ENVIRONMENTAL CONTAMINANTS ENCYCLOPEDIA

ASPHALT 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 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 search for power key section headings and how to use this document in general, 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).

Asphalt (Asphaltic bitumen, bitumen, petroleum asphalt, asphalt cements, CAS number 8052-42-4)

Brief Introduction:

Br.Class: General Introduction and Classification Information:

Asphalt is a complex mixture of many chemical compounds, the exact composition of which depends upon the individual source. According the US Coast Guard Emergency Response Notification System (ERNS), asphalt is one of the most commonly spilled petroleum products the U.S [635].

Asphalts are bituminous materials which occur naturally or are derived from nondestructive separation of petroleum fractions [749]. Typically, this is achieved through fractional distillation or solvent de-asphalting [749]. Asphalt should not be confused with tar, which is obtained through destructive processing of coal, wood, or petroleum [749]. Asphalt contains aliphatic hydrocarbons [749] in addition to the mononuclear aromatics and polycyclic aromatic hydrocarbon (PAH) mixtures found in both asphalt and tars [749].

Structurally, asphalt is considered to be either a colloid consisting of asphalt micelles suspended in oils or an intermicellar resin phase; or a solution of asphaltenes dissolved in the oil-resin phase [749]. Asphalt materials are categorized as asphalt cements or liquid asphalts (see Forms section below) [749].

Asphalt paving materials typically are composed of aggregate and/or sand (90-95% by weight) and asphalt (5-10% by weight). The aggregate and/or sand is responsible for the primary load-bearing properties, while asphalt serves as the binder and as a protective coating. The asphalt binder functions best when the aggregate/sand particles are "wetted" with asphalt. To ensure good adhesion between the asphalt and the aggregate or sand particles, moisture and clays are to be avoided [749].

Hazardous Substances Lists including Asphalt or Asphalt Parameters:

The following state lists were provided by Vera Hudson of the National Library of Medicine in April of 1993. The format calls for the CAS number (with hyphens deleted) followed by the name of the substance, with no space between the CAS number and the start of the substance name. To convert the

CAS number to the more standard style, move one digit to the left of the (right) end of the number and place a hyphen between the last two numbers, then move two more spaces over to the left and insert another hyphen. Using this conversion, the CAS number listed below for lactic acid, 000050215, becomes 50-21-5. Substances with no CAS number are listed last.

Massachusetts Toxic Substances List:

008052424Asphalt (CAS number 52-42-4)

008052424Asphalt (cutback)

008052424Asphalt (liquid rapid-curing)

Illinois Toxic Substances List:

008052424Asphalt (petroleum) vapor

Hazardous Substances, New Jersey Right-to-Know List

008052424Asphalt fumes

Br.Haz: General Hazard/Toxicity Summary:

Hazards to fish, wildlife, and aquatic life:

The main hazard associated with asphalt is from the PAHs and alkyl PAHs in asphalt that can move into the ecosystem from the breakdown of asphalt (see Br.Fate section below). Since asphalt contains so many toxic and carcinogenic compounds and since leaching of harmful PAH compounds has been documented even in water pipe use, asphalt should be kept out of rivers, streams, and other natural waters to the extent possible (see Water Data Interpretation section below).

According to the Coast Guard CHRIS manual, the effects of low concentrations of asphalt to aquatic life or waterfowl is unknown [367].

Hazards to Humans:

Hazards include inhalation of compounds in heated or fresh asphalt as well as ingestion of PAHs entering the food chain as the result of breakdown of asphalt (see Br.Fate Section below). Finished waters from various treatment sites are transported to consumers through a variety of pipelines. PAH's (polynuclear aromatic hydrocarbons) leach from the tar or asphalt linings of these pipes, resulting in increased concentrations of these compounds in water reaching the consumers [366]. Cement-lined pipes produce lower PAH concentrations [366].

NIOSH urges caution related to human exposure to asphalt. Current NIOSH research indicates that asphalt products are carcinogenic to laboratory animals and, therefore may be more toxic to humans than previously believed [366].

Air concentrations of PAHs have been shown to increase to potentially dangerous levels in National Parks in response to forrest fires and asphalt roads burned by lava flows; although the human health risks from low levels of PAHs is not precisely known, the National Institute of Occupational Safety and Health position is that any exposure to certain carcinogenic PAHs is too much and therefore the exposure should be limited as much as possible (Dr. Dawn Tharr, NIOSH, Cincinnati, personal communication).

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

Asphalt is considered a potential carcinogen due to the fact it typically may contain many carcinogenic compounds, including many PAHs. See also: PAHs as a group entry. Current NIOSH research indicates that asphalt products are carcinogenic to laboratory animals and, therefore may be more toxic to humans than previously believed [366].

Found to contain carcinogens. Positive [609].

The debates on which PAHs and alkyl PAHs found in this product to classify as carcinogens, and the details of 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 usually occur in complex mixtures rather than alone. Perhaps the most unambiguous thing that can be said about complex PAH mixtures is that such mixtures are often carcinogenic and possibly phototoxic. One way to approach site specific risk assessments would be to collect the complex mixture of PAHs and other lipophilic contaminants in a semipermeable membrane device (SPMD, also known as a fat bag) [894,895,896], retrieve the contaminant mixture from the SPMD, then test the mixture for carcinogenicity, toxicity, and phototoxicity (James Huckins, National Biological Service, and Roy Irwin, National Park Service, personal communication, 1996).

Toxic Hazard Rating [609]:

> There is inadequate evidence that bitumens alone are carcinogenic to humans. /Bitumens/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V35 71 (1985)].
>
> There is sufficient evidence for the carcinogenicity of extracts of steam-refined bitumens, air-refined bitumens and pooled mixtures of steam- and air-refined bitumens in experimental animals. /Bitumens/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V35 71 (1985)].
>
> There is limited evidence for the carcinogenicity of undiluted steam-refined bitumens and for cracking-residue bitumens in experimental animals. /Bitumens/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V35 71 (1985)].
>
> There is inadequate evidence for the carcinogenicity of undiluted air-refined bitumens in experimental animals. /Bitumens/ [IARC. Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man. Geneva: World Health Organization, International Agency for Research on Cancer,1972-PRESENT. (Multivolume work).,p. V35 71 (1985)].

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

There is some evidence of mutagenic effects and DNA damage in animals due to asphalt exposure [609]. Asphalt may cause irreversible yet not life threatening toxic reproductive effects to humans [369].

See also: PAHs as a group entry.

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

Asphalt is often a residue from petroleum refining, and consists primarily of PNA (polynuclear aromatic hydrocarbons) and alkylated PNA, as well as highly polar compounds [497]. PNA is usually a synonym of PAH (see PAHs as a group entry). Asphalt contains paraffinic and aromatic hydrocarbons and heterocyclic compounds containing carbon, sulfur, nitrogen, and oxygen [363].

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

Asphalt used on roads and in water pipes is supposedly used in a manner which binds most of the harmful compounds together as part of a tough, cement-like solid. In layman's terms, the good news is that the many harmful compounds typically found in asphalt are presumably bound in place fairly tightly in many roadway and other controlled uses. The bad news is that some of these harmful compounds may not always be as firmly and as universally "locked in place" as some have assumed (Roy Irwin, National Park Service, personal communication, 1996).

Asphalt and other solidification and stabilization products are designed to lower contaminant leaching rates [478]. However, the amount the leaching is lowered depends on the physical and chemical characteristics of the particular environment.

Chemical and physical insults as diverse as cattle urine and molten lava have been known to breakdown asphalt roadways. Greases can soften asphalt, while xylene and toluene can diffuse through it [478]. In spite of such potential complications, various formulations of asphalt and binders have been used to cover or encapsulate hazardous waste. Under certain conditions, solvents and road salts can accelerate breakdown of asphalt. However, at present (1989), there are no established standards and protocols for testing and predicting the performance of solidification and stabilization (S/S) products such as asphalt for treating non-radioactive hazardous wastes [478].

Road dust and other erosion fractions originating from slowly wearing-away asphalt roadways are considered one potential source of PAHs in the sediments of urban rivers and bays, although the amount of PAHs coming from this source versus other sources would be difficult to assess. Asphalt wear products were suggested to be responsible for some of the petroleum in urban runoff as well as for some of the PAHs found in the sediments of some urban lakes [750]. The fraction of hydrocarbons contributed from asphalt should decline as the pavement ages. Asphalt can also contribute to hydrocarbon loads by physical abrasion [750].

Asphalt generally contains some of the heaviest and least volatile fractions of petroleum distillates. In the aquatic environment, asphalt will sink to bottom as a dark tarry substance [368].

The CHRIS manual states that the food chain concentration potential of asphalt is unknown [367]. However, it is known that a few of the PAHs known to be found in asphalt have a moderate to low bioaccumulation potential (see PAHs entry).

Petroleum distillates in order of decreasing volatility include [366]:

1. Petroleum ether or benzine
2. Gasoline
3. Naphtha
4. Mineral spirits
5. Kerosene
6. Fuel oil
7. Lubricating oils
8. Paraffin wax
9. Asphalt or tar.

Since asphalt coating in water pipes have been documented to slowly leach PAH compounds into water [366], asphalt in rivers and other natural waters may also slowly leach harmful compounds into the water.

A controversial topic is "asphalt incorporation" of petroleum contaminated soils. Asphalt incorporation at petroleum contaminated sites involves mixing the contaminated soils with asphalt as a whole or partial substitute for the customary aggregate. Subsequently the asphalt is either used in road construction or is broken up and landfilled, or crushed and used for road base. Low molecular weight hydrocarbons are volatilized and pyrolyzed; higher molecular weight hydrocarbons are incorporated into the asphalt [661].

Synonyms/Substance Identification:

Road Oil [560]
Slow Curing Asphalt [560]
Petroleum Asphalt [367, 560, 609]
Liquid Asphalt [560]

Asphaltic bitumen [367, 609]
Bitumen [367, 609]
Asphalt cements [367]
Asphaltum [609]
Judean pitch [609]
Mineral pitch [609]
Petroleum bitumen [609]
Petroleum pitch [609]
Petroleum refining residues, asphalts [609]
Trinidad pitch [609]
Caswell No. 062 [609]
Caswell No. 106 [609]
EPA Pesticide Chemical Code 022001 [609]
EPA Pesticide Chemical Code 022002 [609]
Bituminous materials, asphalt [609]
Mineral rubber (VAN) [609]

Associated Chemicals or Topics (Includes Transformation Products):

See also individual entries:

Oil Spills
Petroleum, General
PAHs as a group
Individual PAH entries

Site Assessment-Related Information Provided by Shineldecker (Potential Site-Specific Contaminants that May be Associated with a Property Based on Current or Historical Use of the Property) [490]:

General Types of Associated Materials:

- Petroleum hydrocarbons
- Solvents
- Tar

Raw Materials, Intermediate Products, Final Products, and Waste Products Generated During Manufacture and Use:

- Copper
- Creosote
- Dichloroethane
- Ethylenediamine
- Phenols
- Polynuclear aromatic hydrocarbons

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

W.Low (Water Concentrations Considered Low):

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

W.High (Water Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

W.Typical (Water Concentrations Considered Typical):

Experiments were conducted to find out whether the use of petroleum-asphalt seal coating in ductile-iron pipe would contribute significant concn of polynuclear aromatic hydrocarbons (PAH) in drinking water distribution systems [609]. The results of the analyses were compared with the WHO recommendation for maximum allowable concn of PAH in drinking water of 200 ng/l. The highest concn found in 3 experiments was 5 ng/l [609]. [Miller HC et al; AM Water Works Assoc J 74 (3): 151-6 (1982)].

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):

W.Plants (Water Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

W.Invertebrates (Water Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

W.Fish (Water Concentrations vs. Fish):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

Finished waters from various treatment sites are transported to consumers through a variety of pipelines. PAHs (polynuclear aromatic hydrocarbons) leach from the tar or asphalt linings of these pipes, resulting in increased concentrations of these compounds in water reaching the consumers. Cement-lined pipes produce lower PAH concentrations, possibly because PAHs are adsorbed from water [366]. Water uses threatened: potable supply, fisheries, industrial, irrigation [368].

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

Sed.Low (Sediment Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.High (Sediment Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Typical (Sediment Concentrations Considered Typical):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Plants (Sediment Concentrations vs. Plants):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Invertebrates (Sediment Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Fish (Sediment Concentrations vs. Fish):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Sed.Human (Sediment Concentrations vs. Human):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

Polycyclic aromatic hydrocarbons (PAH) in sediment cores from Lake Lucerne, Lake Zurich and Greifensee, Switzerland, and Lake Washington, northwest USA, were isolated, identified and quantified by glass capillary gas chromatography and gas chromatography/mass spectrometry [609]. A comparison of PAH distributions in the same sediments and in possible source materials shows that urban runoff of street dust may be the most important PAH input to these lacustrine sediments [609]. A significant contribution to the PAH content of street dust comes from material associated with asphalt [609]. [Wakeham SG et al; Geochim Cosmochim Acta 44 (3): 403-14 (1980)].

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

Soil.Low (Soil Concentrations Considered Low):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Soil.High (Soil Concentrations Considered High):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Soil.Typical (Soil Concentrations Considered Typical)

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Soil.Plants (Soil Concentrations vs. Plants):

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Soil.Invertebrates (Soil Concentrations vs. Invertebrates):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Soil.Human (Soil Concentrations vs. Human):

No information found on this complex and variable mixture. See Chem.Detail section for chemicals found in this product, then look up information on each hazardous compound. Some individual compounds found in petroleum products have low-concentration human health benchmarks for soil (see individual entries in individual compound).

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

A controversial topic is "asphalt incorporation" of petroleum contaminated soils. Asphalt incorporation at petroleum contaminated sites involves mixing the contaminated soils with asphalt as a whole or partial substitute for the customary aggregate. Subsequently the asphalt is either used in road construction or is broken up and landfilled, or crushed and used for road base. Low molecular weight hydrocarbons are volatilized and pyrolyzed; higher molecular weight hydrocarbons are incorporated into the asphalt [661]. Studies that discuss the advantages and disadvantages of asphalt incorporation are listed below:

1) Support for asphalt incorporation methodologies:

   Research sponsored by the EPA, the Electrical Research Institute, and several state agencies has suggested that asphalt incorporation may be useful for treating petroleum contaminated soils and other wastes. However, the most often cited reservation about this technology is the potential for PAH releases and hydrocarbon air emissions. In most cases, these studies were based on the use of hot batching technologies (see also Forms section) [749].

While cold mix technologies produces a lower grade pavement, these pavements may be suitable for light duty use. The asphalt grade employed in this technology is characterized by a low PAH content and, in the case of slow curing blends, are relatively nonvolatile. Hydrocarbon emissions are also reduced because the mixing occurs at ambient temperatures avoiding the potential emissions from fuel combustion and volatilization of the lighter asphalt fractions. For this reason, cold mix asphalt incorporation is not subject to permitting by the South Coast Air Quality Management District in California [749].

As part of a California feasibility study conducted in the spring of 1989 to determine whether sandy soils contaminated with residual fuel oil could be stabilized with an asphalt binder and used as a paving mixture, biossay testing determined that [749]:

> The asphalt pavement produced from fuel oil contaminated sands represented no greater environmental risk that pavement produced from clean sands.
>
> Neither the control or experimental asphalt pavement would be classified as a hazardous waste pursuant to existing California regulation.

The control sample yielded 78.2 mg of extractable hydrocarbon per gram of sample. Four organics (2,6-Dimethylnaphthalene; 2,3,5-Trimethylnaphthalene; Phenanthrene; and Benzo(a)anthracene) were just over their limit of detection (0.5 ug/kg). The experimental sample yielded 80.6 mg of extractable hydrocarbon per gram of sample. The same four organics detected in the control were found in the experimental sample. In each case, the concentration of the four organics was less in the experimental than in the control. This suggest that the source of PAHs is from the asphalt and less from the fuel oil. All other volatile and semivolatile organic compounds were below their respective detection limits [749].

The study results indicate that sandy soils contaminated with residual fuel oil can be successfully stabilized with liquid asphalt, and the resultant pavement does not pose a significant environmental risk. Study results indicate that both experimental and control asphalt pavements would not be classified as hazardous under current California hazardous waste testing protocol.

> NOTES: The authors of this study acknowledge that the PAH content observed in this study may reflect the characteristics of the slow curing liquid asphalt and may not be characteristic of other asphalt grades (see the Forms section above). This technology cannot be universally applied to all petroleum contaminated soils, and is not yet applicable to contaminated clay soils. Stabilizing soils contaminated with residual fuel oil with an asphalt binder has limited application for treating petroleum contaminated soils with high clay fractions and a high capacity for water retention. The applicability of this technology to other petroleum contaminates such as gasoline was not determined by this study [749].

2) Cautions and limitations on asphalt incorporation methodologies:

Very few contaminated soils are actually suited to the manufacture of asphalt for roadway use. Lighter molecular weight hydrocarbons are incompatible with asphalt; they act as solvents and soften and degrade the asphalt. Soils should be incorporated at a rate of less than 5% of the final asphalt product. Clays and sands do not incorporate well. Gravels and conglomerate are suitable [661].

Soils heavily contaminated with volatile hydrocarbons, such as gasoline, are not suitable for this method. Soil parameters which complicate asphalt incorporation include high moisture content and the presence of other contaminants. Other problems that will preclude or limit the use of asphalt incorporation include the following [661]:

A high metal content;

High organic content, which reduces efficiency;

Soil contaminated with waste or used oil;

Large particle size, which limits the surface area and reduces volatilization necessary for combustion;

Large debris such as boulders, concrete or asphalt blocks, roots, branches, etc., which will damage equipment;

Plastic, which will foul the mixing chamber.

Asphalt incorporation is currently (1990) classed as developmental. The basic engineering research to fix the parameters for asphalt incorporation has not been done, at least to the extent of carefully defining the type and mix of contaminants and soils that can be successfully incorporated. Therefore, this method remains largely empirical and dependent on the experience of the facility operator. Even when the experience is there, the method may not meet approval of regulatory agencies [661].

No other information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for

compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Tis.Invertebrates:

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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 as yet. However, there is information available on some of the compounds found in this product (see individual PAH entries in individual compound).

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):

From OHM-TADS [368]:
Toxicity to animals:
Livestock toxicity (ppm): 30

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Tis.Human:

A) Typical Concentrations in Human Food Survey Items:

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Tis.Misc. (Other Tissue Information):

No information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

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

Some of the PAHs in asphalt can accumulate in certain biota such as shellfish, but biomagnification potential is low.

Information from OHM-TADS [368]:

Food chain Potential for accumulation: NEGATIVE
Food chain concentration: NEGATIVE

Interactions:

Asphalt may act as a synergist to pesticides [368].
The PAHs in asphalt interact with sunlight and other things (see PAHs as a group entry in individual compound).

Uses/Sources:

Major Uses [609]:

Making roads, roofs; making tanks watertight [the merck index. 10th ed. Rahway, new jersey: merck co., Inc., 1983. 122].

Paints; adhesive in electrical laminates & hot-melt compositions; diluent in low-grade rubber products; fluid loss control in hydraulic fracturing of oil wells; medium for radioactive waste disposal; pipeline & underground cable coating; rust-preventive hot-dip coatings; base for synthetic turf; water-retaining barrier for sandy soils; supporter of rapid bacterial growth in converting petroleum components to protein [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 102].

Paving material for airfields, road construction-eg, as asphalt mix; construction material for dams, reservoirs & sea defenses, roofs & flooring, for corrosion protection of metals; wrapping & jointing compounds for electrical insulation; sound insulation material-eg, car bodies & machine mounts; coatings for oil & water pipelines; binder for coal briquettes & for recovery of steel wastes; coating for paper; component of electrical batteries, paints; rubber-processing agent.

Asphalt blocks [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 55].

Natural Sources [609]:

Occurs in west indies (chiefly trinidad), venezuela, dead sea, switzerland, etc. [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

Occurrence: California ... Cuba, Canada (Athabasca tar sands). [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 102].

Artificial Sources [609]:

Waste gases from an asphalt plant contained hydrocarbons, tars, hydrogen sulfide, & mercaptans. Anthracene was only polycyclic aromatic cmpd detected in the gases. [Mutko B et al; Ochr Powietrza 8 (5): 134-8 (1974)].

Vapors from asphaltic bitumen can be neglected as factor injurious to plants because of small amt generally released by hot mix asphalt plants. Vegetation damage observed was due to sulfur dioxide, dust and soot. [KRONBERGER W, HALBWACHS G; EUR J FOR PATHOL 5 (5): 267-74 (1975)].

Particle resuspension caused by moving vehicles were determined by solid zinc sulfide tracer particles placed on a road. The fraction of particles resuspended from the road by surface stresses was determined by a tracer mass balance. The downwind airborne tracer exposure & tracer ground deposition were measured at vehicle speeds of 5-50 mile/hr. The fraction resuspended/vehicle pass was from 1x10-5 to 1x10-2 with the greater resuspension corresponding to increased vehicle speeds & driving directly through the deposited tracer. For constant vehicular conditions and no intervening traffic, the fraction of particles initially present were resuspended & markedly with an incr in days after the tracer was placed on the road. [SEHMEL GA; ERDA SYMP SER 38 (ATMOS- SURF EXCH PART GASEOUS POLLUT): 859-82 (1974 & 1976)].

This program was undertaken to develop a quantitative estimate of the emission of volatile organic cmpd (VOC's) from drum-mix asphalt plants. This study was carried out by field sampling of 5 drum-mix plants under a variety of operating conditions.

The sampling method used was EPA Proposed Method 25, modified to filter out particulate emissions which would interfere with the lab determination of VOC concn in the collected samples. The VOC emission factors for drum-mix plants are on the order of 0.1-0.4 lb of VOC (as Carbon) per ton of asphalt concrete produced. The nationwide emission of VOC's from all drum-mix asphalt plants is estimated to be about 20,600 tons/yr.[Beggs TW; Report: 78 pages (1981) EPA-600-2-81-026; Order No PB81-157943].

... Etching grounds /from intaglio printmaking/ contain asphalt in an oil or solvent (asphaltum). [Hart C; Journal of Environmental Health 49 (5): 282-86 (1987)].

Forms/Preparations/Formulations:

Asphalt materials are categorized as asphalt cements or liquid asphalts [749] (reprinted by permission of CRC Press):

> Asphalt cement - is the heaviest fraction of asphalt. Consistency ranges from between solid to semiliquid at room temperature. In general, the heavier fractions of asphalt are characterized by high concentrations of aromatics (both mononuclear and polynuclear rings), nitrogen, sulphur, oxygen, and trace amounts of metals or organo-metallic compounds. Asphalt cements are typically used in hot mix technologies.
>
> Liquid asphalts - are produced from the lighter fractions of the residual asphalt, or by dissolving asphalt cements in solvent or emulsifying asphalt cements in water. These materials are used in cold mix technologies. Types of liquid asphalts include:
>
> > Rapid curing (RC) - are produced by dissolving relatively hard asphalt cements in a kerosene or naphtha solvent. These materials may be expected to contain PAH compounds originating from the heavy asphalt solute and are characterized by a high volatile organic compound (VOC) content due to the solvent carrier.
> >
> > Medium curing (MC) - are produced by dissolving softer asphalt cements in a kerosene type solvent. These material may also contain PAH compounds, but in lower concentration than the RC liquid asphalts, because they are derived from the lighter fractions of asphalt cement. These materials may also contain a high VOC content due to the solvent carrier.
> >
> > Slow curing (SC; or road oil) - may be derived from distillation, being the lightest fraction of the

asphalt, or by fluxing the lightest fraction of the asphalt cements with lighter oils. These materials are most similar to residual fuel oils, which also are derived from the lighter ends of the petroleum distillate. SC liquid asphalts are expected to be composed primarily of chain-type aliphatics rather than aromatic compounds. Trace concentrations of PAHs may be present. The SC liquid asphalts are semivolatile or nonvolatile, and therefore the potential for VOC emissions is not a major concern.

Asphalt emulsions - are produced by using surfactants to emulsify asphalt cements in water. Anionic, cationic and nonpolar asphalt emulsions are available. These material may contain PAHs, depending upon the grade of asphalt cement from which they are derived. Emulsions are relatively nonvolatile [749].

Information from HSDB [609]:

Formulations/Preparations: Each of the following is available in several grades: asphalt cement, rapid-curing liquid asphalt, medium-curing liquid asphalt, slow-curing liquid asphalt (road oil), emulsified asphalt, invented asphalic emulsion, oxidized (air-blown) asphalt. [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5.].

Grade: Solution of residue from distillation in carbon tetrachloride, 99.5% [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 102].

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

Caution: Every individual petroleum product has a unique "fingerprint," or distinct set of constituents most commonly identified by a gas chromatograph analysis. Due to the varying properties of the same general category of a petroleum product (each source and weathering stage of asphalt has a unique gas chromatograph "fingerprint"), careful assessment of the toxicity, specific gravity, and other physical characteristics of each individual oil must be taken into consideration to determine the exact effects of the product on the environment. Therefore, the below comments on asphalt are to be considered as representative, but not absolute values typical of every batch of the product with the same name.

Since PAHs are important hazardous components of this product, risk assessments should include analyses of PAHs and alkyl PAHs utilizing the NOAA protocol expanded scan [828] or other rigorous

GC/MS/SIM methods.

Information from [560] and [609]:

DENSITY (g/mL) [560]:

For temperatures of oil (T) between 0 and 30 C:
Density = 0.97871 - 0.000710 T

NOTE: The densities of crude oils and oil products are dependent on the temperature and degree of weathering. The following density values are at "0% Weathering Volume" - in other words, fresh road oil.

Temp(C)	Density (at 0% Weathering Volume)
25	0.9970 to 1.1964

Density/Specific Gravity [609]:

1.00-1.18 [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

Solubilities [609]:

Insol (sic, actually "relatively insoluble") in water, alc, acids, alkalies; sol in oil turpentine, petroleum, carbon disulfide, chloroform, ether, acetone [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

Among the hazardous polycyclic aromatic hydrocarbons found in asphalt and/or in emissions from asphaltic processing are [366]:

1) Acenapthene

A constituent in asphalt.

2) Anthracene

Associated with coke ovens and asphalt processing and use. In an outlet water spray tower of asphalt hot road mix process. In an outlet of asphalt air blowing process: 220,000 ng/cu m.

3) Benzo(a)anthracene (CAS number 56-55-3)

Emissions from asphalt hot-mixing plant: 5 to 24 ng/cu m; (in high volume particulate matter): avg 11 ng/cu m.

4) Benzo(a)pyrene

In asphalt up to 0.027 wt%.

5) Benzo(e)pyrene (CAS Number 192-97-2)

Concentration of 0.03-52 MG/KG in petroleum asphalts.

6) Benzo(k)fluoranthene

Benzo(k)fluoranthene may be picked up in distribution systems lined with coal tar or asphalt.

7) Fluoranthene (C16-H10, CAS number 206-44-0)

Distribution systems lined with coal tar or asphalt can sometimes contribute measurable amounts of fluoranthene.

Found in leachate samples from petroleum asphalt coatings on ductile-iron pipe.

Leachates from a cement- & asphalt-lined cast-iron pipe were tested using a number of analytical techniques. Fluoranthene (4-6 ng/l) was identified in water that had been in contact with asphalt lining.

Distribution systems with asphalt or coal tar linings can contribute fluoranthene to the tap water. In one extreme case (Portland Oregon) the raw water had 4 ng/l and the distributed water 640 ng/l fluoranthene. Fluoranthene has been found in Nordic tap water <0.58-24 ng/l and detected at >0.1 ug/l in finished water from 5 of 10 utilities in Ohio River Basin.

8) Phenanthrene (CAS number 85-01-8)

An evaluation conducted by/ NIOSH of a coal tar pitch tear-off, and the application of hot asphalt operations; total of 16 personal breathing-zone total dust samples were collected on seven workers. Analyses of the bulk tear-off dust revealed the presence of phenanthrene.

9) Pyrene (The following statements were included under the pyrene heading in the HSDB):

Finished waters from various treatment sites are transported to consumers through a variety of pipelines. PAH's (polynuclear aromatic hydrocarbons) leach from the tar or asphalt linings of these pipes, resulting in increased concentrations of these compounds in water reaching the consumers [366].

NIOSH considers coal tar products carcinogenic and conditions should be made to keep exposures as low as possible. Current NIOSH research indicates that asphalt products are carcinogenic to laboratory animals and, therefore may be more toxic to humans than previously believed.

Additional Physicochemical information from Environment Canada on liquid asphalt (road oil) [560]:

> NOTE: In this section, for properties with more than one value, each value came from its own source; in other words, if Density was measured several times and several different answers were obtained, all of the answers are provided [560]:

INTERFACIAL TENSIONS

NOTE: Interfacial tension is the force of attraction between molecules at the interface of a liquid. These tensions are essential for calculating the spreading rates and the likely extent to which the oil will form oil-in-water and water-in-oil emulsions. The interfacial tensions of crude oils and oil products are dependent on the temperature and degree of weathering. The following tension values are at "0% Weathering Volume" - in other words, fresh road oil.

Air-Oil (mN/M or dynes/cm):

Temp(C)	Air-Oil Tension (at 0% Weathering Volume)
20	25 (estimated)

Oil-Water (mN/M or dynes/cm):

Temp(C)	Oil-Seawater Tension (at 0% Weathering Volume)
20	50 (estimated)

FIRE AND REACTIVITY

Flash Point (C):
148.9 to 287.8

SENSATION

Colour
Dark brown to black

OTHER

Reid method Vapor Pressure (kPa):

Temp(C)	Pressure
37.8	0.689 (estimated)

Information from HSDB [609]:

Color/Form:

The "syriac" asphalt (from dead sea) forms deep black, shining, brittle masses of conchoidal fracture; pitch-like luster [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

Dark-brown to black cementitious material, solid or semisolid in consistency [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 102].

Softens to viscous liquid above 90 deg C [ITII. Toxic and Hazarous Industrial Chemicals Safety Manual. Tokyo, Japan: The International Technical Information Institute, 1982. 55].

Odor:

Pitch-like odor [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

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

Boiling Point:

Greater than 700 deg F [National Fire Protection Association. Fire Protection Guide on Hazardous Materials. 9th ed. Boston, MA: National Fire Protection Association, 1986.,p. 325M-16].

Viscosity:

Liquid: 93.250 cp @ 220 deg F, 85.889 cp @ 230 deg F, 79.299 cp @ 240 deg C, 73.379 cp @ 250 deg C, 68.049 cp @ 260 deg C, 63.240 cp @ 270 deg C, 58.880 cp @ 280 deg C, 54.930 cp @ 290 deg C, 51.930 cp @ 300 deg C, 48.060 cp @ 310 deg C, 45.080 cp @ 320 deg C, 42.340 cp @ 330 deg C, 39.840 cp @ 340 deg C, 37.540 cp @ 350 deg C, 35.420 cp @ 360 deg C, 33.420 cp @ 370 deg C, 31.670 cp @ 380 deg C, 30.000 cp @ 390 deg C (estimated) [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Other Chemical/Physical Properties:

Burns with bright flame /syriac asphalt (from dead sea)/ [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 122].

Solid softens to viscous liq @ about 200 deg f; penetration value (paving) 40-300 (roofing) 10-40; good electrical resistivity [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 92].

Black, friable solid obtained by blowing air @ high temp through petroleum derived asphalt, with subsequent cooling; penetration value 10-40; softening point 85-121 deg C /asphalt, blown/ [Sax, N.I. and R.J. Lewis, Sr. (eds.). Hawley's Condensed Chemical Dictionary. 11th ed. New York: Van Nostrand Reinhold Co., 1987. 102].

Saturated vapor pressure: 0.018 lb/sq in @ 210 deg F, 0.026 lb/sq in @ 220 deg F, 0.037 lb/sq in @ 230 deg F, 0.053 lb/sq in @ 240 deg C, 0.074 lb/sq in @ 250 deg F, 0.103 lb/sq in @ 260 deg F, 0.142 lb/sq in @ 270 deg F, 0.193 lb/sq in @ 280 deg F, 0.262 lb/sq in @ 290 deg F, 0.352 lb/sq in @ 300 deg F, 0.470 lb/sq in @ 310 deg F, 0.622 lb/sq in @ 320 deg F, 0.817 lb/sq in @ 330 deg F, 1.067 lb/sq in @ 340 deg F, 1.384 lb/sq in @ 350 deg F, 1.783 lb/sq in @ 360 deg F, 2.284 lb/sq in @ 370 deg F, 2.909 lb/sq in @ 380 deg F (estimated) [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Consists of saturated cmpd (naphthenic or cycloparaffinic), aromatic cmpd (single ring mainly structures with long side chains & condensed ring systems avg 3 rings with shorter side chains & dimers of these molecules connected by saturated rings or chains), & asphaltenes (high mol wt, highly condensed ring cmpd in range of 2000 & upward) [Gosselin, R.E., R.P. Smith, H.C. Hodge. Clinical Toxicology of Commercial Products. 5th ed. Baltimore: Williams and Wilkins, 1984.,p. II-158].

Liquid water interfacial tension: 70 dynes/cm = 0.07 N/m @ 77 deg C [U.S. Coast Guard, Department of Transportation. CHRIS - Hazardous Chemical Data. Volume II. Washington, D.C.: U.S. Government Printing Office, 1984-5].

Thermal asphalts (products of a cracking process which make them differ from other asphalts) have high specific gravity, low viscosity, & high temperature susceptibility and they contain cokelike bodies (carbenes) [Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed., Volumes 1-26. New York, NY: John Wiley and Sons, 1978-1984.,p. V3 304].

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

No detailed information found; see Chem.Detail section for compounds in this product, then see individual compound entries for summaries of information on individual components of this mixture.

Laboratory and/or Field Analyses:

The relative proportions of hazardous compound constituents present in petroleum-based oil contamination is typically quite variable. The lab analyses most appropriate for measuring different types of oil contamination depend upon the type of oil involved and the reason for measuring the contamination. The farther one progresses from lighter towards heavier oils (the general progression from light towards heavy is the following: Diesel, No. 2 Fuel Oil, Light Crudes, Medium Crude Oils, Heavy Crudes, No. 6 Fuel Oil, etc.) the greater the percentage of PAHs and other semi-volatiles (many of which are not so immediately toxic as the volatiles but which can result in long term/chronic impacts). These heavier oils thus need to be analyzed for the semi volatile compounds which typically pose the greatest long term risk, PAHs and alkylated PAHs.

Asphalt contains paraffinic and aromatic hydrocarbons and heterocyclic compounds containing carbon, sulfur, nitrogen, and oxygen [363]. Asphalt is often a residue from petroleum refining, and consists primarily of PNA (polynuclear aromatic hydrocarbons) and alkylated PNA, as well as highly polar compounds [497]. For lab methods for PAHs, see also: PAHs as a group entry.

Recent (1991) studies have indicated that EPA approved methods used for oil spill assessments (including total petroleum hydrocarbons method 418.1, semivolatile priority pollutant organics methods 625 and 8270, and volatile organic priority pollutant methods 602, 1624, and 8240) are all inadequate for generating scientifically defensible information for Natural Resource Damage Assessments [468]. These general organic chemical methods are deficient in chemical selectivity (types of constituents analyzed) and sensitivity (detection limits); the deficiencies in these two areas lead to an inability to interpret the environmental significance of the data in a scientifically defensible manner [468]. A great deal of uncertainty remains in the use of dose-response relationships based on crude oil as a whole mixture [734].

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Crude oil consists of thousands of individual compounds. The major groups include the saturated alkanes, alkenes, benzene, alkylated and aryl benzenes, polynuclear aromatics, heterocyclic aromatics, and hetro-atom substituted alkanes, alkenes and aromatics [783]. Some of the more toxic compound classes are: low molecular weight aromatics (such as benzene, toluene, xylene, other monocyclic aromatics), and polynuclear aromatic hydrocarbons (PAH) [713, 745]. Due to the presence of light aromatics and PAHs in fuel crude oil, we recommend the following decision tree:

As mentioned in the introductory sections of this entry, the good news is that the many harmful compounds such as PAHs typically found in asphalt are presumably bound in place fairly tightly in many roadway and other controlled uses. The bad news is that some of these harmful compounds may not always be as firmly and as universally "locked in place" as some have assumed (Roy Irwin, National Park Service, personal communication, 1996).

Asphalt is heavier and more solidified than "heavy oils." Nevertheless, in deciding which lab methods to use for asphalt, it is still instructive to consider the following characteristics of heavy oil products [741]:

Heavy Oils (Heavy Crude Oils, No. 6 fuel, Bunker C) [741]:

-Heavy oils with little or no evaporation or dissolution (also true of asphalt)
-Water-soluble fraction likely to be <10 ppm (also true of asphalt)
-Heavy contamination of intertidal areas likely (not as true of asphalt)
-Severe impacts to waterfowl and fur-bearing mammals (coating and ingestion) (not as true of asphalt)
-Long-term contamination of sediments possible (true of asphalt mostly just as solid chunks)
-Weathers very slowly (even more true of asphalt)
-Dispersion seldom effective (true)
-Shoreline cleanup difficult under all conditions (not as true of asphalt)

The following decision tree (dichotomous key) for selection of lab methods for measuring contamination from midrange to heavy crude oils, number 6 and heavier fuel oils, bunker C and all other oils considered to be heavy) has some bearing on asphalt decisions since asphalt is a heavy product (in using this key, understand that asphalt is heavier and more immobile than the heavy crudes and other heavy oils discussed herein):

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. Note: although heavy products have a lower percentage of BTEX and other relatively soluble compounds which typically threaten drinking water, ground water, or water column organisms, some heavy oils including crudes do contain some of these water soluble compounds, so they cannot be ignored.......................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. Another option for fresh oil: in cases where an inexpensive screening scan is desired, consider using an HPLC/Fluorescence scan method for sediment or bile metabolite samples. Such scans are available from laboratories at Texas A. and M., Arthur D. Little, and the NOAA lab in Seattle. This scan is not much more expensive, and less prone to false negatives and various other problems than some of the more common screening methods (TPH-EPA 418.1 and Oil and Grease). Screening measures the total fluorescence of oil components while GC/MS measures individual aromatic compounds [521]. Thus, HPLC/fluorescence screening allowed detecting lower concentrations of petroleum-related aromatic compounds in samples contaminated by Prudhoe Bay Crude Oil than did analysis by GC/MS [521].

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

4. Analyze for Benzene, Toluene, Ethyl Benzene, and Toluene (BTEX) compounds in water as part of a broader scan of volatiles using EPA GC/MS method 8240. The standard EPA GC/MS method 8240 protocol will be sufficient for some applications, but the standard EPA method 8240 (and especially the less rigorous EPA BTEX methods such as method 8020 for soil and method 602 for water) are all inadequate for generating scientifically defensible information for Natural Resource

Damage Assessments [468]. The standard EPA methods are also inadequate for risk assessment purposes. Thus, when collecting information for possible use in a Natural Resource Damage Assessment or risk assessment, it is best to ask the lab to analyze for BTEX compounds and other volatile oil compounds using a modified EPA GC/MS method 8240 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 8240), and PAHs (NOAA protocol expanded scan***). The magnitude of any residual soil contamination will provide insight about the likelihood of recontamination of groundwater resources through equilibria partitioning mechanisms moving contamination from soil to water.

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

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

6. Perform the NOAA protocol expanded scan*** for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs. If there is any reason to suspect fresh* or continuing contamination of soils or sediments with lighter volatile compounds, also perform EPA GC/MS method 8240 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]. The HPLC/fluorescence scan looks for the presence of metabolites of PAHs: naphthalene, phenanthrene, and benzo[a]pyrene. The technique does not identify or quantify actual PAH compounds, but subsequent gas chromatography analyses can be done to confirm the initial findings. Even the semi-quantitative Total Scanning Fluorescence (TSF) done inexpensively by labs such as GERG are a better measure of PAH contamination than GC/FID, which measures less persistent and less hazardous aliphatics. 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 8240 and the NOAA protocol expanded scan*** for PAHs could be performed to see if Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX), naphthalene, and other potentially toxic compounds are above known acute toxicity benchmark concentrations. Zooplankton populations impacted by oil usually recover fairly quickly unless they are impacted in very confined** or shallow environments [835] and the above BTEX and PAH water methods are often recommended rather than direct analyses of zooplankton tissues.

11a. The concern is for benthic invertebrates: analyze invertebrate whole-body tissue samples and surrounding sediment samples for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs using the NOAA protocol expanded scan***. If the spill is fresh* or the source continuous, risk assessment needs may also require that the sediments which form the habitat for benthic invertebrates be analyzed for Benzene, Toluene, Ethyl Benzene, and Xylene (BTEX) and other volatile compounds using EPA GC/MS method 8240 or modified EPA method 8240 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 8240 or modified EPA method 8240 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 expanded scan protocols for polycyclic aromatic hydrocarbons (PAHs) and alkyl PAHs have been published by NOAA [828].

End of key.

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

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

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

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

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

A few notes related to screening scans versus asphalt:

1) Although EPA method 418.1: Petroleum Hydrocarbons expressed as Total Petroleum Hydrocarbons (TPH), is recommended by many State agencies, some consulting firms, and some laboratories for certain regulatory and screening applications (often leaking underground storage tanks), this method is not well suited to asphalt contamination or to the more persistent hazardous constituents in oil. Low values tend to give the mistaken impression that a site is clean when it really isn't (prone to false negatives). This method is said to readily detects the heavy petroleum products such as motor oil, tar, and asphalt [497] (but misses many hazardous heavy PAHs.

2) EPA Method 8015 (for Non-halogenated Volatile Organics): not appropriate for asphalt

> Method 8015 is a gas chromatographic method that is excellent for the analysis of volatile and semivolatile compounds. It can be used to characterize light and midrange petroleum distillates such as gasoline, diesel, fuel oil, and kerosene. This method can be used to obtain some gross fingerprint information for differentiation between petroleum products, as well as detailed information that can be used to differentiate between different batches of the same product. The major limitation of Method 8015 is its inability to detect nonvolatile compounds. Residual petroleum products such as asphalt and tar will not be seen using EPA Method 8015 [497].

Asphalt Summary from Calabrese [497]:

> The Thin-Layer Chromatography (TLC) pattern, using hexane as the eluting solvent, will resemble an elongated teardrop stretching from Rf 0.0 to Rf 0.5 and will be visible under both short and long wave UV light. At high concentrations, this teardrop will extend from Rf 0.0 to 0.8 and at low concentrations from 0.0 to 0.2. This band is visible with iodine staining. A band at Rf 0.9 will sometimes be seen which consists of saturated hydrocarbons that are left in the product.

See also: PAHs as a group entry.