

ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

DIBENZOTHIOPHENE ENTRY

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COMPILERS/EDITORS:

ROY J. IRWIN, NATIONAL PARK SERVICE

WITH ASSISTANCE FROM COLORADO STATE UNIVERSITY

STUDENT ASSISTANT CONTAMINANTS SPECIALISTS:

MARK VAN MOUWERIK

LYNETTE STEVENS

MARION DUBLER SEESE

WENDY BASHAM

NATIONAL PARK SERVICE

WATER RESOURCES DIVISIONS, WATER OPERATIONS BRANCH

1201 Oakridge Drive, Suite 250

FORT COLLINS, COLORADO 80525

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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 uninformed 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:

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

on the internet or NTIS: 1998).

Dibenzothiophene (DBT, CAS number 132-65-0)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Although opinions differ as to whether dibenzothiophene is a PAH, it is listed as such in several sources [468,495,795]. In one reference, dibenzothiophene is listed as a three-ring aromatic PAH [795]. Others say that dibenzothiophene (DBT) is a heterocyclic rather than a PAH compound, yet nevertheless include it with lists of PAHs [971].

It is notable as a very persistent compound compared to most PAHs and other crude oil aromatics [856].

Dibenzothiophene is a sulfur-containing, high molecular weight compound and can be present in significant amounts in petroleum-contaminated samples [468]. Petroleum-contaminated samples also tend to contain the homologous series (alkylated compounds C1 through C3) of dibenzothiophene [468].

Dibenzothiophene is included on the expanded scan list used by the Geochemical and Environmental Research Group (GERG) Laboratory at Texas A&M [828]. This list includes most of the PAHs recommended by the NOAA's National Status and Trends program [680]. Dibenzothiophenes and related dibenzothiophenol compounds in expanded scans for PAHs help complete "fingerprinting" for petroleum-contamination-source identification [942].

The related compound "thiophene," is an organic heterocyclic compound containing a diunsaturated ring of four carbon atoms and one sulfur atom [495]. Thiophene is an aromatic compound [495]. See Chem.detail section below for more discussion of the generic compound thiophene.

Not one of the PAHs found by NASA in 1996 on a rock alleged to be a meteorite from mars; lack of this compound used as one argument that the mix of PAHs was different than that found in typical earth atmosphere. (see Uses/Sources section below for details).

Br.Haz: General Hazard/Toxicity Summary:

This compound has many alkyl homologues; this is important because within an aromatic series, acute toxicity of PAHs tends to increase with increasing alkyl substitution on the aromatic nucleus [851,853].

Probably the most important target analytes in natural resource damage assessments for oil spill are PAHs and the homologous series (alkylated) PAHs [468]. Alkylated PAHs are more abundant, persist for a longer time, and are sometimes more toxic than the parent PAHs [468]. Alkyl Substitutions usually decreases water solubility [754]. They also tend to bioaccumulate to a greater degree [347,885]. 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.

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. Thus, for now, risk assessment experts suggests adding (lumping) all alkyl homolog concentrations with its constituent parent concentration, and interpreting that grouped value (Bill Stubblefield, ENSR, personal communication, 1995). For example, add the reported concentrations for C1-, C2-, C3-, and C4-dibenzothiophenes to the reported dibenzothiophene concentration, and interpret that group value against known toxicological effects benchmarks or criteria for dibenzothiophene.

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 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).

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

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

No information found. However, this compound often occurs together with other PAHs, some possibly more carcinogenic (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. Perhaps the most unambiguous thing that can be said about complex PAH mixtures is that such mixtures are often hazardous in many ways, including carcinogenicity and phototoxicity. (James Huckins, National Biological Survey/USGS, and Roy Irwin, National Park Service, personal communication, 1996).

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

No information found.

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

Dibenzothiophene, C1 Dibenzothiophene, and C2 Dibenzothiophene were still present after 10 years in sediment experimentally polluted with crude oil, long after most aromatics had disappeared [856].

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

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.

Synonyms/Substance Identification:

2,2'-Biphenylene sulfide [365]
Dibenzo(b,d)thiophene [365]
Diphenylene sulfide [365]
9-Thiafluorene [365]

Molecular formula:
C12-H8-S [365]

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

PAHs as a group
Dibenzothiophene, C1-
Dibenzothiophene, C2-
Dibenzothiophene, C2-
PAHs, Alkyl Homologs of
Petroleum, General

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

W.Low (Water Concentrations Considered Low):

No information found.

W.High (Water Concentrations Considered High):

No information found.

W.Typical (Water Concentrations Considered Typical):

No information found.

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):

No information found.

W.Plants (Water Concentrations vs. Plants):

No information found.

W.Invertebrates (Water Concentrations vs. Invertebrates):

LC50 for a 96-hour exposure of *Palaemonetes pugio* (grass shrimp) to dibenzothiophene was 0.28 ppm [851].

LC50s for *Daphnia magna* (water flea) were 0.420 and 0.466 mg/L (ppm) for 48-hr exposures [998].

W.Fish (Water Concentrations vs. Fish):

LC50 for a 96-hour exposure of *Cyprinodon variegatus* (sheep's-head minnow) to dibenzothiophene was 3.18 ppm [851].

LC50 for *Poecilia reticulata* (guppy) was 0.70 mg/L (ppm) for a 96-hr exposure [998].

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

No information found.

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

No information found.

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

No information found.

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):

Dibenzothiophene was detected in 80.1 % of urban-bay samples from the Puget Sound area. The mean concentration was 337 ug/kg dry weight (ppb), while the median concentration was 61 ug/kg (ppb) [852].

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

Sed.Typical (Sediment Concentrations Considered Typical):

Dibenzothiophene was detected in 75 % of non-urban-bay samples from the Puget Sound area. The mean concentration was 5 ug/kg dry weight (ppb), while the median concentration was 3 ug/kg (ppb) [852]. NOTE: these values based on only three samples where dibenzothiophene was detected.

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

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):

No information found.

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):

No information found.

Soil.Typical (Soil Concentrations Considered Typical):

No information found.

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):

No information found.

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):

No information found.

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:

No information found.

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 dibenzothiophene 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):

Dibenzothiophene:	260 ug/kg = ppb
C1-Dibenzothiophene:	1344 ug/kg = ppb
C2-Dibenzothiophene:	2743 ug/kg = ppb
C3-Dibenzothiophene:	2743 ug/kg = ppb

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):

No information found.

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 dibenzothiophene 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):

Dibenzothiophene:	19.65 ug/kg = ppb
C1-Dibenzothiophene:	19.68 ug/kg = ppb
C2-Dibenzothiophene:	15.96 ug/kg = ppb
C3-Dibenzothiophene:	7.44 ug/kg = ppb

Whole-body dibenzothiophene concentrations in 3-year old brown bullhead catfish from the contaminated Black River in Ohio in 1980, 1981 and

1982 were 509, 832, and 92 ug/g wet weight, respectively [890].

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):

Mouse LD50; Route: Oral; Dose: 470 mg/kg; Toxic effects: Behavioral - General anesthetic; Behavioral - Coma; Reference: Fundamental and Applied Toxicology 12:787, 1989. [365].

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

No information found.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found.

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):

No information found.

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

No information found.

Tis.Misc. (Other Tissue Information):

No information found.

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

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).

Interactions:

No information found.

Uses/Sources:

During the summer of 1996, NASA announced that PAHs had been found on a martian meteorite. Three to 6 ring PAHs found included phenanthrene, pyrene, chrysene, perylene, and benzo(a)pyrene, with less than 10% of the mass being alkyl PAHs. It was said that the meteorite PAHs were typified by little alkylation and a lack a dibenzothiophene, making the PAH mixture different than typically found in the earth's atmosphere. However, another unidentified mass of alkyl PAH compounds were also found and NASA acknowledged that PAHs have been found in a wide range of extraterrestrial materials [McKay et.al. 1996, manuscript entitled "Search for Life on Mars: Possible Biogenic Activity in Martian Meteorite ALH84001," a NASA paper available at the time of the NASA press release].

Note from Roy Irwin: This represents an interesting and somewhat speculative attempt to link fingerprinting of PAH combinations to possible life on mars. NASA admits that the PAHs alone do not prove there was life on mars.

See also Chem.detail section below for dibenzothiophene concentrations in various petroleum products.

Forms/Preparations/Formulations:

No information found.

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

Log Kow values for PAH related DBTs [971]:

Dibenzothiophene:	4.49
C1-Dibenzothiophene:	4.86
C2-Dibenzothiophene:	5.5
C3-Dibenzothiophene:	5.73

Molecular weight [365]: 184.26

Dibenzothiophene concentrations were determined for three different crude oil sample types taken from the Exxon Valdez oil

spill. Concentrations in 1) unweathered oil from the tanker itself (March 1989), 2) oil skimmed from the water immediately after the spill and held in the skimmer barge for about 90 days (July 1989), and 3) weathered oil from Prince William Sound shorelines (May 1989) were: 189, 150, and 73 ug/g oil sampled, 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].

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

Dibenzothiophene:	217 mg/kg = ppm
C1-Dibenzothiophene:	449 mg/kg = ppm
C2-Dibenzothiophene:	635 mg/kg = ppm
C3-Dibenzothiophene:	579 mg/kg = ppm

According to Alaska fish and game information on the internet, aged Exxon Valdez oil also has higher concentration of alkyl DBTs than the parent compound. DBT was also detected in edible tissues of various aquatic species around the Exxon Valdez spill.

Dibenzothiophene content in one fresh sample of NSFO (Fuel Oil 5, Chuck Rafkind, National Park Service, Personal Communication, 1996): 25.7 ng/mg (ppm).

Dibenzothiophene 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): 8377.8 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).

Dibenzothiophene concentration in Used Engine Oil: 1.9 ppm [519; Reprinted with permission from Environmental Toxicology and Chemistry, Volume 12, Upshall, C., J.F. Payne and J. Hellou. 1992. Induction of MFO enzymes and production of bile metabolites in rainbow trout (*Oncorhynchus mykiss*) exposed to waste crankcase oil].

Discussion of related compound "thiophene" (not dibenzothiophene):

Thiophene resembles benzene in many of its physical properties, but is more reactive, especially in the positions adjacent to sulfur [495]. Thiophene is nearly insoluble in water (forming 0.02-0.04% solutions at 20 or 68 F) [495]. Thiophene has a resonance energy of 29-31 kcal/mole (121-130 kilojoules/mole), is stable to heat, and undergoes electrophilic substitutions (nitration,

sulfonation, acetylation, halogenation, chloromethylation, and mercuration) [495].

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

Detailed information about the biocatalysis/biodegradation fate of this compound is included on the University of Minnesota Biocatalysis/Biodegradation Database (Available on the internet in July, 1997, www.nmsr.labmesd.umn.edu).

Laboratory and/or Field Analyses:

Lab methods utilized must be able to quantify alkyl dibenzothiophenes, and most standard EPA scans [861,1010,1013] do not do that. For risk assessment, damage assessment, drinking water, or to determine if biodegradation has occurred, the NOAA expanded scan for PAHs and alkyl PAHs [828], or equivalent rigorous and comprehensive scans (such as SW-846 method 8270 modified for Selective Ion Mode detection limits and an equivalent list of alkyl PAH analytes), are recommended.

Recommended detection limits:

Most of the PAH methods which have been commonly used historically for routine monitoring, including PAH parent compound standard methods:

EPA 8270 (8270 includes several PAH parent compounds along with a long list of other organics) for solid waste/RCRA applications [1013], and

EPA NPDES method 610 as specified in 40 CFR Part 136 (method 610 includes 16 PAH parent compounds) [1010],

EPA method 625 for Base/Neutral Extractables (method 625 includes several PAH parent compounds along with a long list of other organics) as specified in 40 CFR Part 136 [1010],

are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These standard EPA scans do not cover important alkyl PAHs and do not utilize low-enough detection limits. When biological effects, ecological risk assessment, damage assessment, or bio-remediation are being considered, detection limit should be no higher than 1-10 ng/L (ppt) for water and 1 ug/kg (ppb) dry weight for solids such as tissues, sediments, and soil.

Note: Utilizing up to date techniques, many of the better labs can use detection limits of 0.3 to 1

ppb for tissues, sediments, and soils. When no biological resources are at risk, detection limits for solids should nevertheless generally not be above 10 ppb. One reason that low detection limits are needed for PAHs is that so many of the criteria, standards, and screening benchmarks are in the lower ppb range (see various entries on individual PAHs).

In the past, many methods have been used to analyze for PAHs [861,1010,1013]. However, 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 in separate "PAHs as a group" entry for more details).

In a similar vein, if the Park Service sediment investigation at Petersburg National Historical Battlefield (see Chem.Detail section in separate "PAHs as a group" 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.

When taking sediment samples for toxic organics such as PCBs, PAHs, and organochlorines, one should also routinely ask for total organic carbon analyses so that sediment values may be normalized for carbon. This will allow comparison with the newer EPA interim criteria [86,127]. TOC in sediments influences the dose at which many compounds are toxic (Dr. Denny Buckler, FWS Columbia, personal communication).

In some cases (where the expanded scans are too expensive) an alternative recommendation is that one screen sediments with a size-exclusion high-performance liquid chromatography (HPLC)/fluorescence method. The utility and practicality of the HPLC bile and sediment screening analyses were demonstrated on board the NOAA R/V Mt. Mitchell during the Arabian Gulf Project. Estimates of petroleum contamination in sediment and fish were available rapidly, allowing modification of the sampling strategy based on these results [522].

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].

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 naphthalene PAHs, 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. In fact, as mentioned in the disclaimers section at the top of this entry, 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].

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 to insure data comparability or method validity. Even volunteer monitoring programs are now strongly encouraged to develop and use quality assurance project plans [1015,1017].

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

It should be kept in mind that quality control field and lab blanks and duplicates will not help in the data quality assurance goal as well as intended if one is using a method prone to false negatives. Methods may be prone to false negatives due to the use of detection limits that are too high, the loss of contaminants through inappropriate handling, or the use of an inappropriate methods such as many of the EPA standard scans. This is one reason for using the NOAA expanded scan for PAHs [828]; or method 8270 [1013] modified for Selective Ion Mode (SIM) detection limits (10 ppt for water, 0.3 to 1 ppb for solids) and additional alkyl PAH analytes; or alternative rigorous scans. These types of rigorous scans are less prone to false negatives than many of the standard EPA scans for PAH parent compounds (Roy Irwin, National Park Service, Personal Communication, 1997).

For a much more detailed discussion of the great many different lab and field methods for PAHs in general, see the entry entitled PAHs as a group (file name starting with letter string: PAHS). There the reader will find much more detailed discussions of lab methods, holding times, containers, comparability of data from different methods, field sampling methods, quality assurance procedures, the relationship of various methods to each other, the various EPA standard methods for various EPA programs, the pros and cons of various methods, and additional documentation concerning why many standard EPA methods are inadequate for certain applications. A decision tree key for selecting the most appropriate methods for oil or oil products spills is also provided in the lab section of the PAHs entry. Due to the length of these discussions, they are not repeated here (see PAHs entry).