ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

OIL SPILLS ENTRY

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Like a library or many large databases (such as EPA's national STORET water quality database), this document contains information of variable quality from very diverse sources. In compiling this document, mistakes were found in peer reviewed journal articles, as well as in databases with relatively elaborate quality control mechanisms [366,649,940]. A few of these were caught and marked with a "[sic]" notation, but undoubtedly others slipped through. The [sic] notation was inserted by the editors to indicate information or spelling that seemed wrong or misleading, but which was nevertheless cited verbatim rather than arbitrarily changing what the author said.

Most likely additional transcription errors and typos have been added in some of our efforts. Furthermore, with such complex subject matter, it is not always easy to determine what is correct and what is incorrect, especially with the "experts" often disagreeing. It is not uncommon in scientific research for two different researchers to come up with different results which lead them to different conclusions. In compiling the Encyclopedia, the editors did not try to resolve such conflicts, but rather simply reported it all.

It should be kept in mind that data comparability is a major problem in environmental toxicology since laboratory and field methods are constantly changing and since there are so many different "standard methods" published by EPA, other federal agencies, state agencies, and various private groups. What some laboratory and field investigators actually do for standard operating practice is often a unique combination of various standard protocols and impromptu "improvements." In fact, the interagency task force on water methods concluded that [1014]:

> It is the exception rather than the rule that water-quality monitoring data from different programs or time periods can be compared on a scientifically sound basis, and that...
>
> No nationally accepted standard definitions exist for water quality parameters. The different organizations may collect data using identical or standard methods, but identify them by different names, or use the same names for data collected by different methods [1014].

Differences in field and laboratory methods are also major issues related to (the lack of) data comparability from media other than water: soil, sediments, tissues, and air.

In spite of numerous problems and complexities, knowledge is often power in decisions related to chemical contamination. It is therefore often helpful to be aware of a broad universe of conflicting results or conflicting expert opinions rather than having a portion of this information arbitrarily censored by someone else. Frequently one wants to know of the existence of information, even if one later decides not to use it for a particular application. Many would like to see a high percentage of the information available and decide for themselves what to throw out, partly because they don't want to seem uniformed or be caught by surprise by potentially important information. They are in a better position if they can say: "I knew about that data, assessed it based on the following quality assurance criteria, and decided not to use it for this application." This is especially true for users near the end of long decision processes, such as hazardous site cleanups, lengthy ecological risk assessments, or complex natural resource damage assessments.

For some categories, the editors found no information and inserted the phrase "no information found." This does not necessarily mean that no information exists; it simply means that during our efforts, the editors found none. For many topics, there is probably information "out there" that is not in the Encyclopedia. The more time that passes without encyclopedia updates (none are planned at the moment), the more true this statement will become. Still, the Encyclopedia is unique in that it contains broad ecotoxicology information from more sources than many other reference documents. No updates of this document are currently planned. However, it is hoped that most of the information in the encyclopedia will be useful for some time to come even without updates, just as one can still find information in the 1972 EPA Blue Book [12] that does not seem well summarized anywhere else.

Although the editors of this document have done their best in the limited time available to insure accuracy of quotes or summaries as being "what the original author said," the proposed interagency funding of a bigger project with more elaborate peer review and quality control steps never materialized.

> The bottom line: The editors hope users find this document useful, but don't expect or depend on perfection herein. Neither the U.S. Government nor the National Park Service make any claims that this document is free of mistakes.

The following is one chemical topic entry (one file among 118). Before utilizing this entry, the reader is strongly encouraged to read the README file (in this subdirectory) for an introduction, an explanation of how to use this document in general, an explanation of how to search for power key section headings, an explanation of the organization of each entry, an information quality discussion, a discussion of copyright issues, and a listing of other entries (other topics) covered.

See the separate file entitled REFERENC for the identity of numbered references in brackets.

HOW TO CITE THIS DOCUMENT: As mentioned above, for critical applications it is better to obtain and cite the original publication after first verifying various data quality assurance concerns. For more routine applications, this document may be cited as:

> **Irwin, R.J., M. VanMouwerik, L. Stevens, M.D. Seese**, and **W. Basham.** 1997. Environmental Contaminants Encyclopedia. National Park Service, Water Resources Division, Fort Collins, Colorado. Distributed within the Federal Government as an Electronic Document (Projected public availability

on the internet or NTIS: 1998).

Oil Spills (Petroleum Hydrocarbon Spills, Spilled Oil in General)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

NOTE: This entry is different from all the others in this volume in that it is a topic rather than a specific compound or petroleum product. As such, it does not fit well into the standard format. As a result, some sections are quite long and there is some overlap between sections. One lengthy non-standard section, abstracts, was added at the end to benefit digital users. The hardcopy reader is encouraged to scan all the sections for the information desired.

Although non-petroleum type oils, such as coconut and other edible oils, might also spill into aquatic environments (approx. 12% of all reported oil spills) [635], this entry is limited to petroleum and/or petroleum product spills. By a wide margin, most of the products derived from petroleum find use as fossil fuels to run vehicles, produce electricity, and to heat homes and businesses. About 65% of the petroleum used as fuel is consumed as gasoline in automobiles [661].

According to the Emergency Notification Response System (ERNS), crude oil, automotive gasoline, and diesel oil are the most often spilled products in the U.S., both by number of notifications and volume [635]. For additional details on the effects of such spills, see Crude Oil, Gasoline, Diesel, and Petroleum General entries. Petroleum products are ubiquitous in the modern environment, leading to contamination problems both for the environment and in sampling activities [661].

Oil spills have occurred in all 50 States [713]. An average of 15 million gallons of petroleum products are spilled yearly in and around the U.S. Approximately one-third of all oil spills occur in inland areas, and over half (55%) of oil spills occur in river channels. Spills in coastal and oceanic areas comprise only 35% of all spills. Other opportunities for exposure to oil occur in association with oil production sites, petroleum refineries, and industrialized locations within the U.S. Most (43%) spills occur during transport over water; another 23% are spilled during land and pipeline transport, 17% are spilled from non-transport land facilities, 11% from marine facilities, and 6% from unknown sources. Winter storms increase the likelihood of transport spills, making January, February, and March the peak spill season [713].

More than 13,000 oil spills of varying magnitude occur in the United States each year [340]. The main source of petroleum product releases between 1987 and 1993 were: fixed facility (36%), marine/offshore incidents (30%), pipeline (13%), highway/rail (13%), unknown (6%), air (1%), and other (1%) [635]. In addition to large oil spills (such as the Ixtoco I, 1979; Exxon Valdez, 1989; and deliberate inputs during the Persian Gulf War, 1990), petroleum hydrocarbons are released into the aquatic environments from natural seeps as well as nonpoint-source urban runoffs [773].

Depending on the exact location of an oil spill, several local, state, and federal agencies may become involved in the response. While taking into account that every oil spill incident is unique, Emergency-preparedness Specialists wishing to maintain familiarity with the myriad laws, regulations, contingency plans and response teams, need to be conversant with:

> EPA's National Oil and Hazardous Substances Pollution Contingency Plan (40 CFR Part 300, March 8, 1990 Federal Register, pages 8666-8865).
>
> The Oil Pollution Act of 1990, which now results in the need to update all the various contingency plans.
>
> National Agency Response Plans, for example, The Fish and Wildlife Service (National) Response Plan of April 18, 1986.
>
> Regional EPA and other agency response plans.
>
> The National Response Team (NRT), Telephone number 800 424-8802 or RCRA Superfund Hotline number 800 424-94346.
>
> Regional Response Teams (RRT)
>
> State Contingency Plan
>
> The Clean Water Act, section 311
>
>> Under section 311 of the Clean Water Act, any person who releases oil and hazardous substances must report the release to the appropriate Federal Agency, who will then immediately notify the appropriate state agencies in states that may be affected by the discharge. A discharge must immediately report an oil spill to the NRC if it: 1)

causes a sheen to appear on the surface of the water, 2) violates applicable water quality standards, 3) causes sludge or emulsion to be deposited beneath the surface of the water or upon adjoining shorelines. If immediate notification to the NRC is not feasible, the spiller may notify the Coast Guard or EPA in the region. Oil notifications account for 57% of all spill notifications to the Emergency Response Notification System (ERNS) [635].

There are electronic sources of information for quickly assessing the extent of risk to biological resources (including human resource issues not completely summarized herein) posed by various hazardous chemicals spilled. The electronic version of this document is useful for fish, wildlife, and other ecotoxicology toxics. However, if human toxicology or safety are the main concerns, another (no government endorsement implied) useful resource is the Micromedex CD-ROM, which includes the entire Coast Guard Chris Manual, EPA's emergency response OHM/TADS data base, the Hazardous Substances Data Bank (developed by the National Library of Medicine), and various other data bases [366]. The National Response Team uses this CD-ROM as one source of information.

Br.Haz: General Hazard/Toxicity Summary:

Acute impacts from massive one-time spills are obvious and substantial. The impacts from small spills and chronic releases are the subject of much speculation and continued research. Clearly, these inputs of petroleum hydrocarbons have the potential for significant environmental impacts, but the effects of chronic low-level discharges can be minimized by the net assimilative capacities of many ecosystems, resulting in little detectable environmental harm [773].

Oil spill effects are related not so much to the gross amount of oil present as to the levels of key toxic components in the particular spilled oil product [468]. Every individual petroleum product has a unique "fingerprint," or distinct combination of concentrations of various polycyclic aromatic hydrocarbons (PAHs) and other petroleum constituents. Due to the varying properties of the same general category of a petroleum product (for example, each source and weathering stage of a No. 6 fuel oil has a unique gas chromatograph "fingerprint"), careful assessment of the toxicity, specific gravity, and other physical characteristics of each individual oil must be considered in order to determine the exact effects of the spilled product on the environment.

See also: PAHs as a group entry.

In general, spilled oil is most harmful when shallow, productive waters, porous sediments, low energy aquatic environments, or special-use habitats are affected. Examples of high risk locations are wetlands, sheltered tidal flats, shallow bays, coarse sand and gravel beaches, and sites with concentrated reproductive and migratory activities [782].

For information on hazardous effects of burning spilled oil, see the "Burning spilled oil" information in the Fate.Detail section below.

Lengthy discussion of the effects of spilled oil vs. plants, invertebrates, fish, and wildlife are found below in the W.Misc. section.

See also Fate.Detail section below for details on the use of chemical dispersants and bioremediation.

Hazard details depend on the exact product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Other sources of information [623]:

> The literature on effects resulting from discharges of oil is extensive and highly multidisciplinary. Much of the literature is "gray" in that it is published in conference proceedings, agency reports, and company documents. One major source of information is the Proceedings of the International Oil Spill Conferences. These conferences have been held biennually since 1969, and the Proceedings published by the American Petroleum Institute in Washington, D.C.

The aquatic toxicity in the water soluble fraction of a sample of middle distillate coal oil was mostly from phenols; the order of impact from the most to the least effected was [970]:

> Cladocerans, fish reproduction, algae, bacteria, and rotifers [970].

Br.Car: Brief Summary of Carcinogenicity/Cancer Information:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

See also: PAHs as a group entry.

Br.Dev: Brief Summary of Developmental, Reproductive, Endocrine, and Genotoxicity Information:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

See also: PAHs as a group entry.

Br.Fate: Brief Summary of Key Bioconcentration, Fate, Transport, Persistence, Pathway, and Chemical/Physical Information:

Alkanes of various types of crude oils and various petroleum products were biodegraded faster than the "unresolved fractions" [975]. Different types of crude oils and products biodegraded at different rates in the same environments [975].

Fate issues vs. generalized response guidelines (clean up methods/ issues):

Selecting appropriate protection, response, and cleanup techniques, both before and following an oil spill, affects the ultimate environmental impact and cost resulting from a spill [777]. Natural resource managers should be familiar with the following key document, prepared by NOAA's Hazardous Response and Assessment Division and the American Petroleum Institute (API), and summarized below [777]:

National Oceanic and Atmospheric Administration (NOAA)/ Hazardous Materials Response and Assessment Division (HMRAD), and the American Petroleum Institute (API). 1994. Options for Minimizing Environmental Impacts of Freshwater Spill Response. 126 pp. [777]

The water environment, shoreline habitat, and the type of oil spilled must be considered when attempting to choose the least adverse response/cleanup method [777]. Water environments include open water (like oceans and seas), large rivers, small lakes/ponds, and small rivers/streams [777]. Shoreline habitat includes bedrock, man-made, sand, vegetated shores, sand and gravel, gravel, mud, and wetlands [777].

There are several different ways to group the various petroleum products. One way is by generalized spill cleanup strategies. Oil properties important for characterizing an oil include flash point, specific gravity/API gravity, viscosity, emulsion formation, and adhesion [777] (see the Chem.Detail sections of individual oil product entries for this information). The following generalized groupings and characteristics (from light to heavy) are used by NOAA to identify basic cleanup options [741,771,777]:

Gasoline Products:

- -Highly volatile.
- -Evaporate quickly, often completely within 1 to 2 days.
- -Highly soluble.
- -Narrow cut fraction with no residue.
- -Low viscosity, spreads rapidly to a thin sheen.
- -High acute toxicity to biota.
- -Do not emulsify.
- -Will penetrate substrate; nonadhesive.
- -Specific gravity less than 0.8.

Diesel-like Products and Light Crudes (Jet Fuels, Diesel, No. 2 Fuel Oil, Kerosene, West Texas Crude):

- -Moderately volatile.
- -Refined products can evaporate with no residue.
- -Light crude will leave residue (up to one-third of spill amount) after a few days.
- -Moderately soluble, especially distilled products.
- -Low and moderate viscosity; spread rapidly into thin slicks.
- -Can form stable emulsions.
- -Moderate to high acute toxicity to biota; product-specific toxicity related to type and concentration of aromatic compounds.
- -Will "oil" intertidal resources; long-term contamination potential.
- -Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments).
- -Tend to penetrate substrate; fresh spills are not adhesive.
- -Stranded light crudes tend to smother organisms.
- -No dispersion necessary.
- -Cleanup can be very effective.
- -Specific gravity of 0.80-0.85; API

gravity of 35-45.

Medium-grade Crude Oils and Intermediate Products (South Louisiana Crude, No. 4 Fuel Oil, Lube Oils):

- About one-third will evaporate within 24 hours.
- Typical water-soluble fraction 10-100 ppm.
- Moderate to high viscosity.
- Variable acute toxicity; depending on amount of light fraction.
- Can form stable emulsions.
- May penetrate substrate and persist.
- May be significant clean-up related impacts.
- Oil contamination of intertidal areas can be severe/long term.
- Stranded oil tends to smother organisms.
- Impact to waterfowl and fur-bearing mammals can be severe.
- Chemical dispersion is an option within 1-2 days.
- Cleanup most effective if conducted quickly.
- Specific gravity of 0.85-0.95; API gravity of 17.5-35.

Heavy Crude Oils and Residual Products (Venezuela Crude, No. 6 Fuel Oil, Bunker C):

- Heavy oils with little/no evaporation or dissolution.
- Water-soluble fraction typically less than 10 ppm.
- Heavy surface and intertidal area contamination likely.
- Highly persistent, long-term sediment contamination possible.
- Less acute toxicity relative to other oil types.
- Very viscous to semisolid; may become less viscous when warmed.
- Can form stable emulsions.
- Weather very slowly. May form tarballs.
- May sink depending on product density and water density.

> NOTE: For a detailed discussion of oil products sinking vs. floating, see the Fate.Detail section below.

- May be significant clean-up related

impacts.
-Heavy contamination of intertidal areas likely.
-Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion).
-Stranded oil tends to smother organisms.
-Dispersion seldom effective.
-Little penetration of substrate likely, but can be highly adhesive.
-Shoreline cleanup difficult under all conditions.
-Specific gravity of 0.95-1.00; API gravity of 10-17.5.

Low API Fuel Oils (LAPIO, Heavy Industrial fuel oils):

-Neutrally buoyant or may sink depending on water density.

> NOTE: For a detailed discussion of oil products sinking vs. floating, see the Fate.Detail section below.

-Weathers slowly; sunken oil has little potential for evaporation.
-May accumulate on bottom under calm conditions and smother subtidal resources.
-Sunken oil may be resuspended during storm events, providing a chronic source of shoreline oiling.
-Highly variable mixtures; often blended with oils.
-Blends may be unstable and the oil may separate when spilled.
-Specific gravity < or = 1.0; API gravity < or = 10.

Additional Source of Information - Oil Spill Bibliography
URL = http://www.lib.lsu.edu/osradp/osradp.html

The Selected Abstracts and Bibliography of International Oil Spill Research is available at the URL listed above. Sponsored by the Louisiana Oil Spill Coordinator's Office/Office of the Governor, in cooperation with the American Petroleum Institute and the Marine Spill Response Cooperation, the bibliography was compiled from searches conducted in 43 separate databases. Over 4,000 citations, some accompanied by abstracts, were retrieved, duplicates eliminated, and the citations were organized alphabetically. A list of the databases searched and keywords and phrases used in the searches are provided. It is noted that the list of keywords used for searching is consistent with the mission of the Louisiana Oil Spill Coordinator's Office; consequently some of the keywords are relevant only for oil spill issues in Louisiana. Abstracts accompany those citations that were pulled from databases providing annotations. The bibliography is available both in WordPerfect 6.0 for Windows or as an ASCII text version. It is not searchable at this time.

See also: PAHs as a group entry.

Synonyms/Substance Identification:

Not applicable, depends on substance spilled.

Associated Chemicals or Topics (Includes Transformation Products):

Readers interested in Oil Spills should also be aware of the following entries:

Petroleum, General
Gasoline, Unleaded
Fuel Oil Number 6
Jet Fuels
Diesel Oil, General

See Crude Oil entry for a more complete list of compounds in Petroleum. For more information on refining, see the "Petroleum, General" entry.

Water Data Interpretation, Concentrations and Toxicity (All Water Data Subsections Start with "W."):

W.Low (Water Concentrations Considered Low):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.High (Water Concentrations Considered High):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Typical (Water Concentrations Considered Typical):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Concern Levels, Water Quality Criteria, LC50 Values, Water Quality Standards, Screening Levels, Dose/Response Data, and Other Water Benchmarks:

W.General (General Water Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Water Concentrations Versus Mixed or General Aquatic Biota):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Plants (Water Concentrations vs. Plants):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

See also: W.Misc. section below.

W.Invertebrates (Water Concentrations vs. Invertebrates):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Fish (Water Concentrations vs. Fish):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Wildlife (Water Concentrations vs. Wildlife or Domestic Animals):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Human (Drinking Water and Other Human Concern Levels):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

W.Misc. (Other Non-concentration Water Information):

General information on oil vs plants:

Mangroves are particularly sensitive to oil pollution [622].

Several experiments were performed to determine the effects of fresh and artificially weathered South Louisiana crude oil on physically isolated plots in a York River, Virginia saltmarsh. Both weathered and unweathered oil had similar effects on Spartina alterniflora: standing stocks were lower than those in the unoiled control treatment [622].

Additional support exists for the contention that weathered oil is at least as toxic to plants as fresh oil. Weathered oil was found to be more toxic to kelp than fresh oil [622].

General information on oil vs invertebrates: See Crude oil entry.

General information on oil vs fish:

Certain life stages may be more vulnerable than others. For example, planktonic fish larvae have a greater potential for exposure because they tend to drift at the same rate as the oil, while adult fish may be able to avoid contaminants [771]. See also: Crude oil entry.

General information on oil vs. birds:

Oiling of feathers is considered to be the primary cause of most bird deaths following oil spills. This results largely in hypothermia and loss of buoyancy [713].

The volume of oil required to cause death of birds is not well known. A small spot of oil on the belly is sufficient to kill murres, and 3-5 mL killed 2 of 3 Cassin's auklets (Ptychoramphus aleuticus). Other species appear to be less sensitive. Visibly oiled gulls, guillemots, and razorbills have successfully cleaned themselves after several weeks. Species that are able to leave the water and thereby reduce or avoid hypothermia (such as gulls, wading birds, and some waterfowl) are presumably more tolerant than more pelagic species (such as auks and murres) [713].

Alcids, cormorants, pelicans, sea ducks, diving ducks, and many other groups exhibit certain types of behaviors that make them vulnerable to spilled oil. These behaviors include feeding, flocking, and roosting in such a way that contact with oil is prolonged or repeated. Other birds, especially herons, egrets, and other wading birds, most shorebirds, and raptors have much lower vulnerability because they are rarely immersed in water and do not flock or roost on the water [713]. The most susceptible birds are those that spend most of their time on the water, and dive rather than fly up when disturbed [713]. Field studies have also shown that some species of birds (such as northern fulmars) are capable of actively avoiding oil on water [713].

Captive birds have been observed to regurgitate and defecate after internal exposure to oil. Mallards dosed internally with oil regurgitated the oil at higher dose levels. Gulls fed oil-stained fish also regurgitated shortly after feeding, and gulls receiving an oral dose of oil in a capsule commonly defecated oil within 10 min [713]. Whether wild oiled birds react to exposure through regurgitation and rapid defecation is not known [713].

Most birds tend to avoid consuming food contaminated with oil [713].

Depressions in food consumption have been documented following acute oral exposure to oil in Coturnix quail [713]. Yet, despite initial avoidance of oil-contaminated food, another common effect of oil exposure is hyperphagia, or increased food consumption. Mallards provided food contaminated with South Louisiana crude oil ate significantly more than birds given uncontaminated food [713].

One experiment found the feeding requirements of birds exposed to relatively low (external) oil coverage (20 g oil/900 g bird) doubled. This increase was associated with an increase in the basal metabolic rate (due to a decrease in body temperature) [713]. These changes vary with species, plumage type, ambient temperature, dose, and oil type [713]. Thermoregulation is also affected by oil that is ingested [713].

The effects of low levels of oil or PAHs on birds is less well documented. Migratory birds can pick up some PAHs from soils, which is reflected in elevated metabolites in bile, but most of these birds are migratory and move on after the original oil insult. Thus, most workers have not found death or reproductive problems, or other chronic impacts upon the birds from low levels of oil or PAHs in soils (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

See also: Crude oil entry.

General information on oil vs. marine mammals:

The nine major groups of marine mammals are baleen whales, toothed cetaceans (like whales and porpoises), fur seals and sea lions, hair seals, walruses, manatees, dugongs (herbivorous), polar bears, and sea otters [713].

There are relatively few oil effect studies on marine mammals, and most of these have involved a small number of animals placed in holding pens with water. From the studies that have been done, the researchers extrapolate to free-ranging animals and sometimes to other species [713]. Because of variation in anatomy, biochemistry, physiology, feeding habits, and behavior among species, responses to oil contamination will vary. Marine mammal response should be considered group by group, and in most cases, species by species [713].

There are few chronic exposure studies with marine mammals. More mobile marine mammals may be able to avoid chronic exposure if they are able to leave the contaminated area [713].

Oil ingested in large quantities can kill polar bears, but seals and cetaceans (whales and porpoises, for example) are more resistant to toxic effects because renal clearance is rapid and they can metabolize petroleum [782].

A spill of crude oil could cause pelagic prey to be temporarily reduced (numbers or availability) for seals, sea lions, fur seals, and toothed whales; and plankton prey of baleen whales could be reduced or contaminated within localized areas. The severity of these effects would depend on the animal's reliance on local and/or seasonally available prey, diversity of preferred prey, and the long-term vulnerability and sensitivity of prey to oil spills [713].

Walruses and bearded seals feed on benthic fauna. Bivalve mollusks, the major prey of walrus, may take up to 10 years or more to recover if the bottom sediment were contaminated by oil. Bearded seals also feed on benthic fauna, but are able to feed on other prey and may not be as severely impacted as walrus. Walruses and bearded seals could consume significant amounts of hydrocarbons from prey in heavily contaminated benthos. Gray whales also scoop food from the benthos and could be affected by contamination [713].

Species that specialize in eating seals or birds might consume raw oil from the pelage (coat) or plumage of contaminated seals or birds. Oiled prey could be more vulnerable to capture, thus increasing the amount of oil predators ingest [713].

The effects of oil on marine mammal reproductive behavior is currently (1994) speculative [713]. Oil could affect mother-young bonds, especially in pinnipeds (seals, walruses) where scent is used to establish mother-pup bonds [713].

An estimated 345 seals were killed due to the Exxon Valdez spill [622].

Killer whale numbers have declined in the area of Prince William Sound since 1989 with 13 known (photo-identified) whales reported missing from a well-studied killer whale pod. Some experts believe that circumstantial evidence links the loss of the 13 whales to the oil discharge. Other experts think the deaths are unrelated to the oil discharge [622].

Impaired responses due to oil contamination could affect an animal's vulnerability to predation [713].

Oil can adversely affect growth rates as indicated by a study on gray seals [713].

The few studies on cetaceans and pinnipeds indicate rapid clearance of oil accumulations. Gastrointestinal clearance in seals is more rapid than for many mammals [713]. Interestingly, after the 1989 Exxon Valdez spill, oil residues found in seal bile were five to six times higher in oiled areas compared with unoiled areas [622].

Oil will probably not adhere to the smoother skinned cetaceans [713]. It is generally not a problem for pinnipeds either because they depend more on a layer of blubber than fur for insulation against cold (except for newborn pups which might be vulnerable to hypothermia for a few days until they accumulate enough fat to insulate them). Also, pinnipeds do not groom as otters do, thus they do not ingest oil from cleaning their pelage (coat) [713].

The effects of oil inhalation depend on the quantity and quality of inhaled vapors [713]. Even just a few milliliters of aspirated regurgitated oil is generally acutely fatal; while relatively large quantities of ingested oil may be tolerated if the oil is rapidly excreted from the gastrointestinal tract. The larynx in a whale has an adaptation to avoid aspirating regurgitated oil [713].

SEA OTTERS:
The sea otter (Enhydra lutris) is considered one of the most vulnerable of marine mammal species to the threat of oil contamination. Otters spend a great deal of their time at the water's surface and also have a relatively strong fidelity to their home range, even if contaminated. Oil exposure may occur through either direct contact with the skin, inhalation, or ingestion, although the evidence suggests that ingestion appears to be the most significant route, especially due to grooming [713]. However, hypothermia is by far the greatest immediate threat to survival for the sea otter after initial oiling [713]. (Contamination by oil eliminates the air layer, allows water to penetrate to the skin, and reduces insulation up to 70% [622].) An oil spill during winter months would be even more hazardous to otter because of the additional energy demands imposed on the animals due to lower water temperatures and rough seas [713].

An estimated 3,500 to 5,500 sea otters were killed by the Exxon Valdez oil discharge (crude oil). Post-discharge surveys showed measurable differences in populations and survival between oiled and unoiled areas in 1989, 1990, and 1991. Dead prime-age animals were still found on beaches in 1990 and 1991 suggesting continuing effects [622].

Sea otters in California show a strong site attachment (fidelity) to kelp beds. These kelp beds have been shown to accumulate oil, leading to the probable contamination of a large number of otter in the event of a spill [713].

Because of the known tendency for benthic macroinvertebrates (clams, mussels, crab, sea urchins, abalone) to accumulate hydrocarbons in their tissues, otters could be impacted through the contamination of their primary food source. This could occur either through direct exposure by eating contaminated food, or indirectly through a reduction in food source [713].

POLAR BEARS:
Research has also shown that a single, 15 min contact with an oil slick can be fatal to polar bears through ingestion of oil by grooming, with subsequent renal failure [713].

Mortality from oil contamination has yet to be documented in free ranging polar bears [713]. It is likely that polar bears would scavenge oil-covered animals (like seals). Polar bears show no aversion to the taste of oil, and have even been noted to bite oil and fuel containers [713].

SUMMARY--MARINE MAMMALS:
No long-term population effects of oil pollution on pinnipeds have been documented (or rigorously examined for long enough periods to do so). Vulnerability of cetaceans to discharges is highest for species with small ranges (coastal, ice-dwelling, and/or riverine habitats), limited diets, poor behavioral flexibility, and small populations. For pinnipeds, stressed or nursing animals and recently weaned pups are most vulnerable. Sea otters and other fur-bearing mammals are the most vulnerable species [622].

General information on oil vs. freshwater mammals:

EUROPEAN and RIVER OTTERS:
Although less information is currently (1994) available, it is clear that both European otter and river otter--both of which inhabit freshwater ecosystems primarily and inter- and sub-tidal zones secondarily--experience a fate similar to sea otter once oiled. While initial mortality was not believed to be extensive, changes in otter diet, body weight, blood parameters, and habitat utilization all indicate that this species continued to experience negative effects at least two years after the Exxon Valdez spill [713].

MUSKRATS:
Little information exists on the effects of oil contamination on the muskrat (Ondatra zibethicus) [713]. One study concluded that it would be doubtful that a moderately oiled, free ranging muskrat could meet the additional energy requirements imposed by the increased heat loss and decreased swimming efficiency [713].

General information on oil vs. Terrestrial mammals:

BROWN BEAR (Ursus arctos):
After the Exxon Valdez spill, several bears were observed with oil on their fur, consuming oiled carcasses [713].

BLACK BEAR (Ursus americanus):
Although the possibility certainly exists for this species to come into contact with a coastal oil

spill, intensive searches of oiled beaches following the Exxon Valdez spill failed to observe any oiled, live bears, or find any oiled carcasses [713].

SITKA BLACK-TAILED DEER (Odocoileus hemionus sitkensis):
One concern is that Sitka deer may be exposed to oil via the contamination of one of their main wintertime food sources, kelp [713].

CARIBOU (Rangifer tarandus):
No information relating oil spills to caribou mortality, physiological impairment, or behavioral changes was found. However, an oil spill on the tundra would undoubtedly degrade for many years the vegetative community, including forage species important to caribou [713].

General information on oil vs. amphibians and reptiles:

There are few data on oil effects on amphibians and reptiles (like sea turtles) [713]. Extrapolating results from tests of amphibians and reptiles is difficult because of the phylogenetic diversity within each group [713]. And, too little is known to extrapolate safety standards from other kinds of vertebrates. Amphibians are more sensitive to some chemicals than most fish that are commonly tested, but are also much more resistant to some cholinesterase-inhibiting compounds than other classes of vertebrates [713]. Reptiles have fewer routes of exposure and life stages than amphibians, but predictability from one group to another is still largely unknown [713].

See also: Laboratory and/or Field Analyses section below.

See also: the Fate.Detail section below for surface water, groundwater, and water column pathway information.

Sediment Data Interpretation, Concentrations and Toxicity (All Sediment Data Subsections Start with "Sed."):

Sed.Low (Sediment Concentrations Considered Low):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.High (Sediment Concentrations Considered High):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Typical (Sediment Concentrations Considered Typical):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Concern Levels, Sediment Quality Criteria, LC50 Values, Sediment Quality Standards, Screening Levels, Dose/Response Data and Other Sediment Benchmarks:

Sed.General (General Sediment Quality Standards, Criteria, and Benchmarks Related to Protection of Aquatic Biota in General; Includes Sediment Concentrations Versus Mixed or General Aquatic Biota):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Plants (Sediment Concentrations vs. Plants):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Fish (Sediment Concentrations vs. Fish):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Wildlife (Sediment Concentrations vs. Wildlife or Domestic Animals):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Human (Sediment Concentrations vs. Human):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Sed.Misc. (Other Non-concentration Sediment Information):

In sedimentary environments (as opposed to gravel or rocky environments) such as sheltered tidal flats and salt marshes, the sediments are characterized by fine silts with high organic content. Here oil may be thoroughly incorporated into the sediments and persist for very long periods [784]. As mentioned in the introduction, spilled oil is most harmful when shallow, productive waters, porous sediments, low energy aquatic environments, or special-use habitats are affected. Examples of high risk locations are wetlands, sheltered tidal flats, shallow bays, coarse sand and gravel beaches, and sites with concentrated reproductive and migratory activities [782].

Increased sediment exposure may occur where machinery and foot traffic force oil into the substrate, and equipment staging areas may also be severely impacted [771].

Oil holding capacity and the depth of penetration depends on sediment size. Oil will penetrate coarse-grained sediments much more rapidly and more deeply than fine sediments [771].

Some of the literature on sediment contamination by petroleum hydrocarbons was summarized in Olsen's 1984 annotated bibliography of the effects of contaminated sediments on fish and wildlife [449].

The following case study illustrates how a crude oil trapped in mangrove sediments experienced very little weathering [622]:

> On April 27, 1986 a storage tank at the Texaco Refineria Panama on the Caribbean coast of Panama ruptured, releasing about 240,000 barrels of medium weight crude oil into Cativa Bay. On May 4, a storm broke the containment booms, releasing about 150,000 barrels of oil into the Atlantic Ocean. Winds, tides and rain runoff washed part of the oil onto exposed shorelines. Some of the oil was carried back into Cativa Bay, and some was washed into adjacent embayments with mangrove shorelines. By May 15, oil had spread along the coast and washed across fringing reefs and into mangrove forests and small estuaries [622].
>
> Initial weathering removed labile (unstable) oil components such as n-alkane hydrocarbons from oiled surface sediments within 6 months after the discharge. However, total oil concentrations remained high, up to 20% of dry weight in surface sediments, for at least the first 4 years following the discharge. Residual pools of oil in mangrove sediments were sufficiently fluid to flow out when sediments were cored or disturbed 5 years after the

discharge. Most of the oozing oil was highly degraded, but one oiled stream contained a fresh oil residue with a full suite of n-alkanes. Subsequent chemical analysis confirmed that this oil was the crude oil mixture discharged in 1986. Release of oil from pools under and around the collapsed Refineria Panama storage tank and from mangrove sediments caused chronic reoiling for at least 5 years following the discharge, and undegraded oil residues were found in some heavily oiled sediments 6 years after the discharge. Thus, the discharge site, initially injured by a single point-source of oil, became a chronic source of oil contamination. Hydrocarbon chemistry confirmed the long-term persistence of crude oil in mangrove sediments, with pools of trapped oil maintaining consistent hydrocarbon composition. The frequency and amount of reoiling differed among habitats. Secondary reoiling was heaviest in sheltered drainage systems of the mangrove environment, where oil continuously leaked from the sediment, but also occurred along the open coast and along channels. Seasonal variation in weather, water levels and tidal flushing affected the amount of oil released [622].

See the below Fate.Detail section for sediment pathway information. See also case studies in the Sed.Misc section of the Crude Oil entry.

See also: Laboratory and/or Field Analyses section below.

Soil Data Interpretation, Concentrations and Toxicity (All Soil Data Subsections Start with "Soil."):

Soil.Low (Soil Concentrations Considered Low):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Five to fifteen ppm TPH in soil is a realistic background level on a Texas intercoastal waterways spoil island. Such levels should not be a problem for most birds (Brian Cain, Fish and Wildlife Service Contaminants Specialist, Houston, personal communication, 1995).

Soil.High (Soil Concentrations Considered High):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Typical (Soil Concentrations Considered Typical):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Concern Levels, Soil Quality Criteria, LC50 Values, Soil Quality Standards, Screening Levels, Dose/Response Data and Other Soil Benchmarks:

Soil.General (General Soil Quality Standards, Criteria, and Benchmarks Related to Protection of Soil-dwelling Biota in General; Includes Soil Concentrations Versus Mixed or General Soil-dwelling Biota):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Plants (Soil Concentrations vs. Plants):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Wildlife (Soil Concentrations vs. Wildlife or Domestic Animals):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Human (Soil Concentrations vs. Human):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Soil.Misc. (Other Non-concentration Soil Information):

Phtoremediation: To address the broader problem of oil contamination, Exxon and other companies (Science News: 8/5/95, p. 84) find that plants stimulate bacteria that break down hydrocarbons [1023]. However, researchers must then contend with herbicides that companies sometimes use on contaminated spots to prevent fires, says Evelyn Drake of Exxon in Annandale, N.J [1023].

Issues depend on the product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

The trend of thinking towards natural attenuation of petroluem spilled in soil was given a boost by a Lawrence Livermore National Laboratory (LLNL) report entitled "Recommendations to Improve the Cleanup Process for California's Leaking Underground Fuel Tanks;" which stressed the use of passive bioremediation for petroleum product contaminated soils, whenever possible, based on the relatively low number of cases where drinking water was impacted [969]. EPA has pointed out some limitations of the LLNL report, including the lack of adequate consideration of PAHs and additives such as MTBE, as well limited consideration of (non-human) exposure pathways and various geologic conditions [969].

See also Sed.Misc. section above as well as Crude Oil and Petroleum, General entries.

Tissue and Food Concentrations (All Tissue Data Interpretation Subsections Start with "Tis."):

Tis.Plants:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Plants:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

B) Body Burden Residues in Plants: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Tis.Invertebrates:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Invertebrates:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

B) Concentrations or Doses of Concern in Food Items Eaten by Invertebrates:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

C) Body Burden Residues in Invertebrates: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Tis.Fish:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Fish (Includes FDA Action Levels for Fish and Similar Benchmark Levels From Other Countries):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

B) Concentrations or Doses of Concern in Food Items Eaten by Fish:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

C) Body Burden Residues in Fish: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Tis.Wildlife: Terrestrial and Aquatic Wildlife, Domestic Animals and all Birds Whether Aquatic or not:

A) As Food: Concentrations or Doses of Concern to Living Things Which Eat Wildlife, Domestic Animals, or Birds:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

B) Concentrations or Doses of Concern in Food Items Eaten by Wildlife, Birds, or Domestic Animals (Includes LD50 Values Which do not Fit Well into Other Categories, Includes Oral Doses Administered in Laboratory Experiments):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Selected Abstract from Compact Cambridge CD-ROM: Life Sciences 1982 - 1983:

TITLE: Ingestion of Petroleum by Breeding Mallard Ducks: Some Effects on Neonatal Progeny.
AUTHOR: Gorsline J; Holmes WN
SOURCE: ARCH. ENVIRON. CONTAM. TOXICOL.; vol. 11, no. 2, pp. 147-153; 1982
ABSTRACT:
Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers. When incubated, fertilized eggs laid by the females consuming South Louisiana crude oil yielded ducklings that upon emergence possessed high levels of naphthalene-metabolizing activity associated with hepatic microsomes. In contrast, ducklings derived from eggs laid by females consuming food contaminated with Prudhoe Bay crude oil showed no increases in total hepatic naphthalene-metabolizing activity and only those ducklings hatched from eggs laid by females consuming food contaminated with 3% crude oil showed significantly induced levels of specific naphthalene-metabolizing activity at hatching.

C) Body Burden Residues in Wildlife, Birds, or Domestic Animals: Typical, Elevated, or of Concern Related to the Well-being of the Organism Itself:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

B) Concentrations or Doses of Concern in Food Items Eaten by Humans (Includes Allowable Tolerances in Human Food, FDA, State and Standards of Other Countries):

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

C) Body Burden Residues in Humans: Typical, Elevated, or of Concern Related to the Well-being of Humans:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Tis.Misc. (Other Tissue Information):

Factors to consider when interpreting residues of petroleum hydrocarbons in wildlife tissues were summarized by Hall and Coon in 1988 [128].

See the below Fate.Detail section for physical (dermal) exposure and ingestion pathway information.

See also Laboratory and/or Field Analyses section below for information on this topic including the use of biological tissues as an indicator of oil exposure.

See also: Petroleum, General and Crude Oil entries.

Bio.Detail: Detailed Information on Bioconcentration, Biomagnification, or Bioavailability:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

During the Exxon Valdez spill, bioconcentration explained the buildup of PAHs in tissues better than biomagnification; most accumulation was of an equilibrium partitioning nature across the gills rather than from the food chain [971]. Immature fish seem have higher bioconcentration of PAHs than adults, perhaps because their PAH breakdown systems are not fully developed and at times perhaps because of a higher percentage of lipid tissues (yolk tissues, etc) [971] (confirmed by Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996). See also: Chem.Detail section for Kow values for PAHs.

Interactions:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Uses/Sources:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Forms/Preparations/Formulations:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Chem.Detail: Detailed Information on Chemical/Physical Properties:

Depends on product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

As a general rule, spilled petroleum oils are complex mixtures. Although often composed of many of the same compounds, the quantities of the individual components differ in crude oils from different locations [773]. For additional details, see: Petroleum, General and Crude Oil entries.

Since PAHs are important hazardous components of many spilled oils, risk assessments should include analyses of PAHs and alkyl PAHs utilizing the NOAA protocol expanded scan [828] or other rigorous GC\MS\SIM methods.

See also Sinking vs. Floating oil and Oil Weathering information in Fate.Detail section below for more information on chemical/physical properties.

Details of PAH content (mg/kg or ppm) in one fresh sample of Exxon Valdez Crude Oil [971]:

Note: these values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene:	622 mg/kg = ppm
C1-Naphthalene:	1400 mg/kg = ppm
C2-Naphthalene:	1780 mg/kg = ppm
C3-Naphthalene:	1410 mg/kg = ppm
C4-Naphthalene:	696 mg/kg = ppm
Acenaphthylene:	0 mg/kg = ppm
Acenaphthene:	2 mg/kg = ppm
Fluorene:	93 mg/kg = ppm
C1-Fluorene:	224 mg/kg = ppm
C2-Fluorene:	366 mg/kg = ppm
C3-Fluorene:	394 mg/kg = ppm
Anthracene:	0 mg/kg = ppm
Phenanthrene:	262 mg/kg = ppm
C1-Phenanthrene:	572 mg/kg = ppm
C2-Phenanthrene:	722 mg/kg = ppm
C3-Phenanthrene:	576 mg/kg = ppm
C4-Phenanthrene:	446 mg/kg = ppm
Dibenzothiophene:	217 mg/kg = ppm
C1-Dibenzothiophene:	449 mg/kg = ppm
C2-Dibenzothiophene:	635 mg/kg = ppm
C3-Dibenzothiophene:	579 mg/kg = ppm
Fluoranthene:	2 mg/kg = ppm
Pyrene:	10 mg/kg = ppm

C1-Fluoranthene/pyrene: 82 mg/kg = ppm
Benzo(a)anthracene: 2 mg/kg = ppm
Chrysene: 46 mg/kg = ppm
C1-Chrysene: 89 mg/kg = ppm
C2-Chrysene: 138 mg/kg = ppm
C3-Chrysene: 115 mg/kg = ppm
C4-Chrysene: 0 mg/kg = ppm
Benzo(b)fluoranthene 6 mg/kg = ppm
Benzo(k)fluoranthene: 0 mg/kg = ppm
Benzo(a)pyrene: 0 mg/kg = ppm
Indeno(1,2,3-c,d)pyrene: 1 mg/kg = ppm
Dibenz(a,h)anthracene: 1 mg/kg = ppm
Benzo(g,h,i)perylene: 2 mg/kg = ppm
Total PAHs 11,317 mg/kg = ppm

Details of PAH content (mg/kg or ppm) in salmon carcass (fatty viscera removed, so the concentrations may have been higher from whole body samples) from Snug Harbor, Alaska, an area heavily oiled by the Exxon Valdez Crude Oil, 4/15/89 [971]:

Note: Concurrent measurements of water quality, as well as equilibrium partitioning estimates of water quality based on concentrations in fish and mussels, both confirm that PAH concentrations did not exceed water quality criteria at the time these concentrations were measured in fish tissues [971]. These values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene: 7.15 ug/kg = ppb
C1-Naphthalene: 65.11 ug/kg = ppb
C2-Naphthalene: 29.75 ug/kg = ppb
C3-Naphthalene: 93.95 ug/kg = ppb
C4-Naphthalene: 36.63 ug/kg = ppb
Acenaphthylene: 0 ug/kg = ppb
Acenaphthene: 0 ug/kg = ppb
Fluorene: 6.86 ug/kg = ppb
C1-Fluorene: 12.63 ug/kg = ppb
C2-Fluorene: 22.87 ug/kg = ppb
C3-Fluorene: 13.64 ug/kg = ppb
Anthracene: 0 ug/kg = ppb
Phenanthrene: 22.97 ug/kg = ppb
C1-Phenanthrene: 28.48 ug/kg = ppb
C2-Phenanthrene: 20.45 ug/kg = ppb
C3-Phenanthrene: 12.43 ug/kg = ppb
C4-Phenanthrene: 1.71 ug/kg = ppb
Dibenzothiophene: 19.65 ug/kg = ppb
C1-Dibenzothiophene: 19.68 ug/kg = ppb
C2-Dibenzothiophene: 15.96 ug/kg = ppb
C3-Dibenzothiophene: 7.44 ug/kg = ppb
Fluoranthene: 0 ug/kg = ppb
Pyrene: 0 ug/kg = ppb
C1-Fluoranthene/pyrene: 0.62 ug/kg = ppb
Benzo(a)anthracene: 0.72 ug/kg = ppb

Chrysene:	2.5 ug/kg = ppb
C1-Chrysene:	0.71 ug/kg = ppb
C2-Chrysene:	0.48 ug/kg = ppb
C3-Chrysene:	0.16 ug/kg = ppb
C4-Chrysene:	0.56 ug/kg = ppb
Benzo(b)fluoranthene	0 ug/kg = ppb
Benzo(k)fluoranthene:	0 ug/kg = ppb
Benzo(a)pyrene:	0 ug/kg = ppb
Indeno(1,2,3-c,d)pyrene:	0 ug/kg = ppb
Dibenz(a,h)anthracene:	0 ug/kg = ppb
Benzo(g,h,i)perylene:	0 ug/kg = ppb
Total PAHs	436 ug/kg = ppb

Details of PAH content (ug/kg or ppb) in whole body samples of mussels) from Snug Harbor, Alaska, an area heavily oiled by the Exxon Valdez Crude Oil, 4/15/89 [971]:

Note: Concurrent measurements of water quality, as well as equilibrium partitioning estimates of water quality based on concentrations in fish and mussels, both confirm that PAH concentrations did not exceed water quality criteria at the time these concentrations were measured in mussel tissues [971]. These values are wet weight (Jerry Neff, Battelle Ocean Sciences, Duxbury, MA, personal communication 1996):

Naphthalene:	12.9 ug/kg = ppb
C1-Naphthalene:	17.3 ug/kg = ppb
C2-Naphthalene:	247 ug/kg = ppb
C3-Naphthalene:	905 ug/kg = ppb
C4-Naphthalene:	850 ug/kg = ppb
Acenaphthylene:	0 ug/kg = ppb
Acenaphthene:	0 ug/kg = ppb
Fluorene:	38.3 ug/kg = ppb
C1-Fluorene:	383 ug/kg = ppb
C2-Fluorene:	1317 ug/kg = ppb
C3-Fluorene:	1535 ug/kg = ppb
Anthracene:	0 ug/kg = ppb
Phenanthrene:	356 ug/kg = ppb
C1-Phenanthrene:	1924 ug/kg = ppb
C2-Phenanthrene:	3834 ug/kg = ppb
C3-Phenanthrene:	2438 ug/kg = ppb
C4-Phenanthrene:	796 ug/kg = ppb
Dibenzothiophene:	260 ug/kg = ppb
C1-Dibenzothiophene:	1344 ug/kg = ppb
C2-Dibenzothiophene:	2743 ug/kg = ppb
C3-Dibenzothiophene:	2743 ug/kg = ppb
Fluoranthene:	10.7 ug/kg = ppb
Pyrene:	32.9 ug/kg = ppb
C1-Fluoranthene/pyrene:	302 ug/kg = ppb
Benzo(a)anthracene:	0 ug/kg = ppb
Chrysene:	411 ug/kg = ppb
C1-Chrysene:	658 ug/kg = ppb
C2-Chrysene:	521 ug/kg = ppb

C3-Chrysene:	239 ug/kg = ppb
C4-Chrysene:	43.9 ug/kg = ppb
Benzo(b)fluoranthene	27.4 ug/kg = ppb
Benzo(k)fluoranthene:	0 ug/kg = ppb
Benzo(a)pyrene:	65.8 ug/kg = ppb
Indeno(1,2,3-c,d)pyrene:	0 ug/kg = ppb
Dibenz(a,h)anthracene:	2.63 ug/kg = ppb
Benzo(g,h,i)perylene:	7.41 ug/kg = ppb
Total PAHs	24,051 ug/kg = ppb

Log Kow values for PAHs [971]:

Naphthalene:	3.37
C1-Naphthalene:	3.87
C2-Naphthalene:	4.37
C3-Naphthalene:	5.0
C4-Naphthalene:	5.55
Acenaphthylene:	4.07
Acenaphthene:	3.92
Fluorene:	4.18
C1-Fluorene:	4.97
C2-Fluorene:	5.2
C3-Fluorene:	5.5
Anthracene:	4.54
Phenanthrene:	4.57
C1-Phenanthrene:	5.14
C2-Phenanthrene:	5.51
C3-Phenanthrene:	6
C4-Phenanthrene:	6.51
Dibenzothiophene:	4.49
C1-Dibenzothiophene:	4.86
C2-Dibenzothiophene:	5.5
C3-Dibenzothiophene:	5.73
Fluoranthene:	5.22
Pyrene:	5.18
C1-Fluoranthene/pyrene:	5.72
Benzo(a)anthracene:	5.91
Chrysene:	5.86
C1-Chrysene:	6.42
C2-Chrysene:	6.88
C3-Chrysene:	7.44
C4-Chrysene:	8
Benzo(b)fluoranthene	5.80
Benzo(k)fluoranthene:	6.0
Benzo(a)pyrene:	6.04
Indeno(1,2,3-c,d)pyrene:	7.0
Dibenz(a,h)anthracene:	6.75
Benzo(g,h,i)perylene:	6.50

For details of PAH content in spills of Fuel Oil 5 or Diesel, See entries by those titles.

Fate.Detail: Detailed Information on Fate, Transport, Persistence, and/or Pathways:

Fate details depend on the exact product spilled; see Petroleum, General and Crude Oil entries, and entries on individual aromatics.

Low molecular weight components evaporate readily; the amount of evaporation varies from about 10% of the spilled oil for very heavy crudes and refined products (No. 6 fuel oil) to as much as 75% for light crudes and refined products (No. 2 fuel oil, gasoline). Less than 5% of a crude oil or refined product will dissolve in water [782].

In general, microbial degradation is most rapid when dissolved oxygen, nutrients, and water temperature are elevated. Approximately 40-80% of a crude oil can be degraded by microbial action [782].

Biodegradation rates of hydrocarbons are dependent on the type of bacteria, presence of limiting nutrients, temperature, and types of hydrocarbons [657]. Most biodegradation occurs from about one week to many months after the spill [771]. Bacteria generally degrade hydrocarbons according to the following sequence (first to last): n-alkanes > branched alkanes > aromatic hydrocarbons > cyclic alkanes. Within a PAH homologous series, bacteria degradation rates generally are inversely proportional to the degree of alkylation. So, the sequence of bacterial degradation within a PAH homologous series would be (from first to last degraded) [657]:

C0-PAH > C1-PAH > C2-PAH > C3-PAH > C4-PAH

Behavior and fate of discharged oil can be affected by the following physical, chemical and biological processes [713]:

PHYSICAL [713]: spreading (thinning of the oil slick); dispersion (by wind); movement (by currents or gravity flow); dissolution; sedimentation or settling; emulsification; evaporation or volatilization; aeolian transport (when oil droplets become airborne and are blown long distances by strong winds).

CHEMICAL [713]: photolysis or photooxidation or photodegradation; oxidation or chemical degradation.

BIOLOGICAL [713]: microbial degradation or biodegradation; ingestion and depuration by organisms [713].

NOTE: See "Crude Oil" entry for additional information on the environmental fate of crude oil.

Pathways of oil spill injuries: Pathways for injuries due to incidents involving oil can be either direct or indirect [713]. Direct pathways occur when the natural resource is exposed to the oil or to a chemical compound originating from the oil. Indirect pathways occur when the natural resource is not directly exposed to the oil or to any chemical compounds originating from the oil:

instead, the presence of the oil interferes with a physical, chemical or biological process important to the natural resource; or a use of the natural resource is impaired by the presence of the oil in that environment [713]. More specifically, an exposure pathway can be either [771]:

> DIRECT: A sequence of events by which the oil traveled through the environment and physically came into contact with the natural resource. For example, direct oiling of a shellfish bed may result in mortality and decreased growth [771].
>
> INDIRECT: A sequence of events by which the effect of exposure to oil was transferred to the natural resource of concern, without the oil directly contacting the natural resource. For example, a decreased bait fish population caused by a spill may result in the starvation of a piscivorous bird, or a fishery may be closed to prevent potentially tainted fish from being marketed [771].

There are a number of potential exposure pathways. In some cases, these pathways may have multiple steps. For example, a common exposure pathway for birds is a surface water pathway, leading to physical exposure, leading to ingestion from preening [771]. Although it is difficult to list all of the potential direct and indirect exposure pathways, several of the predominant pathways for discharges of oil are discussed below [771]:

> SURFACE WATERS: Because most oils float, surface waters are often the exposure pathway of greatest concern. Surface waters may provide a pathway for exposure of open-water natural resources such as birds, mammals, and plankton in the surface microlayer; or a pathway to shoreline and intertidal resources. The surface waters themselves are a resource, and floating oil may disrupt a number of resource services including recreation, transportation, and aesthetic values. This pathway is relatively straightforward to document using aerial overflights, surface vessel observations, and computer models designed to simulate the behavior and transport of surface oil slicks [771].
>
> INGESTION: Ingestion is a common exposure pathway. Oiled birds will ingest oil during preening. Turtles feed on objects floating at the water surface, therefore they are susceptible to ingestion of tar balls, which can block the oral cavity and digestive tract (Van Vleet and Pauly, 1987). Injuries to river otters have been related to ingestion pathways, both from preening and from contaminated food (Bowyer et al., 1993). Ingestion pathways also have been observed for invertebrates. Christini (1992) noted that blue crabs were attracted to and ingested tarballs. Because many organisms can metabolize petroleum, biomagnification via trophic pathways is not considered an important pathway (McElroy et al., 1989; National Research Council, 1985); however, organisms may be exposed by ingesting contaminated prey (that is,

bioavailability). For example, bivalve mollusks such as mussels may accumulate petroleum hydrocarbons in their tissues, and pass contamination on to higher trophic level predators such as birds or marine mammals. This pathway has been linked to the persistent reproductive failure of Harlequin Ducks in Western Prince William Sound following the Exxon Valdez incident (Patten, 1993). Approaches to studying ingestion and food web pathways include direct observation of feeding, preening behavior, and oiling of mouth parts; analysis of gut contents; tissue analysis of prey species; and feces analysis [771].

INHALATION: The potential for inhalation pathways depends on the volatility of the oil and degree of weathering. Inhalation pathways have been hypothesized to be important, especially to marine mammals. For example, following the Exxon Valdez incident, Frost and Lowry, (1993) found central nervous system injuries and edema in harbor seals that was similar to that present in humans that die from inhaling solvents. Researchers postulate that killer whales were killed by exposure to volatile hydrocarbons after the Exxon Valdez incident (Dalheim and Matkin, 1993) [771].

PHYSICAL (DERMAL) EXPOSURE: Surface water and other pathways may lead to direct physical exposure of a natural resource to oil. This contact may directly cause injury (smothering), may impair the physiology of the organism, resulting in injury (hypothermia in birds and mammals from impaired thermoregulation), or may cause a service loss (dermal exposure in fish resulting in tainting). Direct contact through a dermal absorption pathway also may lead to contamination of organs, fluids and tissues [771].

ATMOSPHERIC: The atmosphere may provide a pathway to natural resources, or affect the service flows from these resources. The 1993 Braer incident in the Shetland Islands provides an example of an aeolian pathway. High winds carried the oil as a mist inland and contaminated approximately 20 square miles of crop lands, as well as oiling houses, cars, and a lake used for drinking water (Harris, 1995). Other less dramatic examples include the 1993 Colonial Pipeline incident in Virginia (Koob, 1995) where a break in a pipeline sprayed oil into the air and oiled a number of natural resources, including an upland forest area. The burning of oil (either deliberately or by chance) could increase atmospheric impacts. Atmospheric pathways may be especially important in determining the potential for lost use. For example, oil from the Colonial incident eventually flowed into the Potomac River, where odors resulted in the closure of Great Falls National Park and impairment of air quality along the Capital Mall area [771].

SEDIMENTS: Subtidal and intertidal sediments are an important pathway in most discharges, affecting biological resources, habitats, and service flows. In most instances, intertidal sediments are the primary pathway of concern, but extensive subtidal sediment contamination has been observed in a number of large incidents, such as the Amoco Cadiz, Exxon Valdez, Braer, and Morris J. Berman. Chronic exposure to oiled sediments has been correlated with reduced feeding, growth, and reproduction, and with histopathological changes in benthic fish. Sediment pathways also are important in recreational lost use. Beaches, for example, may be closed because of oiled sediments. Subtidal sediments may provide a pathway for chronic beach oiling (Burns et at., 1995) [771].

GROUNDWATER: Groundwater petroleum contamination can involve large amounts of oil and affect huge areas. One tank farm facility alone has been estimated to have released between 84 and 252 million gallons of petroleum into groundwater (Mould et al., 1995). Chronic groundwater contamination may result from leaking underground storage tanks or from chronic surface discharges (refineries, tank farms), while acute contamination may result from the sudden failure of storage tanks or other terrestrial incidents. Groundwater may provide a pathway for exposure to terrestrial and aquatic resources. In fact, many groundwater problems are first discovered when oil begins leaching into surface waters. Studying groundwater pathways generally involves the use of monitoring wells, or sampling of existing drinking water wells in the aquifer [771].

WATER COLUMN: The potential for a significant water column exposure pathway depends on the dispersion and dissolution characteristics of the oil, response countermeasures, and ambient environmental conditions. Because of the ephemeral nature of water column exposure, studying water column pathways in-situ must be done quickly after a discharge, and can be very costly. Alternatively, this pathway may be demonstrated based on literature information, laboratory studies on the physical behavior of the oil, or through the use of models [771].

SINKING VS. FLOATING OIL:

Heavy fuel oils or crude oils which are high in density should be subjected to a rigorous determination of submergence characteristics so that on-scene response groups can be warned about the possibility of the oil sinking [554]. Sinking oil could lead to a significant environmental impact because the sensitive and often economically valuable benthic environment could become contaminated with oil and resultant PAHs. More research in this area should lead to suggested protocols for a density increase assessment of spilled oils [554].

In general, even though density of oil increases through weathering, the density will rarely increase to that of freshwater (specific gravity approximately 1.00, density 1000 kg/m3) or marine water (specific gravity approximately 1.024, density 1024 kg/m3). However, heavy fuels such as no. 6 may weather to densities heavier than water since the unweathered density already exceeds 900 kg/m3 (for example, a typical No. 6 fuel oil has an API gravity around 12.3, which corresponds to a density of 971 kg/m3 at 22 +or- 2 degrees Celsius) [554].

When does one have to be concerned about heavy oil fractions sinking through the water column and ending up in bottom sediments? Many of the heavier PAHs have specific gravities much higher than 1.0. So why don't they sink out of oil slicks, and head for the bottom sediments, more often than they do? According to Jackie Michel, Research Planning Inc., S. Carolina, a member of a team that provides support to NOAA at spills, the reasons and considerations include the following (Personal Communication to Roy Irwin, 1993):

> Oil fractions seldom sink out of slicks right away. Little separation occurs in most marine spills. The oil mass usually stays together. Only a very little bit of the oil typically dissolves in water.
>
> Oil is pretty viscous and it hangs together. The heavier PAHs are dissolved in the lighter fractions (toluene, benzene, xylene) and are more attracted to these compounds than to water. These forces can overcome the forces of gravity, at least for a time.
>
> It is true that as the light fractions are removed over time by evaporation, sinking can begin to occur as the oil gets heavier and begins to picks up particulates. As emulsification sets in, water surrounds oil droplets.
>
> It should be kept in mind that sinking oil fractions are less likely in marine waters (specific gravity approx. 1.034) than in freshwaters (specific gravity of 1.00) and that the heavy compounds of most concern, PAHs, only make up 2-10% of many spilled petroleum products.
>
> In addition to PAHs, there are other heavy compounds in typical oil slicks, such as heavy asphaltines (compounds with specific structures, not "asphalt", waxes, resins, tars, etc.).

There are a few scenarios and specific conditions which can cause an oil to sink rather than float [775,777]:

1) Spills of very heavy oils in freshwater, such as spills of heavy No. 6 fuel oil or LAPIO (Low-API gravity oils) in freshwater [777]:

> Specific gravity is the ratio of the density of a material to fresh water. Although nearly all crude oils and most refined products have a specific gravity less than 1.00 and thus float, some of the residual refined products are so heavy that their specific gravity is greater than 1.00 (very heavy fuel oils, asphalt). Spills

of these oils can sink immediately and flow along with the bottom currents or as droplets in the water column. However, sinking oils can re-float in response to very small changes in water density. There have been several spills which occurred in the freshwater sections of a river, where the oil originally sank and moved along the bottom; however, at the fresh/salt mixing zone, where the water density increased with salinity, some of the oil rose to the surface. In other spills, oil has been reported to sink with very cold temperatures at night, only to re-float after absorbing heat from the sun through the water [777].

> NOTE: Submerged oil can refloat, as was observed during the Puerto Rico spill. There are three possible mechanisms for refloating: 1) the sand can separate from the oil; 2) wave-generated currents can loosen and resuspend pieces of oil from the bottom; and 3) increases in water and/or oil temperature can make the oil more buoyant [775].

2) Spills of heavy oils in areas where there is a very high suspended sediment load in the water, and very stable emulsions form [775,777]:

Water-in-oil emulsions can contain up to 80 percent water, which will increase the specific gravity accordingly. Also, during the emulsification process, some sediment can be incorporated into the emulsion, either from the suspended sediments in the water mixed into the oil, or those adhered to the floating slick. A very small amount of sediment is needed to sink oil. Only residual refined products (No. 6 fuel oil, Bunker C) have a specific gravity of 0.99 or greater [777].

3) Spills where the oil comes ashore, picks up sediment, and then is eroded from the shore [775,777]:

> NOTE: The Tampa Bay (1993) and Puerto Rico (1994) spills were the first documented instance of oil sinking caused by oil mixing with sand in the surf zone, prior to contact with the beach [775].

Medium and heavy oils can pick up sediment when they strand (that is, run ashore), making the oil heavier than water [777]. However, the oil/sediment mixture must be eroded from the shoreline, usually by waves, which tend to break up the oil slicks. The oiled sediment can be deposited in the nearshore zone, but as small tarballs or widely scattered contaminated sediment, rather than a layer of sunken oil. In some instances, the tarballs can stick to each other, forming a tarmat just offshore [777].

In these spills situations, the oil often remains liquid, initially floats, but then sinks after picking up sand [775]. This behavior was observed recently during the Tampa Bay (Bouchard 155, 1993) and Puerto Rico (Barge Morris J. Berman, 1994) spills [775]. The oil behaves very much like a conventional #6 fuel oil at first, including rapid loss of the light fractions by evaporation and an increase in viscosity. However, when the oil is transported into shallow water, it is more likely to be temporarily mixed into the water column by wave turbulence because it is heavy. Where the bottom is sandy, the sand is also suspended in the water column by the waves, and some sand is mixed with the oil. The specific gravity of quartz is 2.65 and calcium carbonate is 2.71, so it only takes about 2-3 percent sand by weight mixed into oil with a specific gravity of 1.00 [=API of 10] to make it heavier than seawater. The oil/sand mixture is deposited in relatively sheltered areas where it can form extensive, thick layers of oil on the bottom. In Puerto Rico, submerged oil was found in sheltered pockets in the lee of offshore rocks in an otherwise relatively high wave energy setting [775].

It appears that oil sinks in this manner only when it is mixed with sand [775]. There have been several spills where oil has picked up sand after being stranded on sand beaches (IXTOC I and Alvenus). After being eroded from the beach by wave action, the oil/sand mixture was deposited at the toe of the beach or just offshore in the form of tarmats. However, the Tampa Bay and Puerto Rico spills were the first documented instance of oil sinking caused by oil mixing with sand in the surf zone, prior to contact with the beach [775].

Submerged oil can form thick, continuous deposits that are hundreds of feet long, or small tarballs [775]. Where there is current activity, especially generated by waves, the oil/sand mixture can form cigar-shaped "rollers" that can be scattered on the bottom or accumulated into mats. These rollers pick up more sand and shell fragments as they move, making them heavier. They can eventually be deposited on nearby beaches after storms. The extent to which the oil weathers prior to sedimentation has a profound effect on the viscosity and character of the resulting oil/sediment mixture.

4) Spills where the oil is a blend of light and heavy refined products, and the light fraction is lost by evaporation [777]:

Many intermediate fuel oils are actually mixtures of No. 2 and No. 6 oils. If the spill conditions were such that the light oil completely evaporated, and the heavy oil was particularly heavy, the weathered oil might sink [777].

> NOTE: Experiments designed to study the effects of weathering on density of four common heavy fuel oils studied the five processes believed to contribute to an increase in oil density: evaporation, dissolution, photolysis, attachment of foreign matter, and water uptake [554]. The study concluded that the primary causes of increased density are evaporation of the more volatile and less dense components of the oil (although the study results show that No. 6 fuel oil is unlikely to sink by evaporation alone), and the incorporation of denser-than-water mineral matter into the oil [554].

5) Spills of very heavy oil where low current conditions do not keep the oil in suspension (oil remains liquid, but the majority does not float) [775]:

> In this case, the oil has a specific gravity greater than the receiving water. Some of the oil will float, but the majority does not. As the oil mixes in the water column, it will form small drops. This oil is not expected to adhere to debris or vegetation in the water column [775]. When oil encounters water-wet surfaces, it generally does not stick. Where currents are greater than about 0.1 knots, the oil droplets will be kept in suspension. An oil with an API gravity of 0.0 degrees at 60 degrees F has a specific gravity of 1.076, so even very heavy oils can be suspended by alongshore currents. Thus, in most nearshore coastal settings, the oil is not likely to accumulate on the bottom because the currents are strong enough to mobilize the oil [775]. The size of the oil drop is likely to range from 0.5 microns to one millimeter or so. Weathering processes such as evaporation and photo-oxidation will be slower relative to floating slicks, but the drops should eventually weather faster than floating tarballs because of their smaller size [775].
>
> In low-flow zones (less than about 0.1 knots), the suspended oil could sink and accumulate on the bottom [775]. Direct sinking in low-flow areas was observed during the Sansinena (Los Angeles, CA, 1976) and the Mobil Oil (Columbia River, 1984) spills. Thus, it is possible that suspended oil could settle out and accumulate in estuaries in locations similar to those where fine-grained sediments are deposited during slack periods of the tide. However, oil drops are expected to be readily remobilized by tidal currents, so long-term accumulation is likely only in areas little affected by tidal or riverine currents. Examples of such areas would include abandoned channels, dredged channels or pits, depressions adjacent to piers caused by prop wash of anchoring vessels, dead-end canals, and in the lee of

> manmade structures. The oil drops will re-coalesce into pools of liquid oil, which can be up to several feet thick, although it can also spread into a thin layer when there are no depressions [775].

Summary of Low API Oil (LAPIO) Behavior [775]:

> Spills of LAPIO-type oils can have complex behavioral patterns, depending on the API gravity of the oil, the homogeneity of the mixture, the density of the receiving water, and the physical setting of the spill site. Oil is only likely to sink straight to the bottom where the currents are very low. Also, denser-than-water oil is expected to mix in the water column as oil drops rather than large, cohesive mats. Thick mats are formed on the seafloor only when oil that initially floats mixes with sediment. Oil can accumulate on the bottom under calm currents, so releases of very heavy oil in harbors with dredged channels and berths in canals could readily sink and form pools of oil on the bottom. Releases in areas subject to tidal and riverine flow are likely to be kept in suspension in the water column by currents. If the oil is poorly mixed or unstable, the spill could separate into fractions that can float, suspend, and sink simultaneously [775].

Oil Weathering:

After oil is discharged into the environment, a wide variety of physical, chemical, and biological processes begin to transform the discharged oil. Collectively, these processes are referred to as weathering, and act to change the composition, behavior, routes of exposure, and toxicity of the discharged oil. For example, penetration of oil into marsh vegetation may depend on oil viscosity; weathered oils penetrate less than fresh oil. Weathered oil is composed of relatively insoluble compounds, and often coalesces into mats or tarballs. As a result, the potential for exposure to fish through water column toxicity is lessened, as is the potential for birds or mammals to encounter the oil. Alternatively, certain species are known to ingest tarballs and the potential for exposure to those resources may increase as the oil weathers. Also, the loss of the lighter fractions through dissolution and/or evaporation during the weathering process can cause normally buoyant oil to sink, thereby contaminating subtidal sediment and contributing to water column toxicity [771].

After the loss of the volatile, soluble, and easily biodegraded compounds, the remaining compounds can become concentrated. Weathered oil becomes less acutely toxic, but due to polynuclear aromatic hydrocarbons (PAHs) of high molecular weight, it remains toxic [713].

The primary weathering processes are physical phenomena; these include spreading, evaporation, dissolution, dispersion, emulsification, and sedimentation [771]. (Chemical weathering processes include photodegradation and oxidation; biological weathering processes include (microbial) biodegradation and ingestion and depuration by organisms [713].) These processes occur for all discharges, but the rate and relative importance of each process depends on spill characteristics, environmental conditions, and physicochemical properties of the spilled material [771,791]. Note that due to the confounding effects of site-specific and spill-specific variables, however, the physicochemical data can only help by providing a rough estimate of the persistence of a crude oil or oil product in the aquatic environment [791].

That said, oils and oil products with the least persistence in a water environment would have low molecular weights, high solubilities, high vapor pressures, and low octanol/water partition coefficients (Kow). Oils and oil products with the greatest persistence would have the opposite. The low-molecular-weight hydrocarbons are more soluble, have a higher vapor pressure, and have a lower Kow than heavier products [791].

> NOTE: A comprehensive review of the physicochemical properties of several classes of crude oil and oil products found their persistence in the aquatic environment to rank as follows (from most persistent to least persistent): Residual asphaltenes > Heavy crude oil > Medium crude oil > Fuel oil #6 > Light crude oil > Lube oils > Fuel oil #2 > Jet fuel > Gasoline [791].

A brief discussion of each of the primary (physical) weathering processes is provided as follows:

> SPREADING: As oil enters the environment, it begins to spread immediately. The viscosity of the oil, its pour point, and the ambient temperature will determine how rapidly the oil will spread, but light oils typically spread more rapidly than heavy oils. The rate of spreading and ultimate thickness of the oil slick will affect the rates of the other weathering processes. For example, discharges that occur in geographically contained areas (such as a pond or slow-moving stream) will evaporate more slowly than if the oil were allowed to spread. Most of this process occurs within the first week after the spill [771].

> EVAPORATION: Evaporative processes begin immediately after oil is discharged into the environment [771]. Some light products (like 1- to 2-ring aromatic hydrocarbons and/or low molecular weight alkanes less than n-C15) may evaporate entirely; a significant fraction of heavy refined oils also may evaporate [657,771]. For crude oils, the amount lost to evaporation can typically range from approximately 20 to 60 percent. The primary factors that control evaporation are the composition of the oil, slick thickness, temperature and solar radiation, windspeed and wave height. While evaporation rates increase with temperature, this process is not restricted to warm climates. For the Exxon Valdez incident, which occurred in cold conditions (March 1989), it has been estimated that appreciable evaporation occurred even before all the oil escaped from the ship, and that evaporation ultimately

accounted for 20 percent of the oil. Most of this process occurs within the first few days after the spill [771].

DISSOLUTION: Dissolution is the loss of individual oil compounds into the water. Many of the acutely toxic components of oils such as benzene, toluene and xylene will readily dissolve into water. This process also occurs quickly after a discharge, but tends to be less important than evaporation. In a typical marine discharge, generally less than 5 percent of the benzene is lost to dissolution while greater than 95 percent is lost to evaporation. (For alkylated PAHs, solubility is inversely proportional to the number of rings and extent of alkylation [657].) The dissolution process is thought to be much more important in rivers because natural containment may prevent spreading, reducing the surface area of the slick and thus retarding evaporation. At the same time, river turbulence increases the potential for mixing and dissolution. Most of this process occurs within the first hour of the spill [771].

DISPERSION: The physical transport of oil droplets into the water column is referred to as dispersion. This is often a result of water surface turbulence, but also may result from the application of chemical agents (dispersants). These droplets may remain in the water column or coalesce with other droplets and gain enough buoyancy to resurface. Dispersed oil tends to biodegrade and dissolve more rapidly than floating slicks because of high surface area relative to volume. Most of this process occurs from about half an hour to half a day after the spill [771].

EMULSIFICATION: Certain oils tend to form water-in-oil emulsions (where water is incorporated into oil) or "mousse" as weathering occurs. This process is significant because, for example, the apparent volume of the oil may increase dramatically, and the emulsification will slow the other weathering processes, especially evaporation. Under certain conditions, these emulsions may separate and release relatively fresh oil. Most of this process occurs from about half a day to two days after the spill [771].

SEDIMENTATION or ADSORPTION: As mentioned above, most oils are buoyant in water. However, in areas with high suspended sediment levels, oils may be transported to the river, lake, or ocean floor through the process of sedimentation. Oil may adsorb to sediments and sink or be ingested by zooplankton and excreted in fecal pellets which may settle to the bottom. Oil stranded on shorelines also may pick up sediments, refloat with the tide, and then sink. Most of this process occurs from about two to seven days after the spill [771].

OTHER: Aeolian transport (relocation by wind) can also occur [771].

Several general compositional changes can be expected as an oil weathers [713]:

1. Loss of low boiling (less than 20 carbons) aromatic and saturated hydrocarbons through evaporation.
2. Loss of low boiling (less than 15 carbons) aromatic hydrocarbons through dissolution.
3. An increased relative importance of unresolved naphthenic and naphthenoaromatic compounds.
4. An increased importance of highly branched aliphatic hydrocarbons (like isoprenoids) relative to straight chain and singly methyl-branched molecules due to selective depletion of n-alkanes by biodegradation.
5. An increased importance of alkylated (dimethyl to tetramethyl) phenanthrene and dibenzothiophene compounds relative to other aromatics through combined weathering processes.
6. An increased importance of polycyclic aliphatic (like pentacyclic triterpanes) compounds relative to all saturated compounds [713].

The following table shows how the exposure of a spilled oil to the open environment speeds weathering. Note in the table below that the weathered oil PAH values (third column) are lower even though these samples were collected approximately 2 months sooner than the skimmer barge samples (second column):

Table: PAH concentrations (ug/g oil sampled) for three different crude oil sample types taken from the Exxon Valdez oil spill. Concentrations in 1) unweathered oil from the tanker itself (March 1989), 2) oil skimmed from the water immediately after the spill and held in the skimmer barge for about 90 days (July 1989), and 3) weathered oil from Prince William Sound shorelines (May 1989) were, respectively [790; Reprinted with permission from Environmental Toxicology and Chemistry, Vol.14(11), W.A. Stubblefield, G.A. Hancock, W.H. Ford, and R.K. Ringer, "Acute and Subchronic Toxicity of Naturally Weathered Exxon Valdez Crude Oil in Mallards and Ferrets." Copyright 1995 SETAC]:

Naphthalene: 562, 14, 4
C1-Naphthalene: 1307, 150, 52
C2-Naphthalene: 1739, 740, 283
C3-Naphthalene: 1377, 970, 473
C4-Naphthalene: 767, 760, 423
Acenaphthylene: ND, ND, ND
Acenaphthene: ND, ND, ND
Fluorene: 80, 44, 27
C1-Fluorene: 208, 180, 98
C2-Fluorene: 306, 400, 198
C3-Fluorene: 310, 370, 245
Anthracene: ND, ND, ND
Phenanthrene: 222, 200, 124
C1-Phenanthrene/anthracene: 488, 660, 410

C2-Phenanthrene/anthracene: 629, 870, 564
C3-Phenanthrene/anthracene: 456, 640, 507
C4-Phenanthrene/anthracene: 256, 370, 263
Dibenzothiophene: 189, 150, 73
C1-Dibenzothiophene: 389, 460, 258
C2-Dibenzothiophene: 567, 860, 529
C3-Dibenzothiophene: 508, 880, 593
Fluoranthene: ND, ND, ND
Pyrene: 9, 7, 7
C1-Fluoranthene/pyrene: 63, 68, 70
Benzo(a)fluoranthene: ND, ND, 1
Chrysene: 41, ND, 54
C1-Chrysene: 73, 120, 120
C2-Chrysene: 93, 150, 144
C3-Chrysene: 79, 120, 101
C4-Chrysene: 64, 69, 58
Benzo(a)fluoranthene [sic]: 6, ND, 1
Benzo(k)fluoranthene: ND, ND, 2
Benzopyrene: 12, ND, 1
Indeno(1,2,3-c,d)pyrene: ND, ND, ND
Dibenz(a,h)anthracene: ND, ND, ND
Benzo(g,h,i)perylene: ND, ND, 1

ND = not detected.

The table below shows how as evaporation of a crude oil continues, its solubility decreases. (Although the solubility units in the table below are unfamiliar, the inversely proportional relationship of degree of weathering to solubility remains evident.):

Table: Relationship of weathering to solubility for several crude oils [683]:

CRUDE OIL	DEGREE OF WEATHERING (% evap'd)	SOLUBILITY* (g/m3)
Norman Wells	0	32.3
	6	27
	12	14.6
	20.4	7.3
	36.7	0.68
	43.2	0.14
Prudhoe Bay	0	29.25
	9.8	4.89
	18.2	0.15
	24.4	0.10
Lago Medio	0	25.5
	22.3	0.6

* = estimated subcooled liquid solubility

General discussion of the use of chemical dispersants:

The objective of dispersant use is to remove floating oil from the water surface and disperse it into the water column, in order to reduce impact to sensitive shoreline habitats and animals that use the water surface [777]. To accomplish this, specially formulated products containing surface-active agents are sprayed at concentrations of about 5 percent by volume of the oil onto the slicks by aircraft or boats. The dispersants reduce the oil/water surficial tension and decrease the energy needed for the slick to break into small particles and mix into the water column. Some turbulence is needed to mix the dispersant into the oil and to mix the treated oil into the water [777].

Dispersant use is only applicable in open water and/or large river spills with sufficient depth and volume for mixing and dilution, and when the potential impact of the floating oil has been determined to be greater than the potential impact of mixing oil into the water column [777]. Use in shallow water could affect benthic resources. Dispersant use may increase effects on water-column organisms, particularly plankton and larval fish. The potential impact of dispersed oil on drinking water intakes should also be considered. Also, dispersion is usually only partially effective, so some water surface impact may still occur [777].

Dispersants tend to put small droplets of oil down into the water. Dispersants are typically only used in deeper water, only in the early stages of the spill response while the oil is still light (still has a higher percent of volatile compounds). The oil droplets following dispersant use tend to sink, perhaps a typical max of 10 feet. The idea is to keep droplets down, prevent them from reforming a slick, keep them down where bacteria can get at them. Chemically dispersed oil typically doesn't coat the bottom or anything else (Brian Cain, Fish and Wildlife Service, Houston personal communication to Roy Irwin).

Caution should be used in the use of dispersants, since some detergents are inherently toxic and since the oil is sometimes easier to collect or burn while still on the surface. The question also needs to be asked "where are the toxic compounds in the oil (PAHs, etc.) going to end up?" If they end up in the biota or in water column or sediment locations, they might affect the biota to a greater extent or for a longer time than they would have if left on the surface or burned.

Bioremediation (biological response methods):

The intent of nutrient enrichment or natural microbe seeding is to speed the rates of natural microbial degradation of oil by adding nutrients (generally nitrogen and phosphorus) or adding live microbes with enhanced oil-degrading abilities, respectively [777]. These techniques are most affective with diesel-type medium oils that do not have large amounts of high molecular weight, slow degrading compounds. Bioremediation is not suitable in shallow water or restricted waterbodies where nutrient overloading may lead to eutrophication, or where the toxicity of nutrients, particularly ammonia, is of concern. Also, other chemicals in the product could be toxic to aquatic organisms [777].

Burning spilled oil, To Burn or Not To Burn Spilled Oil:

From a water pollution standpoint, burning oil before it reaches shore is often a good idea, and by late 1994, Regional Response Teams in the U.S. were developing in-situ burning policies (Brendhan Zubricki, National Park Service, Atlanta, personal communication 1994).

In-situ burning is most appropriate on floating slicks, in the early stages of a spill event when the oil can be kept thick enough (the oil must be at least 2-3 millimeters thick for proper burning) [777]. In-situ burning has possible application on land where there is heavy oil in sites not amenable or accessible to physical removal, where there is a water layer to minimize impacts to sediments and roots (such as in wetlands or muddy habitats), or where there is ice [777]. There are few studies on the relative effects of burning oiled wetlands compared to other techniques or natural recovery, but the limited data indicate little impact of burning relative to natural recovery when the soils are saturated [777]. Burning is not appropriate on dry muddy substrates where heat may impact the biological productivity of the habitat [777].

According the 1994 EPA Region IV Regional Response Team Policy draft, some of the potential air pollution products of the burning include PAHs as well as aldehydes, ketones, and esters. Temperature and air quality effects are likely to be localized and short-lived [777].

After participating in an in-situ program to evaluate burning spilled oil, the Mineral Management Service's oil spill research staff documented the following [662]:

> In a Newfoundland experiment in the summer of 1994, the efficiency of the burn was 99%, converting many compounds which would be hazardous as water or air (evaporation) pollution into carbon dioxide and water. Beyond 200 meters, all air pollutant compounds measured were below health concern levels.

Preliminary results from an Alaska study (September 1994), suggested that the addition of emulsion breakers permitted burning of slicks that contained up to 60% water.

Although burning creates a visible smoke plume, it can prevent water and sediment pollution that can continue environmental degradation for years, and it can prevent the air pollution caused when up to 50% of a slick evaporates.

Burning Information from EPA 1994 [663]:

Emissions from fuel oil combustion depend on the grade and composition of the fuel, and many other factors [663]. Because the combustion characteristics of distillate and residual oils are different, their combustion can produce significantly different emissions [663]. Emissions typically include formaldehyde and compounds which can almost exclusively be classed into a group known as polycyclic organic matter (POM), and a subset of compounds called polynuclear aromatic hydrocarbons (PNA or PAH) [663]. There are also PAH-nitrogen analogs [663]. Information available in the literature on POM compounds generally pertains to these PAH groups [663]. Trace elements are also emitted from the combustion of oil; the quantity of trace metals emitted depends on combustion temperature, the composition of the fuel the combustion conditions, and many other factors [663].

Total organic compounds (TOCs) emission from burning fuel oil include VOCs, semi-volatile organic compounds, and condensible organic compounds. Emissions of VOCs are primarily characterized by the criteria pollutant class of unburned vapor phase hydrocarbons. Unburned hydrocarbon emissions can include essentially all vapor phase organic compounds emitted from a combustion source. These are primarily emissions of aliphatic, oxygenated, and low molecular weight aromatic compounds which exist in the vapor phase at flue gas temperatures. These emissions include all alkanes, alkenes, aldehydes, carboxylic acids, and substituted benzenes (benzene, toluene, xylene, and ethyl benzene) [663].

References on emissions from burning oil include [663]:

Particulate Polycyclic Organic Matter, National Academy of Sciences, Washington, DC, 1972.

Vapor Phase Organic Pollutants -- Volatile Hydrocarbons and Oxidation Products, National Academy of Sciences, Washington, DC, 1976.

R.P. Hagebrauck, D.J. Von Lehmden, and J.E. Meeker, "Emissions of Polynuclear Hydrocarbons and Other Pollutants from Heat-Generation and Incineration Process," J. Air Pollution Control Assoc, 14:267-278, 1964.

Heavier oils, diesel and Bunker V fuel oils, did not burn without the addition of gasoline, wood chips, or methanol [AUTHOR: Wakamiya W; Petty SE; Boiarski A; Putnam A PUBLICATION YEAR: 1982 TITLE: Combustion of Oil on Water: An Experimental Program JOURNAL: Available from the National Technical Information Service, Springfield SOURCE: VA 22161, as DE82-014598].

However, when Ceuta crude oil and Bunker C Oil were burned both on water and on ice, the burning of these oils was effected by using peat moss as a wicking agent and diesel fuel as a promoter [AUTHOR: Coupal B PUBLICATION YEAR: 1976 TITLE: Controlled Combustion Tests Carried Out Near Rimouski JOURNAL: Technology Development Report EPS-4-EC-76-2, Environmental Protection Service, Ottawa, Canada SOURCE: March 1976, 15p., 4 fig., 2 tab].

Other notes on response methods vs. fate:

Mechanical methods can lead to physical disturbance, while chemical and biological clean up methods can lead to toxic impacts [777]. Briefly, the main physical, chemical, and biological response measures are [777]:

Physical response methods [777]:

Natural Recovery (meaning no response action), Booming, Skimming, Barrier/Berm, Physical Herding, Manual Removal/Cleaning, Mechanical Removal, Sorbents, Vacuum, Debris Removal, Sediment Reworking, Vegetation Removal, In-Situ Burning, Flooding, Low-Pressure Cold-Water Flushing, High-Pressure Cold-Water Flushing, Low-Pressure Hot-Water Flushing, High-Pressure Hot-Water Flushing, Steam Cleaning, Sand Blasting.

Chemical response methods [777]:

Dispersants, Emulsion Treating Agents, Visco-Elastic Agents, Solidifiers, Chemical

Shoreline Pretreatment, Shoreline Cleaning Agents.

Biological response methods [777]:

Nutrient Enrichment, Natural Microbial Seeding

There are pros and cons associated with each of the above response methods, depending on the particular spill environment (see the original reference [777] for details too lengthy to include in this document). For example, natural recovery may be appropriate on inaccessible habitats, or when cleanup actions will do more harm than natural removal [777]. On the other hand, natural recovery may be inappropriate where there are high numbers of mobile animals using the particular body of water or shoreline [777]. More information on dispersants, bioremediation, and in-situ burning is provided in the Detailed Information section below.

As mentioned above, the appropriateness of the method depends on site-specific factors such as the water environment, the shoreline habitat, and the particular oil spilled [777].

Details on Natural Resource Damage Assessment (NRDA) field methods and issues are summarized in the Laboratory and/or Field Analyses section below.

Misc. Source of Database Information:

Selected Abstracts and Bibliography of International Oil Spill Research is published on a gopher server provided by the LSU Libraries. Write to David Wuolu at notdjw@unix1.sncc.lsu.edu if you have any questions about this edition, which is an ASCII version of the original bibliography, received on two 3.5" floppies in the library on March 23, 1995. Content questions should be directed to the appropriate person listed below.

Selected Abstracts and Bibliography of International Oil Spill Research 1994 (Formatted in WordPerfect 6.0 for WINDOWS) Sponsored by: Louisiana Oil Spill Coordinator's Office/Office of the Governor American Petroleum Institute Marine Spill Response Corporation Available from: Louisiana Applied Oil Spill Research and Development Program Room E302 Howe-Russell Geoscience Complex Baton Rouge, Louisiana 70803 Suggested Citation: Louisiana Applied Oil Spill Research and Development Program. 1995. Selected Abstracts and Bibliography of International Oil Spill Research. Prepared by the Louisiana Oil Spill Coordinator, Office of the Governor, Baton Rouge: Louisiana Applied Oil Spill Research and

Development Program. pp. 578. Louisiana has been a leading producer of oil and gas for nearly 100 years. Many technological innovations in exploration and production have originated in Louisiana's oil fields. Significant innovations in response and knowledge about the impacts of discharges of oil and gas into the environment have also originated in Louisiana. As a part of its legal mandate, the Louisiana Oil Spill Coordinator's Office has established the Louisiana Applied Oil Spill Research and Development Program (OSRADP) to further original research in this field. In order to develop a base from which future research could be initiated, the OSRADP began the systematic compilation of this electronic reference file. We believe the resulting electronic bibliography will be a valuable addition to the growing body of knowledge associated with oil spills and their impacts. Quality research begins with a good idea, a thorough knowledge of the literature, and a well-designed research plan. We hope this work will aid current research as well as provide a catalyst for future research ideas. Roland J. Guidry Louisiana Oil Spill Coordinator DATABASE AND KEY WORDS This electronic bibliography was compiled from a key word list that best fits the mission of the Louisiana Applied oil Spill Research and Development Program (OSRADP). Consequently, some of the words and phrases used in the search may only apply to oil spill issues in Louisiana. Forty-three (43) data bases were searched and over 4,000 citations were downloaded. Duplicates have been deleted. Some citations were accompanied by annotations/abstracts that are included on the diskettes. The bibliography was organized alphabetically rather than chronologically. DATABASES USED IN COMPILING THIS BIBLIOGRAPHY Academic Index Aerospace Database Aluminum Industry Abstracts American Petroleum Institute Energy/Business News American Petroleum Institute Literature American Petroleum Institute Patent Aquatic Science and Fisheries Abstract Biosis Previews Bureau of National Affairs Daily News Chemical Abstracts Commonwealth Agricultural Bureaux Abstracts Chemical Engineering and Biotechnology Abstracts Dialog Sourceone (SM) Engineering Engineering Index Compendex Plus Electrical Power Database Energyline Federal News Service Federal Register Fluidex Geobase Georef INSPEC Information Service in Mechanical Engineering Mechanical Engineering Abstracts Metallurgy Index McGraw-Hill Publications Online National Technical Information Service Oceanic Abstracts Pascal Pollution Abstracts Petroleum Exploration and Production PTS Predicasts Overviews of Markets and Technologies PTS Newsletter Database PIRA Paperchem RAPRA Abstracts Standards and Specifications Trade and Industry ASAP Trade and Industry Index.

KEYWORDS AND PHRASES SEARCHED Assessment of ammoniated organic wastes Aquatic phytotoxicity of oils Bacterial degradation of hydrocarbons Baseline information for a spill risk index Biodegradation of toxic chemicals methods to track biodegradation of petroleum compounds Bioregeneration Bioremediation cleanup techniques and rehabilitation of oil-impacted wetlands monitoring procedures potential index soil oxidants as a means of accelerating oil bioremediation Digital data resources to support oil spill contingency planning Effects of oil contamination on freshwater mesocosms GIS-based oil spill analysis and trajectory modeling LANDSAT TM and synthetic aperture radar to facilitate coastline delineation Micro-sensors for detecting gases in environments. Oil Spill absorbents in removal of use of cleaners for removing oil from vegetation and chemical responses on fresh marsh functions and oil degradation and ground water awareness through education oil spill booms cleanup sorbent materials collective device containment using cationic polymer powder risk index real-time monitoring remote sensing detection and mapping oil/water separation techniques in-situ burning as a method of oil removal meteorological support systems for oil spill trajectory forecasting Pipeline and wellhead oil spill risk Used oil disposal Volunteer for oil spill clean-up project Wave energy and vegetative response to oil degradation DISCLAIMER This electronic bibliography was prepared as a reference tool for the oil spill and research communities to use to stay abreast of developments in oil spill research. The compilation involved searching 43 data bases for relevant material. Because bibliographic style and/or format varies among data bases, where appropriate, the citations have been partially edited to provide consistency to the final product. The bibliography is in WordPerfect 6.0 for WINDOWS. Each citation has been reviewed; however, no attempt has been made to edit annotations. They are reproduced as provided from the original sources. Consequently, any errors that may appear in content, spelling, or word usage are inherent to the citation. REPORT AVAILABILITY Extra copies of this electronic bibliography may be obtained by writing to: The Louisiana Applied Oil Spill Research and Development Program Electronic Bibliography Room E302 Howe-Russell Geoscience Complex Baton Rouge, Louisiana 70803 Telephone Number: (504) 388-3481 FAX Number: (504) 388-0403 or from: The Louisiana Oil Spill Coordinator/Office of the Governor Electronic Bibliography 1885 Wooddale Blvd., 12th Floor Baton Rouge, Louisiana 70806 Telephone Number: (504) 922-3230 FAX Number: (504) 922-3239

Laboratory and/or Field Analyses:

For details on lab method recommendations, see Petroleum, General and Crude Oil entries. See also: PAHs as a group entry. Additional notes on chemical analyses:

The methods required depend on the type of oil or oil product spilled, the age of the spill, and many other factors. The following text applies to oil spills in general:

Recent (1991) studies have indicated that EPA approved methods used for oil spill assessments (including total petroleum hydrocarbons method 418.1, semivolatile priority pollutant organics methods 625 and 8270, and volatile organic priority pollutant methods 602, 1624, and 8240) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These general organic chemical methods are deficient in chemical selectivity (types of constituents analyzed) and sensitivity (detection limits); the deficiencies in these two areas lead to an inability to interpret the environmental significance of the data in a scientifically defensible manner [468]. A better (than EPA method 418.1) "total hydrocarbons" measure would include the sum of resolved and unresolved complex mixture of the chromatographic trace, extracted with methylene chloride, and using cleanup and instrumental analysis similar to methods used for rigorous PAH analyses [468].

For weathered oil-impacted samples for which there is a need to identify the source of the oil, sterane and triterpane determinations may be needed. However, probably the most important target analytes in natural resource damage assessments for oil spill are PAHs and the homologous series (alkylated) PAHs [468]. Alkylated PAHs are more abundant, persist for a longer time, and are sometimes more toxic than the parent PAHs [468]. For example, methyl phenanthrene is more toxic than the parent compound phenanthrene. PAHs are valuable for identifying spilled oil, distinguishing between sources of hydrocarbons in the environment, and providing information on the extent of oil weathering and degradation [468].

Often the most useful chemical analyses of spilled oil include an "expanded" PAH scan which includes the most important alkylated PAHs [468,828]. In cases where a less expensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, the NOAA lab in Seattle, WA.

Petroleum products are comprised of varying amounts of PAHs, n-alkanes and isoprenoids (saturate hydrocarbon fractions of petroleum hydrocarbons). Although the PAHs and alkylated PAHS are usually of greater toxicological concern, all the components of an oil product are valuable for fingerprinting oil sources and tracking weathering [468].

It is important to understand that contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see also, discussion in the disclaimer section at the top of this entry).

As of 1997, the problem of lack of data comparability (not only for water methods but also for soil, sediment, and tissue methods) between different "standard methods" recommended by different agencies seemed to be getting worse, if anything, rather than better. The trend in quality assurance seemed to be for various agencies, including the EPA and others, to insist on quality assurance plans for each project. In addition to quality control steps (blanks, duplicates, spikes, etc.), these quality assurance plans call for a step of insuring data comparability [1015,1017]. However, the data comparability step is often not given sufficient consideration. The tendency of agency guidance (such as EPA SW-846 methods and some other new EPA methods for bio-concentratable substances) to allow more and more flexibility to select options at various points along the way, makes it harder in insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

At minimum, before using contaminants data from diverse sources, one should determine that field collection methods, detection limits, and lab quality control techniques were acceptable and comparable. The goal is that the analysis in the concentration range of the comparison benchmark concentration should be very precise and accurate.

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of inappropriate methods. The use of inappropriate methods is particularly common related to oil products.

Detection limit issues:

> Detection limit objectives and the choice of specific laboratory methods to be used should be derived from oil spill study objectives, not from analytical expedience. EPA method 8270 for PAHs provides for a detection limit of 1 ug/L, at least an order of magnitude above the detection limits desirable for scientifically defensible oil spill assessments [468].
>
> Based on biological concerns, recommended water sample detection limits are 10 ng/L (ppt) for individual PAHs [468]. Recommended tissue and sediment sample detection limits are 0.3 to 1 ppb (have the lab report both dry and wet weight) for individual PAH compounds. Some labs have complained that 10 ppb is as low as they can go on detections limits, but others have achieved 1 ppb, including Fish and Wildlife Service Contract Labs such as Texas A. and M. (John Moore, Patuxent Research Center, Fish and Wildlife Service, personal communication). If possible, the 1 ppb detection limit is better than higher detection limits for tissues or sediments (when trying to interpret biological effects), since effects can occur at such low concentrations.

> Note from Roy Irwin: One reason that low detection limits are needed for PAHs is that so many of the water quality criteria, standards, and screening benchmarks are in the lower ppb range (see various entries on individual PAHs).

There are three major objectives for the chemical analysis of oil, and different analytical methods may be necessary to accomplish these objectives. The three objectives are [771]:

(1) Physical and chemical characterization of the oil, including major constituents, to provide information on how that oil will behave in the environment, its potential fates, persistence, toxicity, and carcinogenicity, and to identify target analytes for fingerprinting;

(2) Fingerprinting, to determine whether the oil in an environmental sample is from the specific incident, or from another source of oil pollution; and

(3) Concentration, to determine the quantity of the oil or important constituents of the oil in environmental samples.

Decision tree keys (dichotomous keys) have been developed for the selection of lab methods for measuring contamination from light, midrange, and heavy oil products. Keys for light, midrange, and heavy products can be found in the Gasoline General, Diesel Oil General, and Crude Oil entries, respectively.

Example Key information for light crudes and mid range products:

> In choosing a lab method, it should be kept in mind that this product (as well as Diesel, No. 2 Fuel Oils, and Light Crudes) can be expected to exhibit the following characteristics [741]:
>
> -Moderately volatile; will leave residue (up to 1/3 of spilled amount)
> -Moderate concentrations of toxic (soluble) compounds
> -Will "oil" intertidal resources with long-term contamination potential
> -Has potential for subtidal impacts (dissolution, mixing, sorption onto suspended sediments)
> -No dispersion necessary
> -Cleanup can be very effective

Decision Tree (dichotomous key) for selection of lab methods for measuring contamination from light crude oils and middle distillate petroleum products (all diesels, jet fuels, kerosene, Fuel oil 2, Heating Oil 2):

1a. Your main concern is biological effects of petroleum products..2

1b. Your main concern is cleanup or remediation but no ecological or human resources are at risk............3

2a. The resource at risk is primarily humans via a drinking water pathway, either the contamination of groundwater used for drinking water, or the fresh* or continuing contamination of surface waters used as drinking water, or the risk is primarily to aquatic species in confined** surface waters from a fresh* spill, or the risk is to surface waters re-emerging from contaminated groundwater resources whether the spill is fresh* or not; the medium and/or pathway of concern is water rather than sediments, soil, or tissues 4

2b. The resource at risk is something else.....................5

3a. The spilled substance is a fresh* oil product of known composition: If required to do so by a regulatory authority, perform whichever Total Petroleum Hydrocarbon (TPH) analysis specified by the regulator. However, keep in mind that due to its numerous limitations, the use of the common EPA method 418.1 for Total Petroleum Hydrocarbons is not recommended as a stand-alone method unless the results can first be consistently correlated (over time, as the oil ages) with the better NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If not required to perform an EPA method 418.1-based analysis for TPH, instead perform a Gas Chromatography/Flame Ionization Detection (GC/FID) analysis for TPH using the spilled substance as a calibration standard. GC/FID methods can be sufficient for screening purposes when the oil contamination is fresh*, unweathered oil and when one is fairly sure of the source [657]. If diesel 1D was spilled, perform TPH-D (1D) using California LUFT manual methods (typically a modified EPA method 8015) [465] or a locally available GC/FID method of equal utility for the product spilled. However, no matter which TPH method is used, whether based on various GC/FID or EPA method 418.1 protocols, the investigator should keep in mind that the effectiveness of the method typically changes as oil ages, that false positives or false negatives are possible, and that the better Gas Chromatography-Mass Spectrometry-Selected Ion Mode (GC/MS/SIM) scans (such as the NOAA expanded scan***) should probably be performed at the end of remediation to be sure that the contamination has truly been cleaned up.

3b. The spilled product is not fresh* or the contamination is of unknown or mixed composition.......................6

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8240 (8240 is being replaced

by SW-846 method 8260 [1013]). The standard EPA GC/MS method 8260 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for possible use in a Natural Resource Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8240 (8240 is being replaced by SW-846 method 8260 [1013]) method using the lowest possible Selected Ion Mode detection limits and increasing the analyte list to include as many alkyl BTEX compounds as possible. Also analyze surface or (if applicable) ground water samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan*** modified for water samples using methylene chloride extraction. If the contaminated water is groundwater, before the groundwater is determined to be remediated, also analyze some contaminated sub-surface soils in contact with the groundwater for BTEX compounds (EPA GC/MS method 8260), and PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

5a. The medium of concern is sediments or soils..................6

5b. The medium of concern is biological tissues..................7

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8240 (8240 is being replaced by SW-846 method 8260 [1013]) using the lowest possible Selected Ion Mode (SIM) detection limits and increasing the analyte list to include as many alkyl Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds as possible.

7a. The problem is direct coating (oiling) of wildlife or plants with spilled oil product.....................................8

7b. The problem is something else...............................9

8. Perform NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs and/or GC/FID fingerprinting of the coating oil only if necessary to identify the source or exact oil. If the source is known and no confirmation lab studies are necessary: dispense with additional chemical laboratory analyses and instead document direct effects of coating: lethality, blinding, decreased

reproduction from eggshell coating, etc., and begin cleaning activities if deemed potentially productive after consolations with the Fish and Wildlife Agencies.

9a. The concern is for impacts on water column organisms (such as fish or plankton)...10

9b. The concern is for something else (including benthic organisms)..11

10. If exposure to fish is suspected, an HPLC/Fluorescence scan for polycyclic aromatic hydrocarbon (PAH) metabolites in bile may be performed to confirm exposure [844]. For bottom-dwelling fish such as flounders or catfish, also analyze the bottom sediments (see Step 6 above). Fish which spend most of their time free-swimming above the bottom in the water column can often avoid toxicity from toxic petroleum compounds in the water column, but if fish are expiring in a confined** habitat (small pond, etc.), EPA GC/MS method 8260 [1013] and the NOAA protocol expanded scan*** for PAHs could be performed to see if Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX), naphthalene, and other potentially toxic compounds are above known acute toxicity benchmark concentrations. Zooplankton populations impacted by oil usually recover fairly quickly unless they are impacted in very confined** or shallow environments [835] and the above BTEX and PAH water methods are often recommended rather than direct analyses of zooplankton tissues.

11a. The concern is for benthic invertebrates: analyze invertebrate whole-body tissue samples and surrounding sediment samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that the sediments which form the habitat for benthic invertebrates be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8240 (8240 is being replaced by SW-846 method 8260 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Bivalve invertebrates such as clams and mussels do not break down PAHs as well or as quickly as do fish or many wildlife species. They are also less mobile. Thus, bivalve tissues are more often directly analyzed for PAH residues than are the tissues of fish or wildlife.

11b. The concern is for plants or for vertebrate wildlife including birds, mammals, reptiles, and amphibians: polycyclic aromatic hydrocarbons (PAHs) and other petroleum hydrocarbons break down fairly rapidly in many wildlife groups and tissues are not usually analyzed directly. Instead direct effects are investigated and water, soil, sediment, and food items encountered by wildlife are usually analyzed for PAHs and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that these habitat media also be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8260 [1013]) or modified EPA method 8260 in the Selected Ion Mode (SIM). Less is known about plant effects. However, the same methods recommended above for the analyses of water (Step 4 above) and for sediments or soils (Step 6 above) are usually also recommended for these same media in plant or wildlife habitats. If wildlife or plants are covered with oil, see also Step 8 (above) regarding oiling issues.

* Discussion of the significance of the word "fresh": The word "fresh" cannot be universally defined because oil breaks down faster in some environments than in others. In a hot, windy, sunny, oil-microbe-rich, environment in the tropics, some of the lighter and more volatile compounds (such as the Benzene, Toluene, Ethyl Benzene, and Xylene compounds) would be expected to disappear faster by evaporation into the environment and by biodegradation than in a cold, no-wind, cloudy, oil-microbe-poor environment in the arctic. In certain habitats, BTEX and other relatively water soluble compounds will tend to move to groundwater and/or subsurface soils (where degradation rates are typically slower than in a sunny well aerated surface environment). Thus, the judgement about whether or not oil contamination would be considered "fresh" is a professional judgement based on a continuum of possible scenarios. The closer in time to the original spill of non-degraded petroleum product, the greater degree the source is continuous rather than the result of a one-time event, and the more factors are present which would retard oil evaporation or breakdown (cold, no-wind, cloudy, oil-microbe-poor conditions, etc.) the more likely it would be that in the professional judgement experts the oil would be considered "fresh." In other words, the degree of freshness is a continuum which depends on the specific product spilled and the specific habitat impacted. Except for groundwater resources (where the breakdown can be much slower), the fresher the middle distillate oil contamination is, the more one has to be concerned about potential impacts of BTEX compounds, and other lighter and more volatile petroleum compounds.

To assist the reader in making decisions based on the continuum of possible degrees of freshness, the following generalizations are provided: Some of the lightest middle distillates (such as Jet Fuels, Diesel, No. 2 Fuel Oil) are moderately volatile and soluble and up to two-thirds of the spill amount could disappear from surface waters after a few days [771,835]. Even heavier petroleum substances, such as medium oils and most crude oils will evaporate about one third of the product spilled within 24 hours [771]. Typically the volatile fractions disappear mostly by evaporating into the atmosphere. However, in some cases, certain water soluble fractions of oil including Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) compounds move down into groundwater. BTEX compounds are included in the more volatile and water soluble fractions, and BTEX compounds as well as the lighter alkanes are broken down more quickly by microbes than heavier semi-volatiles such as alkyl PAHs and some of the heavier and more complex aliphatic compounds. Thus after a week, or in some cases, after a few days, there is less reason to analyze surface waters for BTEX or other volatile compounds, and such analyses should be reserved more for potentially contaminated groundwaters. In the same manner, as the product ages, there is typically less reason to analyze for alkanes using GC/FID techniques or TPH using EPA 418.1 methods, and more reason to analyze for the more persistent alkyl PAHs using the NOAA protocol expanded scan***.

** Discussion of the significance of the word "confined": Like the word "fresh" the word "confined" is difficult to define precisely as there is a continuum of various degrees to which a habitat would be considered "confined" versus "open." However, if one is concerned about the well-being of ecological resources such as fish which spend most of their time swimming freely above the bottom, it makes more sense to spend a smaller proportion of analytical funding for water column and surface water analyses of Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile or acutely toxic compounds if the spill is in open and/or deep waters rather than shallow or "confined" waters. This is because much of the oil tends to stay with a surface slick or becomes tied up in subsurface tar balls. The petroleum compounds which do pass through the water column often tend to do so in small concentrations and/or for short periods of time, and fish and other pelagic or generally mobile species can often swim away to avoid impacts from spilled oil in "open waters." Thus in many large oil spills in open or deep waters, it has often been difficult or impossible to attribute significant impacts to fish or other pelagic or strong swimming mobile species in open waters. Lethality has most often been associated with heavy exposure of juvenile fish to large amounts of oil products moving rapidly into shallow or confined waters [835]. Different fish species vary in their sensitivity to oil [835]. However, the bottom line is that in past ecological assessments of spills, often too much money has been spent on water column analyses in open water settings, when the majority of significant impacts tended to be concentrated in other habitats, such as benthic, shoreline, and surface microlayer habitats.

*** The lab protocols for the expanded scan of polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs have been published by NOAA [828].

End of Key.

Experiments designed to assess oil impacts should examine the effects of both fresh and weathered oil. Exposure times for persistent chemicals in natural ecosystems are probably longer than what is normally used in routine laboratory tests [713].

Although generally not of as much toxicological concern as PAHs and alkylated PAHs, n-alkanes and isoprenoids (saturate hydrocarbon fractions of petroleum hydrocarbons) are valuable for fingerprinting oil sources and tracking weathering [468].

Abstracts on Fingerprinting:

Wade, T.L., T.J. Jackson, T.J. McDonald, J.L. Sericano, and J.M. Brooks. 1993. Oyster Polynuclear Aromatic Hydrocarbon Fingerprinting Applied to the Apex Barge Oil Spill. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks Houston, TX., (Nov. 14-18 1993), p. 17.

> An estimated 692,000 gallons of catalytic feed stock oil was spilled into Galveston Bay on July 28, 1990, when a tanker collided with three Apex barges in the Houston Ship Channel. Oysters were collected and analyzed from Galveston Bay Todd's Dump (GBTD) before the spill (235 days) and after the spill (6, 37, 132, 495, and 851 days). Oysters were also collected from Galveston Bay Redfish Island (GBRI), a site known to be impacted by the spill, 37 and 110 days after the spill. The spilled oil was also analyzed. The concentration of 18 polynuclear aromatic hydrocarbons (PAHs), measured as part of the National Oceanic and Atmospheric Administration's National Status & Trends (NS&T) showed a sharp increase from 100 ng/g (235 days before the spill) to over 600 ng/g (one week after the spill). Concentrations of these 19 PAHs were also found at GBRI. Fingerprinting techniques applied to data from oyster analyses demonstrated the presence of bioavailable Apex Barge oil 37, 110, 132 days after the spill at GBTD and GBRI. Fingerprinting becomes less diagnostic with time due to possible environmental weathering of the oil.

A.G. Requejo, T. McDonald, G. Denoux, M.C. Kennicutt, R. Sassen, and J.M. Brooks. 1993. Multivariate Analysis of Environmental Data: A tool for interpreting results of "fingerprinting" analyses. Society of Environmental Toxicology and Chemistry (SETAC) 14th annual meeting. Westin Galleria and Oaks, Houston, TX., (Nov. 14-18 1993), p. 17.

> Chemical Analyses of environmental samples using "fingerprinting" techniques often result in large quantities of data for each sample. For example, a typical soil or sediment analysis might include concentrations of targeted saturated hydrocarbons, polynuclear aromatic hydrocarbons, chlorinated hydrocarbons, and trace metals, in addition to bulk parameters such as organic carbon and nitrogen content and grain size distributions. The sheer volume and diversity of this type of data can make

its interpretation difficult. Multivariate analytical techniques such as Principal Components Analysis (PCA) are ideally suited for the reduction and synthesis of such data sets. PCA employs eigenvector analysis to evaluate the degree of similarity between samples and establish the interrelationship between measured analytes. The major advantages of PCA in comparison to traditional data interpretation approaches are that it is fast, objective, and employs all the data measured. The utility of this approach will be demonstrated using several different sets of environmental "fingerprinting " data. Included among these are fluorescence and polynuclear aromatic hydrocarbon data from bioremediated soil samples containing petroleum and trace organic and inorganic data from estuarine sediments (Casco Bay, Maine).

Other information:

Metals:

Since metals are a concern with many oil products (Crude Oil entry) an ICP scan for a general suite of metals should supplement organic analyses.

Organics:

Although EPA method 418.1: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH), is recommended by many State agencies, some consulting firms, and some laboratories for certain regulatory and screening applications (often leaking underground storage tanks), this method is not well suited to crude oil contamination or to the more persistent hazardous constituents in oil. (See entry entitled: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons). Low values tend to give the mistaken impression that a site is clean when it really isn't (a false negative). For example, a field test of bioremediation of soils contaminated with Bunker C (a heavy fuel) at a refinery in Beaumont, Texas, utilized oil and grease data, which (although the data was quite variable) seemed to indicate bioremediation was taking place [728]. A comparison of the oil and grease data at this site with TPH data at this site suggested the same thing, that the data was quite variable but if anything, the oil was being slowly being cleaned up by bioremediation (Bruce Herbert, Texas A. and M., Department of Geology, personal communication, 1995). However, a later study of the same site utilizing the expanded scan for PAHs [828] (a modified EPA 8270 including alkyl homologues and lower detection limits) [828], indicated that very little bioremediation of hazardous alkyl PAHs and multi-ring PAHs was actually taking place [727]. Thus, utilizing either oil and grease or TPH analyses would tend to lead one to the faulty conclusion that the harmful compounds were being naturally cleaned up at an acceptable rate. This is partly because the TPH and oil and grease methods tend to favor the lighter and less alkylated PAHs, whereas many of the carcinogenic and longer lasting PAHs are the heavier multi-ringed and alkylated compounds.

Overall damage assessment strategy [545]:

The following are proposed as relevant chemical and biological parameters to monitor based on the proximity of the spill to established monitoring sites, on the size of spill, on the type of spill, etc. These serve as the basic protocols of the Geochemical and Environmental Assessment Response (GEARS) sampling strategy [545]:

Sampling of water column (and possibly slick samples) at selected depths and distances for aliphatic and polynuclear aromatic hydrocarbons (PAH) to establish environmental exposure levels, evaporative loss to the atmosphere, dispersant, or bioremediation effectiveness;

Sampling of surficial sediments to establish inputs to subtidal and intertidal sediments;

Sampling of shellfish (oysters or mussels) tissues to establish contaminant elevations in fauna that are used as biomonitors of chronic contamination;

Sampling of fish bile for PAH metabolites to estimate exposure to toxic aromatic hydrocarbons;

Sampling of fishes and crabs for tissue and liver contaminant concentrations;

Sampling of animals for bioindicator studies (stress proteins, metabolic enzymes, DNA integrity, histopathology, and reproductive impairment);

Sampling of infaunal populations to establish impacts on the benthic biota [545].

Biological indicators of oil exposure:

Because changes in animal growth and reproduction ultimately affect the population as a whole, they are ideal measurements for establishing an effect of oil exposure. Although growth and reproduction are easily measured, changes in these parameters are sometimes difficult to observe, especially in the field. Therefore, it is useful to measure other biochemical and physiological parameters (MFO activity, tissue residues of oil/PAH, histopathological changes, and hormonal changes, to name a few) to aid in interpreting the effects of oil on individual organisms [713].

The following have been proposed as indicators of exposure to oil [713]:

ANIMALS

- -presence of oily odor on body
- -presence of visible oil on skin, fur, plumage, etc.
- -presence of visible oil on eggs
- -presence of petroleum hydrocarbons in tissue (like skin, fat, liver, kidney)
- -presence of fluorescent aromatic carbons (FAC) in bile
- -induction of mixed function oxygenase (MFO) enzyme system
- -changes in glutathione concentration and glutathione-S-transferase activity
- -hemolytic anemia and destruction of red blood cells [713]

PLANTS

- -presence of oily odor on plant
- -presence of visible oil on plant surface
- -presence of petroleum hydrocarbons in tissue [713]

HABITAT

- -presence of oily odor in water, sediment, soil or air, or on rocks
- -presence of visible oil in water, sediment or soil, or on rocks
- -presence of petroleum hydrocarbons in water, sediment, soil or air [713]

One researcher found hydrocarbon concentrations in ringed seals declined less rapidly in muscle than in liver or blubber tissues. Although fat and liver may have higher concentrations of hydrocarbons, muscle tissue may be a better indication of hydrocarbon concentrations over time [713].

MFO activity will vary with species, age, sex, and organ. Because of these differences, there are dangers in extrapolating from one species to another [713].

Natural resource damage assessment methods. Since many oil spill situations involve Natural Resources Damage Assessment issues, natural resource managers should also be familiar with the following NRDA document in progress (1995), summarized below [771]:

> The following information from National Oceanic and Atmospheric Administration (NOAA). Damage Assessment and Restoration Program. August 1995. Injury Guidance Document for Natural Resources and Services under the Oil Pollution Act of 1990 (Public Review Draft). Prepared by M.T. Huguenin, D.H. Haury, and J.C. Weiss (Industrial Economics, Inc.); D. Helton, C. Manen, and E. Reinharz (NOAA); and J. Michel (Research Planning, Inc.) [771], reproduced with permission of E. Reinharz:

Demonstrating exposure [771]:

> Demonstrating exposure is an important step in determining injury, but evidence of exposure alone is not sufficient to conclude that injury to a natural resource has occurred (the presence of petroleum hydrocarbons in oyster tissues is not in itself an injury) [771]. The purpose of the exposure portion of an injury assessment is to determine whether natural resources came into contact, either directly or indirectly, with the oil and to estimate the amount or concentration of the oil and the geographic extent of the oil (see the Fate.Detail section for examples of direct and indirect pathways). This information is necessary to design, interpret and extrapolate the results of the injury studies [771].
>
> A number of factors should be considered when formulating hypotheses regarding the potential for, and significance of, exposure [771]:
>
> Presence of oil in transplanted bivalves [771]:
>
>> Bivalves such as clams, mussels, and oysters can be used as indicators of exposure and bioeffects. Biomonitoring with transplanted bivalves can provide integrated information about the bioavailability and effects of oil which cannot be determined solely through the chemical analysis of discrete water

samples. This capability is particularly important in monitoring oil discharges where exposure can be highly variable. The uptake of the discharged oil by bivalves is evidence of exposure to the bivalves themselves as well as an indication of exposure for other injured natural resources. Bivalve collection and procedures for chemical analysis of tissues have been standardized as part of the National Status and Trends Program (see references 676 - 680) [771].

Surrogate samplers [771]:

Water column and sediment exposure may be integrated over time through the use of surrogate samplers, such as semi-permeable membrane devices (SPMDs) or lipid bags [771].

Pah metabolites [771]:

Many oil components including benzene and polycyclic aromatic hydrocarbons (PAHs) are rapidly metabolized by aquatic organisms and do not tend to accumulate in tissues. For vertebrates, documentation of exposure to petroleum hydrocarbons may be complicated. However, the metabolites of PAH compounds can be detected, especially in bile even though the parent compound may no longer be detectable. Presence of these metabolites is an indication that the organism has been exposed to PAHs, but it may be difficult to determine the exact source of that exposure [771].

Mixed function oxygenase (MFO) enzymes [771]:

Certain organisms possess enzyme systems that can detoxify contaminants. The most important enzymes in the detoxification process are known as MFO enzymes. The activity of these enzymes is evidence that the organism has been exposed to contaminants. However, interpretation of enzyme activity level is complicated because other stresses can lead to elevated levels, so other exposure data may be necessary to confirm that the elevated levels are associated with the contaminant of concern [771].

Hemolytic anemia [771]:

The decreased concentration of red blood cells and/or hemoglobin has been used as an indicator of oil exposure in certain vertebrates. Birds that have been exposed to oil may develop anemia within days. Sea otters exposed to oil from the Exxon Valdez incident also developed anemia [771].

Oil type [771]:

The physical and chemical characteristics of the oil will strongly influence the potential for, and nature of, exposure [771].

Spill volume [771]:

The size of the discharge will affect the nature of the exposure. During small discharges, for example, oil may concentrate in a band along the high tide line. The greatest potential for exposure may therefore occur at the high tide line and in detrital material. Under heavy accumulations, however, oil may cover the entire intertidal zone [771].

Cleanup effects [771]:

If oil is removed from the environment quickly and before it comes in contact with sensitive natural resources, the potential for exposure will be greatly minimized. Response actions also may change the nature of oil exposure. For example, use of chemical dispersants will increase exposure to the water column. Increased sediment exposure may occur where machinery and foot traffic force oil into the substrate, and equipment staging areas may also be severely impacted [771].

Shoreline type and exposure [771]:

The potential for exposure to oil varies with shoreline geomorphology and degree of exposure. In high energy areas, oil may be rapidly dispersed, generally reducing the potential for exposure. However, these same forces may result in oil being deposited above the high-water swash (narrow channel through which the tide flows), or buried by clean sand. Stranded or buried oil may be highly persistent. Oil exposure to rocky headlands may be minimal, but a sheltered beach a few meters away, where wave energy is less, may be heavily oiled [771].

Sediment size [771]:

Oil holding capacity and the depth of penetration depends on sediment size. Oil will penetrate coarse-grained sediments much more rapidly and more deeply than fine sediments [771].

Tide stage [771]:

For certain natural resources, the potential for exposure will depend on tidal height. Subtidal seagrass beds are generally less sensitive to oil discharges than intertidal plants, since they usually do not come into direct contact with the floating oil. Similarly, supratidal vegetation may be exposed to floating oil only on the highest spring tides [771].

Weather conditions [771]:

Flood conditions or storm-driven tides may strand oil in areas that would otherwise be immune from oiling. In freshwater systems, oil may be carried over stream or river banks and stranded in the flood plain. In open water, high winds and waves may break up some oils and minimize shoreline contamination. Weather conditions also can accelerate or retard oil weathering. Temperature can affect species presence and behavior, and thus potential for exposure to oil and injury [771].

Behavior and life history considerations [771]:

Animal behavior is a significant factor in the potential for exposure. For example, the feeding and roosting behavior of birds is a major factor in their potential for exposure to oil (King and Sanger, 1979). Certain life stages may be more vulnerable than others. For example, planktonic fish larvae have a greater potential for exposure because they tend to drift at the same rate as the oil, while adult fish may be able to avoid contaminants. Depending on the season, migratory birds and wildlife may be present and therefore, at risk for exposure. Animals that aggregate during reproduction, such as certain marine mammals, birds, and fish may be highly vulnerable [771].

Duration of exposure [771]:

Time of exposure is a critical consideration in evaluating the potential for injury. A pelagic fish that is briefly exposed to oil while passing through a plume will be less likely to be injured than a fish that remains or is confined in the discharge area [771].

Approaches to exposure assessment [771]:

Exposure is generally evaluated with a combination of quantitative and qualitative methods [771]. As with other elements of the NRDA process, selection of appropriate strategies for determination of oil exposure will depend on the type and volume of discharged oil, natural resources at risk, nature of the receiving environment, and availability of personnel, funds, and equipment. A few of the potential approaches to evaluating exposure are described below [771]:

Computer models [771]:

Trajectory and weathering models may provide the first quantitative information on the fates of oil and the likelihood for exposure to specific natural resources and habitats. Models include NOAA's On-Scene Spill Model (OSSM) and ADIOS, the U.S. Department of the Interior's Type A models, Natural Resource Damage Assessment Model for Coastal and Marine Environments (NRDAM/CME) and Great Lakes Environments (NRDAM/GLE), and the SAIC oil weathering model (Payne et al., 1983) [771].

Visual observation [771]:

Aerial and ground surveys provide a rapid tool for exposure assessment of large areas. This approach is especially useful in documenting the overall distribution of oil-induced injuries by habitat or region, as well as identification of potential reference and impact areas. The qualitative and semi-quantitative information collected in this manner is generally combined with more detailed ground surveys and oil sampling to confirm exposure [771].

Presence of oily odor [771]:

Exposure to oil may also be evaluated qualitatively through organoleptic testing, the sensory evaluation of tainting using taste and smell. The ability to detect oils by smell will vary with the chemical composition of the oil, degree of weathering, and sensitivity of the individual. Low molecular weight oil components tend to be the easiest to smell, while the high molecular weight oil components, which may be of the greatest concern for possible long-term effects, are less volatile and thus harder to detect [771].

Body burden [771]:

Exposure to oil can be evaluated with a suite of analytical chemistry techniques ranging in cost, selectivity, and sensitivity. The choice of the method(s), analytes, and detection limits should be made by the NRDA team, in concert with their analytical laboratory, and should depend on: the circumstances of the discharge; the type of sample; the required sensitivity; the degree of sample degradation, metabolism, and weathering; and whether quantitative or qualitative information is necessary. Chemical analyses for fingerprinting, for example, may provide information on the type and degree of weathering of the oil, but generally will not provide an estimate of the concentration of the contaminant in the sample matrix. However, both fingerprinting and determination of contaminant concentrations can be accomplished simultaneously, depending on how the sample is collected [771].

NOAA Preassessment Phase Recommendations [623]:

Stating a clear objective often seems so obvious that it is not explicitly mentioned by investigators considering sampling projects. However, it is frequently the case that objectives are not well formulated, resulting in inconclusive results. With clearly stated objectives, the trustees can be confident in the design and implementation of data collection plans. During preassessment activities at a discharge of oil, chemical samples are collected primarily to answer the following basic questions [623]:

1. Is this oil the same as the oil which was

discharged?;

2. What is the concentration of the oil in the media being sampled?; and

3. What is the composition of the oil in the media being sampled?

The quality of the results obtained from the sample analysis is directly related to [623]:

Collecting representative samples;

Using appropriate sampling techniques; and

Properly preserving the samples until they are analyzed.

Environmental Samples for Fingerprint Analysis [623]:

Samples for fingerprint analysis are collected to answer the question "Is this oil the same as the oil which was discharged?" Consequently, such samples do not have to be quantified, or related to a measured amount of sample. Fingerprint samples are grab samples, not composites. They are compared with a "source" sample, preferably one carefully collected directly from the original container (i.e., vessel, pipeline, tank), and not from floating slicks or stranded oil.

The following techniques are used to collect thin sheens: for offshore, a special sheen sampler composed of teflon strips on a line is pulled through the sheens; for nearshore, pre-cleaned teflon filter papers are used to pick up small sheens (Henry, 1993). In all cases, special care is taken to prevent contamination with sheens from the exhaust of boat motors or washing off the sides of the sampling platform. Samples for fingerprinting can also include tarballs, oiled sediments, oiled animal parts (i.e., preferably fur/feathers), and oiled vegetation. Biological samples are collected in clean, glass jars or cleaned aluminum foil and kept frozen until analysis. Sample containers, sample volumes, and holding times are listed in the NOAA document [623]. All lids should be cleaned aluminum- or teflon-lined, not plastic.

Collection of Water Samples [623]:

Water samples are very difficult to collect where surface oil slicks are present. When sampling in areas covered by a surface slick, extreme care is needed to "knock" the surface slick aside so that the sampling device can be lowered into the water without becoming contaminated. Water samples should be collected directly in the sample container since oil droplets readily adhere to the inside of most samplers. For shallow water samples, it is necessary to wade into the water or lean over from a platform to collect the sample. The container is opened, allowed to fill, and closed at the desired water depth. Deeper water samples have to be collected by lowering the sampling container to the desired depth and remotely opening and closing the container at that depth. Under most conditions, concentrations in the water will be very low, and the potential for contamination is high. Additionally, surface slicks and the water-accommodated fraction track differently. Therefore, the presence of oil on the water surface is not always an appropriate criteria for collection of water-column samples.

Depending on the analytical method used, minimum sample volumes range from one liter to one gallon. With replication, the volume of water shipped to the laboratory can be significant. Ideally, water samples should be stored no longer than eight hours, although, if they are kept cold (4°C) and dark, water samples may be stored for as long as five days. Background samples should be collected well away from any oiled areas, being careful not to sample along the vessel path or near any boat or aircraft engines, to reduce the chance of contamination.

Additional detail on water sampling [623]:

> Water samples should be collected through deployment of water samplers to the desired depth of sampling, rather than using pumps and tubing. With pumps and tubing, there is always the risk that oil droplets will adhere to the inside wall of the tubing and be released randomly, making collection of a representative water sample difficult. The most commonly used samplers are the Kemmerer, Van Dorn, Niskin, and Nansen samplers. Samplers should be teflon-lined or composed of stainless steel. Multiple water samplers can be fixed on a rosette frame so that several depths can be sampled during one cast or replicate samples can be taken at the same depth.

When collecting water samples, the best technique is to collect the sample directly in the sample container, rather than having to transfer the water from the sampler to the container. This technique will minimize the potential for loss of sample integrity due to adherence of oil droplets to the inside surfaces of the sampler. The sample container is attached to a weighted holder which has a spring-mounted teflon stopper which can be opened once the container has reached the selected depth. Some types of sample bottles are designed for deployment with the stoppers closed. For example, Go-Flo bottles have a pressure sensor which triggers the opening of the stoppers when the sample bottle reaches a depth of about 10 meters. When it is necessary to collect water samples where surface slicks are present, use of a close/open/close type of bottle is required.

When sampling in clean areas, standard water samplers can be used. Prior to deployment, the stoppers of water samplers are cocked open. At this step, it is critical that the stoppers and the interior of the sampler remain free from contamination. All members of the sampling team should avoid touching the stoppers and the insides of the sampler.

Once the sampler reaches the desired depth, it should be allowed to equilibrate with ambient conditions for 2-3 minutes before it is closed. It is recommended that at least two samplers be used simultaneously for each depth. A second sampler provides a backup to the primary sampler in case of malfunction. A second sampler also increases the volume of sample available for subsampling and rinsing. To ensure that all subsamples at a particular depth are collected from the same water parcel, it is essential that they all be taken from a single cast, such as through use of a rosette sampler. Multiple casts using a single water sampler cannot meet this objective.

Once the water sampler is brought on board the sampling vessel, the stoppers should be checked immediately for integrity of the seals. If a stopper is not properly sealed, water from the sampled depth may have leaked out during retrieval and been replaced by water from shallower depths. In such cases, the entire water sample should be rejected.

Because a visual inspection might not detect all leaks, an additional check on sampler function may be conducted when sampling in marine settings. This check involves comparing the salinity of the water sample with ambient salinity determined with a CTD (Conductivity-Temperature-Depth probe) deployed with the sampler. A significant difference between ambient salinity and the salinity of a sample or an inconsistency between the salinity of a sample and the salinity profile determined from water in the other samplers from the same cast are indications that a particular sample is invalid. Water samples for chemical analysis and toxicity testing may consist of a single grab sample or a composite collected over a specific period. Containers must be made of non-toxic materials such as Nalgene, high density polyethylene, or polypropylene, and should be new and thoroughly cleaned before use. In the field, containers should be rinsed with sample water at least three times before collecting the actual sample. Each container should be filled completely to exclude any air and sealed appropriately. All containers should be placed on ice as soon as possible. They should be kept cold (4°C) and dark, never frozen. If the sample is collected directly in the container, care should be taken to assure integrity of the sample label.

Collection of Sediment Samples [623]:

Sediment samples are collected from two general settings: surface sediments (i.e., terrestrial soils and intertidal sediments) which are readily visible and collected by hand; and subtidal sediments which are usually sampled with a remote sampling device. Intertidal surface sediments and soils are relatively easy to sample since variability in the sediment type and degree of contamination can be readily discerned and described. Two of the most difficult issues in sediment sampling at oil discharges are:

Collection of a representative sample where there is extreme variability in the amount of oil. On an oiled marsh, the contamination will range from oil pooled on the surface to patches adjacent to visibly clean sediments. This problem is even more difficult where the sediments are coarse (i.e., in the range of pebbles to cobbles) and where the natural variability is compounded by the size of the clasts compared to the sampling container. One approach is to composite sub-samples, but this approach does not facilitate statistical analysis of the variability at a site.

Prevention of cross contamination when moving between heavily contaminated sites and clean sites. Keeping sampling equipment and supplies clean between sites at an oil discharge is very difficult. The only guarantee against cross contamination is to use new, clean utensils at every sampling site. On-site cleaning of utensils or corers is not recommended. Blanks are extremely important to collect, particularly at the cleaner sites.

Detailed descriptions and photographs of the samples and site are needed. Photoscales are always used when photographing sediment sampling sites. Documentation includes both overview and close-up photographs. To determine oil penetration with depth, trenches are dug, described, and photographed. Grain-size estimators (i.e., field guides that visually show grain-size classes) are used to describe sediment textural parameters. Standard oil descriptors are used to characterize the type and degree of contamination. Sampling site locations are shown on detailed field sketches or maps.

Subtidal or bottom sediment samples pose a different set of problems mainly because they require use of sampling devices deployed from a boat, or diver-held corers. Samplers which take box cores with minimal disturbance of the surface are the preferred device because most of the contamination in the first few weeks is likely to be on the sediment surface. Box corers also allow ready collection of replicates or composites at a site. Cleaning of the sampling device is a second problem, especially when the sediment contamination levels are high. Soap and water, scrub brushes, large volumes of clean water, and solvent rinses are needed to clean the sampling device between stations. Collection of the waste solvent for disposal must also be addressed.

It is important to record water depth, time of collection (i.e., so depth can be corrected to mean sea level in tidal waters), sediment description, visible oiling conditions, depth of bioturbation, presence of oxidized and reduced zones, and presence and relative density of invertebrates. The sediment surface should be photographed prior to collection from the corer.

Samples of approximately 100-200 grams (i.e., approximately one cup) are usually sufficient. The data collection plan should specify the sample intervals and depths. All samples should be numbered uniquely. It is important to have preassigned numbering series for samples when multiple teams are in the field collecting samples. Samples are collected with clean metal utensils or wooden tongue depressors and placed in precleaned glass jars with teflon-lined caps.

Detailed information from NOAA guide [623]:

> Collection of Subtidal Surficial Sediments: This section describes the procedures required to collect an acceptable subtidal surficial sediment sample for chemical analysis and/or toxicity testing. In the past, sampling crews were given relatively wide latitude in deciding how to collect samples. However, because sample collection procedures influence the results of all subsequent laboratory and data analyses, it is critical that samples be collected using acceptable and standardized techniques. Detailed methods are provided here because few groups routinely collect subtidal samples.
>
> Design and Operation of Sediment Samplers [623]: The primary criterion for an adequate sampler is that it consistently collects undisturbed samples to the required depth below the sediment surface without contaminating them. An additional criterion is that the sampler can be handled properly onboard the survey vessel. An otherwise acceptable sampler may yield inadequate sediment samples if it is too large, heavy, or awkward to be handled properly. A common sampling device for subtidal surficial sediments is the modified van Veen bottom grab. However, various coring devices (e.g., box corer, Kasten corer) are also used.
>
> Collection of undisturbed sediment requires that the sampler:`
>
>> Creates a minimal bow wake when descending;

Closes to form a leak proof seal after the sediment sample is taken;

Prevents sediment washout and excessive sample disturbance when ascending; and

Allows easy access to the sample surface.

Most modified van Veen grabs have open upper faces that are fitted with rubber flaps. Upon descent the flaps are forced open to minimize the bow wake, whereas upon ascent the flaps are forced closed to prevent sample washout. Some box corers have solid flaps that are clipped open upon descent and snap shut after the corer is triggered. Although most samplers seal adequately when new, the wear and tear of repeated field use eventually reduces this sealing ability (i.e., through chipped or improperly aligned jaws). A sampler should therefore be properly maintained and monitored constantly for proper operation and minimal sample leakage. If unacceptable leakage occurs or the sampler malfunctions in any manner, the sampler should be repaired or replaced. If a sampler is borrowed or leased for a project, its operation and sealing ability should be evaluated prior to sampling. Further, it is prudent to have a backup sampler onboard the survey vessel if the primary sampler begins leaking during a cruise.

The required penetration depth below the sediment surface is a function of the desired sample depth. Generally, it is better to penetrate below the desired sample depth to minimize sample disturbance when the sampling device closes. Penetration depth of most sampling devices varies with the sediment character; it is greatest in fine-grained sediments and least in coarse-grained sediments. In both cases, penetration depth can be modified by adding or removing weights from the samplers. Thus, it is optimal to use a sampler that has a means of weight adjustment. If a sampler cannot consistently achieve the desired penetration depth, an alternate device should be used.

The sampler should be brought aboard the vessel with a minimum amount of swinging to minimize sample disturbance. Once the sampler is secured onboard the survey vessel, it is essential that the surface of the sample be made accessible without substantially disturbing the sample. Most samplers have hinged flaps on their upper face for this purpose. The openings in the upper face of the sampler should be large enough to allow convenient subsampling of the sediment surface. If an opening is too small, the sample may be unduly disturbed during subsampling.

The sampling device should be attached to the hydrowire of the vessel boom using a ball-bearing swivel. The swivel will minimize the twisting forces on the sampler during deployment and ensure that proper contact is made with the bottom. For safety, the hydrowire, swivel, and all shackles should have a load capacity at least 3 times greater than the weight of a full sampler. In addition, screw-pin shackles should have wire through the eye and around one side of the shackle to prevent the pin from rotating.

The sampler should be lowered through the water and retrieved at a controlled speed of approximately l foot per second. Under no circumstances should the sampler be allowed to "free fall" to the bottom, as this may result in premature triggering, an excessive bow wake, or improper orientation upon contact with the bottom. The sampler should contact the bottom gently, and only its weight or piston mechanism should be used to force it into the sediment.

Sediment Sampling Interval [623]:

> The upper 2 cm of sediment is recommended for analysis because that is the sediment horizon in which most infaunal organisms reside and the horizon that is contacted most frequently by epifaunal organisms. When collecting the upper 2 cm of sediment, it is recommended that a minimum penetration depth of 4-5 cm be achieved for each acceptable sample. The portion of sample below the upper 2 cm of sediment can be discarded after the surficial sediment is collected (unless the study design specifies otherwise). Although the 2-cm specification is arbitrary, it will ensure that:

Relatively recent sediments are sampled;

Adequate volumes of sediment can readily be obtained to satisfy the needs of most study objectives; and

Data from different studies (historical or ongoing) can be compared validly.

Sampling depths other than the upper 2 cm may be appropriate for specific purposes, or when baseline data are available for a different interval.

Example Recommendation for a Standard Emergency Field Kit [623]:

The standard kit contains the equipment and supplies most likely needed for NRDA activities at most discharges. At the time of the discharge, nautical charts, topographic maps, and road maps for the discharge site are added.

92-quart cooler with side handles (can be used as carrying case for the kit)

-- Day pack

-- Box-type plastic clipboards

-- Waterproof logbooks with numbered pages

-- Expanding file folders, containing the following paper/forms

  - Original and copies of field forms to be used

  - Waterproof paper for copying field forms

  - Chain-of-custody forms

  - Activities checklist

  - Organization phone lists

  - QA protocols for selected sampling methods

  - Sample tags and labels

  - Field estimator guides for percent cover, grain size, etc.

- Camera: 35-mm, SLR with 50-mm lens, UV and polarizing filters, carrying case
- Film: five rolls each of ASA 64, 100, and 400 slide film; color print film
- Photoscales: 15 cm and 30 cm
- Mechanical pencils with replacement lead and erasers
- Waterproof ink markers
- Color pencil and marker sets
- Pads of paper
- Ruler and dividers
- Large, heavy rubber bands
- Various types of tape: masking, cellophane, strapping, electrical, and duct tape
- Plastic bags: various sizes of Ziploc bags; whirl-pak bags; large trash bags
- Calculator
- Micro-cassette tape recorder, with extra tapes and batteries
- Hand lens
- Tally meter
- Flashlight with extra batteries
- Binoculars
- Compass
- Refractometer
- Thermometer
- Rubber gloves, both surgical and heavy-duty vinyl
- Ear plugs

-- Tar-off towelettes

-- First-aid kit

-- Field pocket knife

-- Folding shovel

-- Wooden tongue depressors in small packs

-- Roll of paper towels

-- Disposable plastic scoops and stainless steel spatulas

-- Precleaned aluminum foil and extra rolls

-- Evidence tape

-- Sample jars: precleaned glass jars with teflon lids

  - 100-ml: box of 24

  - 500-ml: box of 12

  - 1,000-ml: box of 12

  - 1-gallon bottles: box of 4, with shipping containers

-- Prepaid overnight carrier shipping forms

-- Field guide books (birds, fish, invertebrates, mammals, plants, macroalgae, etc.)

Optional Equipment for Standard Kits [623]:

In addition to the items listed above, there are larger and more expensive pieces of equipment which can be extremely valuable on-scene. It is usually possible to lease these from local vendors at the discharge site or ship them on-scene once the need arises. These include:

Pager for each team member, assuming that there is coverage for the discharge site

-- Portable cellular phone, assuming that there is coverage for the discharge site

-- All-weather video camera, with extra

batteries, extra tapes, and cigarette lighter recharger option

- -- Portable computer with FAX modem and extra disks
- -- Portable printer
- -- Global Positioning System (GPS) hand-held unit

Specialized Survey Kits [623]:

In addition to the items listed above, special kits can be developed for the following types of surveys:

Shoreline Survey Kit [623]:

Profile rod set

- -- 50-m fiberglass tape measure
- -- Hand level
- -- Flagging tape
- -- Cement trowel for scraping the surface of trenches
- -- Precleaned aluminum core barrels
- -- Grain-size estimators 0.25 m2 and 1.0 m2 quadrats

Water Sampling Kit [623]:

Water samples need to be kept cold and dark immediately after collection to minimize sample degradation. Samples should be collected directly in the sample jar rather than transferred from the collecting bottle into the sample jar.

Water-sample holder to collect water samples directly in the sampling jar

- -- Additional boxes of precleaned glass jars (1,000-ml and 1-gallon)
- -- Teflon squeeze bottle for rinsing solvents

- Rinsing solvents for cleaning sample holder
- Preserving chemicals, if needed
- Solvent waste container
- Alconox cleaner soap
- Scrubbing brush
- Collapsible containers
- Salinity, temperature, and conductivity meter

Aquatic Biological Sampling Kit [623]:

- If the kit is to be shipped by a commercial carrier, the need for special packages or volume limits for fixatives and preservatives should be determined.
- Small dip net
- Small grab or dredge (e.g., Ponar grab, Ekman dredge)
- Small beach seine
- Kick net
- Small plankton net with several replacement nets and collecting bottles
- Sieve bucket
- Wash bottle and graduated cylinder
- Collapsible plastic containers
- Fish measuring board
- Nalgene sample bottles, various sizes
- Identification keys (e.g., invertebrates, fish)
- Field balance
- Fixatives
- Preservatives

-- Sorting pans with white bottoms
-- Field forms
-- Meter sticks
-- Photoscales
-- 0.25 m2 and 1.0 m2 quadrats
-- Sample vials, various sizes
-- Sample labels
-- Permanent markers
-- Random number table
-- Magnifier