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# Research and Development

Investigation of the Fate of Oily Wastes  
in Streams as a Tool for Hazardous  
Waste Screening: A Preliminary  
Identification of Research Approach  
and Model Development

## Prepared for

Office of Solid Waste  
Office of Solid Waste and Emergency Response  
U.S. Environmental Protection Agency

## Prepared by

Environmental Research  
Laboratory  
Athens GA 30613

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INVESTIGATION OF THE FATE OF OILY WASTE IN STREAMS AS A TOOL FOR  
HAZARDOUS WASTE SCREENING: A PRELIMINARY IDENTIFICATION  
OF RESEARCH APPROACH AND MODEL DEVELOPMENT

by

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(on the sections defining oily waste  
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#### ABSTRACT

An approach is established for the development of procedures for analyzing the impact on streams of oily waste disposal practices. The approach includes a review of the present state of scientific knowledge concerning the processes that affect the transport and transformation of oily materials in water. An initial screening level model for evaluating potential harmful exposures is proposed for use on a nation-wide basis. The data and procedures developed will be available should more site specific models be needed in the regulatory process.



## ACKNOWLEDGMENTS

Dr. Steve C. McCutcheon wrote the majority of this document and is therefore, responsible for its content. Mr. William Vocke of the office of Solid Waste and Emergency Response researched and wrote the definition of oily wastes. Both Dr. McCutcheon and Mr. Vocke are responsible for the definition of what constitutes an oily waste. Much of the background information on water quality criteria was compiled by Mr. Vocke and Dr. McCutcheon incorporated this research into the manuscript.

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PROBLEMS PRESENTED BY OILY WASTES INTRODUCED INTO STREAMS

Re-concentration of Oily Wastes

Aquatic contaminants generally disperse in the environment and become less harmful because many wastes easily dissolve in water. When wastes easily dissolve and disperse, it is a simple matter to determine the critical effect of the waste at or near the source before dispersive processes take full effect in reducing the concentration. Oily, immiscible wastes are an exception to this general rule because of their ability to reconcentrate after some initial dispersion in the environment. As a result of this reconcentrating ability, "hot spots" of acute or chronic toxicity may develop downstream of a source when flow conditions change from highly turbulent to quiescent. Equally detrimental is the formation of visible manifestations of the oily materials as films and sheens on the water and as coatings on bed materials and plants. These visible manifestations are important because they are not in accordance with past and of present criteria [EPA 1973, 1976, and 1986 and Federal Water Pollution Control Administration (FWPCA)1968] and lead to the perception that a stream is more polluted and seriously impaired than may actually be the case.

The ability to reconcentrate arises because oily wastes may have an interfacial tension with significantly different from that of water. Thus the wastes may rise to the surface to form a film, sink to the bottom to coat sensitive benthic surfaces and to form pools and globs of oily materials, or form suspended globs.

The ability of oily wastes to reconcentrate may cause both direct and indirect effects. Oily wastes can be directly toxic to wildlife and plants in streams. Oil films, pools, globs, emulsions, and dissolved oily materials kill and impair the growth of plants, fish and other wildlife. The indirect effect of greatest concern occurs when the oily waste concentrates otherwise immobile hydrophobic organic contaminants. The hydrophobic contaminants of concern may already be present from other sources of pollution (FWPCA 1968 discusses pesticide mobilization) or in the stream maybe mobilized from a landfill, lagoon, or in the bed of the stream and associated surficial aquifer connecting the landfill or lagoon of interest to the nearest stream.

#### Definition of Oily Wastes

There is no single accepted definition for oily waste. Within the U.S. EPA, each program office uses a definition appropriate for their particular regulatory activity. Because the procedure being developed in this effort is intended to support many different program areas, it is difficult to provide a precise definition of oily wastes. Therefore, a general definition suitable for the many uses of the procedure is being proposed. To further aide in

defining oily wastes, important examples and typical characteristics are summarized.

An oily waste contains sufficient oils of animal, vegetable or mineral origin to form a separate non-aqueous phase in water. These waste will have a significant interfacial tension with water that allows the formation of separate phases. Waste that do not have an interfacial tension with water and thus readily dissolve, except where mixing may be precluded by density differences, are typically not considered to be oily wastes. Wastes that form a separate aqueous phase due to density differences resulting solely from temperature differences or the concentration of dissolved chemicals (e.g. brines) are not considered oily wastes. Generally the density of the waste will be different from water but not necessarily in every case. Complex waste mixtures such as those derived from wood preserving may contain oils heavier and lighter than water that have a combine density of water. Peter Shanahan notes in his review in Appendix I that cresote is typically mixed with a carrier that is lighter-than-water fuel oil. Therefore, interfacial tension with water seems to be the only fully distinguishing characteristic but density differences with water are very typical.

Important examples of oily waste include wood preserving wastes (K001 - waste designation by Industry and the U.S. EPA - see 40 CFR, Chap. 1, Subpart D, Section 261), by-products from petroleum production and refining (K048 through K052), distillate bottoms or residues (F024), and by-products from processes that employ petroleum-based materials (written communication, Ben Smith, Waste Characterization Branch, Office of Solid Waste, U.S. EPA, December 1986).

Waste properties, at the least, cover the spectrum of oil properties. In addition, oily wastes may contain appreciable levels of water and solids. When water is present, emulsions often are formed and may be either water in oil or oil in water. Significant volumes of wastes come from: 1) pond sludges, 2) product and crude oil storage tank bottoms, 3) API (American Petroleum Institute) separator sludge, 4) contaminated near surface soils, and 5) used motor oils (written communication, Ben Smith, Waste Characterization Branch, Office of Solid Waste, US EPA, December 1986).

Typical volumes for oily wastes include 500 to 200,000 gallons per disposal event. One to two million metric tons of oily wastes are generated by approximately 180 refineries each year. Surface impoundments typically cover 405 to 405,000 square meters (0.01 to 100 acres) at refineries and other facilities (written communication, Ben Smith, Waste Characterization Branch, Office of Solid Waste, US EPA, December 1986).

There seems to be four important categories of constituents in oily wastes. Metals, such as Arsenic (As), Lead (Pb), Nickel (Ni), Chromium (Cr), Selenium (Se), Cadmium (Cd), and Mercury (Hg) comprise the first category. The second category includes benzene, toluene, and xylene. The third category contains polynuclear aromatic hydrocarbons, especially benz(a)pyrene, benz(a)anthracene, and dibenz(a,h)anthracene. Halogenated dioxins and furans make up the fourth category of constituent types (written communication, Ben Smith, Waste Characterization Branch, Office of Solid Waste, US EPA, December 1986).

The Office of Solid Waste has determined that, as of early 1987, oil and gas wastes were disposed of in 125,074 surface impoundments and on 726 separate land application areas. The number of landfills accepting these wastes has not yet been determined.

Wastes that are derived from vegetable and animal oils are not expected to present a significant problem (McKee and Wolf, 1963). Unlike petroleum-based oils, animal and vegetable oils of recent origin, are unlikely to be toxic or contain materials that are toxic. In addition, mineral oils may produce less detectable tastes and odors. Therefore, it is anticipated that mineral oils will not present a significant problem.

#### DEVELOPMENT OF PROCEDURES TO ANALYZE THE POTENTIAL IMPACT OF OILY WASTE DISPOSAL ON STREAMS

##### Determination of When Oily Wastes Become Hazardous

The objective of this study is to determine when oily materials should be treated as hazardous wastes. Once this determination is made, the wastes would be disposed of in a subtitle C hazardous waste disposal facility.

The analysis procedure to be initially pursued will consist of a simple, well-concieved out, screening level model. The model will be designed for application to all potential sites in the continental United States. We hope to balance scientific rigor, conceptual simplicity, and environmental conservatism in such a screening-level model. The model will be combined with

Monte Carlo analysis of the variation in site characteristics that can occur across the nation to provide estimates of uncertainty. The analysis will be further improved by compensating for uncertainty in environmental process and data for streams and oily waste disposal. The proposed Monte Carlo procedure will allow officials to chose a level of protection based on defined regulatory risk managemnet polices.

We seek to incorporate the necessary scientific understanding of the principle processes that influence the assimilation of oily wastes into the stream environment. Initially we will focus only on processes that are involved in the potential transport of the material to critical exposure zones in streams. To judge what is necessary, we will review, in greater depth than is needed for the initial screening level model, the present understanding of processes that influence the transport and transformation of oily material in streams. The objective of this review will be to separate processes that affect the transport and concentration of oily materials from those that transform the waste into lower concentrations.

If we incorporate only the processes that transport or oncentrate the oily wastes in the initial screening model, we expect to be able to determine if current or projected waste disposal practices are environmentally sound. If the screening analysis indicates that disposal practices are not sound, then we expect that the development of more rigorous models will be necessary to demonstrate the extent of the problem. Additional model development and data collection will focus on the processes that reduce the exposure of stream biota and humans. Therefore, later phases will develop more precise models if the need to do so is demonstrated.

As a part of the development of a procedure to analyze oily waste disposal on a nationwide basis, we will also determine the processes that effect concentrations of the material. As a result, this work will also lay the groundwork for more site-specific models that may be useful in a wavier process if that is later deemed necessary.

#### Investigation of Low Intensity Nonpoint Sources

In this investigation, we have concentrated on the effect of low intensity, approximately constant nonpoint sources of oily materials. In doing this, we have excluded full consideration of spills and the more dynamic introduction of oily materials into streams until a later date. As a result, we do not expect to be able to address problems associated with spills where large quantities overwhelm the stream ecosystem for a short time until some later date.

We are currently advising others on the application of the WASP model (Water Quality Analysis and Simulation Package, early 1988 Ambrose et al. 1988) in a post-audit study of the Ohio River oil spill. From the emergency response to that event we have found that there is a clear need to develop an operational model and we expect that this review of the processes that affect the fate of oily materials will better position us for such an investigation in the future. At this time, however we will do no more than take note where this effort may later be useful for other problems.



## Sources of Oily Wastes

In this analysis, we will consider oily liquids and sludges placed in landfills, in lagoons, and on land application units as potential sources of stream contamination (see Figure 1A through 1D). We expect that liquid oily wastes in leaking drums and other containers, sludges, and tank bottoms will be placed in landfills. Liquid effluents and sludges will be placed in lagoons and sludge drying beds. Migration out of lagoons such as those in a wastewater treatment plant may be a significant source. Oily wastes, especially those from wood preserving operations, have frequently been disposed of by application to land. These practices are presently under review, however.

## Pathways to Streams

We have considered two pathways from the sources of oily materials to the stream -- overland flow and groundwater flow. We have assumed that volatilization from the source and subsequent deposition in the stream is not a significant pathway for this type of material.

At this time, we have not fully considered the dynamic nature of the pulse loading to streams by overland flow. Initially, we will treat overland flow by averaging over periods of time that may be inconsistent with the period of time during which some events may actually occur. In the meantime, we have commissioned a consulting firm to determine the importance of this pathway for oily wastes and other materials. In the interim, the modeling approach that we will take will assume that the waste will enter the stream as a combination of

POTENTIAL SOURCES AND PATHWAYS OF  
OILY WASTES TO STREAMS

A. ORDINARY "TITLE D" LANDFILLS

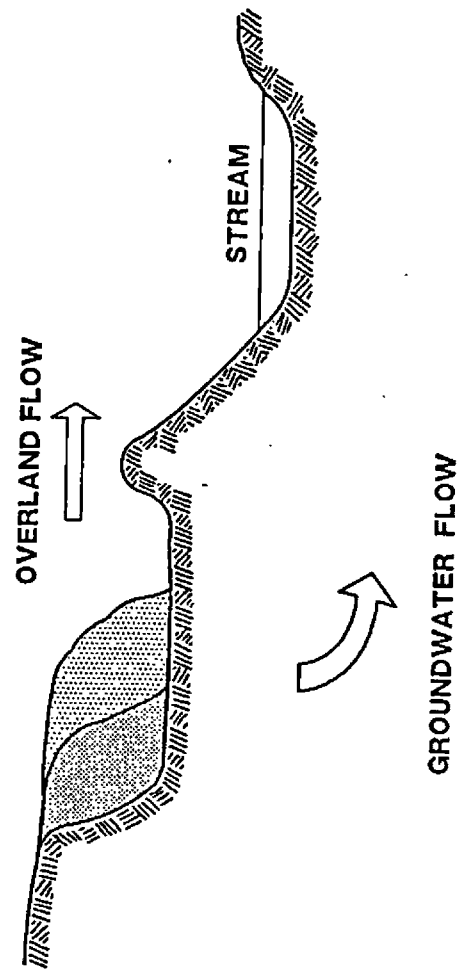


FIGURE 1-A.

POTENTIAL SOURCES AND PATHWAYS OF  
OILY WASTES TO STREAMS

B. OTHER LANDFILL FACILITIES

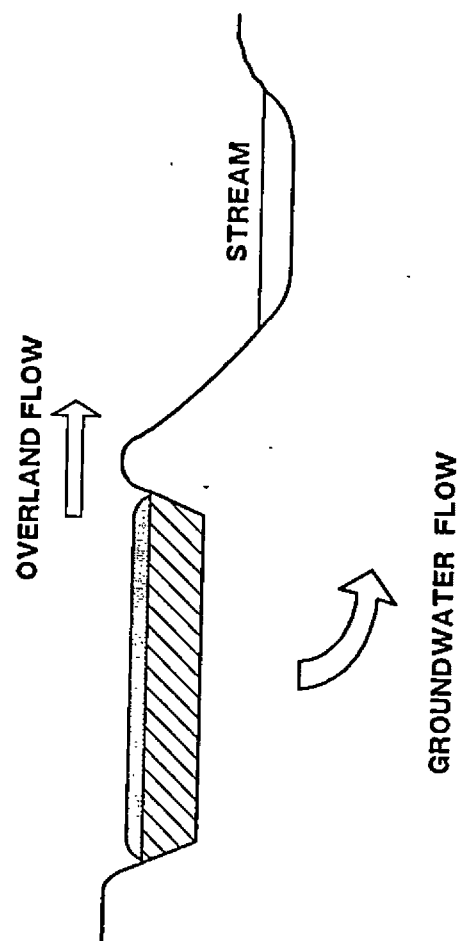


FIGURE 1-B.

POTENTIAL SOURCES AND PATHWAYS OF  
OILY WASTES TO STREAMS

C. LAGOONS

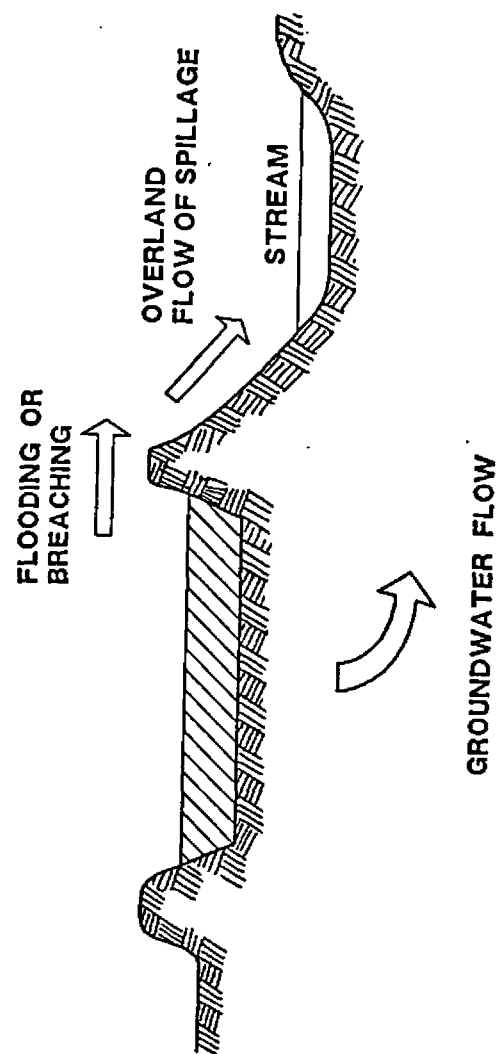


FIGURE 1-C.

POTENTIAL SOURCES AND PATHWAYS OF  
OILY WASTES TO STREAMS

D. LAND APPLICATION

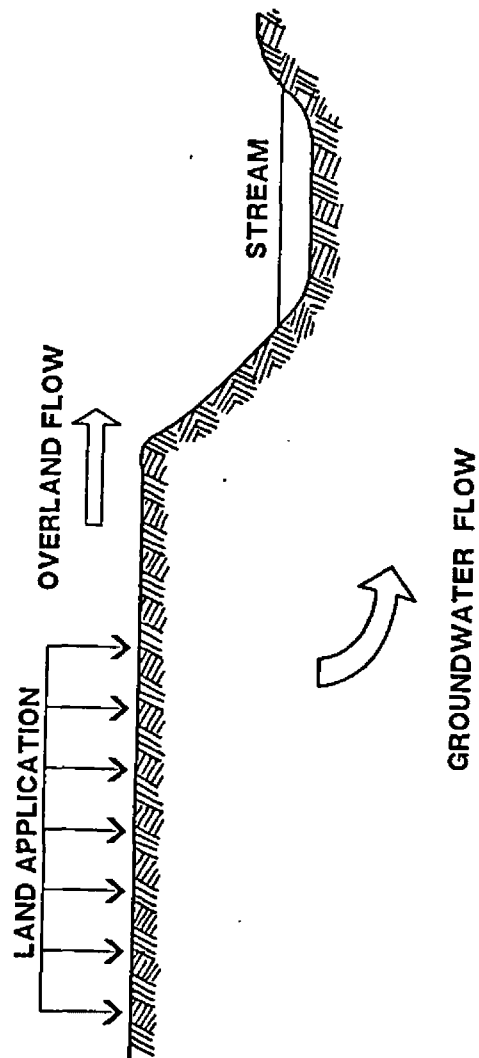


FIGURE 1-D.

a separate phase, partially dispersed droplets, emulsions, or a dissolved component of the overland flow.

The density of the waste will control whether the waste will tend to form a film on the surface or pool along the bottom of the stream. As illustrated in Figure 2, lighter than water oily wastes will tend to form a surface film. Heavier-than-water oily wastes will tend to sink to the bottom (see Figure 3). Emulsions of oil in water and dissolved components will begin to mix in the stream. Partially dispersed droplets also will tend to mix and disperse if the turbulence in the stream is sufficient. Otherwise, droplets will tend to coalesce into films, pools or globs.

We expect the groundwater path to be the predominant route to the stream. As a result, screening level procedures will focus initially on approximately continuous, steady-state introduction of oily materials to streams. Depending on the density of the waste relative to water, and the processes that attenuate concentrations, we expect that the waste may arrive at the stream in a number of forms. This is illustrated in Figure 4.

Oily wastes migrating through groundwaters are expected to be in the following forms:

1. A separate oil phase moving along the surface of the aquifer or the bottom (perhaps moving towards the bottom) of the aquifer (interface with the aquiclude),
2. A mixture of partially dispersed oil droplets,
3. An emulsion of oil in water, and
4. A solution of oil and water.

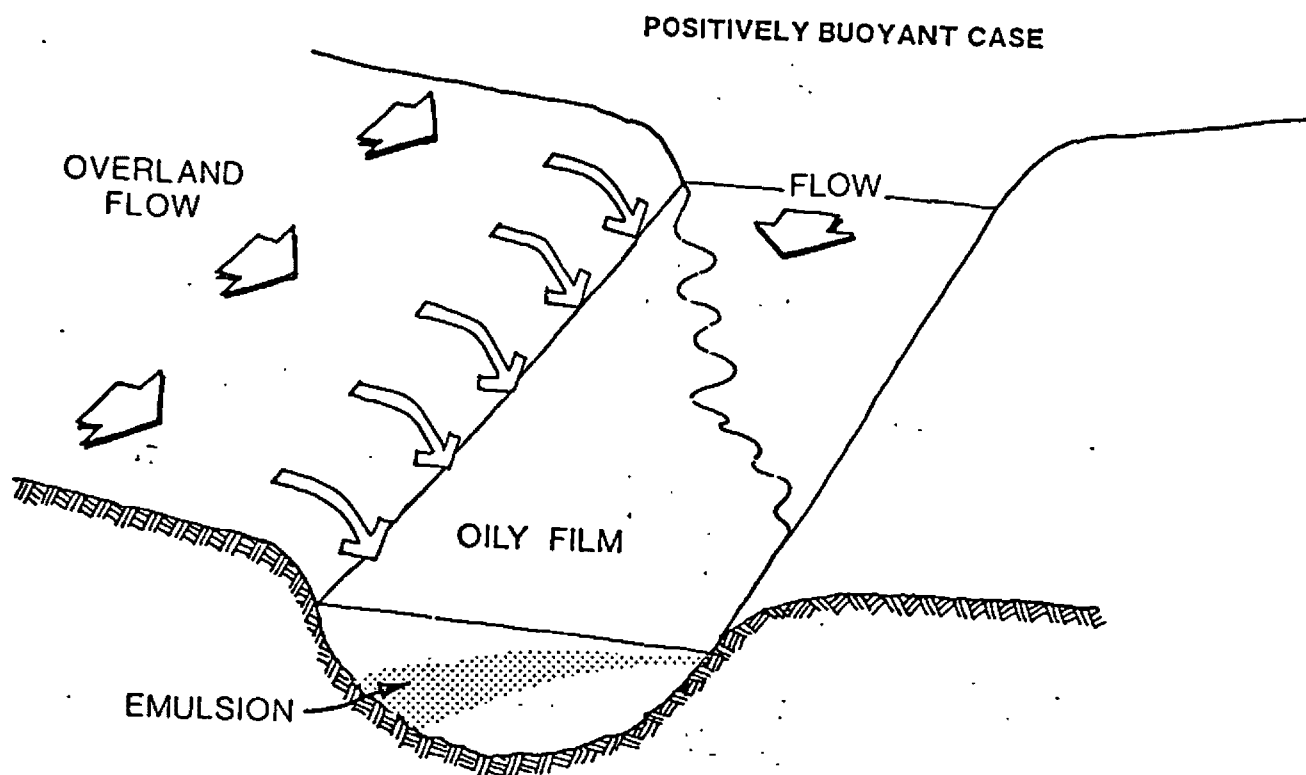


FIGURE 2. Lighter Than Water, Oily Waste  
Entering a Stream as Overland  
Flow

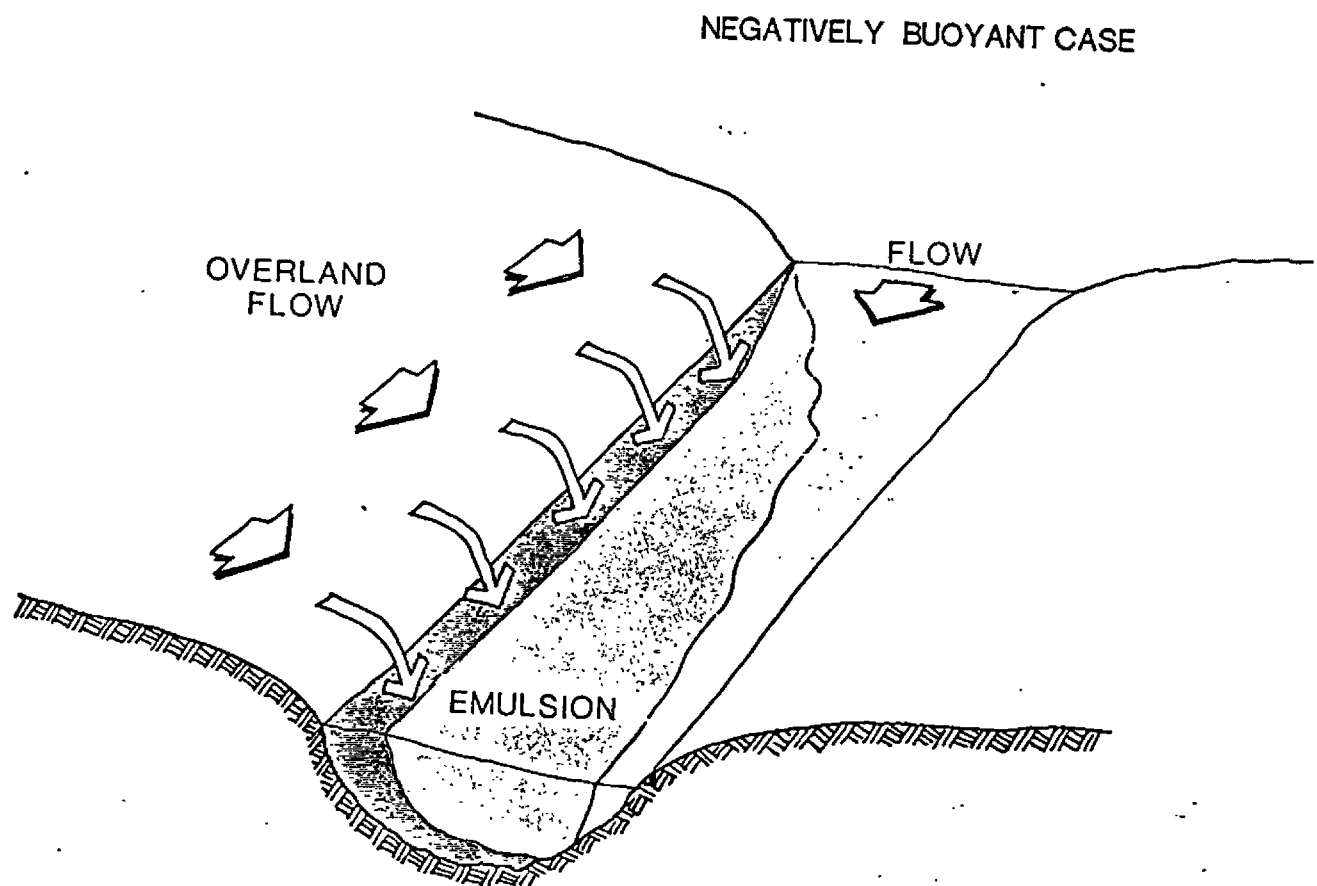


FIGURE 3. Heavier Than Water, Oily Waste Entering a Stream  
As Overland Flow



# PATHWAYS THROUGH GROUNDWATER SYSTEM

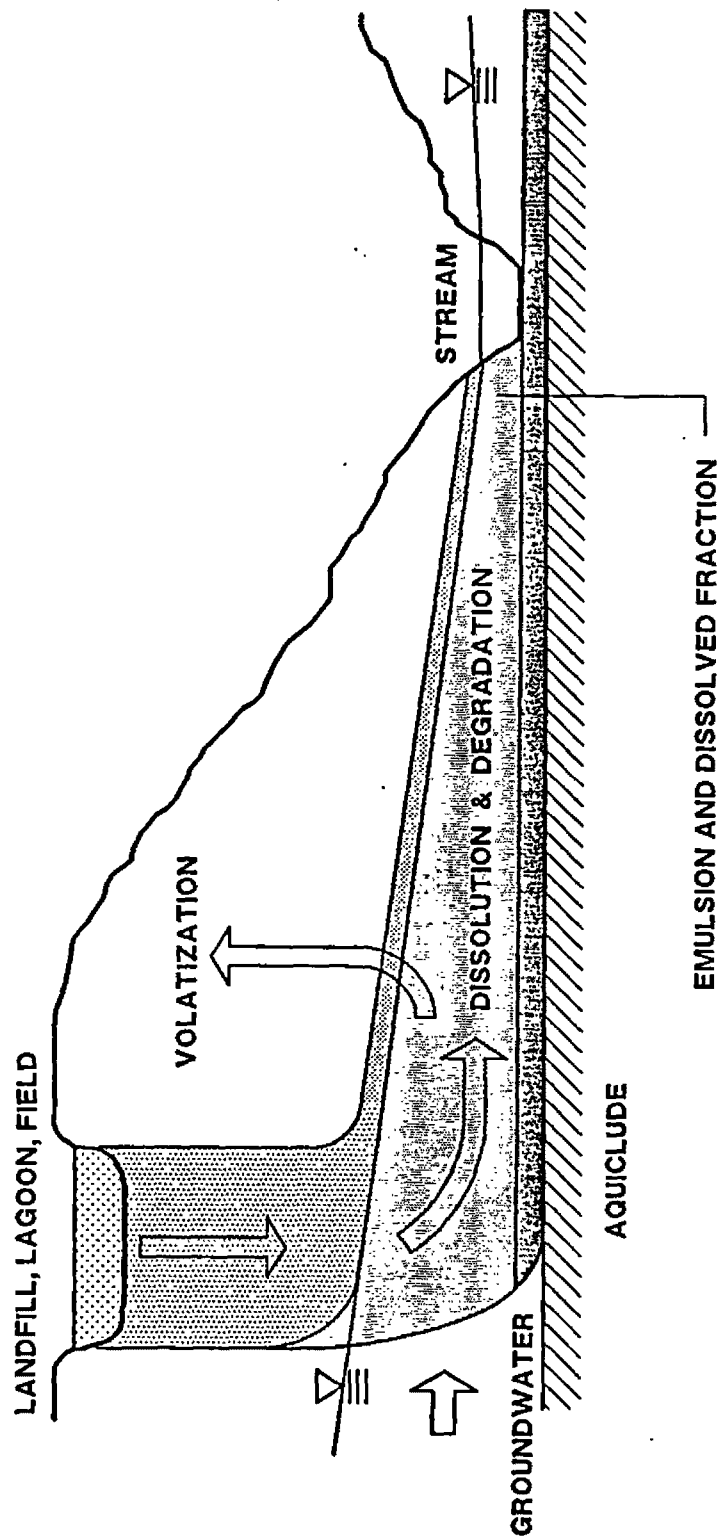


FIGURE 4. Pathways and Potential Attenuation of Oily Waste Migrating Through the Groundwaters to Streams

In addition, emulsions of water in oil may occur in groundwater systems. At this time, however, we do not fully understand whether such an occurrence will significantly change the properties of the separate oily phase enough to influence the mixing and dispersion of the waste in a stream.

The density of the waste will control, to some extent, what combination of forms the waste will be in as it enters the stream. Lighter-than-water oily wastes will tend to move along the top of the groundwater table and almost all of this material will eventually reach a stream or other water body (see Figure 5). Heavier-than-water oily wastes will tend to migrate to the bottom of the surficial aquifer. If the slope of the aquiclude (impermeable layer underlying an aquifer) is towards a stream and the stream fully cuts through the surficial aquifer as shown in Figure 6, then all of this form of the waste also will eventually arrive at the stream.

If the aquiclude slopes away from streams into depressions or into connections with deeper aquifers, it is unlikely that any of the heavier-than-water non-aqueous liquid phase will be introduced into the stream unless it pools in the depressions and spills out. If the stream does not fully cut through the aquifer, then some heavier-than-water wastes may move under the stream. In either case, heavier-than-water oily wastes may not arrive at a stream or other surface water body. These cases are serious groundwater contamination problems because the reservoirs for these wastes in groundwater are finite. In determining the impact on streams, however, these transport processes represent a reduction of the mass of material that reaches the stream.

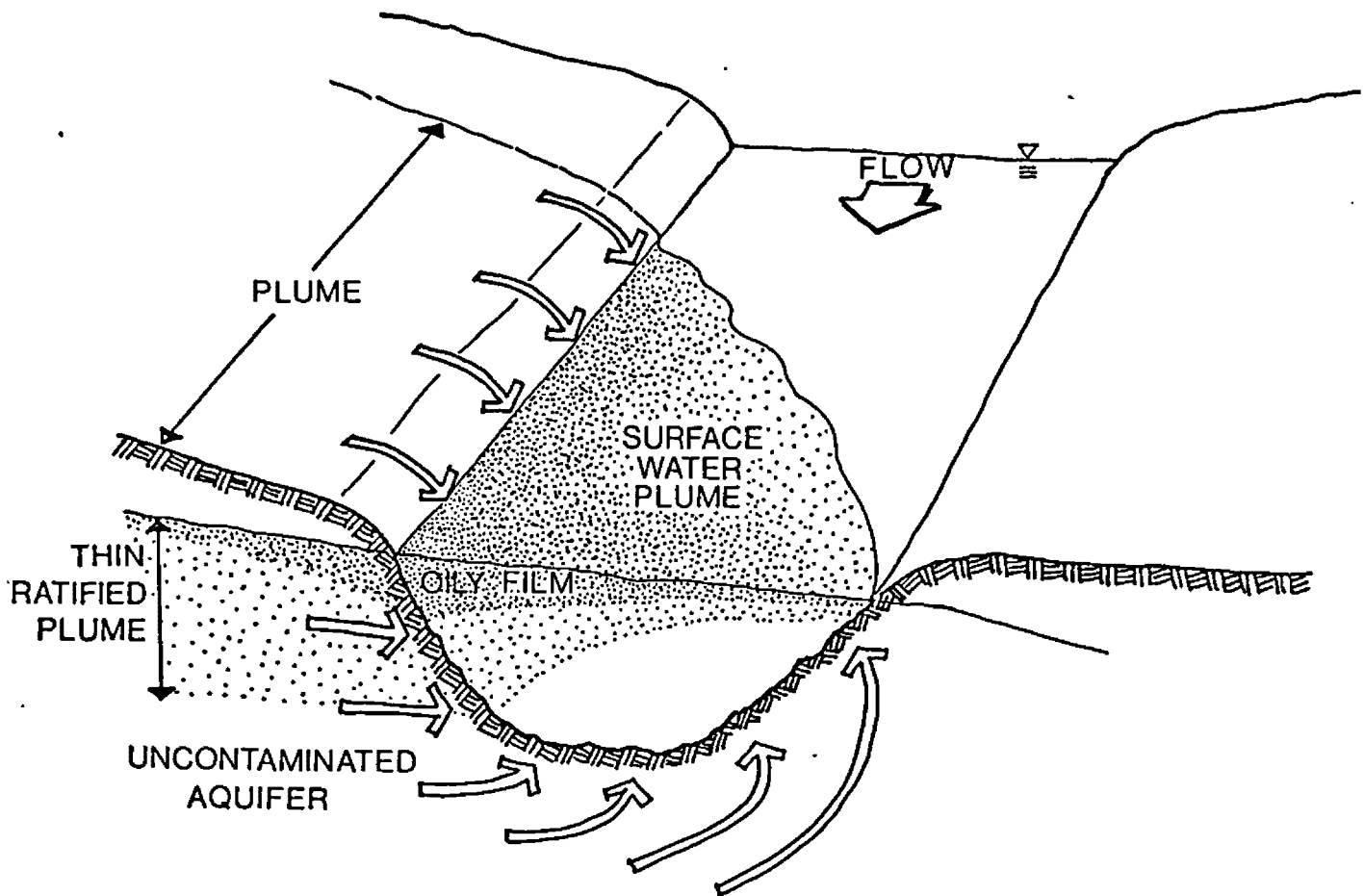


FIGURE 5. Thin Stratified Oil Waste Plume Intersecting a Stream

## NEGATIVELY BUOYANT PLUME

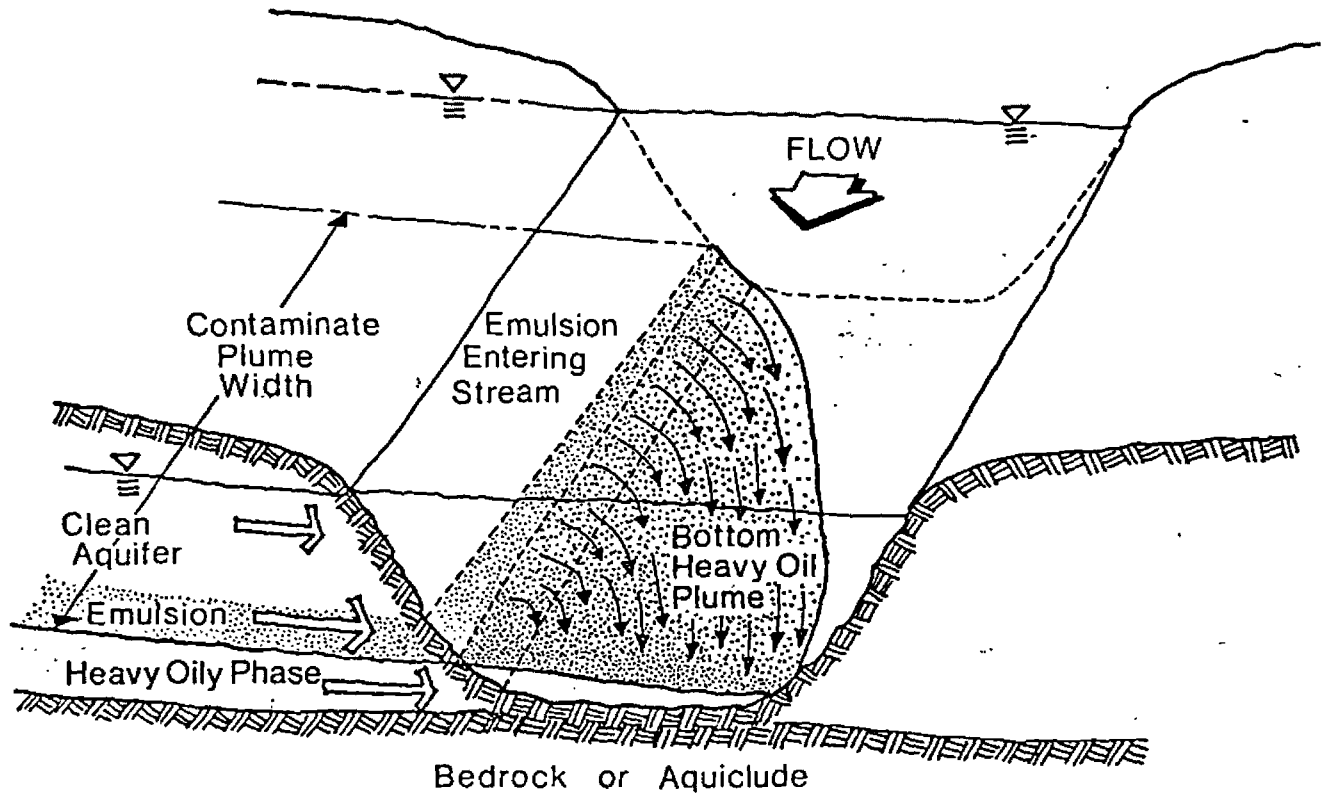


FIGURE 6. Interception of a Plume of Heavier than Water Oily Waste by a Stream that Fully Penetrates the Surficial Aquifer

We have not fully investigated the formation of partially dispersed droplets or emulsions in groundwaters but we do believe that they occur based on our limited understanding of the groundwater pathway. In addition, a recent review of this work (Danny Reible, Department of Chemical Engineering, Louisiana State University, personal communication, February 26, 1988) indicates that this is a reasonable assumption. Dispersed droplets and emulsions are important if the leachate plume is thicker than the depth of the stream penetration into the surficial aquifer. In such a case, not all of the material will be intercepted by the stream as illustrated in Figures 7 and 8. Some of the partially dispersed droplets and emulsified plume will continue downgradient past the stream.

In earlier studies (Ambrose et al. 1987), we have investigated the behavior of dissolved materials such as those that will dissolve from oily wastes at the source and in transit to the stream. From our previous work, we anticipate that the dissolved phase will migrate in a fashion similar to that shown in Figures 4 through 8. If the dissolved plume is shallower than the penetration of the stream into the surficial aquifer, then we expect all of the plume to be intercepted. If this is not the case, we anticipate that some of the dissolved material in the lower part of the plume will not be intercepted and will continue downgradient past the stream. Ambrose et al. (1987) describe the analytical procedures to handle mixing of dissolved materials into streams.

In our initial analysis, we will conservatively assume that all of the oily material will reach the stream. This is equivalent to assuming that the source is at the edge of the stream. We will design the initial model to accept oily waste in the form of a non-aqueous phase liquid, partially dispersed

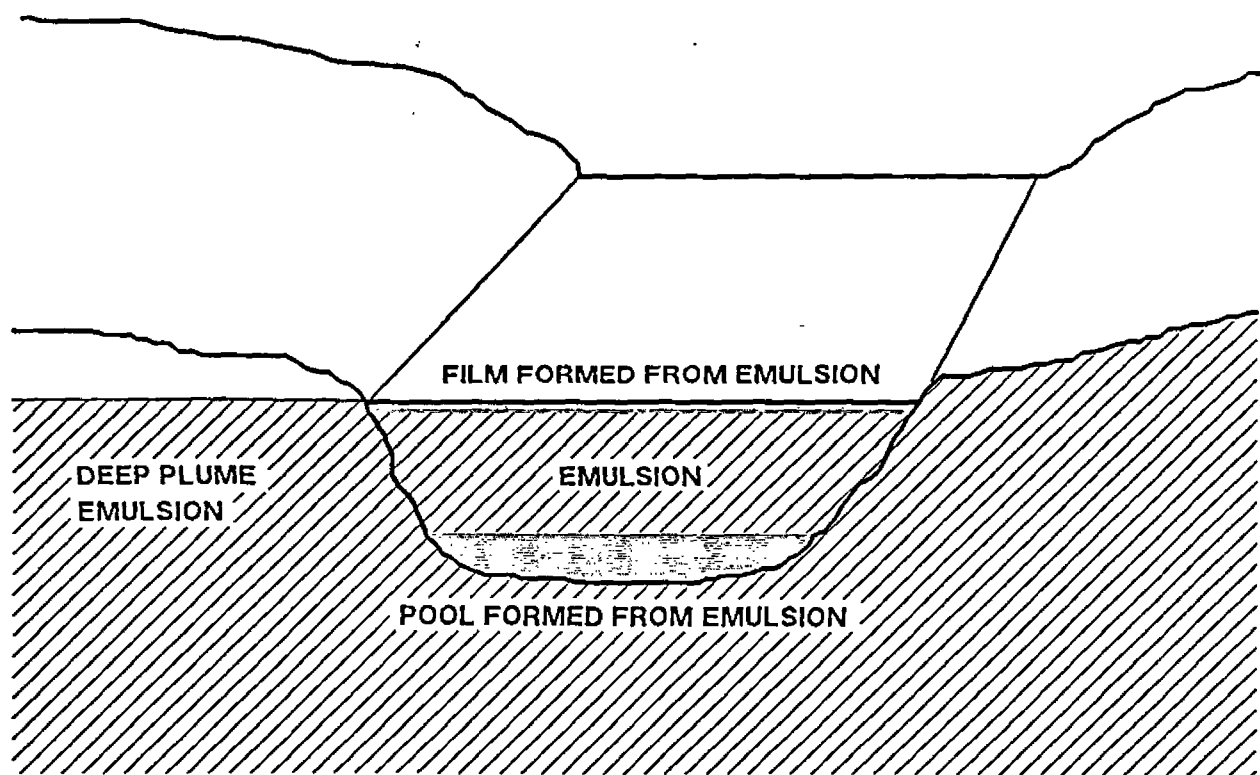


Figure 7. Deep Plume Emulsion Intercepted by a Stream that Does Not Fully Penetrate the Surficial Aquifer

DEEP PLUME :  
POSITIVELY BUOYANT CASE

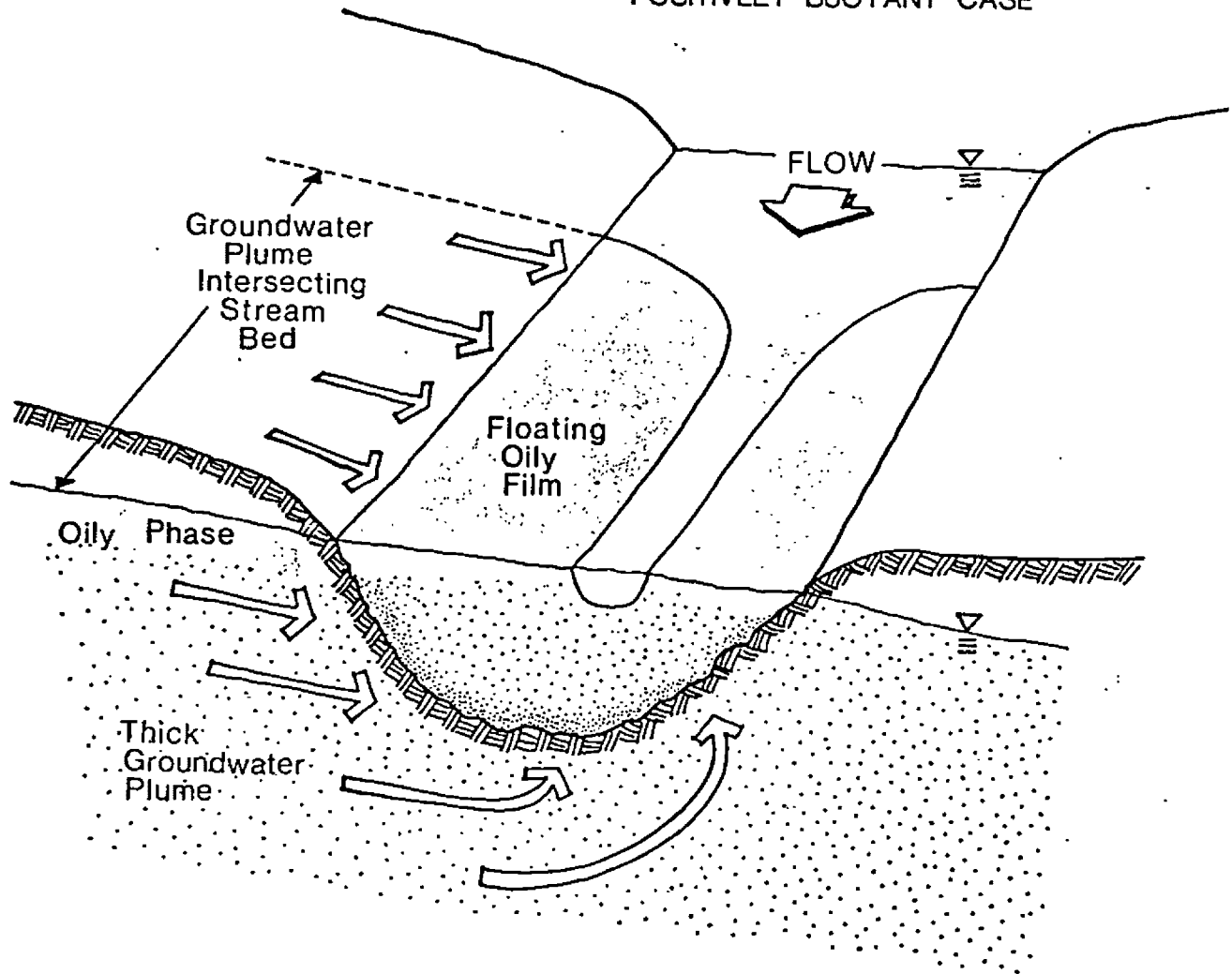


FIGURE 8. Thick Groundwater Plume not Fully Intercepted by a Stream that only Partially Penetrates the Surficial Aquifer

droplets, emulsions, and a dissolved component. We do this so that this effort will mesh with other work that the Office of Solid Waste is doing on the attenuation of oily materials in the groundwater pathway. Specifically, the Office of Solid Waste is currently designing a compatible analysis procedure to simulate the groundwater transport of oily waste leachate. Eventually, we anticipate that the allied effort will be able to simulate the amount of the leachate that is intercepted by streams. We also expect that the groundwater modeling will be designed to predict how much of the intercepted plume is partitioned between the non-aqueous liquid phase, partially dispersed droplets, emulsion, and dissolved components. We also anticipate that the allied project will quantify any attenuation of the leachate caused by volatilization and biodegradation if these prove to be important.

#### Screening Level Model

The initial screening model will ignore the processes that tend to attenuate or dissipate the waste until a need to consider these effects is demonstrated. As a result, the initial screening level model will be conservative in most cases. There may be a few cases where, the analysis may not be fully conservative because of a lack of full knowledge about geomorphology and ecology of streams and the fate of oily wastes in streams.

Ideally, a screening level model should also always conservatively predict effects as shown in Figure 9. In Figure 9, we illustrate the relationship between an environmentally conservative screening model and perfect knowledge of the system under investigation. Unfortunately, we do not know where the line



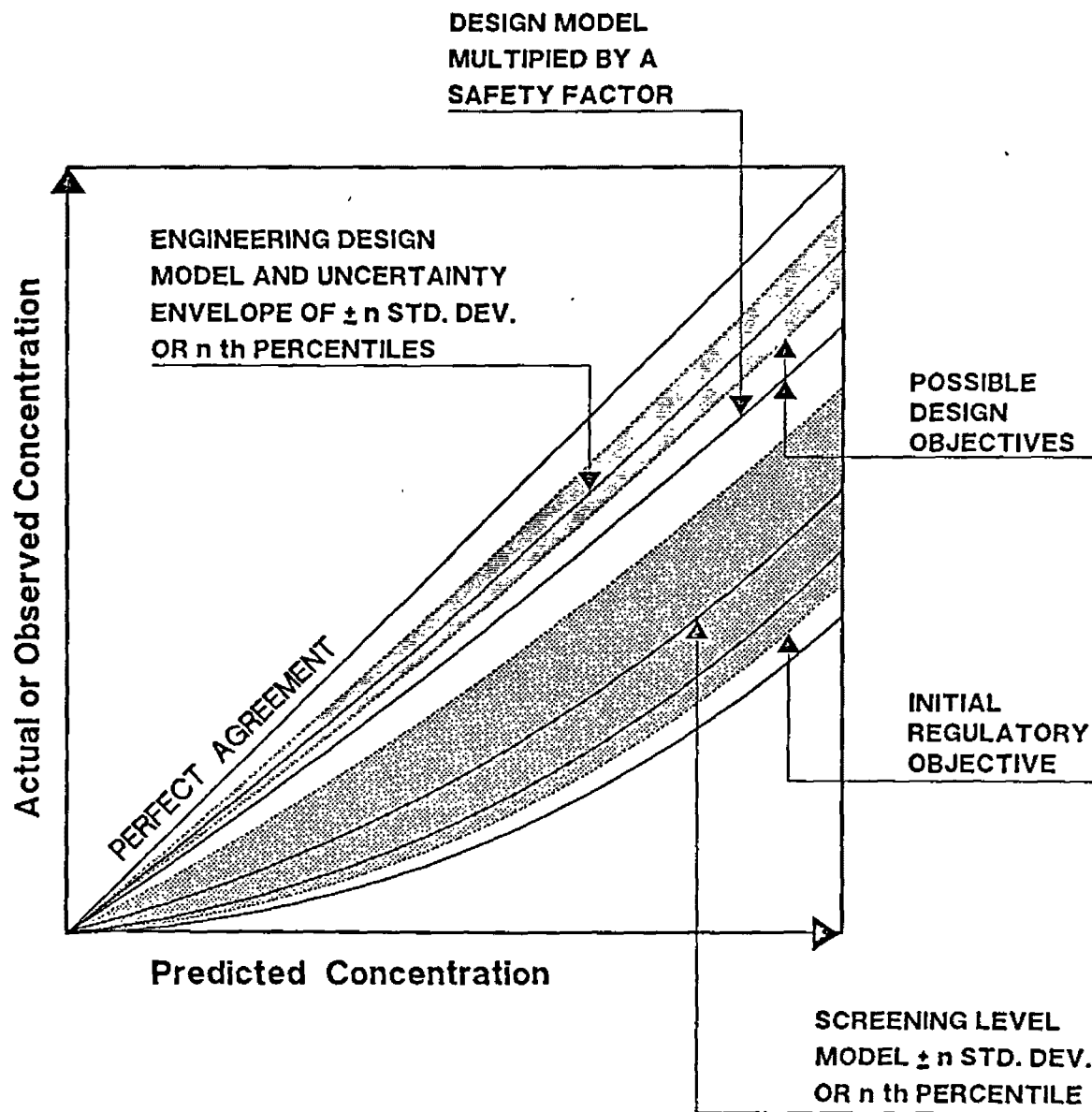


FIGURE 9. Ideal Relationship Between Screening and Design Models

of perfect agreement lies unless we are able to precisely measure impacts. Under practical conditions, we can not be absolutely sure that the screening level model is, in fact, conservative for all conditions. We can usually be reasonably sure that the model is conservative over a limited range of conditions where we have collected validation measurements, however.

Figure 9 also illustrates the relationship one would expect between screening models and precise design models. Ideally, we would hope that design models are only slightly conservative and that the discrepancies between the line of perfect agreement and the predictive ability of the design model are small. In practice, however, design models may be slightly nonconservative or, at the very least, the uncertainty envelope about the predictive curve of the design model (defined by  $\pm n$  times the standard deviation, or  $\pm$  the  $n^{\text{th}}$  percentile) may be nonconservative. Traditionally, the possibility of non-conservative design is taken into account by strictly limiting the conditions over which the method is applied and by multiplying results by a conservative safety factor (see Figure 9). Safety factors of 2 or 2.5 are typically used for bridge and building design. Factors as high as an order of magnitude may be used when the risks are perceived to be high and the predictive method is based on limited knowledge.

Better risk management is possible if the uncertainty is quantified using the standard deviation or similar statistic. In this case, we will use a Monte Carlo analysis to quantify uncertainty and use a designated percentile to provide a quantifiable margin of safety for the analysis. Figure 9 contrasts the approach of using a traditional safety factor versus a margin of safety based on the uncertainty of the design method. The percentile chosen as the

margin of safety will be designated by the regulatory decision makers as part of the risk management process.

The  $n^{\text{th}}$  percentile may or may not be less conservative than a traditional safety factor. However, the  $n^{\text{th}}$  percentile can be quantified whereas the traditional safety factor does not seem readily applicable to risk analysis because of its empirical and subjective nature. In either case, information about the response of the ecological system under study must be collected to determine the appropriate factors. Traditional engineering approaches have relied on an accumulation of observational evidence. Current risk assessment procedures are based upon these same observational data but provides a more rational organization of the information available. This approach helps to determine if the observations available are adequate to validate the designated margin of safety and to provide more precise extrapolation.

The use of a margin of safety for a screening level analysis when a conservative approach is used is necessary when the effect of assumptions are not known to be fully conservative. Initially, there will be only very limited data (if any is available) to validate the conservative nature of the screening model. As a result, we propose to develop a conservative screening model with a margin of safety based on the  $n^{\text{th}}$  percentile (as shown in Figure 9) as the initial objective to support the this regulatory process.

Such a screening model will allow us to conservatively determine when the disposal of oily wastes will not present an environmental problem. The screening analysis will not allow us to definitively determine if a problem

will occur but it will tell us when refinement of the modeling approach is necessary. In refining the model, we expect the curve representing the screening model in Figure 9 to migrate towards the position of the design model and we would expect that generally the uncertainty envelop would shrink. If necessary, the final model would be an engineering design model for the evaluation of waivers (if permissible under present or future regulations).

Incremental improvement of the screening model should be focussed on limited ranges of known applicability or in the vicinity of criteria as shown in Figure 10. This is consistent with limited validation over the range of expected stream conditions and for the potential range of properties of oily wastes that can be generated.

We presently conceive of the initial model as a screening tool because our introductory investigation indicates that only a simple, conservative model is achievable in the initial phases of this work. One preliminary assessment of the nature of the model to be proposed indicates that we may underpredict the amounts of oily materials reaching streams by an order of magnitude (Danny Reible, written communication, 1988 - see Appendix I). If this is true, we expect to develop the necessary modeling refinements in increments until we have developed an adequately incorporated the important processes.

To design an environmentally conservative approach, we have focussed on critical exposure zones in streams and the important pathways between the sources of interest and these zones (see Figure 11). This involves consideration of the following potential effects of oily wastes in streams:

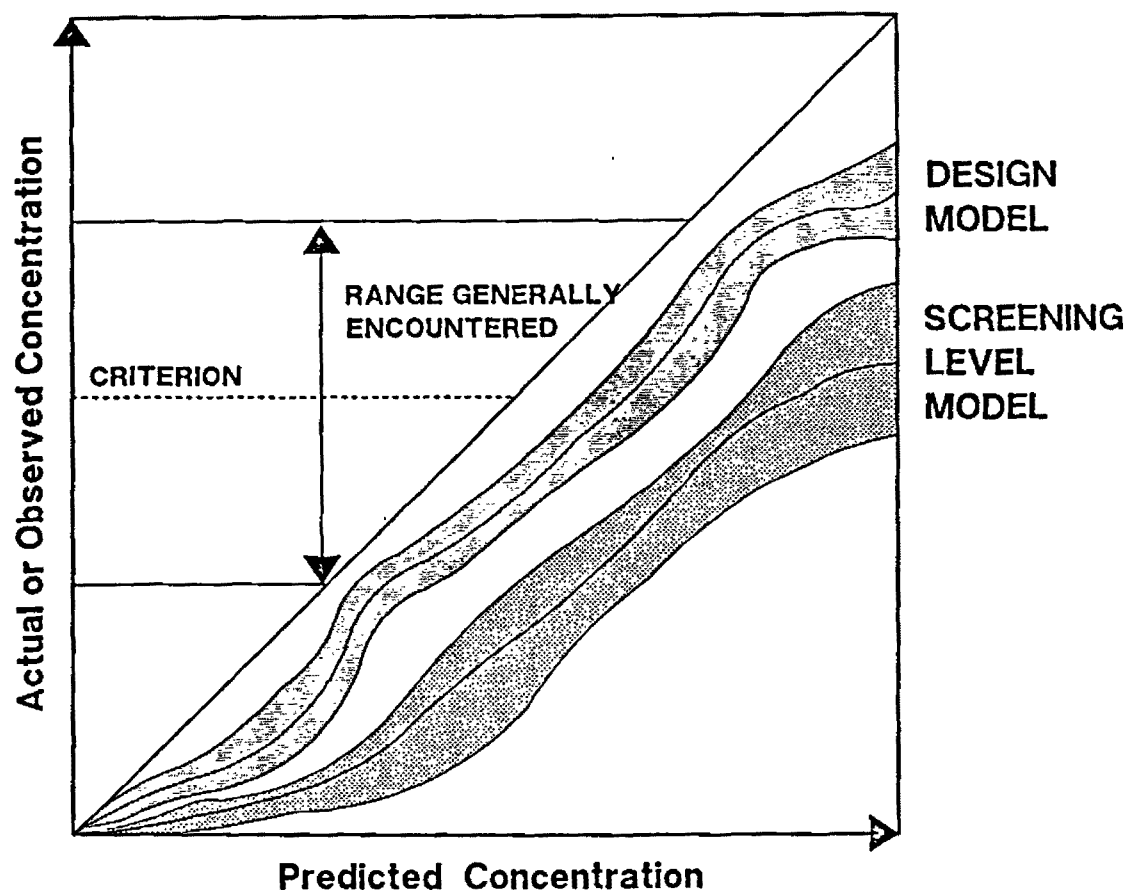


FIGURE 10. Goals for Incremental Improvement of the Screening Model Over the Range Generally Encountered or in the Vicinity of Criteria

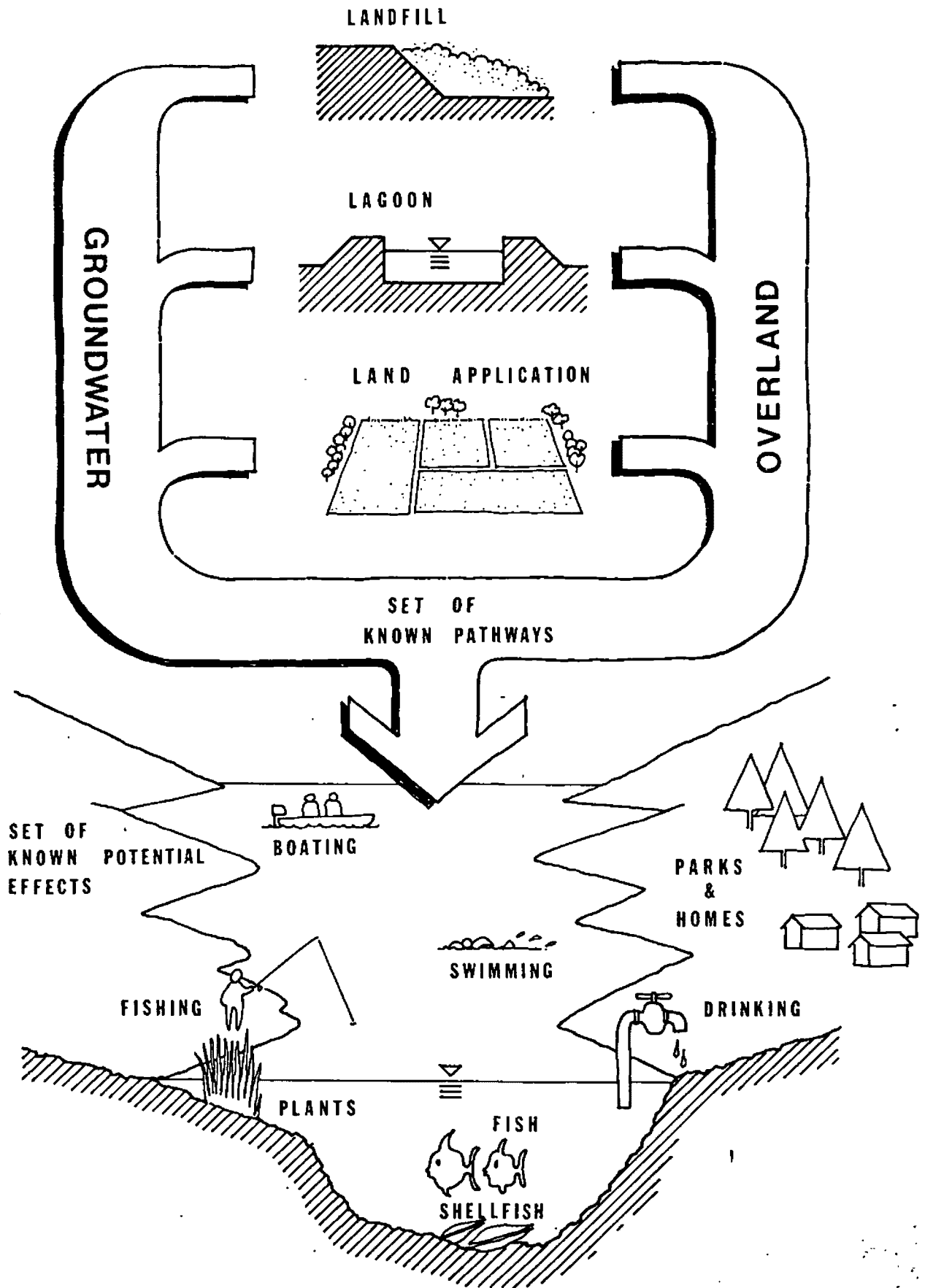


FIGURE 11. The Set of Known Pathways and Potential Effects of Oil Wastes in Strea

- 1) Toxicity to fish and shell fish,
- 2) Taste and odor of the water,
- 3) Tainting of fish flesh,
- 4) Toxicity to plants, and
- 5) Aesthetic impairment.

To be sure we have considered the important processes and pathways, we will briefly review our current understanding in this report. We expect that an expanded review in the future should compile a full understanding of the processes to determine when and if additional model development will be necessary.

To select the appropriate endpoints, we will list the important effects and classify these in a manner that will simplify the development of a screening, exposure model. We will use the current criteria reviewed in the next section and other information to determine endpoints that are easily modeled and useful in dose-response relationships.

#### CRITERIA GOVERNING OILY WASTES

The analysis of oily wastes is hampered to some extent by a lack of numerical criteria governing acceptable levels of oily materials in the aquatic environment. The most recent criteria (U.S. EPA, 1987, see Appendix II) is based on a narrative statement for protection of water supplies and aquatic life. In addition, the latest criteria also recommends that one percent of the lowest continuous flow 96-hour  $LC_{50}$  (lethal concentration for 50 percent of

the test organisms) for important freshwater and marine species be used as protection against harm to aquatic wildlife. It is recommended in the criteria document that any test species demonstrably high susceptibility to oils and petrochemicals.

In part, precisely defined numerical criteria are not available because of the diverse nature of oily wastes. The oil and grease in oily wastes are not definitive chemical classes but are diverse materials that do not readily mix with water. Thousands of organic compounds with very different physical, chemical, and toxicological properties are lumped into this category. The compounds may be volatile or not volatile, soluble or insoluble, and persistent or easily degraded (U.S. EPA 1987).

If there were precise criteria for oily wastes, then this work to develop regulatory procedures and standards might be unnecessary. As it is, the current criteria are not sufficient, as we will indicate in the following review. As a result, we will need to refine the interpretation of existing criteria and develop new exposure endpoints.

McKee and Wolf (1963) seem to be the first to extensively compile water quality criteria. They reviewed the effects of animal and vegetable oils as well as petroleum-based oils. The Federal Water Pollution Control Administration (FWPCA 1968) later provide refined narrative criteria. The 1972 Water Quality Criteria (EPA 1973) offered further refinements and the Quality Criteria for Water 1976 (EPA 1976) seem to offer an even more practical approach. The Quality Criteria for Water 1986 (1987) does not seem to offer



any significant advance over the 1976 criteria for oil and grease. A review of the criteria indicates that little interpretive work has occurred since the early 1970s. In part, this may be one reason why a significant amount of work is needed to develop regulatory methods.

#### Drinking Water Criteria

The FWPCA (1968, p. 25) recommends the avoidance of oil and grease in water supplies because of the occurrence of scum lines, taste, and odor. To achieve these conditions, the FWPCA (1968, p. 6) recommends that discharges be free of oily substances that:

1. Settle to form objectionable deposits,
2. Float to form oil films and scum, and
3. Produce objectionable color, odor and taste.

The more recent criteria (EPA 1987) modifies the recommendation to indicate that drinking water supplies should be "virtually free" of oil and grease.

The 1968 drinking water criteria seem to be overly strict in that a ban on oily waste disposal upstream of locations where drinking water supplies are withdrawn is implied. Given the widespread use of surface waters for drinking in the United States, the strict application of these criteria indicates a potential ban on oily waste disposal over large areas of the country. Such a wide-scale ban is presumed to occur if one traces the stream water at a potential water withdrawal point upstream to all points in the basin and assumes that there is some potential for any amount of oily contaminant to flow through the basin. As an extreme example, if one assumes (as some experiments

indicate - see McKee and Wolf 1963) that oily wastes are not fully degraded in streams and rivers, the strict interpretation of the drinking water criteria for the withdrawal at New Orleans would seem to preclude disposal of oily wastes in almost all of the Mississippi River Basin.

The more recent refinements of the criteria (EPA 1976, 1987) which indicate that water supplies should be "virtually free" of oily material, especially those that cause foul tastes and odors, seem to offer the latitude to determine threshold concentrations that are to be avoided. Therefore, we intend to investigate what guidance is available (McKee and Wolf 1963, EPA 1973) on threshold concentrations causing oily taste and odor and determine whether the available data are sufficient to support the adoption of a single criterion for all oily wastes. Otherwise criteria for broad classes of oily wastes will be investigated. To be most successful, we project that a chemical-by-chemical determination of taste and odor thresholds should be avoided if at all possible.

According to the 1968 criteria, waters also should be free of oils to avoid scum lines in water treatment plants. McKee and Wolf (1963) reviewed other operational difficulties in water treatment plants that indicated the need to have water supplies free of oil and grease. Unfortunately, there seems to be little work defining what amounts of oil cause scum and other operational difficulties. As a result, we will rely on the Monte Carlo analysis to provide some margin of safety in this area where our knowledge is limited.

## Discharge Criteria

Criteria (FWPCA 1968) governing point source discharges of oil and grease are somewhat more specific but are also subjective narrative descriptions that must be quantified if reasonable regulatory procedures are to be proposed. In general, objectionable deposits, odors, tastes and colors have not been defined by numerical criteria. However, such a definition seems possible for at least most of the narrative objectives. In a few cases, it is anticipated that some new guidance will need to be developed in later stages of this study. Initially, we find that "objectionable deposits" are difficult to quantify. Odors, tastes and colors should be reasonably quantifiable.

More recent criteria do not specifically refer to point sources. The 1976 and 1986 criteria do indicate, however, that surface waters shall be virtually free from floating oils. This is much better adapted to the design of analysis procedures if we assume that "virtually free" implies that limited amounts of oily wastes are permissible as long as the film is not visible, does not kill or impair the growth of aquatic life, and does not contribute any other effect.

The 1968 criteria that discharges be free of oily materials if oil films will be formed also has the practical effect of banning disposal of lighter-than-water oily wastes. By definition, immiscible wastes with a density less than water will form a film on the surface. The only condition that may not lead to the formation of a film involves conversion of the oily phase to an emulsion in the groundwater. Otherwise, a film should be expected whenever the leachate plume reaches the stream. Therefore, this criterion seems overly restrictive in light of current practice. As a result, it is proposed to

investigate specific criteria for protection of aesthetic qualities and wildlife and to regulate the wastes on the basis that streams will be virtually free of films if the film is not visible, does not contribute to taste and odors, and does not present a hazard to wildlife.

In considering the restrictive nature of the 1968 discharge criteria, it should be noted that the migration of oily wastes from landfills, lagoons and fields result in nonpoint sources of pollution. This distinction should make no difference, however, because the more recent criteria seem to refer to receiving water quality without regard to the nature of the source.

#### Protection of Wildlife

For the protection of wildlife in streams, the FWPCA criteria (1968, p. 34) recommend that oils and petrochemicals not be added to receiving waters in quantities that cause:

1. A visible color film on the surface,
2. An oily odor to the water,
3. An oily or noxious taste to edible fish and invertebrates,
4. Coating of banks and bottoms of the stream,
5. Tainting of the benthic biota, and
6. Toxicity.

In addition, all of the criteria documents give specific examples of concentrations of oily materials that cause acute and chronic toxicity. The most recent documents (EPA 1976, 1986) organize the state of our knowledge up

until about 1973 into criteria for the effects of classes of oily materials on sensitive or indicator species. The 1986 criteria also establish that the appropriate level of protection is that concentrations should not exceed one percent of the median lethal concentrations ( $LC_{50}$ ) for sensitive freshwater and marine indicator species. The recommendation that the appropriate criteria to avoid chronic toxicity is one percent of the  $LC_{50}$  may also be an additional safety factor to consider.

Tables 6 and 7 in Appendix II compile the most recent readily available information on  $LC_{50}$  values for sensitive species exposed to classes of oily materials. There is a need to review these classes of oily materials to determine if these adequately cover the oily wastes that are currently of interest to the Office of Solid Waste. In addition, there is a need to re-examine what are important freshwater indicator species of fish. In this regard, we anticipate that the Office of Solid Waste will take a lead role in indicating what important species should be included. In any event, we will examine the present guidance and make recommendations as needed. If important classes of oily wastes and indicator species are neglected in the current criteria document, we will also be prepared to indicate to our colleagues at the Environmental Research Laboratory at Duluth what bioassays are needed to support this work.

The exposure criteria given in Appendix II, Tables 6 and 7, represent an excellent basis for this analysis. However, the data in these tables do not extend past 1974. Therefore, we will list other studies uncovered in our review that can be used to update Tables 6 and 7.

It should also be noted that Tables 6 and 7 do not distinguish between the effects of exposure to specific oily waste components such as films or emulsions. Therefore, additional review of past dose-response studies to distinguish between the effects of films, droplets, emulsions, and dissolved components as well as indirect effects such as deoxygenation is indicated.

The Office of Solid Waste has not been able to find criteria protecting fish and wildlife from the U.S. Fish and Wildlife Service.

#### EFFECTS OF OILY WASTES IN STREAMS

There are at least six effects of oily wastes in streams. First, aesthetics are impaired by visible films on the water surface, pools of heavy oily wastes, and coatings of oily wastes on the surfaces of stones and vegetative debris in streams. Second, oily materials, especially petroleum products, cause edible fish and invertebrates (such as clams) to taste bad. Third, oily materials cause foul tastes and odors in drinking water. Fourth, and perhaps most serious, pools, contaminated sediments, films, emulsions, and the dissolved component of oily wastes are toxic to wildlife and biota. Fifth, oily waste may serve as a solvent that mobilizes or concentrates materials that are more toxic than oily waste components. Finally, oily wastes may have an indirect effect on water quality due to influence on photosynthesis, reaeration and other components of the dissolved oxygen balance.

These effects fall into at least three general categories. Aesthetic impairment, foul tastes and odor, and tainting of fish flesh are human effects.

Toxic effects on wildlife represent a second category. Indirect effects represent a useful third category.

#### Human Effects

Past investigations (McKee and Wolf 1963, EPA 1987, also see John Hopkins University 1956 in the Selected Bibliography originally cited in EPA 1987) indicate human toxicity only occurs at concentrations much higher than the criteria for taste and odor. Apparently the same is true for other effects of oily materials. Odor detection thresholds seem to be lower than levels at which oily coatings become detectable to swimmers.

#### Aesthetics

Very minute quantities of an oily phase are visibly detectable on the water surface because of the change in surface tension. The effect of a film on the order of one to ten molecules in depth covering part of the surface can be observed despite the fact that the oil is not visible. Very thin films that partially cover the surface are detectable because of the suppression of capillary waves. Capillary waves are very small irregularities visible on an agitated water surface. The contrast between slick patches of oil and the remaining agitated surface is one manifestation of oily wastes that may present at least a minor concern. In the event that the surface is completely covered with an oily film too thin to be visible and the flow is very quiescent, it may

not be possible to visibly detect the affect of the oily film. It seems rare, however, that stream flows will not be sufficiently turbulent to break up the very thin films or patches that are not visible. As a result, it seems reasonable to conclude that oily wastes cause an aesthetic problem only when the wastes are present in great enough quantities to cause a visible film on the surface. However, this may be one important distinction for oily wastes entering a quiescent lake that should be taken into account in extending these methods to analyze other water bodies.

Visible detection of an oil film remains a subjective exercise. However, the American Petroleum Institute (API) has long-standing criteria regarding what thickness of an oily film is visible on a water surface (Nelson-Smith 1972, API 1963). Evidently, these criteria are traceable to a 1930 report to the U.S. Congress by Stroop (see Selected Bibliography). Therefore, these criteria should be unbiased and useful.

Table 1 is a listing of the thickness of an oily film having different visible characteristics. The thickness of a barely visible film (0.038 microns) would seem to be the most appropriate criterion for this analysis. Depending on the regulatory objective, however, some of the other criteria may be useful under different circumstances. For example, in secluded areas where it may be rare that anyone visits the stream, a less restrictive criterion such as avoidance of a silver sheen (thickness of 0.076 microns) may be useful. If this analysis is later extended to include site-specific analyses of larger streams where navigational uses and industrial development exclude recreational activity, then less severe standards may be appropriate. Multiple film thickness criteria can be incorporated into the Monte Carlo analysis but this



involves a much more extensive mapping of stream reaches and the appropriate reach criteria for film thickness.

Table 1.

Criteria governing the visible detection of oil films on water surfaces.

[source Nelson-Smith 1972, and American Petroleum Institute, 1963, originally adopted from Stroop, 1930].

	<u>Thickness</u>		<u>Quantity of oil</u>	
	inches	microns	gal/mile <sup>2</sup>	liter/km <sup>2</sup>
Barely visible	0.0000015	0.038	25	44
Silvery sheen	0.0000030	0.076	50	88
Trace of color	0.0000060	0.152	100	176
Bright bands of color	0.0000120	0.305	200	352
Colors dull	0.0000400	1.016	666	1170
Colors dark	0.0000800	2.032	1332	2340

We intend to determine if criteria governing visibility of oil under ice exists in the literature. However, it is anticipated that criteria related to oil films under ice would be less restrictive than criteria governing the visibility of films on open waters.

Oily material deposited on the bottom by either coagulation of light oils with suspended sediments or the sinking of heavy oils, may be a less detectable aesthetic problem. At this time, it is not clear how well this potential aesthetic problem can be explored without reliance on fully subjective criteria

(that will be difficult to defend from a technical viewpoint). However, the difficulty in defining criteria to govern the regulation of oily coatings and sinking oily waste may not be critical to the overall analysis procedure because other criteria related to acute and chronic toxicity may be more restrictive. At this time a more restrictive criteria based on benthic toxicity is expected because of the intimate influence of the benthic interface on food chains in streams. There are many rooted and attached plants subject to harm. Many aquatic animal species either begin or spend a significant portion of their life cycle on the stream bed. Nevertheless, coatings on rocks, winter ice, plants, and debris at the edge of a stream may represent a significant and critical aesthetic problem that must be considered in the analysis until additional study indicates otherwise. In addition, toxicity criteria for benthic exposure is expected to also be difficult to define. Therefore, aesthetic concerns can not be completely deferred until criteria based on toxicity are derived.

In this regard, we will investigate any criteria related to the amount of oil coatings that are visible. We will look for studies that quantify how thick oil coatings must be to be visible or what quantity of oil in streams leaves detectable coating on rocks, debris and vegetation and scum lines in water treatment plants.

To better define the aesthetics of oil on stream bottoms, we will consider what recreational and commercial activities may be impacted. The preliminary review (see Appendix I) has provided some suggestions in this matter that should be investigated.

## Tainting of Fish Flesh

Ingested oily wastes may not only affect the growth of fish but may also impair the taste of sport fish (i.e. bass) and other edible fish. In addition, oily wastes may impart oily and noxious tastes to edible invertebrates (i.e. shellfish). Given the arbitrary and subjective nature of how humans distinguish tastes and given the fact that various types of edible fish and invertebrates may either enhance or mask objectionable tastes, it is expected to be difficult to define precise, general criteria for the purpose of avoiding taste problems. At this time it seems that it may be necessary to accept whatever guidance is presently available and to determine if more work in this regard is necessary. McKee and Wolf (1963), FWPCA (1968) and EPA (1973) provide the best guidance of which we are aware.

Table 2 summarizes the readily available information on amounts of oily substances that taint edible fish and invertebrates. We expect to use these data and other data being compiled from EPA (1973) and McKee and Wolf (1963) to determine what guidance may be formulated to develop concentration criteria for all oily wastes or classes of oily wastes. For example, we anticipate that the most useful criteria will be those for wood preserving wastes (because of the phenolic compounds expected in the waste) and the five categories of refining wastes (K48 through k52).

Table 2.  
Concentrations of oily materials or components of oily wastes that  
taint edible fish and invertebrates.

Oily Material	Species	Concentrations or Amount	Reference	Comment
kerosene or diesel	bass and bluegill	20 gal./acre	FWPCA (1968)	persists for 4 to 6 weeks
chlorophenol	fish	0.0001 mg/L	Boetius (1954)	
PURE COMPOUNDS from FWPCA (1968)				
Phenol	Trout, carp, eel, minnow, blue gill, pike	15 to 25 mg/L	FWPCA (1968)	
Cresols	Trench, carp, eel, trout	10.0 mg/L		
Xylenols	Roach, perch, carp	1 to 5 mg/L		
Pyrocatechol [C <sub>6</sub> H <sub>4</sub> (OH) <sub>2</sub> ]	Perch, carp, roach	2 to 5 mg/L		
Pyrogallol [C <sub>6</sub> H <sub>3</sub> (OH) <sub>3</sub> ]	Roach, carp	20 to 30 mg/L		
P-Quinone (C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> )	Carp, trench, roach	0.05 mg/L		
Pyridine	Roach, carp	5.0 mg/L		
Naphthalene	Roach	1.0 mg/L		
Alpha Naphthol	Roach, carp	0.5 mg/L		
Quinoline (C <sub>9</sub> H <sub>7</sub> N)	Roach, carp	0.5 to 1.0 mg/L		
Chlorophenol	Roach, carp	0.01 mg/L		
MIXED PHENOLIC WASTES from FWPCA (1968)				
Coal cooking waste	Freshwater fish	0.02 to 0.1 mg/L		
Coal tar waste	Freshwater fish	0.1 mg/L		
Phenols in polluted river	Minnows	0.02 to 0.15 mg/L		
Sewage contain- ing phenols	Freshwater fish	0.1 mg/L		

We expect that definition of sensitive or indicator species will be necessary. In this case, appropriate indicator species may be game fish or commercially important species. Alternatively, it may be necessary to define classes of organisms for which criteria can be defined using existing bioassays. We will determine if additional bioassay and bioconcentration work would be useful.

#### Taste and Odor

Oily wastes may cause odor when introduced into a stream and, if in the course of swimming, water is consumed, a bad taste may be detected. Similarly and perhaps more importantly, the taste and odor of drinking water may be impaired by excessive oily wastes in stream waters. Because taste and odor are subjective responses, differing from one person to another, criteria useful for avoiding taste and odor problems also will be subjective. Nevertheless, McKee and Wolf (1963) seem to provide enough useful information to derive initial guidance.

The associate author (Vocke) also investigated drinking water standards and determined that there are none available. A health advisory on gasoline in water is expected by the summer of 1988. Upon reflection, the absence of drinking water standards is not unexpected since taste and odor thresholds seem to be lower than concentration that cause human toxicity (EPA 1987, McKee and Wolf 1963).

## Toxicity to Plants and Animals

In this investigation, we are primarily interested in the physical mechanisms that cause death and impair growth. These include coating of gills and sensitive surfaces (i.e. feathers), ingestion (recognizing the overlap with chemical toxicological mechanisms), and prevention of surface breathing. There are a number of documented chemical toxicological effects as well that we will not emphasize here. Chemical mechanisms causing toxicity can be chiefly related to dissolved components. But since the dissolved components of oily wastes must derive from the non-aqueous liquid phase in the form of films, pools, globs, droplets, or emulsions, we can not completely defer the consideration of these effects to the allied investigations such as those underway at the Duluth Environmental Research Laboratory. Studies that concentrate on the effects of dissolved components are not complete without consideration of the transport mechanisms being incorporated in this analysis. If more elaborate models are needed, we expect them to be based on mass balances of the separate components of oily materials. The dissolution of oil will be a critically important process to be included in these mass balance simulations for streams. Furthermore, we can easily include the effects of critical dissolved concentrations in the proposed analysis procedure.

In regard to the previous discussion, we will catalog the readily available information on chemical toxicity, but will not adopt a chemical-specific approach in this analysis. The U.S. EPA has extensive listings of specific chemicals and limitations on their concentrations that should adequately cover the toxicity of most, if not all, of the highly toxic components of oily wastes when those components are present in extraordinary

quantities. Instead, we are interested in the composite effects of mixtures of thousands of organic chemicals present in widely varying percentages, most of which are below the regulatory thresholds for specific chemicals. We are particularly interested in the effects of larger amounts of oily materials that overwhelm physical mechanisms of plants and animals contrasted with trace quantities that usually disable chemical mechanisms.

We propose to investigate toxicity to dissolved components at the same time that we review the information in Tables 6 and 7 (Appendix II) and elsewhere to determine the separate effects of oily films, pools, globs, and emulsions. In this regard, consideration of the dissolved component merely completes the full picture on the effect of oily waste.

In the long term, it will be necessary to fully understand partitioning of chemicals between oily materials, solids and the water to explore suspicions that oily materials may serve as physical concentrators of trace toxicants in the stream or carry otherwise immobile toxicants from the source (i.e. landfills).

It is also important for consistency with proposed work at the Duluth Laboratory to consider all mechanisms of toxicity and the critical transport mechanisms. We expect that the Laboratory at Duluth will conduct much needed bioassays of oily materials and we hope to be able to suggest which waste classifications are the most important to focus upon. We suspect that new bioassay work may be important because the current criteria, as summarized in Tables 6 and 7, have not been updated in 15 years.

## Toxicity of the Oily Phase

Coating of the gills by oily materials is one known mechanism that kills fish (FWPCA 1968, p. 45) and presumably the coating of other sensitive surfaces can kill fish and other invertebrates. FWPCA (1968, p. 45, McKee and Wolf 1963) notes that oily coatings kill plankton. Partial coatings of gills impair respiration and thus contribute to indirect and chronic toxicity. Ingestion of the oily phase is also toxic in a number of cases, especially for refinery wastes. The oil may be directly ingested or oily coatings on food may be ingested. Coatings on food may occur when the food particles fall through a surface film or intersect oily patches on the bottom. As a result, oily films on the surface can take on some added importance. Oily wastes can, in addition, threaten water fowl by destroying the natural buoyancy and insulation of feathers. Invertebrates, especially those in a larvae stage, may be killed when a surface film prevents breathing. This mechanism has long been used to control mosquitoes, but surface films can affect more desirable species of invertebrates such as water boatmen, back swimmers, adult and larvae aquatic beetles, and Diptera (flies) (FWPCA 1968). We expect to investigate the film thickness required to kill and otherwise affect mosquitoes and other invertebrates.

Table 3 summarizes our limited compilation of studies from FWPCA (1968) that document the effects of the oily phase on aquatic wildlife. If time permits, we will review other work on toxicity to fish (p. 72-72 FWPCA 1968, also see Cairns 1957, Academy of Natural Science 1960, Galtsoff 1936, Chipman and Galtsoff 1949, Gutsell 1921, Cairns and Scheier 1958). We also hope to include studies by Hartung (p. 96 FWPCA 1968) concerning egg laying inhibition



in ducks and other effects on waterfowl and terrestrial animals that use streams.

Table 3.  
Concentrations of the oily phase that are toxic to aquatic wildlife.

Oily Material	Species	Concentrations or Amount	Reference	Comment
Crude oil	bass and bream	—	Wiebe (1935) cited in FWPCA (1968)	Found mortality caused by coating gills and soluble fraction also very toxic. Chronic toxicity caused by lower concentrations partially coating the gills.
Crude oil	oysters	—	Galtsoff et al (1935) cited by FWPCA (1968)	anesthetic effect from the soluble fraction.
Crude oil	algae and plankton		FWPCA (1968)	Coats and destroys
Settleable oily substances	benthic organisms, spawning organisms		FWPCA (1968)	Coats and destroys.
Oil film	aquatic insects: water boatmen, back swimmers, aquatic beetles, and aquatic flies.		FWPCA (1968)	Film prevents respiration.
Oil	Waterfowl		FWPCA (1968)	Destroy natural buoyancy and insulation.

Table 3.  
Concentrations of the oily phase that are toxic to aquatic wildlife - Continued

Oily Material	Species	Concentrations or Amount	Reference	Comment
Motor oil	crayfish	5 to 50 mg/L	Seydell (1913) cited in FWPCA (1968)	30 to 35 g organisms died within 18 to 60 hours.
	European small perch and white fish (fam. Corregonida)	4 to 16 mg/L		Lethal within 18 to 60 hours.
Russia crude oils: methano-aromatic type high in asphalt, tar compounds, sulfur, and benzene-ligroin but low in paraffin.	crucian carp (Carassius carassius) 7 to 9 cm in length	0.4 mL/L ((340 mg/L) (average survival: 17 days)  4 mL/L ((3400 mg/L) (average survival: 3 days)	Veselov (1948) cited in FWPCA (1968)	Crucian carp considered to be a hardy fish. Soluble oil extracted by shaking 15 mL of oil in 1 L for 15 minutes. Oil film removed by filtration. DO controlled. Involved 154 tests of 242 fish. Seydell (1913) indicated that toxicity is due to naphthenic acids, small quantities of phenol, and volatile acids.
Gasoline	fish and macro-vertebrates: midge-Orthocladius mayflies, stone flies	not known	Bugbee and Walter (1973)	gasoline spill probably ranging from undiluted to highly diluted killed fish and prevented invertebrate recolonization for at least six months.

Table 3.  
Concentrations of the oily phase that are toxic to aquatic wildlife - Concluded

Oily Material	Species	Concentrations or Amount	Reference	Comment
Crude oil	fish	0.3 mg/L	Chipman and Galtsoff (1949) cited in FWPCA (1968)	extremely toxic
Oil refinery effluents	fathead minnows	—	Dorris et al. (1960) cited in FWPCA (1968)	3.1 to 21.5 percent mortality after 48 hours exposure to untreated effluents. Toxicity due to chemical reactivity rather than depleted oxygen.
Oil	marine mollusks (Mya arenaria)	—	Nelson (1925) cited in FWPCA (1968)	Killed on tidal flats.
Diesel oil	sea urchins (Strongylo- centrotus purpuratus)	0.1 percent emulsion	North et al. (1964) cited in FWPCA (1968)	dies in about one hour.

#### Toxicity of Contaminated Sediments

Although the exact mechanisms causing organisms to die are not well understood, contaminated sediments have also been shown to be toxic to fish and other organisms, including organisms not in direct contact with the sediments (McKee and Wolf 1963). Bioassays of four species involving crude oil absorbed by carbonized sand (a product developed during World War II to soak up spills of oil on water) were reported by FWPCA (1968) and are summarized in Table 4.

In addition, a reviewer of this document (Dr. Robert Swank, Athens Environmental Research Laboratory) points out studies by the Environmental Research Laboratories at Corvallis, Duluth, and Naragansett on sediment criteria that may be of interest. This will be followed up as time permits.

Table 4.  
Concentrations or amounts of oily wastes in sediments  
that are toxic to aquatic wildlife.

Oily Material	Species	Concentrations or Amount	Reference	Comment
Crude oil in carbonized sand with no free oil	Toadfish (Opsanus tau)		Chipman	Very hardy marine fish in the yolk sac stage.
	Barnacle (Balanus balanoides)			
	Oyster (Crassostrea virginica)			
	Hydrozoan (Tubularia crocea)			

At this time it is not clear that the exact mechanisms causing toxicity to fish in the water column can be clearly elucidated. Furthermore, the effects on benthic organisms may need to be defined with additional bioassay studies.

## Toxicity of Emulsions

It is not clear in all bioassay studies of the toxicity of oily materials that the effects of emulsions have been clearly identified. It is expected that the important mechanisms will be ingestion and coalescence of emulsions on the gills and skin. The formation of emulsions will also greatly increase surface area of contact between water and oil. Enhanced toxicity of the dissolved phase due to increased dissolution will be an indirect effect of the formation of emulsions. This seems to have been observed in a few studies of the toxicity of emulsions.

In terms of relative impacts, it is expected that emulsions will be less effective than films and heavy pools of oily wastes in causing coatings on gills and outer surfaces. However, emulsions can represent a greater danger to organisms that will not ordinarily be in contact with the surface and bottom. Therefore, it is not clear that it is conservative to assume that criteria for films and pools will be fully adequate to protect wildlife from emulsions. It is anticipated that criteria describing the effect of ingestion is equally applicable to emulsions and separate oil phases.

It is expected that the indirect effect of enhanced dissolution of the oily waste due to the formation of an emulsion will be difficult to quantify. In a pure water-oil system, surface tension will dictate the formation of a uniform size emulsion. Conceptually, it would seem to be a straightforward task to formulate mass transfer descriptions for an emulsion of uniform droplets. However, in natural systems, a variety of unpredictable combinations of natural surfactants will be present. These surfactants are expected to change the

surface tension and thus affect the droplet size. Being unable to readily predict droplet size indicates that mass transfer will be difficult to predict. Therefore, the importance of enhanced dissolution will need to be investigated.

The effect of surfactants on the emulsions is to form micelles. Micelles are, as illustrated in Figure 12, droplets with surfactant molecules forming a layer between the water and oil phases. Given the diverse number of different surfactants in natural waters, and a paucity of knowledge about the interaction of surfactants, it seems unlikely that surface tension effects on droplet size and mass transfer can be readily determined.

As of yet, the effect of emulsions on fisheries has not been fully investigated. The most useful criterion discovered so far is from the work of Grushko (1968) indicating that a limit of 0.05 mg/L for dissolved and emulsified oils may be adequate protection for fisheries. The U.S. Fish and Wildlife Service does not seem to have similar criteria.

The results of further review of the literature (McKee and Wolf 1963) will be reported in Table 5 if time permits.

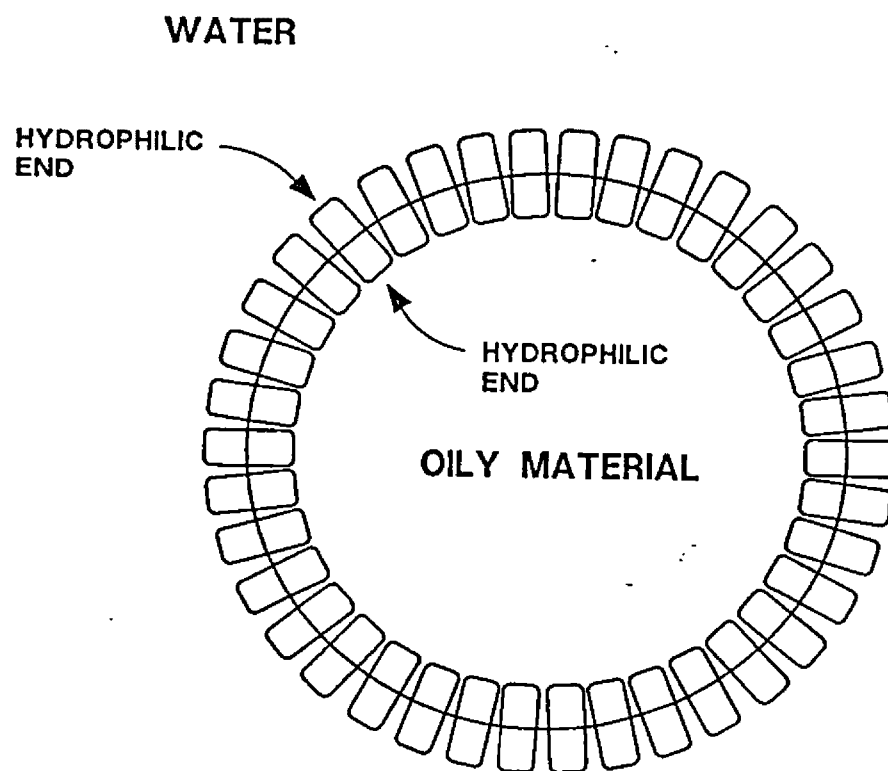


Figure 12, Typical Micelle

Table 5.  
Concentrations of emulsions that are toxic to aquatic wildlife.

Oily Material	Species	Concentrations or Amount	Reference	Comment
Oily wastes	Fish	0.05 mg/L	Grushko (1968)	
Diesel oil	Sea urchins	0.1 %	North et al.	

#### Toxicity of the Dissolved Phase

A significant fraction of oily materials, especially crude oils and their derivatives, dissolve in water. For some oily materials, these fractions may be the most toxic component. Examples of toxic soluble fractions include phenols.

There is some guidance on the weathering of petroleum products that should allow us to compute the dissolution from oil films, pools and emulsions. These methods, however, will be difficult to implement. It will be necessary to investigate mass transfer rates. These rates are governed by the geometry of the nonaqueous phase liquid in the stream. Films, droplets and pools will have different geometries.

It is also recognized that oily wastes act as solvents for other more toxic materials that can be dissolved into the water or remain concentrated in the oily carrier. It is suspected that films, and especially oily wastes pools on stream beds, may concentrate pesticides in streams (FWPCA 1968). These are potential effects that we do not expect to be able to address initially because the need to do so is not presently clear.

Limited data describing the effects of dissolved oily waste components are given in Table 6. We do not intend to imply that a chemical-specific approach will be pursued from this listing of specific components.



Table 6.  
Concentrations of the dissolved components of oily wastes that are toxic.

Component	Species	Concentrations or Amount	Reference	Comment
Petrochemicals:	fathead	12 to 368 mg/L	Pickering	Standard bioassays
benzene,	minnows,	(96-hour $TL_m$ )	and	in hard and soft
chlorobenzene,	bluegills,		Henderson	water. Chemical
0-cresol**,	guppies, and		(1966b)	blended into 500
0-chlorophenol**,	goldfish.		cited in	mL water before
chloropropene,			FWPCA	dilution in test.
cyclohexane			(1968)	Pure oxygen was
( $C_6H_{12}$ ),				
ethyl benzene,				added to keep
isoprene*,				dissolved oxygen
methyl				high.
methacrylate*,				
phenol,				*least toxic
0-phthalic				** most toxic
anhydride,				
styrene,				
toluene,				
vinyl acetate, and				
xylene [ $C_6H_4(CH_3)_2$ ].				

Table 6.  
Concentrations of the dissolved components of  
oily wastes that are toxic - Concluded.

Component	Species	Concentrations or Amount	Reference	Comment
		96-hour $TL_m$ <u>Soft</u> <u>Hard</u> <u>Water</u>		
Naphthenic acid (cyclohexane carbolic acid)	bluegill	5.6 7.1 mg/L	McKee	Petroleum extract used in the manufacture of insecticides, paper and rubber.
	sunfish	(18 to 20 °C)	and	
	(Lepomis macrochirus)	5.6 7.0 mg/L (30°C)	Wolf (1963)	
	pulmonate	6.6- 11.8 mg/L		
	snail	7.5		
	(Physa heterostropha)	(20°C) 18-19 11.7 mg/L (20°C)		
	diatoms	41.8 79.8 mg/L		
	(Navicula seminulum)	(22°C) 41.8 56.0 mg/L (28°C)		
		43.4 28.2 mg/L (30°C)		
	European perch	4 to 16 mg/L		
	Crayfish	5 to 50 mg/L		18 to 60 hours
	minnows	5.0 mg/L		72 hours
	snail and fish	2.0 mg/L (20°C)		when dissolved oxygen is low.

## Other Effects of Oily Wastes

Oil films on the surface may reduce gas transfer and affect photosynthesis. In addition, there has been some suspicion that oily materials add appreciable oxygen demand (McKee and Wolf 1963).

Surface films are expected to have an indirect effect on the dissolved oxygen balance of a stream by reducing reaeration and photosynthesis. We intend, if time permits, to review the work of Tsivoglou and Wallace (1972) and Thibodeaux (1979 also see Reible's comment in Appendix I) to determine if the effect can be readily quantified. However, we expect only a marginal influence at the present time. Nevertheless, we recognize that many disposal areas may be near urban areas where dissolved oxygen levels are chronically depressed.

The effect of reduced sunlight penetration on photosynthesis is a concern that arises from the water quality criteria of 1968 (FWPCA 1968) and McKee and Wolf (1963). We also intend to consider this further when time is available. If we fully investigate the photooxidation of oil at a later stage, it may be appropriate to determine the adsorptive capacity that oil has for sunlight.

Several older studies indicate that oily wastes may also add appreciable oxygen demand (McKee and Wolf 1963). Evidently, there has been some debate over the exact effect of refinery wastes. Some have held that fish kills resulted from lack of oxygen during oil spills rather than from the toxic effect of the dissolved phase. Some discharges seemed to have involved large amounts of oxygen demand as well. Therefore, when we have estimated typical amounts of oily wastes that may be permitted in streams based on other factors, it should be possible to estimate the influence on the oxygen balance as well.

## BEHAVIOR OF OILY WASTES IN STREAMS

The transport of oily wastes in streams is important because of the mechanisms that concentrate waste constituents. Processes that transform wastes may attenuate concentrations of some components, but if wastes are transformed into components that are more toxic, then transformation processes may take on added importance in defining critical processes.

The processes that may affect the weathering of oily wastes are summarized in Figure 13. The most important expected in streams (see Figure 14) are advection, spreading, formation of films and pools, partial dispersion of droplets, emulsification, volatilization, dissolution, photochemical reaction and hydrolysis, biodegradation, sedimentation, and attachment to surfaces (coating, wetting, and sorption). These important processes are shown in Figure 14 and are briefly discussed below.

### Advection and Spreading

The transport of oily wastes is complicated by the tendency to concentrate and move at different velocities than the average stream velocity. The different average velocity of the oil causes spreading not found in other water bodies or dilution by association with larger than expected volumes of stream water.

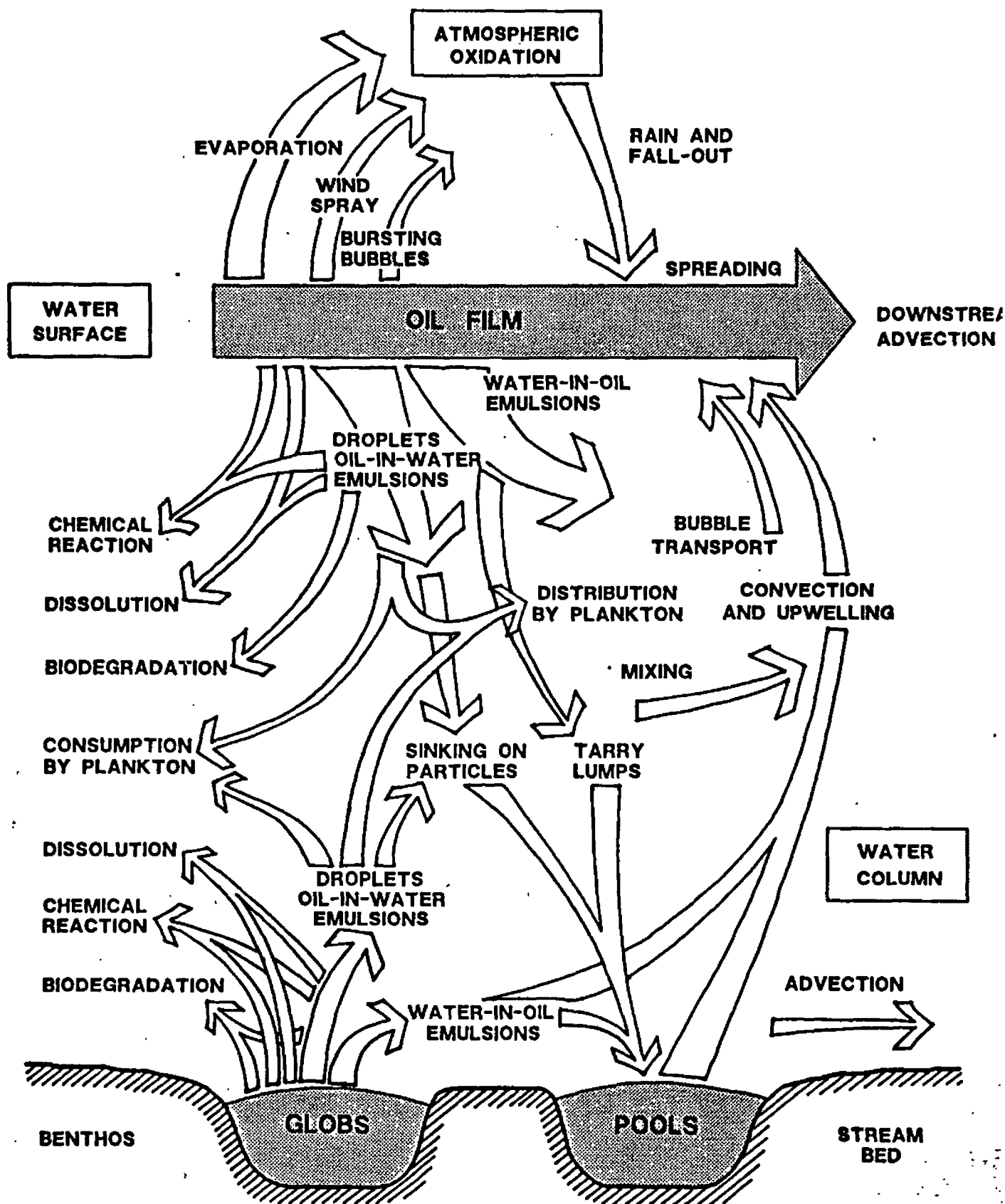


FIGURE 13. Processes Affecting Heavier and Lighter Than Water Oily Wastes. Adopted in part from Nelson-Smith (1972) who credits FAO (1970) and Parker, Freese and Hatchard (1971).

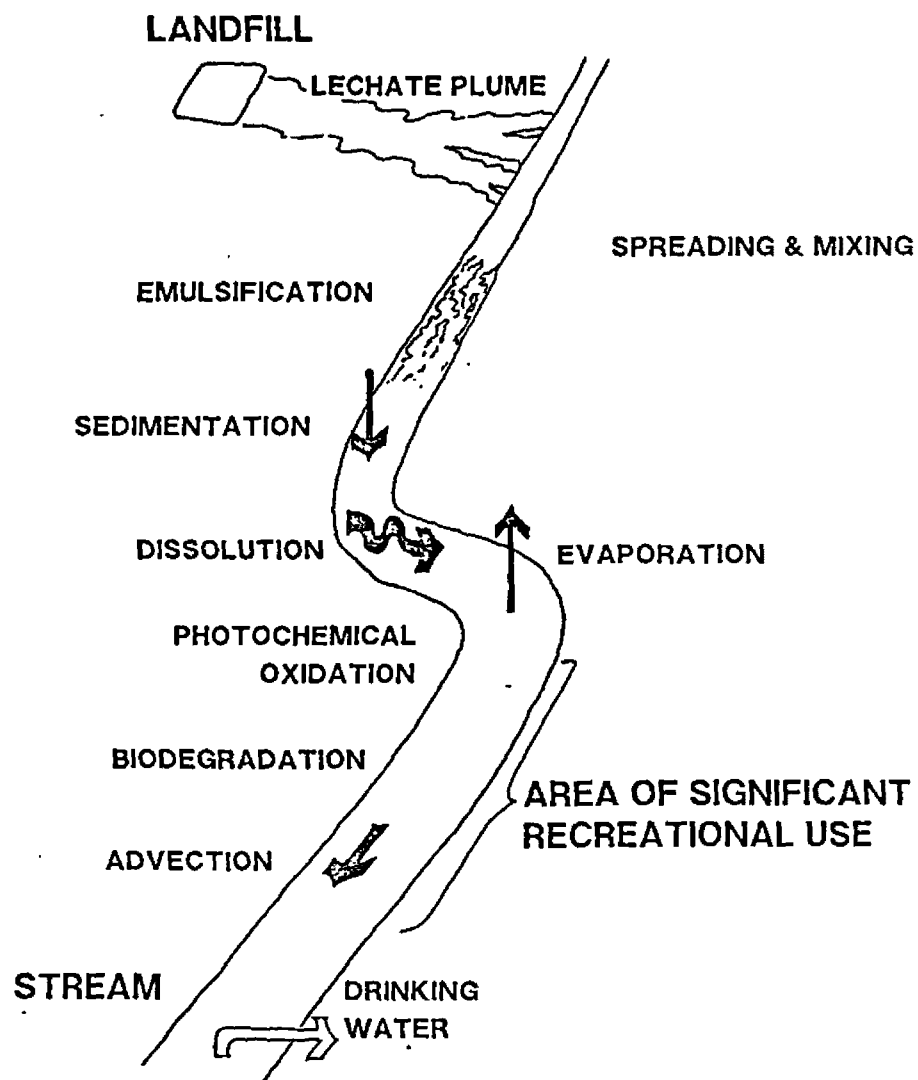


Figure 1b. Processes that effect concentrations of oily wastes in streams.

In general, oil films spread over the surface until buoyancy forces are balanced by interfacial tension between the oil and water. There are a number of spreading regimes of films in open water. However, until there is time to investigate more thoroughly, it seems probable that lateral spreading (usually on the order of 10 to 100 kilometers) is limited by the banks. Spreading along the stream channel occurs because the oil film at the surface moves faster than the average stream velocity.

The longitudinal spreading process is illustrated in Figures 15 and 16. When a film or pool exists or when partially dispersed droplets are unevenly spread over the depth of flow, the oil moves faster or slower than the average stream velocity. Lighter-than-water oily wastes tend to move faster than the average water velocity. Heavier-than-water wastes move slower. When the waste is completely dissolved or dispersed evenly over the depth, the velocity of the waste is equal to the water velocity. Wastes introduced by a continuous source do not spread longitudinally after the leachate plume is well mixed over the depth and across the width of the stream.

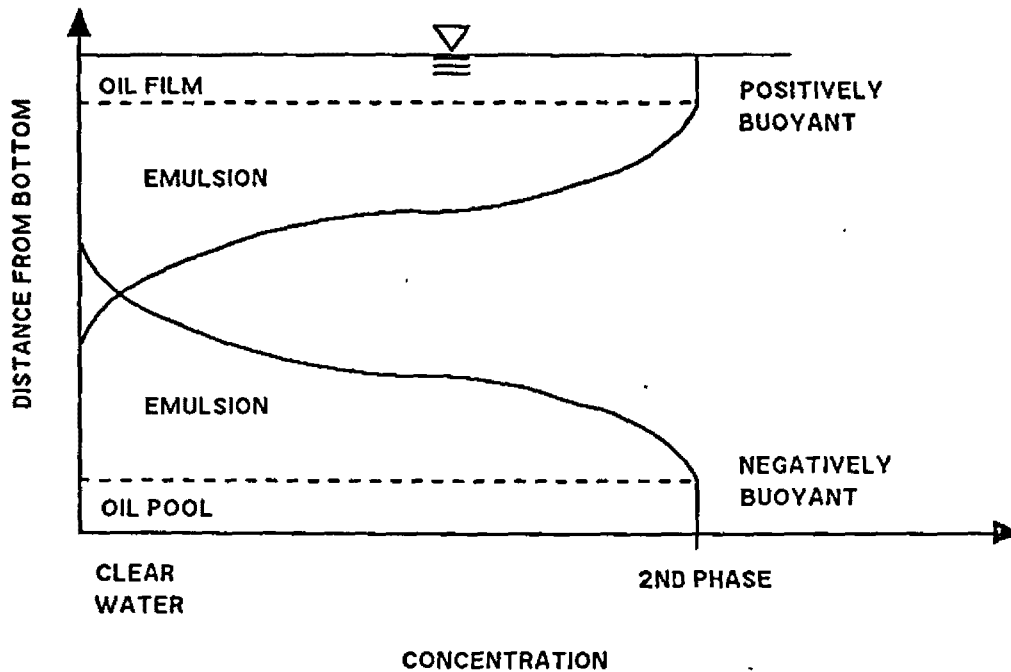
Figure 16 illustrates the difference in velocity of a film and the water and the difference in velocity in a pool and of the water. In this case, the thickness is greatly exaggerated. In most streams, the ratio of oil film velocity,  $u_p$ , to the average water velocity,  $U$ , is

$$u_p/U = u_{\max}/U \quad (1)$$

where  $u_{\max}$  is the maximum water velocity at the surface. For a significant number of streams throughout the continental United States,  $u_{\max}/U = 1.15$

RIFFLES AND TURBULENT FLOWS

# VERTICAL PROFILES



## RIFFLES AND TURBULENT FLOWS

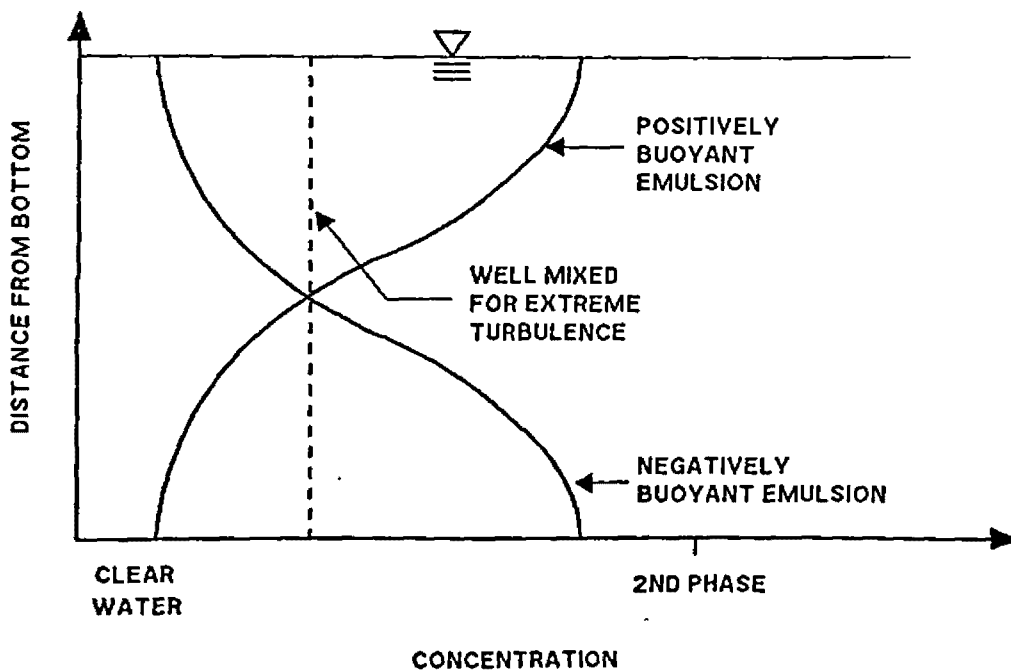


FIGURE 14. Vertical Distributions of Oily Immiscible Wastes in Streams with a Density Different from the Density of Water



## TYPICAL VELOCITY PROFILE IN STREAMS

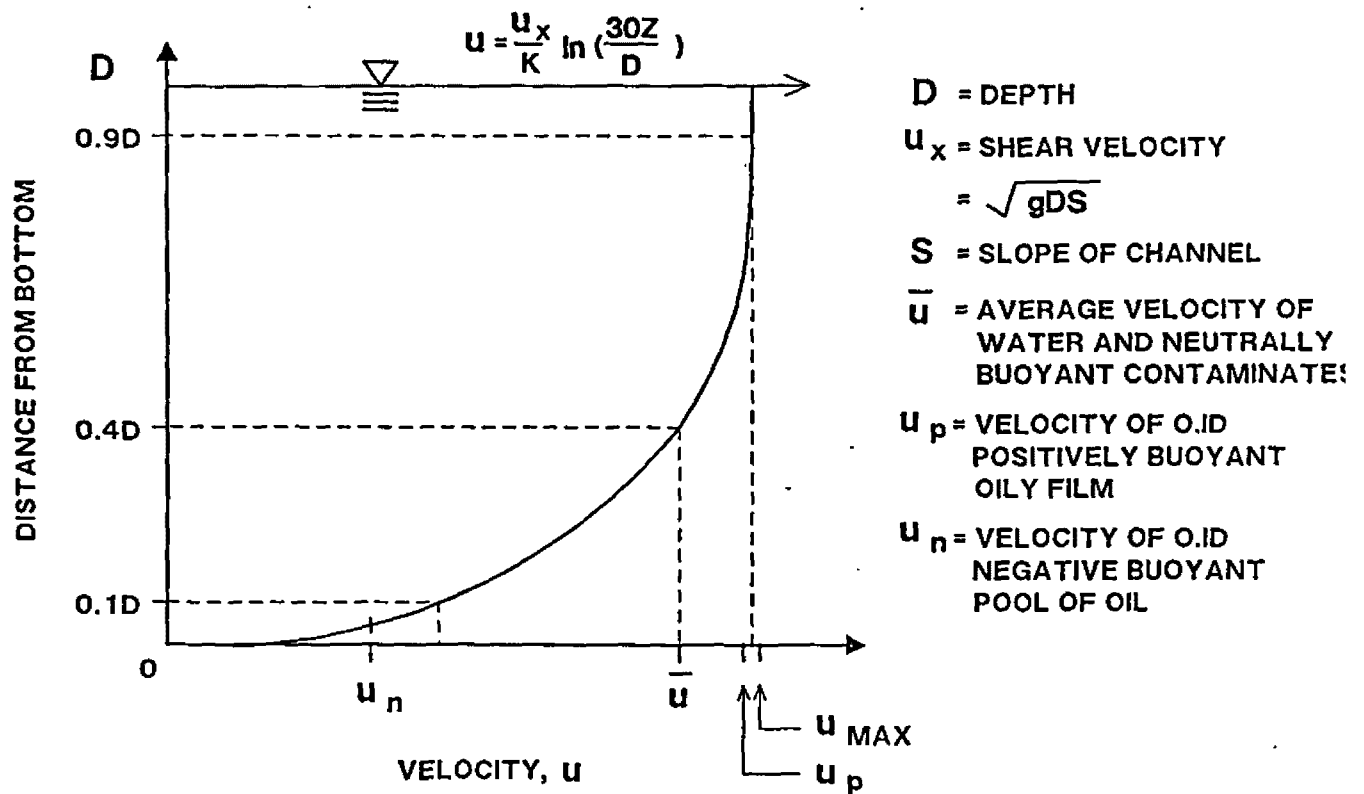


FIGURE 16. Velocity Differences in Streams that Have a Surface Film or Pool of Oil with a Thickness of 10 percent of the Depth of Water Flow.  $Z$  is the depth above the stream bottom,  $k$  is von Karman's coefficient (0.41), and  $U_{\max}$  is the maximum stream velocity that usually occurs at or near the surface.

(McCutcheon 1989, Rantz et al. 1982, Corbett et al. 1962). This ratio has been derived from at least two different assumptions about the mathematical form used to represent the water velocity profile -- namely that the velocity profile can be described by a logarithmic or power law function. More importantly, the ratio of 1.15 is consistent with a number of observations at U.S. Geological Survey stream gaging sites and other locations on streams (Rantz 1982, Hulsing et al. 1966) summarized in Table 7. The effects of secondary circulation accounted for in the USGS observations are, therefore, minor. Secondary circulation in a stream is the cross current circulation that arises because of the irregularity of stream channels. It causes the maximum vertical velocity that would otherwise occur at the surface to be depressed to a depth on the order of 1 to 10 percent of the total depth.

Table 7  
Relationship between point velocities and vertically-averaged mean velocities  
[McCutcheon 1989, originally from Rantz et al., 1982]

Relative depth (from surface)	Ratio of point velocity to vertically-averaged velocity
0.05	1.16
0.1	1.16
0.2	1.15
0.3	1.13
0.4	1.11
0.5	1.07
0.6	1.02
0.7	0.95
0.8	0.87
0.9	0.75
0.95	0.65

The near-vertical shape of the velocity profile near the water surface indicates that the ratio  $u_p/U$  is very insensitive to the film thickness. Just the opposite is expected for oil pools on the stream bottom where the velocity changes very rapidly with depth. In this area,  $u_n/U$  will be very sensitive to oil thickness and channel irregularities will be a significant influence. Secondary circulation, however, will not be important.

In general, a nonhomogeneous distribution of oily wastes is expected downstream of a continuous source because the intensity of mixing will vary. Mixing intensity and the transition from surface films and globs on the bottom to dispersions of droplets and emulsions will be especially pronounced in pool-and-riffle streams (see Figure 17). Of greatest interest is the reformation of bottom globs and surface films downstream where the water is pooled or where debris dams and obstructions operate to skim or pool wastes (see Figures 17 and 18). These areas of reconcentration seem almost certain to occur in any stream. These potential hot spots of concentrated exposure to oily wastes also will generally coincide with the most important ecological area of typical streams.

In this regard, the information available about the distribution of pools and riffles is sparse. It is believed that riffles are separated along the stream by an average distance of seven times the depth (Edwin Herricks, Department of Civil Engineering, University of Illinois, personal communication, February 26, 1988 -- also see Appendix I). We will investigate typical stream geomorphology further, but at this time we are unable to adequately predict the occurrence of quiescent areas where oily waste may accumulate. As a result, we are initially forced to assume (our observations generally support this) that quiescent areas will always be present and we will base the analysis on this assumption.

# EXPECTED LONGITUDINAL BEHAVIOR OF OILY WASTES

## - CONTINUOUS SOURCE

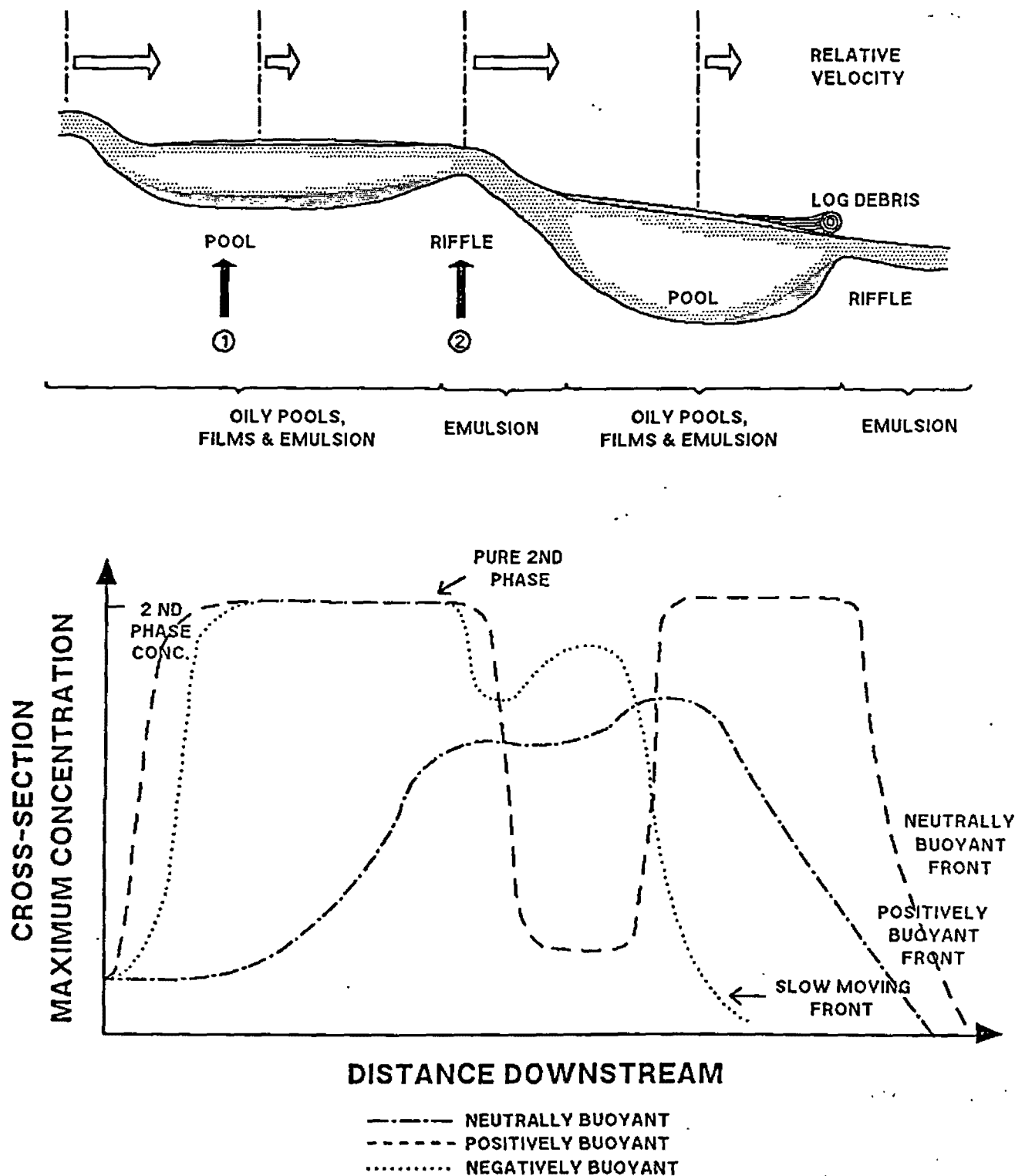
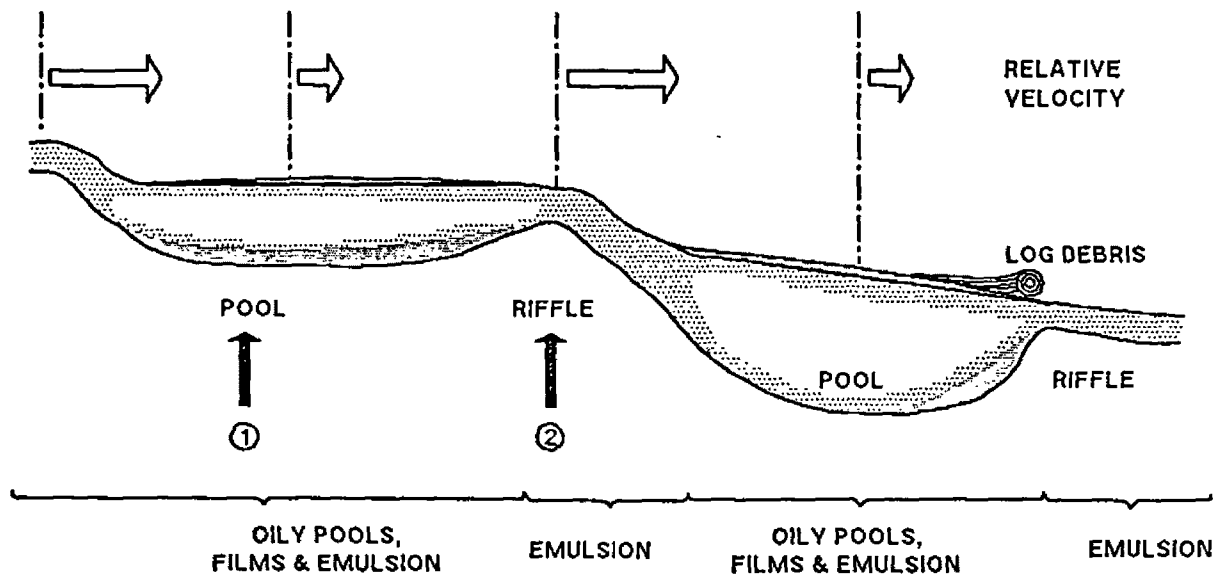


FIGURE 16. General Behavior of Heavy and Light Oily Wastes in Pool and Riffle Streams. Note the potential to form hot spots of exposure in critical ecological zones. Stations (1) and (2) refer to illustrations of vertical profiles in Figure 14.

# EXPECTED LONGITUDINAL BEHAVIOR OF OILY WASTES

## - CONTINUOUS SOURCE



## - DISCONTINUOUS SOURCE (OVERLAND FLOW OR LAGOON FAILURE)

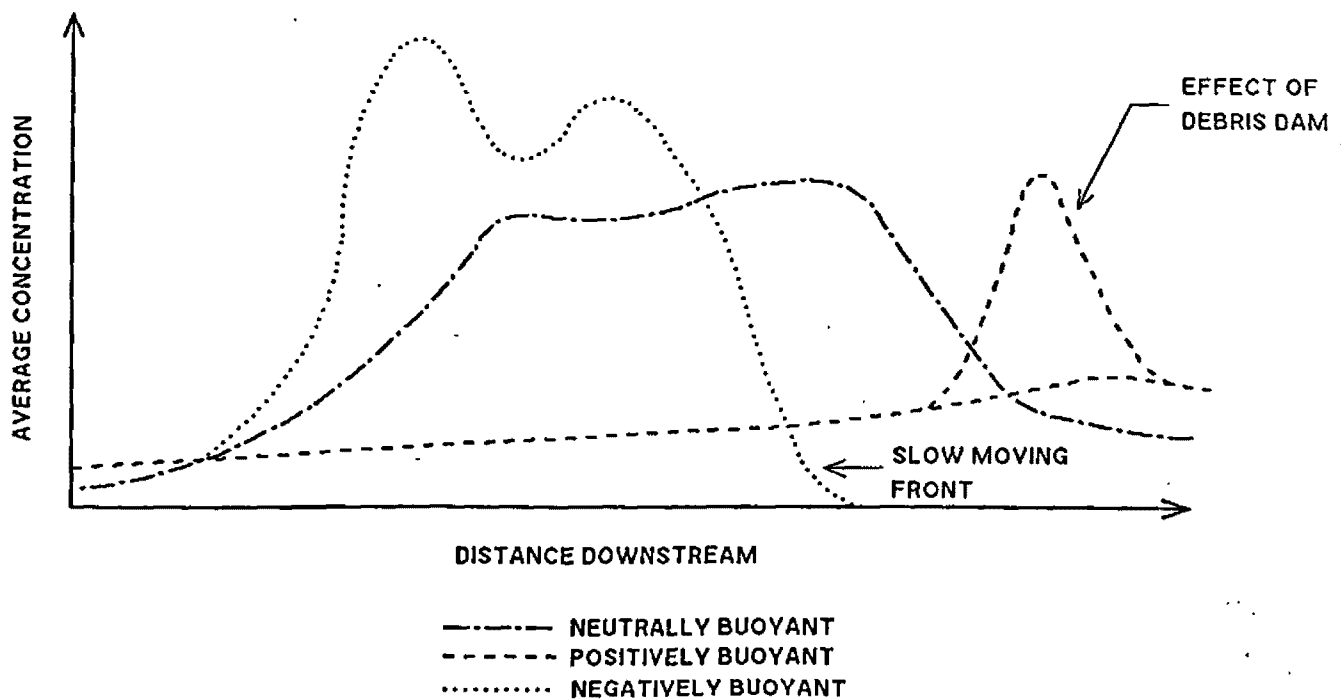


FIGURE 17. Longitudinal Distribution of Heavy and Light Oil Wastes Downstream of a Discontinuous Source. Stations (1) and (2) refer to illustrations of vertical velocity profiles in Figure 14.

We anticipate some differences in distribution of oily wastes downstream of discontinuous sources. We will investigate this matter further.

#### Formation of Films, Globs, Pools, Mixed Droplets, and Emulsions

Oily wastes have been observed in a number of forms in streams. Lighter-than-water oils form floating films in many streams. We can think of only rare instances where there would be no potential for a film to form. All natural streams have quiescent areas at either bank and many streams are connected to backwaters or wetlands. Natural streams usually have debris and natural dams that acts as skimmers. A number of streams are a series of pools and riffles during periods of low flow. As a result, it is rare that films would not form and casual observations of streams in urban areas where oily materials are usually present, bear this out. In addition, many water quality sampling plans assume that films are present when designing stream sampling procedures (McCutcheon et al. 1985).

It is less readily observed, but heavier oil can pool on stream bottoms or sit on the bottom in discrete volumes frequently referred to as globs. Globs or slugs of heavy or light oils may also be broken off from a floating film or pool and move through the water column in a suspended fashion (Perziosi 1987). More frequently observed are smaller droplets that break away from the separate oil phase and become partially dispersed. When intensive mixing is present, extremely fine droplets can be formed that are fully dispersed in the water. These are oil-in-water emulsions that remain approximately well mixed when a minimum level of turbulence is maintained after complete mixing has occurred.

The fine droplets in an emulsion that are covered with surfactants are Micelles.

A typical micelle is shown in Figure 12. The droplet is covered with surfactants that originate from waste sources or from natural materials. Natural surfactants are assumed to be widely available in all natural waters but it is not clear how much is known about the properties of natural surfactants as they relate to the formation of micelles. Ideally it would be useful to know how the type of surfactant is related to the diameter of emulsion droplets to be able to estimate dissolution from droplets. It would also be useful to know what effect surfactants have on the formation of droplets. Since surfactants influence interfacial tension, it is assumed that the presence of surfactants must affect droplet formation and size.

At present we do not understand the relationship of suspended globs, droplets, emulsions, and micelles and intend to investigate further. We will investigate maximum drop sizes (Hu and Kintner 1955) and interfacial stability.

We are most interested in the potential for globs, droplets, and emulsions to reform separate oil films and pools after stream turbulence decreases. At this point, we suspect that an important distinction between micelles and other discrete oil particles (droplets too big to be covered by surfactants and globs) are that micelles do not coalesce into films, pools, globs or other larger droplets whereas other oil bodies do when the flow becomes quiescent.

We have investigated simple parameters to describe interfacial stability to determine if it is possible use gross stream properties such as depth and

velocity and readily available chemical properties of wastes to determine if films and pools will break down into globs, droplets, or emulsions. At this time, we have been unable to derive the appropriate simple criteria that matches the few data available -- flow, depth, velocity and major chemical characteristics of oily wastes. For this reason the initial screening model must be less elaborate than we had originally hoped. Because we are unable to conveniently determine how much of an oily waste will be dispersed, we must conservatively assume that there are reasonable opportunities within a stream for the waste to exist solely as a surface film or pool on the bottom and that at other locations along the stream the wastes could be fully dispersed as droplets. It is very likely that every stream of interest will have quiescent areas where films will form. It is not as likely that all streams of interest will completely convert a source of oily waste into dispersed droplets. This represents a distinct divergent from calculating a mass balance of oily materials. However, for an initial screening, it is not unrealistic.

We have initially investigated the use of the densimetric Froude number to determine when films or pools of oily waste on the bottom and emulsions can be expected to be present in a stream. The densimetric Froude number is defined as

$$Fr = \frac{U}{\left(gD \frac{\rho_o}{\rho}\right)^{1/2}} \quad (2)$$

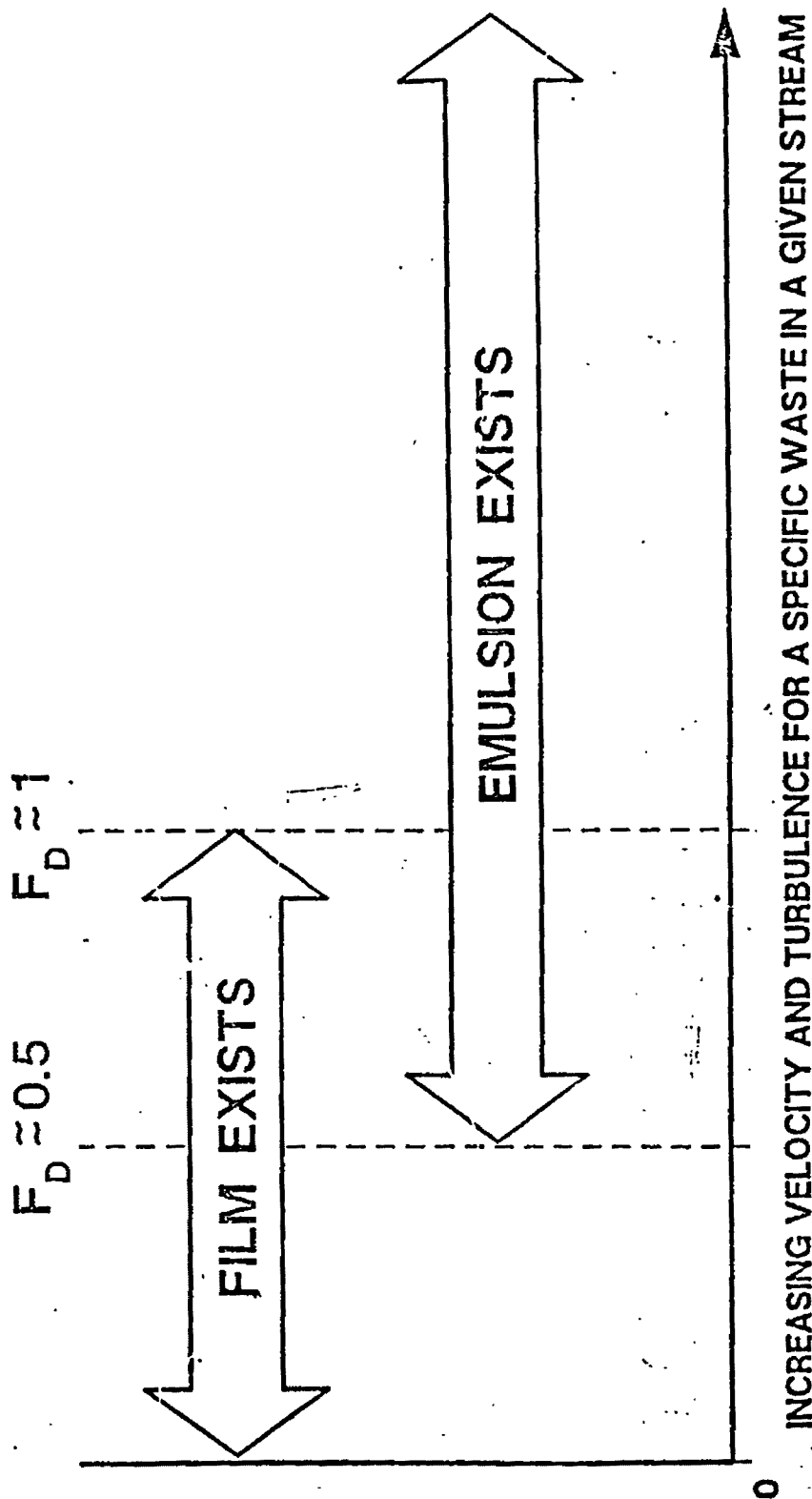
where U was defined earlier as the average stream velocity, g is the acceleration of gravity,  $\rho_o$  is the difference in density between water and the oily waste, and  $\rho$  is the density of water. The densimetric Froude number is also the inverse of the gross Richardson number, which has been used extensively to crudely characterize mixing in density-stratified waters. As



such, the Froude number does not fully take into account important physical characteristics of streams and chemical characteristics of the oily waste. Specifically, the effects of interfacial tension, fluid viscosity, and fluid turbulence and shear are not explicitly taken into account when the Froude number is used to define interfacial stability between oil and water.

We expect that the Froude number may be of limited usefulness based on the work of Wilkinson. Wilkinson (1972, 1973) found that oil slicks behind barriers began to mix with the water underneath if the densimetric Froude number based on depth of flow exceeded 0.5. Between 0.5 and 1.0 both an emulsion and film will coexist if we assume that any film will break up as the flow becomes supercritical (see Figure 19). Interfacial instability at Froude numbers less than one is consistent with the observations of thermal discharges in streams (Polk et al. 1968) where interfacial tension between warm and cold water does not exist. Polk found that miscible density interfaces of the general geometric type that Wilkinson studied were stable if the densimetric Froude number was less than 0.75.

The difficulty in applying the densimetric Froude number as a measure for interfacial stability in this investigation is that there are significant geometric differences in the flows. Wilkinson (1973) studied an oil slick trapped behind a dam that extended part way into the flow from the water surface. Shear stresses arose from the flow of water underneath the stationary slick and dam. With a film on the surface, the film and surface of the water move at almost the same velocity. Therefore, the more significant source of turbulent mixing would seem to be local eddies near the interface that were generated by shear on the bottom of the stream channel rather than shear at the



$$F_D = \frac{u}{\sqrt{gD \left( \frac{\rho}{\rho'} \right)^{1/2}}}$$

FIGURE 19. Crude Parameterization of Oil Film Stability Based on the Theoretical and Observational Study of Wilkinson (1972, 1973) with Extrapolation to Other Conditions

interface. As a result, it is necessary to further investigate interfacial stability criteria.

From the study of the mixing of miscible fluids (i.e. water stratified by heat, salt, or sugar - McCutcheon 1977, French 1975, McCutcheon and French 1977, French 1979, McCutcheon 1980), we know that there is a more elaborate dependence of interfacial stability on the Reynolds number and channel friction. We will revisit the derivation of the Keulegan parameter, which is a combination of the Reynolds number,  $Re$ , and densimetric Froude number,  $Fr$ . The Keulegan parameter is written as

$$K = U^3 / (v_o g \nu_o / \rho) \quad \text{or} \quad K = 1 / (Re Fr^2) \quad (3)$$

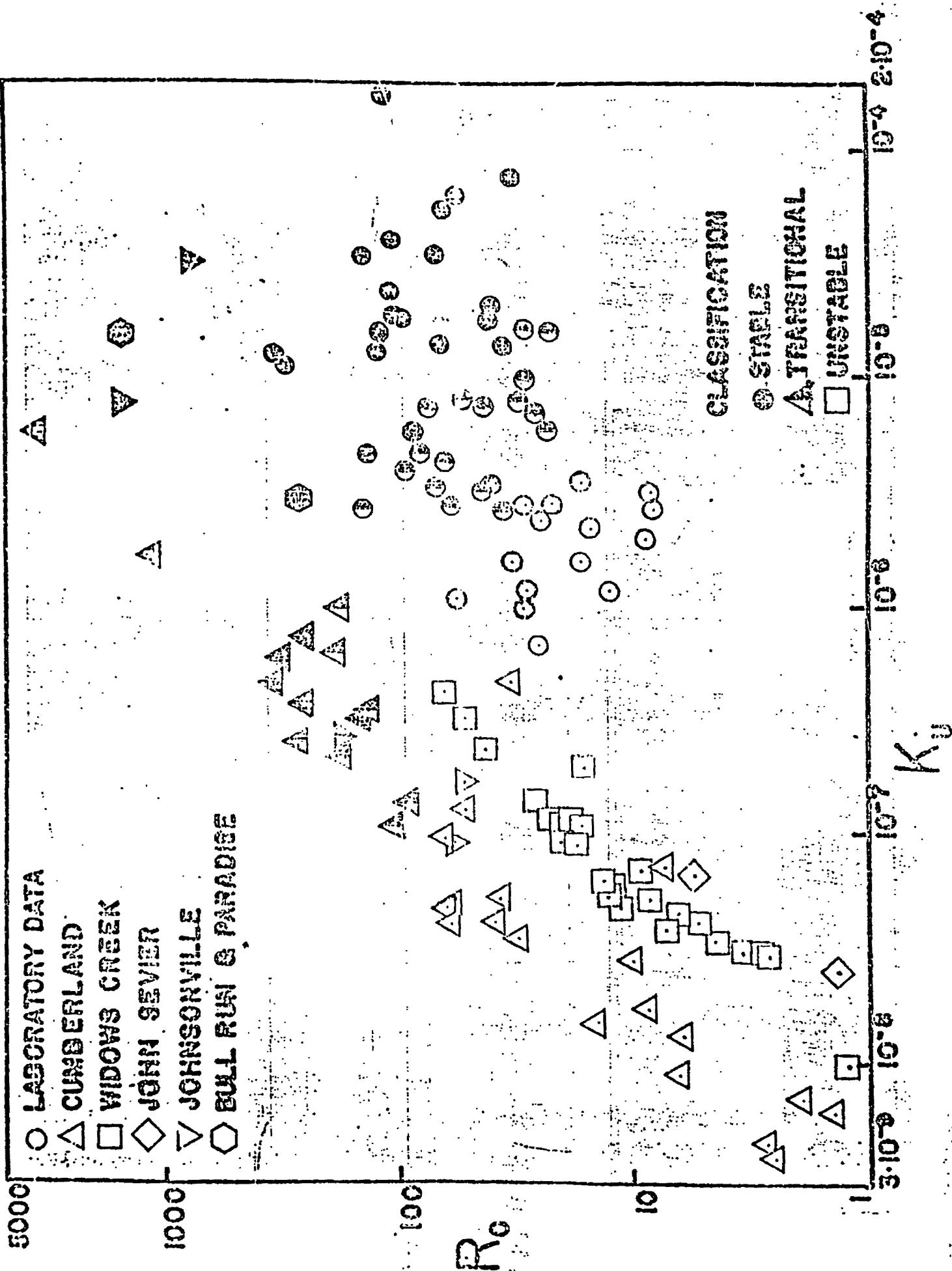
where  $\nu_o$  is the kinematic viscosity of oil. The critical value of this parameter was 180 for entrainment to begin. French (1979) determined that other parameters were also important, including a flow Richardson number

$$Ro = g(\nu_o / \rho)(D) / u_*^2 \quad (4)$$

(where  $u_*$  is the shear velocity) and a friction factor  $U/u_*$  relatable to the Manning  $n$  (a channel roughness coefficient). Figure 20 is the appropriate form of the stability diagram for miscible fluids.

In addition, we will enlarge the necessary dimensional analysis to include effects of interfacial tension. Here we expect that the Weber number must be introduced to account for the effect of surface tension on the formation of emulsions and drops. The Weber number is written as

FIGURE 2: INTERFACIAL STABILITY AS A FUNCTION OF  $K_U$  AND  $R_0$



$$W = \frac{\rho U^2 D}{s} \quad (5)$$

where  $s$  is interfacial tension.

Important variables that should be considered in any dimensional analysis include:

- water velocity,  $U$  in  $L/T$
- density of water,  $\rho$  in  $M/L^3$
- density difference,  $\rho_o$  in  $M/L^3$
- interfacial tension,  $s$  in  $M/T^2$  -usually in dynes per cm or ergs per  $cm^2$  [(force along a length  $l$ ,  $F=ls$  (CRC 1987))]
- depth of flow,  $D$  in  $L$
- stream slope (shear determinate),  $S$  in  $L/L$
- depth of the oil pool,  $d$  in  $L$
- water viscosity,  $\eta$  in  $L^2/T$
- oil viscosity,  $\eta_o$  in  $L^2/T$

where  $L$  designates units of length,  $M$  designates units of mass, and  $T$  designates units of time.

From the work in miscible fluid interfacial stability, we expect that an approximate analog of the Froude number may be possible. However, significant laboratory and field investigations may be necessary to establish critical parameter values.

Interfacial stability controls the formation of drops and emulsions as shown in Figure 21. A qualitative outline of the forces involved is presented in Figure 22.

We expect pools of oily wastes to form in the irregularities of the

## EXISTANCE OF FILMS, POOLS AND EMULSIONS

### - INTERFACIAL STABILITY PROBLEM

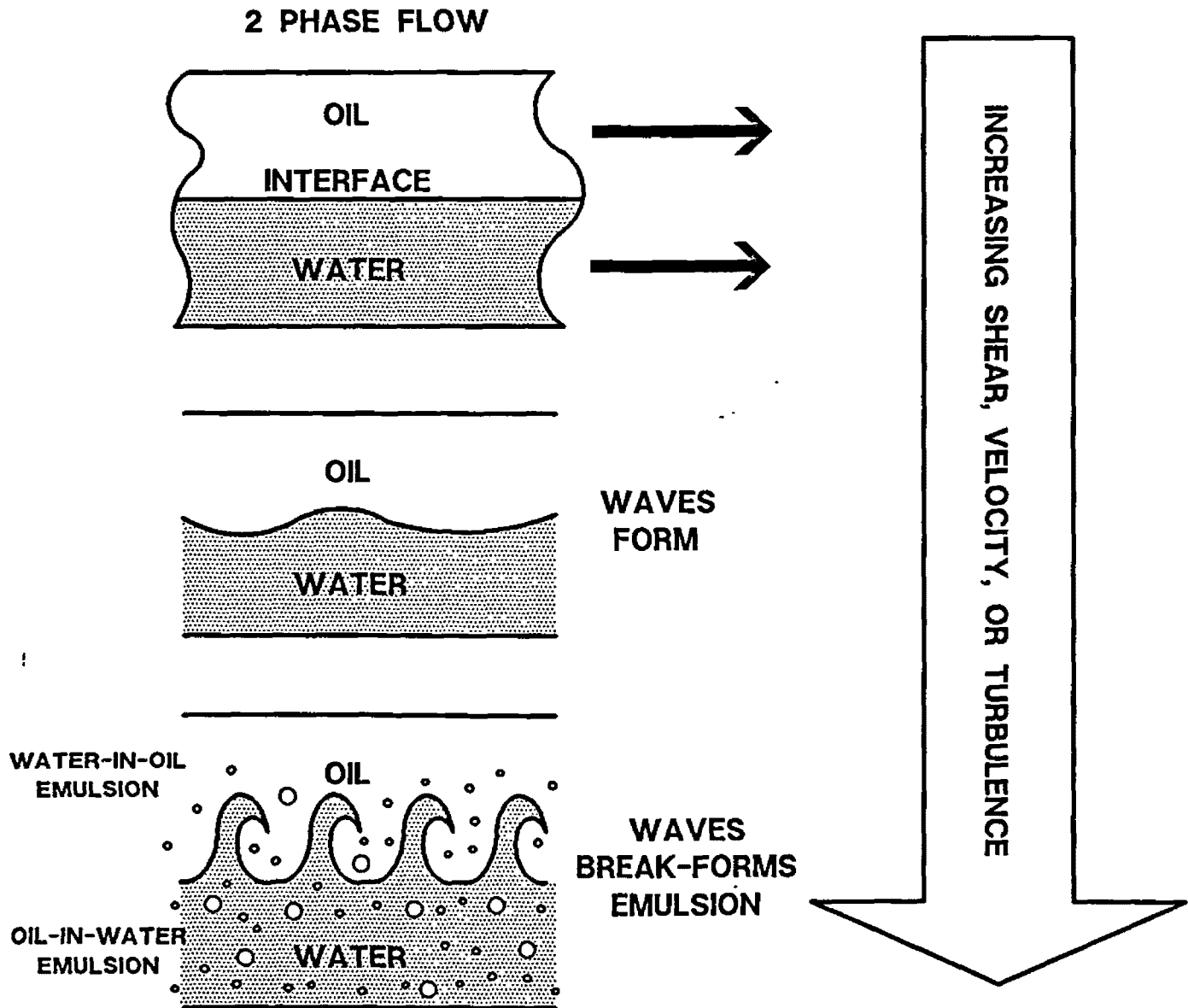


FIGURE 21. Influence of Interfacial Stability on the Formation of Emulsions.

# FORCES AT THE INTERFACE



**VISCOUS FORCES**

**INTERFACIAL TENSION FORCES**

**FORCES DUE TO DENSITY DIFFERENCES**

**IMPORTANT PARAMETERS**

**STREAM VELOCITY OR VELOCITY DIFFERENCE**

**DEPTH OR DISTANCE OVERWHICH  $\Delta V$  ACTS**

**BUOYANCY-DENSITY DIFFERENCE  $g \frac{\Delta \rho}{\rho}$**

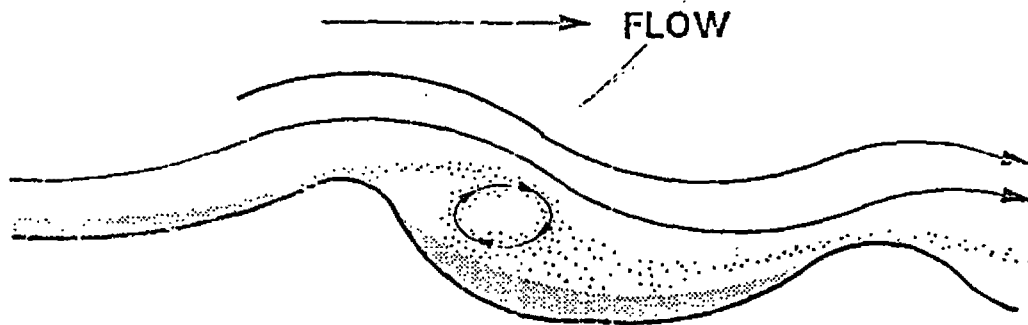
**VISCOSITY**

**TURBLENCE-SHEAR VELOCITY  $U_* = \sqrt{gDS}$**

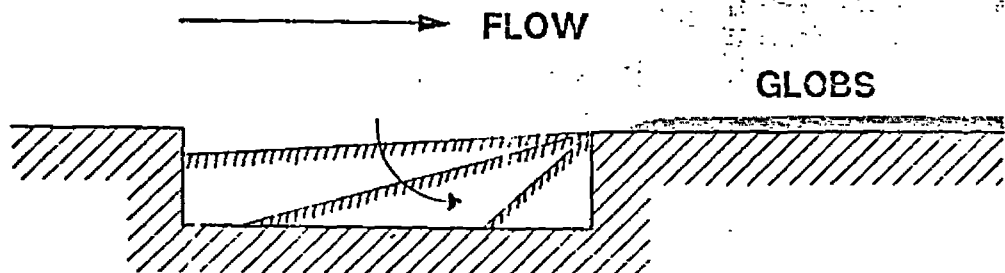
**INTERFACIAL TENSION - (EFFECT OF SURFACTANTS)**

FIGURE 22. Forces at the Interface

# DUNES

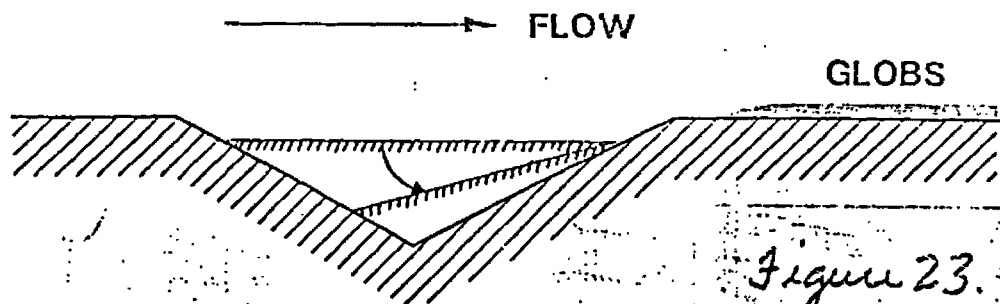


# POTHOLES AND DEPRESSIONS



GLOBS

SURFACE TILT INCREASES  
WITH INCREASED VELOCITY



GLOBS

Figure 23. Potential  
occurrences of pools  
and globs on irregular



channel bed as shown Figure 23. The existence and depth of pools will depend on the shear of flowing water shear pulling oil out of the depression, turbulence entraining droplets, and dissolution. At low stream velocity, we expect pools to be deep. At high velocity we expect the pools to shallow because of increased dissolution, entrainment, and shear.

### Volatilization

From oil spills on the oceans, we know that significant amounts of crude oil and fuels evaporate (Nelson-Smith 1972). Usually 20 to 30 percent of the light fractions of crude oil volatilize within a few days. However, the heavy ends (or fractions) may not volatilize. McKee and Wolf (1963) report that water in long term tests evaporates before some types of oils can be significantly volatilized. Therefore, evaporation can be important and should be investigated further. In this regard, it should be possible to develop the appropriate mass transfer theory and use the extensive work in stream reaeration and lake evaporation to adequately quantify volatilization.

### Dissolution

Nelson-Smith (1972) also indicates the importance of dissolution in reducing the mass of the oil phase. Dissolution is enhanced by the increase in surface area that occurs when droplets form. The influence of surfactants is not presently understood.

Dissolution will not only control how fast oily wastes are dispersed in

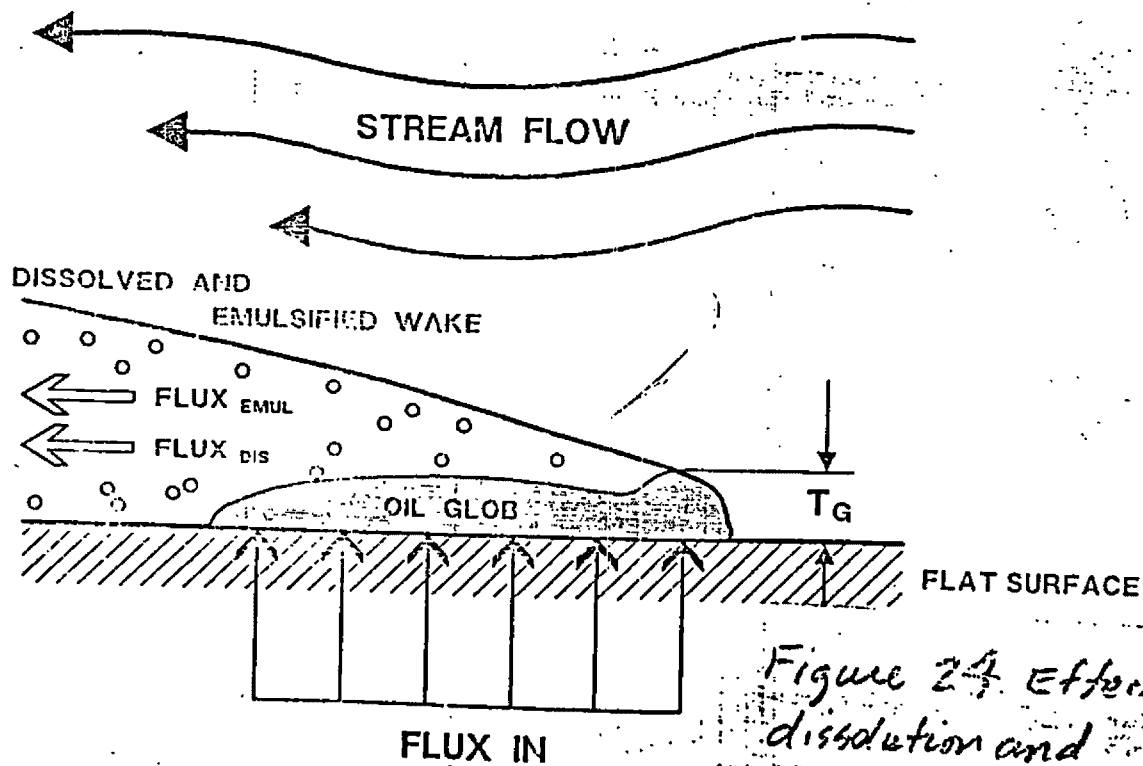
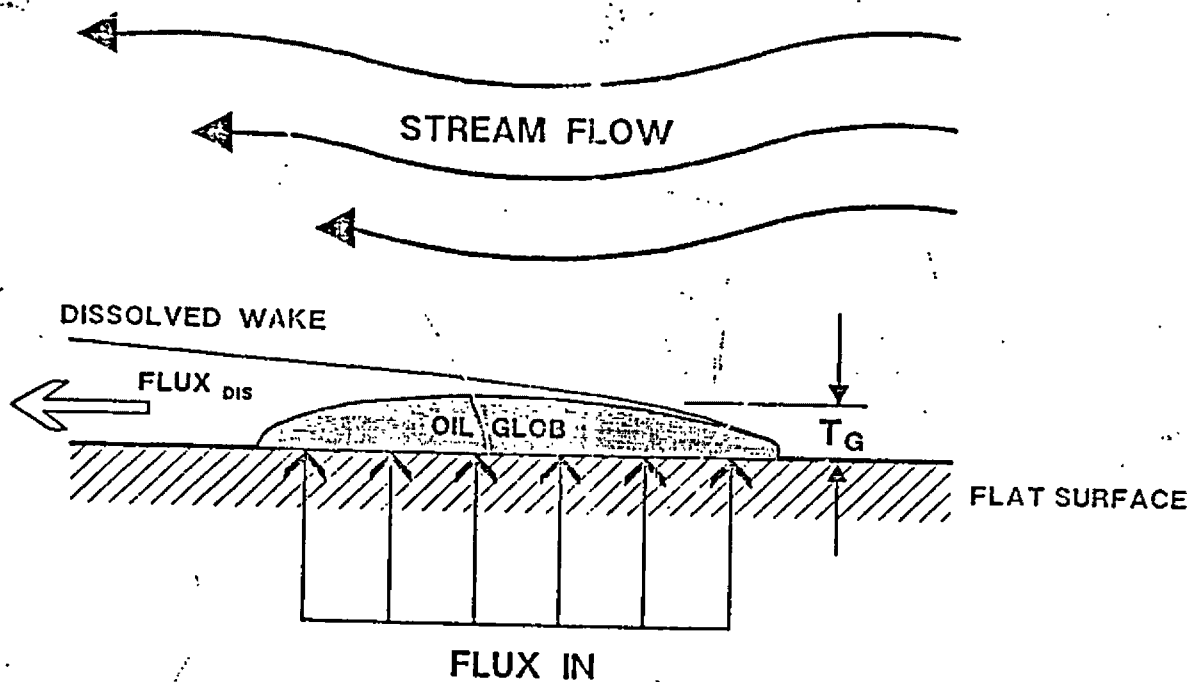


Figure 24 Effect of dissolution and emulsification on the thickness of globs on a flat stream

streams but it also will control the amounts of oily wastes accumulate at various places in streams. At equilibrium between the flux out of the stream bed at the point where globs and pools form and the flux into the water column due to dissolution, the rate of dissolution and emulsification controls the size (thickness and extent) of oil globs (see Figure 24).

The rate of dissolution can be quantified for simple geometry (see Thibodeaux 1977, for example) but it appears that the mass transfer calculations for complex natural conditions have not been fully explored.

As a conservative approach, we intend to investigate specification of the soluble fraction of oily materials from measurements and determine if we can conservatively assume that the dissolution of oily waste components occurs simultaneously from surface films later when we attempt a better mass balance analysis. We will also investigate the same procedure for computing the toxicity of the dissolved phase when a non-aqueous phase is originally present in the stream. This may require that some solubility measurements be considered. In this regard, we intend to investigate the WASTBASE data set being put together for Office of Solid Waste by Development Planning Research Associates, Inc. to determine if the parameter SOLUB will be adequate for this purpose. Appendix III describes WASTBASE and the parameter SOLUB. The mass transfer rates must still be considered in other cases (i.e., computing the thickness of globs on the bottom), however.

## Photochemical Oxidation, Hydrolysis, and Toxic Daughter Products

The effect of chemical reactions has not been fully explored as a need to do does not seem to be indicated. The primary interest in this process is the possible formation of more toxic daughter products (Edwin Herricks, Department of Civil Engineering, University of Illinois, personal communication, February 26, 1988, preliminary review) rather than a significant reduction of the mass of oil.

## Biodegradation

We have not investigated the effect of biological assimilation. We suspect that it is more important for long term weathering of oils in open waters and the eventual assimilation of spills. Lags in acclimation of native bacteria lead to a reduction in immediate importance for discontinuous releases of oily material into streams. However, a continuous source should allow acclimation of native flora if the waste is biodegradable and especially if a lengthy aerobic groundwater pathway is involved. At this time, it is not clear how many oily wastes are readily biodegradable. Nor is it known how important biodegradation may be in the assimilation of wastes.

## Sedimentation

In oil spills, a significant amount of the oil can be removed from the water column by attachment to particles that settle. In general, the

partitioning between the nonaqueous phase, dissolved phase, and solid surfaces is not well understood. At this time, however, we believe that sorption mechanisms are important to the overall fate of oily wastes in streams.

### Coating Surfaces

The coating and wetting of surfaces and adsorption solids are important not only in the removal of oil from the water column but also relative to aesthetic and toxicological impacts. The formation of scum lines in water treatment plants is to be avoided (FWPCA 1968). The coating of banks, debris, and vegetation is a serious but presently unquantifiable problem. There is some guidance on the amounts of oil that attach to shorelines during oil spills that may be useful (Shen et al. 1987). Beyond this, we have discovered no other guidance of significance.

### INVESTIGATION OF REASONABLE ENDPOINTS

#### Concentration vs. Thickness Criteria

We have earlier identified at least ten criteria that may be appropriate as exposure endpoints. These include:

1. Drinking water standards,
2. Taste and odor criteria,
3. Threshold concentrations causing tainting of fish and shellfish,
4. Concentration of emulsions that are toxic,

5. Concentration of dissolved components that are toxic,
6. Visibly-detectable surface film thickness,
7. Thickness of surface films killing or impairing surface breathers,
8. Thickness of detectable bottom deposits of heavy oil,
9. Detectable coatings on banks, debris, and plants, and
10. Quantities of oil phase that are toxic.

These endpoints are, with one ambiguous exception, of two types. The first five endpoints (1 through 5) can be expressed as a concentration criteria. The next four (6 through 9) can be expressed as a limiting thickness of oil on the surface of the stream or elsewhere. The tenth endpoint is ambiguous at this time because it is not clear if it would be best to specify the concentration of oil averaged over the volume of stream reaches as a criteria or to specify a limiting thickness of oil on gills, skin or other surface (i.e., the water surface). Suitable classification requires further investigation.

The categorization of endpoints into two groups simplifies model calculations. Both types of computations are based, however, on a selective mass balance of oil and water. All endpoints specified as a concentration can be related to the amount of oily wastes to be disposed of over a specified period of time,  $q_{oil}$ , as shown in Figure 25. A mass balance of the stream segment shown in Figure 25 is written as

$$q_{oil}C = QC_0 + (Q + q_{oil})C_{CRIT} \quad (6)$$

If we assume that the concentration of oily wastes disposed of in a landfill or other facility is 100 percent oily waste or nearly so (such that  $C = 1.00$ ), that the background concentration of oily material is approximately zero upstream of the intersection of the stream with the leachate plume ( $C_0 = 0$ ), and that the volume of oily waste is small compared to the volume of water that flows in the stream, then Equation (6) reduces to

$$q_{oil} = C_{CRIT}Q \quad (7)$$

If the waste is diluted with water either before disposal or during transit between the source and the stream and the diluting flow is included in the measurement of stream flow,  $Q$ , then these occurrences are easily taken into account. It is also a simple matter to account for upstream oily waste disposal by assuming that  $C_0$  is not equal to zero. Therefore, more than one disposal facility per watershed can be included in the analysis.

The mass balance to relate allowable disposal rates of oily material to critical film or pool thickness is similar as shown in Figure 26.

$$q_{oil} = U_{oil}TW = TWKQ/WD = TKQ/D \quad (8)$$

Note that it is not necessary to know the width of the stream for this calculation. This follows from the definition of relationships between average water velocity and discharge ( $U_{H2O} = Q/DW$ ), the average velocity of the oil film and the disposal rate ( $U_{oil} = q_{oil}/TW$ ) and the relationship between the average velocity of the oil film and the stream as noted earlier ( $U_{oil} = U_{H2O}K$ ). It is assumed that an oil film does not exist upstream, but any effect of this type can be easily incorporated. It is further assumed that  $Q$  is much larger than  $q_{oil}$ , which is expected for low intensity leaching of this type.

To conceptually simplify the basis of the screening approach, the analysis method is focussed on the volumetric flux of oily material being deposited in landfills, in lagoons, and on field application units. For consistency with the preferred regulatory approach (stressing intensive parameters such as leachate concentration of oily wastes), it is conceptually straightforward to relate  $q_{oil}$  to leachate concentration,  $C$ , as

$$C = Q_L/q_{oil} \quad (9)$$

where  $Q_L$  is the leachate flow rate into a stream.  $Q_L$  can be estimated using leachate and groundwater models or may be measured for specific site investigations.



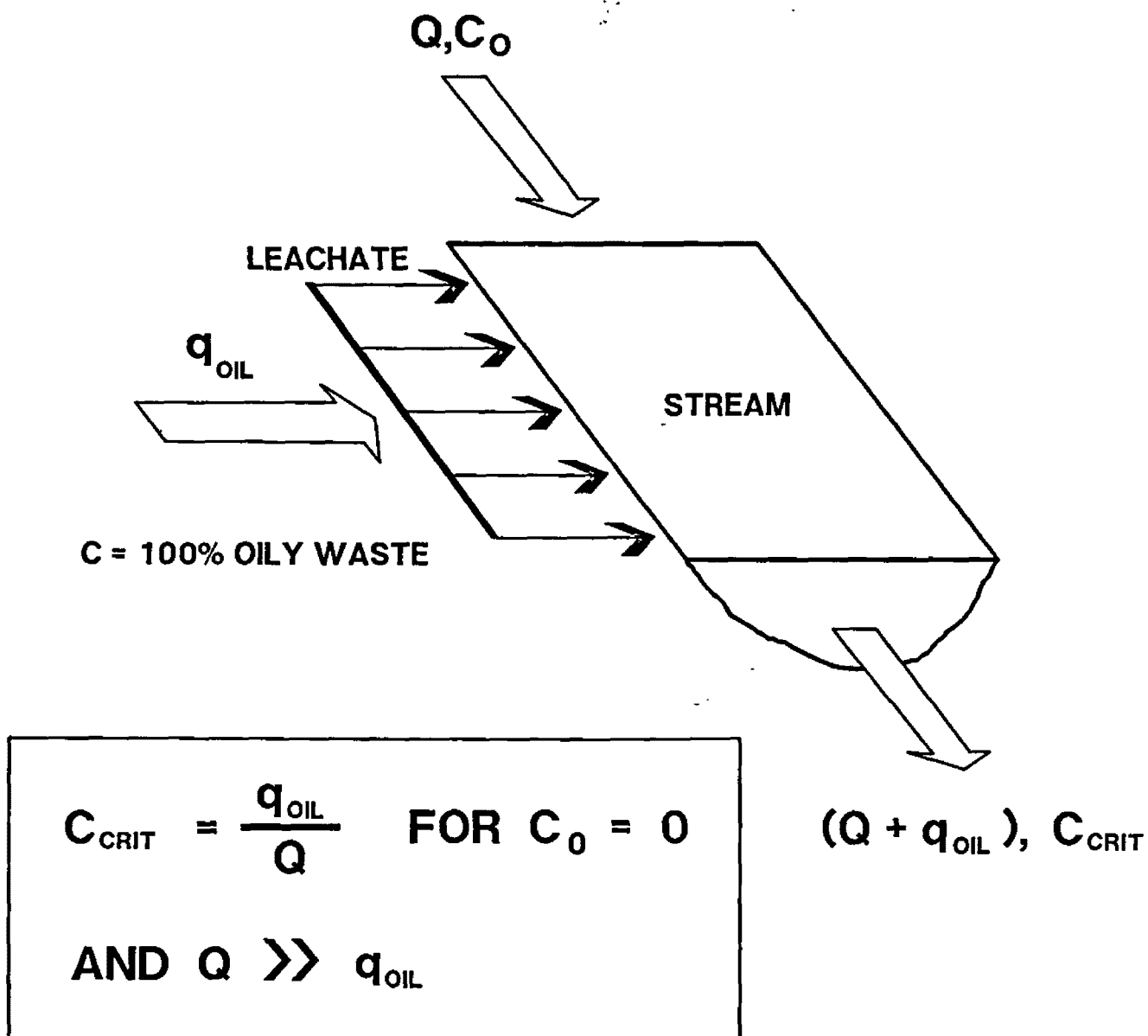


FIGURE 25. Mass balance for dispersed oily wastes or for components where dose-response relationships are based on average amounts of oily waste present.

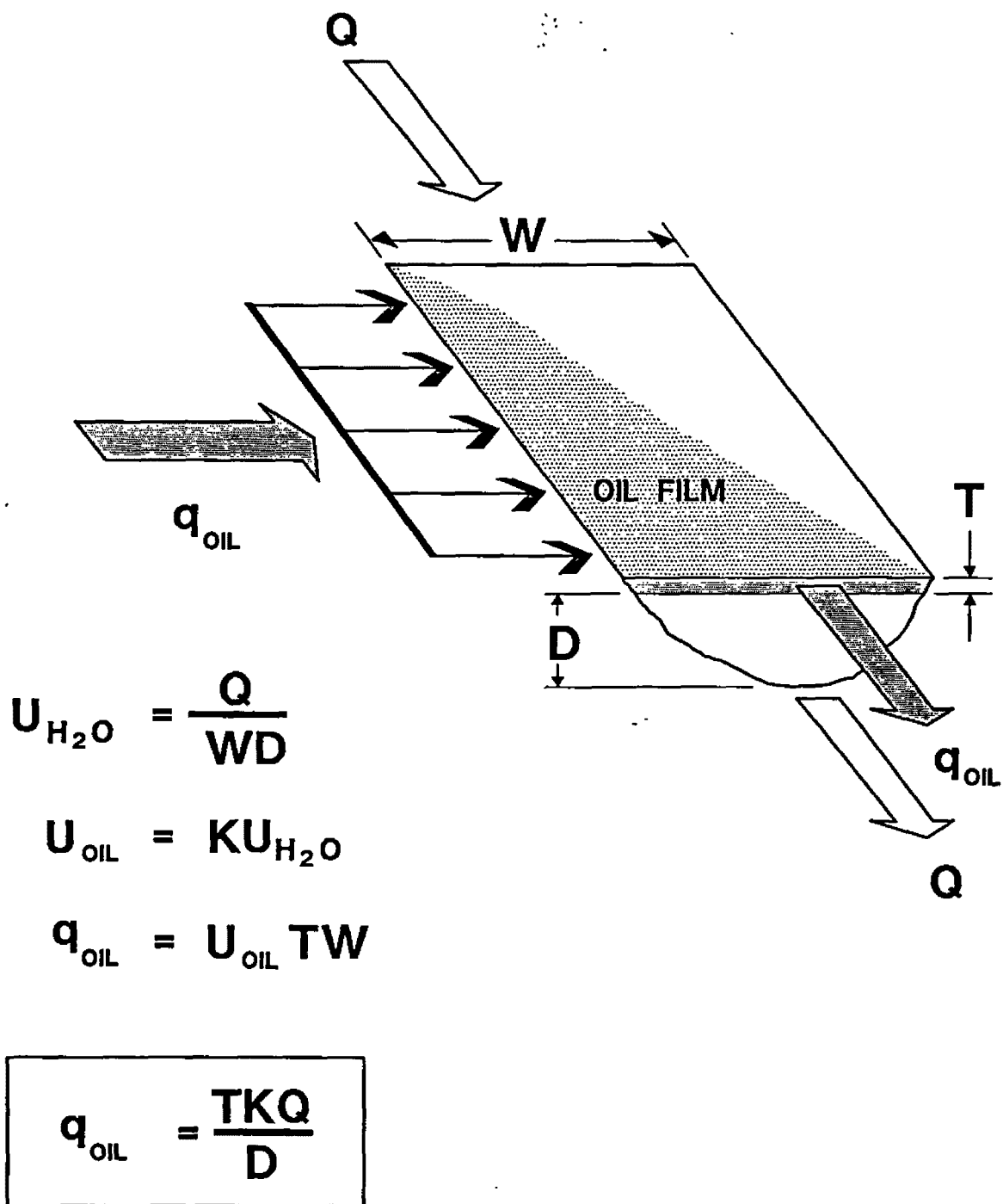


FIGURE 26. Mass balance for oil film on streams.  
 Note that the Thickness, T, can be used to characterize average film thickness, pool depth, glob thickness or even conceptual, average coating thickness on banks, debris or vegetation.

At this point, we have developed the two important computational forms for concentration and thickness criteria to be applied in the initial screening level model.

#### Calculation of the Amount of Oily Waste that May Cause Detectable Oily Tastes and Odors

For the initial analysis procedure, it will be assumed that significant recreational uses and drinking water withdrawals will occur as soon as the oily wastes are well mixed across the stream. In general, stream segments in which recreational use is prevalent and drinking water withdrawals may be located at some distance downstream of the point at which the oily leachate enters the stream. Over the distance from the point where the leachate enters the stream to the recreational areas and water withdrawals, the oily waste can volatilize, settle attached to particles, biodegrade, and photooxidize as illustrated in Figure 13. Of the processes that may affect oily waste concentrations, volatilization and dissolution may be the most important based on current knowledge.

In the initial analysis, however, all processes attenuating exposure concentrations will be ignored until it becomes clear that these processes are important for a significant number of potential sites. In effect, it will be assumed that recreation use and drinking water withdrawals will occur at the location where the leachate enters the stream. It is proposed that the importance of processes that reduce oily concentrations be systemically investigated if it is found that the initial assessments will significantly affect current or future disposal practices.

The minimum concentration from odor thresholds and taste thresholds will be applied to avoid oily tastes and odors in recreational areas based on the expectation that some recreational uses (e.g., swimming) will involve the same close contact with the water experienced in consumption. Boating, wading, and fishing will involve similar close contact where any odors will be detectable. In fact, the odor at the stream may be more detectable than any odor criteria may account for. For instance, if the ratio of the volume of contaminated water in the stream to the limited volume of air just above the stream is larger than that on which the criteria are based, then the volatilized components of the oily waste may be present in higher concentrations in the vicinity of the stream and cause a more intense odor for the same concentration of oily wastes in the water. Therefore, the basis for odor criteria will need to be investigated in light of this proposed application.

As an initial calculation, the amount of oily wastes that can be disposed of on a continuous basis in a disposal facility can be expressed as

$$\min(C_{\text{taste}}, C_{\text{odor}}) \geq \frac{q_{\text{oil}}}{Q} \quad (10)$$

where  $\min(C_{\text{DW}}, C_{\text{taste}}, C_{\text{odor}})$  is a mathematical abbreviation indicating that the smaller of the criteria for oily waste concentrations governing taste,  $C_{\text{taste}}$ , and odor,  $C_{\text{odor}}$  should be larger than or equal to the ratio of the rate of disposal of oily materials,  $q_{\text{oil}}$ , to the flow rate of water in the stream,  $Q$ .  $q_{\text{oil}}$  and  $Q$  may be specified in units of volume or mass per time as long as the units are the same or the appropriate conversions are applied. Convenient units might be gallons per day, or pounds per month for the oily waste and cubic feet per second for the stream flow.

Backcalculation of Allowable Amounts to Avoid  
Oily Tastes in Fish and Invertebrates

Limiting concentrations will be computed as

$$C_{\text{taint}} \geq \frac{q_{\text{oil}}}{Q} \quad (11)$$

If the readily available criteria are in terms of concentrations in the fish flesh,  $C_{\text{flesh}}$ , and a bio-concentration factor relating concentration in the water to the concentration in the edible flesh, BF, is known, then the limiting concentration in the water can be computed as

$$C_{\text{taint}} = C_{\text{flesh}}(\text{BF})^{-1} \quad (12)$$

Exposure to Emulsions

Exposure criteria will be expressed simply as

$$X C_{\text{emul}} \geq \frac{q_{\text{oil}}}{Q} \quad (13)$$

where the allowable concentration of the emulsion for a class of oily waste exposed to an important species or group of species must be specified from past or future bioassay work. This value should be the lowest 96-hour  $\text{LC}_{50}$  or an equivalent. The safety factor X is specified as 0.01 in the current criteria

(EPA 1987). The bioassays should be designed to maintain an emulsion during the 96-hour test.

#### Exposure to Soluble Fraction and Other Dissolved Components

Exposure criteria will be expressed simply as

$$X C_{dis} \geq \frac{(q_{oil})SOLUB}{Q} \quad (14)$$

where the dissolved concentration for a class of oily waste exposed to an important species or group of species should be specified from past or future bioassay work that partitions the waste into a dissolved fraction if SOLUB is taken as unity. This value should be the lowest 96-hour  $LC_{50}$  or an equivalent. The current criteria (EPA 1987) specifies that  $X$  should be 0.01. If the bioassay does not partition the waste into a dissolved component, SOLUB must be measured or estimated by theoretical mass transfer calculations.

#### Calculation of Oily Material Flux to Avoid Formation of Visible Oil Films, Films that Affect Surface Breathers, Pools on the Bottom, and Coatings

The allowable oily waste disposal rate (or leachate concentration if leachate flow rate into the stream is known) can be computed from a mass balance as

$$q_{oil} = T K Q/D \quad (15)$$

where T is the thickness of the oil film permissible to avoid a visible oil film outside the mixing zone, K is a coefficient relating average stream velocity to surface velocity and has a value of approximately 1.09 to 1.15, Q is the stream velocity, and D is the depth of flow. We expect that a value of 0.038 microns will be an appropriate specification of T. If the film thickness affecting surface breathers,  $T_{sb}$ , is less than T, this value should be used in place of T.

For oily waste pools, the permissible thickness based on aesthetic considerations should be used to specify T in Equation (15). The coefficient, K, (in effect a dilution factor) will assume a much smaller value of at least less than 0.65. The exact factor can be derived later. In addition, the dilution factor should also incorporate a correction for the difference in width of pools or globs (on average) compared to the width of the stream. This can also be developed at a later date.

The thickness of oily waste pools or globs on the bottom should be compared to the capillary thickness determined from the interfacial tension and density difference (Thibodeaux 1977). Thibodeaux expresses that thickness as

$$T_g = \left( \frac{2s}{g\Delta\rho} \right)^{1/2} \quad (16)$$

where s is the interfacial tension between the oily waste and water and  $\Delta\rho$  is the difference in density between the waste and water.

The smaller of the arbitrarily selected value for the oily pool depth or the capillary height defined in Equation (16) should be specified for T in Equation (8) or (14). As a first approximation, we intended to compute the capillary height from Equation (16) assuming that the bottom is a flat plate. the thickness on a flat surface.

It remains to be determined what quantity of oily material on the bottom constitutes an aesthetic nuisance. This criterion must be in terms of areal extent and thickness. We expect that wetting characteristics of the oil onto sediments and the porous nature of the bed must be considered. Until we can more precisely determine potential aesthetic impacts, these criteria will be under continued investigation.

The correction of the dilution factor, K, for width difference may also need to be considered to account for the filling of holes and depressions in the bed that may not extend across the channel. We will continue to consider the use of the Manning n and any geomorphological observations to determine what estimate may be appropriate. In addition, the geological and morphological trends given in Table 8 will be considered.



Table 8..  
Geomorphological trends of bed forms and sediment type

Bed material	Bed form			
	flat	ripples	dunes	anti-dunes irregular
clay-silt	X	X		
sand	X	X	X	X
gravel-boulders			X	X

#### Calculation of Detectable Oil Coatings on Shores, Banks, Vegetation and Debris

This calculation has not been formulated because of a lack of data quantifying the amount or thickness of coatings that are detectable. If average thicknesses criteria can be located in the literature, these will be used to specify T. If volumes of oil released are reported with length of shoreline coated, we will attempt to estimate benthic surface area to estimate T or, perhaps better, we may be able to express the allowable quantity of oil as an average concentration.

## Effect of Oily Films on Gills and Benthic Biotic Surfaces

These calculations also have not been formulated. We expect to use our experience in estimating gill surface areas for selected species of fish plus any reports of oil thicknesses that cause mortality or impairment and apply the one percent safety factor suggested by the criteria document (EPA 1987) unless there is more information on this subject in the literature than we suspect.

## DEVELOPMENT OF A SCREENING LEVEL MODEL

The initial screening level model will be based on calculation of the minimum thickness criteria and minimum concentration criteria for sensitive species and important classes of oily wastes. The next phase of development will define data needs and the exact structure of the model. This will be subject of the next progress report.

## PROJECTION OF FUTURE MODEL DEVELOPMENT NEEDS

We have not yet had time to compile our detailed expectations for future model development needs outlined in earlier sections. This will be done later if necessary, but we already see a need to reduce the conservative nature of the screening model in several areas. Chiefly we need to employ a mass balance. To refine the endpoints, we need to incorporate the work on Habitat Suitability Indices by the U.S. Fish and Wildlife Service to better define the following important classifications:

### Classification by vertical location:

- Benthic fish, larvae, and invertebrates
- Water column fish
- Surface insects

### Classification by stream velocity:

- Quiescent zone fish, larvae, and plants
- High velocity zone fish

Classification by vertical location:

- Benthic fish, larvae, and invertebrates
- Water column fish
- Surface insects

Classification by stream velocity:

- Quiescent zone fish, larvae, and plants
- High velocity zone fish

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## APPENDIX I

### Reviews of the Proposed Analysis Method Conducted February 26, 1988

1. Review Comments of: Dr. Danny Reible  
Associate Professor  
Department of Chemical Engineering  
Louisiana State University  
Baton Rouge, Louisiana
2. Review Comments of: Dr. Peter Shanahan  
Consultant  
HydroAnalysis Inc.  
Acton, Massachusetts
3. Preliminary Suggestions of: Dr. Edwin E. Herricks  
Associate Professor of  
Environmental Biology  
Department of Civil Engineering  
University of Illinois  
Urbana-Champaign, Illinois



11/11

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March 14, 1988

Brian Bicknell  
Aqua Terra Consultants  
2672 Bayshore Parkway, Suite 1001  
Mountain View, CA 94043-1011

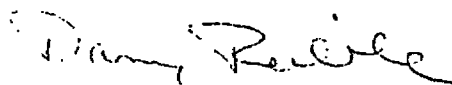
Dear Brian:.

I have attached brief comments on the methodology proposed at our recent meeting with Steve McCutcheon in Atlanta to assess the stream impact of oily discharges from landfills. As I indicated over the phone, the comments are directed toward the preliminary modeling strategy and are general in nature. Since any decision to pursue a more sophisticated modeling approach is dependent on the results of the preliminary model, I felt that it would be premature to focus too much attention on the specific processes that must be included in such a model. In keeping with the focus of the meeting, I have not addressed the transport and attenuation processes between the disposal site and the stream although these processes would likely have a very strong effect on the ultimate stream impact.

I have also not addressed the specific wording of the draft document that was mailed to me prior to the meeting. It seemed to me that much of the document is focused on the more sophisticated second level model and therefore need not be addressed at this time.

I look forward to the results of the preliminary model. If a more sophisticated modeling approach is warranted by the results, I will be happy to provide any assistance possible including literature references that I have found on oil phase behavior in soils and streams. Please feel free to contact me if you have any questions.

Sincerely,



Danny Reible  
Associate Professor

DDR

ATTACHMENT

Comments on  
"Proposed Method to Analyze Oily Wastes Expected to Enter Streams"

by Steve C. McCutcheon

The proposed method is divided into at least two stages:

1. Preliminary assessment assuming no loss or attenuation of the oily wastes.
2. More sophisticated estimate(s) as suggested by preliminary assessment.

This is clearly the logical and appropriate approach to assessing the potential need for regulations limiting the disposal of oily wastes in landfills. My primary concern is that the initial assessment may not provide a significant amount of information and that it will be necessary to implement some level of stage 2 analysis. It seems likely that sufficiently conservative assumptions can be made to ensure that a potential problem with the disposal of oily wastes exists. The stage 1 analysis is still, however, the necessary starting point to begin to identify the magnitude of the problem and procedures for its quantitative assessment. Since the meeting with Dr. McCutcheon of February 26 was focused on the preliminary assessment let me focus my comments on that stage of the analysis.

The key requirement of the preliminary assessment is conservatism. Dr. McCutcheon's plan to neglect loss and attenuation between the landfill and the stream discharge and to treat the entire discharge as contained in

the phase causing the most significant impact is appropriate. In addition, the consideration of both health and aesthetic impacts ensures that both criteria will be satisfied. The procedures outlined for surface film and in-stream impacts are reasonable and appropriate. It is important to recognize, however, that the term oily discharges encompasses a large range of materials. It will prove difficult to adequately characterize the physical and environmental properties of the oily wastes. Wherever possible specific important compounds or classes of compounds should be examined in the analysis.

Some questions were raised during the meeting with Dr. McCutcheon regarding the procedures to handle submerged pools of oily wastes. I indicated at the time and still feel that a reasonable and conservative estimate can be made by assuming that the pool spreads over the entire stream bottom to the limiting thickness imposed by the surface tension with water. From Thibodeaux (Chemodynamics, Wiley, 1979), this thickness is

$$h = \sqrt{(2\sigma/\Delta\rho)}$$

Since the density difference between water and typical oily phases is  $\leq 0.5$  g/cc and the interfacial tension is of the order of 50 dyne/cm (0.05 g/cm), this height is about 5 mm. An estimated water profile over an uncontaminated sediment can be used to estimate the velocity of the oil layer by assuming continuity of shear stresses at the interface. The specific form of the approximation for the oil layer velocity would depend on the thickness, density and viscosity of the oil. Since the above procedures provide an oil phase volume and velocity, the treatment of the bottom-residing pool is essentially identical to the proposed procedure for the surface film.

The assumption of steady state stream flow and oily discharge conditions is appropriate as a preliminary analysis but it should be recognized that these conditions may not represent conservative assumptions. The worst case condition may be the accumulation of oily discharges over time in a lake or pond adjacent to a disposal site. In addition, the contamination may only affect some fraction of the stream or stream bed. It is therefore suggested that some preliminary assessment calculations be made to identify the impact of stream or discharge heterogeneity might have on the results.

Examples of potential problems include the tendency of small oily discharges to form a patchy oil film rather than a continuous film. Thus aesthetic problems could result from a much smaller discharge of oil than predicted by the outlined procedure. In addition, an oil film will tend to form in quiescent regions of a stream rather than in the main channel or in riffles, again suggesting that the proposed preliminary assessment procedure may underestimate the actual aesthetic impacts. Since oily contaminants are likely to concentrate in quiescent regions, the greatest impact on aquatic life will also be noted in these regions rather than in the entire stream.

My expectation is that these problems will lead to a preliminary impact assessment that might be as much as an order of magnitude too low (that is, a conservative estimate of the allowable oily discharges might be an order of magnitude lower than the preliminary assessment might suggest). I suggest, therefore, that the stream oily discharge impacts be increased by a factor of ten, or alternatively the allowable disposal level decreased by a factor of ten, over the estimates of the planned preliminary procedure. This correction can be viewed as neglecting stream

contamination that affects less than 10% of the total stream area. Since the purpose of the preliminary assessment is identification of potential problems requiring further analysis, I do not feel that this factor is unduly conservative.

Let me close by making a few statements about the more sophisticated analysis that will be necessary to more quantitatively assess the impact of landfill disposal of oily wastes on stream quality. The basic transport processes as outlined by Dr. McCutcheon should be included in the analysis. In addition, however, the original listing of contaminant and stream processes neglected the importance of adsorption and subsequent redistribution of contaminants through sediment movement. The oil spill literature would indicate that this is a significant fate and transport mechanism.

The partitioning of the oily wastes between films, drops, pools and emulsions is heavily dependent upon the stream velocity. This suggests that the more sophisticated modeling approach planned for the second stage must explicitly consider the pool-riffle nature of most streams. Stream morphology will likely control the fate and transport of the oily wastes. If the preliminary assessment suggests that this more detailed analysis is necessary, I would be happy to provide additional information such as current references in this area, and provide any other assistance that I can.

# HydroAnalysis Inc

PO Box 6  
Acton, Massachusetts 0172  
(617) 263-48

March 11, 1988

Ref: JOE-REV

Mr. Brian Bicknell  
Aqua Terra Consultants  
2672 Bayshore Parkway, Suite 1001  
Mountain View, CA 94043-1011

Subject: Review of USEPA Draft Oily  
Wastes Procedure

Dear Brian:

The following are my review comments on the draft procedure to analyze oily wastes in streams prepared by Steve McCutcheon of the USEPA Athens Environmental Research Laboratory. My review includes two main sections: one focusing on technical comments and the other on the draft document. My comments in these two sections have rather different focuses. The first section is primarily technical in nature. The second section derives, at least in part, from my experience in working for the American Petroleum Institute (API). My experience with API includes critical review and drafting letters of comment on past proposed EPA regulations and guidance. I have tried to anticipate the kind of comments that might be received from API and the wood-treating industry. I hope this perspective will be helpful in preparing the final document.

## Technical Comments

In general, I believe the proposed procedure is technically sound as a preliminary screening procedure. I think that eventually it would be useful to investigate a more complete phenomenological model of oil behavior in streams. Such an investigation would initially be a research effort but could lead to a useful assessment and regulatory tool.

There are several specific technical items that I believe need further review. Some of these are a reiteration of comments I made in the review meeting on February 26, but I thought it would be useful to record them in writing.

One technical concern (that also has regulatory implications) is the definition of oily wastes. The oily wastes of the wood-treating industry may behave very differently in the environment than petroleum fuel oils. The major oily wastes from the wood-treating industry include the following:

- o Creosote oils and coal-tar derived oils - Coal-tar derived oils are substantially heavier than water and behave in the environment accordingly.
- o Creosote/oil mixtures - Creosote is often mixed with a carrier oil for use as a wood preservative. Typically, a lighter-than-water fuel oil is used as the carrier.
- o Pentachlorophenol - Pentachlorophenol is also often mixed with a carrier oil. The type of oil depends upon the application. Fuel oils are used for most woods, but mineral oil may be used for some fine woods (for example, treated wood doors and windows).

The density of creosote oil and coal tar is a significant factor in their environmental transport. I am sending to Steve McCutcheon two papers by Villaume et al. (1983 and 1985) on a coal-tar contamination site and his analysis of the density effects on subsurface transport. The particular site he worked on is an inactive coal-gas plant that was first discovered to be a problem when coal tar seeped into an adjacent stream. I am also sending another paper by Lafornera et al. (1982) on the same site and a chapter from the rough draft of a wood-treating site handbook prepared by

ERT. The handbook was never completed, so I am sending a draft as the best copy available. Nonetheless, I think it supplies useful general background on oils from the wood-treating industry.

The discussion in the draft oily wastes document of regulations for solvents is somewhat misplaced. As far as I know, there are no regulations for solvents per se. Rather, certain solvents (including many chlorinated organic solvents) are regulated because they are toxic. On the other hand, a great many solvents are not particularly toxic and thus are not regulated. The latter include alcohols, ethers and many petroleum-based solvents.

The formula presented in the document to calculate the limit on oily material flux to avoid formation of visible oils may not be conservative. The formula is:

$$q_{oil} = T K Q/D$$

This formula assumes a uniform distribution of oil over the entire water surface. This neglects the ability of floating oily material to collect and reconcentrate in a small fraction of the water-body surface. Perhaps a quiescent area coefficient that accounts for the turbulence of the stream could be included in the formula. In a highly turbulent stream the quiescent area would be a small fraction of 1. In a very slow-moving stream or backwater it would be nearly 1.

The turbulence environment of riffle-and-pool streams was discussed several times in the February 26 meeting. I am sending to Steve a paper by Bencala and Walters (1983) on solute transport in a riffle-and-pool stream that might be useful in developing an oil transport model.

The issue of toxicity is somewhat confused in the draft document. I recommended in the meeting that this procedure should deal with the physical and toxicological properties that pertain to oily wastes generically. For example, toxic effects that this procedure can validly address include interference with gill mechanisms by oil emulsion droplets, toxicity to benthic organisms by blanketing with oil, effects on insects through interference with emergence, etc. The method should not include toxicity due to trace compounds found in some oils. This type of toxicity is adequately treated by chemical-specific criteria and approaches. Moreover, the trace chemical makeup of various



oils may differ widely (for example, wood-treating oils vs petroleum hydrocarbon fuels). But the toxicity of oils due to their oily character should be generically similar.

On a related topic, the last section of the document discusses more work on dissolution of chemicals from oily wastes. I think this is worthwhile, but again I recommend a generic approach. For example, rather than assume specific chemicals to be present at certain concentrations in oily wastes, the procedure should be a general method to calculate dissolution of any chemical species from the oil. The method could then be applied to a particular oily waste using specific data on the constituents in that oil.

Overall, I was impressed with the literature research that went into the proposed procedure and found it a very credible piece of work. The complexity of oil transport necessitates an incremental approach to model development, and the proposed procedure is an appropriate and valid first step. Eventually, more complex models may be desired, but the general approach proposed in the draft procedure is valid and useful for screening analyses. Nonetheless, the special properties of oil are incompletely accounted for in the current approach and the approach is vulnerable to criticism if it is characterized as anything more than a simple screening tool.

#### Comments on Document

I found the document that presents the procedure to be confusing and difficult to follow. A particular confusion is a failure to distinguish discussions that apply to eventual future development of a sophisticated model and those which apply to the formulae presented in the procedure. Many concepts are presented that are not actually used in the proposed procedure. To correct this confusion a reorganization of the document is needed. One suggestion for overall organization is the following:

- o Introduction - objectives of the proposed procedure with a specific discussion of use in the RCRA permitting process
- o Background - why oily waste is a problem requiring the special attention of this procedure as a part of landfill permitting

- o Criteria - water quality criteria applicable to oily waste (including the formal EPA criteria and the API classification of oil thickness visibility)
- o Physical phenomena - a generic discussion that catalogs the important physical, chemical and biological phenomena affecting oily waste in the environment
- o Proposed procedure - presenting the proposed procedure as a screening approach
- o Future work - discussing technical areas needing further study and planned future work, perhaps proposing eventual development of a sophisticated model of oily wastes

I think an organization such as this that clearly separates the proposed procedure from physical phenomena that are discussed but not actually included in the procedure would make the document much easier to follow.

The language in the document is equivocal in many places. Phrases like "it seems that", "it may be that", "it is not clear how", etc. make the document seem ambiguous and less well thought through than it is. Before releasing the document for public comment, the tone of the document should be strengthened by eliminating the type of phrases listed above.

The document also needs to be edited with respect to references to criteria and regulations. The references to regulations should include specific citations of the Code of Federal Regulations or Federal Register. The references as they are now are not specific and give an impression that the procedure is only vaguely related to a regulatory purpose.

The discussion of criteria would benefit from a review by the criteria experts in the Criteria and Standards Division. While I do not believe there are any errors in the discussion as it is now, the document is not written with the usual terminology of water-quality criteria. There are also many more recent references available on oil toxicity to aquatic species that should be included in the discussion. I do not believe any of these would change the proposed procedure, but would strengthen the document prior to release for public comment.

I hope these comments and the references I have furnished will be helpful. I appreciate the opportunity to participate in reviewing this approach to a very interesting technical problem, and I look forward to following the work as it progresses. If you have any questions on the above or if I can supply further information, please call me at (617) 263-4857.

Sincerely,

*Pete Shanahan*

Peter Shanahan, Ph.D., P.E.

cc: S. McCutcheon, EPA

*Return to Jim*

March 7, 1988

Dr. Steve C. McCutcheon  
USEPA FRL-Athens  
Athens, GA 30613

Dear Steve,

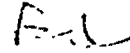
I have begun the process of collecting the material I said I would provide. Enclosed you will find a disk and the manuals for the FWS habitat evaluation procedure (HEP) and the microcomputer version of the habitat suitability index (HSI) models. With the report I left with you should be able to figure out what is going on with the HSI models. We have found that you will need the species reports available from Ft. Collins to select the proper responses in the HSI analysis. I think you should be able to adapt an HSI analysis as a add on to your proposed model although the run time of this version is pretty slow. You might want to begin interacting with the people at Ft. Collins where HSI and HEP is centered. I am enclosing a copy of the new HEP newsletter, you might want to request some of the new HSI models listed in this issue. You might also want to contact the R&D people at the Division of Biological Services, USFWS in Washington. Also you might want to get a copy of Biological Report 25(6), December 1984 Proceedings of a Workshop on Fish Habitat Suitability Index Models which reviews the scientific underpinning of HSI models.

I have also included a copy of the report I mentioned which may help in developing width and depth values for analysis. This report is one of a series produced by Skip Stall and Ted Yang in the early 70's. I recommended that this approach be used in a 13a assessment of instream flow needs. Back in 1976-77 the FWS was developing initial approaches to IFN analysis. I am enclosing my recommendation memo, you may be interested in the development of climo-physiographic regions. I can reconstruct who was doing this work, but after ten years I am sure few of the same people are around now. Please share this report with Tom, he said he needed an approach to develop width and depth for another project.

I have begun my search for pool/riffle information. To that end I am enclosing a copy of another Stall and Yang report which touches on the issue and a copies of several papers on riffles and pools. I also looked through my collection of reprints and am enclosing a paper by Keller and Melhorn which is directly related to the pool-riffle question, and a section from Richard's book on pool-riffle spacing. This is a big topic and these papers only scratch the surface. I think it will be enough to further thinking on stream impact assessment.

I am received the copies of your overheads on Friday and will work to finalize a short critique paper based on those materials and our phone conversation. If you have any questions, please call (217)333-0997.

With best regards,



Edwin E. Herricks  
Associate Professor of  
Environmental Biology

cc:Brian Bicknell

## APPENDIX II

### 1986 "Gold Book" Criteria for Oil and Grease

The following criteria are reproduced from Quality Criteria for Water 1986 (U.S. EPA Rep. 440/5-86-001 with updates 1 & 2, 1987). Tables 6 and 7 referred to in the criteria document are reproduced from the "Red Book," Quality Criteria for Water 1976 (U.S. EPA 1976).

## OIL AND GREASE

### CRITERIA:

For domestic water supply: Virtually free from oil and grease, particularly from the tastes and odors that emanate from petroleum products.

For aquatic life:

- (1) 0.01 of the lowest continuous flow 96-hour LC50 to several important freshwater and marine species, each having a demonstrated high susceptibility to oils and petrochemicals.
- (2) Levels of oils or petrochemicals in the sediment which cause deleterious effects to the biota should not be allowed.
- (3) Surface waters shall be virtually free from floating nonpetroleum oils of vegetable or animal origin, as well as petroleum-derived oils.

### INTRODUCTION:

It has been estimated that between 5 and 10 million metric tons of oil enter the marine environment annually (Blumer, 1970). A major difficulty encountered in the setting of criteria for oil and grease is that these are not definitive chemical categories, but include thousands of organic compounds with varying physical, chemical, and toxicological properties. They may be volatile or nonvolatile, soluble or insoluble, persistent or easily degraded.

### RATIONALE:

Field and laboratory evidence have demonstrated both acute lethal toxicity and long-term sublethal toxicity of oils to aquatic organisms. Events such as the Tampico Maru wreck of 1957 in Baja, California, (Diaz-Piferrer, 1962), and the No. 2 fuel oil spill in West Falmouth, Massachusetts, in 1969

(Hampson and Sanders, 1969), both of which caused immediate death to a wide variety of organisms, are illustrative of the lethal toxicity that may be attributed to oil pollution. Similarly, a gasoline spill in South Dakota in November 1969 (Bugbee and Walter, 1973) was reported to have caused immediate death to the majority of freshwater invertebrates and 2,500 fish, 30 percent of which were native species of trout. Because of the wide range of compounds included in the category of oil, it is impossible to establish meaningful 96-hour LC50 values for oil and grease without specifying the product involved. However, as the data in Table 6 show, the most susceptible category of organisms, the marine larvae, appear to be intolerant of petroleum pollutants, particularly the water soluble compounds, at concentrations as low as 0.1 mg/L.

The long-term sublethal effects of oil pollution refer to interferences with cellular and physiological processes such as feeding and reproduction and do not lead to immediate death of the organism. Disruption of such behavior apparently can result from petroleum product concentrations as low as 10 to 100 ug/L (see Table 7).

Table 7 summarizes some of the sublethal toxicities for various petroleum pollutants and aquatic species. In addition to sublethal effects reported at the 10 to 100 ug/L level, it has been shown that petroleum products can harm aquatic life at concentrations as low as 1 ug/L (Jacobson and Boylan, 1973).

Bioaccumulation of petroleum products presents two especially important public health problems: (1) the tainting of edible,



aquatic species, and (2) the possibility of edible marine organisms incorporating the high boiling, carcinogenic polycyclic aromatics in their tissues. Nelson-Smith (1971) reported that 0.01 mg/L of crude oil caused tainting in oysters. Moore et al. (1973) reported that concentrations as low as 1 to 10 ug/L could lead to tainting within very short periods of time. It has been shown that chemicals responsible for cancer in animals and man (such as 3,4-benzopyrene) occur in crude oil (Blumer, 1970). It also has been shown that marine organisms are capable of incorporating potentially carcinogenic compounds into their body fat where the compounds remain unchanged (Blumer, 1970).

Oil pollutants may also be incorporated into sediments. There is evidence that once this occurs in the sediments below the aerobic surface layer, petroleum oil can remain unchanged and toxic for long periods, since its rate of bacterial degradation is slow. For example, Blumer (1970) reported that No. 2 fuel oil incorporated into the sediments after the West Falmouth spill persisted for over a year, and even began spreading in the form of oil-laden sediments to more distant areas that had remained unpolluted immediately after the spill. The persistence of unweathered oil within the sediment could have a long-term effect on the structure of the benthic community or cause the demise of specific sensitive important species. Moore et al. (1973) reported concentrations of 5 mg/L for the carcinogen 3, 4-benzopyrene in marine sediments.

Mironov (1967) reported that 0.01 mg/L oil produced deformed and inactive flatfish larvae. Mironov (1970) also reported inhibition or delay of cellular division in algae by oil

concentrations of  $10^{-4}$  to  $10^{-1}$  mg/L. Jacobson and Boylan (1973) reported a reduction in the chemotactic perception of food by the snail, Nassarius obsoletus, at kerosene concentrations of 0.001 to 0.004 mg/L. Bellen et al. (1972) reported decreased survival and fecundity in worms at concentrations of 0.01 to 10 mg/L of detergent.

Because of the great variability in the toxic properties of oil, it is difficult to establish a numerical criterion which would be applicable to all types of oil. Thus, an application factor of 0.01 of the 96-hour LC50 as determined by using continuous flow with a sensitive resident species should be employed for individual petrochemical components.

There is a paucity of toxicological data on the ingestion of the components of refinery wastewaters by humans or by test animals. It is apparent that any tolerable health concentrations for petroleum-derived substances far exceed the limits of taste and odor. Since petroleum derivatives become organoleptically objectionable at concentrations far below the human chronic toxicity, it appears that hazards to humans will not arise from drinking oil-polluted waters (Johns Hopkins Univ., 1956; Mckee and Wolf, 1963). Oils of animal or vegetable origin generally are nontoxic to humans and aquatic life.

In view of the problem of petroleum oil incorporation in sediments, its persistence and chronic toxic potential, and the present lack of sufficient toxicity data to support specific criteria, concentrations of oils in sediments should not approach levels that cause deleterious effects to important species or the

bottom community as a whole.

Petroleum and nonpetroleum oils share some similar physical and chemical properties. Because they share common properties, they may cause similar harmful effects in the aquatic environment by forming a sheen, film, or discoloration on the surface of the water. Like petroleum oils, nonpetroleum oils may occur at four levels of the aquatic environment: (a) floating on the surface, (b) emulsified in the water column, (c) solubilized, and (d) settled on the bottom as a sludge. Analogous to the grease balls from vegetable oil and animal fats are the tar balls of petroleum origin which have been found in the marine environment or washed ashore on beaches.

Oils of any kind can cause (a) drowning of waterfowl because of loss of buoyancy, exposure because of loss of insulating capacity of feathers, and starvation and vulnerability to predators because of lack of mobility; (b) lethal effects on fish by coating epithelial surfaces of gills, thus preventing respiration; (c) potential fishkills resulting from biochemical oxygen demand; (d) asphyxiation of benthic life forms when floating masses become engaged with surface debris and settle on the bottom; and (e) adverse aesthetic effects of fouled shorelines and beaches. These and other effects have been documented in the U.S. Department of Health, Education and Welfare report on Oil Spills Affecting the Minnesota and Mississippi Rivers and the 1975 Proceedings of the Joint Conference on Prevention and Control of Oil Spills.

Oils of animal or vegetable origin generally are chemically nontoxic to humans or aquatic life; however, floating sheens of

such oils result in deleterious environmental effects described in this criterion. Thus, it is recommended that surface waters shall be virtually free from floating nonpetroleum oils of vegetable or animal origin. This same recommendation applies to floating oils of petroleum origin since they too may produce similar effects.

(QUALITY CRITERIA FOR WATER, JULY 1976) PB-263943  
SEE APPENDIX C FOR METHODOLOGY

Table 6

Summary of lethal toxicities of various petroleum products to aquatic organisms (a thorough discussion of duration and test conditions is found in Moore, Dwyer & Katz, 1973)

TYPE ORGANISM	Substrate	Dispersants	1,2 Dodecyl Benzene	Crude Oil	Gasoline	Diesel Fuel	Marine Oil	Substrate Residuals	Acute Toxicity Grade
Marine Flora	(29) (29) 10 ppm-100 ppm	(29) (31) 1.0 ppm-100 ppm	(31) 100 ppm	(31) Toxic to many salt water plants			(14) 10 ppm		(29) C <sub>32</sub> H <sub>66</sub> note
Fish	(29) (29) 10 ppm-100 ppm	(29) (29) 1.0 ppm-100 ppm	(40) 550 mg/L (ppm)	(31) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	Significant than lethal toxicity
Larvae and Eggs	(28) (29) 0.1 ppm-1 ppm	(29) (29) 1 ppm-10 ppm	(31) 100 ppm	(31) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Pelagic Crustacea	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Benthic Crustacea	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Gastropods	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Bivalves	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Other Benthic Invertebrates	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Freshwater Fish	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Freshwater Flora	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	
Marine & Birds	(29) (29) 10 ppm-100 ppm	(29) (29) 1 ppm-10 ppm	(29) 100 ppm	(29) 100 ppm	(29) 10 ppm	(29) 10 ppm	(14) 10 ppm	(29) 100 ppm-1000 ppm	

Note: 1) Numbers in brackets represent reported values (volume to volume or weight to volume basis) converted to ppm.  
 2) Numbers in parentheses refer to references.  
 3) Asterisks indicate values estimated by Moore, Dwyer, & Katz, 1973 (no other estimates are supported by examples given therein).  
 4) In some cases, the above values have been taken from summary type publications (for example: Moore, Dwyer & Katz, 1973); the corresponding reference numbers therefore do not necessarily refer to the original publication.  
 5) The number in which the above values are reported is only an attempt to summarize the ranges in threshold lethal toxicities, based on some of the existing published data, and should not be regarded as absolute limits of toxicity for a given category of toxicant or test organism. It must be understood that there are numerous additional published data that fall within the ranges suggested above, and possibly data that may suggest further extending these ranges. It is not the author's intention to herein summarize all of the toxicity values reported thus far for petroleum and petroleum products.

TABLE 7  
SUMMARY OF SOME SUBLETHAL EFFECTS OF PETROLEUM PRODUCTS ON MARINE LIFE

TYPE ORGANISM	SPECIES	REFERENCE	TYPE PETROLEUM PRODUCT	CONCENTRATION	SUBLETHAL EFFECTS
Marine Flora					
	phytoplankton ( <i>Chlorella vulgaris</i> )	Enns, et al., 1972 <sup>1</sup>	crude Naphthalene	1 ppm	suppress growth Reduction of bicarbonate uptake
	phytoplankton ( <i>diatoms and dinoflagellates</i> )	Mironov, 1970 <sup>1,2</sup>	"oil"	10 <sup>-1</sup> 10 <sup>-4</sup> ppm	Inhibition or delay in cellular division
	phytoplankton ( <i>Asterionella muhlenbergii</i> )	Aubert, et al., 1969 <sup>1</sup>	Kerosene	0.01-35 ppm	Depression of growth rate
	phytoplankton ( <i>Phaeodactylum tricornutum</i> )	Lacaze, 1967 <sup>1</sup>	Kuwait crude	"1 ppm"	Depression of growth rate
	phytoplankton ( <i>Nannochloris lutheri</i> )	Strand, et al., 1971 <sup>1</sup>	Kuwait crude; dispersant emulsions	20-100 ppm	Inhibition of growth; reduction of bicarbonate uptake at 50 ppm
	phytoplankton ( <i>Phaeodactylum tricornutum</i> , <i>Skeletonema costatum</i> , <i>Chlorella</i> sp., <i>Chlamydomonas</i> sp.)	Shari, 1973 <sup>1</sup>	Extracts of oilboard motor oils, No. 6 fuel oil, No. 2 fuel oil.		
	phytoplankton	Jordan and Prouse, 1973 <sup>1</sup>	Venezuelan crude, No. 2 and 6 fuel oils.	10-200 µg/l (ppm)	stimulation of photosynthesis at 10-20 µg/l decrease in photosynthesis at 100-200 µg/l No. 2 fuel oil.
Larvae and Eggs	Yelp ( <i>Paracalanus crassirostris</i> )	Wilber, 1968 <sup>1,2</sup>	Toluene	10 µg	75% reduction in photosynthesis within 96 hr
	Lichen ( <i>Lichen pyrenaeus</i> )	Brown, 1972 <sup>1</sup>	Kuwait crude, 10 <sup>100</sup>	0.1-100 ppm	0.1 ppm significantly decrease total C <sup>14</sup> fixation
	Pink Salmon fry ( <i>Oncorhynchus gorbuscha</i> )	Rice, 1973	Trudhoe Bay crude	1.6 ppm	avoidance effects; could have effect on migration behavior
	Black sea turbot ( <i>Psetta maxima</i> )	Mironov, 1967	"oil"	0.01 ppm	Irregularity and delay in hatching—resulting larvae deformed and inactive
	Pluteo larvae ( <i>Alpheoidea</i> )	Wilson, 1970 <sup>1,2</sup>	No. 1002	0-10 ppm	Disruption of embryonic and feeding behavior
	Cod fish larvae ( <i>Gadus morhua</i> )	McDonald, 1970 <sup>1</sup>	Iranian Crude	Aqueous extracts from 10 <sup>10</sup> ppm, 10 <sup>100</sup> ppm	Adverse effect on behavior leading to death
	Labster larvae ( <i>Homarus americanus</i> )	Wells, 1972 <sup>1</sup>	Venezuelan crude	5 ppm	Delay molt to 4th stage
	Sea Urchin larvae ( <i>Echinocysta</i> )	Allen, 1971 <sup>1,2</sup>	extracts of Number C	0.1-1 ppm	Interference with fertilized egg development
	Paramecia larvae ( <i>Paramecium</i> )	Mironov, 1970	"oil"	0-100 µg/l (ppm)	Stimulated development
	Crab larvae ( <i>Decapodidae</i> )	Mironov, 1970	"oil"	10-100 µg/l (ppm)	Initial increase in population

SUMMARY OF SOME SUBLETHAL EFFECTS OF PETROLEUM PRODUCTS ON MARINE LIFE

TYPE ORGANISM	SPECIES	REFERENCE	TYPE PETROLEUM PRODUCT	CONCENTRATION	SUBLETHAL RESPONSE
FISH	Chinook salmon ( <i>Oncorhynchus tshawytscha</i> )	Kneib & Bailey, 1975 <sup>1</sup>	Kerosene	5, 10 ppm	Initial increase in respiration.
	Striped bass ( <i>Morone saxatilis</i> )	Gardner, et al, 1973	Crude (volatile fractions water-soluble) (water-insoluble)	150 ppm (v/v) 10 ppm estimated 450 ppm (v/v)	Metabolic damage to chemoreceptors.
CRUSTACEANS	Lobster ( <i>Homarus americanus</i> )	Blumer, et al, 1973	Crude, kerosene	10 ppm	Effects of chemoreception, feeding time, stress behavior, aggression, growth.
	<i>Polydora polychaeta</i>	Straughan, 1972	Crude-Santa Barbara	Field study after blowout.	Apparent decrease in adult breeding; no recruitment in ciliated areas.
	Lobster ( <i>Homarus americanus</i> )	Arma and Stein, 1972	No. 2 Fuel oil	Extracts	Delay in feeding.
	<i>Pachystacus crassius</i>	Kittredge, 1971 <sup>1</sup>	Crude	Extractions of diethyl ether extracts (100%)	Inhibition of feeding.
	<i>Uca pinnata</i>	Krebs, 1973 <sup>1</sup>	No. 2 Fuel oil	Field observations after N. Falmouth spill	Adverse effects on sexual behavior.
MOLLUSCS	Mussel ( <i>Mytilus edulis</i> )	Gillfillan, 1973 <sup>2</sup>	Crude	1 ppm	Reduction in carbon budget (increase in respiration; decrease in feeding.)
	Snail ( <i>Massaria abscissa</i> )	Blumer, et al, 1973	Kerosene	Saturated extract diluted 10:10	80% reduction in chemotactic perception of food.
	Snail ( <i>Massaria abscissa</i> )	Jackson & Boylen 1973	Kerosene	0.001 - 0.004 ppm	Reduction in chemotactic perception of food.
	Clam ( <i>Vespa arenaria</i> )	Kerry and Yovich, 1974	No. 2 fuel oil	collected from field	Oncosal tumors.
	Oyster ( <i>Crassostrea virginica</i> )	Hackin and Hopkins, 1961	Bleedwater		Reduced growth and nitrogen content.
	Shell ( <i>Littorina littorea</i> )	Perkins, 1970 <sup>1</sup>	BP 1002	30 ppm	significant inhibition to growth.
	Oyster ( <i>Crassostrea virginica</i> )	Menzel, 1948; in Holsay-Smith, 1973	"oil"	0.01 ppm	marked tainting.
	Mussel ( <i>Mytilus edulis</i> )	Blumer, et al, 1971 <sup>1</sup>	No. 2 fuel oil	collected from field after spill	Inhibition in development of adults.
OTHER MARINE INVERTEBRATES	Polychaeta ( <i>Capitella capitata</i> )	Bellan, et al, 1972 <sup>1</sup>	Detergent	0.01-10 ppm	Decrease in survival, fecundity.

Note: <sup>1</sup> Taken from National Academy of Sciences, 1975  
<sup>2</sup> Taken from Moore, Beyer, and Katz, 1973.

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APPENDIX III

PARAMETERS EXPECTED IN THE DATA BASE FOR HAZARDOUS CHEMICALS  
DEVELOPED FOR THE OFFICE OF SOLID WASTES

Parameters in the Data Base - WASTBASE



# DPRA

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1/15/87

Agnes Ortiz  
EPA  
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Dear Ms. Ortiz:

Here is a list of the variables contained in the data set WASTBASE, for use with the dBASE III menu system WASTE BASE. The following chemical parameters: molecular weight; acid- and base-catalyzed and neutral hydrolysis; half-life for volatilization from water; Henry's law constant; Octanol-Water partition coefficient; water solubility; and vapor pressure are present in the data set. The number and percentage of records for which non-blank, non-zero values for these parameters exist are given along with variable definitions.

ACIDH<sup>1</sup>DR: *acid hydrolysis rate constant* units are  $M^{-1}$   
Half-life for acid-catalyzed hydrolysis, in hours  
unless otherwise noted;  
(15 non-zero values; 2.5% of compounds).

updating → APP8: Flag indicating appearance of substance in 40 CFR part appendix VIII.

APP9: Flag indicating appearance on groundwater monitoring list, "Appendix IX".

BASEHYDR: *base hydrolysis rate constant*  $M^{-1} hr^{-1}$   
~~Half-life for base-catalyzed hydrolysis, in hours~~  
unless otherwise noted;  
(58 non-zero values; 9.6%).

pdating → CA: Maximum concentration of substance in a waste under "California list" (FR vol. 51 no. 102).

CANCER: Flag indicating carcinogenicity.

→ CASNAME: Chemical Abstracts Service Registry name (9th Collective Index).

→ CASNO: CAS Registry number.

CHARACT: Characteristic(s) for which substance is listed.

→ COMPOUND: Common name of substance used in some regulatory documents.

CYN: Indicates presence of cyanide moiety and form (free or bound).

DESCRIP1: For F and K wastes, first 200 characters of description given in 40 CFR part 261, subpart D. (261.3)

DESCRIP2: Second 200 characters of description.

DESCRIP3: Third 200 characters of description.

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FN1ST3RD: Flag indicating assignment of substance to first third of schedule for land disposal restriction under the final rule (FR vol. 51 no. 102).

FN2ND3RD: Indicates assignment to second third of schedule for land disposal restriction under final rule.

FN3RD3RD: Indicates assignment to third third of schedule for land disposal restriction under final rule.

GROUPA: Flag indicating assignment to group A of first third of schedule for land disposal restrictions under proposed relisting.

GROUPB: Indicates assignment to group B of first third of schedule for land disposal restrictions under proposed relisting.

GROUPC: Indicates assignment to group C of first third of schedule for land disposal restrictions under proposed relisting.

HFLF: Half-life, for volatilization from water at STP; (137 non-blank values; 23%).

HLAW: Henry's law constant (unitless); (137 non-zero values; 23%).

HORG: Element symbol for halogen present in substance.

LOG\_KOW: Log of the Octanol-Water partition coefficient (unitless); (137 non-zero values; 23%).

METAL: Element symbol for toxic metal in substance.

MOLEWT: Molecular weight of substance; (344 non-blank values; 57%).

NAME: Common name used in other regulatory documents.

NEUTHYDR: ~~Half-life for hydrolysis under neutral conditions, in hours unless otherwise noted;~~ <sup>neutral rate constant</sup> ~~in~~ <sup>hr</sup> (64 values; 10.6%).

PCB: Flag indicating that substance is a poly-chlorinated biphenyl.

REFNO: Number by which published data source is indexed in CIS.

OTC REGLEVEL: Threshold concentration, in mg/l, of a substance in a leachate of a waste obtained by the Toxicity Characteristic Leaching Procedure (TCLP; FR vol. 51 no. 114)

RELIST: A list of F and K wastes of which substance is a constituent, taken from the document presenting the proposal for relisting the schedule for land disposal restrictions.

RL1ST3RD: Flag indicating assignment to first third under proposed relisting.

RL2ND3RD: Flag indicating assignment to second third under proposed relisting.

RL3RD3RD: Flag indicating assignment to third third under proposed relisting.

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SOLTEMP: Temperature at which solubility measurement was taken.  
SOLUB: Solubility in water;  
(137 non-zero values; 23%).  
SOLUNITS: Units for solubility measurement.  
SORTK: String beginning with first alphabetic character of  
COMPOUND; key by which substances are sorted in some  
published lists.  
SORTKEY: Corresponds to SORTK, but based on NAME rather than  
COMPOUND.  
VPRESS: Vapor Pressure at one atmosphere;  
(12 non-zero values; 2%).  
VPTMP: Temperature of vapor pressure measurement.  
WASTCODE: EPA Hazardous Waste Number (40 CFR part 261).  
WSTREAM: Corresponds to RELIST, but based on 40 CFR part 261  
appendix VII.

Data quality assurance is continuing for all variables.

Yours truly,



Karl A. Anderson  
Analyst