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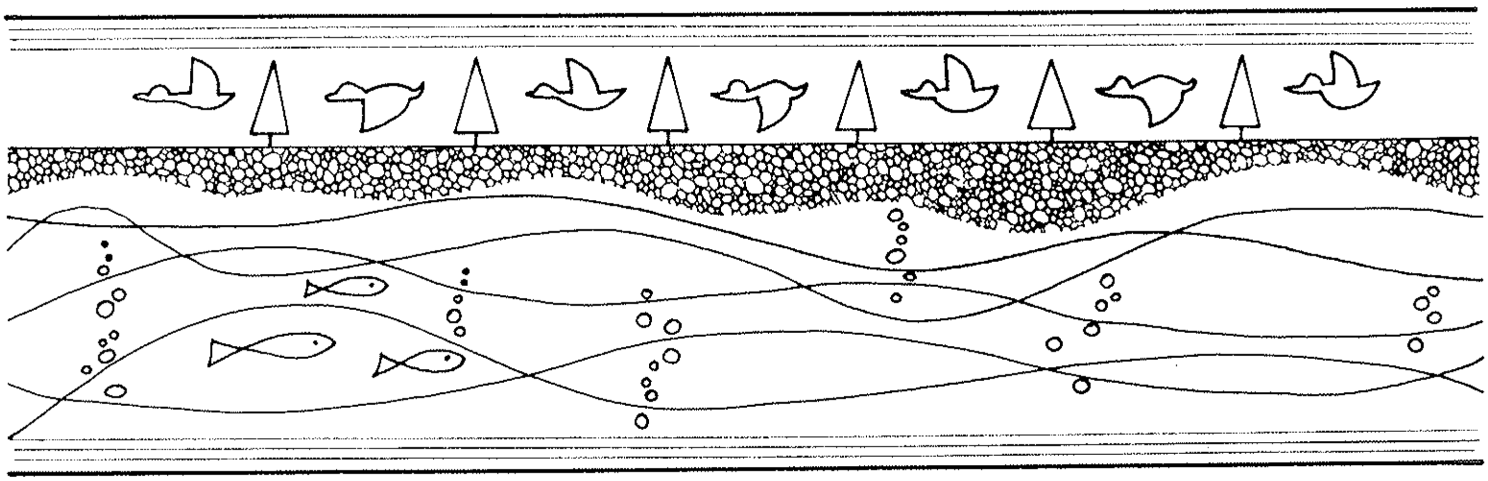

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The Spill Technology Newsletter was started with modest intentions in 1976 to provide a forum for the exchange of information on spill countermeasures and other related matters. We now have over 1600 subscribers in over 50 countries.

To broaden the scope of this newsletter, and to provide more information on industry and foreign activities in the field of spill control and prevention, readers are encouraged to submit articles on their work and views in this area.

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et demandez Bulletin de la lutte contre les déversements

INTRODUCTION

This issue is the third one of the four to be produced in 1986, and it would appear that our past production problems have finally been overcome. Hopefully this will have the desired effect of again attracting technical articles and reports from our readership. In that regard, please note that the invitation to contribute on the inside cover page of previous issues was incorrect in limiting the field to oil spill control and prevention; chemical spills control and prevention reports and articles are equally welcome. Please note that we do not publish commercials; we may on occasion and at our discretion announce new products or services together with the appropriate contact for details.

We have recently reviewed our distribution list and were very gratified to find that, although the number of subscribers has dropped to just under 1600, the number of other countries currently receiving one or more copies has grown to 50.

This newsletter is not the only means used by the Environmental Emergencies Technology Division (EETD) for the dissemination of information on spill countermeasures technology. Detailed reports are available on EETD projects and are announced in this Newsletter as they become available.

EETD also holds two annual technical seminars; one is the Technical Seminar on Chemical Spills and the other is the Arctic and Marine Oilspill Program (AMOP) Technical Seminar. The third one of the former series took place in Montreal 5-7 February 1986 with 310 registered attendees, and there were 116 registrants at the ninth AMOP seminar in Edmonton 10-12 June 1986. We will be holding the next chemical spill seminar in Toronto 10-12 February 1987 and the next AMOP seminar will be in Edmonton 9-11 June 1987; registration forms and program information can be obtained from the Technology Transfer and Training Division of the Environmental Protection Directorate (Mr. M. Cloutier) at the address provided on the inside of the front cover. Papers for both are by invitation only; anyone wishing to be considered should provide EETD (Meikle or Fingas) with an overview of their related activities and the work to be reported.

Although proceedings are published for both seminars, the number of copies is limited so we have reprinted two of the 1986 papers for the benefit of those who could not be there. The first is by Gord Tidmarsh and describes fish tainting. The second article is by Dave Wilson and Don Mackay who describe a very interesting project about oil in freezing situations.

FISH TAINTING AND HYDROCARBONS IN THE ENVIRONMENT: A PERSPECTIVE

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1. INTRODUCTION

Under the Effects Monitoring priority study area, the Environmental Studies Revolving Funds initiated a study in 1984 to review the question of possible fish tainting caused by the introduction of hydrocarbons into the marine environment as a result of offshore oil and gas exploration and development activities.

The objectives of the study were:

- to review case histories to attempt to identify concerns associated with tainting and determine how recorded incidents have been handled in other jurisdictions;
- to assess the validity of available assessment techniques and analytical methods for determining whether or not a product is tainted;
- to recommend a series of investigations to develop a reasonable scientific basis for conducting an evaluation of a possible tainting situation.

Essentially, the study was designed to provide an overview of the subject and identify a possible future course of action which the Funds may choose to pursue with respect to tainting. The study concentrated on the scientific aspects of the problem and avoided the perceptual questions (e.g., marketing, economic impacts) for which little factual information is available. This paper contains a summary of the study findings and attempts to place the subject of tainting in some perspective.

2. BACKGROUND

Tainting is the development of an unnatural flavour in finfish and shellfish as a result of exposure to contaminants present in an aqueous medium. Tainting is not caused solely by hydrocarbons but the strongest tainters tend to be organic compounds. It is one human-related effect associated with the bioaccumulation by marine organisms of more soluble, polar as well as cyclic and aromatic hydrocarbons, artificially introduced into the aquatic environment.

Although it is only one element of the hydrocarbon contamination problem, real or potential tainting associated with petrogenic hydrocarbons, i.e., condensate and crude oil, has become a concern to fishermen because of the increasing exploration, production, and transportation of oil at sea in recent years (GESAMP, 1977). Until recently, this concern has not been matched by concerted scientific or regulatory effort at national levels or within the international community to develop mechanisms for dealing with the problem (GESAMP, 1983). Currently, there are no generally accepted standard scientific methods for assessing or verifying tainted produce (Howgate, pers. comm.).

For the purposes of this study, a basic definition of the term "tainting" developed by the GESAMP Working Group on the Evaluation of the Hazards of Harmful Substances Carried by Ships (EHS) (GESAMP, 1985) is considered as generally applicable for finfish or shellfish prior to processing.

> "(Tainting is) the development of a flavour or odour in the organism when caught or harvested which is not typical of the flavour or odour of the organisms themselves."

It should be noted that this definition does not make a statement about the nature of the atypical flavour or odour or attempt to quantify the degree of taint. The importance lies in whether the flavour or odour of the product is altered, not whether a contaminant impairs or improves the flavour.

The EHS Working Group (GESAMP, 1985) have noted that there is one order of magnitude difference in contaminant concentrations between the detection and recognition thresholds of off-flavours. It is important to remember that it is the off taste, not the determination of what is causing the off flavour, which will cause product rejection.

Tainting of seafood produce can arise from either the natural spoilage of improperly handled whole or processed produce, or the exposure of living organisms to anthropogenic contaminants present in the aquatic environment. The latter is of greatest concern because it can result in substantial economic losses to innocent parties (GESAMP, 1977). Economic losses as a result of perceived or actual tainting associated with hydrocarbon losses are impossible to evaluate because of inadequate documentation, and technical data on the subject are sparse (GESAMP, 1982).

Fear of tainting can be as serious a problem as an actual tainting incident. Consumer resistance, closures imposed by regulatory authorities, and embargoes on harvesting activities by producers resulting from even the remote possibility that seafoods are tainted can cause severe economic losses. Tainting per se is essentially an economic problem associated with the wider environmental or public health concerns arising from exposure of exploited fish stocks to anthropogenic hydrocarbons and is as much a perceptual problem as a real concern. Unlike the presence of carcinogens such as PNAH, which are known to bioaccumulate but are not detectable by normally human sensory systems, the presence of hydrocarbons causing a taint is readily detectable.

Tainting is a difficult subject to treat quantitatively because it is a sensory perception based on individual experience and preference. The flavour of a food is determined by a blend of taste and odour evoked by a substance in or near the mouth. As a sensory perception, individual experience as well as preference can greatly infuence a determination as to whether a product is "off". In fish, the flavour can be strongly influenced by the diet of the living organism prior to harvesting, as well as by natural degradation or spoilage after death. Separating flavours associated with natural processes, compared with those resulting from exposure to contaminants such as hydrocarbons released into the environment, can be difficult.

From the point of view of marketability of fish and shellfish and acceptance or rejection of a product by inspectors and the public, not only raw odour, but also tissue or shell colour, tissue texture, and general aesthetic quality of the product will influence the decision. External contamination or fouling by hydrocarbons, as well as a taint, may be cause for product rejection, although external contamination of an organism does not necessarily mean that tainting of the underlying tissue has occurred (GESAMP, 1977). Generally, tainted product can be readily detected by initial grading but in rare cases, the potential presence of an "off-flavour" or taint may not be detectable until the product is prepared for eating or is actually consumed.

Increases in body burdens of hydrocarbons leading to the acquisition of a taint arises from four mechanisms (Connell and Miller, 1981). These are:

- absorption of hydrocarbons on the skin;
- absorption of dissolved hydrocarbons from the water through the skin;
- absorption of dissolved hydrocarbons through the gills, i.e., respiration; and
- ingestion of food contaminated with petroleum.

The mechanism varies from situation to situation depending upon the species exposed, the type and concentration of hydrocarbons present, the exposure time, and the season. Generally, the increase in body burden is reversible but the depuration rate varies. This is important because it means that live contaminated produce which has acquired a taint need not be destroyed. Placement of produce in uncontaminated holding facilities for a period of time will restore product quality and should not compromise market acceptability.

Tainting as a result of absorption on the skin has been observed when a catch has accidentally come in contact with oily water from storage tanks (Stansby, 1978) or from fouled nets. The contaminant and to some extent the acquired odour can be removed by washing in running water and detergents although a residual odour may remain after cleaning.

Each species of finfish and shellfish has its own characteristic flavour (McGill et al., 1984). The flavouring components occur in both the lipid and the protein of the fish. Ordinarily, however, in the absence of putrification, the most volatile and flavourful components are the chemicals dissolved in the lipid (Stansby, 1978). It is generally accepted that there is a greater storage and persistence of aromatic and polynuclear hydrocarbons in lipid-rich than in lipid-poor tissues of most marine species (GESAMP, 1977). Whittle and Mackie (1976) have suggested that the amount of "free" lipids present in a fish indicates the susceptibility of that organism to acquire a taint.

Although the total lipid content is important with respect to bioaccumulation, the lipid content of edible tissue may be important with respect to the presence of a taint. Hence, for most groundfish where the lipid content of edible tissues is low (<3% wet weight), the susceptibility to acquiring a taint is far less than for pelagic species such as herring (Clupea harengus) and mackerel (Scomber scombrus) where the lipid content may be as high as 20-24% of the wet weight of edible tissue. The lipid content of the muscle can show marked seasonal variation which is reflected in the tainting potential, or the threshold concentrations at which an off-flavour is noticeable.

In shellfish, the distribution of taint producing hydrocarbons in organisms varies. In molluscs, they would tend to be widely distributed while in crustaceans, they would tend to be concentrated in the hepatopancreas which is normally not eaten. Exposure of crustaceans may not necessarily lead to tainting, but releases of metabolized hydrocarbons from the hepatopancreas may lead to relatively long-term low level contamination in the edible tissue. This may or may not impair the taste.

The threshold level of exposure necessary to cause a taint in finfish and shellfish depends on the chemical composition of the hydrocarbon contaminant and on the species affected. Tainting has been associated with diesel fuel (Mackie et al., 1978), crude oil (Motohiro and Inoue, 1973), Bunker C (Shenton, 1973, Scarratt, 1980), and gasoline (Kerkhoff, 1974) present in the environment, as well as with refinery effluents (Nitta 1972; Connell, 1974). The principal components of crude and refined oil causing tainting include the phenols, dibenzothiophenes, naphthenic acids, mercaptans, tetradecanes and methylated naphthalenes (GESAMP, 1977). Some of these compounds are polar, some volatile, and most are somewhat soluble in water and lipids. Due to their lipid solubility they are readily transferred by partitioning into the blood and tissues of organisms. Due to metabolic processes of organisms that alter the chemical characteristics of contaminants, it is difficult to unequivocally identify, by chemical analytical techniques, compounds in crude oil or condensates that exactly match hydrocarbons isolated from fish deemed to be tainted. The chemical verification of tainting is also difficult due to biogenic hydrocarbons produced by the living organisms themselves. Pristane, some n-alkanes and isoprenoid hydrocarbons are widespread in the food chain (GESAMP, 1977) and overlap to a large extent with petrogenic hydrocarbons.

Given this rather complicated background, it is not surprising that there is considerable contradiction in the literature on the subject of tainting. As indicated above, it is a subject that has received relatively little systematic attention from the scientific community until recently. The study revealed a number of areas where information is lacking or available evidence is conflicting on the subject of tainting. The principal findings of the study are described in the following section.

3. SUMMARY OF FINDINGS AND RECOMMENDATIONS

The discussion which follows is divided into three subsections - case histories, regulatory mechanisms, and methods of determination. In each, the results of the study are summarized and the conclusions drawn are highlighted.

3.1 Case Histories

Available case histories of tainting of marine organisms resulting from oil pollution were reviewed in an attempt to identify the common factors associated with incidents of reported tainting and the responses of regulatory authorities to a real or perceived tainting situation. The case histories were broken down into tainting arising from industrial discharges, shipping accidents, and offshore oil and gas activities. Much of the available information about tainting incidents is anecdotal, or is located in government reports and the gray literature which cannot be readily accessed (GESAMP, 1982).

Tainting incidents and residual tainting is generally associated with organisms present in shallow protected coastal waters where circulation is limited. It is more often associated with shellfish than finfish. To date, most of the tainting incidents have arisen from shipping accidents involving losses of large volumes of crude oil, or distillate into confined coastal waters. Relatively few instances of tainting have been reported as a result of industrial discharges into marine waters.

Numerous shipping accidents have resulted in reported tainting but the best documented cases are the Torrey Canyon and Amoco Cadiz incidents where incidents of shellfish and finfish contamination were reported (e.g., Shelton, 1982). In the Amoco Cadiz case, considerable economic losses in the oyster industry were experienced (Chassé, 1978). Generally, available information indicates that the fisheries affected by an oil spill resulting in tainting gradually recover, and long-term impacts are not apparent. In Canada, tainting as a result of shipping accidents has not been reported but it has been a concern to authorities (see Scarratt, 1980).

The study revealed that little, if any, contamination has occurred as a result of blowouts associated with offshore oil and gas activities. The Ekofisk and Uniacke blowouts did not cause discernible tainting although, in both situations, some evidence of hydrocarbon exposure was apparent (Whittle et al., 1978; Zitko et al., 1984). There were no other discernible effects on the fisheries as a result of these incidents. Tainting was not reported during or after the Ixtoc blowout although there were other impacts on the fisheries. The only recent documented case of seafood becoming tainted was as a result of the Funiwa 5 blowout in the Niger Delta.

The risk of tainting is higher in coastal waters than in offshore areas. Where blowouts at offshore wellsites have occurred and oil or condensate released during the accident has not reached the coast, fish tainting as a result of hydrocarbon uptake from the dissolved or particulate material in the water column has not been apparent. The hydrocarbons are rapidly dispersed in the environment and concentrations rapidly decrease to levels below which exposure of organisms will cause a taint. In coastal areas, the hydrocarbons do not disperse as quickly and can become trapped in sediments. These factors substantially increase the risk of finfish and shellfish resources acquiring a taint as a result of a spill.

Of particular interest from the oil spill countermeasures standpoint is the finding that dispersant usage after a spill in the past has been responsible for fish resources in coastal areas becoming tainted. The risk of this is now thought to be lessened because of the chemical composition of the second generation dispersants, but some doubt remains.

3.2 Regulatory Mechanisms

The regulatory mechanisms within the 19 jurisdictions canvassed during the study revealed that few countries have established protocols for dealing with a tainting incident. Monitoring produce for tainting is usually the responsibility of public health authorities who only act to condemn produce deemed to be unwholesome after landing. Closures are occasionally imposed. They are not a consistent practice and fishermen are responsible for deciding where and when to fish. In some cases, fisheries authorities have the power to invoke closures but firm guidelines for determining when a fishery may be reopened after a tainting incident are lacking.

From the review, it is evident that regulatory responsibility for management of a tainting incident is generally fragmented. The exception is in the United Kingdom where the Food and Environment Protection Act specifies the responsibilities of the various authorities in the event of a spill of toxic substances.

Where major spills of hydrocarbons from tanker incidents or offshore well blowouts have occurred, large exclusion zones established to ensure public safety and to facilitate cleanup or well-capping activities have, as a side-effect, led to a temporary fishing closure. These closures are not enforced after the emergency has passed and as indicated above there are no established procedures for determining the quality of affected finfish and shellfish resources before a fishery is reopened.

3.3 Methods of Determination

Determination of suitable methods for identifying a taint proved to be a relatively easy task compared with the subjects considered above. Methods for determining taste quality are well developed in the food sciences, and chemical analytical methods are available. The literature on the latter is voluminous. From the determination of taint standpoint, the real concern is developing suitable and consistent methods for separating natural flavours, and variants thereof, from those introduced as a result of exposure to hydrocarbons.

Because tainting is a sensory perception, sensory (organoleptic) methods are required to evaluate the quality of suspect produce. Sensory testing, however, is subjective and is difficult to quantify. On the other hand, chemical analysis of the product will yield quantitative results, but will only identify the types of hydrocarbons present and will not always identify the taint-producing agent. Chemical analysis will not, by itself, determine whether a product is tainted.

Sensory evaluation methods involve using the senses of taste and odour to establish differences or preference of a suspect product with a known standard or control. Trained or untrained people assembled in a taste panel are used in the comparison. Specific sensory methods include the triangle test, multiple comparison test, a hedonic test, and category scaling. The method chosen depends on the number of samples, quantity of product available, the information desired, and the qualifications of the panel members. In any evaluation to identify a possible taint, the objective is simply to determine whether there is a detectable difference in the taste of produce from contaminated and uncontaminated areas, and not to classify the nature of any difference. Using this premise, it was concluded that the basic triangle test would prove to be the most useful and reliable tool to identify a possible taint. This is consistent with the GESAMP (1985) recommendations.

Sample preparation for these tests is critical. It would appear that the "boil-in-a-bag" method is preferable to the casserole method because it is easier to standardize and results should be more readily reproducible. Variations in oven temperature and sample handling associated with the casserole method could inadvertently bias the results.

The review of chemical analytical techniques determined that the most suitable method involves mincing the sample and subjecting it to steam distillation, followed by hexane extraction of the distillate, drying and concentration. Hydrocarbon determinations should be made using capillary GC-MS. The method is proven and has the advantage of speed and simplicity. As a procedure to support sensory evaluations, the chemical analysis should concentrate on the same tissues (e.g., fish fillet, whole oyster, scallop muscle, etc.) that have been tested by taste panels.

To date there has only been limited research to establish a relationship between sensory testing and chemical analysis. In the case of hydrocarbon contamination, case histories provide little guidance in this area because the methods used are often only very generally described in available reports. Where comparisons have been made, it has proven difficult to specifically identify the tainting agent because of biomodification and masking by biogenic hydrocarbons.

3.4 Recommendations

Seven recommendations were developed from the study. In summary these were:

- standardization and refinement of sensory evaluation methodologies to ensure reproducible results and to satisfy any legal requirements for handling compensation claims;
- correlation of taste panel results with tissue analysis to attempt to establish threshold concentrations;
- establishment of depuration rates for contaminated fish;

- establishment of background levels of aromatic hydrocarbons in stocks resident near exploration areas;
- monitoring of possible uptake of hydrocarbons from production water discharges;
- determination of the effects of dispersant usage during an oil spill on the risk of tainting; and
- assessment of the risk of tainting from oil present in sediments or in drilling muds.

By design, the recommendations did not extend into the consideration of perceptual problems associated with tainting. It was felt that if the problem of tainting can be placed on a more factual basis, perceptions can be readily dealt with.

It is recognized that the recommendations cover a wide range of scientific subjects associated with the problem of tainting and may in fact duplicate some work already done. However, the widely divergent results published in the literature suggest that some reappraisal work is needed if we are to be in a position to effectively deal with a fish tainting situation should one arise in Canadian waters in the future.

4. FUTURE DIRECTIONS

This final section contains some general observations arising from the study and ideas which perhaps should be considered when planning future work on the subject of fish tainting.

4.1 Scientific

Although the effect of hydrocarbon contaminants on the quality of exposed finfish or shellfish is well known, there are a large number of scientific questions which remain outstanding. Although the EHS Working Group of GESAMP has been evaluating the effects of hazardous substances carried by ships over a period of 12 years, the question of tainting only formally entered their deliberations in 1981. Recently, the group has devoted considerable effort to developing a reasonable definition of the term tainting, organoleptic testing protocols for determining a taint and attempts to determine the threshold concentration of tainting substances (see GESAMP, 1983, 1985). It is generally recognized that considerable effort is needed to attempt to systematize the process of evaluating a taint, and place it on a more quantifiable basis. The committee has recognized that the primary method of evaluation must be sensory, and that it would not be valid to base measurement solely on chemical analysis. Crude oil is not considered within the mandate of the working group although many of the derivatives (e.g., benzene, cyclohexane, etc.) have been assigned hazard profiles. The deliberations of the group reflect the scientific complexity of the problem and reinforce the recommendations made for further investigation described above.

Some recent work on tainting and threshold concentrations has been undertaken in the United Kingdom (McGill, pers. comm.) and the results will be published in the near future.

At the risk of restating the obvious, it is evident that the most recent work should be reviewed in detail, before any future programs are finalized.

4.2 Economic and Regulatory Aspects

From the point of view of impacts, tainting is probably the most tangible potential effect of a large scale oil pollution incident on the fishing industry, not because of problems of off-flavour but rather because of problems of marketing. It is a scientific problem which also manifests itself as an economic issue. In a situation where produce is harvested from a well-defined area near or adjacent to a spill site, uncontaminated material may have to be withheld from market in order to protect future markets, or present investments. During the Amoco Cadiz incident, the oyster industry in Brittany was forced to destroy in excess of $2 million worth of produce (Chassé, 1978). Obviously, fishing operations in coastal waters will be more vulnerable to these pressures than harvesting activities offshore. The risk is increasing substantially because aquaculture facilities on the east and west coasts contain stocks of finfish and shellfish which are vulnerable to acquisition of a taint as a result of chronic or acute oil pollution. The investments in these facilities are substantial.

To date, the regulatory focus related to tainting has been the protection of public health. In Canada, as elsewhere, regulatory responsibility for tainting is somewhat fragmented with both the Departments of Fisheries and Health and Welfare having some responsibilities. Fisheries has primary responsibility for monitoring fish quality during landing and processing to ensure that unwholesome product does not reach market, but if a health question is raised in the market place, health officials become involved. The orientation of both groups is, of course, to protect public health but there may be a need to reorient Fisheries inspection practices at the outset of a pollution incident to protect the industry. It will be argued that this would be unjustified intervention, but the present level of public investment in many fishing related enterprises through loans, grants and subsidies, is such that some regulation of the produce entering the market place may be justified to protect this investment.

A conundrum for regulatory agencies is the qualitative methods available for assessing possible taint. We only have to consider the recent "tainted tuna" affair to realize that the subjective nature of a decision to accept or reject product is vulnerable to outside pressure. The GESAMP EHS Working Group's guidelines for sensory testing for possible taint place existing methods on a more legitimate basis. Their adoption as a standard testing method would remove the element of suspicion about the validity of the test methods.

5. ACKNOWLEDGEMENTS

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THE BEHAVIOUR OF OIL IN FREEZING SITUATIONS

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ABSTRACT

An experimental study of the behaviour of an oil spill in a developing (grease) ice field is described. It was found that significant quantities of oil may be entrained within and beneath a grease ice field. The amount of oil entrained is increased by:

i) a high oil density occurring naturally or induced by weathering.
ii) the presence of sufficient turbulence to disperse the surface oil at an appreciable rate and induce mixing within the forming ice field.
iii) a high oil viscosity occurring naturally or induced by weathering.
iv) the formation of emulsions and sea water and/or ice in the oil.
v) the formation of smaller oil droplets.
vi) the formation or coalescence of ice particles to a size of approximately 5 mm in diameter.

It is suggested that the results and observations obtained here be used as a component in an "expert system" computer model that would aid in the prediction of the fate and behaviour of an oil spill in the presence of a developing ice field and in other regimes in which oil may interact with ice. This model may then be included as part of a comprehensive model encompassing the entire spectrum of oil spills conditions which may occur in the Arctic marine environment.

INTRODUCTION

The exploration and developing of the Arctic as an important petroleum producing region has resulted in a significant number of research programs pertaining to the presence of oil in the Arctic environment. In particular, much effort has been devoted to modelling, environmental assessment, countermeasures and recovery of oil spills in Arctic waters. However, while detailed studies have been performed and models proposed with regard to oil spills underneath ice, above ice and in open waters, very little research has been performed on the topic of spills in freezing conditions, or on the interaction of oil with a developing ice field. The purpose of this study is thus to investigate and quantify the nature of the oil and developing ice field interactions. The knowledge gained with regard to this phenomenon may be used to assess possible countermeasures or clean up techniques for the oil. It is also intended that the data accumulated may be used to formulate a predictive model for the behaviour and fate of oil spilled in a developing ice field.

Existing oil spill models, as reviewed in four previous papers, (Mackay, 1984) tend to fall into certain defined classes such as (i) open-water trajectory models which may include interaction with shorelines, (ii) open-water behaviour models which describe the changing properties and configuration of oil spills with time, (iii) descriptions of oil behaviour on shore, (iv) descriptions of behaviour in rising plumes reaching the sea surface or ice under surface, (v) descriptions of oil movement under ice and entrapment in ice and subsequent release during thaw. As has been pointed out by Bobra and Fingas (1986) there is a lack of model capability treating the situation in which a spill on water is subjected to freezing conditions. Behaviour in leads has also been studied (MacNeil and Goodman, 1985), but there remains a need to quantify the processes of oil splashing onto or under ice and determine the extent of emulsification and weathering.

It is believed that there is also a need to develop an overall modelling capability which can bring together these various models in one system and allow the user to predict oil spill behaviour under a wide variety of situations - open water, shorelines, and ice of various conditions and thus exploit the considerable experience which has been built up over the years in programs such as AMOP. In effect, this would be close to an "expert system" which has been successfully used in fields such as medical diagnosis and shows promise of applicability to environmental emergencies as discussed recently by Hushon (1986).

This study thus has several facets. At the most general level it will attempt to provide a structure for an expert oil spill modelling system and assess the feasibility of that system. This aspect is not reported here. There are more specific components being considered such as oil behaviour in open water (based on past work), oil behaviour at shorelines (based largely on the work of others such as Gundlach et al. in these and previous proceedings, e.g., Gundlach et al., 1985) and oil behaviour in the presence of ice (based on the work of many authors). As one of these components we have studied and report here experimental work on oil behaviour in developing ice fields, which we regard as contributing one component of the overall system.

OIL INCORPORATION IN DEVELOPING ICE

The pertinent question in this study is that of whether, and how, oil may become incorporated within the developing or "grease" ice, hence removing it from sight and from access to most conventional recovery processes. The theory underlying the phenomenon of oil incorporation in a developing ice field is multi-faceted. An ice field's ability to retain quantities of oil within its structure below the surface of the water is presumably a function of the oil's density, viscosity and interfacial tensions as well as the thickness of the oil layer, the porosity of the ice field and the level of turbulence present. While the subsurface behaviour of oil in water has been explored to some extent by Wilson et al., (1985) the presence of ice particles in water complicates the theory underlying this process. In the aforementioned paper it was demonstrated that significant quantities of oil may be entrained below the surface of the water if the upward buoyancy force exerted upon the oil particles is balanced by the downwards driving force of subsurface currents created by turbulence in the form of breaking waves or local downswelling regions. The upward buoyancy force may be quantified on the basis of a Stokes' Law analysis of the oil particles while the downwards force may be related to wind speeds directly above the water surface. Hence, a developing ice field or grease ice may be treated similarly with an ice/water mixture replacing water alone in the theoretical analysis. However, it is also necessary to consider the movement of the oil between the individual ice particles. This requires correlation of ice porosity and oil/ice/water interfacial tension with the wind derived turbulent behaviour of the ice-water mixture. It is also necessary to correlate this information with oil properties and the dynamic behaviour of both the oil and ice with changing environmental conditions.

It appears that the number of variables affecting the process of oil incorporation in a developing ice field is sufficiently large to render a theoretical approach to this phenomenon extremely complex and probably inaccurate and inconclusive. Thus, the initial intent of this paper is to obtain a quantity of data on the probable fate of an oil spill under freezing conditions. This empirical approach will allow the prediction of probable oil-ice behaviour under various environmental conditions. In future, theoretical approaches may then be attempted to enhance the interpretation and correlation of experimental results.

EXPERIMENTAL

The principal experimental apparatus, illustrated in Figure 1 consisted of a clear lucite tank of dimensions 35 cm by 35 by 35 cm deep into which various mixtures of ice, oil and water were placed. Agitation of the mixture was obtained by use of an oscillating hoop apparatus, powered by a 12 volt battery and a D.C. motor. The hoop could be oscillated vertically at a maximum rate of approximately 12 oscillations per minute. The vertical oscillations of the hoop, just below the surface of the water-oil interface created a low energy ripple/wave effect. The apparatus was placed within a cold room in which selected subzero temperatures could be maintained.

A series of experiments was performed to investigate the phenomenon of oil incorporation in grease ice fields. Since oil density is obviously an important parameter it was desired to test a series of oils of varying density, but of relatively constant viscosity. Unfortunately, weathering a crude oil results in a marked increase in viscosity. After some investigations it was decided to use a mixture of a light hydrocarbon oil and a dense organo-chlorine solvent. Bayol 35, a white oil, (SG of 0.790) was mixed with measured quantities of tetrachloroethylene (SG of 1.615) in order to vary the net oil density and was introduced into various grease ice fields. Oils of various densities and oil layer thicknesses were used as well as grease ice fields of varying ice particle diameter and field depths. The grease ice fields were not artificially compressed and were allowed to attain their own thickness and ice-to-water ratio. The experiments were carried out in large glass, graduated beakers of 2500 to 3500 mL volume and the oil was dyed red using Sudan Red dye in order to facilitate the observation of the oil incorporated within ice. The oil-ice mixture was allowed to freeze solid after which volumes of oil incorporated within the ice could be measured. Ice-to-water volume ratios within the grease ice fields were also measured by displacement of water upon introduction of ice to the water. Fresh water was used since this greatly simplifies the experimental procedure and some

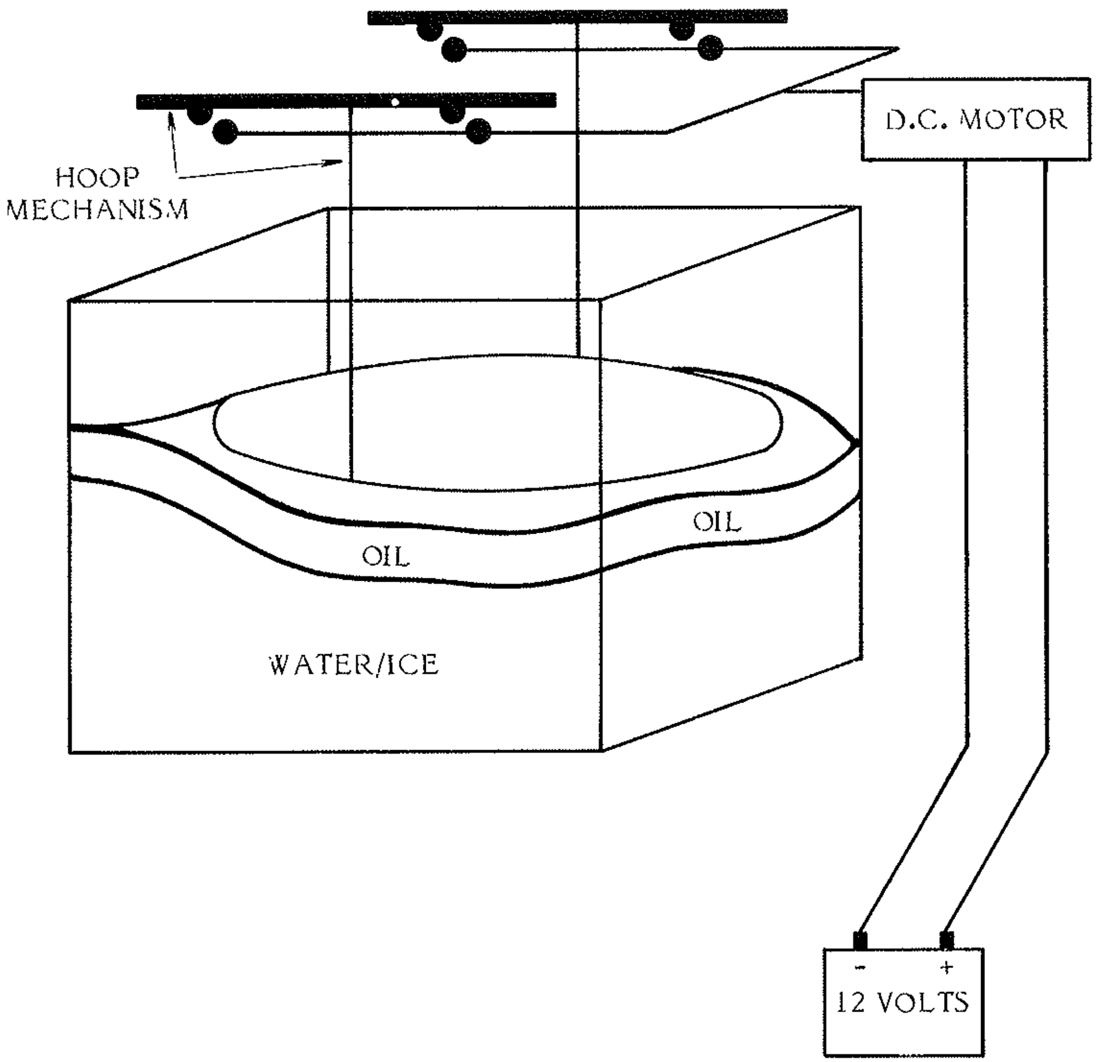


FIGURE 1 OSCILLATING HOOP AND TANK APPARATUS

fresh over salt water stratification is quite prevalent under Arctic conditions especially in close proximity to rivers, icebergs or floes.

A number of experimental runs were performed in conjunction with the incorporation of oil in grease ice experiments. After oils of various densities had been incorporated into grease ice fields and allowed to freeze solid the beakers of ice and oil were placed in an ambient environment (temperature of 21°C) and allowed to thaw. Measurements of the volume of oil released as a function of time, density of oil, and extent of incorporation were obtained in order to determine the effect of the entrained oil on the thawing process. Non-oiled ice samples were also allowed to thaw in the same ambient environment in order to compare rates of thaw of oiled and non-oiled ice.

A number of emulsions were formed under freezing conditions using a rotating shaker placed in an incubator and maintained at a temperature of -5°C. Emulsions were created using a 70/30 combination of No. 2 and No. 6 fuel oils as well as Arabian heavy crude oil. The oils were mixed with salt water in a ratio of 90% water to 10% oil. Also, a number of samples included ice crystals of various sizes in order to investigate the possibility of emulsification of oil within a grease ice field. The rotating shaker was operated at a speed of 48 rpm over a period of 3-4 hours in order to produce the emulsions. Once formed the emulsions were introduced into grease ice fields and observed. Density and percent water content were also measured.

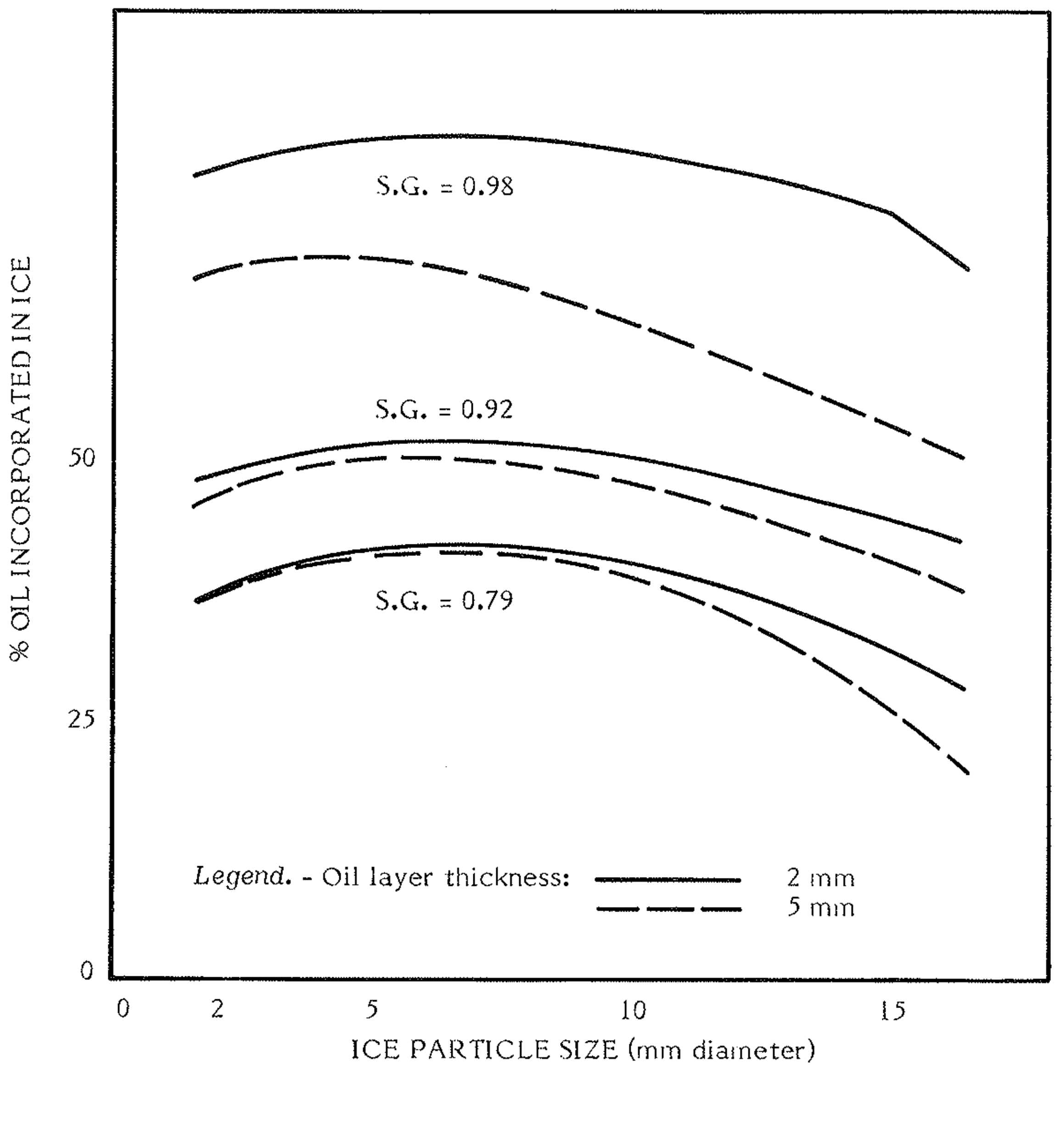
Experiments were performed in the hoop and tank apparatus using a 70/30 mixture of No. 2 and No. 6 fuel oils with different thicknesses of oil layers in order to explore the effects of thermal insulation by the oil versus the oil's damping effect on turbulence. The hoop was operated at maximum oscillatory speed while the cold room was maintained at a temperature of -5°C. Observations were recorded and the time for initial ice formation was noted and compared with the time for ice formation in the absence of oil.

An actual spill of No. 6 fuel oil in the St. Lawrence River, Quebec, in a developing ice field, was observed in December of 1985. Oil and ice mixture samples were obtained and observed. The oil was also analyzed for density increase as a result of weathering using a densitometer at the Environment Canada River Road Environmental Technology Centre Laboratory in Ottawa, Ontario.

RESULTS

Figure 2 illustrates the results from the oil incorporation in grease ice experiment. The percent by volume of an oil layer, of known thickness, which was incorporated into the grease ice layer is plotted. Grease ice fields were obtained using ice particles of different size in order to simulate the coalescence and compaction of ice particles that naturally occur as grease ice becomes pancake ice. Hence, percent of the oil present which is incorporated into the ice is plotted against ice particle size with initial oil layer thickness and oil density as parameters.
The very dense oil tested, with a specific gravity of 0.98 was incorporated into the agitated grease ice field to a maximum level of 78 percent. The oil with a specific

OIL/ICE INCORPORATION



gravity of 0.92, similar to that of ice itself, was incorporated to a maximum level of 52% while the least dense oil, with a specific gravity 0.790, was incorporated to a maximum of only 47 percent. The extent of incorporation appears to reach a maximum when the ice particle size is in the range of 5 mm to 8 mm. When the ice particles are very large the extent of incorporation is considerably reduced. This appears to be a result of the effect that with larger ice particles there were larger spaces between the individual particles and hence the oil was able to flow more easily to the surface of the grease field through these gaps. Less incorporation also occurred for very small ice particles (less than 3 mm diameter). This appeared to be a result of the small particles being of insufficient diameter to "trap" oil droplets below them with the result that the oil droplets pushed through and past the ice particles as they surfaced.

For the two lower density oils tested there appears to be little variation in oil incorporation as oil layer thickness increases. However for the very dense oil (specific gravity of 0.98) the amount of oil incorporated was reduced significantly with increasing oil layer thickness. This result appears to be related to the effect that as thicker layers of oil were introduced, the oil droplets (which dispersed throughout the grease ice as a result of agitation) tended to be much larger than those created with a thin oil layer. The thick layer drops tended to be on the order of 4 mm to 6 mm diameter while the thin layer drops were on the order of 1 mm to 3 mm diameter. Because the thick layer oil droplets were much larger their positive buoyancy driving force was greater than that for small droplets.

It appears that a simple "rule of thumb" is that the oil droplet size will be similar to the thickness of the oil slick from which they were derived.

The results from the thawing experiments are illustrated in Figure 3 as a plot of percent oil remaining incorporated within the ice as a function of the time that the oil-ice mixture has been exposed to an ambient environment. Oil density is the parameter.

The deviation from linearity of the plots after as short a time as five hours is probably a result of the growing oil layer on top of the ice. Because the oil was less dense than the ice it remained on top of the ice once released from within the ice. The oil then insulated the ice from the warm environment and retarded the rate at which the ice thaws and hence slows down the rate at which oil is released from the ice.

The curves plotted show that the denser oils required significantly larger amounts of time to be released from the ice.

Exploratory experiments were performed to observe the effects of oil incorporation on the actual rate that the ice thaws. However, in no case was the oil layer completely incorporated within the ice and hence the situation reverted to the case of ice with an oil film above it which has previously been studied by other authors.
An emulsion of Arabian heavy crude and salt water was formed which has a net specific gravity of 0.946 and was composed of approximately 40% salt water and 60% oil. The emulsion was obtained after three hours of shaking at 48 rpm. It is possible that more

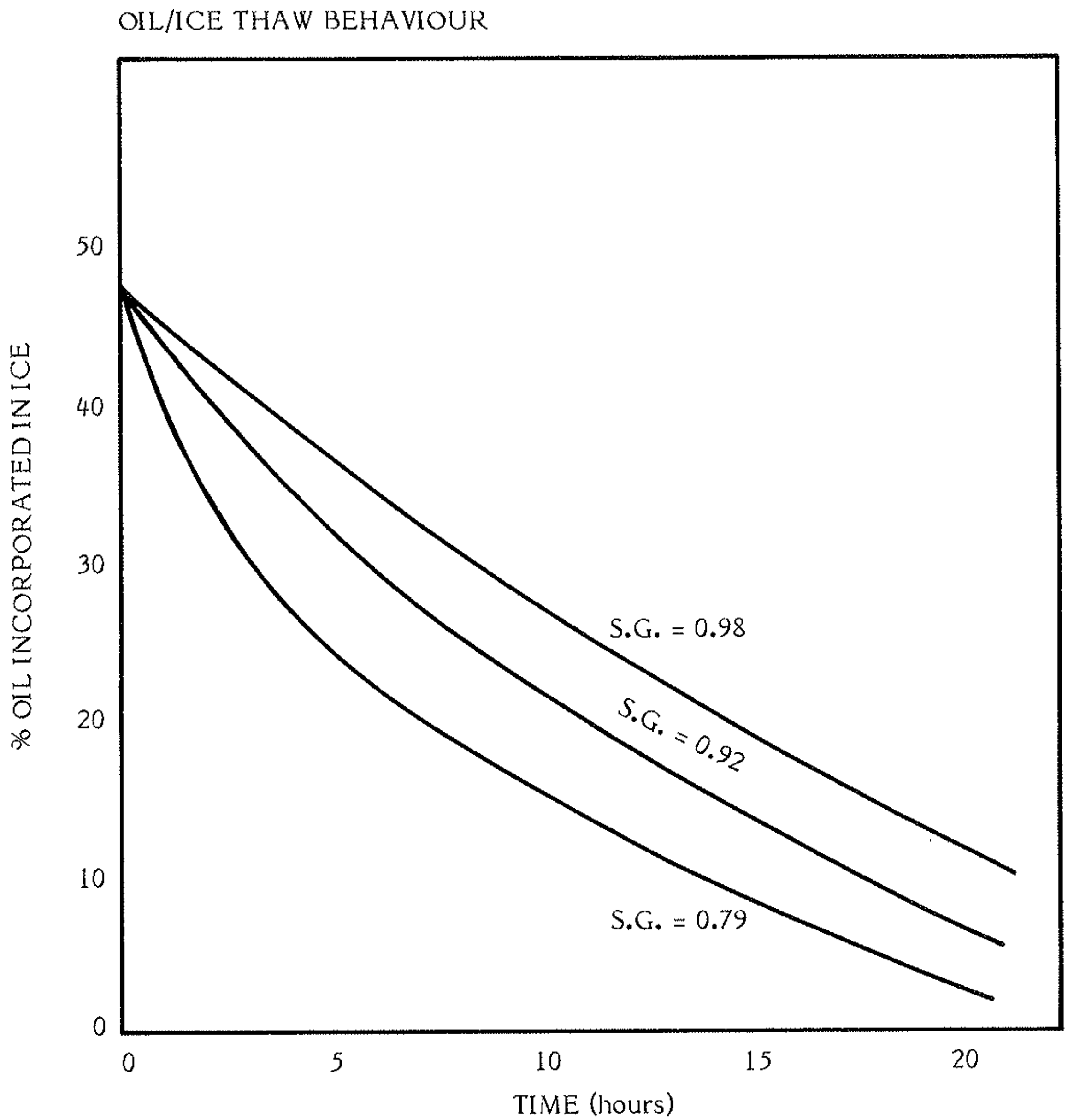


FIGURE 3 PLOT OF % OIL INCORPORATED IN ICE VS. TIME DURING THAWING OF OIL/ICE MIXTURE

vigorous shaking would have produced a higher water content and hence higher specific gravity emulsion. The emulsion was not highly stable and remained in emulsified form, in the absence of ice, for only about 50 hours.

The emulsion was poured into a grease ice field within a 3500 mL beaker and stirred. Figure 4 is a photograph of the resulting emulsion in ice incorporation. It was observed that the oil bubbles incorporated within the ice field were much larger than those formed using low viscosity oils. The high viscosity oil droplets were as large as 10-20 mm in diameter. Continuous agitation reduced many of the oil droplets to a size as small as 5 mm in diameter. However, the relatively large size of the emulsified oil droplets prevented their movement upwards through the ice field. An estimate of the amount of oil incorporated was obtained by pouring the remaining surface layer of oil into another beaker. The amount of oil incorporated was measured as 80% to 90% of the initial quantity.

In order to investigate the effect of oil on the growth of the turbulent ice fields tests were performed using the principal experimental apparatus and a 2 mm layer of the 70/30 No. 2 and No. 6 fuel oils mixture. Turbulence was provided by the oscillating hoop mechanism. While the expected frazil/grease/pancake ice formation was not noted, a slushy, crystal-like, porous frozen mixture initially formed which trapped significant quantities of oil within its internal structure. Below this layer, columnar ice formation was observed and in the first few cm of columnar ice round oil droplets of varying diameter became trapped within the growing ice. The droplets of oil ranged in diameter from as small as 0.5 mm to as large as 10 mm. The upper layer of the ice-oil mixture was solid but porous in nature with the pores in the ice containing significant quantities of oil. During the early period of the freezing process the oil was wave driven downwards by the hoop and would then resurface due to its positive buoyancy in the water. However, as freezing progressed, the ice chunks formed and then broken by the hoop became more numerous and hence formed a thicker mixture in the oil and water. This broken ice increasingly inhibited the ascent of the oil to the surface. However the oil of initial specific gravity 0.919 was sufficiently close to neutral 10 cm layer of water and ice by the downward motion of the hoop. Shortly thereafter the ice and water mixture was of sufficient consistency to trap even large droplets of oil and also allow the formation of columnar ice around and beneath the oil. The resulting oil-ice mixture was of porosity such that when pressure was exerted downwards upon it oil would flow upwards through pores and channels within the ice.

The wave or ripple effect produced by the hoop was not of sufficient energy to break up the oil layer except about the actual perimeter of the hoop. Because of this, it was not possible to quantify the balance between the oil's insulating, ice growth retarding, behaviour and its wave dampening, ice promoting behaviour. The experiments performed support the suggestion that the oil layers of thickness that would be expected in an actual spill would not be of sufficient depth to dampen swells of the magnitude expected in an ocean. Oceanic wave action is expected to break up the oil slick and hence severely retard its ability to dampen waves and insulate the water below from the subzero atmosphere. While the times recorded for wave formation are not believed to have a high

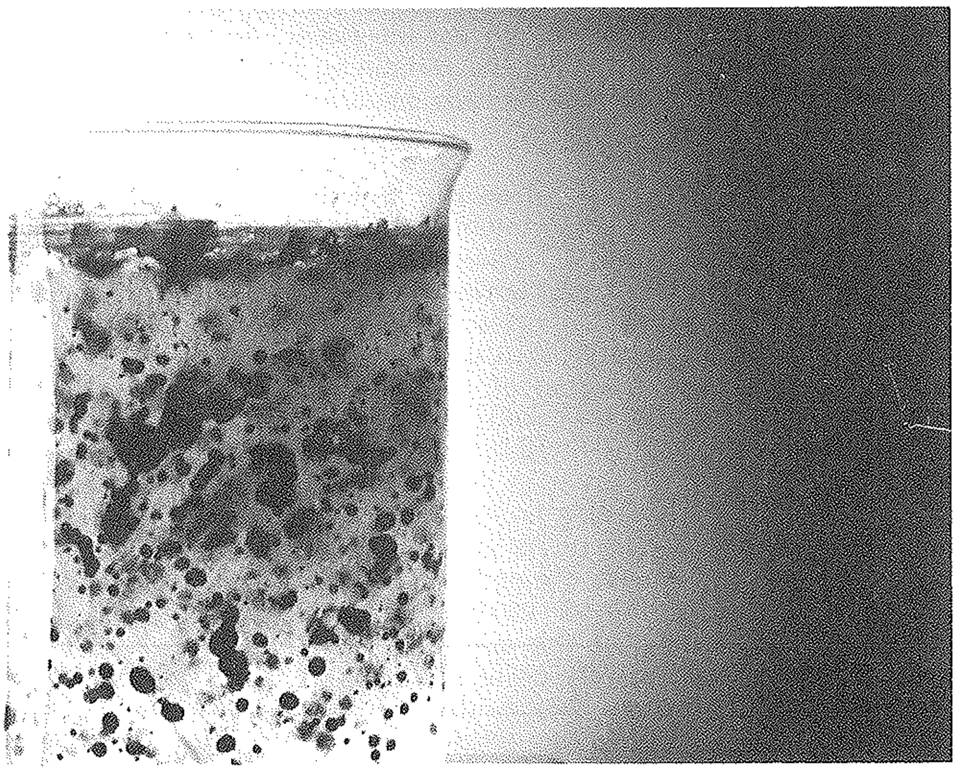


FIGURE 4 WATER-IN-OIL EMULSION INCORPORATED IN DENSE GREASE ICE

degree of accuracy there was no significant difference between time for ice formation in the presence or absence of a thin oil layer under turbulent water conditions.

Matane Spill

As previously noted a spill of No. 6 fuel oil occurred in the Gulf of St. Lawrence River in December of 1985. The author (David G. Wilson) was able to travel to the site of the spill and arrived three days after the spill had occurred. At that time, for a width of about five metres from shore, there existed a mixture of grease and pancake ice and for the next twenty metres a mixture of frazil and grease ice. The spill occurred about 100 m offshore and was blown into the grease/pancake ice mixture by the wind and current of the river. At the time of observation no oil was visible within or above the grease ice and the only visible oil was that washing up on shore. The oil washed up on shore was grease ice that had been compressed and had the water forced from between the individual ice particles by the pressure of the ice against the shore. The result was a porous crystalline ice-oil mixture that contained up to 50% oil. Figure 5 is a photograph of the ice-oil mixture which was observed at the shoreline. Samples of the oil were analyzed at the Environment Canada River Road Environmental Technology Centre Laboratory in Ottawa on a Parr densitometer. Table 1 provides a summary of the results. The specific gravity of the oil near freezing temperatures is quite close to that of the sea water at the spill site which was estimated to be 1.02. This raises the possibility that although there was no oil visible from above the grease and frazil ice there may have been large quantities of oil below or within the ice. There was also a high level of turbulence in the water during the period of the spill and hence it is possible that water-oil emulsions may have been formed.

CONCLUSIONS

A series of experiments has been performed which investigate the phenomenon of oil entrainment within a developing ice field. The observations recorded from the laboratory experiments have been complemented by observations from an actual oil spill during freezing conditions.

It is concluded that significant quantities of oil may be entrained within a developing ice field under freezing conditions. The extent of incorporation is enhanced by:

i) a high oil density occurring naturally or induced by weathering.
ii) the presence of sufficient turbulence to disperse the surface oil at an appreciable rate and induce mixing within the ice field.
iii) a high oil viscosity occurring naturally or induced by weathering.
iv) the formation of emulsions of seawater and/or ice in oil.
v) the formation of smaller oil droplets.
vi) the formation or coalescence of ice particles to a size of approximately 5 mm in diameter.

It is concluded that under non-turbulent water conditions an oil layer will behave as an insulating layer and retard ice development beneath it. Under turbulent water conditions

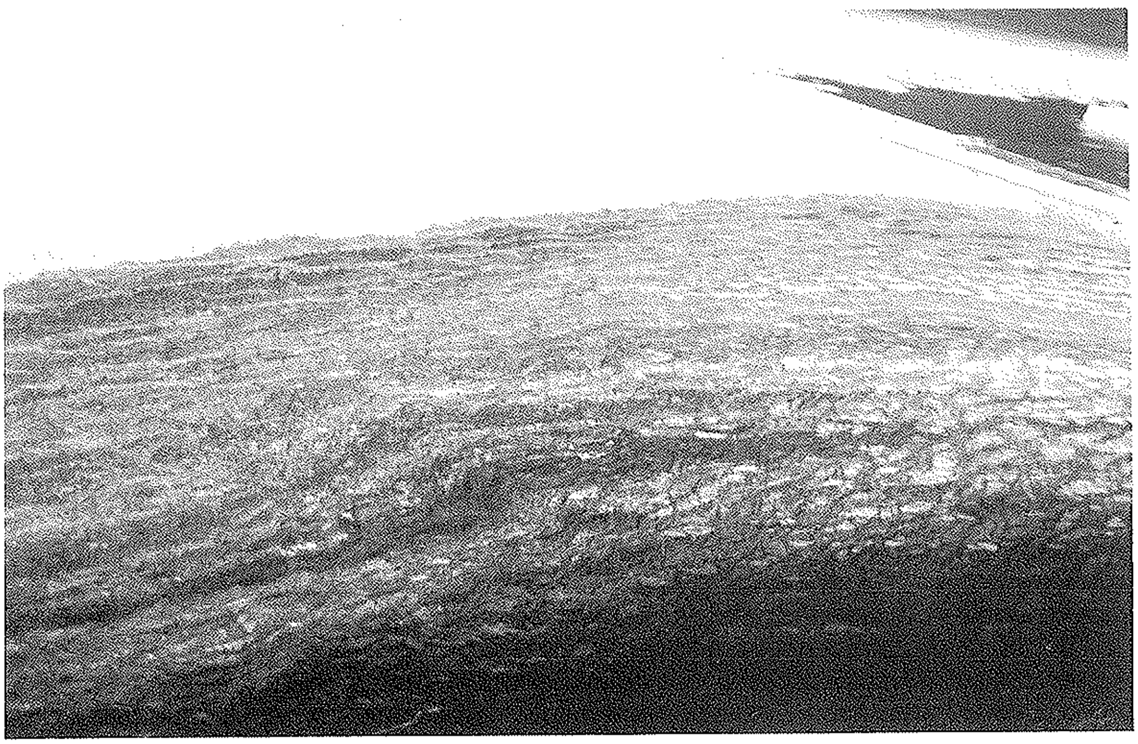


FIGURE 5 OIL/ICE MIXTURE AFTER MATANE OIL SPILL

TABLE 1

Temperature (°C)	DENSITY	
	Sample 1	Sample 2
25	0.9996	1.0020
20	1.0033	1.0061
15	1.0073	1.0098
0	1.0178	1.0204

it is likely that the presence of oil will have a negligible effect on the development of ice except for its possible incorporation within the developing ice.

Furthermore it appears that solar radiation has little effect on the development of an ice field in the presence of oil unless environmental conditions are non-turbulent. In such a case solar radiation may significantly retard the ice formation process.

The least buoyant oils (of highest density) will require the greatest amount of time to be released from a frozen ice pancake during the thawing process. Once the oil begins to collect on the surface of the ice, solar radiation will tend to hasten the thawing process.

It has been suggested that an empirical and theoretical approach be taken to model the process of oil incorporation within a developing ice field in order to predict the extent of oil entrainment under given circumstances.

Finally, it is believed that this study will contribute information concerning one component of the overall expert oil spill modeling system. The structure and success of that system remains to be assessed.

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