10

Degradation Rates of Various Petroleum Hydrocarbons in Fresh Water (from Lee 1977)

Compound	Measured Degradation Rate ug l^{-1} d^{-1}	Instantaneous Rate % d^{-1}
Phenol	200-580	4-6
Naphthol	240	2.4
Benzene	200-330	1.3-3.3
Heptadecane	50-240	1-1.6
Hexadecane	29-130	0.4-1.2
Toluene	150	0.7
Naphthalene	70-1200	0.2-2.7
Methylnaphthalene	18-460	0.1-2.3
Anthracene	0-8	0.05
Benzo(a)pyrene	0-2	0.02
Fluorene	0-12	0.01

molecular weight. Oudot et al. (1981) found that only larger isoprenoids (notably pristane and phytane) could be detected in petroleum-contaminated sediments one year after the Amoco Cadiz spill and after 18 months all traces of even these compounds had been eliminated.

Cycloalkanes (cycloparaffins or naphthenes) are unsaturated hydrocarbons made up of one or more ring structures. The vast majority are composed of up to five- or six-carbon rings and normally single- or double-ring structures predominate. Cycloalkanes are toxic at high concentrations, but are metabolized at moderate rates at low concentrations. Certain cycloalkanes are microbially degraded although at a slower rate than the corresponding *n*-alkanes. Susceptibility varies with the number of rings and with the degree of alkyl substitution. There appears to be little kinetic data available for specific cyclic alkane compounds, but according to Oudot et al. (1981) one year after the Amoco Cadiz spill only the pentacyclictriterpanes could be identified in sediments. All others had been degraded. Even after 18 months triterpanes were still present in detectible quantities.

Aromatic Hydrocarbons

Aromatic hydrocarbons contain one or more benzene rings. Molecules contain up to five rings as either fused rings (e.g. phenanthrenes) or lined rings (e.g. biphenyls) existing either in unsubstituted form or with alkyl substituents. As a group, aromatics are abundant constituents of crude oils, making up a somewhat smaller proportion than alkanes (Table 2.9). As the name suggests, some aromatic compounds are quite odoriferous and have often been implicated in fish tainting in past studies (Table 2.7). Lighter aromatics (lower molecular weight molecules with single or double rings) are highly soluble and are apparently readily degraded; but resistance to degradation appears to increase with the number of rings. Oudot (1984) classified aromatics according to their degradation potential as follows:

i) susceptible to degradation, single ring aromatics and sulphur aromatics;
ii) moderately susceptible to degradation, two- and three-ring aromatics;
iii) resistant to degradation, four-ring aromatics; and
iv) highly resistant to degradation, five-ring aromatics.

The degradation data summarized in Tables 2.10 and 2.11 show that rapid mineralization rates (>1% per day) have been observed in water and/or sediments for aromatics of one to three rings. This suggests that under the appropriate environmental circumstances these compounds might be readily mineralized (eliminated in less than one year). Mineralization rates for benz(a)pyrene, a five-ring compound, are much slower (<0.1% per day). Assuming first-order kinetics, this represents a half-life for degradation of benz(a)pyrene of almost two years.

Several authors have reported the persistence of alkylated polynuclear aromatic hydrocarbons (PNAs) over their unsubstituted parent compounds in intertidal and subtidal

TABLE 2.11

Degradation Rates for Aromatic Hydrocarbons in Sediments (Herbes 1981, Herbes and Schwall 1978)

Compound	Number of Rings	Hydrocarbon Degradation Rate			
		Study No. 1		Study No. 2	
		k (h^{-1})	t ½ (d)	k (h^{-1})	t ½ (d)
Napthalene	2	7.6×10^{-2}	0.4	1.4×10^{-1}	0.2
Anthracene	3	1.6×10^{-2}	1.8	2.5×10^{-3}	12
Benzathracene	4	3.3×10^{-3}	8.7	1.0×10^{-4}	288
Benzopyrene	5	3.4×10^{-4}	85	$<3 \times 10^{-5}$	>962
Dibenzanthracene	5	1.2×10^{-4}	240	---	---

sediment samples following the Amoco Cadiz (Atlas et al. 1981; Oudot et al. 1981) and Buzzards Bay spills (Teal et al. 1969). Kennicutt (1988) found that resistance to microbial degradation increased with the degree of alkylation when crude oil was weathered in sea water. Davies and Tibbetts (1987) suggested, however, that in sediments the relative persistence of members of a homologous series was somewhat more complex. The latter authors suggested that unsubstituted aromatics were less persistent in sediments due greater solubility rather than due to greater susceptibility to degradation and that the more highly alkylated homologues (C3 and C4) might be more susceptible to degradation rather than less susceptible.

In general, the available data suggest that the lighter aromatics would be lost quickly from slicks or oiled sediments by solution or degradation. Parent compounds of three- and four-ring compounds would be lost from sediments over a period of weeks or months, but certain alkyl-substituted homologues might persist for years. The five-ring compounds would be highly persistent and would also remain in sediments for years.

Asphaltenes

Asphaltenes are a heterogeneous and poorly characterized assortment of compounds with high molecular weights, low solubility and low volatility. Members of this group have not been implicated in tainting studies. They represent a minor constituent of most crude oils, but are common in some crude oils and certain refined products (Tables 2.6 and 2.9). Traditional chemical analytical techniques have been inadequate to define the chemical structures of asphaltenes and hence their degradation is poorly understood. Oudot (1984) and other authors agree that asphaltenes are highly resistant to degradation, although Oudot (1984) found that 10% to 20% of the asphaltenes in a light Arabian crude oil were degraded in 60 days in sea water.

Polar Compounds (Resins)

Resins are a heterogeneous assemblage of polar and heterocyclic (NSO) compounds that make up a minor proportion of most crude oils, though a significant proportion of some (Tables 2.6 and 2.9). The low molecular weight compounds of this group (phenols, cresols, thiols) are somewhat susceptible to degradation. The data in Table 2.10 show that phenol is readily mineralized in fresh water. Oudot (1984), however, found that the resin fraction of a light Arabian crude oil was "totally resistant to microbial attack". Clearly in this diverse and heterogeneous assemblage of compounds persistence will be highly variable and should be considered on a compound by compound basis. One significant component of this group is the benzothiophene group. This group is a common constituent of petroleum. It is commonly found as a contaminant in intertidal and bed sediments during spills and has been implicated in tainting situations (Table 2.7). Several authors have identified dibenzothiophene as being very persistent in contaminated sediments (Sinkkonen 1989, Marchand and Caprais 1981). The latter authors reported that following the Amoco Cadiz spill dibenzothiophenes were highly persistent in sediments being detectible at least two years after the spill. Sinkkonen (1989) reported

that dibenzothiophenes were the most persistent of all petroleum hydrocarbons studied following the Antonio Gramsky spill in the Baltic Sea in 1979. To date no specific data concerning the degradation kinetics of aromatic thiophenes in sediments has been found.

Summary

Based on existing knowledge of petroleum degradation, the following predictions might be made concerning degradation of sedimented hydrocarbons in deep, offshore areas. Short- and medium-chain length *n*-alkanes should be eliminated quickly followed closely by isoalkanes. Long chain alkanes would persist for years. The lighter aromatics (benzene and naphthalene) would have been lost by solution or degradation. Unsubstituted 3- and 4-ring structures would be lost within months, but alkylated 3- and 4-ring compounds and all 5-ring compound might persist for years. The asphaltenes and certain resins might be expected to persist for years.

HYDROCARBON TAINTING IN FLATFISHES RESULTING FROM PETROLEUM HYDROCARBON-CONTAMINATED SEDIMENTS

INTRODUCTION

Flatfish have been shown to become contaminated with hydrocarbons and suffer adverse effects as a result of exposure to hydrocarbons from either oil spills or from routine discharges from petroleum operations. In assessing the hazard to flatfish posed by these discharges it is essential to understand the relationship between the effects caused in the flatfish and exposure conditions causing them (oil concentrations in the sediments and the duration of exposure). The objective of this section is to consider exposure conditions in relation to the effects caused in flatfish. Although a variety of effects are discussed, the main emphasis here is organoleptically detectible tainting[8].

EFFECTS OF SPILLED OIL ON FLATFISH

Flatfish have been shown to suffer a wide variety of effects as a result of exposure to oil. These effects have ranged from simple contamination of fish tissues to more serious conditions such as extensive tissue necrosis and reproductive failure. These effects are summarized below.

In several spill situations authors have observed that flatfishes have become contaminated with hydrocarbons although without suffering any apparent adverse physiological effects. For example, in the months following the Tsesis spill of No. 5 fuel oil in the Baltic Sea, flounders exhibited temporarily elevated concentrations up to 440 ug/g total hydrocarbons in muscle tissue (Elmgren et al. 1983). In addition, several authors have identified petroleum-derived hydrocarbons in tissues of flatfish caught in the immediate vicinity of seabed oil drilling operations where authors have postulated that fish have become contaminated by hydrocarbons from oil-based drilling muds (Middleditch et al. 1979, Davies et al. 1989).

In some cases exposures to oil have been sufficient to cause "off-flavours" or detectible "oily" odours in commercial flatfish species. For example, following the Torrey Canyon spill plaice were reported to give off an unpleasant odour when cooked (Simpson 1968). Similarly, following the British Mallard spill fishermen reported that certain items of the catch, including plaice, gave off an oily odour (Palmork and Willhelmsen 1974). Nitta (1972) reported that flatfish taken in a nearshore area gave off an offensive odour, potentially due to contamination with hydrocarbons from petrochemical plant effluents. Flatfish taken near North Sea drilling platforms appear to exhibit some hydrocarbon tainting. In some cases this evidence of tainting appears to be conclusive (Randlov and Poulsen 1986), while in other cases evidence is less conclusive

8 Organoleptically detectible tainting is tainting that is detectible by taste testing.

(McGill et al. 1987, Davies et al. 1989). The occurrence of tainting and exposure conditions causing tainting are discussed in more detail below.

Rarely are mortalities or gross tissue injuries in flatfish observed during spills (although these effects have commonly been observed in association with sediments contaminated with hydrocarbons from other sources). However, certain effects were noted in flatfish populations following the Amoco Cadiz spill, 1978. Following this spill, several workers conducted extensive studies of the flatfish in the abers (estuaries) and the coastal bays. These authors noted reduced growth rates and fin necrosis in plaice and soles in the months immediately following the spill. In addition, these workers found that there were no juvenile flatfish in coastal bays and concluded that reproduction of flatfish populations had been ineffective during the spill year, although no cause-effect relationship was identified (Conan and Friha 1981, Desaunay 1981, Haensley et al. 1982, Moissec 1980).

Oil spills and routine discharges from petroleum operations have clearly resulted in mortalities of fin and shellfish in the past, but there is little evidence in the literature concerning lethality of spills to flatfishes. The above examples demonstrate, however, that flatfishes have indeed suffered a variety of sub-lethal injuries or conditions as a result of routine or accidental discharges of hydrocarbons from petroleum operations. In the following sections we will examine the relationship between sediment contamination with hydrocarbons and the appearance of effects in flatfish. In this analysis our primary concern is for tainting resulting from the type of exposures likely to be encountered by flatfish in deeper offshore areas such as the Grand Banks. As discussed above, in these environments flatfish would be exposed primarily to heavily weathered hydrocarbons in sediments. Unfortunately, information concerning flatfish exposed under these specific conditions is extremely limited and hence the scope of the study has been expanded slightly to include exposures of flatfish to sediments containing drilling wastes, and sediments containing fresh oil, reflecting exposure conditions experienced by flatfish in shallow, nearshore areas; and sediments containing drill wastes, reflecting exposures to benthic conditions in the immediate vicinity of the drilling site.

EXPOSURE CONDITIONS CAUSING TAINTING IN FLATFISH

The "effect" on flatfish that is emphasized here is tainting. Tainting is defined as the presence of an atypical or "off-flavour" in fish flesh caused by spoilage or the presence of chemical contaminants in the flesh. Although the contaminants causing the tainting may not be present in the tissues in sufficient concentrations to do damage to individual fishes, the potential economic impact of tainted fish on the fishery may still be significant. Tainting of finfish and shellfish by petroleum hydrocarbons have been reviewed extensively in the past (GESAMP 1977, Connell and Miller 1980, and Motohiro 1986). A particularly comprehensive review of the subject is presented in Tidmarsh et al. (1986). These reviews represent an excellent summary of the subject and no further review of tainting will be offered here other than to summarize a few key

points concerning tainting as an introduction to the present analysis of tainting in flatfish.

As mentioned above, tainting is caused by the presence in fish tissues of odoriferous contaminants. In order to cause taint these contaminants must be present in the tissues in at least minimum threshold concentrations. The tainting contaminants themselves may be accumulated from food, water, or sediments. Of particular interest in the present context are the exposure conditions, namely the oil concentrations in sediments, that would be required to cause tainting in flatfish under conditions of prolonged exposure.

Tainting by oil is a somewhat complex problem to study for at least two reasons. First, taint is a subjective assessment rather than an objective analytical one, and the detection threshold of tainting chemicals in fish tissues may vary somewhat from person to person. Second, the threshold tainting concentration varies from compound to compound (Table 3.1) and since oil is a mixture of compounds, oil tainting is the result of a mixture of odoriferous compounds acting together. Although no single compound may be present at a sufficient concentration to cause tainting on its own, the group of compounds acting together may collectively cause taint. As a result it is difficult or impossible to establish a direct relationship between the concentration of petroleum hydrocarbons in the fish flesh and the occurrence of tainting. Hence, the only truly reliable measure of the presence or absence of taint is a taste test using a taste testing panel. Only studies involving taste panels are considered here.

Tainting By Weathered Oil in Sediments

The above discussion demonstrated that for oil spills in deeper, offshore waters, the primary vector of oil exposure for flatfish would be via sediments rather than via the water vector and that the oil reaching the sediments in offshore spills would be weathered rather than fresh. Unfortunately no published studies involving tainting of flatfish by weathered oil in sediments has been identified in our thorough literature search or in our extensive international mail survey of fisheries scientists and oil spill experts. This lack of experimental work may reflect several things including:

i) the perception among scientists that flatfish tainting during deeper offshore spills may not be a problem; and
ii) the difficulty of experimentally reproducing oil-exposure conditions that realistically simulate oil-exposure conditions in deeper shelf environments.

The absence of any observational evidence of tainting of flatfish may simply reflect the rarity of major offshore oil spills.

In the absence of any observational or empirical data consider the following. Based on available evidence there are conflicting arguments concerning the hazard potential to flatfish of heavily weathered oil in sediments. On the one hand, based on evidence from historical spills and empirical work on oil sedimentation, it appears unlikely that deep offshore sediments would become heavily contaminated (>1000 ppm) with oil during

TABLE 3.1

Taste Thresholds of Some Petroleum Compounds in Water

(From Hart 1974)

Hydrocarbon	Taste Threshold in Water, ppm
Cresol	.7
Ethanethiol	.24
Toluene	.25
Ethylbenzene	.25
Naphthalene	1.00
Phenol	1.0-10.00

spills. In addition, it appears that the weathered oils that reach the seabed would be depleted in the more water-soluble, low molecular weight hydrocarbon compounds that have been implicated in the past in tainting cases and would therefore be unlikely to cause tainting even at high concentrations. This would suggest that tainting of deeper-water flatfish stocks would not be a significant problem. On the other hand, certain taint-causing compounds such as the sulphur-bearing heterocyclic hydrocarbon compounds, dibenzothiophenes, have been identified as being common in heavily weathered oils. Dibenzothiophenes are also strongly resistant to degradation and hence are very persistent[9]. There therefore appears to be at least a weak argument suggesting that heavily weathered oil may still pose some tainting threat to flatfish. This suggests that some effort might be expended to determine the exposure threshold for inducing tainting in flatfish by heavily weathered oil under conditions continuous exposure.

On balance, however, there appears to be little evidence to suggest that spills in deeper offshore waters pose a tainting risk to flatfish. However, even though organoleptic tainting may not be a problem, the higher molecular weight aromatic hydrocarbons present in sediments may represent a contamination problem which could be significant since certain of these are known to be carcinogenic.

Tainting By Fresh Oil in Sediments

Some published information has dealt with the problem of potential flatfish tainting via sediments contaminated with fresh oil from nearshore spills. The observational evidence cited above of tainting in flatfish following the Torrey Canyon and British Mallard spills (Simpson 1968, Palmork and Wilhelmsen 1979), suggest that tainting is possible. However, in neither spill is there any indication of whether the tainting hydrocarbons might have been accumulated via acute exposure to elevated oil concentrations in the water-column or possibly via chronic exposure to oil-contaminated sediments.

There is however, some clear empirical evidence of the fact that flatfish can become tainted by exposure to fresh oil in sediments. Howgate et al. (1977) studied the tainting of plaice exposed to hydrocarbon-contaminated sediments in order to identify the compounds responsible for the taint. Fresh North Sea crude oil was mixed with sand at a single concentration of 5% (v/v) (approximately 50,000 ppm, dry weight) and plaice were exposed to these sediments in a flow-through system for up to eight days. Plaice acquired a clearly detectable taint after only two days of exposure at this concentration. Unfortunately there is no indication concerning the compounds causing the taint in this case. Nitta et al. (1965) investigated disagreeable odours acquired by fish taken near oil refining plants. They reported that fish exposed under controlled experimental conditions

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9 The great persistence of dibenzothiophenes in sediments suggests a very strong affinity for the sediments and thus a very low bioavailability and a low potential for uptake by flatfish.

to mud containing 2000 ppm (dry weight) of oil acquired taint[10], but there is again no indication of the compounds responsible for the taint or even whether the oil involved was fresh oil. It appears reasonable that the compounds responsible for tainting under these circumstances would be the water-soluble, low molecular weight aromatics and/or alkanes that would be leached out of the sediments and would be taken up by flatfish via the gills.

These studies suggest that continuous exposures to 2000 ppm of fresh oil in sediments may cause taint in flatfish, but the threshold may be lower than this. Additional work should be devoted to this area to determine the approximate threshold exposure concentration of fresh oil in sediments causing tainting under conditions of continuous exposure. These data would be necessary for predicting the potential for tainting in nearshore benthic environments in which fresh or lightly weathered oil has become mixed with the seabed sediments.

Tainting of Flatfish by Oil-Based Drilling Muds

Another potential source of petroleum taint in flatfish fisheries are oil-based drilling muds. These products are used in offshore exploratory oil well drilling and drill cuttings contaminated with these products are discharged in the immediate vicinity of the offshore platforms where they settle immediately to the seafloor in the area surrounding the rigs. McGill et al. (1987) found evidence in the North Sea of hydrocarbon contamination in dabs (Limanda limanda) caught within 1 km of a gas well platform where hydrocarbon concentrations in sediments ranged in concentration from several hundreds to several thousand ppm dry wt. There was some indication of tainting in the dabs, but results were inconclusive.

Ernst et al. (1989) demonstrated conclusively that drilling muds might cause tainting in fish. These authors exposed cod[11] to a water-soluble extract of Conoco base oil, a constituent of drilling mud, and were able to cause organoleptic tainting in the cod fish. This study unfortunately does not demonstrate whether or not the tainting compounds might be present in sufficient quantities or be sufficiently bioavailable in spent drill cuttings to cause taint in flatfish under "real-world" exposure conditions. Payne et al. (1989) studied the bioaccumulation of hydrocarbons by flatfish exposed to drill cuttings by exposing flounder to undiluted drill cuttings continuously for one month. These authors demonstrated that some of the hydrocarbons in the drill cuttings were indeed bioavailable to the flounder. They found that the water-soluble, low m.w. aromatics such as naphthalene were accumulated to a measurable degree in the liver. The less soluble, higher m.w. hydrocarbons such as the higher m.w. PNAs were not accumulated to a measurable degree. This study demonstrated conclusively that flatfish could

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10 It is not at all clear from the available material that the work involved flatfish or that the exposure medium involved fresh crude oil.

11 An economically important demersal species, but not a flatfish species.

bioaccumulate measurable amounts of hydrocarbons from drill cuttings, but it remains unclear whether flatfish might accumulate sufficient hydrocarbons from drilling muds into their muscle to cause organoleptic tainting.

The above suggests that spend drill cuttings contaminated with oil-based drilling mud discharged at sea may indeed pose a threat of tainting to flatfish exposed under certain conditions. However it appears from the work of McGill et al. (1987) that even were tainting to occur, only flatfish taken within 1 to 2 km of the drilling site might be affected; flatfish taken outside this area would be free from taint[12]. On the Grand Banks flatfish are broadly distributed and are fished over a wider area, so that even if a small area near drilling rigs were to be affected, the net impact on the fishery as a whole might be negligible. It is important to consider, however, that the level of contamination and the size of the area contaminated depends upon a number of variables. The level of sediment contamination near the drill site and the areal extent of contamination would depend at least on the volume of drill cuttings discharged, current speed and water depth at the drill site. It would be useful to obtain an estimate of the threshold concentration of oil in drill cuttings required to cause tainting in order to estimate the size of a potential "area-of-effect" for tainting around specific drill sites. In addition, it would be useful to monitor the hydrocarbon concentrations in flatfishes near drill sites in order to confirm the conclusions of McGill et al. In assigning priorities for research in this area it should be considered that while the overall impact on a flatfish fishery from spent drill cuttings might be far less than that from a major nearshore spill, the threat of seabed contamination by discharged drill cuttings is a virtual certainty while the risk of a major inshore spill is only a remote possibility.

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12 Randlov and Poulsen (1986, cited in Reierson et al 1989) reported finding definite evidence of tainting arising from drilling muds after they reported finding tainted plaice at a distance of 20 to 45 km from a drilling platform in the North Sea. This would appear to be inconsistent with the findings of McGill et al (1987), but since few details of the former work are available it is difficult to evaluate their findings.

AVOIDANCE OF HYDROCARBON-CONTAMINATED SEDIMENTS BY FLATFISHES

INTRODUCTION

The aim of this section is to assess whether in nature flatfish might be able to detect and avoid sediments contaminated with petroleum hydrocarbons in the same way that certain pelagic fishes appear to be able to avoid elevated oil concentrations in the water-column. The ability to avoid hydrocarbons would be important in the present context because it would allow flatfish to avoid exposure to hydrocarbons in sediments and hence avoid pathological effects and tainting even if sediments were to become contaminated. Thus even if areas of seabed might become contaminated with hydrocarbons there might be very little impact on the flatfish population or its fishery.

The role that behaviour plays in habitat or substrate selection in nature involves a combination of environmental and physiological factors including: i) the availability of a variety of alternative environmental choices; ii) the ability to detect environmental cues associated with the environmental choices; iii) the behavioral ability to respond appropriately to the detected cues; and iv) the locomotory powers to move the appropriate distances at the speeds needed to implement the behaviours. The objective of this section is to review the possible behaviours of flatfish related to oil and the detection abilities of flatfish with respect to oil in sediments.

Unfortunately an exhaustive literature search and conversations with experts in various areas of flatfish and hydrocarbon research have revealed a general lack of knowledge of flatfish behaviour, and an almost complete dirth of work on flatfish concerning their ability to detect and avoid hydrocarbon contamination in sediments. Our objective in this section is to review the limited available information on behavioral responses of fish to hydrocarbons and to summarize the fragmentary evidence of the presence or absence of avoidance behaviour in flatfish.

RESPONSES OF FISHES TO PETROLEUM HYDROCARBONS IN THE WATER PHASE

Much of the research involving flatfish and hydrocarbons has focused on pathological effects of hydrocarbons on flatfish (Fletcher et al. 1982, McCain et al. 1978, Payne et al. 1978). Behavioral research involving finfish and hydrocarbons has usually involved pelagic species such as salmons (e.g., Bax 1987, Beitinger and Freeman 1983, Folmar et al. 1981, Maynard and Weber 1981) and demersal species such as cod, and sea catfish (Bohle 1986, Hellstroem and Doeving 1983, Wang and Nicol 1977, Williams and Kiceniuk 1987). Almost all behavioural work has involved exposures to water-borne hydrocarbons rather than sediment-borne hydrocarbons.

Various workers have ably demonstrated that finfish can detect and successfully avoid high concentrations of hydrocarbons in the water-column by behavioural means. Weber et al. (1981) conducted field experiments involving avoidance of hydrocarbons by adult Pacific salmon (Onchorhynchus sp.) during upstream spawning migration. The up-stream migrating salmon were offered three choices: migrating up-stream via an uncontaminated salmon ladder; migrating upstream via a hydrocarbon-contaminated ladder (water was contaminated with a mixture of monocyclic aromatics and levels of contamination were varied during the experiment), or remaining below the dam. The experiment revealed that the migrating salmon avoided the contaminated ladder at hydrocarbon concentrations in the water of 3.2 ppm or greater (total monocyclic aromatic hydrocarbons), but did not avoid the hydrocarbon-contaminated ladder at concentrations below this level showing that adult salmon can detect and avoid dangerously high concentrations of hydrocarbons in the water-column. This is consistent with work of Maynard and Weber (1981) who found that juvenile Pacific salmon avoided petroleum hydrocarbons at concentrations of 3-4 ppm during downstream migrations. In subsequent work Bohle (1986) found that cod could possibly detect and avoid hydrocarbon concentrations in the water- column one order of magnitude lower than was the case with salmon. Bohle (1986) provided cod with clean and contaminated sea water (WSF of No. 2 fuel oil at a variety of concentrations) in different compartments in a maze. The cod selected compartments where hydrocarbon contaminations were lower than 0.1 ppm in preference to those when concentrations exceeded that level. Clearly cod were capable of detecting hydrocarbon concentrations in water of 0.1 ppm and avoiding them, although it is unclear from the experiment how such behaviours might function under natural conditions in the sea.

RESPONSES OF FISH AND SHELLFISH TO HYDROCARBONS IN SEDIMENTS

Clearly at least some finfish species can detect and avoid potentially harmful concentrations of hydrocarbons in the water-column. There is also limited information regarding the effect of hydrocarbons in sediments on the behaviours of sediment-burrowing benthic species. Much of the work has focused on the burrowing behaviours of invertebrates such as clams (Hartwick et al. 1982, Olla and Bejda 1983, Taylor and Karinen 1977) and gastropods (Chapman et al. 1988). At least one study, however, has dealt with the effect of hydrocarbons on burrowing behaviour of a finfish. Pearson et al. (1984) studied the effect of hydrocarbon contaminated sediments on burrowing behaviour of sand lance, Ammodytes hexapterus. Sand lance were not given any choice of substrate so habitat selection/avoidance was not a criterion here, but the author did monitor the amount of time sand lance spent buried in sediments to which they were exposed. Under natural conditions sand lance burrow in the substrate when not feeding in order to escape predation, hence burrowing has survival value. Under normal conditions (clean sand and water) sand lance spend 85 to 90% of their time buried in the sand. At 25 ppm contamination with hydrocarbons burrowing behaviour was unaffected, but sand lance spent markedly less time in the substrate and more time swimming in conditions where sediments contained 250 and 3000 ppm hydrocarbons. This suggests that high

concentrations of hydrocarbons in sediments might influence the behaviour of benthic fishes.

BEHAVIORAL RESPONSES OF FLATFISHES TO HYDROCARBONS IN SEDIMENTS

The natural habits of flatfish place them in intimate contact with sediments throughout the year. A flatfish species such as winter flounder inhabits nearshore areas with soft mud and sand-gravel bottoms (Fletcher et al. 1981), where they spend much of their time resting on or buried in the sediments and where they ingest some sediment material while feeding. Between October and April winter flounder spend 90% of their time buried in the sediments. As a result of this behaviour, flatfishes are uniquely vulnerable to effects of hydrocarbons that might be associated with ambient sediments.

The available evidence concerning behavioural responses of flatfish to hydrocarbon-contaminated sediments is fragmentary at best. In the months following the Amoco Cadiz spill, Desaunay (1981) found that plaice did not avoid the highly hydrocarbon-contaminated areas in nearshore zones of the French coast. The author found that plaice that were marked (tagged) in heavily contaminated zones were all recaptured in the same zones within the three months following tagging. The average oil concentrations in sediments in these areas were in the 100 to 1000 ppm range (Marchand and Chaprais 1981). These authors also reported that flatfish found in these areas displayed a variety of physiological, histopathological and gross pathological conditions. This evidence suggests that plaice were unable to avoid hydrocarbon contaminated areas that were sufficiently contaminated to cause major pathological effects in exposed individuals.

In a laboratory study Weber et al. (unpublished) determined that when offered both uncontaminated and heavily contaminated sediments, juvenile English sole did not actively select clean sediments over those containing an average of 10,000 ppm of fresh Prudhoe Bay crude oil. Fish continued to burrow in sediments so heavily contaminated with oil that the burrowing fish dislodged oil droplets which resurfaced forming a highly visible sheen on the surface of the test tank. This result suggests that at least some flatfish species cannot discriminate between clean and heavily contaminated sediments when burrowing. In the latter study Weber et al. suggested that the lack of avoidance behaviour might have been due to a disruption of chemosensory modalities resulting from the initial contact with the extremely high concentrations of hydrocarbons in the contaminated sediments. To my knowledge this experiment has not been repeated to attempt to address this possible problem.

In experiments with winter flounder, Payne et al. (1988) found that flounder exposed to sand containing hydrocarbon concentrations ranging from 100 to 11,000 ppm continued to burrow in the sediments regardless of the presence of hydrocarbons. This in some ways confirms the flounder's apparent indifference to the contamination present in the

sediments suggested by Weber et al., but sheds no new light on the question of whether flatfish might have selected clean sediments for burrowing if they had been offered.

These results although fragmentary suggest that flatfish are behaviourally indifferent to the presence of oil in sediments and do not avoid dangerously high concentrations of hydrocarbons in sediments in the same way that other species avoid high concentrations of hydrocarbons in the water phase. Studies performed during a real spill suggested that some species clearly do not vacate areas where sediments contain dangerously high concentrations of hydrocarbons. Indeed they appear to remain in these areas and as a result suffer major pathological effects. Under laboratory conditions other species apparently do not distinguish between clean and contaminated sediments when selecting substrate even when the substrate contains very high concentrations of oil. These results suggest that flatfish are unable to detect and avoid sediments contaminated with very high concentrations of oil. These studies were all conducted with fresh oil so there is no indication that flatfish might be able to avoid weathered sedimented oil.

IS AVOIDANCE AN OPTION FOR FLATFISH?

The information-base concerning the ability of flatfish to detect and avoid oil-contaminated sediments as other fishes avoid oil-contaminated water masses is fragmentary. The very limited available data suggest that flatfish do not avoid hydrocarbons, but the results are not conclusive. Before setting out to determine empirically whether a flatfish can avoid sediment contaminated with fresh or weathered oil, it is necessary to consider whether any such data would be useful in the context of impact prediction.

During large spills oil entering the water-column might generate clouds of noxious dispersed oil in the water-column that may be harmful to fish upon prolonged exposure. These clouds are ephemeral since they quickly disperse through outward diffusion of the noxious components. A short-term chemotactic or chemokinetic behaviour is sufficient to allow pelagic species to avoid areas of high hydrocarbon concentrations and thus minimize the risk of exposure of fishes to the short-lived environmental hazard. Spill-contaminated sediments present a different kind of problem however.

Spills, whether inshore or offshore may cause significant sediment contamination over finite area. This contamination may persist for months or years rather than only hours. Contamination within this area is likely to be highly patchy rather than uniform. In order to allow flatfish to avoid exposure, their behaviour must allow them to avoid areas of high oil contamination or minimize the time spent resting or burrowing in contaminated patches, electing rather to burrow in clean or less contaminated patches. To achieve this, the flatfish must be able to detect either specific hydrocarbon concentrations or steep hydrocarbon concentration gradients in sediments. In addition, the ability to detect elevated hydrocarbon concentrations must not accommodate to the

hydrocarbons upon prolonged exposure. It is unlikely that any organism would possess a capability of detecting hydrocarbons that does not accommodate to the presence of hydrocarbons and hence become useless over prolonged exposure. Any experimentation in this area must focus on the ability of flatfish to detect steep concentration gradients of fresh and weathered oils and to select the less contaminated end of the gradient. It must focus on the specific compounds which the flatfish are detecting and responding. Finally, the experiment must from the outset determine how quickly the flatfish accommodate to the presence of the hydrocarbons and hence over what period any avoidance behaviour might be expected to provide protection.

RECOMMENDATIONS

CONTAMINATION OF OFFSHORE BED SEDIMENTS WITH HYDROCARBONS FROM SPILLS

Simple models of oil sedimentation have been developed, but their use is hampered by the lack of a suitable data set for validation. It is recommended that in the event of a major offshore "spill of opportunity" an extensive series samples of bed sediments be taken to quantify:

i) the concentrations of hydrocarbons in bed sediments;
ii) the proportion of the spilled hydrocarbons actually reaching the sediments; and
iii) the areal extent of the detectible seabed contamination.

This set of samples could be used for model verification.

One obvious deficiency identified in this study is the apparent lack of a sediment sampling device that can reliably sample and retain the upper 2 to 4 cm of bed sediments including the freshly settled hydrocarbon-contaminated floc it contains. Such a sampler must at least avoid scattering the floc layer as it arrives at the sea floor and must retain the light floc material as it is raised through the water-column and hauled aboard.

Recognizing the practical difficulties associated with sampling the bed sediments and determining the areal extent of seabed contamination, it would be important during a "spill of opportunity" to obtain a series of samples of whole water, suspended sediments, and sediment trap material taken at various locations, depths and times post-spill also in order to "ground-truth" oil sedimentation models. During such a sampling exercise it would be useful to characterize the material collected in sedimentation traps through microscopic analysis.

In order to adequately model the sedimentation of oil in offshore areas it will be necessary to understand the factors that control the partitioning of oil between the larger particles that sink rather quickly and the smaller particles that sink only very slowly. It would be important to gain an understanding of the role of suspension-feeding zooplankton and their fecal pellets in contributing to the sinking of oil in both nearshore and offshore environments.

A significant deficiency in the information-base concerning the fate of sedimented oil is the apparent lack of data concerning the microbial degradation of commonly occurring sulphur heterocyclic compounds in sediments. It would be appropriate to study the degration products and the rates of degradation of dibenzothiophenes in sediments relative to rates of other persistent hydrocarbon species such as pyrenes and benzopyrenes.

TAINTING OF FLATFISH

Based on the present study, there is little evidence to suggest that spilled oil poses a significant threat to flatfish stocks in deeper, offshore areas because most alkane and aromatic hydrocarbons compounds that have been linked with tainting in past work are relatively water-soluble and hence would be largely depleted in oil reaching sediments in deeper, offshore areas. Unfortunately, the question concerning the hazard potential of persistent petroleum constituents such as the larger aromatic molecules or sulphur heterocycle compounds remains largely unanswered. In order to address this question it would be important to determine whether sedimented, weathered oil can cause tainting (or any other sublethal effect) under conditions of continuous exposure.

The threat of tainting of flatfish by spilled oil is probably far greater during inshore spills than offshore spills. During nearshore spills sediments may become contaminated with relatively fresh oil that still contains some water-soluble hydrocarbons. The existing database suggests that oil concentrations in sediments at least as low as 2000 ppm total oil can cause tainting in flatfish exposed to them. Unfortunately the minimum exposure threshold, which may be considerably less than 2000 ppm total oil has not been determined for any type of oil. Since the results of the present review suggest that there appears to be some risk of flatfish tainting in nearshore flatfish populations from nearshore spills, it would be useful if the exposure threshold for causing tainting in flatfish could be determined.

There are data to suggest that flatfish might become tainted through exposure to spent drill cuttings contaminated with oil-based drilling mud (OBM). To date, despite research activities in various parts of the world, no one has determined the exposure threshold concentration for OBM-contaminated cuttings. This is an obvious data gap. In view of the results obtained by Payne et al. 1989, a single series of experiments should demonstrate whether or not tainting might be a problem. It would be prudent, however, to monitor flatfish stocks in the vicinity of drilling operations to confirm the conclusion of McGill et al. 1987 that flatfish containing OBM contaminants are restricted to within a few kilometres of the drill site.

AVOIDANCE OF OIL-CONTAMINATED SEDIMENTS BY FLATFISH

Existing information regarding avoidance by flatfish of hydrocarbons in sediments is fragmentary, but the limited available evidence there is suggests that flatfish are indifferent to even dangerously high concentrations of fresh hydrocarbons in sediments. Experiments could be designed to study the ability of flatfish to detect and avoid hydrocarbons in sediments, but there is little justification for conducting these tests until such time as there is some observational evidence of avoidance behaviour in flatfish.

APPENDIX A
EXAMPLE OF LETTER SENT TO EXPERTS

Dear Colleague:

This letter is to request your assistance in identifying information concerning the tainting of flatfishes by petroleum hydrocarbons absorbed from sediments.

Our firm is assessing the feasibility of developing a model to estimate the risk of tainting of flatfish stocks by petroleum hydrocarbons during spills from offshore petroleum operations. As part of this work, we are attempting to quantify the relationship between the level of hydrocarbon contamination of seabed sediments and the occurrence of off-flavours in the flatfishes exposed to them, based on published studies. To date in our literature search we have been able to identify only a very limited number of studies in this subject area (see attached Table). In order to determine whether any additional work has been done, we are contacting a number of workers, world-wide, who like yourself have published in this or closely related areas. Would you please assist us in this work by:

i) identifying any of your publications on this subject that we have overlooked in our literature search;

ii) aiding us in obtaining copies of your publications that have appeared as limited circulation reports; and

iii) identifying colleagues that may have special knowledge concerning petroleum tainting in flatfishes.

Please note that in this survey a negative reply is just as valuable to us as a positive reply.

Your assistance in this matter would be greatly appreciated.

Yours truly,

B. Kenneth Trudel
Encl.

APPENDIX B

NAMES AND ADDRESSES OF PERSONS CONTACTED

J.Albaiges
Centro de Investigacion y Desarrollo
Consejo Superior de Investigacions Cientificas
Jorge Girona Salgado, 18-26
08034 Barcelona
Spain

Jack W. Anderson
Southern California Coastal Water Research Project
646 West Pacific Coast Highway
Long Beach, California, 90806
United States

M.E.Bender
Virginia Institute of Marine Science
College of William and Mary
Gloucester Point
Virginia, 23062
United States

R.A. Blackman
Ministry of Agriculture, Fisheries and Food
Fisheries Laboratory
Remembrance Avenue
Burnam-on-Crouch
Essex
CMO 8HA
United Kingdom

P.D.Boehm
Marine Sciences
Arthur D. Little Inc.
20 Acorn Park
Cambridge
Massachusetts 02140
United States

T. Bohn
Norsk Institut for Vannsorskreng (NIVA)
Postboks 333
Blindern
Oslo 3
Norway

D.W. Connell
School of Australian Environmental Studies
Griffith University
Nathan, Queensland
Australia

J.M. Davies
Marine Laboratory
P.O.Box 101
Victoria Road
Aberdeen
AB9 8DG
United Kingdom

R.Elmgren
Department of Zoology
Asko Laboratory
University of Stockholm
S-10691
Stockholm
Sweden

Anders Goksoyr
Department of Biochemistry
Arstadveien 19
University of Bergen
N-5009 Bergen
Norway

W.Grogan
Marathon Oil U.K. Ltd.
Marathon House
Rubislaw Hill
Anderson Drive
Aberdeen AB2 4AZ
United Kingdom

R.Hardy
Torry Research Station
P.O. Box 31
135 Abbey Road
Aberdeen
AB9 8DG
United Kingdom

P.Howgate
Torry Research Station
P.O. Box 31
135 Abbey Road
Aberdeen
AB9 8DG
United Kingdom

I.Kimura
Laboratory of Oral Oncology
Aichi Cancer Center Research Institute
Chikusu-ku
Nagoya 464, Japan

J. Kuiper
TNO Marine Research Laboratory
Department of Biology
Den Helder
The Netherlands

R.J.Law
Ministry of Agriculture, Fisheries and Food
Fisheries Laboratory
Remembrance Avenue
Burnam-on-Crouch
Essex
CM0 8HA
United Kingdom

O.Linden
Swedish Water and Air Pollution Research Institute(IVC)
Studsvik, S-611 82 Nykoping
Sweden

B.B.McCain
Environmental Conservation Division
Northwest and Alaska Fisheries Center
National Marine Fisheries ServiceNOAA
2725 Montlake Boulevard East
Seattle
Washington,98112
United States

A.S.McGill
Torry Research Station
P.O. Box 31
135 Abbey Road
Aberdeen
AB9 8DG
United Kingdom

A.D.MacIntyre
Marine Laboratory
P.O.Box 101
Victoria Road
Aberdeen
AB9 8DG
United Kingdom

P.R.Mackie
Torry Research Station
P.O. Box 31
135 Abbey Road
Aberdeen
AB9 8DG
United Kingdom

D.Malins
Environmental Conservation Division
Northwest and Alaska Fisheries Center
National Marine Fisheries Service
NOAA
2725 Montlake Boulevard East
Seattle, Washington,98112
United States

L. Massie
Marine Laboratory
P.O.Box 101
Victoria Road
Aberdeen
AB9 8DB
United Kingdom

G.J.Miller
School of Australian Environmental Studies
Griffith University
Nathan, Queensland
Australia

B.S.Middleditch
Department of Biophysical Sciences
University of Houston
Houston
Texas, 77004
United States

T.H.Moller
The International Tanker Owners Pollution Federation
Staple Hall
Stonehouse Court
87-90 Houndsditch
London,EC3A 7AX
United Kingdom

T.Motohiro
Faculty of Fisheries,
Kagoshima University
Shimoarata
Kagoshima
Japan

Masana Ogata,M.D.
Department of Public Health
Okayama University Medical School
2-5-1 Shikata-cho
Okayama City
Japan

T. Ogura
Department of Public Health
Okayama University Medical School
2-5-1 Shikata-cho
Okayama City
Japan

J.G.Parker
Shell UK Exploration and Production
1 Athens Farm Road
Nigg
Aberdeen
United Kingdom

J.D. Peterson
North Sea Operators Committee
Maersk Oil and Gas, A.S.
Esplanaden 50
DK-1263
Copenhagen K
Denmark

Anders Randlov
COWIconsult Consulting Engineers and Planners
19 Parallelvej
DK_2800 Lyngby
Denmark

L.O.Reiersen
State Pollution Control Authority
P.O.Box 8100 Dep.
0032 Oslo 1
Norway

G.Roesijadi
Center for Environmental and Estuarine Studies
University of Maryland
Chesapeake Biological Laboratory
Box 38
Solomons
Maryland, 20688-0038
United States

C.E.Sjogren
Nycomed Imaging
P.O.Box 4220 ^Torshov
N-0401 Oslo 4
Norway

R.B.Spies
Environmental Sciences Division
Lawrence Livermore National Laboratory
University of California
Livermore
California, 94550
United States

M.E.Stansby
Northwest Fisheries Science Center
Environmental Conservation Division
2725 Montlake Boulevard East
Seattle, Washington, 98112
United States

G.G.Stott
College of Veterinary Medicine
Texas A. and M. university
College Station
Texas

U.Varanasi
Northwest Fisheries Science Center
Environmental Conservation Division
2725 Montlake Boulevard East
Seattle, Washington, 98112
United States

K.J.Whittle
Torry Research Station
P.O. Box 31
135 Abbey Road
Aberdeen
AB9 8DG
United Kingdom

REFERENCES CITED

Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. Microbiol. Rev. 45:180-209.

Atwood, D.K. (convenor). 1980. Proceedings of a symposium on preliminary results from the September 1979 Researcher/Pierce Ixtoc-1 cruise. U.S. Dept. of Commerce, Key Biscayne, Florida, June 9-10, 1980, December 1980.

Bax, N.J. 1987. Effects of a tanker accident and an oil blowout in Bristol Bay, Alaska, on returning adult sockeye salmon (Oncorhynchus nerka) - a simulation study. Mar. Env. Res. 22: 177-203.

Beitinger, T.L. and L. Freeman. 1983. Behavioral avoidance and selection responses of fishes to chemicals. Residue Rev. 90: 35-55.

Bobra, M.A. and S. Callaghan. 1990. A catalogue of oil properties. (1990 version). Environmental Emergencies Technology Division, Environment Canada, March 1990, 542 pp.

Boehm, P.D., J.E. Barak, D.L. Fiest and A.A. Elskus. 1982. A chemical investigation of the transport and fate of petroleum hydrocarbons in the littoral and benthic environments: the Tsesis oil spill. Mar. Env. Res. 6:157-188.

Boehm, P.D., and D.L. Fiest. 1980. Aspects of the transport of petroleum hydrocarbons to the offshore benthos during the Ixtoc-1 blowout in the Bay of Campeche. In Atwood, D.K. (Convenor). 1980. pp 207-236.

Bohle, B. 1986. Avoidance of petroleum hydrocarbons by the cod (Gadus morhua). Fisk Dir. Skr. Ser. Hav Unders 18: 97-112.

Chapman, H.F., R.L. Kitching and J.M. Hughes. 1988. Behavioral responses of Polinices incei (Gastropoda: Naticidae) to diesel oil contamination in sediments. Aust. J. Mar. Freshw. Res. 39: 435-440.

Conan, G., and M. Friha. 1981. Effets des pollutions par les hydrocarbures du petrolier Amoco Cadiz sur la croissance des soles et des plies dans l'estuaire de l'Aber Benoit. In. Amoco Cadiz: Fates and Effects of the Oil Spill. Proc. Int. Symp. Centre Ocean. Bretagne. Brest, France, 19-22 novembre 1979, pp. 749-755.

Connell, D.W., and G.J. Miller. 1981. Petroleum hydrocarbons in aquatic ecosystems - Behaviour and effects of sublethal concentrations. CRC Crit. Rev. Environ. Control 11(2): 105-162.

Davies, J.M. and P. Tibbets. 1987. The use of in-situ benthic chambers to study the fate of oil in sub-littoral sediments. Estuar. Coast. Shelf Sci. 24:205-223.

Davies, J.M., D.R. Bedborough, R.A.A. Blackman, J.M. Addy, J.F. Appelbee, W.C. Grogan, J.G. Parker, and A. Whitehead. 1989. Environmental fate of oil-based mud drilling in the North Sea. In. F.R.Englehart et al. (eds).1989., pp. 59-90.

de Lappe, B.W., R. Riseborough, A. Springer, F. Schmidt, J. Shropshire, E. Letterman and J. Payne. 1980. The sampling and measurement of hydrocarbons in natural waters. In B. Afghan and D. Mackay (eds). Hydrocarbons and halogenated hydrocarbons in the aquatic environment. Plenum, New York pp. 29-68.

Desaunay, Y. 1981. Evolution des stocks de poissons plat dans la zone contaminée par l'Amoco Cadiz. In Amoco Cadiz: Fate and Effects of the Oil Spill. Proc. Int. Symp. Centre Ocean Bretagne. Brest, France, 19-22 novembre 1979. pp.727-735.

Elmgren, R., S. Hansson, U. Larsson, B. Sundelin and P.D. Boehm. 1983. The "Tsesis" oil spill: Acute and long-term impact on the benthos. Mar. Biol. 73:51-65.

Englehart, F.R., J.P.Ray, and A.H. Gillam (eds). 1989. Drilling Wastes. Proc. 1988 Int. Conf. on Drilling Wastes, Calgary, Alberta, Elsevier Applied Science, New York, N.Y.

Ernst,R.J., W.M.N. Ratnatake, T.E. Farquharson, R.G.Ackman, W.G.Tidmarsh, and J.A. Carter. 1989. Tainting of Atlantic cod (Gadus morhua) by petroleum hydrocarbons. In. F.R.Englehart et al. (eds). 1989., pp. 827-842.

Fieser, L.F. and M. Feiser. 1956. Organic Chemistry. Reinhold Publ. Co., Baltimore, Md.

Fiest, D.L. and P.D. Boehm. 1980. Subsurface distributions of petroleum from an offshore well blowout, the Ixtoc-1 blowout, Bay of Campeche. In D.K. Atwood. (convenor) 1980. pp. 169-188.

Fletcher, G., J.W. Kiceniuk and U.P. Williams. 1981. Effects of oiled sediments on mortality, feeding and growth of winter flounder (Pseudopleuronectes americanus). Mar. Ecol. Progr. Ser. 4: 91-96.

Folmar, L.C., D.R. Craddock, J.W. Blackwell, G. Joyce and H.O. Hodgins. 1981. Effects of petroleum exposure on predatory behaviour of coho salmon (Oncorhynchus kisutch). Bull. Environ. Contam. Toxicol. 27(4): 458-462.

GESAMP. 1977. IMCO/FAO/UNESCO/UMO/WHO/IAEA/UN. Joint Group of Experts on the Scientific Aspects of Marine Pollution. The Impact of Oil on the Marine Environment. Report on Study No. 6. FAO, Rome.

Gearing, J.N., P.J. Gearing, T. Wade, J.G. Quinn, H.B. McCarty, J. Farringtonn, and R.F. Lee. 1979. The rates of transport and fates of petroleum hydrocarbons in a controlled marine ecosystem, and a note on analytical variability. Proc. 1979 Oil Spill Conference, pp. 555-564.

Haensley, W.D., J.M. Neff, J.R. Sharpe, A.C. Morris and M.F. Bedgood. 1982. Histopathology of Pleuronectes platessa from Aber Wrach and Aber Benoit, Brittany, France: long-term effects of the Amoco Cadiz crude oil spill. J. Fish. Dis. 5:365-391.

Hart, B.T. 1974. A Compilation of Australian Water Quality Criteria, Australian Government Publishing Service, Canberra.

Hartwick, E.B., R.S. Wu and D.B. Parker. 1982. Effects of a crude oil and oil dispersant (Corexit 9527) on populations of the littleneck clam (Protothaca staminea). Mar. Env. Res. 6: 291-306.

Hellstroem, T. and K.B. Doeving. 1983. Observations of cod behaviour when stimulated with water soluble fractions of oil. In Doevig, K.B. (ed) Chemoreception in studies of marine pollution. Reports from a workshop at Oslo, July 13 and 14, 1980, Norw. Mar. Pollut. Res. Monit. Programme No. 1. pp. 69-85

Herbes, S.E. 1981. Rates of microbial transformation of polycyclic aromatic hydrocarbons in water and sediments in the vicinity of a coal-coking waste water discharge. Appl. Env. Microbiol. 41:20-28.

Herbes, S.E., and L.R. Schwall. 1978. Microbial transformation of polycyclic aromatic hydrocarbons in pristine and petroleum-contaminated sediments. Appl. Env. Microbiol. 35:306-316.

Howgate,P., P.R.Mackie, K.J.Whittle, J.Farmer, A.D.McIntyre, A.Eleftheriou.1977. Petroleum tainting in fish. Rapp. P.-v. Reun. Cons. Explor. Mer 171:143-146.

Johansson, S., U. Larsson and B.P. Boehm. 1980. The Tsesis oil spill: impact on the pelagic ecosystem. Mar. Poll. Bull. 11:284-293.

Jordan, R.E., and J.R. Payne. 1980. Fate and weathering of petroleum spilled in the marine environment: a literature review and synopsis. Ann Arbor Science Publ., Ann Arbor, Mich.

Keizer, P.D., P. Ahern, J. Dale and J.H. Vandermuelen. 1978. Residues of Bunker C oil in Chedabucto Bay, Nova Scotia, 6 years after the Arrow spill. J. Fish. Res. Bd. Can. 35: 528-535.

Keizer, P.D., J. Dale and D.C. Gordon. 1978. Hydrocarbons in surficial sediments from the Scotian Shelf. Geochim. Cosmochim. Acta 42:165-172.

Kennicutt, M.C. 1988. The effect of biodegradation on crude oil: bulk and molecular composition. Oil Chem. Pollut. 4:89-112.

Law, R.L. 1978. Determination of petroleum hydrocarbons in water, fish and sediments following the Ekofisk blowout. Mar. Pollut. Bull. 9:321-324.

Lee, R.F. 1977. Fate of petroleum components in estuarine waters of the southeastern United States. Proc. 1977 Oil Spill Conf., pp. 611-686.

Lee, R.F. 1980. Processes affecting the fate of oil in the sea. In R.A. Geyer (ed). 1980. Marine Environmental Pollution; 1. Hydrocarbons. Elsevier Scientific Publishing Company. New York, N.Y. pp. 337-352.

Levy, E.M. 1983. Baseline levels of volatile hydrocarbons and petroleum residues in the waters and sediments of the Grand Banks. Can. J. Aquat. Sci. 40 (Suppl. 2):23-33.

McAuliffe, C.D., A.E. Smalley, R.D. Groover, M. Welsh, S. Pickle and G. Jones. 1975. Chevron Main Pass Block 41 oil spill: chemical and biological investigations. Proc. 1975 Oil Spill Conf., pp. 555-566.

McCain, B.B., H.O. Hodgins, W.D. Gronlund, J.W. Hawkes, D.W. Brown, M.S. Myers and J.H. Vandermeulen. 1978. Bioavailability of crude oil from experimentally oiled sediments to English sole (Paraophrys vetulus) and pathological consequences. J. Fish. Res. Bd. Can. 35: 657-664.

McGill, A.S., P.R. Mackie, P. Howgate, and J.G. McHenery. 1987. The flavour and assessment of dabs (Limanda limanda) caught in the vicinity of the Beatrice Oil Platform. Mar. Pollut. Bull. 18:186-189.

Mackay, D. 1984. The fate and behaviour of oil in cold climates. Unpublished report prepared for Environment Canada.

Mackie, P., R. Hardy and K. Whittle. 1978. Preliminary assessment of the presence of oil in the ecosystem at Ekofisk after the blowout, April 22-30, 1977. J. Fish. Res. Bd. Can. 35:544-551.

Marchand, M. and M.P. Caprais. 1980. Suivé de la pollution de l'Amoco Cadiz dans l'eau de mer les sediments marins. In Amoco Cadiz: Fate and Effects of the Oil Spill. Proc. Int. Symp. Centre Ocean, Bretagne. Brest, France, november 19-22, 1979. pp. 23-54.

Maynard, D.J. and D.D. Weber. 1981. Avoidance reactions of juvenile Coho salmon (Oncorhynchus kisutch) to monocyclic aromatics. Can. J. Fish. Aquat. Sci. 38(7): 772-778.

Middleditch,B.S., E.S.Chang, B.Basile, and S.R.Missler. 1979. Alkanes in fish from the Buccaneer Oilfield. Bull. Env. Contam. Toxicol. 22:249-257.

Miossec, L. 1980. Effets de la pollution de l'Amoco Cadiz sur la morphologie et sur la reproduction des plies (Pleuronetesplatessa) dans l'Aber Wrach et l'Aber Benoit. In Amoco Cadiz. Fate and Effects of the Oil Spill. Proc. Int. Symp. Centre Ocean. Bretagne. Brest, France 19-22 november, 1992. pp. 737-747.

Motorhiro, T. 1983. Tainted fish caused by petroleum compounds - a review. Wat. Sci. Tech. 15:75-83.

National Research Council (U.S.). 1985. Oil in the sea: impacts, fates, and effects. National Academy Press, Washington, D.C., 601 pp.

Nitta, T. 1972. Marine Pollution in Japan. In. M. Ruivo (ed). 1972. Marine Pollution and Sea Life. Fishing News (Books) Ltd., Surrey, pp. 77-81.

Nitta,T.,K.Arakawa,K.Ohkubo.,T.Ohkubo,and K.Tabata. 1965. A study on control of oily tainted fish by waste water from petrochemical factories. Bull. Tokai Reg. Fish. Res. Inst., 42:23-37.

Olla, B.L. and A.J. Bejda. 1983. Effects of oiled sediment on the burrowing behavior of the hard clam, Mercenaria mercenaria. Mar. Env. Res. 9:183-193.

Oudot, J., P. Fusey, M. Van Pruet, J. Fesal and F. Gaill. 1981. Hydrocarbon weathering in seashore invertebrates and sediments over a two-year period following the Amoco Cadiz oil spill: influences of microbial metabolism. Environ. Pollut. (A) 26:93-110.

Oudot, J. 1984. Rates of microbial degradation of petroleum components as determined by computerized capillary gas chromatography and computerized mass spectrometry. Mar. Env. Res. 13:277-302.

Palmork, K.H. and S. Wilhelmsen. 1974. Cited in Connell, D.W. and G.J. Miller. 1981. Petroleum hydrocarbons in aquatic ecosystems - behaviour and effects of sublethal concentrations: part 2. Crit. Rev. in Env. Control. CRC Press.

Payne, J.F., J. Kiceniuk, U. Williams, L. Fancey, W. Melvin, and R. Addison. 1989. Bioaccumulation of polycyclic aromatic hydrocarbons in flounder. (Pseudopleuronectes americanus) exposed to oil-based drill cuttings. In F.R. Englehart et al. 1989. pp. 427-438.

Payne, J.F., J. Kiceniuk, L.L. Fancey, U. Williams, G.L. Fletcher, A. Rahimtula and B. Fowler. 1988. What is a safe level of polycyclic aromatic hydrocarbons for fish: subchronic toxicity study on winter flounder (Pseudopleuronectes americanus)? Can. J. Fish. Aquat. Sci. 45: 1983-1993.

Payne, J.R., G.S. Smith, P.J. Mankiewicz, R.F. Stokes, N.W. Flynn, V. Moreno, and J. Altamirano. 1980. Horizontal and vertical transport of dissolved and particulate-bound higher molecular-weight hydrocarbons from the Ixtoc-1 blowout. In Atwood, D.K. (Convenor). 1980. pp. 119-166.

Pearson, W.H., D.L. Woodruff and P.C. Sugarman. 1984. The burrowing behavior of sand lance, Ammodytes hexapterus: Effects of oil-contaminated sediment. Mar. Env. Res. 11: 17-32.

Posthuma, J. 1977. The composition of petroleum. Rapp. P.-v Réun. Cons. int. Explor. Mer, 171:7-16.

Randlov, A., and E. Poulsen. 1986. Environmental impact of low-toxic oil-based drilling mud. Taint in fish and possibilities of reduction of the impact. COWIconsult. Maersk olie og gas a.s. (cited in Reiersen et al. 1989).

Reiersen, L.O., J.S. Gray, K.H. Palmork, and R. Lange. 1989. Monitoring in the vicinity of oil and gas platforms. Results from the Norwegian sector of the North Sea and recommended methods for forthcoming surveillance. In. F.R. Englehardt et al. (eds). 1989., pp. 91-117.

Sanders, H.L., J.F. Grassle, G.R. Hampson, L.S. Morse, J. Garner-Price, and C.C. Jones. 1980. Anatomy of an oil spill: long-term effects from the grounding of the barge Florida off West Falmouth, Massachusetts. J. Mar. Res. 38:265-380.

Simpson, A.C. 1968. The Torrey Canyon disaster and fisheries. Ministry of Agriculture, Fisheries, and Food. Fisheries Laboratory Burnham-on-Crouch, Laboratory Leaflet (new series) 18, 43pp.

Sinkkonen, S. 1989. The fate of some crude oil residues in sediments. Chemosphere, 18:2093-2100.

Taylor, T. and J.F. Karinen. 1977. Response of the clam, Macoma balthica (Linnaeus), exposed to Prudhoe Bay crude oil as unmixed oil, water-soluble fractions, and oil-contaminated sediment in the laboratory. In D.A. Wolfe (ed.), 1977. Fate and effects of petroleum hydrocarbons in marine organisms and ecosystems. Pergamon Press, New York, pp. 229-237.

Teal, J.M., K. Burns and J. Farrington. 1978. Analysis of aromatic hydrocarbons in intertidal sediments resulting from two spills of No. 2 fuel oil in Buzzards Bay, Massachusetts. J. Fish. Res. Bd. Can. 35:510-520.

Tidmarsh, W.G., R. Ernst, R. Ackman, T. Farquharson. 1986. Tainting of fish resources. Environ. Stud. Res. Funds, Rept. No. 21.

Wade, T.L. and J.G. Quinn. 1980. Incorporation, distribution, and fate of saturated petroleum hydrocarbons in sediments from a controlled marine ecosystem. Mar. Env. Res. 3:15-33.

Wang, R.T. and J.A.C. Nicol. 1977. Effects of fuel oil on sea catfish: feeding activity and cardiac responses. Bull. Env. Contam. Toxicol. 18(2): 170-176.

Weber, D.D., W.D., Gronlund, T. Federighi and D.W. Brown. unpublished report. Non-avoidance of oil-contaminated sediment by juvenile English sole (Parophrys vetulus).

Weber, D.D., D.J. Maynard, W.D. Gronlund and V. Konchin. 1981. Avoidance reactions of migrating adult salmon to petroleum hydrocarbons. Can. J. Fish. Aquat. Sci. 38: 779-781.

Williams, U.P. and J.W. Kiceniuk. 1987. Feeding reduction and recovery in cunner, Tautogolabrus adspersus following exposure to crude oil. Bull. Envir. Contam. Toxicol. 38: 1044-1048.

Zurcher, F. and M. Thuer. 1978. Rapid weathering processes of fuel oil in natural waters - analysis and interpretations. Env. Sci. Tech. 12:838-843.

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