ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

NAPHTHALENE ENTRY

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Like a library or most 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 with out 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:

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on the internet or NTIS: 1998).

Naphthalene (CAS number 91-20-3)

Note: since total naphthalenes are sometimes compared to various naphthalene benchmarks and criteria, this entry includes a discussion of total naphthalenes (total NPHs), the sum of C1-C4 alkyl naphthalenes plus naphthalene as a parent compound (naphthalene itself, C0 naphthalene).

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Naphthalene is a very common, relatively light, semi-volatile polyaromatic hydrocarbon (PAH) found in numerous petroleum products and by-products. It is also present in cigarette smoke, wood smoke, tar, and asphalt [766]. Naphthalene is an EPA priority pollutant [446], and a two-ring, low molecular weight PAH [634,653].

Naphthalene is an important PAH and is often present in significant amounts in petroleum products [468], particularly in middle distillates (such as diesel, no. 1 and 2 fuel oils, and heating oil) [661].

The most abundant aromatic hydrocarbon families in oil products have two and three fused rings with one to four carbon atom alkyl group substitutions [773]. Naphthalene is called the parent compound, while naphthalenes with alkyl group substitutions added to naphthalene are called alkyl naphthalenes.

A large percentage of two ringed PAHs are often naphthalene and alkyl naphthalene compounds, although acenaphthene, ancenaphthylene, and biphenyls are also two ringed PAH compounds.

Naphthalene is a toxic pollutant designated pursuant to section 307(a)(1) of the Clean Water Act and is subject to effluent limitations [366].

As of February 1994, the EPA found naphthalene at 520 of 1,350 hazardous waste sites on the National Priorities List (NPL) [766].

Naphthalene and its alkyl homolog series are included on the expanded scan of PAHs and alkyl PAHs recommended by NOAA [828]; this list includes the PAHs recommended by the NOAA's National Status and Trends program [680].

The proportion of naphthalene compounds vs. other hydrocarbons can be a finger-printing clue that the source is indeed a petroleum product rather than some

other biological source (Dr. Mahlon Kennicutt, Geochemical and Environmental Research Group, Texas A. and M. University, personal communication, 1995).

Br.Haz: General Hazard/Toxicity Summary:

Potential Hazards to Fish, Wildlife, and other Non-human Biota:

Probably the most important target analytes in natural resource damage assessments for oil spills are PAHs and the homologous series (alkylated) PAHs [468].

The general stress syndrome (GSS) produced the best estimates of overall risk for aquatic species exposed to napthalene [970].

In the aquatic environment, naphthalenes are especially hazardous PAHs due to their particular combination of mobility, toxicity, and general environmental hazard (summary of details presented below). Some studies have concluded that the toxicity of an oil appears to be a function of its di-aromatic hydrocarbon (that is, two-ring hydrocarbons such as naphthalene) content [770,854].

Naphthalene exposures increased oxygen consumption by benthic invertebrates and reduced photosynthesis of Chlamydomonas angulosa [970].

Toxicity resulting from fresh Prudhoe Bay Crude oil water soluble fractions and dispersed crude oil was likely the result of the combination of monoaromatic and di-aromatic compounds found in fresh oil [854]. Data from shrimp (Pandalus danae) exposure showed a decrease in toxicity with decreasing amounts of total aromatics in the mono- and di-aromatic range (benzene, alkylbenzenes and naphthalenes) as the fresh product was distilled in order to approximate field conditions [854]. The naphthalenes still present in the Stage I oil (that is, the stage where the benzenes and alkylbenzenes had been removed) produced significant mortality [854]. Stage II (which lacked benzenes, alkylbenzenes, and naphthalenes) did not produce significant mortality for shrimp in either the water soluble fraction or dispersed phase [854].

The "relatively soluble" aromatics of an oil (such as benzene, toluene, ethylbenzene, xylenes, and naphthalenes) produce the majority of its toxic

effects in the marine environment [770,853].

Alkyl naphthalenes are usually found in the same petroleum products as naphthalenes, often in higher concentration than the parent compound naphthalene [796]. Since alkyl PAHs are often more abundant in fresh petroleum products than their parent compounds, and the proportion of alkyl PAHs to parent compound PAHs increases as the oil ages, it is very important to analyze oil samples for alkyl PAHs any time that biological effects are a concern.

In general, alkyl naphthalenes pose similar hazards or worse hazards than naphthalene [851]. Within an aromatic series, acute aquatic toxicity increases with increasing alkyl substitution on the aromatic nucleus [851]. Naphthalenes are no exception to this overall generalization for PAHs, as there is an increase in toxicity as alkylation of the naphthalene structure increases [853]. For example, the order of most toxic to least in a study using grass shrimp (Palaemonetes pugio) and brown shrimp (Penaeus aztecus) was dimethylnaphthalenes > methylnaphthalenes > naphthalenes [853]. There is also an increase in toxicity to marine planktonic algae as alkylation of the naphthalene structure increases [366, Jensen K et al; Limnol 15 (2): 581-4 (1984)].

Although there is less toxicity information available for most of the alkyl PAHs than for their parent compounds, most alkyl PAHs appear to be at least as toxic or hazardous as the parent compound. As can be seen from the preceding paragraph, some have been documented to be more toxic.

Total naphthalenes (total NPHs): Until more complete information on the effects of all the alkyl naphthalenes is available, risk assessment experts suggest adding all alkyl naphthalene concentrations plus the parent compound concentration and comparing the sum to known toxicological effects benchmarks and criteria for the respective parent compound (Bill Stubblefield, ENSR, personal communication, 1995). In this method, naphthalenes are the sum of C0-C4 naphthalenes (total NPHs) [521]. In other words, the concentration of total naphthalenes is the sum of the following concentrations: total C1 naphthalenes (including all methyl naphthalenes) + total C2 naphthalenes (including dimethylnaphthalenes) + total C3 naphthalenes (including trimethyl naphthalenes) + total C4

naphthalenes + C0 (naphthalene parent compound concentration). C0-C4 naphthalenes are typically identified in expanded scans [828].

One study indicated that pure naphthalene and alkylnaphthalenes are from 3 to 10 times more toxic to test animals than are benzene and alkylbenzene [770]. However, another source states that naphthalene and its homologous series are less acutely toxic than benzene, but prevalent for a longer period during oil spills [773].

Noncarcinogenic effects of naphthalene exposure include subtle changes in detoxifying enzymes and liver damage [773].

Naphthalene is selectively phytotoxic (Spencer, E. Y. Guide to the Chemicals Used in Crop Protection. 7th ed. Publication 1093. Research Institute, Agriculture Canada, Ottawa, Canada: Information Canada, 1982. 411.) [366].

At the initial stages of the release of naphthalene- and benzene-derived compounds, when these compounds are present at their highest concentrations, acute toxic effects are most common. Noncarcinogenic effects range from subtle changes in detoxifying enzymes to liver damage and interference with reproductive behavior [773].

The heavier (4-, 5-, and 6-ring) PAHs are more persistent than the lighter (2- and 3-ring) PAHs, such as all naphthalenes, and tend to have greater carcinogenic and other chronic impact potential [796].

Acute toxicity is rarely reported in humans, fish, or wildlife, as a result of exposure to low levels of a single PAH compound such as this one. PAHs in general are more frequently associated with chronic risks. These risks include cancer and often are the result of exposures to complex mixtures of chronic-risk aromatics (such as PAHs, alkyl PAHs, benzenes, and alkyl benzenes), rather than exposures to low levels of a single compound (Roy Irwin, National Park Service, Personal Communication, 1996, based on an overview of literature on hand). See also "PAHs as a group" entry.

This compound often occurs together with other aromatics (sometimes including other alkyl PAHs), and a typical complex mixture of aromatics may be more toxic or hazardous in general than this

compound would be alone (see "PAHs as a group" entry).

Potential Hazards to Humans:

The ATSDR summarized potential hazards to humans in 1995 [867]. For humans, the primary source of exposure is from air, especially in areas of heavy traffic or where fumes from evaporating gasoline or fuel oil exist or in the vicinity of petroleum refineries and coal coaking operations [366].

For additional details on immunological effects of PAHs in general, see ATSDR [881].

Inhalation of naphthalene vapor may cause irritation of the eyes, skin, and respiratory tract. Naphthalene exposure has been implicated in the development of cataracts and damage or irritation to lung and nose tissues [867]. In addition to inhalation, other routes of exposure are ingestion, and absorption through the skin; and the organs that may be affected are the eyes, liver, kidney, blood, skin, and central nervous system [480].

Naphthalene is a human poison if ingested [620]. Naphthalene, which is a significant constituent of distillate oils, has been shown to cause hemolytic anemia (too few red blood cells) in humans, as well as animals, exposed for either short or long periods of time [480,824,867].

Naphthalene exposure symptoms in humans have included [366]:

Naphthalene cataracts and ocular irritation.

Skin irritation and, in the case of a sensitized person, severe dermatitis. Lesions clear spontaneously, as soon as the exposure is terminated.

Percutaneous absorption ... inadequate to produce acute systemic reactions except in newborns.

Headache, confusion, and excitement.

Nausea and sometimes vomiting, and extensive sweating.

Dysuria, hematuria, & the acute hemolytic reaction

Rarely optic neuritis is encountered. [Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-309].

Abdominal cramps with nausea, vomiting, and diarrhea.

Profuse perspiration, listlessness, confusion. In severe poisoning, coma with or without convulsions.

Irritation of the urinary bladder ... Signs & symptoms: urgency, dysuria, & the passage of a brown or black urine with or without albumin & casts.

Acute intravascular hemolysis is the most characteristic sign. ... It begins on the 3rd day & is accompanied by anemia, leukocytosis, fever, hemoglobinuria, jaundice, renal insufficiency, and sometimes, disturbances in liver function.

In the absence of adequate supportive treatment, death may result from acute renal failure in adults or kernicterus in young infants. [Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. III-309].

Naphthalene is listed among drugs responsible for hemolysis in G-6-PD-deficient patients. [Haddad, L.M. and Winchester, J.F. Clinical Management of Poisoning and Drug Overdosage. Philadelphia, PA: W.B. Saunders Co., 1983. 888].

Rare cases of corneal epithelium damage in humans have been reported. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 15(81) 713].

Conjunctivitis, swelling of parotid glands, hepatomegaly splenomegaly, tenesmus, and lenticular opacities in peripheral portions. [ITII. Toxic and Hazardous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 353].

A thirty-six-yr-old pharmacist was given 5 g of unpurified naphthalene in an emulsion of castor oil in divided doses in the course of thirteen hr. On awakening eight to nine hr later he had severe pain in the bladder, and found that he was nearly blind, although previously he had good vision. ... A yr later /examination showed/ the vision to be reduced and in both lenses were seen countless fine whitish opacities arranged as a zonular cataract about the nucleus with a narrow clear zone at the equator. [Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 651].

In twenty-one newborns, a rather severe form of hemolytic anemia, associated with jaundice & kernicterus and produced from the inhalation of naphthalene used in blankets & woolen clothing stored for the summer, was reported. [Arena, J.M. and Drew, R.H. (eds.) Poisoning-Toxicology, Symptoms, Treatments. 5th ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 248].

A 69-year-old black female exposed to naphthalene and paradichlorobenzene developed aplastic anemia two months after exposure. [Harden RA, Baetjer AM; J Occup Med 20: 820 (1978) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene (Draft) p.C-21 (1980)].

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

EPA 1996 IRIS Database [893]:

Evidence for classification as to human carcinogenicity; weight-of-evidence classification:

Classification: D; not classifiable as to human carcinogenicity

BASIS: Based on no human data and inadequate data from animal bioassays.

HUMAN CARCINOGENICITY DATA: None.

ANIMAL CARCINOGENICITY DATA: Inadequate.

However, according to information in IRIS [893], naphthalene may soon be upgraded to "possible carcinogen." status (confirmed by Robert McGaughy,

EPA, personal communication, 1996). Further details:

> EPA IRIS Note ADDED IN JULY 1995 [893]: Subsequent to the verification of this cancer assessment in 1990, the National Toxicology Program completed a two-year cancer bioassay (1991); its results suggest that naphthalene may be more appropriately classified as a possible human carcinogen (Group C under current EPA guidelines) [893]. The NTP concluded, "Under the conditions of these 2-year studies, there was no evidence of carcinogenic activity of naphthalene in male B6C3F1 mice exposed by inhalation to concentrations of 10 or 30 ppm for 6 hours daily, 5 days per week, for 103 weeks [893]. There was some evidence of carcinogenic activity of naphthalene in female B6C3F1 mice, as indicated by the increased incidences of pulmonary alveolar/bronchiolar adenomas [893]."

The IARC and EPA carcinogenic classifications for naphthalene are group 3 and group D, respectively (both stand for "not classifiable as to its carcinogenicity to humans") [766,893]. This rating was given by EPA in 1990 and may change [893] (see below discussions for details):

Formerly, naphthalene had not been considered carcinogenic [773]. This compound has not been treated as a carcinogen for model calculation purposes in some EPA risk-based (RBC and PRG) models [868,903], but this tentative distinction was made for the purpose of choosing a modeling scenario based on current (often inadequate) knowledge rather than for the purpose of strongly stating that this compound is definitely not a carcinogen; the non-carcinogenic benchmarks are sometimes nearly as low as the carcinogenic benchmarks (Stan Smucker, personal communication, EPA, 1996).

EPA Historical (modeling purposes only) Classification: Not a Carcinogen [302,446].

There is some (mixed) evidence of naphthalene carcinogenicity to mice exposed by inhalation [867,893] as well as some indications that naphthalene may act as a promoter for lung tumors started by other carcinogens [766]. Since naphthalenes often occur in petroleum hydrocarbon mixtures which contain strong carcinogens, a carcinogenic promoter role may prove environmentally significant.

Data available from animal studies do not agree

regarding the carcinogenic effects resulting from naphthalene exposure. There is some evidence that naphthalene causes lung cancer in female mice but not in male mice, or rats of either sex [867]. The EPA has determined that naphthalene is not classifiable as to its human carcinogenicity based on the absence of animal data [766].

The observations of Adkins et al. (1986) that there was an increased incidence of tumors in each tumor-bearing mouse, but not in the numbers of mice with tumors, supports classifying naphthalene as a promoter for lung tumors rather than a carcinogen. If this hypothesis is correct, naphthalene may be of greatest environmental concern when exposure to naphthalene is accompanied by exposure to pulmonary carcinogens [766]. This is of interest because naphthalene occurs in various petroleum fuel mixtures which also contain know carcinogens such as benzene, 1,3 butadiene, and various carcinogenic PAHs.

Naphthalene was predicted not to be phototoxic using QSAR estimates [891].

Some interactions are known for certain naphthalenes. For example, when either naphthalene, 1-methylnaphthalene, of 2-methylnaphthalene was applied dermally in combination with benzo(a)pyrene (BaP), there was an inhibitory effect on the induction of skin tumors in female mice. The authors suggested that it is likely that certain naphthalenes compete with BaP for the same enzyme site, resulting in alteration of the BaP metabolic pathway and decreased production of the active BaP metabolite [766].

Naphthalene often occurs together with other PAHs, in complex mixtures possibly more carcinogenic than the individual components (see "PAHs as a group" entry). The debates on exactly how to perform both ecological and human risk assessments on the complex mixtures of PAHs typically found at contaminated sites, are likely to continue. There are some clearly wrong ways to go about it, but defining clearly right ways is more difficult. PAHs such as naphthalene usually occur in complex mixtures rather than alone. One of the few things that seems clear is that complex PAH mixtures in water, sediments, and organism internal tissues may be carcinogenic and/or phototoxic (Roy Irwin, National Park Service, personal communication, 1996; see also "PAHs as a group" entry and Arfsten et al [911]).

One way to approach site specific risk assessments is to collect the complex mixture of PAHs and other lipophilic

organic contaminants in a semipermeable membrane device (SPMD, also known as a fat bag) [894,895,896], retrieve the organic contaminant mixture from the SPMD, then test the mixture for carcinogenicity, toxicity, and phototoxicity (James Huckins, National Biological Survey, and Roy Irwin, National Park Service, personal communication, 1996).

Six cases of malignant tumors occurred among 15 workers exposed to vapors of naphthalene and coal tar for a period of up to 32 years at a coal tar naphthalene production facility: 4 individuals contracted laryngeal carcinoma and all were smokers; the other 2 workers developed neoplasms of the pylorus and cecum. No control group was examined. (Wolf O; Deutche Gesundheitwesen 31: 996, 1976) [366].

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

Naphthalene is an endocrine disrupter; when elevated in water to 10 ppm, naphthalene has caused crawfish ovaries to shrink, resulting in fewer eggs and smaller offspring [883,884] (Naphthalene confirmed as an endocrine disrupter by Milton Fingerman, Tulane University, personal communication, 1996).

Noncarcinogenic effects of naphthalene exposure range from subtle changes in detoxifying enzymes to liver damage and interference with reproductive behavior [773].

Histological examination did not reveal damage to male or female reproductive organs in mice exposed by inhalation to 30 ppm naphthalene for two years [766].

Pregnant rabbits were gavaged with 16 mg/kg of metabolite of naphthalene on days 20, 22, and 24 of gestation. Cataracts and retinal damage were found in the offspring [366].

One study results suggested that naphthalene metabolites are responsible for its embryotoxicity and support the hypothesis that a medium that decreased naphthalene bioavailability would also reduce its toxicity during the early stages of reproduction [766].

Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers [886]. 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 [886]. 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 [886].

For naphthalene, there is little evidence for mutagenicity [366,893]. With one exception. naphthalene was not positive when tested in a variety of genotoxicity assays [893].

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

Low molecular weight PAHs (naphthalenes through phenanthrenes) are removed from the water column primarily by evaporation, microbial oxidation, and sedimentation [851]. Naphthalene binds weakly to soils and sediments and easily passes through sandy soils to reach groundwater [867].

The heavier (4-, 5-, and 6-ring) PAHs are more persistent than the lighter (2- and 3-ring) PAHs, such as all naphthalenes [796].

Naphthalene is adsorbed to a moderate extent (10%) by soil. The extent of sorption depends on the organic carbon content of the soil, with rapid movement expected through sandy soils. Because it adsorbs to aquifer material, its passage through groundwater will be somewhat retarded. Nevertheless, naphthalene frequently appears in effluent drainage from disposal sites. However, sorption of naphthalene to aquifer materials with low organic carbon content (<0.03%) may be enhanced by the presence of nonionic low-polarity organics, such as tetracholoroethene, commonly found at hazardous waste sites [766].

In healthy soils, microorganisms will grow and break down naphthalene in 1 to 3 months; if the soil has few microorganisms, it will take about twice as long [867]. If the soil has already been contaminated by PAHs, naphthalene will break down quickly; otherwise it can take up to 80 days [366,599].

Naphthalene is not particularly water soluble compared to all chemicals in general, but among PAHs, naphthalene is relatively soluble and more soluble than alkyl

naphthalenes (see Chem.Detail section below for detailed information on solubility). Naphthalene and 1 methyl naphthalene are calculated to have almost the same solubility, with the alkyl naphthalene being only slightly more soluble, but 1 ethyl naphthalene is considerable less soluble [970].

Naphthalene in surface waters may volatilize to the atmosphere. Due to the vapor pressure and solubility of naphthalene, it is likely that volatilization will be an important route of naphthalene movement from water. The rate of volatilization also depends on several environmental conditions, including temperature, wind velocity, and mixing rates of the air and water columns [766].

Bioconcentration occurs to a moderate extent but since depuration and metabolism readily proceed in aquatic organisms, this is often a short term problem [366].

Many shellfish and other invertebrates do not break down PAHs as well as invertebrates, which is an important reason why invertebrates are more often used as PAH monitors than vertebrates. Some marine organisms have no detectable aryl hydrocarbons hydroxylase enzyme systems, including phytoplankton, certain zooplankton, mussels (Mytilus edulis), scallops (Placopecten sp), and snails (Litternia littorea) [366,599]. Those organisms which lack a metabolic detoxification enzyme system, tend to accumulate polycyclic aromatic hydrocarbons [366,599].

PAH Alkyl naphthalenes were more persistent in sediments [521,885] and amphipod tissues [885] than naphthalene. Persistence increases with increasing alkyl substitution, with methyl naphthalene being more persistent than naphthalene and dimethyl naphthalene being still more persistent in sediments and amphipod tissues [885].

The crude oil aromatic compounds that are most resistant to weathering, include highly alkylated naphthalenes, phenanthrenes, and dibenzothiophenes [521,523]. In one study, the proportions of the C0-C2 naphthalenes are much smaller and proportions of the highly alkylated (C3-C4) naphthalenes, phenanthrenes, and dibenzothiophenes are larger in weathered Prudhoe Bay Crude Oil than in fresh Prudhoe Bay Crude Oil [521].

Alkyl naphthalenes tend to bioaccumulate faster in tissues than naphthalene [851].

Naphthalene evaporates easily and in air, moisture and sunlight can help it break down into 1-naphthol or 2-naphthol, often within one day [867].

For several PAH families (naphthalenes, fluorenes, phenanthrenes, dibenzothiophenes, and chrysenes) if the unsubstituted parent PAH is less abundant than the sum of its counterpart alkyl homologues, the source is more likely petrogenic (from crude oil or other petroleum sources) rather than pyrogenic (from high temperature sources) [942].

Since alkyl versions of this compound are often found in even greater concentrations than the parent compound, the following generalizations concerning alkyl vs. parent compound PAHs should be kept in mind:

Some alkyl PAHs tend to be less volatile than parent compound PAHs [867]. Alkyl substitution usually also decreases water solubility [754].

Introduction or extension of an alkyl group increases not only persistence but also lipophilicity; increased lipophilicity is often associated with increased absorption [856]. Alkyl PAHs tend to bioaccumulate to a greater degree than parent compound PAHs [347,885].

Alkylated PAHs are often more abundant than parent compounds [468], at least those alkyl PAHs originating from petrogenic sources [942].

Alkyl PAHs also tend to persist for a longer time than the parent PAHs [468,856]. PAH persistence tends to increase with increasing alkyl substitution; for example, methyl naphthalene is more persistent than naphthalene (the parent compound) and dimethyl naphthalene is still more persistent than methyl naphthalene in sediments and amphipod tissues [885].

Comparing PAHs and alkyl PAHs, the parent compound is typically the first to degrade. Thus, as mixed composition petroleum products age, the percentage of alkyl PAHs vs. PAHs increases, yet most standard EPA scans (even 8270) do not pick up alkyl PAHs [796]. This, coupled with the need for lower detection limits and the general hazards presented by alkyl PAHs, is one reason the NOAA protocol expanded scan [828] or other rigorous scans using Selected Ion Monitoring (SIM) [942] are often recommended rather than the older standard EPA scans.

Environmental Fate/Exposure Summary [366]:

Once in the atmosphere, naphthalene rapidly photodegrades (half-life 3-8 hr). Releases into water are lost due to

volatilization, photolysis, adsorption, and biodegradation. The principal loss processes will depend on local conditions but half-lives can be expected to range from a couple of days to a few months.

When adsorbed to sediment, biodegradation occurs much more rapidly than in the overlying water column. When spilled on land, naphthalene is adsorbed moderately to soil and undergoes biodegradation. However, in some cases it will appear in the groundwater where biodegradation still may occur if conditions are aerobic.

Synonyms/Substance Identification:

Mothballs [366,620,766]
Camphor Tar [620]
Naphthaline [366,620]
Naphthene [366,620,766]
Naftalen (Polish) [366]
NCI-C52904 [366]
Albocarbon [366,766]
Dezodorator [366]
Moth Flakes [366,766]
Tar Camphor [366,766]
White Tar [366,766]
Naphthalin [366]

Molecular Formula [366]:
C10-H8

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Naphthalene, 2,6-Dimethyl
Naphthalene, 1-Methyl
Naphthalene, 2-Methyl
Naphthalene, 1,6,7-Trimethyl
Naphthalene, 2,3,5-Trimethyl
Naphthalene, C1-
Naphthalene, C2-
Naphthalene, C3-
Naphthalene, C4-
PAHs, Alkyl Homologs of
PAHs as a group

When released in air, moisture and sunlight break naphthalene down. The naphthalene may be changed to 1-naphthol or 2-naphthol [766].

The bacteria Pseudomonas putida and P. multivorans isolated from an oil-polluted estuary metabolized naphthalene into salicylic acid [851].

A high-yielding (98%) process from the oxidation by

microorganisms, has been developed in Japan for the production of salicylic acid from naphthalene [366].

Impurities [366]:

The main impurity in crude 78 deg C coal tar naphthalene is sulfur which is present in the form of thionaphthalene (1-3%). Methyl- and dimethylnaphthalenes also are present (1-2 wt %) with lesser amounts of indene, methylindenes, tar acids, and tar bases. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 15(81) 708].

Bile breakdown products [523]:

Because spilled Prudhoe Bay crude is degraded in time by physical, chemical, and microbial processes, the aromatic fraction of the weathered oil will be dominated by those aromatic hydrocarbons (such as highly alkylated naphthalenes, phenanthrenes, and dibenzothiophenes) that are most resistant to weathering. Therefore, metabolites of these resistant aromatic hydrocarbons should be found in bile of fish exposed to weathered crude oil.

As many of the metabolites as feasible were identified and quantitated in the bile from three of the fish: 158 in the oil-injected halibut, 119 in salmon A, and 54 in the pollock Alkylated naphthols, fluorenols, phenanthrols, dibenzofuranols, and dibenzothiophenols comprised the majority; smaller numbers of alkylated fluoranthenols/pyrenols and benz(a)anthracenols/chrysenols were also identified .

Metabolites, Breakdown Products [366]:

In order to investigate the species difference in toxicity, the metabolism of naphthalene by lung and liver microsomes of the mouse and rat was studied. In all cases, naphthalene was metabolized to a covalently bound product(s) and to two major methanol-soluble products, which co-chromatographed with 1-naphthol and 1,2-dihydro-1,2-dihydroxynaphthalene. However, both the covalent binding and metabolism were approximately 10-fold greater in microsomes prepared from mouse lung compared with those from the rat.

Metabolized via 1,2-epoxide into 1,2-dihydronaphthalene-1,2-diol, 1,2-dihydro-1-naphthol & n-acetyl-s-(2-hydroxy-1,2-dihydronaphthyl)-cysteine, which after further metabolism ... Excreted in urine as 1-naphthylmercapturic acid ... & Conjugates of 1,2-dihydronaphthalene-1,2-diol ... 1-& 2-Naphthols, & 1,2-dihydroxynaphthalene.

Naphthalene 1,2-oxide is intermediate in microsomal

hydroxylation of naphthalene.

Naphthalene ... & Monohalogenated benzenes are metabolized into mercapturic acids, conjugates in which n-acetylcysteine moiety replaces a hydrogen atom.

Naphthalene yields s-(1-naphthyl)glutathione in rabbit: corner, eds, & young, l, biochem j, 58, 647 (1954); bourne, mc, & young, l, biochem j, 28, 803 (1934). Naphthalene yields s-(1-naphthyl)glutathione in rat, in mouse & in guinea pigs. /From table/

Naphthalene yields cis-1,2-dihydro-1,2-dihydroxynaphthalene in pseudomonas: catterall, fa, murray, k, & williams, pa, biochim biophys acta, 237, 361 (1971); catterall, fa, & williams, pa, j gen microbiol, 67, 117 (1971). /From table/

Fish exposed to benzo-a-pyrene (b(a)p) & naphthalene in sediment containing prudhoe bay crude oil. Fish were exposed l3-h: greater extent than naphthalene. Naphthalene was metab to 1,2-dihydro-1,2-dihydroxynaphthalene glucuronide.

Cunninghamella elegans (a filamentous fungus) is capable of oxidizing naphthalene to trans-1,2-dihydroxy-1,2-dihydronaphthalene. Other metabolites were identified as 1-naphthol, 2-naphthol and 4-hydroxy-1-tetralone.

Naphthalene is first metabolized by hepatic mixed function oxidases to the epoxide, naphthalene-1,2-oxide. The epoxide can be enzymatically converted into the dihydrodiol, 1,2-dihydroxy-1,2-dihydronaphthalene or conjugated with glutathione. The dihydrodiol can then be conjugated to form a polar compound with glucuronic acid or sulfate or be further dehydrogenated to form the highly reactive 1,2-dihydroxynaphthalene. This too can be enzymatically conjugated with sulfate or glucuronic acid or spontaneously oxidized to form 1,2-naphthoquinone. [Van Heyningen R; Exp Eye Res 28: 437 (1979) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene (Draft) p.C-7 (1980)].

In rabbits 1,2-dihydroxynaphthalene ... is produced enzymatically and by autoxidation, and /it is/ the metabolic intermediate responsible for naphthalene cataractogenesis. [Grant, W.M. Toxicology of the Eye. 3rd ed. Springfield, IL: Charles C. Thomas Publisher, 1986. 653].

Conjugates of glutathione, cysteinylglycine & cysteine, intermediates in formation of mercapturic acids, are excreted, particularly in bile, as metabolites of ... Naphthalene. ... [Parke, D. V. The Biochemistry of

Foreign Compounds. Oxford: Pergamon Press, 1968. 92].

In the presence of glutathione and glutathione transferases, microsomal fractions prepared from fresh samples of human lung tissue obtained at resection metabolized naphthalene to naphthalene dihydrodiol and 3 glutathione conjugates at easily measurable rates. Addition of varying amounts of human lung microsomal protein markedly inhibited mouse liver microsome-catalyzed naphthalene metabolism in one sample but not the other. These studies suggest that there may be an inhibitor, potential released during tissue homogenization, that makes measurement of human lung xenobiotic metabolism difficult. [Buckpitt AR, Bahnson LS; Toxicology 41 (3): 333-41 (1986)].

In an experimental animal study, doses of naphthalene ranging from 1 ug to 1 g were administered in the feed to 3 young pigs and their urine was collected in 2 sequential 24 hr specimen. The major urinary metabolite, conjugated 1-naphthol, was separated by gas chromatography and detected by electron capture. Most 1-naphthol excretion occurred during the first 24-hr period following dosing. Metabolic 1-naphthol could be detected after administration of as little as 100 ug naphthalene. A linear relationship was observed between urinary 1-naphthol and oral dose (both expressed on the log scale) in 24-hr specimen (r squared = 0.961, $p<0.05$) and 48 hr specimens (r squared = 0.906, $p<0.05$)].

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

W.Low (Water Concentrations Considered Low):

Naphthalene is rarely detectable in drinking water [766]. However, if a concentration is reported as non detected, check to see what the detection limit was; if it was above 1-10 ppb, the detection limit may have been too high and naphthalene may have been present even though it was reported as "non-detected." Detection limits of 10 ppb or less are possible with GC/MS/SIM scans [828]. Also note that alkyl naphthalenes are slower to degrade and may be present in sediment, soils, or invertebrate tissues long after naphthalene has degraded [885] (see fate discussions for details).

Naphthalene was reported in drinking water supplies in one area in the United States at levels up to 1.4 ug/L [766].

Naphthalene has been reported at a mean concentration of 6.3 ng/L (0.0063 ug/L) in seawater in the south Atlantic

Ocean [766].

SURFACE WATER [366]: Lake Zurich, Switzerland - surface water - 8 parts/trillion: water at 30 m depth - 52 parts/trillion(2,3). Kitakyusku area, Japan - detected, not quantified in river water(1). River Glatt, Switzerland - detected, not quantified(4). Mississippi River during summer 1980 - 4 - 34 ppb(5). [(1) Akiyama T et al; J UOEH 2: 285-300 (1980) (2) Grob K, Grob G; J Chromatogr 90: 303-13 (1974) (3) Korte F, Klein W; Ecotox Environ Safety 6: 311-27 (1982) (4) Zuercher F, Giger W; Vom Wasser 47: 37-55 (1976) (5) DeLeon IR et al; Chemosphere 15: 795-805 (1986)].

SEAWATER [366]: Naphthalene measured as follows: Gulf of Mexico - unpolluted (anthropogenic influence) 0.2 parts/trillion mean(2). Cape Cod, MA - Vineyard Sound - 0.5/35 parts/trillion, 12 parts/trillion avg and results displayed a strong seasonal pattern, highest concentrations noted in winter which suggests a source from heating fuels(4). Chemotaxis Dock, Vineyard Sound MA, Dec 78 to Mar 79 - 0 to 27 parts/trillion, with low levels reported in Dec and Jan; high level reported in February, correlating with a late heavy snowfall, indicating runoff or atmospheric inputs(5). Dohkai Bay, Japan - area polluted by domestic and industrial waste as well as airborne particulates - detected, not quantified(3). Kitakyusku area, Japan - detected, not quantified(1). [(1) Akiyama T et al; J UOEH 2: 285-300 (1980)(2) Sauer TC Jr; Org Geochem 3: 91-101 (1981) (3) Shinohara R et al; Environ Int 4: 163-74 (1980) (4) Gschwend PM et al; Environ Sci Technol 16: 31-8 (1982) (5) Mantoura RFC et al; Environ Sci Technol 16: 39-45 (1982)].

W.High (Water Concentrations Considered High):

Naphthalene and 2-methylnaphthalene were detected in groundwater at five wood treatment facilities. Naphthalene was reported in 35% of samples at all five sites at an average concentration of 3,312 ug/L. Naphthalene was also reported in leachate or groundwater plume from industrial and municipal landfills at concentrations ranging from less than 10 to 18.69 mg/L (10,000 to 18,690 ug/L) and 0.110 to 19 mg/L (110 to 19,000 ug/L), respectively [766].

Groundwater samples taken near wood treatment/ storage sites in Canada contained between 0.378 and 66 mg/L naphthalene [864].

The maximum water solubility (in water at 25 degrees C) has been given as 12.5 to 137.4 mg/L, with most stated

values falling in the range of 30-34 mg/L [848]. Therefore, any water concentration above 20 mg/L should be considered as approaching the maximum that water could ordinarily hold at 25 degrees C [848].

Effluent Concentrations [366]:

Industrial effluents- up to 3200 ppb, discharges from sewage treatment plants - up to 22 ppb(1). Water sample from a stream running through an oil tank farm, Knoxville TN - 8 ppb(2) tire manufacturing plant wastewaters - 100 ppb(2,4). Spent chlorination liquors from bleaching of sulfite pulp - 0.8 - 2.0 g/ ton pulp(9). Bekkelaget Sewage treatment plant, Oslo, Norway, secondary sewage water effluent - 88 parts/trillion (dry period, Nov, 1979), 303 parts/trillion (dry period, spring, 1980), 1504 parts/trillion (after rainfall, summer, 1980)(3). Gas phase emission rates, diesel trucks - 7.4 mg/km (filtered), 9.2 mg/km (nonfiltered), gasoline-powered vehicles - 8.6 mg/km (filtered), 8.1 mg/km (unfiltered)(5). 2 representative USA cities, sewage treatment plant influent, city A - 33% frequency, 13 ppb avg, city B - 67% frequency, 14.8 ppb avg; city B effluent - not detected(6). Industries with mean treated wastewater concentrations greater than 200 ppb - paint and ink formulation, electrical/electronic components, auto and other laundries, iron and steel manufacturing (< 920 ppb)(7). Maxey Flats, KY and West Valley, NY - trench leachate - 0.12 to 0.28 ppm (3 of 3 trenches pos) and 0.46 to 1.7 ppm (2 of 3 pos)(8). [(1) USEPA; Ambient Water Quality Criteria: Naphthalene; USEPA 440/5-80-059 (1980) (2) Carlson RM et al; Implications to the Aquatic Environment of Polynuclear Aromatic Hydrocarbons Liberated from Northern Great Plains Coal; pp. 156 USEPA 600/3-79-093 (1979) (3) Kveseth K et al; Chemosphere 11: 623-39 (1982) (4) Jungclaus GA et al; Anal Chem 48: 1894-6 (1976) (5) Hampton CV et al; Environ Sci Technol 17: 699-708 (1983) (6) Callahan MA et al; 8th Natl Conf Munic Sludge Manag Proc; p.55 (1979) (7) USEPA; Treatability Manual; p.I.10.15-1 to 15-5 USEPA 600/2-82-001a (1981) (8) Francis AJ et al; Nuclear Tech 50: 158-63 (1980) (9) Carlberg GE et al; Sci Total Environ 48: 157-67 (1986)].

W.Typical (Water Concentrations Considered Typical):

Naphthalene has been detected in surface and groundwater in the United States. An analysis of 1980-1982 EPA STORET data indicates that naphthalene was detectable in

7% of 630 ambient water samples. The median concentration in the samples was less than 10 ug/L. Analysis of earlier (1978-1980) STORET showed concentrations in positive samples ranging from 0.005 to 17 ug/L. Naphthalene was also detected in 11% of 86 urban runoff samples at concentrations ranging from 0.8 to 2.3 ug/L [766].

PAHs have been detected in surface waters of the United States. In an assessment of STORET data covering the period 1980-82, Staples et al. (1985) reported median concentrations in ambient water of less than 10 ug/L for 15 PAHs (acenaphthene, acenaphthylene, anthracene, benz[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, chrysene, fluoranthene, fluorene, indeno[1,2,3-c,d]pyrene, naphthalene, phenanthrene, and pyrene). The number of samples ranged from 630 (naphthalene) to 926 (fluoranthene); the percentage of samples in which these PAHs were detected ranged from 1.0 (benzo[g,h,i]perylene) to 5.0 (phenanthrene) and 7.0 (naphthalene) [881].

Water Concentrations [366]:

> DRINKING WATER: Naphthalene measured as follows: Washington DC tap water - 1 ppb(1). 3 New Orleans area drinking water plants sampled - detected but not quantified(2). 12 Great Lake municipalities drinking water supplies - 0.9 to 1271 ppb, with levels being generally higher in winter(3). Cincinnati, OH, Feb 1980 - 5 parts/trillion(5). Drinking waters - up to 1.4 ppb(4). 2 representative US cities, tap water - not detected, 14% frequency in source for city A - 7.8 ppb avg, 23% frequency in source for City B - 23.0 ppb avg(6). [(1) Scheiman MA et al; Biomed Mass Spectrom 4: 209-11 (1974) (2) Keith LH et al; pp. 329-73 in Identification and Analysis of Organic Pollutants in Water; Keith LH ed; Ann Arbor MI Ann Arbor Press (1976) (3) Williams DT et al; Chemosphere 11: 263-76 (1982) (4) USEPA; Ambient Water Quality Criteria; Naphthalene, NTIS PB81-117707, Springfield, VA (1980) (5) Coleman WE et al; Arch Environ Contam Toxicol 13: 171-8 (1984) (6) Callahan MA et al; 8th Natl Conf Munic Sludge Manag Proc; p. 55 (1979)].
>
> DRINKING WATER: Naphthalene measured as follows: Rhine River water, the Netherlands, bank-filtered tap water - 100 parts/trillion(1). Kitakyushu area Japan - 2.2 ppb(2). Zurich Switzerland, tap water - 8 parts/trillion(3,6). Ottawa, Ontario - January, 1978 - 4.8 parts/trillion, February, 1978 - 6.8

parts/trillion(4). 4 of 5 Nordic tap water, - 1.2 to 8.8 parts/trillion(5). [(1) Piet GJ, Morra CF; pp.31-42 in Artificial Groundwater Recharge (Water Res Eng Ser); Huisman L, Olsthorn TN eds; Pitman Pub (1983) (2) Akiyama T et al; J UOEH 2: 285-300 (1980) (3) Grob K, Grob G; J Chromatogr 90: 303-13 (1974) (4) Benoit FM et al; Int J Environ Anal Chem 6: 227-87 (1979) (5) Kveseth K et al; Chemosphere 11: 623-39 (1982) (6) Korte F, Klein W; Ecotox Environ Safety 6: 311-27 (1982)].

GROUNDWATER: Naphthalene was detected as follows: Hoe Creek, NY, underground coal gasification site, 2 aquifers sampled 15 months after gasification complete - 380 to 1800 ppb(1). Samples from East Anglica, England chalk aquifer 10, 100-120, and 210 m distance from gasoline storage - 150, 30, and 0.1 ppb resp(2). 3 of 4 rapid infiltration sites, Fort Polk, LA - 0.03 to 0.22 ppb, 1 of 4 sites not quantified(3). Zurich, Switzerland - not detected(4). [(1) Stuermer DH et al; Environ Sci Technol 16: 582-7 (1982) (2) Tester DJ, Harker RJ; Water Pollut Control 80: 614-31 (1981) (3) Hutchins SR et al; Environ Toxicol Chem 2: 195-16 (1983) (4) Korte F, Klein W; Ecotox Environ Safety 6: 311-27 (1982)].

SURFACE WATER: Lake Michigan - a trace detected at 5 of 9 sites(7). Delaware River studies ranged from a trace to 0.9 ppb(1,5). Ohio River between Wheeling and Evansville (5 samples) and 3 tributaries - detected at a detection limit of 0.1 ppb(3). Charles River, Boston - detected at a detection limit of 0.1 ppb(4). Lower Tennessee R, Calvert City, KY - 30.4 ppb (water and Sediment(6). Unspecified US river near industrial sites - 6 to 10 ppb(2). Natural waters - up to 2 ppb(8). [(1) Sheldon LS, Hites RA; Environ Sci Technol 12: 1188-94 (1978) (2) Junglclaus GA et al; Environ Sci Technol 12: 88-96 (1978) (3) Ohio R Valley Water Sanit Comm; Assessment of Water Quality Condition Ohio R Mainstreams 1978-9 Cincinnati OH (1980) (4) Hites RA, Biemann K; Science 178: 158-60 (1972) (5) Sheldon LS, Hites RA; Environ Sci Technol 13: 574-9 (1979) (6) Goodley PC, Gordon M; Kentucky Acad Sci 37: 11-5 (1976) (7) Konasewich D et al; States Report on Organic and Heavy Metal Contaminants in the Lake Erie, Michigan, Huron, and Superior Basins. Great Lakes Quality Board; pp. 273 (1978) (8) USEPA; Ambient Water Quality Criteria: Naphthalene USEPA-440/5-80-059 (1980)].

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):

Canada's interim assessment criteria (similar to screening benchmarks) and remediation criteria provide another indication that the consensus is going in the direction of lower standards and detection limits for PAHs. The interim assessment criteria (that is, approximate background concentration or approximate analytical detection limit) for naphthalene in water is 0.2 ug/L (ppb) [656]. There is currently no listed remediation criteria for naphthalene in water [656].

EPA 1996 IRIS data base, U.S. Water Quality Criteria in ug/L [893]:

Ambient Water Quality Criteria for Aquatic Organisms, Acute Freshwater: 2.3E+3 ug/L [893].

Older reference gave same concentration: Freshwater Acute Criteria: Insufficient data to develop criteria. Lowest Observed Effect Level: 2,300 ug/L [446].

Freshwater Chronic Criteria: Ambient Water Quality Criteria for Aquatic Organisms, Chronic Freshwater: 6.2E+2 ug/L [893].

Older reference: insufficient data to develop criteria; Lowest Observed Effect Level: 620 [446].

Marine Acute Criteria: 2,300 ug/L [893].

Marine Chronic Criteria: None Published [446,893].

Criteria Federal Register Notice Numbers:

45 FR 79337 [446].

45 FR 79318 (11/28/80)[893].

Note: Before citing a concentration as EPA's water quality criteria, it is prudent to make sure you have the latest

one. Work on the replacement for the Gold Book [302] was underway in March of 1996.

Oak Ridge National Lab, 1994: Ecological Risk Assessment Freshwater Screening Benchmarks for concentrations of contaminants in water [649]. For a definition of meaning of each benchmark, see entry entitled: Benchmarks, Ecological Risk Assessment Screening Benchmarks. To be considered unlikely to represent an ecological risk, field concentrations should be below all of the following benchmarks [649]:

Note: Although most of the lab tests done to develop water quality criteria and other benchmarks were originally based on "total" values rather than "dissolved" values, the lab settings were typically fairly clean and the numbers generated by the lab tests are therefore often even more comparable to field "dissolved" values than to field "total" values (Glen Suter, Oak Ridge National Lab, Personal Communication, 1995). For more information on dissolved vs. total concentrations, and EPA suggested conversion fractions for metals, see entry entitled "Dissolved."

NAPHTHALENE (micrograms per liter, ug/L):

353 = SECONDARY ACUTE VALUE
23.4 = SECONDARY CHRONIC VALUE
620 = LOWEST CHRONIC VALUE - FISH
1163 = ESTIMATED LOWEST CHRONIC VALUE - DAPHNIDS
33,000 = LOWEST CHRONIC VALUE - AQUATIC PLANTS
450 = LOWEST TEST EC20 - FISH
> 600 = LOWEST TEST EC20 - DAPHNIDS
1000 = POPULATION EC2O

The maximum permissible concentration of naphthalene in fishery waters in the USSR is 4 ug/l.; (Mosevich MT et al; Izv Gos Nauchno-Issled Inst Ozern Rechn Tyb Khoz 109: 50 (1976) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene p.C-31, Draft, 1980) [366].

W.Plants (Water Concentrations vs. Plants):

Inhibition of photosynthesis of a freshwater, non-axenic unialgal culture of Selenastrum capricornutum at: 1% saturation: 110% (14)C

fixation (vs controls); 10% saturation: 89% (14)C fixation (vs controls); 100% saturation: 15% (14)C fixation (vs controls). (Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 897) [366].

Alkyl naphthalenes were toxic than naphthalene to marine algae (see W.Misc. section below).

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50 Values [851]:

Neanthes arenaceodentata
(marine polychaete) - 3.8 ppm, 96 h
Cancer magister
(Dungeness crab) - >2.0 ppm, 96 h
Elasmopus pectenicrus
(marine amphipod) - 2.68 ppm, 96 h
Palaemonetes pugio
(grass shrimp) - 2.4 ppm, 96 h
Penaeus aztecus
(brown shrimp) - 2.5 ppm, 24 h

A naphthalene concentration of 10 ppm in water in a 48 hour exposure caused crawfish ovaries to shrink, resulting in fewer eggs and smaller offspring [883,884].

Information from the HSDB [366]:

> Larval mud crabs were exposed continuously from hatching through 1st stage to sublethal concn of naphthalene (0, 75, 150 or 300 mug/l). Salinity & temperature were varied. At optimal salinity no consistent effect of naphthalene on growth was apparent. [366, Laughlin & Neff; Mar Ecol: Prog Ser; 5 (3): 319 (1981)].
>
> .. Exposure of the 4th instar larvae of the freshwater dipteran Chironomus attenuatus to 1 mg/l for 1 hr resulted in ... the loss of ionic regulation. ... /This was/ due to inhibition of specific enzyme systems and not to a general alteration of membrane integrity. [Darville RG et al; Environ Toxicol Chem 2 (4): 423-9 (1983)].
>
> LC50 Palaemonetes pugio (grass shrimp) 2600 ug/l/24 hr /Conditions of bioassay not specified/ [Anderson JW et al; The Effects of

Oil on Estuarine Animals: Toxicity, Uptake and Depuration, Respiration. Pollution and Physiology of Marine Organisms (1974) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene p.B-10 (Draft) (1980)].

TLm (median threshold limit) Pandalus goniurus (shrimp) 2.16 ppm/96 hr at 4 deg C; 1.02 ppm/96 hr at 8 deg C; 0.971 ppm/96 hr at 12 deg C /Static bioassay/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 897].

LC50 Parhyale hawaiensis (amphipod) 15 ppm/24 hr open bowl; 6.5 ppm/24 hr closed bottle in a static bioassay. [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 897].

W.Fish (Water Concentrations vs. Fish):

One study reports 4 or 5 mg/L of naphthalene kills sunfish in one hour, but another study set the lethal concentration at 10 mg/L [224].

During an exposure of one hour, 17.1 mg/L did not kill minnows, but caused them to stop eating. A concentration of 4.3 mg/L had no effect [224].

For perch, the killing strength has been given as 40 mg/L in some studies, and as 20 mg/L in another study [224].

One study exposed minnows to naphthalene for six hours in both distilled and hard water. The minimum lethal dose in distilled water at 19 degrees C was 11-13 mg/L, and in hard water at 16 degrees C was 15-18 mg/L [224].

TLm values for mosquito fish (Gambusia affinis) using highly turbid water at 22-24 degrees C were found to be 220 mg/L at 24 hours, 165 mg/L at 48 hours, and 150 mg/L at 96 hours. The naphthalene did not clarify the turbid water [224].

In aerated seawater, the critical level for fingerling silver salmon during 72-hour exposure was reported to be between 1.8 and 3.2 mg/L [224].

Cutthroat trout (Salmo clarki) were exposed for 90 days to four concentrations (ranging from 100 to

520 ug/L) of a Wyoming crude oil in water. Survival was reduced to 52% at 520 ug/L, but was not affected by the 3 lower concentrations. Growth was significantly slower than control fish at all four concentrations. Exposure concentrations of 520 and 450 ug/L induced gill lesions and development of lesions on the retina and lens of the eye. Accumulation of total hydrocarbons in fish tissue was directly related to water concentration, except for fish in the 520 ug/L concentration. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily, and naphthalenes were the dominant aromatic component in oil, water, and fish. Evidence from this research suggests that discharges of 10 mg/L oil and grease allowed by several western states are too high [786].

LC50 Values [851]:

Gambusia affinis
(mosquito fish) - 150 ppm, 96 h
Oncorhynchus gorbuscha
(pink salmon fry) - 0.92 ppm, 24 h
Cyprinodon variegatus
(sheep's head minnow) - 2.4 ppm, 24 h

Information from HSDB [366]:

LC50 Cyprinodon variegatus (sheepshead minnow) 2400 ug/l/24 hr /Conditions of bioassay not specified/ [366, Anderson JW et al; The Effects of Oil on Estuarine Animals: Toxicity, Uptake and Depuration, Respiration. Pollution and Physiology of Marine Organisms (1974) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene p.B-10 (Draft) (1980)].

TLm (median threshold limit) Oncorhynchus gorbuscha (pink salmon) 1.37 ppm/96 hr at 4 deg C; 1.84 ppm/96 hr at 8 deg C; 1.24 ppm/96 hr at 12 deg C /Static bioassay/ [Verschueren, K. Handbook of Environmental Data of Organic Chemicals. 2nd ed. New York, NY: Van Nostrand Reinhold Co., 1983. 897].

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

No information found.

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

The State of New York ambient water quality standard (AWQS) aesthetic limit (that is, whose presence in excess of the limit does not present a risk to human health, but may render the water unpalatable or otherwise unacceptable to the consumer) is set at 10 ug/L (ppb) [859].

U.S. Water Quality Criteria in ug/L [446]:

Human Health (10-6) Risk Level for Carcinogens)

IRIS Recalculated (9/90) Criteria for Water and Organisms: None Published

IRIS Recalculated (9/90) Criteria for Organisms Only: None Published

Drinking Water MCL: None Published

The EPA recommends that children not drink water with over 0.5 ppm naphthalene for more than 10 days or over 0.4 ppm for any longer than 7 years. Adults should not drink water with more than 1 ppm for more than 7 years. For water consumed over a lifetime, EPA suggests that it contain no more than 0.02 ppm naphthalene [766].

The Kansas state drinking water standard for naphthalene is 143 ug/L (0.143 ppm) [776].

Human Water Standards [366]:

For the maximum protection of human health from the potential carcinogenic effects due to exposure of polynuclear aromatic hydrocarbons through ingestion of contaminated water and contaminated aquatic organisms, ... therefore, the levels which may result in incremental increase of cancer risk over the lifetime are estimated at 1x10-5, 1x10-6, and 1x10-7. The corresponding ambient water criteria are 28.0 ng/l, 2.8 ng/l, and 0.28 ng/l, respectively. If the above estimates are made for consumption of aquatic organisms only, excluding consumption of water, the levels are 311.0 ng/l, 31.1 ng/l, and 3.11 ng/l respectively. /Polynuclear aromatic hydrocarbons based on benzo(a)pyrene as the model PAH/ [USEPA; Ambient Water Quality Criteria Doc: Polynuclear Aromatic Hydrocarbons (Draft) p.C-121 (1980)].

NOTE: Typical drinking water levels can

be found in the W.Typical section.

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

The potential impact of motorboat activity on the Occoquan (drinking-water) reservoir east of Washington, D.C. was evaluated at both marina and nonmarina sites. The presence of PAHs (especially the lower molecular weight compounds like acenaphthene and naphthalene) in June during peak boating activity, and the absence of PAHs in October, a period of low boating activity, indicated boating to be a source of PAHs to the water [653].

Petroleum is a complex mixture of thousands of different hydrocarbons and related substances, all with different physical and chemical properties [770]. As such, determination of the fate and toxicity of a particular oil is a difficult task. Solubility-fate relationships must be considered. Generally, the relative toxicity of an oil will be the result of the fractional toxicities of the different hydrocarbons present in the aqueous phase [770].

Because of the low water-solubility of tricyclic and polycyclic aromatic hydrocarbons (that is, those aromatic hydrocarbons heavier than naphthalene), these compounds are generally present at very low concentrations in the WSF of oil. Therefore, the results of several studies conclude that the soluble aromatics of an oil (such as benzene, toluene, ethylbenzene, xylenes, and naphthalenes) produce the majority of its toxic effects in the marine environment [770,853]. Generally, the relative toxicity of an oil will be the result of the fractional toxicities of the different hydrocarbons present in the aqueous phase [770]. This and other findings in this study demonstrate that a prediction of environmental impact must take into consideration the specific characteristics of the particular oil spilled as well as the particular spill environment (that is, whether the spill occurs in the open sea, or a confined water body). A more detailed summary of the study [770] is in the "Petroleum, General" entry.

Information from HSDB [366]:

> The toxic effect of aromatic hydrocarbons, benzene, toluene, naphthalene, 1-methylnaphthalene, anthracene, 9-methylanthracene, phenanthrene, on the productivity of various marine planktonic algae (Dunaliela biocula, Phaeodactylum tricornutum, and Isochysis galbaya) increased with increasing number of aromatic rings. The methylated compounds were

most toxic. Taxonomic differences in sensitivity to aromatic hydrocarbons /was investigated/[Jensen K et al; Limnol 15 (2): 581-4 (1984)].

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

Sed.Low (Sediment Concentrations Considered Low):

No information found.

Sed.High (Sediment Concentrations Considered High):

Naphthalene was detected in contaminated and noncontaminated estuarine sediments. Reported average concentrations were 54.7 and 61.9 ppb (ug/kg) naphthalene at 10 and 25 miles from an offshore coastal multiwell drilling platform. The concentration in nearby noncontaminated estuarine sediments was 2.1 ppb (ug/kg) [766].

Naphthalene was detected in 65.8 percent of urban-bay samples from the Puget Sound area. The mean concentration was 2829.33 ug/kg dry weight (ppb), while the median concentration was 100 ug/kg (ppb) [852].

NOTE: The above [852] values are not normalized for total organic carbon (TOC) content.

Sed.Typical (Sediment Concentrations Considered Typical):

Naphthalene was reported as detectable in 7% of 267 sediment samples entered into the EPA STORET database (1980-1982), with the median concentration for all samples less than 500 ug/kg. Another analysis of STORET data indicated that concentrations in positive sediment samples ranged from 0.02 to 496 ug/kg [766].

Naphthalene was detected in 46.3 percent of non-urban-bay samples from the Puget Sound area. The mean concentration was 339.33 ug/kg dry weight (ppb), while the median concentration was 85 ug/kg (ppb) [852].

NOTE: The above [852] values are not normalized for total organic carbon (TOC) content.

Sediment Concentrations [366]:

Detected in only 1 sediment sample from an industrial location on an unspecified USA river(1). Royal Botanical Gardens, Hamilton, Ontario - 2.0 ppb in pond sediment(2). Lower Tennessee River, Calvert, KY - 30.4 ppb water and sediment(3)

Kitakyusku area, Japan - detected in sediment, not quantified(4). Dohkai Bay, Japan, area polluted by domestic and industrial waste and airborne particulates - detected in sediment, not quantified(5). Saudafjord, Norway, suggested sources - ferro alloy smelter, sediment from 6 sites, station 1 closest to smelter - 483.8 ppb (0-2 cm), 685.9 ppb (2-4 cm), 278.7 ppb (4-6 cm), 328.3 pb (6-8 cm), station 2,2479.5 ppb (0-2 cm), station 3,48.3 ppb (0-2 cm), station 4,10.9 ppb (4-6 cm), not detected stations 5 and 6 (furthest away)(6). South Texas coast, samples taken following the blowout of an exploratory oil well (Ixtoc-1) - detected at trace amount in 3 of 3 samples(7). Cascoe Bay Maine, detected in 1 of 30 samples at 113 ppb(8). Windsor Cove, Buzzards Bay, MA, 0-6 cm - 9.2 ppm (Oct 74), 0.63 ppm (May 75), 0.11 ppm (June 1977), oil spill occurred October 1974(9). Wild Harbor, Buzzards Bay, MA - detected not quantified immediately following September 1969 oil spill, not detected from 1971 to 1976(9). Sediments from various fjords in Norway, 0-5 cm samples: Saudafjord, 800 m from ferro alloy plant - 2,870 ppb; Sorfjord, Tyssedal, 500 m from aluminum plant 3 and 5 km from zinc and calcium carbide plants resp - 220 ppb; Sorfjord, Hovland, 15, 18 and 20 km from above industries - 41.5 ppb. Brofjord, 800 m from petroleum refinery - 70.0 ppb; Oslofjord, Bunnefjord, close to city of Oslo - 53.6 ppb; Oslofjord, Lysakerkilen, close to city of Oslo 45.8 ppb; North Sea 500 m from oil field - 31.6 ppb; North Sea, 10 km from oil field - 4.32 ppb, and Framvaren, a permanent anoxic fjord with no potential local pollution but high PAH values - 292 ppb (0-10 cm), 272 ppb (14-20 cm)(10). March Point, Strait of Juan de Fuca and Northern Puget Sound, unpolluted area, baseline study - not detected in two week sampling intervals(11). [(1) Jungclaus GA et al; Environ Sci Technol 12: 88-96 (1978) (2) Kalas L et al; pp. 567-76 in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment; Afghan BK, Mackay D eds; New York NY Plenum Press (1980) (3) Goodley PC, Gordon M; Kentucky Acad Sci 37: 11-5 (1976) (4) Akiyama T et al; J UOEH 2: 285-300 (1980) (5) Shinohara R et al; Environ Int 4: 163-74 (1980) (6) Bjoerseth A et al; Sci Total Environ 13: 71-86 (1979) (7) Bedinger CA Jr, Nulton CP; Bull Environ Contam Toxicol 28: 166-71 (1982) (8) Larsen PF et al; Bull Environ Contam Toxicol 30: 530-5 (1983) (9) Teal JM et al; J Fish Res Board Canada 35: 510-20 (1978) (10) Sporstal S et al; Environ Sci Technol 17: 282-6 (1983) (11) Brown DW et al; Investigation of Petroleum in the Marine Environs of the Strait of Juan de Fuca and

Northern Puget Sound; p. 33 USEPA 600/7-79-164 (1979)].

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):

NOAA 1995: After studying its own data from the National Status and Trends Program as well as many literature references concerning different approaches to determining sediment criteria, NOAA suggested that the potential for biological effects of this contaminant sorbed to sediments was highest in sediments where its concentration exceeded the 2100 ppb dry weight Effects Range-Median (ERM) concentration and was lowest in sediments where its concentration was less than the 160 ppb dry weight Effects Range-Low (ERL) concentration [664]. To improve the original 1990 guidelines [233], the 1995 report included percent (ratios) incidence of effects for ranges below, above, and between the ERL and ERM values. These numbers represent the number of data entries within each concentration range in which biological effects were observed divided by the total number of entries within each range [664] (see also the entries entitled ERM and ERL):

<ERL	16.0
ERL-ERM	41.0
>ERM	88.9

Oak Ridge National Lab, 1994: Risk Assessment Screening Benchmarks for Sediment Concentrations. To be considered unlikely to represent an ecological risk, field concentrations should be below the following benchmark in mg/kg (ppm) dry weight [652]:

For CAS 91-20-3 NAPHTHALENE (mg/kg dry wt.): 0.407 is the ESTIMATED EQUIVALENT SEDIMENT QUALITY CRITERION at 1% Organic Carbon.

AET from EPA 1988: The apparent effects threshold concentrations for naphthalene in sediments proposed for Puget Sound ranged from 2.1 mg/kg dry weight (microtox) to 2.7 mg/kg dry weight (benthic) [416]. Although the authors of the Puget Sound

AETs have cautioned that Puget Sound AETs may not be appropriate for comparison with data from other geographic areas, so few concern levels for this chemical have been published that the proposed Puget Sound concern level is included in this text as a reference item.

The Canadian AET concentration, adapted from NOAA (1990), for naphthalene sorbed to marine sediments is 0.500 mg/kg dry weight [864].

NOTE: Even lower concentrations of this PAH may be of concern related to its contribution to "total PAH" sums (see "PAHs as a group" entry).

St. Lawrence River Interim Freshwater Sediment Criteria, 1992. No effect: 20 ug/kg dry weight. Minimal effect: 400 ug/kg dry weight. Toxic effect: 60 mg/kg organic carbon [761].

Sed.Plants (Sediment Concentrations vs. Plants):

No information found.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found.

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

No information found.

Sed.Human (Sediment Concentrations vs. Human):

No information found.

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

No information found.

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

Soil.Low (Soil Concentrations Considered Low):

No information found.

Soil.High (Soil Concentrations Considered High):

Naphthalene was reported at concentrations of 6.1 ug/g in coal tar contaminated soil, 16.7 mg/kg in soil from a former tar-oil refinery, and up to 66 ug/kg in sludge-treated soils [766].

Soil Concentrations (mg/kg dry weight) Polycyclic Aromatic Hydrocarbons (PAHs) at Contaminated Sites. Highest values found at wood preserving, gas works, and coking site plants (mg/kg dry weight) [881]:

Naphthalene	5,769

Soil.Typical (Soil Concentrations Considered Typical):

Naphthalene has been reported in untreated agricultural soils at levels ranging from 0 to 3 ug/kg [766].

Soil Concentrations [366]:

Soil near aluminum reduction plant - 48.3 ppn [sic]; unpolluted soil - 46.2 ppb; soil under a March [sic] - 57.7 ppb [Vogt NB et al; Environ Sci Technol 21: 35-44 (1987)].

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):

Canada's interim assessment criteria (similar to screening benchmarks) and remediation criteria provide another indication that the consensus is going in the direction of lower standards and detection limits for PAHs. The interim assessment criteria (that is, approximate background concentration or approximate analytical detection limit) for naphthalene in soil is 0.1 ug/L (ppb) [656]. The interim remediation criteria (considered generally protective of human and environmental health) for naphthalene in soil is 0.1 ug/g (ppm) for agricultural land, 5 ug/g for residential/ parkland, and 50 ug/g for commercial/ industrial land. All values are in dry weight [656].

Soil criteria for evaluating the severity of contamination under the Dutch Soil Cleanup (Interim) Act (1982): 0.1 ppm of naphthalene

indicates a background concentration. 5 ppm indicates a moderate soil contamination. 50 ppm indicates a threshold value which requires immediate cleanup [347].

Acceptable on-site soil concentrations approved by the Ontario Ministry of the Environment for the Texaco and Shell refinery sites (1987): The acceptable soil concentration of naphthalene is 5,400 ppm [347].

Soil.Plants (Soil Concentrations vs. Plants):

No information found.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found.

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

No information found.

Soil.Human (Soil Concentrations vs. Human):

Preliminary remediation goals (PRGs) [868]:

Residential Soil: 8.0E+02 mg/kg wet wt.

Industrial Soil: 8.0E+02 mg/kg wet wt.

NOTE:

1) PRGs focus on the human exposure pathways of ingestion, inhalation of particulates and volatiles, and dermal absorption. Values do not consider impact to groundwater or ecological receptors.

2) These values are based on saturated concentrations of naphthalene in soil.

3) PRGs for residential and industrial landuses are slightly lower concentrations than EPA Region III RBCs, which consider fewer aspects (more limited to ingestion pathway) [903].

EPA RBC to protect from transfers to groundwater:

30 mg/Kg dry weight [903].

EPA 1996 National Generic Soil Screening Level (SSL) designed to be conservative and protective at the majority of sites in the U.S. but not necessarily protective of all known human exposure pathways, land uses, or ecological threats [952]:

SSL = 3100 mg/kg for ingestion pathway [952].

SSL = no benchmark given for inhalation pathway [952].

SSL = 4 to 84 mg/kg for protection from migration to groundwater at 1 to 20 Dilution-Attenuation Factor (DAF) [952].

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

No information found.

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:

No information found.

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

Plant Concentrations [366]:

Southern Norway area, various species marine algae - not detected to 2109 ppb(1). [(1) Knutzen J, Sortland B; Water Res 16: 421-8 (1982)].

Occurs naturally in the essential oils of the roots of Radix and Herba ononidis [PATTY. INDUS HYG & TOX 3RD ED VOL2A, 2B, 2C, 1981-1982 p.3333].

Tis.Invertebrates:

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

No information found.

B) Concentrations or Doses of Concern in Food Items

Eaten by Invertebrates:

No information found.

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

Details of naphthalene 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

Reported naphthalene concentrations ranged from 5 to 176 ng/g in oysters, from 4 to 10 ng/g in mussels, and from less than 1 to 10 ng/g in clams from the United States waters [766].

Measured naphthalene concentrations were (in wet weight) 0.002 ug/g in oysters, 0.036 ug/g in snails, and 0.5 in insects from Canadian and American creosote-contaminated sites [864].

See Tis.Fish section C).

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):

See Tis.Human below.

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

No information found.

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

Details of naphthalene 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

The naphthalene concentration in mosquitofish with extremely elevated total PAH concentrations (60.79 mg/kg) was 0.19 mg/kg [201].

Concentrations of 0.22 ug/g in fish muscle, 0.24 in fish fat, and 50 ug/ml naphthalene/ phenanthrene metabolites in fish bile were found at Canadian and American creosote-contaminated sites [864].

Fish/Seafood Concentrations [366]:

Pike from Detroit River, and Carp and Pike from Hamilton Harbor - detected, not quantified, Lake Trout from Lake Superior - detected, not quantified, estimated conc range detected - 0.01 to 5 ppm(1). Cepangopaludina chinensis, Royal Botanical Gardens, Hamilton Ontario - < 0.01 ppb(2). Polycheates 4.2 to 5.5 ppm, clam 0.43 ppm(3). Mussels, Saudalfjord, Norway suggested source - ferro alloy smelter, 4 stations - not detected(4). Mussels sampled near the Bekkelaget sewage treatment plant, Oslo, Norway - not detected(5). Southern Norway Coast, mussels, 7 of 9 samples pos, trace to 516 ppb; various

invertebrates ND to 241 ppb, results not separable from methyl naphthalene(6). Mussels and oysters from more than 100 US east, west, gulf coast sites, Woods Hole - 2.8 ppb avg, USEPA Natl Res Lab, Narragansett - 4.8 ppb avg Univ New Orleans, Center for Bio-organic Studies 96 ppb avg(7). Several species Nigerian freshwater fish species, traditionally smoked - 1.75 to 7.88 ppb, traditionally solar dried - 0.96 to 7.38 ppb, oven dried - 0.19 to 4.42 ppb(8). March Point mussels, Strait of Juan de Fuca and Northern Puget Sound, unpolluted area baseline study, 3 of 6 two week interval samples pos, 3.3 to 13 ppb(9). [(1) Konasewich D et al; Status Report on Organic and Heavy Metal Contaminants in the Lakes Erie, Michigan, Huron and Superior Basins Great Lakes Qual Board (1978) (2) Kalas L et al; pp. 567-76 in Hydrocarbons and Halogenated Hydrocarbons in the Aquatic Environment; Afghan BK, Mackay D eds; New York NY Plenum Press (1980) (3) Carlson RM et al; Implications to the Aquatic Environment of Polynuclear Aromatic Hydrocarbons Liberated from Northern Great Plains Coal; pp. 156 USEPA 600/3-79-093 (1979) (4) Bjorseth A et al; Sci Total Environ 13: 71-86 (1979) (5) Kveseth K et al; Chemosphere 11: 623-39 (1982) (6) Knutzen J, Sortland B; Water Res 16: 421-8 (1982) (7) Galloway WB et al; Environ Toxicol Chem 2: 395-410 (1983) (8) Afolabi OA et al; J Agric Food Chem 31: 1083-90 (1983) (9) Brown DW et al; Investigation of Petroleum in the Marine Environs of the Strait of Juan de Fuca and Northern Puget Sound; p. 34 USEPA 600/7-79-164 (1979)].

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:

No information found.

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):

In mice, an oral LD50 value may be on the order of 600 mg/kg. Symptoms of respiratory depression and

ataxia were noted [480].

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

After the Exxon Valdez spill, one yearling brown bear (Ursus arctos) found dead had elevated bile naphthalene concentrations of 160,000 ppb [713].

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

See Tis.Fish section C).

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):

Naphthalene has as RfD (Reference Dose; similar to an Acceptable Daily Intake) of:

0.004 (sic) mg/kg/day [824].
0.04 mg/kg/day [868,903].

Although currently regulated as a noncarcinogen, naphthalene may pose other threats. For example, naphthalene has been shown to cause hemolytic anemia in humans exposed for either short or long periods of time [824].

The EPA has calculated a chronic oral exposure dose of 0.04 mg/kg/day for naphthalene based on a NOAEL of 35.7 mg/kg/day for the presence of decreased body weight gain in rats exposed to naphthalene by gavage for 13 weeks [766].

IRIS 1996 states that the status of the reference dose for chronic oral exposure (RfD) is under review; readers should distinguish between carcinogenic and non-carcinogenic reference doses and understand that RfD usually refers to "safe" doses for chronic oral exposures, while RfC usually refers to "safe" inhalation doses for chronic inhalation exposures [893].

For risk to human adults eating fish, separate carcinogenic and non-carcinogenic risk-based fish tissue concentrations were calculated [903]. The following EPA Region III fish tissue risk-based concentration (RBC) benchmark utilizes the lower of the two (carcinogenic vs. non-carcinogenic)

concentrations, rounded to two significant figures [903]:

RBC Benchmark = 54 mg/Kg wet weight. The reader should keep in mind that fish metabolize PAHs, that the concentrations would seldom if ever be this high, that a greater risk, if any, would be from invertebrates, PAH metabolites, or routes other than fish. However, concentrations of individual PAHs often occur in the presence of complex mixtures of PAHs, and that complex mixtures of PAHs often display carcinogenic and phototoxic properties (see "PAHs as a group" entry).

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

Milk Concentrations [366]:

Mother's milk from 4 USA urban areas - detected in 6 of 8 samples quantified. [(1) Pellizzari ED et al; Bull Environ Contam Toxicol 28: 322-8 (1982)].

Body Burdens [366]:

HUMAN ADIPOSE TISSUE CONCENTRATIONS: A National Human Adipose Tissue Survey (NHATS) by EPA for fiscal year 1982 detected naphthalene in wet adipose tissue with a frequency of 40% and conc range <9 ppb - 63 ppb(1). [(1) Stanely JS; Broad Scan Analysis of the FY82 National Human Adipose Tissue Survey Specimens Vol III. Semi-volatile Organic Compounds EPA-560/5-860-037, Washington, DC USEPA pp. 148 (1986)].

Tis.Misc. (Other Tissue Information):

Naphthalene is not generally reported in fish, but has been detected in shellfish in the United States. Naphthalene was not detected in 83 biota samples (median detection limit 2.5 mg/kg) reported from 1980-1982 STORET data [766].

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

The log octanol/water partition coefficient (low Kow) for naphthalene ranges from 3.01 to 4.7 [848]. Based on the magnitude

of the Kow and other information, strong bioaccumulation in the human food chain is not expected to occur [867]. However, naphthalene exposure of cows and chickens could lead to the presence of naphthalene in milk and eggs [766].

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 to 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).

The simple bio-concentration factor (concentration in fish:concentration in water) of naphthalene 426, while for benzo(a)anthracene it is 10,000 and for pyrene, 2690 [832].

The log bioconcentration factor (log BCF) for naphthalene ranges from 1.64 - 4.11 for a variety of fish and aquatic invertebrates [848]. Naphthalene is readily metabolized in fish [849].

Coho salmon were exposed to a dilute water soluble fraction (WSF) of Prudhoe Bay crude oil for five weeks. They accumulated the more highly alkylated naphthalenes in muscle tissue faster than the less-substituted aromatics [851]:

HYDROCARBON	CONCENTRATION (PPB)		BIOACCUMULATION
	Water	Muscle Tissue	FACTOR
Naphthalene	4	240	60
1-Methyl-naphthalene	4	400	100
2-Methyl-naphthalene	4	560	140
C2-Naphthalenes	10	850	85.0
C3-Naphthalenes	6	680	113.3

For invertebrates, depuration naphthalene parent compound is rapid when the organism is placed in water free of pollutant [849,885]. During a constant exposure of 22 ppb total naphthalenes, amphipods reached a threshold of accumulation after about seven days, and the majority of naphthalenes present were alkylnaphthalenes [885]. Bioconcentration of naphthalenes by amphipods was greatest (about 1000 times) in flow through systems. In the sediment exposure system, no naphthalene was present in amphipod tissues after four days and by the 18th day only dimethyl naphthalenes were present [885].

Biomagnification of petroleum hydrocarbons through the food chain has not been demonstrated in marine mammals, probably due to their cytochrome P450 system [713]. The bioaccumulation and persistence of PAHs in the food chain is opposite that seen for other chemicals such as some PCBs and certain other organochlorines which tend to concentrate in the top predators [713]. Because it is the species lower in the food chain that concentrate PAHs, those species (like bowhead whales and walrus) that feed at that lower

level are at higher risk of bioaccumulation than species (like killer whales) that feed higher in the food chain on fish [713]. Fish also have an enzyme system for clearing hydrocarbons, thus they are not likely to bioaccumulate hydrocarbons [713]. However, colder waters can slow down the metabolism and elimination of hydrocarbons, thus animals feeding in arctic waters have a greater chance of bioaccumulating some hydrocarbons [713].

Cutthroat trout (Salmo clarki) were exposed for 90 days to four concentrations (ranging from 100 to 520 ug/L) of a Wyoming crude oil in water. Alkylated mono- and dicyclic aromatic hydrocarbons were accumulated most readily, and naphthalenes were the dominant aromatic component in oil, water, and fish. Survival was reduced to 52% at 520 ug/L, but was not affected by the 3 lower concentrations. Growth was significantly slower than control fish at all four concentrations. Exposure concentrations of 520 and 450 ug/L induced gill lesions and development of lesions on the retina and lens of the eye. Accumulation of total hydrocarbons in fish tissue was directly related to water concentration, except for fish in the 520 ug/L concentration. Evidence from this research suggests that discharges of 10 mg/L oil and grease allowed by several western states are too high [786].

Oil was taken up by Acartia bifilosa and Eurytemora hirundoides copepod invertebrates in the gut system when exposed to Russian crude oil for 24 hours [900]. Super(14)C-1-napthalene is also absorbed by E. hirundoides from emulsions in sea water [900]. Oil was present in E. hirundoides bodies after exposure for 24 hours to 1 ml/1 oil emulsion [900]. Napthalene elimination from E. hirundoides bodies after being transferred into clean sea water was studied [900]. The half-life T sub(b) is 6.2 days and the consumption rate is 6.3 ng napthalene/copepod from 1 mg/1 napthalene emulsions [900]. It is therefore assumed that copepods eating oil form a potential danger to the components of the food chain, as part of the naphthalene accumulated in the bodies [900].

Additional Notes on Bioconcentration [366]:

> Naphthalene bioconcentrates to a moderate amount in fish and aquatic invertebrates (log BCF 1.6-3.0)(1-6). However, at least for invertebrates, depuration is rapid when the organism is placed in water free of the pollutant(6,7) and naphthalene is also readily metabolized in fish (8). [(1) Roubal WT et al; Arch Environ Contam Toxicol 7: 237-44 (1978) (2) Veith GD et al; J Fish Res Board Canada 36: 1040-8 (1979) (3) Southworth GR et al; Water Res 12: 973-7 (1978) (4) Geyer H et al; Chemosphere 11: 1121-34 (1982) (5) Lee RF; pp.60-70 in Fate and Effects of Petroleum Hydrocarbons in Marine Organisms and Ecosystems Vol 6; Wolfe DA ed; (1977) (6) Eastmond DA et al; Arch Environ Contam Toxicol 13: 105-11 (1984) (7) Tarshis IB; Arch Environ Contam Toxicol 10: 79-86 (1981) (8) Callahan MA et al; Water-related Environmental Fate of 129 Priority Pollutants; pp.95-1 to 95-20 USEPA-440/4-79-029b (1979)].

Some marine organisms have no detectable aryl hydrocarbons hydroxylase enzyme systems, namely: phytoplankton, certain zooplankton, mussels (Mytilus edulis), scallops (Placopecten sp), and snails (Litternia littorea). ... Those organisms which lack a metabolic detoxification enzyme system, tend to accumulate polycyclic aromatic hydrocarbons. /Polycyclic aromatic hydrocarbons/ [Malins DC; Ann NY Acad Sci 298: 482-496 (1977) as cited in: Health and Welfare Canada; Polycyclic Aromatic Hydrocarbons p.37 (1979) Report No. 80-EHD-50].

Bioaccumulation, especially in vertebrate organisms, is considered to be short-term, and is not considered an important fate process. /Polycyclic aromatic hydrocarbons/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 95-9].

Polycyclic aromatic hydrocarbons (PAH) were analyzed in surfacial sediments & benthic organisms in southeastern lake Erie, near a large coal-fired power plant. Sediment concn (530-770 ppb PAH) were relatively homogenous throughout most of the 150 square km area, although river & nearshore concentrations reached 4 ppm. Oligochaete worms did not bioconcentrate (on wet wt basis) any of the PAH. Chironomide midges collected 1 km offshore exhibited bioconcentration of 5 pah one of which was pyrene. Further offshore, these apparent bioconcentrations disappeared, with midges at near equilibrium with sediments. [EADIE BJ ET AL; CHEMOSPHERE 11 (2): 185-92 (1982)].

Mallard ducks were given naphthalene in oil over a period of two weeks. The compound was found to distribute in the skin, liver, brain, blood, muscles, and heart. [Lawler GC et al; Environ Sci Technol 12: 51 (1978) as cited in USEPA; Ambient Water Quality Criteria Doc: Naphthalene (Draft) p.C-7 (1980)].

The pattern of naphthalene uptake & accum from a flow-through system into oyster tissues was relatively constant after only a few hr of exposure. Accum was influenced by nutritional state, lipid concn, length of exposure to naphthalene & external naphthalene concn. [RILEY ET AL; MAR BIOL (BERL) 61 (4): 267 (1981)].

Naphthalene was readily taken up by tissue of laying pullets, swine, and dairy cattle after oral administration of a single dose or on a daily basis for 31 days. Adipose tissue, kidneys, livers, and lungs of pullets had the highest naphthalene levels after acute treatment; kidneys had high levels after chronic

treatment. In swine, adipose tissues had high levels of naphthalene after acute treatment; lungs were highest with chronic treatment. In cattle, livers had the highest levels of naphthalene after both treatments. [Eisele GR; Bull Environ Contam Toxicol 34 (4): 549-56 (1985)].

Interactions:

When either naphthalene, 1-methylnaphthalene, of 2-methylnaphthalene was applied dermally in combination with benzo(a)pyrene (BaP), there was an inhibitory effect on the induction of skin tumors in female mice. The authors suggested that it is likely that certain naphthalenes compete with BaP for the same enzyme site, resulting in alteration of the BaP metabolic pathway and decreased production of the active BaP metabolite [766].

Explosive reaction with dinitrogen pentaoxide. Reacts violently with CrO3; aluminum chloride + benzoyl chloride [766].

Ip injection of channel catfish (Ictalurus punctatus) with 100 ug benzo(a)pyrene, Aroclor 1254, or naphthalene, singly and in combinations, affected the levels of the brain neurotransmitters norepinephrine, dopamine, and 5 hydroxytryptamine, but the effect showed no discernible pattern. The effects of combinations of the chemicals did not appear to be predictable from the effects of individual chemicals. In several instances, the change in the level of neurotransmitter in fish receiving a combination of chemicals was greater than in fish receiving either chemical alone. [366, Fingerman SW, Short EC; Bull Environ Contam Toxicol 30 (2): 147-51 (1983)].

Naphthalene exposures increased oxygen consumption by benthic invertebrates and reduced photosynthesis of Chlamydomonas angulosa [970].

Uses/Sources:

Naphthalene is a common PAH found in numerous petroleum products and byproducts, particularly the middle distillate petroleum products (such as diesels, no. 1 and 2 fuel oils, and heating oil) [661]. Most common petroleum products contain naphthalene, including jet fuels and even the very light product stoddard solvent.

Water extracts of crude oils generally produce higher total hydrocarbon values than fuel oils, since they contain a higher proportion of low molecular weight soluble compounds. Monocyclic aromatic compounds (C12 or less) are relatively abundant in water mixtures from crude oils, while refined products or residual oils and their water extracts contain a higher proportion of di- and tri- aromatic compounds [853].

Although PAHs, particularly heavy PAHs, do not make up a large percentage of diesel fuels by weight, there are some PAHs in diesel fuels, including naphthalene and alkyl naphthalenes [497,661,796,822,824].

Of the polynuclear aromatic hydrocarbons, naphthalene, 2-

methylnaphthalene, and phenanthrene are the most commonly found in diesel and are the individual compounds posing the highest calculable risk due to ingestion [497].

Naphthalene, benzo(a)pyrene, fluorene, and phenanthrene are common PAH components of used motor oil [75].

Naphthalene, one of the more important components derived from the second distillation fraction when distilling coal tar from coal, is employed in the production of dyes and synthetic resins [279]. It is also used for lubricants, explosives, fungicides, and moth repellents and as a solvent and preservative [279].

Nearly all naphthalene entering the environment is released directly to the air (92.2%). The largest source of emission (more than 50%) is through inadvertent releases due to residential combustion of wood and fossil fuels [766].

Naphthalene enters the atmosphere primarily from fugitive emissions and exhaust connected with its presence in fuel oil and gasoline. In addition, there are discharges on land and into water from spills during the storage, transport and disposal of fuel oil, coal tar, etc. [366].

About 5% of all naphthalene entering the environment is released to water. Most of that amount is attributable to coal tar production and distillation processes. Some naphthalene (about 60%) from these sources is discharged directly to surface waters; the remainder is distributed to wastewater treatment plants. The only other contributions of any consequence enter the nation's waterways from wood preserving industry effluent and from oil spills [766].

To study water soluble leachates from out-of service railway ties, one gram of wood was shaved from the surface of the railroad ties and agitated in water for 24 hours. Up to 88.9 ug/L of naphthene was found in the water [864].

This compound is found in floor wax and many other products and may be a lab contaminant [971].

Natural Sources [366]:

> Component of crude oil; since naphthalene is a natural combustion product, forest fires, etc may be a source of naphthalene. (SRC) .
>
> One common PAH, naphthalene, occurs naturally in the essential oils of the roots of Radix and Herba ononidis [Patty. Indus Hyg & Tox 3rd ed Vol2A, 2B, 2C, 1981-1982 p.3333].

Artificial Sources [366]:

> Emissions from its production from petroleum refining and coal tar distillation(1); Emissions and wastewater from its use as a chemical intermediate(2); Motor vehicle emissions; tobacco smoke(3); coal tar pitch fumes(1); Oil spills(SRC). [(1) Verschueren K; Handbook of Environmental Data on Organic Chemicals; 2nd ed Van Nostrand Reinhold Co New York NY p.892 (1983) (2) Kirk-Othmer Encyclopedia of Chemical Technology; 3rd ed 15:698

(1978) (3) Graedel THE; Chemical Compounds in the Atmosphere; Academic Press New York NY p.124 (1978)].

Naphthalene has been identified in cigarette smoke condensate(1). [(1) USEPA; Ambient Water Quality Criteria Naphthalene; USEPA 440/5-80-059 (1980)].

Major Uses [366]:

Formerly used as wood preservative. [Gosselin, R.E., H.C. Hodge, R.P. Smith, and M.N. Gleason. Clinical Toxicology of Commercial Products. 4th ed. Baltimore: Williams and Wilkins, 1976.,p. III-242].

MFR of phthalic & anthranilic acids, naphthols, naphthylamines, sulfonic acid, synthetic resins, celluloid, lampblack, smokeless powder, and hydronaphthalenes. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

Use of naphthalene as moth repellent and insecticide is decr due to introduction of chlorinated cmpd such as para-dichlorobenzene. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

Is used in the preparation of anthraquinone. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 2(78) 704].

Is used for the manufacturing of indigo. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 8(79) 367].

Is used in the formation of perylene via the intermolecular Scholl reaction. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 11(80) 278].

A high yielding (98%) process from the oxidn by microrganisms, has been developed in Japan for the production of salicylic acid from naphthalene. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 15(81) 460].

Chem int for phthalic anhydride.

Chem int for 1-naphthyl-n-methylcarbamate insecticide.

Chem int for beta-naphthol & synthetic tanning chems.

Chem int for surfactants-eg, naphthalene sulfonates.

Chem int for 1-naphthylamine (FORMER USE).

VET: has been used as insecticide, antiseptic and vermicide [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

VET: 0.2% ... used in combination-type antiseptic for irrigating wounds & 1% ... On neglected infected wounds. [Rossoff, I.S. Handbook of Veterinary Drugs. New York: Springer Publishing Company, 1974. 377].

Externally, on livestock & poultry ... To control lice. [Rossoff, I.S. Handbook of Veterinary Drugs. New York: Springer Publishing Company, 1974. 377].

Ingredient of some moth repellants and toilet bowl deodorants. [GOSSELIN. CTCP 5TH ED 1984 p.III-307].

Sulfonation of naphthalene with sulfuric acid produces mono-, di-, tri-, and tetranaphthalenesulfuric acids. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 15(81) 700].

Other HSDB Information [366]:

Most abundant single constituent of coal tar. Dry coal tar contains about 11%. Crystallizes from middle or "carbolic oil" fraction of distilled tar. Purified by hot pressing, which may be followed by washing with H_2SO_4, NAOH, & water, then by fractional distillation or by sublimation. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

The petroleum industry is a large producer of naphthalene. In gas treatment facilities of coke plants, the gas is usually cooled by direct contact with water resulting in condensation of naphthalene from the gas. The naphthalene is dissolved by passing the water through a bath of tar in the base of the final cooler. Alternatively, a petroleum oil fraction may be used instead of water to cool the gas and to absorb the naphthalene. The naphthalene is recovered from the oil by steam stripping. [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 6(79) 285].

Therapeutic Uses [366]:

VET: has been used as insecticide, antiseptic and vermicide [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

VET: 0.2% ... used in combination-type antiseptic for irrigating wounds & 1% ... On neglected infected wounds. [Rossoff, I.S. Handbook of Veterinary Drugs. New York: Springer Publishing Company, 1974. 377].

Externally, on livestock & poultry ... To control lice ... Powder usually contains 15-35% concn although 100% ... Occasionally used ... Lower concn ... Used with other insecticides. [Rossoff, I.S. Handbook of Veterinary Drugs. New York: Springer Publishing Company, 1974. 377].

Naphthalene is an insecticidal fumigant of restricted usefulness & of somewhat low potency.... [Worthing, C.R., S.B. Walker (eds.). The Pesticide Manual - A World Compendium. 7th ed. Lavenham, Suffolk, Great Britain: The Lavenham Press Limited, 1983. 390].

Consumption Patterns [366]:

Chem int for phthalic anhydride, 58%; chem int for 1-naphthyl-n-methylcarbamate, 21%; chem int for beta-naphthol, 8%; chem int for synthetic tanning agents, 6%; moth repellant, 3%; chem int for surfactants, 3%; other, 1% (1980 est).

Chem intermediate for phthalic anhydride, 50%; chem intermediate for carbamate insecticides, 20%; chemical intermediate for naphthalene sulfonic acids, 20%; miscellaneous, 10% (1984) [CHEMICAL PRODUCTS SYNOPSIS: NAPHTHALENE, 1984].

Phthalic anhydride, 60%; exports, 15%; 1-naphthol, tetralin, 1-naphthyl methyl carbamate insecticide, 10%; tanning agents, 8%; surfactants and other uses, 7% (1985) [CHEMICAL PROFILE: NAPHTHALENE, 1985].

CHEMICAL PROFILE: Naphthalene. Phthalic anhydride, 60%; 1-naphthyl methyl carbamate insecticide and related products (tetralin and 1-naphthol), 10%; dispersant chemicals, 10%; moth repellent, 6%; synthetic tanning agents, 5%; miscellaneous uses, 5%; exports, 4%. [Kavaler AR; Chemical Marketing Reporter 232 (14): 78 (1987)].

CHEMICAL PROFILE: Naphthalene. Demand: 1986: 250 million lb; 1987: 255 million lb; 1991 /projected/: 270 million lb (Includes exports, imports are negligible).[Kavaler AR; Chemical Marketing Reporter 232 (14): 78 (1987)].

Forms/Preparations/Formulations:

No information found.

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

Gasolines, including unleaded [746], contain a small but significant amount of PAHs including naphthalene and alkyl naphthalenes [797]. Naphthalenes make up from 0.09 to 0.49 weight percent of gasoline and from 0.08 to 0.5 volume percent of various gasolines [796]. Methyl naphthalenes constituted the single largest class of chemicals in soils contaminated by no. 6 fuel oil [814].

Among the compounds in diesel are three polycyclic aromatic hydrocarbons: 0.07 ug/kg benzo(a)pyrene; 0.57-0.91 weight percent methylnaphthalene; and 0.13 weight percent naphthalene [796].

The 100% water soluble fraction of No. 2 fuel oil contains about 6 ppm total hydrocarbons, of which 90% are aromatics, and 30% are specifically naphthalenes [853]. However, naphthalenes represent only 2.2% of the total aromatics and 1.3% of the total hydrocarbons in the water soluble fraction of South Louisiana Crude oil. While it would appear that naphthalenes would contribute less to the toxicity of crude oils than fuel oils, the relative volatility of hydrocarbons in the different mixtures should be considered. Toluene, benzene, and xylenes, which are prominent in crude oil extracts, are more volatile than naphthalene and particularly alkyl naphthalene [853].

Naphthalene content in one fresh sample of NSFO (Fuel Oil 5, Chuck Rafkind, National Park Service, Personal Communication, 1996): 34.3 ng/mg (ppm).

Naphthalene content in one sample of groundwater subjected to long term contamination of NSFO (Fuel Oil 5), possibly mixed with some JP-4, motorgas, and JP-8, Colonial National Historical Park Groundwater Site MW-10 (Chuck Rafkind, National Park Service, Personal Communication, 1996): 530.8 ng/L (ppt).

NOTE: the above two PAH concentrations were analyzed by a GC/MS/SIM NOAA protocol [828] modified with methylene chloride extraction for use with water samples (Guy Denoux, Geochemical and Environmental Research Group, Texas A&M University, personal communication 1996).

Naphthalene concentration in Used Engine Oil: 52.0 ppm [519; Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12, Upshall, C., J.F. Payne and J. Hellou. Induction of MFO enzymes and production of bile metabolites in rainbow trout (Oncorhynchus mykiss) exposed to waste crankcase oil. Copyright 1992 SETAC].

Naphthalene content of a no.2 fuel oil - diesel oil [824]:

CHEMICAL	CONCENTRATION RANGE (ppm)
2-Methylnaphthalene	6,700
Naphthalene	2,730

Concentrations of naphthalene in a reference Bunker C, no. 2 fuel oil, and two crude oils [177]:

NOTE: The following concentrations in mg/kg (ppm) are from API

reference oils:

COMPOUND	South LA crude	Kuwait crude	No. 2 fuel oil	Bunker C residual
Naphthalene	400	400	4,000	1,000
1-Methylnaphthalene	800	500	8,200	2,800
2-Methylnaphthalene	900	700	18,900	4,700
Dimethylnaphthalenes	3,600	2,000	31,100	12,300
Trimethylnaphthalenes	2,400	1,900	18,400	8,800

For comparison, the following table lists some of the specific naphthalene contents (ppm) of water soluble fraction (WSF) from 10% oil-in-water solution of four test oils (measured by gas chromatography) [770]:

COMPOUNDS	SOUTH LA CRUDE	KUWAIT CRUDE	NO. 2 FUEL OIL	BUNKER C RESIDUAL
Di- and tri- aromatics				
Naphthalene	0.12	0.02	0.84	0.21
1-Methylnaphthalene	0.06	0.02	0.34	0.19
2-Methylnaphthalene	0.05	0.008	0.48	0.20
Dimethylnaphthalenes	0.06	0.02	0.24	0.20
Trimethylnaphthalenes	0.008	0.003	0.03	0.10

In one study, the proportions of the C0-C2 naphthalenes are much smaller and proportions of the highly alkylated (C3-C4) naphthalenes, phenanthrenes, and dibenzothiophenes are larger in weathered Prudhoe Bay Crude Oil than in fresh Prudhoe Bay Crude Oil [521].

Aromatic hydrocarbons concentrations (ug/g, ppb) measured in a study using Prudhoe Bay Crude oil [854]:

COMPOUNDS	CONCENTRATION (ppb)
Naphthalene	777
2-Methylnaphthalene	1,711
1-Methylnaphthalene	1,197
1- & 2-Ethylnaphthalene	664
2,6-Dimethylnaphthalene	1,046
1,3-Dimethylnaphthalenes	1,038
1,7-Dimethylnaphthalene	1,063
1,4-Dimethylnaphthalenes	786
1,2-Dimethylnaphthalene	448
2,3,5-Trimethylnaphthalene	466

For comparison, capillary gas chromatograph analyses of aromatic hydrocarbon concentrations (uL/L, ppb) in the water soluble fractions (WSF) of a fresh Prudhoe Bay Crude oil [854]:

COMPOUNDS	CONCENTRATION (ppb)
Naphthalene	118.38
2-Methylnaphthalene	47.03
1-Methylnaphthalene	39.13
1- & 2-Ethylnaphthalene	3.44
2,6- & 2,7-Dimethylnaphthalenes	6.28
1,3- & 1,6-Dimethylnaphthalenes	8.83

1,7-Dimethylnaphthalene	9.29
1,4- & 2,3- & 1,5-Dimethylnaphthalenes	5.84
1,2-Dimethylnaphthalene	1.86
TOTAL NAPHTHALENES	240.09

Naphthalene concentrations (ug/g oil sampled) were determined for three different crude oil sample types taken from the Exxon Valdez oil spill. Listed below are 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), 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

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

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

Physical/Chemical Measures:

Water Solubility (in water at 25 degrees C) [848]: 12.5 to 137.4 mg/L (most values 30 to 34 mg/L).

Solubility (in water at 20 degrees C) [766]: 31.7 mg/L

Solubility (in seawater) [851]:

At 22 degrees C, 32% salinity: 20 mg/L
At 25 degrees C, 35% salinity: 22.0 mg/L

Solubilities [366]:

30 MG/L in water; very sol in 1,2-dichloromethane [Worthing, C.R., S.B. Walker (eds.). The Pesticide Manual - A World Compendium. 7th ed. Lavenham, Suffolk, Great Britain: The Lavenham Press Limited, 1983. 390].

SOL in acetic acid [Weast, R.C. (ed.) Handbook of

Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-357].

1 G/13 ML METHANOL OR ETHANOL [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-357].

1 G/3.5 ML BENZENE OR TOLUENE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

1 G/8 ML OLIVE OIL OR TURPENTINE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

1 G/2 ML CHLOROFORM OR CARBON TETRACHLORIDE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

1 G/1.2 ML CARBON DISULFIDE [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

VERY SOL IN ETHER, HYDRONAPHTHALENES [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

VERY SOL IN FIXED & VOLATILE OILS [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

SOL IN ETHYLENE DICHLORIDE [Spencer, E. Y. Guide to the Chemicals Used in Crop Protection. 7th ed. Publication 1093. Research Institute, Agriculture Canada, Ottawa, Canada: Information Canada, 1982. 411].

Vapor Pressure [766]: 0.087 mmHg

Vapor Pressure at 25 degrees C [848]: 6.6 to 111 Pa (most values 10 to 12).

Density/Specific Gravity [366]:

Density: 0.97021 g/cu cm @ 90 deg C; Specific gravity: 4.4 (gas) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 13-15(81) 466-9].

Density [848]: 1.01 to 1.15 g/cm3 at 20 degrees C.

Density [766]: 1.145 g/mL

Color/Form [366]:

White, crystalline flakes or solid [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 49-66].

White scales, balls, powder or cakes [Rossoff, I.S. Handbook of Veterinary Drugs. New York: Springer Publishing Company, 1974. 377].

Monoclinic plates from alcohol [Weast, R.C. (ed.) Handbook of Chemistry and Physics. 67th ed. Boca Raton, FL: CRC Press, Inc., 1986-87.,p. C-357].

Odor [366]:

Strong coal tar odor. [ITII. Toxic and Hazardous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 353].

AROMATIC ODOR [Sax, N.I. Dangerous Properties of Industrial Materials. 6th ed. New York, NY: Van Nostrand Reinhold, 1984. 1971].

ODOR OF ... MOTH BALLS [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Odor Threshold [766]:

0.021 mg/L (21 ppb) in water
0.44 mg/m3 (84 ppb) in air

Boiling Point [366,766,848]:

217.7 to 218 Degrees C

Melting Point [366,766,848]:

80-83 Degrees C

Molecular Weight [366,766]:

128.16 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 914].

Corrosivity [366]:

Melted naphthalene will attack some forms of plastics, rubber, and coatings. [Mackison, F. W., R. S. Stricoff, and L. J. Partridge, Jr. (eds.). NIOSH/OSHA - Occupational Health Guidelines for Chemical Hazards. DHHS(NIOSH) PublicationNo. 81-123 (3 VOLS). Washington, DC: U.S. Government Printing Office, Jan. 1981. 2].

Critical Temperature and Pressure [366]:

CRIT TEMP: 887.4 DEG F= 475.2 DEG C= 748.4 DEG K [U.S.

Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

CRIT PRESSURE: 588 PSIA= 40.0 ATM= 4.05 MEGANEWTONS/SQUARE M [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Heat of Combustion [366]:

-16,720 BTU/LB= -9287 CAL/G= -388.8X10+5 JOULES/KG [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Heat of Vaporization [366]:

43.5 kJ/mol [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. 15(81) 699].

Henry's Law Constant (Pa m3/mol):

35.8 to 119.5 (most values 40 to 50) [848].

Octanol/Water Partition Coefficient:

The log octanol/water partition coefficient (low Kow) for naphthalene ranges from 3.01 to 4.52 [848].

Log Kow = 3.01-3.59 [366, Hansch, C., A. Leo. Substituent Constants for Correlation Analysis in Chemistry and Biology. New York, NY: John Wiley and Sons, 1979. 249].

Log Kow [766]: 3.29

Log Kow [754,848]: 3.37

Log Kow values for alkyl naphthalenes [971]:

Naphthalene:	3.37
C1-Naphthalene:	3.87
C2-Naphthalene:	4.37
C3-Naphthalene:	5.0
C4-Naphthalene:	5.55

Log Koc (Sorption Partition Coefficient) [766,848]: 2.97

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

Low-molecular-weight PAHS, such as naphthalene, are readily volatilized from the water column. In general, volatilization half-lives from surfaces are shorter than 100 h for low-molecular-weight PAHs such as naphthalene. However, this number may vary depending upon surface wind velocity and turbulence [754].

Naphthalene and methylnaphthalenes are degraded in water by photolysis and biological processes. The half-life for photolysis of naphthalene in surface water is estimated to be about 71 hours, but the half-life in deeper water (5 m) is estimated at 550 days [766].

Naphthalene fate and effects on aquatic biota in a model aquatic system were descrlbed by Bartell et al [970].

Of 14 PAHs studied in two soils, volatilization was found to account for about 20% of the loss of 1-methylnaphthalene and 30% of the loss of naphthalene; volatilization was not an important loss mechanism for the other compounds. Lower molecular weight compounds may also volatilize from sediments; this process is not significant for the higher molecular weight compounds [788].

One study showed how biodegradation of PAHs was related to molecular weight. The 2- and 3-ring PAHs (naphthalene, fluorene, and phenanthrene) degraded rapidly [815].

Of naphthalene and alkyl naphthalenes, the parent compound naphthalene is the first to degrade; so as petroleum products age, the percentage of alkyl naphthalenes vs. naphthalene increases [796].

Breeding female mallard ducks consuming petroleum-contaminated food show significant induced increases in the naphthalene-metabolizing properties of microsomes prepared from their livers [806]. 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 [806]. 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 [806].

Information from HSDB [366]:
Environmental Fate [366,599]:

> TERRESTRIAL FATE: The sorption of naphthalene to soil will be low to moderate depending on its organic carbon content. Its passage through sandy soil will be rapid. It will undergo biodegradation which may be rapid when the soil has been contaminated with PAHs (half-life a few hours to days) but slow otherwise (half-life > 80 days). Evaporation of naphthalene from the top soil layer will be important but the importance of the process will gradually decrease as the soil depth increases. (SRC) .
>
> AQUATIC FATE: Photolysis, volatilization, biodegradation, and adsorption may all be important loss mechanisms for

naphthalene discharged into water. In the Rhine River the half-life has been determined as 2.3 days based upon monitoring data(1). Moderate adsorption to sediment and particulate matter occurs. In surface layers of water, photolysis may be dominant (half-life 3 days). Volatilization is an important loss mechanism especially in rapid streams since the half-life for a river may be a couple of days. In a mesocosm experiment which simulated Narraganset Bay, the half-life in winter was 12 days; loss being primarily due to evaporation(2). These investigators did not mention any photolytic loss which would certainly have been noticed since they used sterile controls(2). In oil contaminated water which is not exposed to sunlight because the water is murky or the water depth is great, biodegradation can be important with half-lives of 7 days in oil polluted streams to a few months in inland and coastal waters.(SRC) [(1) Zoeteman BCJ et al; Chemosphere 9: 231-49 (1980) (2) Wakeham SG et al; Environ Sci Technol 17: 611-7 (1983)].

ATMOSPHERIC FATE: Naphthalene reacts with photochemically produced hydroxyl radicals and degrades with a half-life of 3-8 hr. Although photolysis should occur, no data could be found to assess its importance. In polluted urban air, reaction with NO3 radicals may be an additional sink for night time loss. .

Soil Adsorption/Mobility [366]:

Naphthalene is adsorbed moderately by soil and sediment. 17 soils and sediment had a mean Koc of 871(1) and soils from Switzerland had a Koc of 812(3). A mean Koc of 2400 was measured for 4 silt loams and a sandy loam soil(2) and a Koc of 4100 was measured for natural estuarine colloids(12). Although it adsorbs to aquifer material(10), in simulations of ground-water transport systems and rapid infiltration sites, and in field studies, naphthalene frequently appears in the effluent(4-9). A half-life of 65 hr due to sediment adsorption in a flowing river of 1 m depth and 0.5 m/sec has been predicted(11). In a variety of surface waters only 0.1-.8% of the naphthalene was sorbed to particulate matter(11). [(1) Karickhoff SW; Chemosphere 10: 833-46 (1981) (2) Briggs GG; J Agric Food Chem 29: 1050-9 (1981) (3) Schwarzenbach RP, Westall J; Environ Sci Technol 15: 1360-7 (1981) (4) Goerlitz DF; Bull Environ Contam Toxicol 32: 37-44 (1984) (5) Hutchins SR et al; Environ Toxicol Chem 2: 195-216 (1983) (6) Roberts PV et al; J Water Pollut Control Fed 52: 161-71 (1980) (7) Schwarzenbach RP et al; Environ Sci Technol 17: 472-9 (1983) (8) Piet GJ et al; Int Symp Quality of Groundwater Studies in Environ Sci 17: 557-64 (1981) (9) Rittmann BE et al; Ground Water 18: 236-43 (1980) (10) Ehrlich GG et al; Ground Water 20: 703-10 (1982) (11) Herbes SE et al;

pp.113-28 in Scientific Basis of Toxicity Assessment; Witschi H ed; Elsevier/North Holland Biomed Press (1980) (12) Wijayaratne RD, Means JC; Mar Environ Res 11: 77-89 (1984)].

Volatilization from Water/Soil [366]:

The laboratory determined half-life for the evaporation of naphthalene from water 1 m deep with a 1 m/sec current velocity and a 3 m/sec wind speed is 4.1-5 hr(1,2). In the case of naphthalene the rate of volatilization is much more sensitive to the current velocity and a 10 fold decrease in current to 0.1 m/sec will increase the half-life to 32 hours whereas 10 fold decrease in wind speed to 0.3 m/sec will increase the half-life to 11 hr(1). The rate of evaporation of naphthalene in jet fuel from water relative to the oxygen reaeration rate ranged from 0.2 to 0.5 which when combined with typical reaeration rates for natural bodies of water(4) give a half-life for evaporation of 50 and 200 hr in a river and lake respectively(3). Estimated volatilization half-lives from a soil containing 1.25% organic carbon were 1.1 day from 1 cm soil depth and 14.0 days from 10 cm soil depth(5). In moisture-saturated soil as in the case of flooded soil, volatilization may not be important(6). [(1) Southworth GR; Bull Environ Contam Toxicol 21: 507-14 (1979) (2) Lyman WJ et al; Handbook of Chemical Property Estimation Methods Environmental behavior of organic chemicals; McGraw Hill New York NY p. 960 (1982) (3) Smith JH, Harper JC; 12th Conf on Environ Toxicol; pp. 336-53 (1982) (4) Mill T et al; Laboratory Protocols for Evaluating the Fate of Organic Chemicals in Air and Water; p. 255 USEPA-600/3-82-022 (1982) (5) Jury WA et al; J Environ Qual 13: 573-9 (1984) (6) Bouwer EJ et al; Water Res 18: 463-72 (1984)].

Biodegradation [366]:

Polycyclic aromatic hydrocarbons with 4 or less aromatic rings are degraded by microbes and are readily metabolized by multicellular organisms; biodegradation may be the ultimate fate process. /Polycyclic aromatic hydrocarbons/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 97-17].

Biodegradation is probably slower in the aquatic system than in the soil, and biodegradation may be much more important in those aquatic systems which are chronically affected by contamination. /Polycyclic aromatic hydrocarbons/ [Callahan, M.A., M.W. Slimak, N.W. Gabel, et al. Water-Related Environmental Fate of 129 Priority

Pollutants. Volume I. EPA-440/4 79-029a. Washington, DC: U.S.Environmental Protection Agency, December 1979.,p. 95-11].

There is a moderate amount of data concerning the biodegradability of naphthalene both in standard biodegradability tests and in natural systems. Although there is some conflicting data, the preponderance of data suggests that naphthalene degrades after a relatively short period of acclimation and that degradation can be rapid in oil polluted water, slow in unpolluted water and that the rate of degradation increases with the concentration of naphthalene(5). In laboratory tests with sewage or sludge inoculums, 100% degradation was obtained in 7 days(1,2) while others got 0% BOD in 5 days(3,4). Approximately 70% was lost in a pilot-scale municipal wastewater treatment plant due to biodegradation(6). In water, bacteria can utilize naphthalene only when it is in the dissolved state(7). [(1) Fochtman EG, Eisenberg W; Treatability of Carcinogenic and Other Hazardous Organic Compounds; pp.61 (1979) USEPA-600/2-79-097 (2) Tabak HH et al; J Water Pollut Control Fed 53: 1503-18 (1981) (3) Dore M et al; Trib Cebedeau 28: 3-11 (1975) (4) Heukelekian H, Rand MC; J Water Pollut Control Assoc 23: 1040-53 (1955) (5) Van der Linden AC; Dev Biodegrad Hydrocarbons 1: 165-200 (1978) (6) Petrasek AC et al; J Water Pollut Control Fed 55: 1286-96 (1983) (7) Thomas JM et al; Appl Environ Microbiol 52: 290-6 (1986)].

Twenty percent of naphthalene was degraded to CO2 when incubated in water from an oil polluted creek(1) and rapid degradation, sometimes as fast as 95% degradation in 1.5 hr (3), have been reported in other experiments with inoculums from oil contaminated water or sediment(2). In die-away tests, reported half-lives include 70 hr in water with high PAH levels(4); 7, 24, 63, and 1700 days in an oil polluted estuarine stream, clean estuarine stream, coastal waters and in the Gulf Stream respectively(5); 9 days in water near a coal-coking wastewater discharge(6). In water from the Alaskan Continental Shelf degradation rates avg 0.5%/week; however, when nutrient levels are lower as in late spring-early summer (after algae blooms), the degradation rate is reduced(7). In a mesocosm experiment using Narraganset Bay seawater, the half-life in late summer was 0.8 days and is principally due to biodegradation(8). Biodegradation half-life 43 days in microbe-supplemented filtered superior harbor water and 39 days in nutrient and microbe-supplemented water(9). [(1) Walker JD, Colwell RR; Appl Environ Microbiol 31: 189-97 (1976) (2) Van der Linden AC; Dev Biodegrad Hydrocarbons 1: 165-200 (1978) (3) Herbes SE et al; Appl Environ Microbiol 32: 244-6 (1977) (4) Herbes SE et al; pp.113-28 in The Scientific Basis of Toxicity Assessment; Witschi H ed;

Elseveir/North Holland Biomed Press (1980) (5) Lee RF; 1977 Oil Spill Conf; Amer Petrol Inst pp.611-6 (1977) (6) Herbes SE; Appl Environ Microbiol 41: 20-8 (1981) (7) Roubal G, Atlas RM; Appl Environ Microbiol 35: 897-905 (1978) (8) Wakeham SG et al; Environ Sci Technol 17: 611-7 (1983) (9) Vaishnaw DD & Babeu L; Bull Environ Contam Toxicol 39: 237-44 (1987)].

Degradation rates in sediment are much higher than in water, being 8-20 fold higher than in the water column above the sediment(3). Half-lives in sediment include 4.9 hr and > 88 days in oil contaminated and uncontaminated sediment, resp(3), 9 days in sediment near a coal coaking discharge(2); and 3, 5, and > 2,000 hours in sediments with high, medium and low PAH levels respectively(1). When incubated in a slurry with sediment from an uncontaminated pond, the mineralization rate increases, reaching a peak after 6-12 days corresponding to a half life of 78 days(4). Biodegradation half-life ranged from 2.4 weeks in sediments chronically exposed to petroleum hydrocarbons to 4.4 weeks in sediment from a pristine environment(5). [(1) Herbes SE et al; pp.113-28 in The Scientific Basis of Toxicity Assessment; Witschi H ed; Elseveir/North Holland Biomed Press (1980) (2) Herbes SE; Appl Environ Microbiol 41: 20-8 (1981) (3) Herbes SE, Schwall LR; Appl Environ Microbiol 35: 306-16 (1978) (4) Saylor GS, Sherrill TW; Bacterial Degradation of Coal Conversion Byproducts (polycyclic aromatic hydrocarbons) in Aquatic Environments; Knoxville TN pp. 90 Tenn Elnev Report no 39535 (1981) (5) Heitkamp MA et al; Appl Environ Microbiol 53: 129-36 (1987)].

No degradation under anaerobic conditions was observed in 6 and 11 weeks in a lab reactor with seed from a well near a source of contamination(1), or with sewage seed(2), resp, but complete degradation occurred in 8 days in gas-oil contaminated groundwater which was circulated through sand which had been inoculated with groundwater under aerobic conditions(3). Biodegradation occurred in groundwater contaminated with creosote(4). [(1) Ehrlich GG et al; Ground Water 20: 703-10 (1982) (2) Bouwer EJ, McCarty PL; Appl Environ Microbiol 45: 1295-9 (1983) (3) Kappeler T, Wuhrmann K; Water Res 12: 327-33 (1978) (4) Thomas JM et al; Environ Toxicol Chem 6: 607-14 (1987)].

Abiotic Degradation [366]:

Naphthalene absorbs light with a wavelength greater than 290 nm and will photolyze in water(1,3). Photolysis should also occur in air but no experimental data could be found(SRC). The half-life in surface waters is calculated to be 71 hours(1,2) and longer in deeper or murky water(1). When a mixture of jet fuel was added to

filtered deionized water, salt water or pond water and exposed to sunlight, 44-77% of the naphthalene in the fuel was lost in 7 days(6). The presence of algae in the water can increase the rate of photolysis of naphthalene by a factor of 1.3 to 2.7(5). If nitrite is present in the water, mutagenic products are formed during photolysis(4). Reaction with oxidizing species in natural waters as well as hydrolysis will not be significant(3). [(1) Zepp RG, Schlotzhauer PF; pp. 141-58 in Polynuclear Aromatic Hydrocarbons; Jones PW, Leber P ed; Ann Arbor Press Ann Arbor MI (1979) (2) Herbes SE et al; pp. 113-28 in Scientific Basis of Toxicity Assessment; Witachi H ed; Elseveir/North Holland Biomed Press (1980) (3) Callahan MA et al; Water-related Environmental Fate of 129 Priority Pollutants; pp. 95-1 to 95-20 USEPA-440/4-79-029b (1979) (4) Suzuki J et al; Bull Environ Contam Toxicol 31: 79-84 (1983) (5) Zepp RG, Scholzhauer PF; Environ Sci Technol 17: 462-8 (1983) (6) Smith JH, Harper JC; 12th Conf on Environ Toxicol; pp. 336-53 (1982)].

Naphthalene in air reacts with photochemically generated hydroxyl radicals with a half-life about 8 hr in clean air and 3 hr in moderately polluted air(1,2,3). The loss of naphthalene due to reaction with N2O5 and O3 in air is neglible(1,3). In polluted urban air, reaction with NO3 radicals may be an additional sink for night time loss(4). [(1) Atkinson R et al; Environ Sci Technol 18: 110-3 (1984a) (2) Kloepffer W et al; Chim Zig 110: 57-61 (1986) (3) Atkinson R et al; Environ Sci Technol 21: 1014-22 (1987) (4) Atkinson R et al; J Phys Chem 88: 1210-5 (1984b)].

Absorption, Distribution and Excretion [366]:

Cutaneous absorption of naphthalene in infants is incr by baby oil. [Thienes, C., and T.J. Haley. Clinical Toxicology. 5th ed. Philadelphia: Lea and Febiger, 1972. 231].

Readily absorbed when inhaled. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 3340].

Excreted in urine as 1-naphthylmercapturic acid (15% dose) and as conjugates of 1,2-dihydronaphthalene-1,2-diol (10%), 1- & 2-naphthols & 1,2-dihydroxynaphthalene. [Parke, D. V. The Biochemistry of Foreign Compounds. Oxford: Pergamon Press, 1968. 219].

At 100 mg/kg intraperitoneally, 20 to 30 percent was excreted in the rat urine. 85 to 90 percent of these in the form of conjugates /which are acidic/; 5 to 10 percent was excreted in the bile, of these also 70 to 80

percent as acid conjugates, with the major metabolite naphthalene-1,2-dihydrodiol. [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 3341].

In small oysters transport of naphthalene between tissues is primarily by diffusion. In intact oysters, accum in adductor muscle & body followed accum in gills after a large lag-time. In isolated tissues with no shell to impede water, there was no time lag. [RILEY ET AL; MAR BIOL (BERLIN) 63 (3): 325 (1981)].

The gills of dolly varden char (Salvelinus malma) were the most important pathway for excretion of (14)c from (14)c-labeled naphthalene. In general, fish exposed to toluene excreted more (14)c than fish exposed to naphthalene. [THOMAS RE, RICE SD; BIOL MONIT MAR POLLUT, IN PROC SYMP POLLUT PHYSIOL MAR ORG: 425 (1981)].

English sole exposed to (3)h-benzo(a)pyrene (b(a)9) & (14)c-naphthalene (nph) in sediment containing prudhoe bay crude oil. Bioconcentration values for NPH was greater than values for B(a)P in tissues of fish exposed for 24 hr. [VARANASI U, GMUR DJ; AQUAT TOXICOL 1 (1): 49 (1981)].

The mechanism of transport by polynuclear aromatic hydrocarbons (PAH) into cells & between intracellular membranes is discussed. From the partitioning parameters, the rate limiting step /in the transport of PAH's cells and across intraellular membrane/ involves solvation of transfer species in the interfacial water at phospholipid surface. [PLANT AL ET AL; CHEM-BIOL INTERACT 44 (3): 237-46 (1983)].

Polynuclear aromatic hydrocarbons are highly soluble in adipose tissue and lipids. /Polynuclear aromatic hydrocarbons/ [Sittig, M. Handbook of Toxic And Hazardous Chemicals. Park Ridge, NJ: Noyes Data Corporation, 1981. 564].

Conjugates of glutathione, cysteinylglycine & cysteine, intermediates in formation of mercapturic acids, are excreted, particularly in bile, as metabolites of ... Naphthalene. ... [PARKE; BIOCHEM COMPOUNDS: 92 (1968)].

Laboratory and/or Field Analyses:

Caution: This compound is found in floor wax and many other products and may be a lab contaminant [971].

Detection limits: For risk assessment or drinking water purposes, low detection limits (no higher than 0.3 ppb) should be

specified using Selective Ion Mode (SIM) methods [828] or other rigorous methods. When potential biological effects are being considered, many of the methods historically used have been determined to be inferior to the NOAA protocol expanded scan [828] being recommended by some risk assessment experts in 1996. Most of the historically used methods, including EPA standard semi-volatile scan number 8270, do not cover important alkyl PAHs and do not utilize low-enough detection limits (10 ppt for water, 1-10 ppb for sediments and soil) to use in ecological risk assessments.

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].

If a Park Service groundwater investigation at Colonial National Historical Park performed in response to contamination by Fuel Oil 5 had utilized EPA semi-volatile scan 8270 or any of the other typical EPA scans (625, etc.) all of which only include parent compounds and typically utilize detection limits in the 170-600 ppb range, the false conclusion reached would have been that no PAHs were present in significant (detection limit) amounts. This false negative conclusion would have been made because the parent compound PAHs present constituted only 7.6% of the PAHs detected in groundwater by the expanded scan [828], and the highest concentration found for any parent compound was 8.4 ppb, far below the detection limits used on the older standard EPA scans. Utilizing the NOAA protocol expanded scan [828], it was determined that 92.4% of the total concentration values of the PAHs detected in groundwater were alkyl PAHs, and that all 39 PAHs and alkyl PAHs were present. Of course, all 39 PAHs were also present in the fresh product, in much higher concentrations, and also having alkyl compounds with the highest percentage of higher values compared to parent compounds (see Chem.Detail section of the separate PAHs entry for more details).

In a similar vein, if the Park Service sediment investigation at Petersburg National Historical Battlefield (see Chem.Detail section of the separate PAHs entry, this study was performed in response to contamination by Diesel) had utilized EPA semi-volatile scan 8270 or any of the other typical EPA scans (625, etc.), all of which only include parent compounds and often utilize detection limits no lower than the 170-600 ppb range, the false conclusion reached would have been that only one PAH was present in significant (detection limit) amounts. This false negative conclusion would have been made because the parent compound PAHs present constituted only 2.4% of the PAHs detected in sediments, and the highest concentration found for any parent compound except pyrene was 85.5 ppb, far below the detection limits used on the

older standard EPA scans. Pyrene was 185 ppb, which would have been non-detected on many of the EPA scans, but not all. However, utilizing the NOAA protocol expanded scan [828], it was determined that 97.6% of total quantity of PAHs detected in sediments were alkyl PAHs, and that all 39 PAHs and alkyl PAHs were present in these sediments.

Examples of standard method protocols for PAHs published by various parts of EPA as well as some other agencies are outlined below:

Holding Times:

Water Samples: Both NPDES and RCRA (SW-846) maximum holding times are 7 days until extraction and 40 days after extraction [1010,1013].

Samples of Solids: EPA RCRA methods for semi-volatiles in solids in SW-846 call for holding times of 14 days until extraction and 40 days after extraction [1013]. The need to get rid of headspace to prevent loss of certain PAHs (such as naphthalenes) tends to discourage the freezing of soil and other samples. However, the Fish and Wildlife Service and some other groups nevertheless freeze some soil samples. If this can be accomplished without compromising the sample (for example, breaking a glass container), the freezing tends to stop biodegradation. Once frozen, holding times for samples of semi-volatiles such as PAHs in solids is on the order of decades (John Moore, Fish and Wildlife Service, Personal Communication, 1997).

Containers:

Both EPA and APHA (Standards Methods Book) recommend glass containers for the collection of organic compounds [141,1010,1013]. EPA also recommends teflon lined caps for solids samples of semi-volatiles [1010,1013].

Guidance from other federal agencies (USGS, FWS, NOAA) also recommends glass containers for organics, and discourages the use of plastic containers for a variety of reasons (Roy Irwin, National Park Service, Personal Communication, 1997, based on a glance through recent internal guidance of several agencies).

Some federal agency quality control procedures call for voiding or red-flagging the results of organic analyses if the lab receives the sample in plastic containers (Roy Irwin, National Park Service, Personal Communication, 1997). The APHA pointed out some the potential hazards of the use of certain plastic containers for storing organic samples [141]:

A) Potential contamination of the sample via

leaching of compounds from the plastic, and/or

B) The plastic container walls can sometimes be attacked by certain organics and fail, and/or

C) The possibility that some of organic compound will dissolve into the walls of the plastic container, reducing the concentration of the compound in the container [141].

For the relatively volatile PAHs such as naphthalenes, not even vials are not the best choice for avoiding false negatives in soil samples through volatilization losses, since the use of brass liners for collection resulted in 19 fold higher VOCs than when 40 mL vials were used [798] The third update of EPA's SW-846 RCRA guidance authorizes the storage of soil samples of volatiles in EnCore TM (or equivalent, no government endorsement implied) samplers as long the sample is analyzed within 48 hours after collection [1013]. Several states also authorize the use of EnCore TM or equivalent containers for temporary (48 hour) storage containers (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997).

Certain plastic polymers present less of a problem related to potential losses of volatiles than others. Some plastic is found in the latest approved EnCore TM samplers. Some states also give the reader the option of using plastic in collecting devices. For example, related to methods for gasoline range petroleum hydrocarbons, Wisconsin states that organics can be collected using a 30 ml plastic syringe with the end sliced off, a brass tube, an EnCore TM sampler or other appropriate devices (Donalea Dinsmore, State of Wisconsin DNR, personal communication, 1997). A plastic syringe is also mentioned as an option in the third update of RCRA methods in SW-846 [1013]. The thinking appears to be that plastic is less of a threat in a collecting device, with momentary contact, than in a storage container where contact times are longer.

Typical "standard method" protocols recommend proper cleaning of glass containers before use. Some collectors simply use pre-cleaned jars from I-Chem or Eagle Pitcher (no government endorsement implied) or equivalent suppliers. EPA [1010], USGS, and most other federal agencies recommend cleaning procedures for the glass containers, usually involving detergent rinsing, baking, and sometimes HCL rinses (Roy Irwin, National Park Service, Personal Communication, 1997).

Field Protocols:

Standard field collection method protocols are published

or internally distributed by the Fish and Wildlife Service, the USGS, DOE, NOAA, and EPA. These recommendations change over time, with the newest recommendations sometimes being quite different than the old, thereby producing different results. The USGS NAWQA protocols call of sieving of sediment samples composites, a practice that might result in the loss of relatively volatile PAHs such as the naphthalenes.

The Fish and Wildlife Service methods are similar in many ways to NOAA field protocols [676]. Many recommended EPA field methods for organics are not very detailed, although the 3rd update of SW-846 for RCRA solid waste methods is becoming more detailed [1013].

The various EPA methods for organics are different from each other, with the selection of the appropriate method depending upon the specific application (RCRA vs. CERCLA vs. NPDES permits, vs. Drinking Water, etc.) [861,1010,1013]. The EPA-recommended field methods are scattered through various EPA and ASTM publications.

EPA methods typically include recommendations that grab samples rather than composites be utilized for organics, and require the proper cleaning of collection bottles and collecting gear for both volatile and semi-volatile organics [1010,1013]. In other publications, EPA recommends caution in the use of composite soil samples whether organic or inorganic, citing statistical complications and stating that the compositing of samples cannot, in general, be justified unless for a stated specific purpose and unless a justification is provided [1017].

For PAHs (lab method 610) and other semi-volatiles, EPA recommended in 1994: that "conventional sampling practices" be followed as specified by ASTM D-3370 (3370-95a is a recent number), "Standard Practices for Sampling Water from Closed Conduits" [1010,1012]. No field methods are specified when not sampling for pipes [1010,1012].

Regardless of what lab methods are used, the investigator should take special precautions to prevent the escape of relatively light PAHs during sample shipment, storage, extraction, and cleanup [798]. This is especially true for soil and sediment sampling. The results of analyses of the lighter semi-volatiles (such as naphthalenes) can be dramatically effected by small details such as how the samples are collected, stored, held, and analyzed in the lab, since volatile compounds can readily volatilize from samples in both field and lab procedures. If the investigator knows that the sample will contain significant quantities of the lighter semi-volatiles such

as naphthalenes, field and lab precautions should be taken just as if the investigator were handling volatiles (see Benzene entry for details). For example, for the lighter semi-volatiles, it may be prudent to use EPA method 5021 in SW 846, a generic "headspace" method for the collection of volatiles in soils and sediments [1013].

Standard field methods for sampling contaminated soils for various types of contaminants were summarized by EPA in 1991 [1020]. These methods seem generally consistent with SCS recommendations, but are not necessarily 100% consistent with other protocols suggested by other parts of EPA [1013], and are not consistent with methods suggested by other agencies, such as the Fish and Wildlife Service.

Variation in concentrations of organic contaminants may sometimes be due to the typically great differences in how individual investigators treat samples in the field and in the lab rather than true differences in environmental concentrations. This is particularly true for volatiles and for the relatively lighter semi-volatiles such as the naphthalenes, which are so easily lost at various steps along the way. Contaminants data from different labs, different states, and different agencies, collected by different people, are often not very comparable (see 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]. The basics of these quality assurance plans for chemical analyses should include the following quality control steps:

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. Typical lab quality control techniques should have included the

following considerations (Roy Irwin, National Park Service, Personal Communication, 1997, summary based on various EPA and FWS documents):

Procedural Blanks should be analyzed to assure that no contaminants are added during the field and lab processing of the samples. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits. For one program, NOAA stated that at least 8% of samples should be blanks, reference or control materials [676].
>
> The basic idea is that neither samples nor blanks should be contaminated. Because the only way to measure the performance of the modified procedures is through the collection and analysis of uncontaminated blank samples in accordance with this guidance and the referenced methods, it is highly recommended that any modifications be thoroughly evaluated and demonstrated to be effective before field samples are collected [1003].
>
> It should be kept in mind that blanks will not help in the way intended if one is using a method prone to false negatives due to the use of detection limits that are too high, the loss of contaminants in handling, use of an inappropriate method, etc. This is one reason for using the NOAA expanded scan for PAHs [828], method 8270 modified for SIM detection limits and more alkyl analytes, or other rigorous scans rather than many of the standard EPA parent compound scans which are prone to false negatives (Roy Irwin, National Park Service, Personal Communication, 1997).

Duplicate samples are analyzed to provide a measure of precision of the methods. The standards for adequacy depend on the method and the media being measured.

> Different federal agencies publish different acceptable limits. There appears to be an inverse relationship between precision and sensitivity [676].
>
> Some EPA methods state that a field duplicate must be collected at each sampling site, or one field duplicate per every ten samples, whichever is more frequent [1003]. Some protocols call for the preparation of one Ongoing precision and recovery (OPR) standard for every ten or fewer field samples. Great care should be taken in preparing ongoing precision and recovery standards [1003].

Spiked samples are analyzed to provide a measure of the accuracy of the analysis methods. The standards for adequacy

depend on the method and the media being measured.

Different federal agencies publish different acceptable limits.

Pros and cons of various lab and field methods for PAHs and data comparison issues for PAHs may be found in the separate PAHs entry. Due to the length of these discussions, they are not repeated here (see separate PAHs entry).

PAHs are often analyzed when crude oil or oil products are spilled. This is as it should be, since PAHs are among the more hazardous of the constituents in crude oil and many oil products (see Chem.Detail section of separate PAHs entry). However, it is not always easy to determine which combinations of lab methods to use for crude oil and oil products. The following is a proposed decision Tree (dichotomous key) for selection of lab methods for measuring contamination from mid-range petroleum products (Roy Irwin, National Park Service, Personal Communication, 1997):

In choosing a lab method, it should be kept in mind that many mid range products (such 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 8260. The older standard EPA GC/MS method 8240 protocol was 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 8260 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) [1013], 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 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] (see discussion at the end of this key). 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 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 8260 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 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 decision tree key.

Some labs use screening HPLC fluorescence methods to screen for alkylated naphthalenes and dibenzothiophenes that fluoresce at naphthalene wavelengths and the alkylated phenanthrenes that fluoresce at phenanthrene wavelengths [521]. Other HPLC/fluorescence scans are used to examine fish bile directly for the presence of metabolites of PAHs such as naphthalene [523].

Certain labs use screening HPLC fluorescence methods to screen for alkylated naphthalenes and dibenzothiophenes that fluoresce at naphthalene wavelengths and the alkylated phenanthrenes that fluoresce at phenanthrene wavelengths [521].

Other HPLC/fluorescence scans are used to examine fish bile directly for the presence of metabolites of PAHs such as naphthalene [523]. In these methods, ratios of phenanthrene or naphthalene equivalents to benzo(a)pyrene (BaP) equivalents from bile screening can be used to differentiate the source of the aromatic hydrocarbons contamination [523]. The naphthalene/BaP ratios should be higher in fish exposed to crude oil than those exposed in pyrogenic urban PAHs in sediments [523].

Routine (often less rigorous methods) used in the past have included the following:

In the past, many methods have been used to analyze for PAHs [861,1010,1013]. Parent compound semi-volatile PAHs have often been analyzed using routine monitoring methods EPA 8270 for solid waste/RCRA purposes [1013] or by EPA NPDES method 610 as specified in 40 CFR Part 136 [1010]. However, the standard EPA methods 8270, 610, and 625 are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. For risk or damage assessment purposes, or to determine if biodegradation has occurred, the NOAA expanded scan generally gives more rigorous and comprehensive results.

Various EPA Methods (Note: as mentioned above, many of the standard EPA methods are inadequate for risk or damage assessment purposes):

EPA (RCRA Group) publishes requirements for solid waste methods in 40 CFR Part 261, Appendix III, with details in the following periodically updated publication [1013]:

> Environmental Protection Agency. 1997. Test methods for evaluating solid waste, physical/chemical methods, SW-846, EPA Office of Solid Waste and Emergency Response, EPA, Washington, D.C. Update 3 finalized in 1997. Available from NTIS or GPO. Previous 1995 update 2 was available on CD-ROM [1013].

RCRA (SW-846) methods tend to include provisions for using the specified method or something better. RCRA SW-846 methods typically require instrument calibration before analyses, but some labs don't do it, and many labs actually use some kind of hybrid between RCRA, CERCLA, or various other "standard protocols" (Roy Irwin, Park Service, Personal Communication, 1997, based on conversations with various EPA and private lab staff members). The guidance in SW-846 must be used in some states, but is considered "guidance of acceptable but not required methods" in most federal applications. In the past, EPA has also published separate (not SW-846) guidance documents with suggestions on field sampling and data quality assurance related to sampling of sediments [1016] and soils [1017,1018,1019].

EPA (CERCLA) publishes various Contract Laboratory Program (CLP) methods documents periodically, available from EPA and NTIS. CLP methods were designed for use in contaminated areas and often have detection limits that are not low enough for use in relatively clean areas or where low detection levels are needed in comparison with low concentration criteria or benchmarks. CERCLA CLP methods tend to require things done exactly per contract specifications. A few examples of CLP publications (this list is not complete) [861]:

> User's Guide CLP CERCLA User's Guide to the Contract Laboratory Program. USEPA - Office of Emergency and Remedial Response. Dec 1988

> 9240_0-0XFS Multi-Media/Conc Superfund OSWER CERCLA Multi-Media, Multi-Concentration Organic/Inorganic Analytical Service for Superfund, Quick Reference Fact Sheets, 9240.0-08FS (organic) and 9240-0-09FS (inorganic), August 1991. The

organic/inorganic analytical service provides a technical and contractual framework for laboratories to apply EPA/Contract Laboratory Program (CLP) analytical methods for the isolation, detection and quantitative measurement of 33 volatile, 64 semi-volatile, 28 pesticide/Aroclor, and 24 inorganic target analytes in water and soil/ sediment environmental samples.

AOC/Contract Laboratory Program (CLP), Routine Analytical Services, Summary on EPA Home Page under Superfund Subdirectory, EPA Office of Remedial and Emergency Response, 1997, Internet.

Less rigorous scanning methods for various PAHs in drinking water have included High pressure liquid chromatography (EPA 550, 550.1); gas chromatographic/mass spectrometry (EPA 525): PQL= 0.0002 mg/L [893].