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Critical Review of Draft EPA Guidance on Assessment and Control of Bioconcentratable Contaminants in Surface Waters

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Critical Review of Draft EPA Guidance on Assessment and Control of Bioconcentratable Contaminants in Surface Waters

Health and Environmental Sciences Department

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ABSTRACT

In 1991, EPA proposed guidance, "Assessment of Bioconcentratable Contaminants in Surface Water," for the identification of potential bioconcentratable compounds which are not currently regulated under the NPDES program. This API technical review of EPA guidance is intended to provide the industry with a better understanding of the proposed manner to determine bioconcentratable contaminants as well as a subject matter review of bioaccumulation in aquatic organisms. The EPA draft guidance does not provide a sound basis for identifying and predicting bioaccumulation of nonpolar organic chemicals of the types found in petroleum industry effluents. Nearly all potentially bioconcentratable organic chemicals (log K_{ow}>3.5) in oil industry effluents are saturated and aromatic hydrocarbons. If present in the effluent at a concentration higher than 100 ng/L, they will not pass the initial screening test if initial dilution in the receiving waters is less than 100-fold. The difficult analytical methods proposed for identifying bioconcentratable chemicals in effluents, tissues of aquatic animals, and sediments may produce analytical artifacts in samples containing hydrocarbons. Further, the methods are unlikely to positively identify additional chemicals, not already known to be present in the effluent, for which physical/chemical data required to predict bioconcentration and toxicity, are available.

Bioconcentration models relating the bioconcentration factor (BCF) to log K_{ow} tend to greatly overestimate concentrations of hydrocarbons in tissues of aquatic organisms. Hydrocarbons are absorbed from the food inefficiently and are metabolized and excreted rapidly by most aquatic animals. Therefore, they do not biomagnify in aquatic food chains. Concentrations of bioconcentratable chemicals in tissues of free-swimming aquatic animals or in sediments of depositional areas near an outfall cannot be used to identify bioconcentratable chemicals in a particular effluent because of uncertainties about the sources of the chemicals, particularly hydrocarbons.

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EXECUTIVE SUMMARY

As part of its mission to develop an integrated, multifaceted approach to protect aquatic life, wildlife, and human health from toxic chemicals in surface waters, the U.S. Environmental Protection Agency has developed draft guidance on the "Assessment of Bioconcentratable Contaminants in Surface Waters" (EPA, 1991b). The draft bioconcentration guidance (DBG) provides a methodology for assessing the identity and concentrations in effluents of nonpolar organic chemicals with a strong potential to bioaccumulate in aquatic food chains. Two alternative methods are described: the effluent option; and the tissue residue option. Procedures for assessing sediments are also included.

In the tissue residue option, tissues of aquatic organisms in the receiving water are analyzed for residues of bioconcentratable organic chemicals. If the concentrations of any chemicals in tissues are above permissible levels, the sources of the chemicals are traced by target analysis and the chemicals are limited in the point sources. In the effluent option, representative samples of the effluent are analyzed for chemicals that bioconcentrate. If any bioconcentratable chemicals are detected in the effluent at concentrations above a threshold value, a determination (based on a bioconcentration model) is made as to whether bioaccumulation by fish and shellfish in the receiving waters could occur at levels that might pose a health hazard to human consumers of the fishery products.

This report presents a critical review of methods proposed in the DBG with particular emphasis on their suitability for assessing bioconcentratable chemicals in National Pollution Discharge Elimination System (NPDES) permitted effluents from oil refineries, petroleum marketing terminals, and crude oil production activities. The major focus of this review was on the effluent option.

As defined in the DBG, bioconcentratable chemicals are nonpolar (unionizable) organic chemicals with a log octanol/water partition coefficient (log K_{ow}) of 3.5 or higher and a concentration in the final effluent of 100 ng/L (parts per trillion) or higher. The most abundant potentially bioconcentratable chemicals in NPDES-permitted oil industry effluents are saturated and aromatic hydrocarbons and related heterocyclic compounds. Halogenated organics, phthalate esters, pesticides, and other potentially bioconcentratable compounds of

major environmental concern usually are absent, present as trace contaminants, or are analytical artifacts. Therefore, any assessment of bioconcentratable chemicals in oil industry effluents should focus on hydrocarbons.

The guidance proposed by the EPA for identifying and quantifying bioconcentratable organic chemicals in NPDES-permitted effluents does not provide a sound basis for predicting bioaccumulation of toxic chemicals in the edible tissues of fish and shellfish. A great many conservative assumptions are made in deriving screening parameters for each stage of the assessment. The net result is an extremely conservative, overprotective, estimate of potential bioaccumulation and tissue residue concentrations in fishery products consumed by man. Because of the multiple conservative assumptions, tissue residues are likely to be overestimated by as much as two to three orders of magnitude. This over-estimation is particularly true for hydrocarbons, which are the potentially bioconcentratable chemicals most frequently encountered in oil industry effluents. These chemicals are absorbed poorly from the gut of aquatic animals and man and are metabolized and excreted rapidly. Hydrocarbons do not biomagnify in aquatic food webs.

In the effluent option, effluent samples are collected from point source discharges and analyzed by a high pressure liquid chromatography (HPLC) method that produces three fractions of nonpolar organic chemicals with different ranges of log K_{ow} between 3.5 and 8.2. Each fraction is analyzed by gas chromatography/mass spectrometry (GC/MS) to identify and quantify individual bioconcentratable chemicals. Various screening steps are then performed for each chemical identified to determine if it poses a hazard and may require subsequent regulatory action. The initial screen identifies bioconcentratable chemicals of concern based on log K_{ow}, concentration in the whole effluent, and initial dilution in the mixing zone of the outfall. Chemicals that do not pass the first screen are evaluated by regression models that relate log K_{ow} to bioconcentration factor (BCF). Predicted concentrations of chemicals in tissues of aquatic animals are evaluated with respect to the risk of harm to human consumers of fishery products from the vicinity of the waste water outfall.

Although the effluent option provides a means for identifying and quantifying potentially bioconcentratable chemicals in oil industry effluents, the extraction, cleanup, and analytical methods may degrade many hydrocarbon analytes and produce a variety of artifacts. Reverse

searches of mass spectral libraries probably will produce tentative identifications for many chemicals for which no physical/chemical or toxicological data are available. It will not be possible to determine if these chemicals pose a health hazard to humans at the concentrations at which they occur in the effluent.

The complex screening process is so conservative that nearly all chemicals in fraction 1 and all chemicals in fractions 2 and 3 will not pass the initial screen and will require additional assessment if their individual concentrations in the full-strength effluent are 100 ng/L or higher and the allowable initial dilution of the effluent in the mixing zone of the discharge is 100-fold or less. The screening analysis is time-consuming and expensive. Because it contributes little to identifying chemicals that should or should not be listed in Report 2, it should be eliminated.

Concentration decision points for water, tissues, and sediments are set unrealistically low, particularly for saturated and polycyclic aromatic hydrocarbons (PAHs). Natural background concentrations of hydrocarbons of the types found in oil industry effluents are likely to be similar to or higher than the decision point concentrations, particularly in sediments (5 μg/kg dry wt.) and tissues (5 μg/kg wet wt.). The decision point concentrations are very near the detection limits of available analytical methods for most chemicals of concern in oil industry effluents. This will result in a high variance in measured concentrations near the decision points and lack of confidence in the value of the decision point concentrations.

However, the main weakness of the effluent option, as discussed in greater detail in the following sections of this review, is the uncertainties about many of the assumptions used to mathematically link (model) the relationship between concentrations of a bioconcentratable chemical in an effluent and concentrations of that chemical in the edible tissues of an animal living in the receiving water environment. The models assume that there is an equilibrium among concentrations of bioconcentratable chemicals in the receiving water, sediments, food organisms, and aquatic animals consumed by man in the receiving water environment. This is almost never the case. Concentrations in a receiving water environment of chemicals derived from a point-source effluent are continuously varying on both temporal and spatial scales. Animals, particularly motile ones, are nearly always actually exposed to time-averaged concentrations of the chemicals of concern that are much lower than the concentrations

predicted by conventional dilution models. The kinetics of partitioning of nonpolar organic chemicals among water, sediments, food organisms, and consumer organisms is poorly understood, particularly under conditions of highly variable concentrations in solution in the aqueous phase. Wide differences in the ability of food chain organisms to metabolize and excrete hydrocarbons (Stegeman, 1981; Stegeman and Kloepper-Sams, 1987), the most abundant bioconcentratable compounds in oil industry effluents, further complicates prediction of net bioaccumulation in aquatic animals consumed by man.

The technical basis for calculating values for BCFs using a log K_{ow}/log BCF model is very weak. Regression equations between log K_{ow} and log BCF, based on data primarily for chlorinated hydrocarbons, do not produce good estimates for BCFs for saturated and aromatic hydrocarbons of the types found in oil industry effluents and for other nonpolar organic chemicals that are rapidly metabolized in tissues of aquatic animals and excreted. Because most hydrocarbons are absorbed poorly from food and metabolized/excreted rapidly by active enzymatic processes, estimated food chain multipliers (FMs) based on food chain behavior of non-metabolizable chemicals overestimates bioaccumulation of petroleum hydrocarbons and possible biomagnification. Metabolic degradation and excretion of hydrocarbons may substantially increase the elimination rate constants for the chemicals from tissues, decreasing the equilibrium BCF. Hydrocarbons do not biomagnify in aquatic and marine food webs.

The tissue residue option is not appropriate for regulation of potentially bioconcentratable chemicals in oil industry effluents because is not possible, in most cases, to identify the source(s) of chemical residues in the tissues of feral animals, particularly motile species such as fish and most crustaceans, in the receiving water environment.

Analysis of sediments in depositional areas near an outfall may not provide much useful information about the chemical content of ongoing discharges. Sediments represent a long-term reservoir for nonpolar chemicals. It usually is difficult or impossible to determine the source(s) of chemicals in sediments of depositional areas remote from point sources. In addition, most fine-grained sediments contain concentrations of natural (biogenic) and anthropogenic hydrocarbons well above the sediment concentration decision point (5 μg/kg wet wt). The co-occurrence of a bioconcentratable chemical in sediments and in animals living in, or in close association with, the sediments does not constitute proof that the animals

accumulated the chemical from the sediments. Both the sediments and the animals may have accumulated the chemical from the overlying water column. Current models for predicting bioaccumulation of nonpolar organic chemicals from sediments by demersal and benthic animals have not been adequately validated, to date, to be used for regulation.

The problem of identifying the source or sources of tissue residues of bioconcentratable chemicals in aquatic animals in a receiving water environment is particularly great when effluents from oil industry operations are involved. As discussed in Section 2 of this review, the most frequently encountered and most abundant potentially bioconcentratable chemicals in oil industry effluents are saturated and aromatic hydrocarbons and related hetero compounds. These chemicals have a wide variety of natural and anthropogenic sources in aquatic environments, only a few of which are related to oil industry operations (Neff, 1979). Therefore, it will not be possible, in most cases, to definitively attribute hydrocarbon residues in tissues of aquatic organisms to a particular oil industry effluent.

The draft guidance, if applied in its present form to regulation of NPDES-permitted effluents from oil industry operations would be unnecessarily stringent. These initial results indicate that substantially more field validation is required of the applicability of the draft bioconcentration assessment guidance to oil industry effluents that contain almost exclusively hydrocarbons. Results of validation studies are essential for a complete evaluation of the soundness of the assumptions and simplifications incorporated in the model linking chemicals in effluents to chemical residues in tissues of aquatic animals. In particular, validation studies are required for organic chemicals that may have an anomalous environmental behavior, such as alkanes and PAHs. These chemicals are natural biogenic materials that are subject to a variety of degradative processes in the environment not considered in the models. The DBG should not be accepted as final and used for regulatory purposes until such time as the results of the field studies have been reported and thoroughly evaluated and validated by independent reviewers. Industry should not be required to eliminate discharges or to develop new costly technologies to remove traces of organic chemicals (mostly hydrocarbons) that, because of their behavior in aquatic food webs, do not pose a health hazard to human consumers of fishery products.

Section 1
INTRODUCTION

The U.S. Environmental Protection Agency (EPA) is developing an integrated, multifaceted approach to protect aquatic life, wildlife, and human health from toxic chemicals in surface waters (EPA, 1991a). The integrated approach will be based on whole effluent, chemical-specific, and biological assessments. Implementation of this draft guidance is intended to provide early information on unregulated compounds discharged to surface waters that may bioconcentrate.

The whole effluent approach to toxics control uses acute and chronic toxicity tests to measure the toxicity of waste waters. The chemical-specific approach to toxics control uses specific limits on concentrations of specific chemicals in National Pollution Discharge Elimination System (NPDES) permits to control the discharge of toxic chemicals. Permit limits are derived from numeric water quality criteria adopted in the State's water quality standards. State standards also include chemical-specific limits for protection of human health with respect to consumption of drinking water and fishery products. Biological assessments, still in the early stages of development, are intended to monitor the ecological integrity of biological communities in the receiving water environment. Ecological integrity is measured as the structure and function of biological communities.

The most important pathways for exposure of humans to toxic chemicals in surface waters are through drinking water and consumption of fish and shellfish. Direct exposure to toxic chemicals in surface waters through bathing and swimming rarely is sufficient to pose a health hazard (National Research Council, 1990). In order to pose a significant human health hazard, chemicals in surface waters must be able to sorb, or pass readily through biological membranes by active or passive means. Not all bioavailable chemicals accumulate in the tissues of the organism in contact with the water; some are lost from the organism by active or passive means as rapidly as they enter the tissues. The food route of exposure to toxic chemicals is important only for those chemicals that are accumulated from the water and are retained in the tissues of fish and shellfish species consumed by humans, and that can be absorbed in significant amounts through the human gut.

As part of the chemical-specific approach to toxics control, EPA (1991b) has developed draft guidance on the "Assessment and Control of Bioconcentratable Contaminants in Surface Waters (March 1991)." This document, referred to subsequently as the DBG (draft bioconcentration guidance), provides guidance for identifying and monitoring nonpolar organic chemicals in effluents that have the greatest potential to bioaccumulate in aquatic food chains leading to humans. The major goal of bioconcentration assessment is to protect humans from consumption of toxic quantities of contaminated fish and shellfish products.

The DBG describes:

- Analytical chemical procedures to identify and quantify bioconcentratable pollutants in environmental samples (water, sediments, tissues of aquatic animals),
- Methods for deriving criteria for aquatic organisms and receiving waters, and
- Approaches for the control of these pollutants from point sources.

EPA has not yet developed guidelines to be used by NPDES-permitting authorities to identify point dischargers or to set priorities for identifying dischargers that will be required to perform an assessment for bioconcentratable chemicals in NPDES-permitted effluents. EPA has asked for public comment on selection of point-source dischargers for assessment. The final guidance document will provide recommendations for the selection process.

The DBG describes two approaches for assessing bioconcentratable contaminants in effluents and receiving waters: 1) the tissue residue option, and 2) the effluent option. It also includes procedures for assessing sediments. In the tissue residue option, tissues of aquatic organisms in the receiving water are analyzed for residues of bioconcentratable organic chemicals. If the concentrations of any chemicals in tissues are above permissible levels, the sources of the chemicals are traced by target analysis and the chemicals are limited in the point sources. In the effluent option, representative samples of the effluent are analyzed for chemicals that bioconcentrate. If any bioconcentratable chemicals are detected in the effluent at concentrations above a threshold value, a determination (based on a bioconcentration model) is made as to whether bioaccumulation by fish and shellfish in the receiving waters could occur at levels that might pose a health hazard to human consumers of the fishery products.

The objective of this review is to evaluate the proposed methods and underlying assumptions for assessing bioconcentratable contaminants in petroleum industry effluents. The main focus of this review is on the effluent option and its application to NPDES-permitted effluents from oil refineries, petroleum product marketing terminals, and oil/gas production platforms (produced water discharges). However, there will be some general evaluation of the suitability of the tissue residue option for evaluating oil industry effluents. The review will, in general, discuss and evaluate the different aspects of the DBG in the order in which they appear in the draft guidance document.

Section 2

CHEMICALS WITH BIOCONCENTRATION POTENTIAL IN PERMITTED EFFLUENTS FROM OIL INDUSTRY OPERATIONS

INTRODUCTION

NPDES-permitted, treated effluents from oil refineries, petroleum product marketing terminals, and oil/gas production platforms (produced water) often contain low or trace concentrations of a wide variety of chemicals. Some of the nonpolar (unionizable) chemicals in these effluents have a strong potential to bioconcentrate, as defined in the DBG. The DBG criteria for identifying potentially bioconcentratable organic chemicals are: concentration in the effluent greater than 100 ng/L (0.1 μg/L or parts per billion); and log octanol/water partition coefficient (log K_{ow}) greater than 3.5. The concentration criterion is the lowest concentration at which adequate quantification can occur with the analytical methods proposed in the DBG. The value of 100 ng/L also is the approximate solubility in fresh water of a nonpolar organic chemical with a log K_{ow} of about 8.2 (Brüggemann and Altschuh, 1991), the highest log K_{ow} used in the bioconcentration assessment. The log K_{ow} criterion was based on the observation that nonpolar organic chemicals with log K_{ow} values lower than 3.5 do not bioconcentrate to any great extent in aquatic organisms. Only organic chemicals that meet the above criteria are considered. Metals and polar (ionizable) organic chemicals were not considered in the DBG.

This section of the review provides a summary of the published scientific literature on the identity and measured concentrations of organic chemicals in permitted, treated oil industry effluents. This is followed by a brief discussion of the physical-chemical properties that affect bioconcentration of nonpolar organic chemicals. A representative group of 18 potentially bioconcentratable compounds, covering the range of log K_{ow} values in the three analytical fractions recommended by the DBG, were selected as model compounds for evaluation of the proposed bioconcentration evaluation methods. The identity of these compounds and the basis for their selection is described in the last part of this section.

ORGANIC CHEMICALS IN OIL INDUSTRY EFFLUENTS

The composition and relative concentrations of nonpolar organic compounds in permitted, treated effluents from oil refineries, petroleum marketing terminals, and production

platforms/produced water treatment facilities are summarized in Appendix A, Tables A-1 through A-10. The dominant nonpolar organic chemicals in all three types of effluents are saturated hydrocarbons, aromatic hydrocarbons, and related nitrogen-, oxygen-, and sulfur-substituted (hetero) compounds. A few pesticides were identified in raw refinery effluents (EPA, 1982; Versar, 1982), but not in the treated effluents. Low molecular weight organochlorine compounds, phenols, and phthalate esters were detected in refinery effluents from several sources and marketing terminal effluents monitored by Borey *et al.* (1989). Most of these compounds have values for log K_{ow} lower than 3.5, and so are not of concern in the current assessment. Phthalate esters occur frequently at relatively high concentrations in waste effluents. Most often, they also occur in laboratory solvents, equipment, and various procedural blanks in the analytical laboratory and are considered contaminants in the analytical protocols (Lopez-Avila *et al.*, 1990). Phthalates, in particular di(2-ethylhexyl)phthalate, are physical plasticizers in plastics and are ubiquitous trace contaminants of the environment. Because phthalates are so widely distributed in the environment and because they have a high affinity for adsorption to surfaces (Södergren, 1982; Sullivan *et al.*, 1982), they are very difficult to analyze at trace levels in environmental samples (Giam *et al.*, 1975; Ehrhardt and Derenbach, 1980). Unless elaborate precautions are taken during sampling, sample handling, and analysis, water and air samples nearly always contain phthalates from sources other than the sample being evaluated (Giam *et al.*, 1980; Lopez-Avila *et al.*, 1990).

Low molecular weight chlorinated compounds may be produced if any effluent stream (e.g., from activated sludge treatment) is chlorinated before discharge. Chlorination of wastewater streams containing PAH results in oxidation of most of the PAH (Harrison *et al.*, 1976) but also may result in the production of small amounts of several chlorinated aromatic compounds, including chlorinated biphenyls, naphthalenes, fluorenes, and phenanthrenes (Smith *et al.*, 1977; Oyler *et al.*, 1978). These halogenated aromatics are only rarely found in modern oil industry effluents. Phenols appear to be normal constituents of refinery effluents. The low molecular weight chlorinated compounds and phenols usually are moderately soluble and have values for log K_{ow} below 3.5.

Raphaelian and Harrison (1978) provided quantitative data for only the effluent from the dissolved air floatation unit of a refinery. The effluent from the dissolved air flotation unit

subsequently passed through an extended aeration type activated sludge unit and a final clarifier before discharge. Some of the effluent from the final clarifier was passed through a pilot scale mixed-media filter and activated carbon unit before sampling. The effluent from the final clarifier and the activated carbon unit contained many of the chemicals quantified in the effluent from the dissolved air floatation unit, but at very low, usually unquantifiable concentrations. Therefore, concentrations of chemicals in the effluent that were actually discharged were much lower than the concentrations listed for the effluent from the dissolved air floatation unit. Raphaelian and Harrison (1978) reported low concentrations of several pyridines, quinolines, and anilines in an effluent sample from the dissolved air floatation unit from a class-B refinery in Ohio. These compounds are quite soluble and have low K_{ow}s.

Produced water contains high concentrations of several organic acids (Somerville *et al.* 1987; Boesch and Rabalais 1989; Barth, 1991). The acids include a homologous series from acetic to at least decanoic acid, plus aromatic acids, such as benzoic acid, and cyclic acids, such as cyclohexane carboxylic acid. They are very water-soluble and so are not of concern in the present context.

PHYSICAL-CHEMICAL PROPERTIES OF ORGANIC CHEMICALS IN OIL INDUSTRY EFFLUENTS

Appendix B contains a summary of the physical/chemical properties of saturated, olefinic, aromatic, and hetero-hydrocarbons frequently found in petroleum industry effluents. Only chemicals with measured or predicted log K_{ow}s greater than 3.5 are included in the Appendix table.

In the effluent option for assessing bioconcentratable chemicals in effluents, bioconcentration factors (BCF) are estimated by a regression of log K_{ow} versus log BCF. As a general rule, for each chemical class, aqueous solubility decreases and the log K_{ow} increases as molecular weight increases. The slope of the molecular weight/solubility and molecular weight/log K_{ow} curves for n-alkanes are particularly steep (solubility decreases and log K_{ow} increases sharply as molecular weight increases) (Coates *et al.*, 1985). Hydrocarbons with log K_{ow}s greater than about 3.5 include mono-aromatic hydrocarbons with molecular weights greater than about 118 (indan and isobutylbenzene), polycyclic aromatic hydrocarbons (PAHs) with molecular weights greater than about 130 (methylnaphthalenes; however some estimates of the log K_{ow}

of naphthalene are higher than 3.5), saturated hydrocarbons with molecular weights greater than about 90 (dimethylbutanes and n-heptane), olefins with molecular weights greater than about 100 (1-octene), and heterocyclic compounds with molecular weights greater than about 140 (methylbenzothiophenes and carbazole). The highest molecular weight PAH that is considered mobile in the environment is coronene (MW 300.4). It has an estimated solubility of about 0.14 μg/L and a log K_{ow} of 7.64 (Eastcott *et al.*, 1988). By comparison, the C_{20} n-alkane docasane has a molecular weight of 310.6, an estimated aqueous solubility of 0.008 ng/L, and an estimated log K_{ow} of 11.46 (Coates *et al.*, 1985). Because of the low aqueous solubility of n-alkanes, the highest molecular weight member of this group of hydrocarbons that might be considered in the bioconcentration assessment is the C_{14}-n-alkane, pentadecane (MW 212.4, solubility 0.076 μg/L, log K_{ow} 7.72).

SELECTION OF MODEL COMPOUNDS FOR EVALUATION

Table 2-1 is a summary of the range of concentrations of the most abundant potentially bioconcentratable hydrocarbons with K_{ow}s greater than 3.5 in the three types of effluents. As a general rule, based on the very limited data available, the lower molecular weight compounds are more abundant in produced water than in either refinery effluents or marketing terminal effluents. The few higher molecular weight compounds detected usually are more abundant in refinery or marketing terminal effluents than in produced water. The C_{14} and C_{15} n-alkanes are the saturated hydrocarbons present at highest concentration in the limited number of samples of untreated refinery effluent and treated produced water analyzed to date for saturated hydrocarbons. Phthalate esters were not included because they usually are contaminants introduced into the samples during sample collection, processing, and analysis, and are not known to be constituents of the effluents themselves. Chloronaphthalene was reported once in a refinery effluent sample at a concentration of 4 μg/L. It probably was a byproduct of chlorination of a refinery wastewater stream.

The effluent fractionation/analysis method proposed in the DBG is a high-performance liquid chromatography (HPLC) method that produces three fractions of nonpolar organic compounds with different ranges of log K_{ow}: 3.5 to 4.5; 4.5 to 5.7; and 5.7 to 8.2. As part of the evaluation of the draft guidance, we have evaluated the methodology for estimating bioconcentration potential using 18 nonpolar organic chemicals characteristic of oil industry effluents. These compounds (referred to below as evaluation compounds) were chosen based

on their abundance in oil industry effluents (Table 2-1) and K_{ow} values (Appendix B) representative of the log K_{ow} ranges in the three HPLC fractions (Table 2-2).

The compounds that were evaluated include representatives of the three chemical classes (saturated hydrocarbons, aromatic hydrocarbons, and heterocyclic compounds) identified most often at highest concentration in oil industry effluents and span the range of K_{ow}s considered in the DBG. In developing the list from among the candidate compound classes in Table 2-1, consideration was given to the potential availability of data needed to estimate a reference ambient concentration (RAC). The RAC is used as a basis for assessing if bioconcentratable chemicals are present at unacceptably high concentrations in an effluent or the tissues of aquatic animals. EPA recommends using the IRIS database to calculate RAC values (see Section 5 of this review). However, only six of the 18 evaluation compounds are in the IRIS database: fluorene, phenanthrene, fluoranthene, benz(a)anthracene, chrysene, and benzo(a)pyrene. Information for carbazole was found in another risk assessment database.

Table 2-1. Range of Reported Concentrations (μg/L) of Aromatic and Heterocyclic Compounds with Log K_{ow}s Greater than 3.5 in Refinery Effluents, Marketing Terminal Effluents, and Produced Water. Data are From Appendix A.

Compound	Refinery Effluent	Marketing Terminal	Produced Water
C-3 Benzenes			5 - 159
C-4 Benzenes			12 - 102
Methylnaphthalenes	0.10		18 - 240
C-2 Naphthalenes	0.1 - 65		27 - 360
C-3 Naphthalenes	3.0 - 44		15 - 395
Biphenyl	+		1.8 - 2.1
Acenaphthene	0.1 - 10		tr - 6
Fluorene	5 - 6		ND - 18
C-1 Fluorenes	0.10		0.3 - 13
Carbazole	2.2		
C-1 Carbazoles	4.8		
C-2 Carbazoles	4.6		
Anthracene	ND - 1.0	ND - 8	ND - 10[a]
Phenanthrene	0.1 - 13	ND - 42	ND - 120
C-1 Phenanthrenes	+		tr - 260
Dibenzothiophene	tr		ND - 14
C-1 Dibenzothiophenes	+		ND - 30
Pyrene	ND - 3.0	ND - 300	ND - 0.67
Fluoranthene	ND - 1.0	ND - 100	ND - 0.56
Chrysene	0.02 - 9.0	ND - 2	ND - 1.95
Triphenylene	2.8		
Benz(a)anthracene	ND - 9.0	ND - 2	ND - 0.90
Benzo(a)pyrene	ND - 0.5		ND - 1.2[a]
Benzo(e)pyrene	3.9		
Methylbenzopyrenes	5.3		
Perylene	0.7		ND - 0.48
Benzo(ghi)perylene	0.7		

ND, Not detected

tr, Present but below quantifiable concentration

+, Identified but not quantified

a, Data from Middelditch 1984

Table 2-2. Nonpolar Organic Chemicals (Evaluation Chemicals) Used to Evaluate the Effluent Option of the Draft EPA Guidance. These Chemicals are Representative of the Most Abundant Bioconcentratable (Log K_{ow} > 3.5) Chemicals in Oil Industry Effluents and Span the Range of log K_{ow} Values in the Three HPLC Fractions of the Proposed Fractionation Method.

Chemical	Class	Log K_{ow}[1]
Fraction 1: Log K_{ow} 3.5 to 4.5		
Carbazole	heterocyclic	3.84
1,2,4-Trimethylbenzene	monoaromatic	3.85
2-Methylnaphthalene	alkyl-PAH	3.86
n-Octane	n-alkane	4.00
Fluorene	unsub. PAH	4.18
Dibenzofuran	heterocyclic	4.21
Dibenzothiophene	heterocyclic	4.49
Fraction 2: Log K_{ow} 4.5 to 5.7		
Phenanthrene	unsub. PAH	4.57
Methyldibenzothiophene	alkyl-heterocyclic	4.86
n-Decane	n-alkane	5.01
1-Methylphenanthrene	alkyl-PAH	5.08
Fluoranthene	unsub. PAH	5.22
Fraction 3: Log K_{ow} 5.7 to 8.2		
Chrysene	unsub. PAH	5.79
Benz(a)anthracene	unsub. PAH	5.90
Benzo(a)pyrene	unsub. PAH	6.40
5-Methylchrysene	alkyl-PAH	6.42
7,12-Dimethyl-benz(a)anthracene	alkyl-PAH	6.93
n-Tetradecane	n-alkane	7.20

[1] Representative values were chosen from the scientific literature, mostly from Eastcott *et al.* (1988).

SUMMARY

- The major potentially bioconcentratable nonpolar organic chemicals in permitted effluents from oil refineries, petroleum product marketing terminals, and oil/gas production platforms are saturated and aromatic hydrocarbons and related S-, N-, and O-substituted hydrocarbons.

- A group of 18 hydrocarbons, representative of the most abundant bioconcentratable chemicals in oil industry effluents, was selected to evaluate the effluent option methods described in the DBG. Chemicals that fall in the three HPLC fractions (log K_{ow} 3.5 to 4.5, 4.5 to 5.7, and 5.7 to 8.2) were included.

Section 3

SELECTION OF AN APPROPRIATE ASSESSMENT OPTION

This section of the review is a general description and critique of Chapter 1 of the DBG. Chapter 1 provides a general overview of the approach EPA recommends for evaluation of bioconcentratable nonpolar organic chemicals in effluents. The major focus of this chapter is a discussion of reasoning and justification behind the selection of an appropriate assessment option from the two available.

Following is a brief discussion of the different rationales and justifications EPA proposes for each assessment option. This is followed by a review of some of the strengths and weaknesses of each option. A detailed critique of specific scientific issues related to the DBG follows in Sections 4 and 5.

The DBG describes a seven-step process for the assessment and control of bioconcentratable contaminants in surface waters. In the seven steps, EPA or the discharger:

1. Selects dischargers or receiving waters for assessment;
2. Selects the appropriate assessment option, effluent concentration or tissue residue concentration;
3. Analyzes effluent or tissue samples for bioconcentratable chemicals;
4. Calculates reference ambient concentrations (RACs) and/or reference tissue concentrations (RTCs) for the bioconcentratable chemicals identified in the effluent or tissues, respectively;
5. Determines if bioconcentratable chemicals are present at concentrations that have a reasonable potential to pose health risks for human consumers of fish and shellfish; and, if so
6. Develops wasteload allocations; and
7. Develops permit limits.

EPA has not yet developed guidelines for step 1. An indepth evaluation of Steps 3, 4, and 6 is the main focus of Sections 4 and 5 of this review. The focus of this section of the review is on Step 2, selection of an appropriate assessment option.

SELECTION OF AN ASSESSMENT OPTION

Responsibility for Selecting an Assessment Option

Selection of either or both of the assessment options for evaluating an NPDES-permitted effluent appears to be the responsibility of the regulatory authority (page I-5 of DBG: "The regulatory authority should select the assessment approach based on the available site and facility specific information and the objectives of each application."). EPA, or a state agency designated by EPA, is responsible for issuing NPDES permits. Presumably the NPDES permit-granting agency in each state would be responsible for selecting the assessment option for each discharge identified in step 1 as requiring assessment. It is unclear whether the discharger may recommend an assessment option and whether the regulatory authority may consider recommendations of the discharger in selecting an assessment option.

Possible Functions of Each Assessment Option

The two assessment options (effluent concentration and tissue residue concentration) provide different types of information and cannot be used interchangeably to accomplish different possible assessment objectives. Chapter 1 of the DBG provides some general guidance to the responsible regulatory authority in selecting the appropriate assessment option, depending on site-specific circumstances and specific objectives or questions that the assessment is being required to address. However, the discussion is extremely simplistic and the DBG does not relay how dynamic and how variable in time and space most natural aquatic ecosystems are.

The DBG (page I-5) states that: "In general, EPA recommends that a discharger be required to conduct the effluent option if existing fish tissue and/or facility information suggests the potential presence of bioconcentratable contaminants." In the effluent option, concentrations of bioconcentratable chemicals are measured in representative samples of a point-source effluent. For bioconcentratable chemicals measured at higher than a low threshold concentration of 0.1μg/L or 5μg/kg, a mathematical model is then used to predict the concentrations of the chemicals which would be expected to be found in the tissues of fish and shellfish in the receiving water environment.

The DBG also states (page I-6) that: "EPA recommends that the tissue residue option be required if the objective of the regulatory authority is to assess existing ambient bioconcentration or bioaccumulation problems in the absence of existing water body or facility information on the presence of these contaminants."

The tissue residue option can be used to identify and characterize existing bioaccumulation problems in a water body. It can identify the net effects of multiple point, non-point, and sediment sources of chemicals of environmental concern. It cannot identify or differentiate among multiple sources of most chemicals. It cannot be used alone to identify and control bioconcentratable chemicals in a particular effluent. However, when combined with targeted analysis of effluent samples, it may be able to contribute to identifying some of the sources of a bioconcentratable chemical in a water body.

The recommended frequency of monitoring (quarterly to annually; page I-9) is insufficient to identify introductions of new bioconcentratable chemicals before they reach equilibrium with the food web of the receiving water system. In addition, the guidance implies that one year is required "for the required samples and analyses to be conducted and the results submitted to the regulatory authority prior to issuance of a permit." Just because the effluent option may identify potential problem chemicals in the effluent before discharge, does not mean that it can be used to "prevent tissue contamination from occurring" (page I-7).

Tissue Residue Option

Because of the complexity in determining the sources of tissue residues in aquatic animals consumed by man, the tissue residue option cannot ordinarily be used to identify the contribution of particular permitted effluents to tissue residue levels in animals in the receiving water environment. Although the tissue residue option provides a measure of the concentrations of bioconcentratable chemicals in tissues of animals sampled in the receiving waters, it often is difficult or impossible to identify with any certainty the sources of the chemical residues in tissues.

The problem of identifying the source or sources of tissue residues of bioconcentratable chemicals in aquatic animals in a receiving water environment is particularly great when effluents from oil industry operations are involved. As discussed in Section 2 of this review, the most frequently encountered and most abundant potentially bioconcentratable chemicals in oil industry effluents are saturated and aromatic hydrocarbons and related hetero compounds. These chemicals have a wide variety of natural and anthropogenic sources in aquatic environments, only a few of which are related to oil industry operations (Neff, 1979). Therefore, it will not be possible, in most cases, to definitively attribute hydrocarbon residues in tissues of aquatic organisms to a particular oil industry effluent.

Concentrations of anthropogenic nonpolar organic chemicals in solution in a natural water body, particularly a well-mixed river, estuarine, or coastal marine ecosystem, receiving point-source effluents show tremendous variability over small temporal and spacial scales. In well-mixed receiving waters, there usually is a very sharp declining gradient of concentrations of dissolved chemicals with distance from the point source (e.g., Brandsma *et al.*, 1992). Temporal variability in mixing of receiving waters due to tides, winds, and variations in stream flow result in large temporal variations in rates of dilution of effluent plumes. Rates of photodegradation and biodegradation of organic chemicals in receiving waters vary diurnally and seasonally.

Nonmotile aquatic animals sample this variable ambient medium at only one location, whereas motile animals, such as most fish and many crustaceans, sample the variable medium over larger, generally unpredictable spacial scales. Concentrations of a chemical in the tissues of an aquatic animal reflect the time-integrated exposure history of the animal. For chemicals that are not readily metabolized or excreted, the exposure history of concern may be the entire life of the animal.

However, no aquatic animal in its natural environment is exposed to bioconcentratable chemicals in aqueous solution alone. Any bioconcentratable chemical in solution in the water will have a strong tendency to sorb to suspended and deposited particles and to be bioaccumulated by food chain organisms (partitioning of nonpolar organic chemicals among water, sediments, and animal tissues is discussed in greater detail in Section 4 of this review). Thus, an aquatic animal will be exposed simultaneously to bioconcentratable chemicals in solution in the water, in food, and in suspended or deposited sediments.

There is growing recognition that aquatic sediments are both a sink for and a long-term source of chemicals in aquatic ecosystems (Salomons *et al.*, 1987). Sediments may be a source of bioconcentratable chemicals for aquatic animals that live and feed in sediments or at the sediment/water interface (benthic and demersal fauna). However, **the co-occurrence of a bioconcentratable chemical in sediments and in animals living in, or in close association with, the sediments does not constitute proof that the animals accumulated the chemical from the sediments.** Both the sediments and the animals may have accumulated the chemical from the overlying water column.

The Effluent Option

The effluent option does identify and quantify bioconcentratable chemicals in specific effluents and, therefore, is in line with the chemical-specific approach to toxics control in effluents. As with any chemical-specific assessment, it may be difficult to obtain water samples that are truly representative of the average, time-integrated composition of the effluent stream. Until the temporal variability in the chemical composition and concentrations in a particular effluent are established, it will be difficult to determine if quarterly or annual sampling and analysis are adequate to characterize bioconcentratable chemicals in an effluent.

However, the main weakness of the effluent option, as discussed in greater detail in the following sections of this review, is the uncertainties about many of the assumptions used to mathematically link (model) the relationship between concentrations of a bioconcentratable chemical in an effluent and concentrations of that chemical in the edible tissues of an animal living in the receiving water environment. The models assume that there is an equilibrium among concentrations of bioconcentratable chemicals in the receiving water, sediments, food organisms, and aquatic animals consumed by man in the receiving water environment. This is almost never the case. Concentrations in a receiving water environment of chemicals derived from a point-source effluent are continuously varying on both temporal and spatial scales. Animals, particularly motile ones, are nearly always actually exposed to time-averaged concentrations of the chemicals of concern that are much lower than the concentrations predicted by conventional dilution models. The kinetics of partitioning of nonpolar organic chemicals among water, sediments, food organisms, and consumer organisms is poorly understood, particularly under conditions of highly variable concentrations in solution in the aqueous phase. Wide differences in the ability of food chain organisms to metabolize and excrete hydrocarbons (Stegeman, 1981; Stegeman and Kloepper-Sams, 1987), the most abundant bioconcentratable compounds in oil industry effluents, further complicates prediction of net bioaccumulation in aquatic animals consumed by man.

The proposed analytical methods themselves pose many unique problems (discussed in greater detail in Section 5 of this review) for typical effluent, ambient water, tissue, and sediment samples. The proposed analytical methods may be completely unsuitable, in particular, for oil industry effluents in which nearly all the nonpolar organic chemicals with log K_{ow}s greater than 3.5 are hydrocarbons. The following statement is made on page I-8 of the DBG:

> "Another limitation of the effluent option also arises as a result of the analytical methods used. Hydrocarbons, such as those found in lubricants, oils and gasoline, are not removed by the aforementioned cleanup step. These chemicals rarely form residues in aquatic organisms but do cause interferences in the analyses. Specifically, these types of compound prevent successful GC/MS analysis of the third fraction of the effluent extracts. For this reason, application of this option to discharges expected to contain very large numbers of hydrocarbons, such as refineries, is not recommended. However, since this type of chemical does not form residues, the tissue residue option is not subject to this analytical interference and may be applied."

It is clear from this statement, that the DBG as presented is not applicable to oil industry effluents, given, as discussed in Section 2 of this review, that the only potentially bioconcentratable chemicals consistently found at concentrations greater than 100 ng/L are hydrocarbons and closely related hetero-substituted hydrocarbons. According to EPA, these compounds interfere with the proposed analytical methods for water samples (the effluent option) and do not form residues in aquatic organisms (the tissue residue option).

Field Validation

Section 1.7 of the DBG identifies field validation studies that are being performed to evaluate the applicability of the two options for control of bioconcentratable chemicals in NPDES effluents. The Environmental Risk Watch (1992) reported that EPA's National Effluent Toxicity Assessment Center announced preliminary results of two validation studies of its bioconcentration guidance procedures for nonpolar organic chemicals in aqueous effluents. One of these studies evaluated residues of five PAHs in the tissues of crayfish and sunfish living downstream from coking operations. The results indicated that the tissue residues of "nonmetabolizable" chemicals are more predictable than those readily metabolized by aquatic organisms. The models overestimated tissue residues of readily metabolized PAH in fish tissues.

These initial results indicate that substantially more field validation is required of the applicability of the draft bioconcentration assessment guidance to oil industry effluents that contain almost exclusively hydrocarbons. Results of validation studies are essential for a complete evaluation of the soundness of the assumptions and simplifications incorporated in the model linking chemicals in effluents to chemical residues in tissues of aquatic animals. In particular, validation studies are required for organic chemicals that may have an anomalous environmental behavior, such as alkanes and PAHs. These chemicals are natural biogenic

materials that are subject to a variety of degradative processes in the environment not considered in the models. The DBG should not be accepted as final and used for regulatory purposes until such time as the results of the field studies have been reported and thoroughly evaluated and validated by independent reviewers.

Monitoring of Sediments

Section 1.8 of the DBG is a discussion of the evaluation of potentially bioconcentratable chemicals in sediments. It is unclear in this section or in Section 3.4 (Sediment Assessment) how assessment of potentially bioconcentratable chemicals in sediments relates to the assessment of bioconcentratable chemicals in effluents and tissues of aquatic animals. In Section 1.8, the DBG states that analysis of sediments may "facilitate detection of contaminants which are present in an effluent or other sources at very low concentrations or are only released periodically." It is unclear if EPA may itself or may require an NPDES permittee to analyze sediments near an outfall, and how sediment chemical data generated in this way might be used as a basis for regulating the discharge.

As mentioned above, the linkage between potentially bioconcentratable chemicals in sediments and the concentrations of the same chemicals in effluents and the tissues of animals in the receiving water environment is a complex one. A variety of possible uses for sediment contamination data are suggested in Section 1.8. Some of these uses are highly equivocal unless a great deal is known about the physical limnology/oceanography and sedimentology of the water body. Highly nonpolar organic chemicals are extremely persistent in fine-grained sediments, particularly if the sediments contain high concentrations of organic carbon or are hypoxic. Concentration gradients of chemicals in sediments have been used many times to aid in identifying point sources of chemicals. However, the possible confounding effects of sediment resuspension and transport, sediment grain size, and concentration of dissolved and particulate organic matter in sediments on the distribution of nonpolar organic chemicals in sediments must be considered, especially where multiple sources of the chemicals of concern are possible (Baudo, 1990).

Sediments may be an important source of nonpolar organic chemicals in the tissues of plants and animals in the receiving water environment (Landrum and Robbins, 1990). However, sediments also are long term repositories of these chemicals. It cannot always be determined

with any certainty what fraction of nonpolar organic chemicals is bioavailable, where chemicals in sediments came from, and when they were deposited. This is particularly true for some chemicals, such as PAHs, that may have been derived from multiple point and nonpoint sources over long periods of time (Hites *et al.*, 1977).

SUMMARY

- Chapter 1 of the DBG provides a broad overview of methods for selection of an appropriate assessment option, which appears to be the responsibility of EPA. The role, if any, of the NPDES permittee is not clear.

- The two assessment options, the effluent option and the tissue residue option, provide different types of information and cannot be used interchangeably. Neither assessment option is really effective in identifying future potential bioconcentration problems in a water body.

- The major problem with the tissue residue option is that it is difficult or impossible to definitively identify the source or sources of the tissue residues with respect to the effluent from a particular discharger. This problem is particularly severe for potentially bioconcentratable chemicals, such as hydrocarbons (the major chemicals of concern in oil industry effluents), that have a multitude of natural and anthropogenic sources in the environment.

- The main weakness of the effluent option is the uncertainty about many of the assumptions used to model the relationships between concentrations of bioconcentratable chemicals in an effluent and their concentrations in aquatic animals in the receiving water environment.

- The analytical methods proposed for the effluent option cannot be used for effluents containing mostly hydrocarbons. Therefore, the methods are not suitable for permitted effluents from oil industry operations.

- Inadequate information is available from field validation studies to judge whether either or both of the assessment options provide technically sound and useful information for a wide variety of effluents under different discharge and natural environmental conditions.

- The role of sediment analysis in bioconcentration assessment is unclear and should be clarified. The co-occurrence of a bioconcentratable chemical in sediments and in animals living in or on the sediments does not constitute proof that the animals accumulated the chemical from the sediments.

Section 4

BIOCONCENTRATION AND BIOACCUMULATION

Chapter 2 of the DBG provides a brief discussion of the principles of bioconcentration and bioaccumulation of nonpolar organic compounds by aquatic and marine organisms. The discussion is based on results of controlled laboratory studies and does not adequately discuss the limitations to our ability to extrapolate from laboratory data and theoretical concepts of bioconcentration to actual bioaccumulation under field conditions.

This section of the review includes a discussion of the major limitations of bioconcentration and bioaccumulation extrapolations, with particular emphasis on problems encountered in dealing with bioconcentratable chemicals commonly found in petroleum industry effluents. Bioconcentration, bioaccumulation, and biomagnification are defined and discussed as they relate to prediction of concentrations potentially bioconcentratable chemicals in tissues of aquatic organisms. This is followed by a description of the use of physical/chemical properties of chemicals to predict (model) their bioaccumulation by aquatic animals. Emphasis is placed on limitations of the models, particularly for chemicals that are readily degraded and excreted by aquatic organisms. Finally, the limitations of the proposed models in the DBG for predicting tissue residues of hydrocarbons are discussed.

DEFINITIONS

The definitions of bioconcentration, bioaccumulation, and biomagnification as presented on page II-1 of the DBG are adequate but incomplete. The definitions of Brungs and Mount (1978) and Spacie and Hamelink (1985) are used most frequently in the scientific community and are discussed below. Only bioavailable compounds can be bioconcentrated, bioaccumulated, or biomagnified. A chemical is bioavailable if it is in a form that can move through or bind to the surface coating (e.g., skin, gill epithelium, gut epithelium, cell membrane) of an organism and thereby elicit biological responses.

Bioaccumulation

Bioaccumulation is the uptake and retention of a bioavailable chemical from all possible external sources (water, food, substrate, air). For bioaccumulation to occur, the rate of uptake must be greater than the rate of loss of the chemical from the organism. Many highly soluble

chemicals, such as ammonia and some inorganic ions, are bioavailable and rapidly penetrate the tissues of aquatic organisms. However, they are not retained and are lost just as rapidly from the tissues by diffusion or active transport. Their concentrations in tissues are equal to or lower than their concentrations in the ambient medium or they are regulated at a particular level independent of concentrations in the ambient medium. Some other bioavailable chemicals are taken up rapidly, but are transformed and/or excreted rapidly by metabolic processes of the organism, and so are not bioaccumulated.

As the concentration of a chemical in the tissues of an aquatic organism increases, there is a tendency for the rate of loss of the chemical from the tissues to increase. During continued exposure to a relatively constant concentration of the chemical in the water, food, and sediments, the rate of active plus passive loss of the chemical will increase to equal the rate of uptake. At this point, a steady state or equilibrium is reached. The equilibrium concentration of the chemical in the tissues of an aquatic organism usually is measured as the bioaccumulation factor (BAF), the ratio of the concentration of the chemical in the tissues of the organism to its concentration in all ambient compartments in equilibrium with the organism. Alternatively, and more appropriately, the BAF is the ratio of the sum of the uptake rate constants of the chemical from all environmental compartments accessible to the organism to the sum of release rate constants by active and passive mechanisms from the organism. BAFs are difficult to measure directly because a variety of factors (discussed in more detail below) affect the rates of accumulation of hydrophobic chemicals from different environmental compartments, and their rates of loss from tissues of organisms by active and passive routes (Esser and Moser, 1982).

Bioconcentration

Bioconcentration is a special case of bioaccumulation. Bioconcentration is defined as uptake and retention of a chemical from water alone. Uptake from other sources is not considered. In most laboratory studies of uptake by aquatic organisms, the organisms are exposed to water containing the chemical(s) of interest in solution. Food and substrate are not provided or are not contaminated, so uptake from these sources is not measured. Bioconcentration is a completely artificial parameter because natural populations of aquatic animals never are exposed solely to chemicals in solution.

The magnitude of bioconcentration is measured as the bioconcentration factor (BCF). The BCF is the ratio at equilibrium between the concentration of the chemical in the tissues of the organism to the concentration of the chemical in solution in the water to which the organism was exposed. The BCF can also be measured as the ratio of the uptake rate constant, or clearance, to the release rate constant at equilibrium. Uptake clearance has units of unit mass of chemical/unit mass of tissue/unit time, which translates to time^{-1} (Spacie and Hamelink, 1982). The elimination rate constant also has units of time^{-1}; therefore, BCF is unitless. The BCF is not, as indicated on page II-2 of the DBG, the ratio of the uptake rate to the elimination rate; by definition, the uptake rate equals the release rate at equilibrium.

At least some of the external body surfaces of all water-breathing aquatic animals are permeable (e.g., the gills) and bioavailable nonpolar organic chemicals can partition passively (both inward and outward) between the lipids of the animal and the surrounding water through these surfaces (equilibrium partitioning). According to equilibrium partitioning theory (Davies and Dobbs, 1984; Bierman 1990), when an aquatic animal is exposed to a nonpolar organic chemical dissolved in the ambient water, the chemical partitions into the tissue lipids until an equilibrium defined by the octanol/water partition coefficient (K_{ow}) for the chemical is reached. At equilibrium, the rates of absorption into and desorption from the lipid phase of the animal are equal. Because of the relationship between log K_{ow} and bioaccumulation, it is possible to predict the equilibrium BCF for a particular compound from its log K_{ow}, if all the underlying assumptions are met (Veith and Kosian, 1983; Davies and Dobbs, 1984).

Many of the underlying assumptions in the model of the relationship between BCF and log K_{ow} may not be met under field conditions. For highly hydrophobic chemicals (having high K_{ow}s), true equilibrium may not be reached in a reasonable amount of time, especially if, as is usually the case, concentrations of dissolved nonpolar organic chemicals in the receiving waters are highly variable over time and space. Hawker and Connell (1985, 1986) estimated that one or more years would be required for a fish to reach equilibrium with a dissolved chemical with a log K_{ow} of 6 or greater. *Daphnia* and small molluscs may reach equilibrium more quickly; however, these invertebrates usually have shorter life spans than most fish. When the equilibration rate is slow, growth in mass of aquatic animals has the effect of diluting accumulated chemicals, decreasing the equilibration rate (Thomann, 1989).

The BCF/K_{ow} model assumes that an accumulated chemical can only be lost from tissues through passive partitioning between tissue lipids and water. Most aquatic animals, particularly fish, can metabolize most of the hydrocarbons found in oil industry effluents and, thus, release them much more rapidly than the model predicts. True BCFs for chemicals that are actively metabolized and excreted are lower than theoretical equilibrium BCFs (de Bruijn and Hermans, 1991; de Wolf *et al.*, 1992).

Because nonpolar organic chemicals dissolved in water have a strong tendency to partition from the water onto or into all hydrophobic interfaces, the chemicals become distributed rapidly among different liquid and solid compartments of the environment according to various interphase partition coefficients. An aquatic animal in its natural environment is never exposed for an extended period of time to only the dissolved chemical in the ambient water. Food consumed by the aquatic animal tends to accumulate the chemical from the water as well as from its own food sources. Animals living near or buried in bottom sediments are exposed to the chemicals bound to sediment particles and in sediment pore water. Thus, an aquatic animal is exposed to and may accumulate the chemical simultaneously from the water, food, and sediments in its environment.

The vast majority of the published scientific literature on uptake considers or models only bioconcentration and does not consider uptake from all sources available to the organisms in its natural environment (bioaccumulation). The DBG gets around this problem "by 'adjusting' the BCF using a food chain multiplier (FM) for the organism of concern" (page II-3). Values for FM are presented in Table 4.1 on page IV-6 of the DBG. The FM is a factor, between 1.0 and 103.8, by which the BCF is multiplied to account for bioaccumulation from food and to thereby convert the BCF to a BAF. Estimated values for FM are based on values of log K_{ow} and trophic level of the animal under consideration. As discussed below, food chain transfer (accumulation of chemicals from food) is a complex process that cannot readily be predicted from log K_{ow} and trophic level alone. Such factors as chemical- and species-specific variability in absorption efficiency of chemicals from the gut, active metabolism and excretion by the gut epithelium of some chemicals such as PAHs, the complexity of most aquatic food chains, and variable growth efficiencies of aquatic animals affect the importance of food as a source of tissue residues.

Biomagnification

Biomagnification is the process of bioaccumulation whereby a chemical is passed through the food web by trophic transfer, its concentration increasing in tissues of organisms at each higher trophic level. Several conditions are required for trophic transfer and biomagnification of nonpolar organic chemicals (Gobas *et al.*, 1988). The chemical must be present in the food in a bioavailable form (digestion may increase or decrease bioavailability). The chemical must be at least slightly soluble in the fluids in the gastrointestinal tract and it must be able to permeate the intestinal mucosa by diffusion. Once it has moved into the cells and tissues of the digestive tract, the chemical must partition into tissue lipids or bind to tissue macromolecules so that the rate of passive loss back to the external medium is slower than the rate of influx. Finally, active metabolic breakdown or excretion of the chemical must be slow, so that the chemical can accumulate in tissues over time. If these conditions prevail and the food continues to contain elevated concentrations of the chemical, the consumer will, over a long period of time, eat several times its own weight of contaminated food and may retain the chemical in its tissues at a concentration higher than the concentration of the chemical in the food.

PREDICTION OF BIOCONCENTRATION

Estimation of BCF from K_{ow}

The DBG Approach. The DBG recommends that values for BCF should be calculated from the log K_{ow}/log BCF relationship and that these calculated or predicted values should be used in the calculation of reference tissue and ambient concentrations (page II-5). Actually, for chemicals with log K_{ow} greater than about 5, the required parameter is BAF, not BCF. The BAF is estimated by multiplying the predicted BCF by the FM (page II-3). Food is considered to be a quantitatively important source of tissue residues for nonpolar organic chemicals with log K_{ow}s of 5 or higher (Thomann, 1989). Compounds with lower log K_{ow}s are accumulated almost exclusively from the water.

Regression of Log BCF Versus Log K_{ow}. The use of a single formula to predict values for BCF for a wide variety of different types and structural classes of nonpolar organic compounds in different size classes of aquatic animals is subject to substantial error, particularly if estimated values for K_{ow} are used. The linear equation relating BCF to K_{ow} usually takes the form of:

$$\log BCF = a \log K_{ow} + b \quad (4\text{-}1)$$

where a and b are the slope constant and intercept constant, respectively, and are determined empirically. Values for a and b are estimated by performing a regression of empirically determined values for log BCF against literature values of log K_{ow} for several nonpolar organic chemicals. A linear regression line with the "best fit" is calculated and the goodness of fit is estimated statistically. A large number of these regressions has been performed using different numbers and classes of nonpolar organic chemicals spanning different ranges of log K_{ow}.

The equation recommended in the DBG (page II-4) for estimation of BCF from log K_{ow} was derived from a regression of log BCF in 13 species of fish (nearly all freshwater species) versus log K_{ow} for 122 nonpolar organic chemicals (Veith and Kosian, 1983). The resulting equation and values for a and b are:

$$\log BCF = 0.79 \log K_{ow} - 0.40 \quad (4\text{-}2)$$

There is a good correlation between log BCF and log K_{ow} ($R^2 = 0.86$) for the data set used. Use of a regression equation derived for one class of compounds to predict bioconcentration of chemicals from another class produces BCFs that may be inaccurate. Only five of the 122 chemicals used to derive the equation were PAHs (nonpolar organic chemicals found in oil industry effluents). There were no alkanes or heterocyclic compounds in the data set. The draft guidance indicated that the equation, derived from data for freshwater fish, is applicable to marine fish and invertebrates (Zaroogian *et al.*, 1985). Actually, Zaroogian *et al.* (1985) used earlier equations of Veith *et al.* (1979, 1980) that had different values for the constants a and b. None of the chemicals evaluated by Zaroogian *et al.* (1985) were petroleum hydrocarbons. The log K_{ow}/log BCF relationship for petroleum hydrocarbons is different from that for chlorinated aromatics and other classes of nonpolar organic chemicals, as discussed below.

Veith *et al.* (1979) reported that the BCF for organic chemicals spanning a log K_{ow} range of 6 can be predicted to within an order of magnitude by a formula similar to that presented above. Thus, a BCF of 1000, estimated by the formula, may actually be somewhere between 100 and 10,000. However, for classes of chemicals under-represented or not represented in the data

set used to derive the formula, it is probable that deviations between predicted and actual BCFs will be even greater than one order of magnitude (factor of 10), and the uncertainty in the predicted BCF values may not be known.

Schüürmann and Klein (1988) summarized 20 published versions of the BCF/K_{ow} equation derived for different groups of nonpolar organic chemicals. Values for a ranged from + 0.54 to + 1.16; values for b range from -1.82 to + 0.75. They observed that, for a set of 19 chlorinated hydrocarbons, 11 PAH, and 19 other organic compounds, the overall correlation between log BCF and log K_{ow} was only moderate (r^2 = 0.79). Restriction of the data set to just chlorinated hydrocarbons and PAH improved the correlation (r^2 = 0.90).

Variability of Estimates of K_{ow}. There often are large differences between measured and predicted values for K_{ow}. Use of measured values for K_{ow} improved the correlation between BCF and K_{ow} (Shüürmann and Klein, 1988). The accuracy of log K_{ow} values used in the equation may have a large effect on the reliability of the assessment of bioconcentration potential of chemicals in effluents. A variety of methods are used to measure or predict the K_{ow} of organic compounds. The different methods often yield widely different results (e.g., Doucette and Andren, 1988; Klein *et al.*, 1988; Shüürmann and Klein, 1988; Brooke *et al.*, 1990). Therefore, published values for K_{ow} for a single compound may span an order of magnitude or more. Pavlou *et al.* (1987) reported that published log K_{ow} values for 10 PAH were quite variable. Güsten *et al.* (1991) reported the following range of published K_{ow}s for several aromatic hydrocarbons:

	Log K_{ow} Range	K_{ow} Range
n-Butylbenzene	3.62 - 4.44	4,169-27,542
Naphthalene	3.01 - 4.70	1,023-50,119
Pyrene	4.50 - 6.80	31,623-6,309,573
Perylene	5.82 - 6.53	660,693-3,388,442
Benzo(a)pyrene	5.97 - 6.83	933,254-6,760,830
3-Methylcholanthrene	6.42 - 7.11	2,630,268-12,882,495
Benzo(ghi)perylene	6.25 - 7.10	1,778,279-12,589,254
Coronene	5.40 - 7.64	251,189-43,651,583

This variability in published values for K_{ow}s must be kept in mind when using the DBG to evaluate an effluent because the choice of which published value of log K_{ow} to use has a marked effect of the predicted value for BCF. For example, if log K_{ow}s for naphthalene in the range reported by Güsten *et al.* (1991) are used in the equation for PAHs of de Voogt *et al.* (1991) (see equation 4-3 below), the estimated BCFs for naphthalene range from 523 to 25,562.

Opperhuizen *et al.* (1988) showed that part of the reason for the variability in the BCF/K_{ow} relationship for different classes of nonpolar organic compounds is that octanol is not a good model for animal lipids. K_{ow} provides a variable and unpredictable estimate of the animal lipid/water partition coefficient. The thermodynamics of octanol/water and lipid/water partitioning are different for different classes of nonpolar organic compounds. Therefore, BCF/K_{ow} regressions developed for one class of chemicals cannot readily be extrapolated to predict the partitioning behavior of another class of compounds.

Estimates of BCFs for Bioconcentratable Chemicals in Oil Industry Effluents. Log K_{ow}/BCF Regressions have been developed by several investigators for PAH and related heterocyclic compounds. Even within these relatively narrow classes of nonpolar organic compounds, values for a and b are quite variable (Table 4-1). The most recent derivation was that of de Voogt *et al.* (1991). The regression equation for log BCF of a group of 19 parent PAH and related O-, N-and S-heterocyclic compounds determined empirically with the guppy (*Poecilia reticulata*) was:

$$\log BCF = 0.51 \log K_{ow} + 1.28 \qquad (4\text{-}3)$$

In order to assess the effect of use of different published regression equations to predict BCFs, equation 4-2 (Veith and Kosian, 1983) and equation 4-3 (de Voogt *et al.*, 1991) were used to estimate the BCF for the 18 evaluation compounds typical of oil industry effluents (Table 4-2). All BCF estimates were corrected for 3 percent lipids. The equation of Veith and Kosian (1983) gave lower predicted log BCF values than the equation of de Voogt *et al.* (1991) for compounds with log K_{ow}s less than about 6.0. For compounds with log K_{ow}s greater than about 6.0, the de Voogt *et al.* (1991) equation produced lower estimated values for BCF. The largest difference between BCFs estimated by the two equations was log 0.52 (about 3.3-fold).

Table 4-1. Values for a and b in the Equation, Log BCF = aLog K_{ow} + b, for PAHs and Heterocyclic Compounds. Number of Chemicals (n) and Correlation Coefficient (r) for the Equations are Given.

Compound Class	Species	n	a	b	r	Reference
PAH, O-, N-, S- heterocyclics	*Phoecilia*	19	0.51	1.28	0.91	de Voogt *et al.*, 1991.
PAH, 5- heterocyclics	*Daphnia*	6	0.66	-0.05	0.81	Eastmond *et al.*, 1984.
PAH	*Daphnia*	7	0.75	-0.44	0.92	Southworth *et al.*, 1978.
PAH	Fish spp.	11	0.83	-0.55	0.99	Mackay, 1982.
PAH	Goldfish	17	0.71	-0.92	0.98	Ogata *et al.*, 1984.
Alkyl-dibenzothrophenes	Clam	14	0.16	1.52	0.71	Ogata *et al.*, 1984.
PAH	*Mytilus*	5	0.96	-1.40	--	Pruell *et al.*, 1986.
PAH, Cl-hydrocarbons	Fish spp.	22	0.78	-0.55	0.95	Schüümann & Klein, 1988

A large fraction of the bioconcentratable chemicals identified in NPDES-permitted effluents by the analytical methods proposed in the DBG (Section III) have not been well characterized. It is unlikely that empirical physical/chemical data will be available for most of these compounds. Therefore calculated, rather than empirically-determined, K_{ow}s most likely will be used to predict BCFs, increasing the uncertainty of the resulting BCF values.

The BCF values produced by de Voogt *et al.* (1991) were based on exposures lasting only two to four days in which uptake and elimination rate constants were estimated by monitoring concentrations of chemicals in the exposure water (Banerjee *et al.*, 1984). Therefore, these estimated BCF values do not consider metabolism and active excretion of the PAH and heterocyclic compounds (Lech and Bend, 1980; Kleinow *et al.*, 1987). Longer exposures probably would have produced decreasing body burdens of hydrocarbons and lower values for BCF. However, for chemicals with log K_{ow}s greater than about 6, equilibrium may not be reached in a year or more (Hawker and Connell, 1985). PAHs of this type (those in Fraction 3 of the DBG) never reach equilibrium in the tissues of fish and other aquatic animals that have an active enzymatic system for metabolism and excretion of PAHs and certain other nonpolar xenobiotics.

Measured BCFs for several PAH in the water flea (*Daphnia magna*) were substantially lower than the values predicted by either the Veith and Kosian (1983) or De Voogt *et al.* (1991) formula (Newstead and Giesy, 1987). These very small animals may be able to eliminate accumulated PAH very rapidly by passive diffusion.

Table 4-2. Values for Log BCF for 18 Evaluation Chemicals Frequently Found in Oil Industry Effluents Estimated by the Regression Equation of Veith and Kosian (1983) (BCF_1) and Regression Equation of de Voogt *et al.* (1991) (BCF_2).

Chemical	Log K_{ow}	Log BCF_1	Log BCF_2
Fraction 1: Log K_{ow} 3.5 to 4.5			
Carbazole	3.84	2.23	2.75
1, 2, 4-Trimethylbenzene	3.85	2.24	2.76
2-Methylnaphthalene	3.86	2.25	2.77
n-Octane	4.00	2.36	2.84
Fluorene	4.18	2.50	2.93
Dibenzofuran	4.21	2.53	2.95
Dibenzothiophene	4.49	2.74	3.09
Fraction 2: Log K_{ow} 4.5 to 5.7			
Phenanthrene	4.57	2.81	3.13
Methyldibenzothiophene	4.86	3.03	3.28
n-Decane	5.01	3.16	3.36
1-Methylphenanthrene	5.08	3.21	3.39
Fluoranthene	5.22	3.32	3.46
Fraction 3: Log K_{ow} 5.7 to 8.2			
Chrysene	5.79	3.77	3.75
Benz(a)anthracene	5.90	3.86	3.81
Benzo(a)pyrene	6.40	4.26	4.06
5-Methylchrysene	6.42	4.27	4.07
7,12-Dimethylbenz(a)anthracene	6.93	4.67	4.33
n-Tetradecane	7.20	4.89	4.47

There is growing evidence that the BCF/K_{ow} relationship overestimates the BCF for chemicals with log K_{ow}s greater than about 5. The simple linear equations assume simple first-order kinetics for both uptake and elimination of chemicals (Spacie and Hamelink, 1982; Hawker and Connell, 1985). Thus, as K_{ow} increases, the uptake rate constant must increase. However, the point is reached when uptake rate is limited by the solubility of the chemical in water, the water and blood flow rates between and through the gill lamellae, the efficiency of transfer across membranes, and solubility of the compounds in lipids (Hawker and Connell, 1985; Gobas *et al.*, 1989; Banerjee and Baughman, 1991; Schmieder and Weber, 1992; Streit and Siré, 1993). The importance of biotransformation in controlling actual BCFs also may

increase with increasing K_{ow} (de Wolf *et al.*, 1992). McKim *et al.* (1985) and Pärt (1989) showed, in uptake experiments with isolated, perfused gills of rainbow trout, that uptake rate increases in a linear fashion with increasing log K_{ow} to a log K_{ow} of about 4 to 5. Uptake rates do not increase at higher values of K_{ow}, and even tend to decrease at log K_{ow}s of about 6 or greater.

Factors Affecting the BCF/K_{ow} Relationship

Many factors affect the BCF/K_{ow} relationship. Biotic factors include active metabolism and excretion of the chemical, animal species, lipid content and distribution in the animal (which often varies widely depending on age, sex, and stage of the reproductive cycle), feeding status, metabolic rate of the animal (which varies with the species, age, and nutritional status of the animal), and behavioral effects of experimental exposures (Spacie *et al.*, 1982; Zaroogian *et al.*, 1985; Jiminez *et al.*, 1987; Landrum *et al.*, 1992). Physical factors that affect the relationship between BCF and K_{ow} include temperature, salinity, and the physical form of the chemical in the water.

Predicted values for BCF and BAF provide a weak basis for regulation of chemicals in permitted effluents. Quite frequently, there is a poor correlation between predicted BCFs and actual tissue residues in aquatic animals in the field (e.g., Gossett *et al.*, 1983; Farrington and Westall, 1986). Our understanding of the processes of bioconcentration, and particularly bioaccumulation, are very incomplete. For the most part, empirical and theoretical studies of bioconcentration have utilized relatively few major taxa of aquatic organisms (mostly fish) and have focused primarily on a few classes of nonpolar organic chemicals (primarily organochlorine compounds). Many bioconcentration studies have used exposure concentrations, particularly of highly lipophylic chemicals (log $K_{ow} \geq 6$), that are greater than the aqueous solubility of the compound and many times higher than realistic environmental concentrations, producing anomalous BCFs (Geyer and Muir, 1993). In the field, there usually are large interspecies differences in tissue concentrations of nonpolar organic chemicals that cannot be explained simply as differences in tissue lipid concentrations or feeding habits (e.g., Gossett *et al.*, 1983; Farrington and Westall, 1986; Connollly, 1991). Zaroogian *et al.* (1985) showed that for some species of marine animals, such as oysters (*Crassostrea virginica*) and sheepshead minnows (*Cyprinodon variegatus*), the agreement between predicted and measured BCFs was low ($r^2 = 0.29$ and 0.42, respectively). For all

species evaluated, calculated BCFs usually overestimated the measured BCF values. This may be due in part to the fact that only chemicals that are in true solution in the water are modeled by the BCF equations. Much of the nonpolar organic chemicals of environmental concern in natural water bodies are sorbed or complexed with dissolved and particulate organic matter in the water column.

All models relating log K_{ow} to BCF assume that the chemical in the water, food, and sediments is in a readily bioavailable form. Relationships between log BCF and log K_{ow} are assumed to be linear and based on first-order uptake and elimination kinetics. As discussed below, these simplifications of the model may introduce substantial error into the prediction of BCFs.

The effluent option does not consider the physical form of potentially bioconcentratable organic chemicals in the water. The form of the chemical in the water is particularly important in determining its bioavailability (Spacie and Hamelink, 1982). Hydrophobic chemicals have a high affinity for sorption to or complexation with particles and dissolved/colloidal organic matter in the water. Several studies have shown that sorption/complexation of dissolved nonpolar organic chemicals increases with increasing K_{ow}, decreasing the bioavailability of chemicals to aquatic organisms (Spacie and Hamelink, 1982; Leversee *et al.*, 1983; McCarthy and Jiminez, 1985a; McCarthy *et al.*, 1985; Farrington, 1991). Eadie *et al.* (1990) showed that approximately 50 percent of benzo(a)pyrene added unfiltered to Lake Michigan water rapidly became sorbed to natural particulate and dissolved organic matter in the water. The extent of sorption/complexation varied seasonally in response to varying concentrations of dissolved and particulate matter in the water.

Organic matter in the water column, primarily dissolved humic substances and colloidal organic material with molecular weights in the range of about 500 to 10,000 daltons (Wijayaratne and Means, 1984; Whitehouse, 1985), tends to complex reversibly with dissolved nonpolar organic chemicals, increasing their apparent solubilities (Chiou *et al.*, 1987; Shinozuka *et al.*, 1987) and decreasing sorption to solid phases (Caron *et al.*, 1985) and bioavailability to aquatic organisms (Servos *et al.*, 1989).

Water that has been in contact with petroleum products (e.g., many of the effluents from oil industry operations) has a strong tendency to contain small amounts of very finely dispersed

oil droplets, even after treatment (Neff *et al.*, 1987). The hydrocarbons in these droplets are not as bioavailable as hydrocarbons in true solution (Neff and Anderson, 1981). Estimates of the bioconcentration potential of the chemicals in an effluent will be greatly exaggerated if all nonpolar organic chemicals extracted from an unfiltered effluent sample are assumed to be in true aqueous solution.

Theoretically, complexation of a dissolved nonpolar organic compound with dissolved or colloidal organic matter is completely reversible. The slope of the sorption isotherm should be the same as the slope of the desorption isotherm. McCarthy and Jiminez (1985a) reported that this is the case for benzo(a)pyrene and its association with dissolved humic material following association times of up to seven days and dissociation times of up to four days. However, Johnsen (1987) reported that when polycyclic aromatic hydrocarbons are incubated with natural aquatic humic substances for periods of up to 70 days, desorption of the hydrocarbons from the humic substance decreases with time. The extent of irreversible binding increases with increasing hydrophobicity and decreasing solubility of the aromatic hydrocarbons. The concentrations of dissolved organic matter from terrestrial origin are high enough in runoff, many fresh water bodies and coastal/estuarine waters, and the pore water of sediments to bind significant amounts of polycyclic aromatic hydrocarbons (Whitehouse, 1985).

Suspended particulate organic matter/water and dissolved organic matter/water partition coefficients are similar to octanol/water partition coefficients for several PAHs (Broman, 1990). Therefore, dissolved and suspended particulate matter compete directly with aquatic plants and animals for uptake of PAH and other hydrophobic chemicals from solution in the ambient water. The analytical methods proposed in the draft guidance will not necessarily distinguish between the fraction of total nonpolar organic chemicals in the effluent or receiving water that is sorbed/complexed and, therefore, not readily bioavailable, and the fraction that is in true solution and bioavailable.

Metabolism and Excretion of Accumulated Chemicals

Most models assume that active metabolic degradation and excretion of accumulated chemicals are negligible. The model relating BCF to K_{ow} assumes that both the uptake rate constant (k_1) and the elimination rate constant (k_2) are directly correlated to K_{ow} (Spacie and

Hamelink, 1982; Hawker and Connell, 1985). The only mechanism in the model for elimination of chemicals from tissues is through partitioning between body lipids and body and external water with passive outward diffusion. Passive elimination through equilibrium partitioning is very slow for high molecular weight compounds with high K_{ow}s and low aqueous solubilities. If active metabolism and excretion do not occur, these compounds may accumulate to high concentrations in aquatic animal tissues. However, most aquatic animals have the ability to metabolize some nonpolar organic compounds and convert them to more polar, soluble byproducts that are rapidly excreted by active or passive means (Stegeman, 1981; Kleinow *et al.*, 1987; Stegeman and Kloepper-Sams, 1987; Pritchard and Bend, 1991; Goksøyr and Förlin, 1992).

When fish and some higher invertebrates are exposed to petroleum hydrocarbons or certain other nonpolar organic chemicals, such as polychlorinated biphenyls and polychlorinated dibenzodioxins, dissolved or dispersed in the water column, in food, or in sediments, an enzyme system, known as the cytochrome P450 mixed function oxygenase system (MFO), is induced (its activity is increased) in the liver and some other tissues (Stegemen, 1981; Stegeman and Kloepper-Sams, 1987). This enzyme system aids in the breakdown and excretion of many bioaccumulated nonpolar organic chemicals via the bile and urine (Pritchard and Bend 1991).

Metabolic degradation and excretion of certain nonpolar organic compounds may substantially increase the elimination rate constants for the chemicals from tissues, decreasing the equilibrium BCF. Werner and Kimerle (1982) reported that the empirically determined BCF for a C_{12}-alkylbenzene in bluegills was 35, compared to a predicted value of 6,300. The lower actual than predicted BCF was attributed to metabolic breakdown of the compound. Lu *et al.* (1977) showed that mosquitofish (*Gambusia affinis*) in a freshwater mesocosm containing ^{14}C-benzo(a)pyrene in solution accumulated much less radioactivity if the mesocosm water was also dosed with an excess of piperonyl butoxide, a powerful inhibitor of MFO, than if the inhibitor was not present. The BCF for benzo(a)pyrene in the absence of piperonyl butoxide was 30 after 33 days, compared to 140 in the presence of the MFO inhibitor. By comparison, BCFs in pond snails (*Physa* sp.), which have only a low, uninducible activity of MFO, were 4,860 and 7,520, respectively. The large differences in BCFs for the different species and treatments were attributed to large differences in MFO activity.

Southworth *et al.* (1980) showed that bioconcentration of three azaarenes (nitrogen-substituted heterocyclic compounds of the type sometimes found in oil industry effluents) by fathead minnows was much less than predicted by K_{ow}/BCF models. Bioconcentration of these compounds also was much less in the fish than in *Daphnia pulex*. The authors showed that these differences were due to the rapid metabolic alteration of the azaarenes in the fish tissues.

Kayal (1991) estimated the distribution of three PAH in the Brisbane River, Australia, based on a fugacity model and compared the results to actual measurements. There was reasonably good agreement between predicted and observed phase distributions of pyrene, benzo(a)pyrene, and coronene in water, suspended particles, and sediments, but not in fish tissues (Table 4-3). The fugacity model used by Kayal predicted that 0.05 percent of all three PAH should be in the fish. Only 0.0003 percent of the pyrene and none (below detection limit) of the benzo(a)pyrene and coronene were in the fish. The results of these studies and the field studies of Broman (1990), discussed below, indicate that natural populations of fish in an aquatic environment containing near-background concentrations of PAHs are able to metabolize PAH and heterocyclic compounds fast enough to significantly decrease their net bioaccumulation in tissues. K_{ow}/BCF and fugacity models always overestimate equilibrium BCFs and BAFs for such compounds. Even shortly after a large oil spill in Alaska, salmon and other commercial and subsistence fisheries species from the spill area contained only traces of PAHs in their tissues (Varanasi *et al.*, 1990). The fish contained high concentrations of PAH metabolites in their bile, indicating rapid metabolism and excretion of the PAHs accumulated from the spilled oil (Krahn *et al.*, 1992).

Similar results have been obtained for other classes of nonpolar organic chemicals, lending additional support to the conclusion that nonpolar organic chemicals that are actively metabolized do not accumulate to high concentrations in aquatic food webs. Lower chlorinated polychlorinated dibenzo-*p*-dioxins and dibenzofurans do not bioaccumulate in the tissues of fish to the concentrations predicted based on their K_{ow}s (Opperhuizen and Sijm, 1990). The authors showed that this was due to biotransformation of the compounds by the MFO system. Similar results have been obtained for coplanar polychlorinated biphenyls (Boon *et al.*, 1989), chlorinated anilines (de Wolf *et al.*, 1992), and organophosphorus pesticides (de Bruijn and Hermans, 1991).

Table 4-3. Comparison of observed and predicted distribution of PAHs in the Brisbane River Estuary (From Kayal, 1991).

	% Associated with Each Phase							
	Water		Particulates		Sediments		Fish	
PAH	O*	P*	O	P	O	P	O	P
Pyrene	0.4	6.2	1.0	2.4	98.6	91.3	0.0003	0.05
Benzo(a)pyrene	0.7	0.9	1.1	2.6	98.4	96.4	ND	0.05
Coronene	ND	0.2	0.3	2.6	97.1	97.1	ND	0.05

*O=Observed, P=Predicted

In summary, there are a great many uncertainties surrounding estimation of BCFs based on linear regression equations between log BCF and long K_{ow}. These uncertainties can produce a large amount of variation in predicted BCFs for different compounds. Major sources of variation in estimating BCFs arise from violations of the simplifying assumptions underlying the first-order linear regression model, variability in the values for the constants, a and b, in regression equations derived from different groups of chemicals, wide variations in the published values for K_{ow}, variability in the fraction of the total amount of a chemical in an effluent that is in true solution and therefore bioavailable, and lack of consideration of the effects active metabolism and excretion on the release rates of some nonpolar organic chemicals from animal tissues. It is difficult to estimate the effects of these uncertainties, taken together, on the accuracy of predicted BCFs. However, errors of one or more orders of magnitude are likely.

BIOACCUMULATION OF CHEMICALS FROM FOOD

Accumulation Mechanisms

Thomann (1989) and others have shown that as log K_{ow} increases above a value of about 5, the efficiency of bioconcentration of a nonpolar organic chemical from the water alone decreases, and the importance of food as a source of the chemical increases. Thus, for hydrophobic chemicals with a log K_{ow} greater than about 5, the more appropriate measure of net accumulation is the bioaccumulation factor (BAF) rather than the BCF.

For moderately hydrophobic compounds (log K_{ow} 4 to 6), uptake rate constants are relatively insensitive to hydrophobicity (Gobas *et al.*, 1986; 1989), and there is a good correlation between K_{ow} and bioaccumulation. However, for chemicals with log K_{ow} greater than about 6, the relationship between K_{ow} and assimilation efficiency breaks down, resulting in variable absorption efficiencies for these highly hydrophobic compounds. These very hydrophobic chemicals are accumulated much more efficiently from food than from the water (Bruggeman *et al.*, 1984). Their aqueous solubilities are so low that very little of the free, uncomplexed compound can exist at the external water/permeable membrane interface (e.g., gills) for partitioning into the animal. Higher concentrations of the chemical in gut fluid may be attained by a digestion/concentration mechanism described by Paterson and Mackay (1985, 1987) and Clark and Mackay (1991). For highly hydrophobic compounds with K_{ow}s greater than about 6, elimination through the gills becomes so inefficient that the main avenue of excretion is via the feces, probably as metabolites in bile (if the chemical can be metabolized) (Gobas *et al.*, 1989) and the main mechanism for the decrease in concentration of chemical residues in the tissues is by growth dilution (Thomann, 1989).

As molecular size and hydrophobicity increase, partitioning into the tissue lipid phase decreases, due to hinderance of diffusion of the large molecules into lipid membranes or to reduced solubility of these compounds in lipids (Banerjee and Baughman 1991). Chemicals with molecular weights greater than about 600 or log K_{ow}s greater than about 8 to 9 are absorbed very inefficiently, if at all, from the gut of fish, and so are not transferred through aquatic food chains.

The Food Chain Multiplier

The BAF is difficult to measure directly or to estimate. The approach recommended in the DBG is to multiply the BCF by a food chain multiplier (FM) to generate an estimate of the BAF. The FM table was developed from a statistical model developed by Thomann (1987). The values for FM in Table 4.1 of the DBG exceed a value of 1.0 (a value of 1.0 indicates that no significant net trophic transfer and biomagnification is taking place) at or above a log K_{ow} of 4.1 for all trophic levels. Thus, nearly all chemicals in the three fractions in the analysis scheme (log K_{ow} range of 3.5 to 8.2) will require application of a food chain multiplier. The FM becomes a quantitatively significant factor in estimating bioaccumulation when it reaches a value of two or higher (more than half the tissue residues come from food)

at all trophic levels, which is the case for chemicals with values for log K_{ow} greater than about 5.

There are several serious technical problems with this approach to estimating the BAF. Most aquatic food webs are complex and variable, making it difficult to assign a particular species to a definite trophic category. More important, there is a wide variability in the efficiency of absorption of different nonpolar organic chemicals from the digestive tracts of aquatic animals. In addition, species differences in absorption efficiency have been documented but not fully categorized. Many aquatic animals, particularly those at higher trophic levels, can metabolize and actively excrete some accumulated nonpolar organic chemicals. Some metabolism may occur in the gut, even before the chemical is assimilated (Van Veld *et al.*, 1987), contributing to low absorption efficiency. Because of rapid excretion, food chain transfer of some chemicals, particularly the hydrocarbons characteristic of oil industry effluents, does not contribute significantly to concentrations of some nonpolar organic chemicals in the tissues of aquatic animals at upper trophic levels.

The DBG offers an alternative to use of the FM; experimentally determined BAFs can be used in place of BCF x FM. However, there are very few data in the scientific literature that provide empirically-derived values for BAFs following prolonged exposure (long enough to allow full induction of the MFO system) to aromatic and heterocyclic compounds with bioconcentration potential. BAFs are very difficult to determine empirically because so many factors affect uptake of chemicals from food, sediments, and water and elimination of chemicals by active and passive means in fish. In addition, the composition of the average diet of feral aquatic animals rarely is known.

Aquatic Food Webs

Three trophic steps are included in the estimation of FM in the DBG. Trophic step 1 is from primary producers to primary consumers (plants to herbivores); step 2 is from secondary consumers (herbivores) to predators; the third step is from lower level predators to top predators. The DBG recommends using the third trophic step (trophic level 4) for most calculations because the top predators usually are the preferred commercial and recreational species consumed by man (at least in freshwater ecosystems). If the ecosystem under investigation has fewer than three trophic steps or the species of concern is known to be at a

lower trophic level (e.g., oysters or clams), the FM for fewer than three trophic steps can be used. An empirically-derived BAF, if it is available for the ecosystem under investigation and "has been measured accurately" (page IV-5 in DBG), may be used in place of the FM*BCF term.

The complexity of freshwater, estuarine, and marine food chains varies widely. Many of the lakes of glaciated regions of temperate northern North America have relatively simple food chains, characterized by few trophic steps and few species at each step (Oliver and Niimi, 1988; Rasmussen *et al.*, 1990; Whittle *et al.*, 1992). In these simple food webs, there is a factorial increase in tissue residues of certain non-metabolizable organochlorines (polychlorinated biphenyls, dibenzodioxins, and dibenzofurans) with each successive trophic step. In many cases, contaminant concentrations in tissues of fish (usually lake trout) at the highest trophic level increased as the number of trophic steps in different lakes increased (Rasmussen *et al.*, 1990). Similar simple food webs have been described in oligohaline regions of the Baltic Sea (Broman, 1990). Food chain models applied to these relatively simple lake food chains provide reasonably good (within an order of magnitude) estimates of the distribution of certain poorly metabolized nonpolar organic chemicals, such as PCBs (Gobas, 1993). Application of the food chain multiplier seems appropriate in most cases where the food chain in the receiving water environment is known to be simple and where the chemicals of concern are not readily biodegraded at one or more steps in the food chain.

However, food chains and trophic relationships in many aquatic, estuarine, and marine communities are very complex and only partly understood. Simple food chains, hierarchies of monophagous consumers (Paine, 1980; Gray, 1981), are very rare, particularly in marine ecosystems. Instead, most consumers are polyphagous, feeding on a variety of foods, often from different trophic levels. Groupings of polyphagous consumers constitute a food web. Even the concept of trophic levels in most aquatic ecosystems is inaccurate. For example, Darnell (1961), in describing the trophic relationships in coastal Louisiana, argued that most estuarine/freshwater consumers derive nutrition from numerous prey categories, most of which cannot readily be assigned to any particular trophic category. For instance, the grass shrimp (*Palaemonetes pugio*), a common estuarine species along the U.S. coasts of the Gulf of Mexico and the Atlantic, can function as a herbivore, detritivore, or carnivore, depending on prey availability (Welsh 1975). In fact, most of the consumers in estuarine food webs practice two or three different modes of feeding (Simenstad *et al.* 1990).

For most animals at higher trophic levels in aquatic and marine food chains, actual diet at any particular time depends in large part on availability of different types of prey. For example, winter flounder (*Pseudopleuronectes americanus*) in Charlestown Pond, Rhode Island, consumed a wide variety of benthic prey, including crustaceans, polychaetes, tunicates, mollusks, and plant material. Diet composition varied seasonally, depending on availability of different prey items (Worobec 1984). In most seasons, the most abundant foods in winter flounder stomachs are detritus and polychaetes. However, particularly in the spring, a large part of the diet includes benthic crustaceans and grasses. Thus, a particular species may function at different trophic levels depending on local conditions and food availability.

The polyphagous nature of most aquatic, estuarine, and marine animals makes it difficult to apply simple FM estimates to predict the concentration of bioconcentratable chemicals in top consumers or at other trophic levels. Because the concentrations of nonpolar organic chemicals in tissues of aquatic animals vary widely from one species to another, bioaccumulation of nonpolar chemicals from the food is related to the mean concentration of the chemicals in the total diet and the relative efficiencies of accumulation of the chemicals from the different food species. Application of the level 3 FM to estimate bioaccumulation in a complex food web usually will overestimate uptake in most animals in the food web.

Uptake Efficiency from the Gut

As with uptake from water and sediments, bioaccumulation of nonpolar organic chemicals from food is a physico-chemical partitioning process between the organism's body fat and body water (Gobas *et al.* 1986). Active transport across membranes probably is not important.

In fish, and possibly in invertebrates as well, the rate and efficiency of bioaccumulation of nonpolar organic chemicals from food seems to increase with weight (size) of the animal (Griesbach *et al.*, 1982, Laake *et al.*, 1982, cited by Ekelund, 1989). The reason for this is unclear, but could be related to a lower retention efficiency of materials in the gut of smaller animals or to lower elimination rates in larger animals (Ekelund, 1989). A positive correlation between animal size and tissue concentrations of PCBs, DDT, and hexachlorobenzene has been reported for cod (Schaefer *et al.*, 1976), herring (Perttila *et al.*,

1982), and salmon (Falandysz, 1982). No such relationship has been reported for the saturated, aromatic, and hetero-substituted hydrocarbons sometimes found in oil industry effluents.

Not all of a nonpolar organic chemical ingested in the food is absorbed. Some of the chemical remains in the gut and is eliminated in the feces or is metabolized by enzymes in the gut epithelium before it can be assimilated. The importance of uptake from water or food in the contamination of aquatic food chains depends in large part on the efficiencies of chemical uptake by the two routes. The same physical-chemical processes govern uptake by both routes, but the environment at the uptake site (gill or general body surface for uptake from water, and gastrointestinal tract for uptake from food) are different.

Gobas *et al.* (1988) studied the relationship between the uptake efficiency of nonpolar organic chemicals from food (E_0) and their K_{ow}s. As a general rule, E_0 falls with increasing K_{ow} (Figure 4-1). The Equation derived for this relationship by Gobas *et al.* (1988) is:

$$1/E_0 = 5.3x10^{-8}K_{ow} + 2.3 \qquad (4\text{-}5)$$

As can be seen in Figure 4-1, there is a large amount of variability in the relationship between E_0 and log K_{ow}. Factors other than hydrophobicity and lipophilicity affect absorption efficiency of nonpolar organic chemicals.

Niimi and Oliver (1988) have evaluated the relationship between E_0 in fish and molecular weight (MW) and molecular volume (MV) of several halogenated nonpolar organic chemicals (Figure 4-1). There was little relationship between MW and E_0. There was a slightly more consistent inverse relationship between MV and E_0 (Niimi and Oliver, 1988) (Figure 1). None of the three indices, K_{ow}, MW, or MV, provide a relationship to E_0 that can be used to consistently estimate the absorption efficiency of nonpolar organic chemicals from food by fish. However, all three parameters affect absorption efficiency. Both MW and MV probably are poor predictors of E_0 for all but the largest chemicals because they do not consider the shape of the chemical molecules. The analysis of Niimi and Oliver (1988) suggests that chemicals with linear or planar configurations, such as n-alkanes and coplanar

PCBs, are absorbed more efficiently than more condensed, globular molecules with similar molecular volumes. Shaw and Connell (1984) showed, for a group of PCBs, that the distribution and positions of chlorines on the biphenyl molecule affected adsorption characteristics of PCB congeners onto biological surfaces, affecting uptake rates and efficiencies. Planar PCBs were adsorbed onto biological surfaces more efficiently than nonplanar congeners.

Other factors that may affect assimilation efficiency of nonpolar organic chemicals from the gut include ingestion rate and the quality of the food (Clark *et al.*, 1990; Parkerton *et al.*, 1993). Usually, there is a roughly inverse relationship between the rate of food ingestion and assimilation efficiency for both nutrients and nonpolar organic chemicals from the gut. Most laboratory studies of assimilation efficiencies use purified laboratory diets spiked with nonpolar organic chemicals. Both the physical form of nonpolar organic chemicals as well as the nutritional quality of the food may affect assimilation efficiency.

There is growing evidence that the route of uptake of a nonpolar organic chemical may have a profound effect on its distribution and persistence in the tissues of the animal. A large fraction of the PAHs that are present in the food of fish are metabolized by an active, inducible MFO system in the intestinal epithelium before they can be absorbed (Vetter *et al.*, 1985; Van Veld *et al.*, 1987, 1988; Varanasi *et al.*, 1989). That fraction of the PAH that is absorbed is carried by the hepatoportal circulation directly to the liver where most is metabolized by the active MFO system there (Van Veld *et al.*, 1988; Lemaire *et al.* 1992). PAH metabolites produced in the liver are excreted via the gall bladder into the intestine. The small amount of PAH and PAH metabolites escaping the hepatoportal circulation is excreted by the kidneys. Little or no PAHs absorbed from the gut accumulate in muscle or other tissues of fish. On the other hand, PAHs and other nonpolar organic chemicals that are accumulated across the gills are transported in the general circulation throughout the body and may accumulate in several tissues, particularly well perfused tissues rich in lipids.

Food Chain Models

Empirical relationships between bioaccumulation and K_{ow}, MW, and MV, although not absolute, have been used as the basis for mathematical models of transfer and biomagnification of nonpolar organic chemicals in marine and freshwater food chains (e.g.,

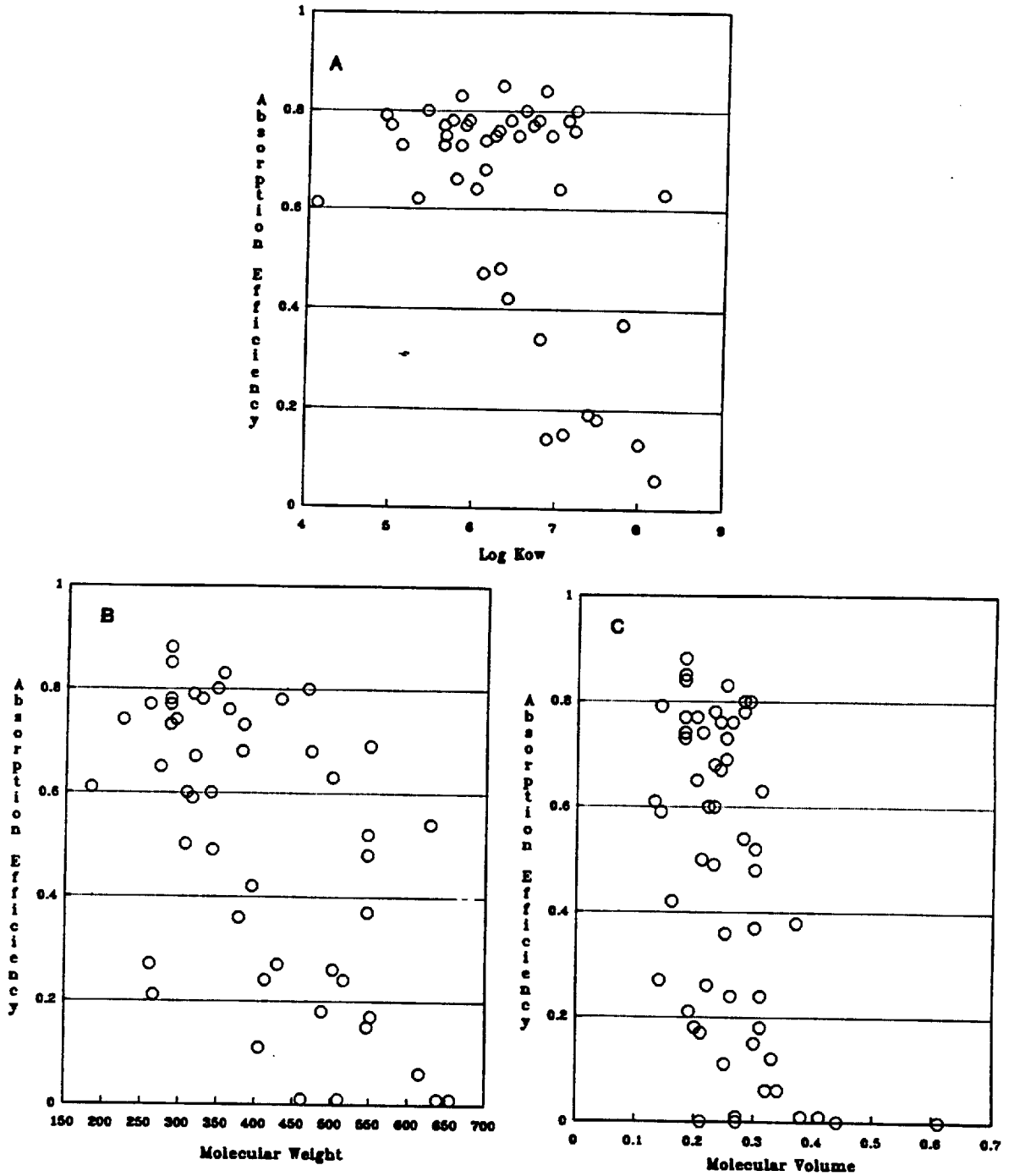

Figure 4-1. The relationship between K_{ow}(A), molecular weight (B), and molecular volume (C) of nonpolar organic chemicals and the efficiency of absorption from the gut of salmonid fish. From Gobas *et al.* (1988), Niimi and Oliver (1988), and Clark *et al.* (1990).

Clark and Mackay 1991; Connolly, 1991; Gobas, 1993). Thomann (1989) developed and evaluated a model to estimate the concentration of organic chemicals in a simple generic freshwater food chain. His model was based on the premise that there is a correlation between the K_{ow} of a nonpolar organic chemical and its uptake efficiency from water, excretion rate, and assimilation efficiency from food. Growth of the consumer may affect the uptake predicted by simple partitioning by a factor of 2 to 5. Estimated efficiencies of uptake from water and food also have important effects on estimates of BAF for chemicals. The model predicts that food chain effects are not significant for nonpolar organic chemicals with log K_{ow}s up to about 5. For chemicals with log K_{ow}s between 5 and 7, trophic transfer is predicted to be a major source of body burdens in animals at higher trophic levels. The potential for trophic transfer and biomagnification of chemicals with log K_{ow}s greater than 7 is predicted to depend on the assimilation efficiency of the chemical from food and the ability of primary producers, particularly phytoplankton to bioconcentrate the chemical.

Food Chain Transfer of PAHs

Most PAHs with log K_{ow}s greater than about 5 are not absorbed efficiently through the gut of aquatic animals. Gut absorption efficiency (E_0) for these compounds ranges from essentially zero (for pyrene and chrysene) to 0.23 (for benzo[a]pyrene) (Table 4-4). Because of their low absorption efficiencies and rapid metabolism and excretion (discussed above), these chemicals are not transferred efficiently through aquatic food chains and do not biomagnify. This conclusion is supported by many laboratory and a few field studies. Laboratory studies have shown that small amounts of PAH can be accumulated from food by polychaete worms (McElroy *et al.*, 1990), bivalve molluscs (Dobroski and Epifanio, 1980), crustaceans (Corner *et al.*, 1976; Lee *et al.*, 1976, O'Connor and Squib, 1989), and fish (Niimi and Palazzo, 1986; Niimi and Dookhran, 1989; O'Connor *et al.*, 1988; McElroy *et al.*, 1991). In no case did the test animals accumulate the PAH in their tissues to concentrations higher than those in their food. These results, as Niimi and Dookhran (1989) concluded, indicate that biomagnification of PAH in aquatic food chains is unlikely.

The limited field studies of PAH in aquatic food chains support the conclusion that **PAHs do not biomagnify**. Broman (1990) and Broman *et al.* (1990) studied the distribution of 19 PAHs (primarily of pyrogenic origin), in a simple food chain from the Baltic Sea consisting of seston (nonliving suspended particles >0.045 μm), blue mussels (*Mytilus edulis*) and

common eider ducks (*Somateria mollissima*). The major food of juvenile eider ducks in the Baltic is mussels. Concentrations of the different PAHs were quite different from one another at different levels in the food chain. This was attributed by the authors to different capabilities of mussels and ducks to metabolize and excrete the different PAHs.

Table 4-4. Efficiency of Absorption of Nonpolar Organic Chemicals from Food by Marine and Freshwater Animals

Compound	Species	Absorption Efficiency	Reference
Naphthalene	*Onchorhynchus kisutch*	0.03	Roubal *et al.* 1977
Fluorine	*Salmo gairdneri*	0.14	Niimi and Palazzo 1986
Phenanthrene	*Salmo gairdneri*	0.04	Niimi and Palazzo 1986
2-Methylanthracene	*Salmo gairdneri*	0.14	Niimi and Dookhran 1989
9-Methylanthracene	*Salmo gairdneri*	0.01	Niimi and Dookhran 1989
Pyrene	*Salmo gairdneri*	0.00	Niimi and Palazzo 1986
Fluoranthrene	*Salmo Gairdneri*	<0.01	Niimi and Palazzo 1986
Benz(a)anthracene	*Salmo Gairdneri*	<0.01	Niimi and Palazzo 1986
7,12-dimethylbenz (a)anthracene	*Salmo Gairdneri*	0.02-0.12	O'Connor *et al.* 1988
Chrysene	*Salmo Gairdneri*	0.00	Niimi and Palazzo 1986
Benzo(a)pyrene	*Mercenaria mercenaria*	0.054	Dobroski an Epifanio 1980
	Salmo gairdneri	0.02-0.12	O'Connor *et al.* 1988
	Pseudopleuronectes americanus	0.23	McElroy *et al.* 1991
Benzo(a)pyrene7,8-dihydrodiol	*Pseudopleuronectes americanus*	0.15	McElroy *et al.* 1991

Approximately 80 percent of the PAHs accumulated by the mussels and virtually all the PAHs accumulated by the ducks were accumulated from the food, demonstrating the importance of trophic transfer in accumulation of PAH in this simple natural food chain. However, concentrations of all PAHs were greater in seston than in the tissues of the ducks,

irrespective of whether PAH concentrations in tissues were expressed on a lipid weight or whole tissue weight basis, indicating that biomagnification was not occurring. PAH concentrations decreased with increasing trophic level in this simple natural food chain.

In similar food chain studies in this simple Baltic food chain, Broman *et al.* (1992) and Rolff *et al.* (1993) showed that isomers of polychlorinated dibenzodioxins and dibenzofurans that could be readily metabolized did not biomagnify, whereas isomers that were resistant to metabolism did biomagnify. Opperhuizen and Sijm (1990) obtained similar results in laboratory studies. These results show that nonpolar organic chemicals that are poorly assimilated from the food and that are readily metabolized and excreted do not biomagnify.

The field studies confirm the conclusions of the laboratory studies that **PAHs, and probably also saturated hydrocarbons and heterocyclic compounds, such as those identified in permitted effluents from oil industry operations, do not accumulate to high concentrations in freshwater and marine food webs and do not biomagnify.** Alkanes are readily metabolized by fish to fatty acids that are then incorporated into tissue lipids (Cravedi and Tulliez, 1986). Hetero-aromatic hydrocarbons are metabolized by the enzyme system responsible for metabolism of PAH. The importance of food as a source of the small amounts of petroleum-derived hydrocarbons in the tissues of populations of aquatic organisms is moderate and variable, even for the higher molecular weight, highly hydrophobic PAHs. Therefore, application of a food chain magnification factor (FM) to estimated BCFs to derive an estimated BAF is inappropriate for the chemicals found most frequently in oil industry effluents.

SUMMARY

The DBG recommends the use of a linear regression equation developed by Veith and Kosian (1983) between log BCF and log K_{ow} to estimate the BCF of bioconcentratable chemicals in effluents. For chemicals with a log K_{ow} greater than 4.1, the DBG recommends multiplying the predicted BCF by an FM to account for accumulation of bioconcentratable chemicals from food.

- The extremely conservative assumptions used in the DBG greatly overestimate equilibrium BCFs and resulting tissue residues. This is especially true for chemicals in oil industry effluents.

- Bioconcentration (defined as uptake of a chemical from the ambient water) is a completely artificial parameter that should not be used as the basis of a model to predict BCFs in wild populations of aquatic animals. Natural populations of aquatic animals are exposed simultaneously to potentially bioconcentratable nonpolar organic chemicals in the ambient water, food, and sediments.

- There are many published versions of the BCF/K_{ow} regression equation derived with different numbers and classes of nonpolar organic chemicals spanning different K_{ow} ranges. The values for the constants, a and b, in these equations vary widely; depending on the equation used to estimate the BCF for a particular compound, results may vary by a factor of five or more.

- Linear regression equations of log BCF and log K_{ow} are inappropriate for saturated and aromatic hydrocarbons that are characteristic of the potentially bioconcentratable fraction of oil industry effluents. Even for chemicals for which the linear regression models may be appropriate, the wide variability and uncertainty in predicting BCFs from K_{ow} indicate that they are not an appropriate basis for regulatory controls.

- Published values of K_{ow} vary widely (occasionally by an order of magnitude) for many nonpolar organic compounds. Predicted BCFs can vary by two orders of magnitude or more depending on the value of K_{ow} used in the regression equation.

- There often is a poor correlation between predicted BCFs and actual tissue residues in aquatic animals in the field because the bioconcentration models upon which the effluent option is based do not consider the physical forms of potentially bioconcentratable chemicals in the water or the ability of fish and many aquatic invertebrates to rapidly metabolize and excrete many accumulated chemicals. Chemicals sorbed to or complexed with dissolved or particulate organic matter in the water are much less bioavailable than chemicals in true solution. Metabolic degradation and excretion of certain nonpolar organic compounds, including PAHs, substantially increases the elimination rate constant for the chemicals from tissues, decreasing the equilibrium BCF.

- Saturated and aromatic hydrocarbons, even those with log K_{ow}s greater than 5.0, do not accumulate efficiently in aquatic food chains because of poor assimilation from the gut and rapid metabolism and excretion from the tissues of most aquatic animals. PAHs do not biomagnify in aquatic food webs. Therefore, food chain multipliers (Fms) are inappropriate for these chemicals.

- Linear regressions between log BCF and log K_{ow} may not be reliably used to estimate BCF or BAF values for chemicals with log K_{ow}s greater than about 5.0. Moreover, the use of such equations will overestimate the BAF hydrocarbons and other organic chemicals that are rapidly metabolized.

Section 5
ASSESSMENT OF BIOCONCENTRATABLE CONTAMINANTS

Chapter III of the DBG provides a detailed description of the two assessment options for identifying bioconcentratable chemicals in permitted effluents. It also provides a description of methods for identifying bioconcentratable chemicals in sediments. The major focus of this review of Chapter III will be on the "effluent option" for identifying bioconcentratable chemicals, because this option has a more direct bearing on the loadings to a receiving water from an individual discharger, whereas the tissue residue option would show the long-term averaged concentrations due to exposure to all sources. However, brief discussions of the tissue residue option and the sediment assessment methods are included, because one or both could be required by EPA for a particular effluent. The analytical chemical methods themselves will not be discussed in detail here.

A brief discussion follows on the general approach recommended in the DBG for analyzing effluent, tissues, and sediments for bioconcentratable chemicals. Emphasis is placed on the applicability of the proposed methods for identifying the hydrocarbons that are the most abundant potentially bioconcentratable chemicals in oil industry effluents. This discussion is followed by a detailed description and critique of each of the proposed steps in the performance of the effluent option for assessment of bioconcentratable chemicals. A brief discussion follows of the important features and limitations of the tissue residue option and recommended methods for assessing bioconcentratable chemicals in sediments.

ANALYSIS OF BIOCONCENTRATABLE CHEMICALS IN WATER AND TISSUES

Section 2.7 of the DBG provides a rationale for the analytical methods recommended for identifying and quantifying bioconcentratable chemicals in effluent, tissue, and sediment samples. The objective of the chemical analyses is to identify any bioconcentratable chemicals in samples, not to determine the concentration in the samples of pre-determined target analytes. Typically, a capillary gas chromatography/mass spectrogram of an extract of the nonpolar organic fraction of a complex effluent or tissue sample contains a very large number of peaks. However, of the tens of thousands of natural and anthropogenic chemicals that could be present in a nonpolar organic fraction analyzed by gas chromatography, only a few thousand have been characterized by mass spectrometry and are in standard mass spectra

libraries. More important, no more than a few hundred of these thousands of nonpolar organic chemicals are listed in toxicology and risk assessment databases or have water quality criteria.

In the proposed analytical scheme, assuming that the analytical methods work, only a fraction of the chemicals in an effluent sample or tissue sample will receive a definite identification by the analytical method. The analytical searching methods proposed in the DBG are not likely to identify many new compounds, not already known to be present under some circumstances in oil industry effluents, for which sufficient toxicological and environmental fate data are available to develop a criterion concentration. Therefore, **the difficult and expensive methodology is not useful for regulating bioconcentratable chemicals in oil industry effluents.**

A better approach would be to use a target analyte approach to first identify different major classes of nonpolar organic chemicals with bioconcentration potential in effluents, then identify and quantify the most abundant components of each fraction, and finally develop criteria for the most abundant bioconcentratable components of the effluent for which adequate toxicological data are available.

The analytical detection limits for modern capillary gas chromatography with quantification by mass spectrometry in the selected ion mode are very close to the concentration decision points for effluent, tissue, and sediment samples (100 ng/L, 5 μg/kg wet wt., and 5 μg/kg dry wt., respectively). Because of sample size constraints and matrix interference problems, particularly for large sample masses, detection limits for nonchlorinated compounds in tissue and sediment samples may be higher than the 5 μg/kg (parts per billion) concentration decision points for these matrices; usually they are approximately 50 μg/kg. Experienced, high-quality analytical chemical laboratories usually can obtain detection limits for individual PAHs in water of about 2 to 5 ng/L (parts per trillion), though reporting limits usually are set at about 10 ng/L, one-tenth of the effluent concentration decision point. The presence of interfering compounds in the effluent sample may increase these detection and reporting limits substantially.

The analytical methods proposed in the DBG for effluents and tissues require expensive, complex analytical instrumentation and are difficult to apply. Although the extraction method is simpler for tissues than for water, analysis of tissues is made more difficult than that of water by the greater difficulties in processing and extracting tissue samples. The extraction and cleanup methods may degrade some analytes and produce byproducts not in the original effluent or tissue samples.

The relative sensitivity of the proposed analytical chemical methods for the effluent and tissue residue options for identifying chemicals of potential concern is difficult to assess. By definition, concentrations of bioconcentratable chemicals always are higher in the tissues of aquatic animals than in the ambient water. However, nonpolar organic chemicals nearly always are much easier to quantify in a water matrix than in a tissue matrix. In addition, it nearly always is possible to analyze a much larger mass of water than tissue. Therefore, analytical detection limits nearly always are much lower for water samples than for tissue samples. Although the tissue samples do not require cleanup to remove non-bioconcentratable chemicals, they do require an even more rigorous and difficult cleanup step to remove natural, biogenic nonpolar organic chemicals (mainly lipids) from the tissue extract. This cleanup step is particularly important and difficult when the target analytes are hydrocarbons of the types that are the dominant potentially bioconcentratable compounds in oil industry effluents.

In summary, the analytical methods proposed in the DBG probably will not serve their intended purpose of identifying bioconcentratable chemicals in effluents and tissues that have not already been identified by other more conventional means. New chemicals that may be identified probably will have insufficient physical/chemical and toxicological data upon which to base a health risk analysis. The analytical methods will be difficult and expensive to apply. They have not been adequately validated with authentic field samples.

THE EFFLUENT OPTION

Overview

The effluent option recommended in the DBG (pages III-11 through III-23) is a multi-step process (Figure 5-1). A representative sample of the effluent is collected. Nonpolar organic chemicals in the effluent are extracted and the extract is cleaned up. The extract is separated

into a fraction containing organic chemicals with log K_{ow}s less than 3.5, which is discarded, and three fractions containing organic chemicals spanning three ranges of lot K_{ow} between 3.5 and 8.2. Each of the three fractions is analyzed by gas chromatography/mass spectrometry (GC/MS). All chemicals in the extracts that are positively or tentatively identified by mass spectral searches are subjected to several evaluation criteria. Those that exceed the criteria values may be subjected to a human health risk assessment at the discretion of the regulatory agency. Each step in the effluent option will be evaluated in the sections that follow.

Sampling and Analysis

Representative samples of the effluent are collected. Twenty-four-hour composite water samples containing 10 to 12 liters of effluent are recommended in the DBG (pp. III-12). Guidance is not provided on sampling and sample storage methods to assure sample integrity and to avoid extraneous contamination of samples. Samples are stored under dark refrigeration and extracted within seven days of collection.

There are several problems with the effluent option that could lead to substantial errors. If the sample has a significant chemical or biological oxygen demand and is not preserved, substantial chemical alteration of organic chemicals in the sample could occur during seven days of cold storage. Refrigeration at 4°C does not completely inhibit microbial activity. Water samples are spiked with three surrogate chemicals (d_{10}-biphenyl, $^{13}C_6$-1,2,4,5-tetrachlorobenzene, and $^{13}C_6$-hexachlorobenzene) at a concentration of 100 ng/L, mixed, and extracted with hexane. The three surrogates have log K_{ow}s that are within the range of the three bioconcentratable fractions. They are used for quantification of the unknown analytes. Because most of the bioconcentratable compounds expected in oil industry effluents are saturated and aromatic hydrocarbons, it would be advisable to empirically compare GC/MS response factors for the surrogates, two of which are organochlorines, with those for various parent and alkyl aromatic compounds expected to be present in oil industry effluents.
The effluent is extracted with n-hexane and cleaned up by elution through a silica gel/Celite/sulfuric acid column to remove biogenic interferences. The effluent from the acid clean-up is fractionated by reverse phase high pressure liquid chromatography (HPLC) to produce a fraction of chemicals with log K_{ow}s less than 3.5 (discarded) and three fractions with log K_{ow}s greater than 3.5 (log K_{ow} 3.5 to 4.5, 4.5 to 5.7, and 5.7 to 8.2).

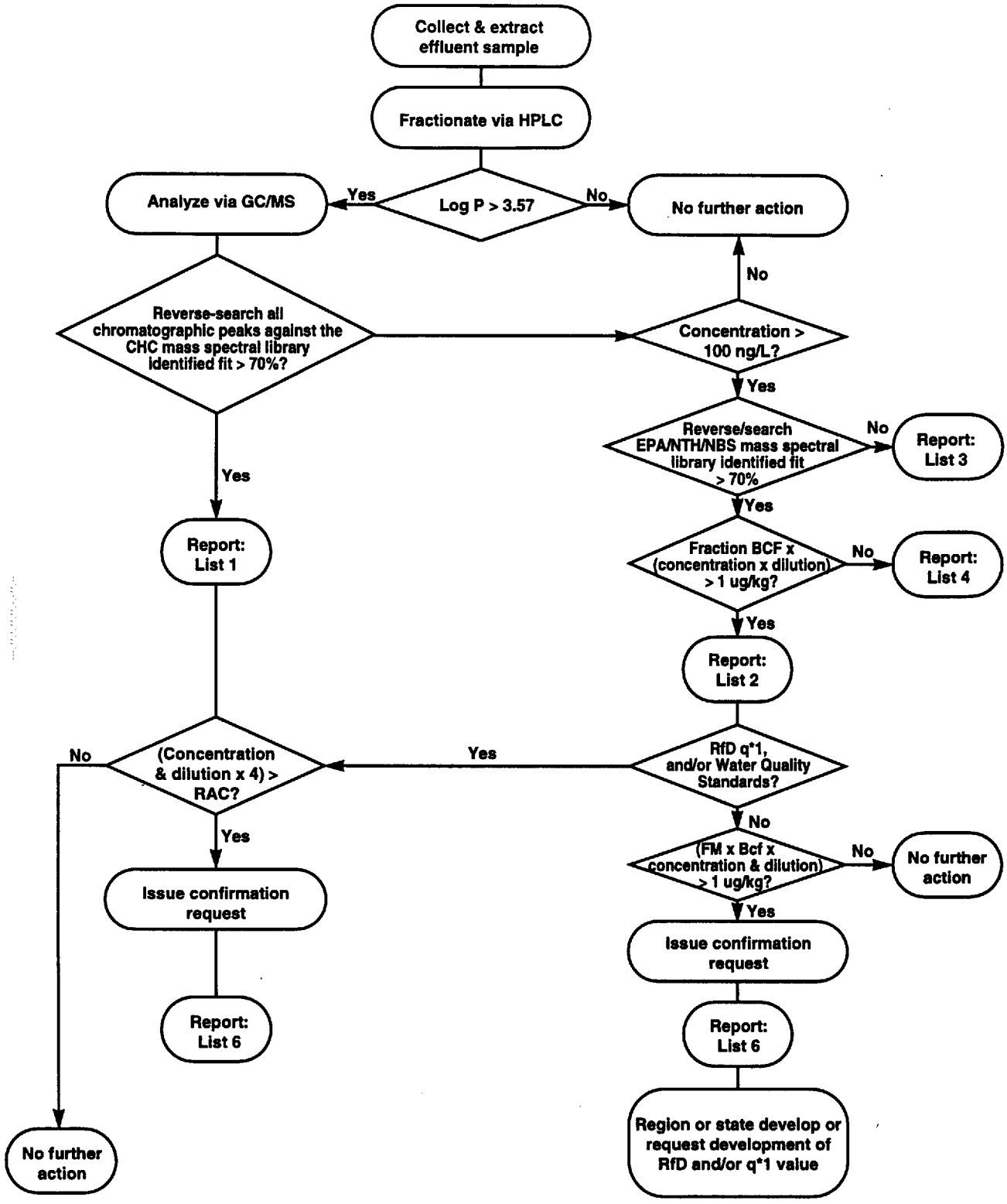

Figure 5-1. Analysis scheme recommended in the DBG for the effluent option.

This extraction, cleanup, fractionation procedure may be completely inappropriate for effluents, such as those from oil industry operations, that contain mainly hydrocarbons. Thisproblem was recognized in the DBG (page I-8). Hexane is not necessarily the best extractant for hydrocarbons. More important, the acid/Celite cleanup is likely to destroy many analytes of interest in the extract.

The three fractions containing potentially bioconcentratable nonpolar organic chemicals are analyzed by GC/MS. Mass spectral data are collected using full scan electron impact ionization mass spectrometry, and analytes are quantified by comparison with responses of the internal standards. All chromatographic peaks in the GC/MS data are compared, using reverse searching algorithms, with a mass spectral library for a group of 33 Chemicals of Highest Concern (CHC) (p. II-9 in DBG). Peaks that match a library spectrum by 70 percent or greater are considered tentatively identified. A Report 1 is produced containing information about all chemicals tentatively identified as being among the CHCs in each fraction.

Chemicals of Highest Concern

The CHCs are 33 chemicals considered by EPA to pose serious risks to human health due to high toxicities and high potential to bioconcentrate (page II-7). Very sensitive analytical methods are available for all or nearly all the chemicals on the CHC list, so it is unclear why EPA considers that "detection of these chemicals will be difficult" (page II-8). The DBG recommends that a specific MS library should be developed and used to identify CHCs in samples.

The CHCs are an unusual, heterogeneous group of chemicals or chemical mixtures. EPA has provided no detailed rationale for singling them out for special consideration nor documentation of their extreme hazard to human health, other than the brief statement on page II-7 of the DBG. Most of the CHCs are pesticides or degradation products of pesticides. Many of the pesticides have been banned in the United States and their concentrations in the environment are declining rapidly. Several of the "chemicals" actually are mixtures of many chemicals spanning a wide range of physicochemical and toxicological properties. These mixtures cannot be evaluated properly in the bioconcentration models discussed in earlier sections of this review.

In particular, commercial Aroclor mixtures of polychlorinated biphenyls (designated with a four-number identifier) are extremely complex mixtures. There are 209 possible PCB congeners with one to ten chlorines. The solubilities of individual congeners range from about 5.1 mg/L for 2-clorobiphenyl to 0.000007 mg/L for decachlorobiphenyl (Miller *et al.*, 1985; Dunnivant and Elzerman, 1988). Values for log K_{ow} range from 4.46 to 8.18, a range of nearly four orders of magnitude (Hawker and Connell, 1988). In order to predict the BCF of a commercial Aroclor mixture, it would be necessary to use an average value for K_{ow}. This is technically unsound and will not yield a meaningful estimate of the bioaccumulation potential of the complex mixture. BCFs of less chlorinated PCB congeners would be grossly overestimated and those of more highly chlorinated congeners would be grossly underestimated.

None of the chemicals on the CHC list are hydrocarbons and none are expected to be typical components of oil industry permitted effluents. Therefore, it is not appropriate that this step in the evaluation process be included for assessment of bioaccumulation potential of chemicals in oil industry effluents. Because the next step in the effluent option methodology is a search of the much more comprehensive EPA/NIH/NBS mass spectral library (which contains all the chemicals on the CHC list), it is unclear what advantage is gained by first performing a search of a much smaller CGC mass spectra library. This step in the assessment could be eliminated without any loss of precision in the overall approach.

Concentration Decision Points

If a GC/MS peak is not identified in the CHC mass spectral library search, chemicals present in the sample extracts at very low concentrations are dropped from the search. EPA proposes a concentration decision point for each of the assessment options. These are:

- Water: 100 nanograms/liter (parts per trillion)
- Tissues: 5 micrograms/kilogram (parts per billion) wet weight
- Sediment: 5 micrograms/kilogram (parts per billion) air dry weight

Any chemicals present in the samples at concentrations higher than the decision point value are evaluated further. An attempt is made to identify each potentially bioconcentratable chemical present in the effluent at a concentration greater than 100 ng/L using the EPA/NIH/NBS mass spectral database. Chemicals with fits/matches less than 70 percent

are included in Report 3. Two subgroups of chemicals are included in Report 3: chemicals with fits/matches less than 70 percent but greater than 25 percent (two best fits are listed); and compounds with fits/matches less than 25 percent (unknowns). Compounds with fits/matches greater than 70 percent are considered tentatively identified. These compounds are evaluated further.

The concentration decision point values are considered to "represent the minimum level at which adequate quantification can occur" (pages III-7 and III-17 in the DBG) and are the concentration of the surrogate compounds added to the different sample types. Therefore, this decision point is based on analytical chemical considerations and not on environmental considerations. No consideration was given to how these concentrations compare to background (sometimes natural) concentrations of the analytes in the environment. This latter consideration is particularly important for the major potentially bioconcentratable chemicals in oil industry effluents, most of which can be derived from a variety of natural and anthropogenic sources.

The background concentrations of saturated and aromatic hydrocarbons in water, sediments, and the tissues of aquatic organisms often exceed the decision point concentrations. Hydrocarbons in the aquatic environment are derived from several natural and anthropogenic sources, including biosynthesis, oil spills and natural oil seeps, combustion of almost any type of organic matter, and the early steps of diagenesis of certain natural organic precursors (Neff, 1979; Venkatesan *et al.*, 1987; Bouloubassi and Saliot, 1993).

There are limited amounts of data on the "background" concentrations of total PAH and saturated hydrocarbons in the fresh and marine waters. Background concentrations undoubtedly vary in relation to proximity to natural (oil seeps) and anthropogenic sources of hydrocarbons. Concentrations of total low and high molecular weight hydrocarbons in the water column of the high arctic north of Svalbard, Norway are in the range of 0.1-0.6 and 0.05-0.2 μg/L, respectively (Fogelqvist *et al.*, 1982). Concentrations of total C_9- through C_{27}-n-alkanes in the water samples from Bermuda range from 0.40 to 1.31 ng/L (Ehrhardt and Burns, 1990). Average concentrations of total saturated hydrocarbons of fossil fuel origin in water samples from the Hibernia oil field and a reference station in the Laurentian Channel south of Newfoundland were 0.165 and 0.074 μg/L, respectively (Gassmann and Pocklington 1984).

Wade *et al.* (1989) reported an average concentration of 0.028 μg/L total PAH in water samples collected near a hydrocarbon seep in 570 m of water in the Gulf of Mexico. The total concentrations of naphthalene, fluorene, phenanthrene, dibenzothiophene, fluoranthene, pyrene, and their alkyl homologues in water samples from 3 nearshore locations around Bermuda ranged from 0.003 to 0.062 μg/L (Ehrhardt and Burns, 1990). A water sample from an offshore reference station contained only 0.01 ng/L (parts per trillion: ppt) fluoranthene. Concentrations of phenanthrene, anthracene, fluorene, pyrene, chrysene, and benzo(a)pyrene in the water column of Lake Michigan were in the range of 10 to 40 ng/L each (Eadie, *et al.*, 1982). These data suggest that background concentrations of individual PAHs in the water column are in the range of less than 0.001 to 0.05 μg/L. Slightly higher concentrations may occur near natural oil seeps or anthropogenic non-point sources. By comparison, the concentration decision point value for chemicals in effluent samples is 0.1 μg/L, about twice the natural background concentration of individual PAHs, but much lower than the naturally and non-point source derived background concentrations of total hydrocarbons and saturated hydrocarbons. Consequently, the decision concentration is so low that it essentially provides no screening.

The tissue concentration decision point of 5 μg/kg wet wt is comparable to or lower than concentrations of PAH in many aquatic invertebrates, even from seemingly clean environments. Because saturated and aromatic hydrocarbons are natural components of all aquatic habitats, most aquatic organisms (even from pristine areas) contain some hydrocarbons in their tissues. For example, copepods from the eastern Gulf of Mexico contained concentrations of total hydrocarbons (mostly saturated hydrocarbons) ranging on a seasonal basis from 135 to 719 mg/kg dry wt (Calder, 1976). Concentrations of total PAH in the tissues of mussels (*Mytilus edulis*) from the U.S. Atlantic and Pacific coasts range from less than 0.4 to 16.9 mg/kg (Freitas *et al.*, 1989). Highest concentrations were associated with contaminated urban sites. Mussels from sparsely populated coastal areas of Scotland contained an average of 109 μg/kg total PAH (Mackie *et al.*, 1980). Marine fish (*Notothenia gibberifrons*) from waters around the Antarctic Peninsula contained 13 to 145 μg/kg total PAH in their livers and 38-90 μg/kg total PAH in their muscle tissues (McDonald *et al.*, 1992). In most cases, concentrations of PAH are highest in aquatic plants and invertebrates and low or undetectable in the tissues of fish and higher vertebrates, reflecting the different capabilities to metabolize and excrete the hydrocarbons (Neff, 1979).

The sediment concentration decision point is 5 μg/kg. This concentration is well below natural concentrations of PAH and saturated hydrocarbons in clean freshwater and marine sediments. Nearly all potentially bioconcentratable saturated and aromatic hydrocarbons will exceed the concentration decision point value in fine grained sediments, irrespective of the distance from point sources of these hydrocarbons. For example, concentrations of total hydrocarbons in sediments of the Beaufort Sea off northern Alaska range from 0.3 to 20 mg/kg in nearshore sediments to 20 to 50 mg/kg in offshore sediments (Shaw *et al.* 1979; Venkatesan *et al.* 1983). Particles entering the Beaufort Sea, Canada, in the Mackenzie River outflow contain an average of about 11.8 mg/kg total alkanes and about 2 mg/kg total PAH (Yunker *et al.* 1991). Background concentrations of total PAH in sediments from the continental slope and rise off southern New England at a depth in the sediment cores of 24 to 35 cm is in the range of 10 to 20 μg/kg dry sediment (Venkatesan *et al.*, 1987). The surficial sediments in these cores contain about 100 μg/kg total PAH. Unpolluted soils in Norway contained an average of 188 μg/kg total PAH; naphthalene, phenanthrene, and chrysene/triphenylene were the most abundant (Vogt *et al.* 1987). Concentrations of total PAH in sediments of Cayuga Lake, NY, were in the range of 104 to 20,000 μg/kg dry weight (Heit 1985). The lowest concentrations were considered background values. The highest concentrations were within about 1,000 meters of point sources of PAH: stacks of a coal-fired power plant; marinas; and highway bridges. These PAH were from both petrogenic and pyrogenic sources.

In summary, because of the ubiquity of saturated and aromatic hydrocarbons from a variety of natural and anthropogenic sources in aquatic environments, nearly all water, sediment, and tissue samples in a receiving water environment are likely to contain traces of hydrocarbons approaching or exceeding the decision point concentrations, irrespective of the concentrations of hydrocarbons in the effluent. Sediments, in particular, nearly always contain concentrations of saturated and aromatic hydrocarbons greater than 5 μg/kg.

Screening for Bioconcentration Potential

The next step in the effluent option is to determine if chemicals that have been tentatively identified by the mass spectral library searches and are present in the effluent at a concentration of 100 ng/L or higher, have a high likelihood of being bioconcentrated in aquatic animals in the receiving water environment of the discharge. These chemicals are evaluated further in the formula:

Fraction BCF x Concentration x Dilution > 1 μg/kg (5-1)

where fraction BCF is the maximum BCF (page III-19 of the DBG) of the HPLC fraction in which the chemical occurred, concentration is the concentration of the chemical in the effluent, and dilution is the expected dilution of the effluent within the mixing zone of the receiving waters. All chemicals exceeding the 1 μg/kg criterion are listed in Report 2 with relevant analytical data. Chemicals whose concentrations are below this criterion are listed in Report 4.

On page IV-4, the DBG recommends using the average BCF for each fraction. If the chemical has been tentatively identified and a measured or estimated K_{ow} value is available for it, it would be more accurate to use this value rather than the maximum or average value for the particular HPLC fraction. Use of the maximum K_{ow} value, in particular, can introduce substantial error into the screening evaluation. For example, the range of BCF values in fraction 3 is from 5,000 to 470,000, a span of nearly two orders of magnitude. The potential for a chemical with a log K_{ow} of 5.7 to bioaccumulate would be greatly overestimated.

The dilution factor is to be specified by the regulatory authority, based on site-specific factors. In the absence of a specified dilution factor, the dilution factor can be set at an extremely conservative value of 1 (no dilution). Based on an evaluation of 26,524 NPDES permittees nationwide, a majority of dilutions are in the range of 100 to 1,000 (dilution factor 0.01 to 0.001) during mean stream flow conditions; during low flow conditions, a majority of dilutions fall in the range of 1 to 10 (dilution factor of 0.1 to 1.0) (EPA, 1991a). Since bioaccumulation is a time-integrated response of organisms in the receiving water environment, the mean stream flow conditions probably best represent a realistic dilution during bioaccumulation. Receiving waters with no dilution of an effluent are not likely to support significant populations of fish and shellfish consumed by man. Therefore, a dilution factor of 0.01 (100-fold dilution) was used here as a conservative value to evaluate this screening step.

Using a dilution factor of 0.01, chemicals with a concentration of 100 ng/L (the concentration decision point for effluent samples) in the effluent will produce estimated tissue

concentrations according to Equation 4-2 of 0.57, 5.0, and 476 μg/kg for chemicals in fractions 1, 2, and 3, respectively. Thus, all chemicals in fractions 2 and 3 will exceed the screening concentration of 1 μg/kg. The effluent would have to be diluted by a factor of 500 for chemicals in fraction 2 to pass the screening analysis; for chemicals in fraction 3 to pass the screening analysis, the effluent would have to be diluted by a factor of more than 5,000.

The 18 evaluation chemicals typical of oil industry effluents (Table 2-2) were evaluated by this screening protocol, using the published values for K_{ow} for each compound (Table 5-1). All chemicals in fraction 1 and phenanthrene in fraction 2 were below the screening criterion when they were present in the effluent at a concentration of 0.1 μg/L and when the dilution was 100-fold (0.01). All the remaining chemicals in fractions 2 and 3 exceeded the screening value of 1.0 μg/kg in the tissues of organisms at the edge of the mixing zone.

This analysis shows that the screening analysis according to the methods proposed in the DBG is not useful for identifying chemicals in fractions 2 and 3 with the greatest bioconcentration potential, unless dilutions substantially greater than 100-fold are allowed by the regulatory agency. All chemicals in all three fractions would have exceeded the screening criterion at their effluent concentration decision point concentration if the conservative dilution of 1 was used, as recommended in the DBG (page III-19). A screening/decision process that, because of the definitions of parameters in the screening equations, always or nearly always indicates an exceedance is not useful. The screening analysis is time-consuming and expensive. Because it contributes little to identifying chemicals that should or should not be listed in Report 2, it should be eliminated.

Chemicals in Report 2 are screened further to determine if water quality standards are available.

Water Quality Standards

The next step in the effluent option is intended to determine if there is a water quality standard or other types of information available that are sufficient to calculate a reference ambient concentration (RAC) (page III-21 of the DBG). Chemicals that exceed the estimated tissue screening bioconcentration value of 1 μg/kg are listed in Report 2 and evaluated further to determine if RfD, q1*, and/or water quality standards are available. The RfD is an

Table 5-1. Evaluation of the Screening Formula for Bioconcentratable Compounds in Oil Industry Effluents (Fraction BCF x Concentration x Dilution > 1μg/Kg). BCFs were Derived from the Formula of Veith and Kosian (1983) Corrected for an Average Lipid Concentration of 3 Percent. Concentration was Set at the Effluent Concentration Decision Point (0.10 μg/L) and Dilution was Set at 0.01.

Chemical	BCF	Tissue Concentration
Fraction 1: Log K_{ow} 3.5 to 4.5		
Carbazole	170	0.17
1, 2.4-Trimethylbenzene	174	0.17
2-Methylnaphthalene	178	0.18
n-Octane	229	0.23
Fluorene	316	0.32
Dibenzofuran	339	0.34
Dibenzothiophene	550	0.55
Fraction 2: Log K_{ow} 4.5 to 5.7		
Phenanthrene	646	0.65
Methyldibenzothiophene	1,072	1.07*
n-Decane	1,445	1.44*
1-Methylphenanthrene	1,622	1.62*
Fluoranthene	2,089	2.09*
Fraction 3: Log K_{ow} 5.7 to 8.2		
Chrysene	5,888	5.89*
Benz(a)anthracene	7,244	7.24*
Benzo(a)pyrene	18,197	18.20*
5-Methylchrysene	18,621	18.61*
7,12-Dimethylbenz(a)anthracene	46,774	46.77*
n-Tetradecane	77,625	77.62*

* Exceeds screening criterion

estimate of the daily exposure to a chemical (oral), measured as mg/kg/day, during a lifetime (70 years) by the human population that is without risk of deleterious effects. The q1* is the carcinogenic potency factor, and is expressed in units of reciprocal mg/kg/day (kg x day/mg). These parameters are used to calculate a RAC. The RAC is the highest concentration in mg/L of a bioconcentratable chemical in the receiving water that will not pose a human health risk from consumption of fish or shellfish. If a RAC can be calculated, the tentatively-identified

chemical is evaluated further by the formula:

$$\text{Concentration} \times \text{Dilution} \times 4 > \text{RAC} \qquad (5\text{-}2)$$

All chemicals in Report 1 (CHCs tentatively identified in the effluent) and those chemicals in Report 2 for which water quality data are available are evaluated in equation 5-2 to determine if the RAC may be exceeded.

The value 4 in this equation is derived from a statistical analysis of the likely coefficient of variation (CV) in concentrations of a tentatively identified chemical in replicate samples of effluent (page III-10). With a CV of 0.6, the maximum ratio of the effluent population mean to one sample is 3.6 at the 99 percent confidence level. It is unclear if empirically determined variability in concentrations of different analytes in a typical effluent was used for this analysis and whether the variability of different types of effluents was considered. The number of "replicates" used in this analysis also was not stated. Therefore, it is not possible to evaluate the reasonableness of the value 4 with respect to oil industry permitted effluents. A lower CV, for example 0.2, would produce a much lower expected ratio between the concentration of the analyte in a single sample and the mean concentration in the effluent, in the range of about 1.6.

This factorial adjustment of the predicted concentration of effluent chemicals at the edge of the mixing zone may not be justified if the effluent sample is truly representative of the average concentration of the discharge and residue concentrations in the tissues of aquatic animals in the mixing zone actually represented the time-integrated equilibrium BCFs.

If the information needed to calculate a RAC for a tentatively identified chemical is not available, the regulatory agency may obtain improved values for BCF and FM, if these parameters are not available. This may be done by calculating or empirically determining the log K_{ow} for the chemical or by empirical determination of the BCF. If the value for the chemical exceeds its RAC, the chemical is listed in Report 5 and the agency may request a confirmation of the identity of the chemical. If the chemical does not exceed its RAC, it is not considered further.

If physical/chemical data are available, the chemicals in report 5 will be evaluated by the formula:

$$FM \times BCF \times Concentration \times Dilution > 1\ \mu g/kg \qquad (5\text{-}3)$$

This formula is the same as the formula (equation 5-1) discussed above for initial screening of potential bioconcentratable compounds, except that the food chain multiplier (FM) is added. If the chemical exceeds this screening criterion, the regulatory authority will request a confirmation of the identity of the chemical. If the chemical passes the screen, it will not be considered further.

As discussed above nearly all chemicals in fraction 2 and all chemicals in fraction 3 will always exceed the initial screening evaluation (equation 5-1). Multiplication of the answer by the FM will produce an even higher value, so even more chemicals in fractions 2 and all chemicals in fraction 3 will always exceed this screen. Values of FM for chemicals in fraction 2 (log K_{ow} 4.5 to 5.7) are in the range of 1.2 to 23.2, depending on the actual value for K_{ow} and the trophic level to which the animal of interest is assigned. The screening value for phenanthrene in equation 5-3 is 0.78 μg/kg, compared to a value of 0.65 μg/kg in equation 5-1. Therefore, this screening process, like the earlier one, provides little useful information. All chemicals in fractions 2 and 3 will most likely have to proceed to the next step in the evaluation.

Derivation of the Reference Ambient Concentration (RAC)

The BCF is estimated for each potentially bioconcentratable chemical tentatively identified in the effluent by the methods discussed in Chapter III of the DBG or the value is taken from the Quantitative Structure Activity Relationship (QSAR) database (Hunter and Culver, 1988). Alternatively, if BCFs cannot be estimated by these means, the average BCF for the fraction in which the chemical elutes from the HPLC column is used. Published literature, water quality criteria documents, or various toxicological databases can be used to obtain empirically determined values for BCF if there is evidence that the chemical is highly biodegradable and readily excreted. All BCF values are normalized to 3 percent lipid in the test animals.

Bioaccumulation (food chain transfer) is considered in this evaluation by including the FM in the equation to derive a RAC. EPA recommends use of the FM values for trophic level 4

(the highest trophic level: top carnivores), because these are considered the fish most sought by fishermen. However, use of high values for FM will considerably bias RACs for some chemicals that are metabolized and excreted rapidly by fish, e.g., nearly all saturated and aromatic hydrocarbons characteristic of petroleum industry effluents, (Lech and Bend, 1980). **Because food chain transfer is low and biomagnification does not occur for aromatic hydrocarbons and heterocyclic compounds, FM values should not be used to calculate RACs for petroleum industry effluents.**

The DBG recommends using the Integrated Risk Information System (IRIS) database to obtain values for reference dose (RfD) or, for known or suspected human carcinogens, the carcinogenic potency estimate or q1*, the cancer-causing potential resulting from lifetime (70 years) exposure to a chemical.

If exposure to the chemical of concern through inhalation, consumption of non-aquatic foods, and in drinking water are not considered to be quantitatively important, the RAC for a non-carcinogenic chemical can be calculated by the equation:

$$\text{RAC (mg/L)} = \frac{(\text{Rfd} \times \text{Wt.})}{\text{FC} \times \text{L} \times (\text{FM} \times \text{BCF})} \qquad (5\text{-}4)$$

where RfD = reference dose (mg chemical/kg human body weight/day)
WT = weight of an average human adult (70 kg)
FC = daily fish consumption (0.02 kg fish/day)
L = ratio of lipid fraction of fish tissue consumed to 3 percent
FM = food chain multiplier
BCF = bioconcentration factor (concentration of chemical in fish/concentration of chemical in solution in ambient water)

The DBG recommends that fish consumption values (FC) reflect the most current relevant and or state/specific information available. EPA (1989) identifies four levels of fish consumption: 6.5 g/day to represent the low estimate of average consumption by the entire U.S. population; 20 g/day to represent a high estimate of the average consumption by the entire U.S.

population; 165 g/day to represent the average consumption by the 99.9th percentile of the U.S. population consuming the most fish; and 180 g/day to represent the reasonable worst case based on the assumption that some individuals would consume fish at a rate equal to the combined consumption of red meat, poultry, fish, and shellfish in the U.S. A value of 20g/day (0.020 kg/day) was chosen to evaluate this formula.

If exposure to the chemical of concern through inhalation, consumption of non-aquatic foods, and in drinking water are not considered to be quantitatively important, the RAC for a suspected carcinogenic chemical can be calculated by the equation:

$$RAC\ (mg/L) = \frac{RL \times Wt.}{(q1^*) \times L \times (FM \times BCF)} \qquad (5\text{-}5)$$

where RL = the risk level (10^{-5})

$q1^*$ = the carcinogenic potency factor (kg x day/mg) = 1/CPF (CPF = the carcinogenic slope factor in mg/kg/day)

EPA and state regulatory agencies frequently use risk factors (RL) ranging from 10^{-4} to 10^{-6}. A risk value of 10^{-5} (1 in 100,000 lifetime cancer risk) was used below to evaluate this formula for chemicals in oil industry effluents.

Human health risk data for the 18 evaluation chemicals typical of oil industry effluents are summarized in Table 5-2. Values for RfD and CPF (carcinogenicity slope factor) were obtained from the July 6, 1992 update of the IRIS database and from the 1992 Human Effects Assessment Summary Tables (EPA, 1992). Human toxicity data were available for only seven of the eighteen chemicals used for this evaluation. The estimated RAC concentrations for the three non-carcinogens ranged from 0.016 to 0.403 mg/L. RAC concentrations for the four suspected carcinogens range from 4.4×10^{-6} to 4.1×10^{-5} mg/L. By comparison, equation 5-2 for comparing concentrations in the effluent with the RAC yields a value of 4.0×10^{-6} mg/L when the concentration in the effluent is set at 0.0001 mg/L (0.1 µg/L) and dilution is set at 0.01. Thus, all seven chemicals evaluated pass the screening test when present in the effluent at a concentration of 100 ng/L (0.0001 mg/L) if the allowed dilution is 100-fold. Carbazole, fluorene, and phenanthrene passed the earlier screen at a concentration of 0.0001

mg/L in the effluent and, therefore, they would not have been evaluated in this screening exercise. They would have failed the earlier screen at concentrations of 0.00018 mg/L (carbazole and fluorene) and 0.00015 mg/L (phenanthrene). However, even at these concentrations, these chemicals would pass this final screen. Any increase in the concentrations of the suspected carcinogens in the effluents above 100 ng/L will most likely result in an exceedance of the RAC.

Table 5-2. Human Health Risk data for Consumption of Fishery Products Contaminated with Typical Potentially Bioconcentratable Chemicals in Oil Industry Effluents. RfD is Reference Dose, CPF is the Carcinogen Slope Factor, and RAC is the Reference Ambient Concentrations. The Screening Concentration is $4.0x10^{-6}$ mg/L for an Analyte Concentration of 0.0001/mg/L and a Dilution of 0.01.

Chemical	RfD (mg/kg/day)	CPF (mg/kg/day)	RAC (mg/L)
Carbazole	ND	$2.0x10^{-2*}$	$4.1x10^{-5}$
1, 2, 4-Trimethylbenzene	ND	ND	
2-Methylnaphthalene	ND	ND	
n-Octane	ND	ND	
Fluorene	$4.0x10^{-2}(4.0x10^{-1})$	ND	$4.0x10^{-1}$
Dibenzofuran	ND	ND	
Dibenzothiophene	ND	ND	
Phenanthrene	4.0^{-3}	ND	$1.7x10^{-2}$
Methyldibenzothiophene	ND	ND	
n-Decane	ND	ND	
1-Methylphenanthrene	ND	ND	
Fluoranthene	$4.0x10^{-2}(4.0x10^{-1})^{*}$	ND	$1.6x10^{-2}$
Chrysene	ND	5.79	$1.3x10^{-5}$
Benz(a)anthracene	ND	5.79	$5.9x10^{-6}$
Benzo(a)pyrene	ND	$7.3(5.8)^{*}$	$4.4x10^{-6}$
5-Methylchrysene	ND	ND	
7, 12-Dimethylbenz(a)anthracene	ND	ND	
n-Tetradecane	ND	ND	

ND No data available from the IRIS database (IRIS, 1992).
* - Value from the Health Effects Assessment Summary Tables, Annual FY 1992 (EPA, 1992)

The protocol for estimating carcinogenic risk is extremely conservative. It is based on linear extrapolation of cancer induction in laboratory mammals (usually rats and mice) by very high

doses of potential carcinogens to very low doses in human foods. Although several higher molecular weight PAH and nitrogen heterocyclic compounds are carcinogenic in laboratory animals, none are proven human carcinogens. Carcinogenic risk usually is estimated as an increased incidence of cancer in 10,000 to 1,000,000 people resulting from life-long exposure to the chemical in food or water. Even disregarding the extremely conservative nature of the carcinogenic potency extrapolation, it is highly unlikely that thousands of people would consume fishery products for a lifetime from the immediate vicinity of a permitted effluent. Therefore, it is unlikely that enough people would be exposed to generate the prediction of even a single excess death.

Of the 11 chemicals considered that do not have sufficient information in either IRIS or EPA (1992), two are known carcinogens: 5-methylchrysene and 7,12-dimethylbenz(a)anthracene (IARC, 1987; National Toxicology Program, 1991). However, 5-methylchrysene is not listed on the EPA Carcinogen Assessment Group's list of carcinogens (IRIS, 1992). The Carcinogen Assessment Group is an advisory group that evaluates chemicals for inclusion in the IRIS database.

RAC concentrations seem more environmentally realistic for non-carcinogenic compounds. The nine chemicals that are not suspect carcinogens and are not listed in the IRIS database also lack federal water quality criteria. For the most part, these hydrocarbons are toxic to aquatic animals at concentrations approaching their aqueous solubilities (Abernethy *et al.*, 1986).

In the context of this assessment, it is assumed that significant numbers of people will obtain and eat 20 g/day of upper trophic level fish from the edge of the mixing zone for the outfall for a full lifetime. This is highly unlikely and certainly represents an extreme case. The mixing zone around an outfall is a relatively small area, compared to the total area of most receiving water environments. The RAC for suspected carcinogens incorporates a risk level of 10^{-5} to 10^{-7} that corresponds to a risk of one additional cancer among 100,000 to 10,000,000 people eating significant amounts every day for a lifetime (70 years) of fish from the edge of the mixing zone of an outfall. According to this scenario, if ten people consumed 20 g of fish each day for a lifetime from the edge of the mixing zone of an outfall discharging a carcinogenic chemical at a concentration above the RAC, there would be one

chance in 10,000 that one of these people would contract cancer as a direct result of consumption of contaminated fish from the vicinity of the outfall. The risk of dying from cancer from another source, other disease, or an accident is much higher than this. For example, the lifetime risk of cancer from cigarette smoking has been estimated to be 1 in about 70 (1.4×10^{-2}) per cigarette smoked daily (Connor, 1984). Even this extrapolation is a very conservative one, because the dose/response slope function for cancer is derived from extrapolation from very high doses in laboratory animals to very low environmental doses using a linear dose/response model.

As suggested above, it would be better to focus the assessment on targeting and quantifying potentially bioconcentratable chemicals in effluents for which appropriate human health risk data are available. As new chemicals are added to the risk assessment databases, they can be added to the list of targeted chemicals for evaluation for potential bioconcentration hazard.

THE TISSUE RESIDUE OPTION

Sampling and Analysis

The DBG recommends that animals from the receiving water environment be collected during at least two seasons when dilution of the effluent in receiving waters is at normal or sub-normal levels. At least two species that are consumed by man should be sampled (page III-3 of the DBG). They should represent different "habitat niches" and be from different trophic levels, preferably including a top predator (trophic level 4). One species each of an invertebrate and fish is recommended.

These recommendations may be difficult to fulfill, particularly if the intent is to sample animal populations that have inhabited the receiving water environment for an extended period of time (at least long enough to attain equilibrium BCFs and BAFs). Top predators are by definition highly motile. Very few species remain in a single location for extended periods of time. They cannot be maintained in field cages near the outfall for long, and are unlikely to feed normally if they are maintained in such cages. If feral fish are collected, there is no way to assure that they have spent a significant amount of time near the outfall. Therefore, it will not be possible in most cases to determine if any residues in their tissues were derived from the effluent being monitored (Cullen and Connell, 1992). Some demersal fish have rather restricted local distributions at least on a seasonal basis and might be suitable for monitoring purposes. However, most are trophic level 2-3 consumers.

Several species of invertebrates are relatively immobile and are suitable for monitoring. However, none of these species in freshwater environments are frequently consumed by man. Some marine and estuarine bivalves, such as mussels and oysters, are consumed by man and have been used widely for monitoring the chemical status of coastal environments (Freitas *et al.*, 1989). They would be suitable for monitoring bioconcentratable chemicals in coastal estuarine and marine environments. However, results for these species cannot be extrapolated to higher trophic levels, particularly fish and crustaceans, because of the marked differences among bivalve molluscs, crustaceans, and fish in MFO activity and ability to metabolize and rapidly excrete accumulated hydrocarbons, as discussed above (Section 4).

The DBG does not recommend collecting animals in the mixing zone of the outfall being monitored (page III-4 of DBG). The DBG assumes that bioconcentratable chemicals in the effluent will accumulate to higher concentrations in sediments of depositional zones downstream of the outfall and result in higher concentrations of the chemicals in food chain organisms there. The DBG also suggests that animals may spend less time in the area of the mixing zone, not allowing for bioaccumulation. At least in theory, concentrations of bioconcentratable chemicals in sediments and tissues of aquatic animals should be directly proportional to the concentration of the chemicals in solution in the water (according to equilibrium theory). If this is not true, the whole basis of the bioconcentration assessment is faulty. One would expect that concentrations of bioconcentratable chemicals from an effluent to be highest in the water column near the outfall and decrease with distance from the outfall. It will be difficult or impossible to attribute tissue residues in aquatic animals collected from the area of a depositional zone to any single point discharge (Cullen and Connell, 1992).

The major problem with the tissue residue option is that it rarely is possible to document the exposure of the aquatic animals to the effluent. Most frequently, motile animals collected near the outfall have been resident in the area for only a short period of time. None are likely to have resided in the area long enough to reach an equilibrium tissue residue concentration represented by a predicted BAF. It is not possible to determine with any certainty the source of tissue residues of bioconcentratable chemicals in feral populations of mobile animals.

Results obtained with the tissue residue option will be very sensitive to the locations in the receiving water environment at which animals are collected and the number of replicate

samples used to characterize the variance in tissue residue levels (controllable) and to the previous history of the animals sampled for analysis (usually not controllable). Therefore, the tissue residue option should be used with great caution as a basis for setting limits on the concentrations of bioconcentratable chemicals in specific permitted effluents, particularly those from oil industry operations.

Tissue Analysis and Evaluation of Tissue Residues

Similar problems to those faced in the effluent option occur in the tissue residue option with respect to chemical analysis and residue data analysis. Conventional extraction and cleanup techniques are used, followed by analysis by GC/MS. This avoids the artifact-prone acid cleanup and HPLC fractionation steps used for effluent samples. However, concentrations of bioconcentratable chemicals usually are much more difficult to measure accurately in a tissue matrix than in water.

Formulas similar to those used to screen bioconcentratable chemicals and determine the RAC of chemicals in effluents are used to screen tissue residues and calculate a reference tissue concentration (RTC). They suffer from the same problems as the formulas used in the effluent option.

SEDIMENT ASSESSMENT

The sediment assessment is intended to determine if bioconcentratable chemicals are present in sediments near a point source at concentrations high enough to represent a "significant source for bioconcentratable chemicals" (page III-25 in DBG). Bioconcentratable chemicals have a strong propensity to sorb to suspended particles and be deposited with them in sediments. The DBG recommends that samples of sediment from the receiving water environment be analyzed for bioconcentratable chemicals. Samples should be taken after periods of normal or sub-normal stream flow and normal weather conditions. One or two sampling events per year should be sufficient. Coarse-grained sediments low in organic carbon should be avoided. No guidance is provided on the depth at which samples should be taken. However, if the sample is to represent recent accumulation from the effluent being monitored, samples of only the upper surficial layer of recently-deposited sediment should be sampled (the upper 2 to 10 cm in most cases). Chemicals at greater depths in the sediment

probably were deposited some time ago (Laflamme and Hites, 1978) and probably are not readily mobilized and bioavailable to aquatic organisms.

Locations of sediment sampling relative to the location of the outfall being monitored are critical to interpretation of the results. Variations in sediment texture will have a greater effect in most cases than distance from the outfall on the relative concentrations of chemicals in the sediments. Yet sampling at a depositional site with fine-grained, organic-rich sediments at some distance down-current from the outfall also creates problems. It may not be possible to identify the sources of chemicals in fine-grained sediments from a depositional site well removed from the outfall under investigation.

Sediment samples are analyzed by the same basic methods as water and tissue samples. As discussed earlier in this section, the sediment concentration decision point (5 μg/kg) is much too low to be useful for screening sediments for bioconcentratable hydrocarbons typically found in oil industry effluents. Nearly all fine-grained sediments rich in organic matter contain concentrations of saturated and aromatic hydrocarbons well above the concentration decision point value, even in regions remote from human activities (Laflamme and Hites, 1978; Neff, 1979).

The sediment assessment is unlikely to provide much useful information concerning hazards from bioaccumulation of chemicals in the vicinity of outfalls discharging permitted effluents. In most cases, it will be difficult or impossible to identify the sources of chemicals in the sediments. Equilibrium theory can be used to model transfer of chemicals from sediments into the overlying aquatic food chain, but such modeling has not been validated to an extent that it can be used to regulate concentrations of chemicals in effluents.

SUMMARY

- The extraction, cleanup, and fractionation procedures recommended for the effluent option may cause degradation of analytes and generate artifacts.
- Only a few chemicals tentatively identified by the proposed analytical scheme and not already known to be present in the effluent will have sufficient physical/chemical and toxicological data for calculation of a RAC. Therefore, the difficult and expensive methodology is not useful for regulating bioconcentratable chemicals in petroleum industry effluents.

The decision point concentrations of potentially bioconcentratable chemicals in sediments and tissues are so low that natural background concentrations of the chemicals (especially the hydrocarbons characteristic of oil industry effluents) will exceed them frequently.

- The use of an average K_{ow} for complex mixtures (such as PCB formulations and toxaphene) will greatly overestimate tissue residues for lower molecular weight components and greatly underestimate tissue residues for high molecular weight components.

- The tissue residue option is not appropriate because it will not be possible to identify the sources of bioconcentratable chemicals in the animal tissues and natural background concentrations often will exceed the 5 μg/kg decision concentration.

- Assessment of concentrations of bioconcentratable chemicals in sediments will have little value. Natural background concentrations of many chemicals, particularly the hydrocarbons found in oil industry effluents, often are higher than the decision point concentration of 5 μg/kg. It will not ordinarily be possible to identify the sources of the chemicals in sediments or when they were deposited. Methods for extrapolating from concentrations of chemicals in sediments to concentrations in tissues of aquatic animals have not been adequately tested and validated.

- Use of food chain multipliers (Fms) derived from a generic bioaccumulation model that was parameterized and validated for persistent chemicals such as PCBs is not generally applicable for other classes of potentially bioconcentratable chemicals, such as PAHs. This conclusion is corroborated by both laboratory and field data. Because PAHs are not transferred efficiently in aquatic food chains and do not biomagnify, FM values should not be used to estimate their RACs.

- Reference ambient concentrations (RACs) are derived on the basis of chemicals in true solution in the water. However, the importance of aquatic fate processes (e.g., partitioning to dissolved and particulate organic carbon phases) in controlling dissolved concentrations and therefore bioavailability of chemicals in effluents was ignored.

- RACs are based on long-term averages of concentrations of bioconcentratable chemicals in effluents since the BAFs upon which these values are derived are based on steady-state assumptions. Therefore, typical CVs characterizing effluent variability on a daily or hourly basis are inappropriate for bioaccumulation assessment.

Section 6

CONCLUSIONS AND RECOMMENDATIONS

CONCLUSIONS

The DBG provides a methodology for assessing the identity and concentrations of nonpolar organic chemicals with a strong potential to bioaccumulate in aquatic food chains to concentrations that could pose a health hazard to human consumers of fishery products. The methods proposed in the DBG have been reviewed critically with particular emphasis on their suitability for assessing bioconcentratable chemicals in permitted effluents from oil refineries, petroleum marketing terminals, and crude oil production activities. The major focus of this review was on the effluent option.

NPDES-permitted effluents from oil refineries, production platforms, and oil marketing terminals contain low concentrations of a complex mixture of nonpolar organic chemicals. The most abundant chemicals are saturated and aromatic hydrocarbons and related heterocyclic compounds. Halogenated organics, phthalate esters, pesticides, and other compounds of major environmental concern usually are absent, present as trace contaminants, or as analytical artifacts. Therefore, any assessment of bioconcentratable chemicals in oil industry effluents should focus on hydrocarbons.

The methodology proposed by EPA for identifying and quantifying bioconcentratable organic chemicals in NPDES-permitted effluents does not provide a sound basis for predicting bioaccumulation of toxic chemicals in the edible tissues of fish and shellfish from the receiving water environment that might be consumed by man. A great many conservative assumptions are made in deriving screening parameters for each stage of the assessment. The net result is an extremely conservative estimate of potential bioaccumulation and tissue residue concentrations in fishery products consumed by man. Because of the multiple conservative assumptions, actual tissue residues are likely to be overestimated by as much as two to three orders of magnitude. This is particularly true for chemicals, such as most of the potentially bioconcentratable chemicals that typically occur in oil industry effluents. These chemicals are absorbed poorly from the gut of aquatic animals and man and are metabolized and excreted rapidly.

The effluent option provides a means for identifying and quantifying potentially bioconcentratable chemicals in oil industry effluents. However, the extraction, cleanup, and analytical methods may degrade many hydrocarbon analytes and produce a variety of artifacts (e.g., degradation products of aromatic hydrocarbons). Reverse searches of mass spectral libraries probably will produce tentative identifications for many chemicals for which no physical/chemical or toxicological data are available. It will not be possible to determine if these chemicals pose a health hazard to humans at the concentrations at which they occur in the effluent.

The complex series of screening steps proposed to identify chemicals with the highest likelihood of posing a human health risk will identify nearly all chemicals in the three HPLC fractions. Nearly all chemicals that are present in the effluent at a concentration greater than the effluent concentration decision point (0.10 μg/L - parts per billion) will not pass the subsequent screens if the allowable dilution is less than about 100-fold. EPA or the responsible state regulatory agency is not likely to allow a greater dilution; therefore, the screening process does not provide useful information.

Concentration decision points for water, tissues, and sediments are set unrealistically low. Natural background concentrations of hydrocarbons of the types found in oil industry effluents are likely to be similar to or higher than the decision point concentrations, particularly in sediments (5 μg/kg dry wt.) and tissues (5 μg/kg wet wt.). The decision point concentrations are very near the detection limits of available analytical methods for most chemicals of concern in oil industry effluents. This will result in a high variance in measured concentrations near the decision points and lack of confidence in the value of the decision concentrations.

The technical basis for calculating values for BCFs and BAFs is very weak. Regression equations between log K_{ow} and log BCF, based on data or model predictions primarily for chlorinated hydrocarbons, will not produce good estimates for BCFs for saturated and aromatic hydrocarbons of the types found in oil industry effluents, and for other nonpolar organic chemicals that are rapidly metabolized in tissues of aquatic animals and excreted. Because most hydrocarbons are absorbed poorly from food and metabolized/excreted rapidly by active enzymatic processes, estimated Fms based on food chain behavior of non-

metabolizable chemicals will overestimate bioaccumulation from food and possible biomagnification. Hydrocarbons do not biomagnify in aquatic and marine food webs.

The tissue residue option is not appropriate for regulation of potentially bioconcentratable chemicals in oil industry effluents because it will not be possible, in most cases, to identify the source(s) of chemical residues in the tissues of feral animals in the receiving water environment.

Analysis of sediments in depositional areas near an outfall will not provide much useful information about the chemical content of ongoing discharges. Sediments represent a long-term reservoir for nonpolar chemicals. It usually is difficult or impossible to determine the source(s) of chemicals in sediments of depositional areas remote from point sources. In addition, most fine-grained sediments contain concentrations of natural (biogenic) and anthropogenic hydrocarbons well above the sediment concentration decision point. Current models for predicting bioaccumulation of nonpolar organic chemicals from sediments by demersal and benthic animals have not been adequately validated, to date, to be used for regulation.

The DBG, if applied in its present form to regulation of NPDES-permitted effluents from oil industry operations would be unnecessarily stringent. Industry should not be required to eliminate discharges or to develop new costly technologies to remove traces of organic chemicals (mostly hydrocarbons) that, because of their behavior in aquatic food webs, do not pose a health hazard to human consumers of fishery products.

RECOMMENDATIONS

A more useful approach to identifying and quantifying potentially bioconcentratable chemicals in oil industry permitted effluents would be to focus on chemicals for which physical/chemical and toxicological information is available. Representative samples of effluent would be analyzed by modern highly sensitive methods. Identification and quantification of chemicals in the extract would be targeted (by selected ion monitoring) to classes or groups of chemicals known or suspected of being present in the particular effluent at a concentration that might result in biologically significant bioconcentration (about 1 μg/L). Specific target analytes would be chemicals for which an adequate validated physical/chemical and toxicological database exists.

EPA should generate and validate physical/chemical and toxicological data for chemicals that are frequently detected in permitted effluents at potentially harmful concentrations, for which the necessary data do not yet exist. As more data are added to available risk assessment databases, new chemicals could be added to the target analyte list.

BCFs should be calculated on a tissue lipid basis (amount of chemical per unit weight of tissue lipid/amount of chemical per unit weight of water), not as proposed in the DBG on a whole tissue basis corrected for percent lipid. Many of the published BCF data can be converted to a lipid basis if the investigators measured the lipid concentration of the whole animals in their studies. Use of lipid-normalized BCFs would substantially reduce the variability of BCF/K_{ow} regressions.

Values for K_{ow}, BCF, and BAF used in evaluating the potential hazard of a particular chemical should be based on empirical data to the extent possible. If models are used, they should be specific for the types of chemicals under scrutiny and should model real-world scenarios, not idealized situations (e.g., linear, first order uptake and release rate constants; efficient uptake from food; very little or no metabolism and excretion of accumulated chemicals). Consideration must be given to partitioning of nonpolar organic chemicals in the receiving water environment. Only chemicals that are in true solution in the water are modeled by the BCF equations. The bioconcentration assessment should become part of an ecological risk assessment, relying on data produced by the ecological risk assessment on the distribution, partitioning, and physical/biological fates of the chemicals of concern in the receiving water environment.

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APPENDIX A

Concentrations of Potentially Bioconcentratable Chemicals in Permitted Effluents from Oil Refineries, Petroleum Marketing Terminals, and Oil/Gas Production Platforms

Table A-1. Aromatic Hydrocarbons and Related Heterocyclic Compounds with K_{ow}>3.5 in Refinery Effluents. Concentrations are in µg/L. From Searl and Brown (1984) and Canviro Consultants (1987).

Compound	Illinois1975	Pace1981	Pace1985	API/A81	API/B81
Acenaphthene			10		
Dimethylnaphthalenes		65			
Fluorene		5.1		6	
Phenenthrene		13	3		1
Anthracene		0.25			1
Methylanthracenes			10		
Fluoranthene	0.06			1	
Pyrene	0.5	1.6	2	3	1
Benz(a)anthracene	0.3	9.0		4	1
Chrysene	ND(0.1)	2.8	9	4	1
Triphenylene	2.8				
Benzo(k)fluoranthene	0.1				
Benzofluoranthenes	ND(0.02)				
Methylbenz(a)anthracenes	0.2				
Benzo(a)pyrene	0.5				
Benzo(e)pyrene	3.9				
Dimethylbenz(a)anthracenes	0.2				
Methylbenzo(e)pyrene	4.4				
Methylbenzo(a)pyrene	0.9				
Perylene	0.7				
Benzo(ghi)perylene	0.7				
Coronene	ND(0.02)				

Table A-2. Statistical Analysis of Average Flow-Weighted Concentrations (μg/L) of Organic Compounds in Refinery Effluents Subjected to Different Treatments. Compounds indicated by * have estimated log K_{ow}s below 3.5. Versar, Inc. 1982; EPA 1982.

Compound	Pretreated Raw & Current	Current/BPT	BAT Op1	BAT Op2	Rev Bat Op1	Rev BAT Op2
Acrolein*	0.7					
Aldrin	0.6					
δ-BHC	0.6					
DDE	0.4					
DDT	0.01					
β-Endosulfan	0.6					
Isophorone*	293.3					
Dichloromethane*	0.1					
Chloroform*	24.6	3.1	4.0	3.9	3.9	3.7
1,2-Dichloroethane*	0.9					
1,1,1-Trichloroethane*	0.5					
t-1,2-dichloroethane*	0.1					
Tetrachloroethane*	0.4					
4-Chlorophenyphenyl ether*	1.4					
Chlorobenzene*	0.1					
Phenol*	1368.7					
2-Chlorophenol*	28.5					
Pentachlorophenol[1]	2.2					
2-Nitrophenol*	65.5					
4-Nitrophenol*	561.4					
Benzene*	148.8	2.3	3.2	2.9	3.1	2.9
Ethylbenzene*	123.8					
Toluene*	398.1	10.1	12.4	10.9	11.9	11.1

(continued)

Table A-2. Statistical Analysis of Average Flow-Weighted Concentrations (µg/L) of Organic Compounds in Refinery Effluents Subjected to Different Treatments. Compounds indicated by * have estimated log K_{ow}s below 3.5. Versar, Inc. 1982; EPA 1982 (continued).

Compound	Pretreated Raw & Current	Current/BPT	BAT Op1	BAT Op2	Rev Bat Op1	Rev BAT Op2
p-Chloro-m-cresol*		0.3	0.5	0.5	0.5	0.5
2,4-Dichlorophenol*		0.2	0.4	0.3	0.4	0.4
2,4-Dinitrophenol*	1068.4					
2,4-dimethylphenol*	1207.7					
4.6-Dinitro-o-cresol*	2.9					
Dimethylphthalate*		0.1	0.1	0.2	0.1	0.2
Diethylphthalate*	1.5	1.5	1.5	2.0	1.5	1.7
Di-n-butylphthalate*	0.1	0.04	0.3	0.4	0.3	0.4
Acenaphthene	188.9	1.1	0.7	0.6	0.7	0.6
Acenaphthylene	81.5					
Anthracene	119.2					
Banz(a)anthracene	0.4					
Benzo(a)pyrene	0.03	0.1	0.1	0.1	0.1	0.1
Chrysene	5.3	0.02	0.03	0.04	0.03	0.03
Fluoranthene	6.3					
Fluorene	50.5					
Naphthalene	581.6					
Phenanthrene	234.7	0.2	0.1	0.1	0.1	0.1
Pyrene	4.6	0.1	0.2	0.2	0.2	0.2

1, Estimated values for log K_{ow} for pentachlorophenol range from about 3.32 to 5.01.

Table A-3. Concentration of Organic Chemicals in the Effluent from the Dissolved Air Floatation Unit of a Class B Refinery and Percent Removal by Activated Sludge and Activated Carbon Units. Concentrations are in μg/L (ppb). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Raphaelian and Harrison (1978).

Compound	Concentration (μg/L)	Activated Sludge	Activated Carbon
n-Alkanes			
C-9	32	NM	ND
C-10	128	99.98	ND
C-11	349	99.97	T
C-12	544	99.83	97.9
C-13	675	99.74	95.9
C-14	683	99.63	93.7
C-15	651	99.61	91.3
C-16	493	99.59	90.9
C-17	355	99.55	87.6
C-18	261	99.54	86.9
C-19	205	99.55	88.4
C-20	160	99.55	85.3
C-21	107	99.60	79.4
C-22	64	99.40	80.3
C-23	61	99.55	82.6
C-24	43	99.41	79.5
C-25	32	99.36	70.2
C-26	27	99.33	77.9
C-27	19	99.43	T
C-28	13	99.36	T
C-29	11	NM	T
C-30	NM	T	T
C-31	NM	T	T
Branched Alkanes			
C-13	159	99.92	T
C-13	77	99.94	ND
C-14	196	99.80	T
C-14	246	99.96	78.7
Pristane	157	99.73	78.1
Phytane	67	99.94	58.8
Cycloalkanes & Alkenes			
Total Resolved	392	99.76-99.96	ND

(continued)

ND, Not detected
NM, Not measured
T, Trace

Table A-3. Concentration of Organic Chemicals in the Effluent from the Dissolved Air Floatation Unit of a Class B Refinery and Percent Removal by Activated Sludge and Activated Carbon Units. Concentrations are in μg/L (ppb). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Raphaelian and Harrison (1978) (continued).

Compound	Concentration (μg/L)	Activated Sludge	Activated Carbon
Monoaromatics			
Toluene*	101	99.87	84.1
Ethylbenzene*	35	99.95	66.7
p-,m-Xylenes*	187	99.97	76.6
o-Xylene*	101	99.97	77.3
i-propylbenzene	5	ND	ND
n-Propylbenzene	13	99.94	T
m-Ethyltoluene	93	99.98	71.2
o-Ethyltoluene	32	99.98	T
1,3,5-Trimethylbenzene	43	99.97	ND
1,2,4-Trimethylbenzene	176	99.98	44.9
1,2,3-Trimethylbenzene	96	99.98	60.0
n-Butylbenzene	8	T	ND
m-n-Propyltoluene	19	99.97	ND
o-n-Propyltoluene	13	99.96	ND
m-Diethylbenzene	13	T	ND
1,3-Dimethyl-5-ethyl-benzene	29	99.98	ND
1,3-Dimethyl-4-ethyl-benzene	37	99.98	ND
1,2-Dimethyl-4-ethyl-benzene	43	99.99	ND
1,3-Dimethyl-2-ethyl-benzene	16	ND	ND
1,2-Dimethyl-3-ethyl-benzene	13	T	ND
1,2,4,5-Tetramethylbenzene	27	99.98	ND
1,2,3,5-Tetramethylbenzene	48	99.98	T
1,2,3,4-Tetramethylbenzene	64	99.99	51.4
Indan*	93	99.98	50.0
1-Methylindan	104	99.98	T
2-Methylindan	61	99.99	ND
Ethylindan	27	T	ND
Dimethylindans	107	99.97	ND
Trimethylindans	35	T	ND

(continued)

ND, Not detected
NM, Not measured
T, Trace

Table A-3. Concentration of Organic Chemicals in the Effluent from the Dissolved Air Flotation Unit of a Class B Refinery and Percent Removal by Activated Sludge and Activated Carbon Units. Concentrations are in µg/L (ppb). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Raphaelian and Harrison (1978) (continued).

Compound	Concentration (µg/L)	Activated Sludge	Activated Carbon
Monoaromatics (continued)			
Tetralin	11	ND	ND
Methyltetralin	64	T	ND
Ethyltetralin	27	99.93	ND
Dimethyltetralin	21	T	ND
Ethylstyrenes	67	99.98	ND
C_3-Styrenes	165	99.97	ND
Diaromatics			
Naphthalene*	197	99.99	37.7
1-Methylnaphthalene	448	99.99	44.9
2-Methylnaphthalene	259	99.99	33.3
Ethylnaphthalene	77	99.98	55.8
Dimethylnaphthalenes	803	99.99	12.0-37.5
C_3-Naphthalenes	820	99.69	T-91.7
Sulfur Heterocyclics			
Methylbenzothiophenes	82	99.87	71.4
Ethylbenzothiophene	11	99.85	ND
Dimethylbenzothiophenes	43	99.81	ND
Dibenzothiophene	13	T	ND
Polycyclic Aromatic Hydrocarbons			
Phenanthrene/Anthracene	168	99.97	52.8
Methylphenanthrenes	152	N	T
1-Methylanthracene	27	99.98	T
2-Methylanthracene	27	99.99	T
C_2-Phenanthrenes/Anthracenes	114	N	ND
Fluorene	27	N	ND
Methylfluorenes	80	99.91	T
Acenaphthene	3	T	ND
Methylacenaphthenes	75	N	ND
Biphenyl	24	T	T
Methylbiphenyls	30	T	T
Pyrene	29	99.88	76.1
Methylpyrenes	11	99.67	ND
Chrysene	5	99.69	ND

(continued)

ND, Not detected
NM, Not measured
T, Trace

Table A-3. Concentration of Organic Chemicals in the Effluent from the Dissolved Air Floatation Unit of a Class B Refinery and Percent Removal by Activated Sludge and Activated Carbon Units. Concentrations are in μg/L (ppb). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Raphaelian and Harrison (1978) (continued).

Compound	Concentration (μg/L)	Activated Sludge	Activated Carbon
Polycyclic Aromatic Hydrocarbons (continued)			
Benz(a)anthracene	13	99.65	ND
Phenols			
Phenol*	22	ND	ND
Cresol*	33	99.98	NM
p-Cresol*	50	ND	ND
Ethylphenols*	11	ND	ND
Dimethylphenols*	53	99.98	ND
Propylphenols*	23	ND	ND
Methylethylphenols*	5	ND	ND
2,4,5-Trimethylphenol*	3	99.89	ND
C_4-Phenols	3	ND	ND
Diethylphenols	1	ND	ND
Pyridines			
Lutidine*	2	97.6	ND
Ethylpicolines*	1	ND	ND
2,4,6-Collidine*	2	ND	ND
Collidine*	2	67.0	99.6
Ethyllutidine*	1	ND	ND
Quinolines			
Quinoline*	6	ND	ND
Methylquinolines*	8	85.1	ND
Dimethylquinolines*	8	91.9	88.9
C_3-Quinolines*	4	96.7	ND
Anilines			
Aniline*	27	99.5	T
Toluidine*	39	NM	ND
N,N-Dimethylaniline*	<1	88.6	ND

ND, Not detected
NM, Not measured
T, Trace

Table A-4. Maximum Concentrations of Nonpolar Organic Chemicals in 12 Samples of Final Effluents from Each of Two Refineries. All Compounds Except Those indicated By 1 Were Detected in Less than 50 Percent of the Samples. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Values in Parentheses are Means. Concentrations in µg/L. Radian Corp. (1981).

Compound	Refinery A	Refinery B
Phenols		
Pentachlorophenol[1]*	23(2)	22(1)
Phenol[1]*	12(2)	5(2)
2,4-Dimethylphenol[1]*	21(1)	10
Polycyclic Aromatic Hydrocarbons		
Acenaphthene	NA	ND
Anthracene/Phenanthrene	10	1
Benz(a)anthracene/Chrysene	4	1
Benzo(a)pyrene	ND	ND
Benzo(b/k)fluoranthene	ND	ND
Fluoranthene	1	ND
Fluorene	6	ND
Indeno(1,2,3-cd)pyrene	ND	ND
Naphthalene	11	1
Pyrene	3	1
Phthalates (probably analytical contaminants)		
Bis(2-ethylhexyl)phthalate[1]	100(10)	200(8)
Butylbenzylphthalate	1	1
Di-n-butylphthalate[1]*	6(1)	6(1)
Di-n-octylphthalate	8	2
Diethylphthalate[1]*	85(3)	94(3)
Dimethylphthalate*	2	NA

NA, Not analyzed or not reported
ND, Not detected

Table A-5. Maximum and Mean (Parentheses) Concentrations of Base Neutral Extractable Organic Compounds in Effluents from Two Canadian Refineries. Concentrations in µg/L. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Canviro Consultants (1987).

Compound	Sarnia	Trafalgar	Detection Limit
Aromatics			
Naphthalene*	NA	ND	1.6
Methylnaphthalene	ND	ND	2.0
Dimethylnaphthalene	ND	12.8	2.0
Trimethylnaphthalene	ND	44	2.0
Phenanthrene	ND	ND	5.4
Anthracene	NA	ND	1.9
Methylanthracene	ND	ND	2.0
Acenaphthene	ND	NA	1.9
Fluorene	ND	ND	1.9
Flouranthene	ND	NA	2.2
Pyrene	ND	NA	1.9
Phthalates			
Bis(2-ethylhexyl)phthalate	78(11)	120(21)	2.5
Di-n-butylphthalate*	10.1	4.9	2.5
Di-n-octylphthalate	3.7	NA	2.5
Diethylphthalate*	4.9	NA	2.5

NA, Not analyzed or not reported
ND, Not detected

Table A-6. Organic Compounds Identified by Gas Chromatography-Mass Spectrometry in Two Samples of Refinery Effluent. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. From deFur *et al.* (1987).

Compound	Effluent #1	Effluent #2
Naphthalene*	+	+
Benzothiophene*	+	-
Methylbenzothiophene	+	-
2-Methylnaphthalene	+	+
Biphenyl	+	+
Ethylnaphthalene	+	+
C-2 Naphthalenes	+	+
C-2 Benzothiophenes	+	-
Acenaphthene	+	+
4-Methylbiphenyl	-	+
3-Methylbiphenyl	+	-
C-3 Naphthalenes	+	+
C-3 Benzothiophenes	+	+
Fluorene	+	-
Methylacenaphthene	+	-
C-4 Naphthalenes	+	+
Methyldibenzofuran	+	-
Methylfluorene	+	-
C-2 Dibenzofuran	+	+
C-5 Naphthalenes	+	-
Dibenzothiophene	+	-
Anthracene	+	+
C-2 Fluorenes	+	+
C-3 Dibenzofurans	+	+
Methyldibenzothiophene	+	-
C-4 Dibenzofurans	+	+
3-Methylphenanthrene	-	+
2-Methylphenenthrene	+	+
C-3 Fluorenes	+	+
C-2 Dibenzothiophenes	+	-
C-3 Dibenzothiophenes	+	+
Fluoranthene	+	-
Pyrene	+	+
Methylcyclopenta(def) phenanthrenes	+	-
Benzo(a)fluorene	-	+
Methylphenylnaphthalenes	-	+

(continued)

Table A-6. Organic Compounds Identified by Gas Chromatography-Mass Spectrometry in Two Samples of Refinery Effluent. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. From deFur *et al.* (1987) (continued).

Compound	Effluent #1	Effluent #2
C-2 Phenylnaphthalenes	-	+
Benzonaphthothiophene	+	+
Chrysene/Triphenylene	+	+
Benzo(j,b & k)fluor-anthrenes	-	+
Benzo(e)pyrene	-	+
Benzo(a)pyrene	-	+
Perylene	-	+
Benzo(ghi)perylene	-	+
Polar Compounds (numbers are concentrations in μg/L)		
Methylaniline*	+	-
C-2 Aniline*	-	+
Phenol*	+	-
o- & p-Cresol*	+	-
m-Cresol*	+	-
C-2 Phenols*	+	-
C-3 Phenols*	+	-
1,3,5-Trithiane*	+	-
Methylsulfonylbenzene*	-	2.0
1-Methyl-4-methyl sulfonylbenzene*	-	8.0
(Methylsulfonyl) methylbenzene*	-	2.4
Carbazole	2.2	-
α-Phenylbenzemethalol	-	2.5
Methylcarbazoles	4.8	-
C-2 Carbazoles	4.6	-
C-3 Carbazoles	1.9	-
C-4 Carbazoles	0.9	-

Table A-7. Range of Concentrations of Organic Chemicals in Wastewater Streams Sampled Four Times Over 16 Weeks from Petroleum Product Marketing Terminals. Concentrations are in µg/L. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Borey *et al.* 1989.

Compound	TX	BX	BCX	RX	FCX	SX	SCX
Aromatic Hydrocarbons							
Benzene*	14000-30000	ND-160	ND-1500	ND-290	ND	ND-1200ND-200	
Toluene*	2100-18000	5-300	ND-2900	ND-480	ND-200	ND-1300ND-200	
Ethylbenzene*	1800-2900	ND	ND-300	ND-3	ND	NDND	
Naphthalene*	ND-970	ND-2	ND	ND	ND	ND-25ND-2	
Phenanthrene	ND-42	ND-3	ND	ND	ND	ND-7ND	
Anthracene	ND-8	ND	ND	ND	ND	ND-3ND	
Fluoranthene	ND-100	ND	ND	ND-1	ND	NDND	
Pyrene	ND-300	ND	ND	ND-1	ND	NDND	
Chrysene	ND	ND	ND	ND-2	ND	NDND	
Benz(a)anthracene	ND	ND	ND	ND-2	ND	NDND	
Phenols							
Phenol*	ND-16000	ND	ND-27	ND-2	ND-7	440-6900ND-1300	
2,4-Dimethylphenol*	220-600	ND	ND	ND	ND	ND-410ND	
Chlorinated Compounds							
Methylene chloride*	ND	ND	ND-3	ND	ND-5	NDND	
bis(2-Chloroethyl)ether*	ND	ND	ND	ND-2	ND	NDND	
bis(2-Chloroisopropyl)ether	ND	ND-24	ND-37	ND	ND	NDND	
2-Chloronaphthalene	ND-4	ND	ND	ND	ND	NDND	
Phthalates							
di-n-Butylphthalate*	ND-100	ND-2	ND-2	ND-3	ND-2	ND-7ND-3	
Diethylphthalate*	ND	ND-1	ND	ND	ND	NDND	
Butylbenzylphthalate	ND	ND	ND-2	ND-1	ND	NDND	
bis(2-Ethylhexyl)phthalate	ND-47	ND-63	ND-16	ND-23	ND-260	10-140ND-25	
di-n-Octylphthalate	ND-4	ND-15	ND	ND	ND-17	NS-89ND	

Table A-8. Concentrations of Nonpolar Organic Chemicals in Produced Water From Coastal Louisiana. Numbers in Parentheses are Concentrations Determined in Samples Collected During a Preliminary Survey in 1985. Concentrations in μg/L. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Neff *et al.* (1989).

Compound	Lake Pelto	Eugene Isle #105	Eugene Isle #120	Ship Shoal
n-Alkanes				
C-10	14.1	19.3		
C-11	29.5	93.1		
C-12	43.7	193		
C-13	54.6	272		
C-14	56.2	308		
C-15	57.2	266		
C-16	54.9	177		
C-17	56.1	142		
C-18	33.4	215		
C-19	38.3	180		
C-20	35.6	171		
C-21	29.5	123		
C-22	24.7	107		
C-23	21.7	85.2		
C-24	19.8	69.2		
C-25	18.5	56.7		
C-26	16.4	50.5		
C-27	11.5	39.8		
C-28	9.7	29.9		
C-29	8.0	25.7		
C-30	6.4	18.7		
C-31	6.6	17.5		
C-32	4.3	10.6		
C-34	2.2	6.6		
Aromatics				
C-2 Benzenes*	24.1(195)	25.8(176)	275	177
C-3 Benzenes	25.4(193)	31.5(174)	86.4	159
C-4 Benzenes	11.6(119)	9.54(94.9)	74.9	102
C-5 Benzenes	0.90(63.4)	0.72(70.3)	42.5	70.3
C-6 Benzenes	0.19		0.00	
Naphthalene*	13.9(53.4)	9.64(48.5)	67.9	70.4
C-1 Naphthalenes	22.5(78.2)	18.4(83.1)	97.6	118
C-2 Naphthalenes	36.0(99.8)	26.7(104)	121	143
C-3 Naphthalenes	18.9(74.8)	15.1(84.1)	110	109
C-4 Naphthalenes	4.31(24.9)	3.69(11.1)	35.2	45.1

(continued)

Table A-8. Concentrations of Nonpolar Organic Chemicals in Produced Water From Coastal Louisiana. Numbers in Parentheses are Concentrations Determined in Samples Collected During a Preliminary Survey in 1985. Concentrations in µg/L. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Neff *et al.* (1989) (continued).

Compound	Lake Pelto	Eugene Isle #105	Eugene Isle #120	Ship Shoal
Aromatics (continued)				
C-5 Naphthalenes	0.00	0.00		
Biphenyl	1.75	2.08		
C-1 Biphenyls	0.26	0.26		
C-2 Biphenyls	0.10	0.10		
C-3 Biphenyls	0.01	0.04		
C-4 Biphenyls	0.00	0.00		
C-5 Biphenyls	0.00	0.00		
Fluorene	1.98(3.06)	0.17(0.11)	1.26	2.10
C-1 Fluorenes	2.81(6.85)	0.31(0.00)	1.26	13.3
C-2 Fluorenes	3.89(10.0)	0.27(0.00)	1.00	23.0
C-3 Fluorenes	2.12(6.66)	0.00(0.00)	0.80	21.2
C-4 Fluorenes	0.51	0.00		
C-5 Fluorenes	0.00	0.00		
Dibenzothiophene	0.56(1.86)	1.02(3.70)	3.43	1.94
C-1Dibenzothiophenes	1.91(3.56)	0.20(0.00)	0.53	6.47
C-2Dibenzothiophenes	1.15(4.31)	0.00(0.00)	0.00	11.8
C-3Dibenzothiophenes	0.98(0.98)	0.04(0.00)	0.00	6.80
C-4Dibenzothiophenes	0.21(0.00)	0.004(0.00)	0.00	1.28
C-5Dibenzothiophenes	0.00	0.00		
Phenanthrene	4.34(7.32)	0.85(0.70)	2.37	9.67
C-1 Phenanthrenes	3.75(22.4)	0.37(0.00)	5.32	34.8
C-2 Phenanthrenes	10.1(22.8)	0.44(0.00)	3.50	39.7
C-3 Phenanthrenes	4.16(7.68)	0.26(0.00)	0.64	16.1
C-4 Phenanthrenes	0.00(0.00)	0.00(0.00)	0.00	1.78
C-5 Phenanthrenes	0.00	0.00		
Pyrene	0.23	0.00		
C-1 Pyrenes	0.62	0.00		
C-2 Pyrenes	0.74	0.00		
C-3 Pyrenes	0.87	0.00		
C-4 Pyrenes	0.49	0.00		
C-5 Pyrenes	0.00	0.00		
Chrysene	0.33	0.00		
C-1 Chrysenes	0.92	0.00		
C-2 Chrysenes	0.73	0.00		
C-3 Chrysenes	0.26	0.00		
C-4 Chrysenes	0.02	0.00		

(continued)

Table A-8. Concentrations of Nonpolar Organic Chemicals in Produced Water From Coastal Louisiana. Numbers in Parentheses are Concentrations Determined in Samples Collected During a Preliminary Survey in 1985. Concentrations in μg/L. Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Neff *et al.* (1989) (continued).

Compound	Lake Pelto	Eugene Isle #105	Eugene Isle #120	Ship Shoal
Aromatics (continued)				
C-5 Chrysenes	0.00	0.00		
Perylene	0.48	0.00		
C-1 Perylenes	0.08	0.00		
C-2 Perylenes	0.02	0.00		
C-3 Perylenes	0.00	0.00		

Table A-9. Organic Chemical Composition of Produced Water Samples from Coastal Louisiana Studied by Boesch and Rabalais (1989). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Concentrations are in µg/L.

Compound	Conoco87	Exxon1	Exxon2	Conoco88	Fourchon	Timbilier
Benzene*	2,900	8,000	1,700	2,400	2,000	1,200
Toluene*	1,800	1,200	640	1,300	660	600
Ethylbenzene*	68	54	37	62	24	25
Xylenes*	140	240	15	420	180	160
Naphthalene*	220	140	88	210	90	190
C-1 Naphthalenes	240	120	Tr	250	170	150
C-2 Naphthalenes	220	81	Tr	360	130	180
C-3 Naphthalenes	98	20	ND	270	54	130
Fluorene	ND	ND	ND	18	Tr	13
Dibenzothiophene	ND	ND	ND	Tr	Tr	5
C-1 Dibenzothiophenes	ND	ND	ND	30	Tr	17
C-2 Dibenzothiophenes	ND	ND	ND	24	Tr	8
Phenanthrene	Tr	120	ND	6	13	23
C-1 Phenanthrenes	Tr	260	ND	83	22	59
C-2 Phenanthrenes	ND	ND	ND	110	25	50
C-3 Phenanthrenes	ND	ND	ND	55	Tr	27
Anthracene	ND	ND	ND	Tr	ND	ND
Fluornathene	ND	ND	ND	Tr	ND	ND
Pyrene	ND	ND	ND	ND	ND	ND
Benz(a)anthracene	ND	ND	ND	ND	ND	ND
Chrysene	ND	ND	ND	ND	ND	ND
Benzo(b & k)fluoranthenes	ND	ND	ND	ND	ND	ND
Benzo(a)pyrene	ND	ND	ND	ND	ND	ND

ND, Not Detected
Tr, Trace Concentration

Table A-9. Organic Chemical Composition of Produced Water Samples from Coastal Louisiana Studied by Boesch and Rabalais (1989). Chemicals Indicated with * Have Estimated Values for Log K_{ow} Lower than 3.5. Concentrations are in µg/L (continued).

Compound	Conoco87	Exxon1	Exxon2	Conoco88	Fourchon	Timbilier
Aromatic Acids						
Phenol*	2,800	1.200	1.200	2,900	1,600	1,800
p-Cresol*	300	110	89	310	150	180
M, o-Cresols*	1,400	500	440	1,300	510	750
Benzoic acid*	2,300	220	260	4,900	3,100	4,00
Polar Compounds						
Pentanoic acid*				1,500		
Hexanoic acid*				1,500		
Heptanoic acid*				950		
Benzoic acid*				4,400		
Octanoic acid*				670		
Methylbenzoic acids*				3,190		
Nonanoic acid*				470		
Decanoic acid*				150		
3-Methyloctanoic acid*				1,300		

APPENDIX B

Physical/Chemical Properties of Mono-aromatic Hydrocarbons, Polycyclic Aromatic Hydrocarbons, Saturated Hydrocarbons, and Heterocyclic Compounds with Log K_{ow}>3.5

Table B-1. Physical/Chemical Properties of Non-Polar Organic Chemicals with K_{ow}>3.5 in Refinery, Marketing Terminal, and Produced Water Effluents.

Compound	Molecular Weight	Aqueous Solubility		Log K_{ow}	Henry's Law Const.
		mg/L	mM/L		
One-Ring Aromatic Hydrocarbons					
Indan	118.1	109	0.920	3.31-3.57	
Isopropylbenzene	120.2	48.3	0.402	3.66	0.614
n-Propylbenzene	120.2	52.2	0.434	3.69	0.417
1-Ethyl 4-methyl benzene	120.2	94.9	0.789	3.63	0.201
1-Ethyl 2-methyl benzene	120.2	74.6	0.621	3.53	0.215
1,3,5-Trimethyl benzene	120.2	48.2	0.401	3.55	0.330
1,2,4-Trimethyl benzene	120.2	51.9	0.432	3.58	0.253
1,2,3-Trimethyl benzene	120.2	65.5	0.545	3.58	0.150
t-Butylbenzene	134.2	29.5	0.220	4.11	0.525
Isobutylbenzene	134.2	10.1	0.0753	4.01	1.33
s-Butylbenzene	134.2	17.6	0.131	--	0.742
1-Isopropyl 4-methylbenzene	134.2	34.2	0.254	--	0.324
n-Butylbenzene	134.2	13.8	0.103	4.28	0.538
1,2,4,5-Tetra-methylbenzene	134.2	3.48	0.0259	4.00	1.03
n-Pentylbenzene	148.3	1.05	0.0071	4.90	0.249
n-Hexylbenzene	162.3	1.02	0.0063	5.52	0.798
Polycyclic Aromatic Hydrocarbons					
2-Methyl naphthalene	142.2	25.6	0.180	3.86	0.0203
1-Methyl naphthalene	142.2	28.4	0.200	3.87	0.0160
Acenaphthylene	152.2	3.470	0.0228		
Biphenyl	154.2	7.0	0.0454	3.95	0.0348
Acenaphthene	154.2	3.93	0.0255	3.92	0.0042
2-Ethyl naphthalene	156.2	8.0	0.0512	3.86	0.0255
1-Ethyl naphthalene	156.2	1.07	0.0069	3.87	0.0148

(continued)

Table B-1. Physical/Chemical Properties of Non-Polar Organic Chemicals with K_{ow}>3.5 in Refinery, Marketing Terminal, and Produced Water Effluents (continued).

Compound	Molecular Weight	Aqueous Solubility		Log K_{ow}	Henry's Law Const.
		mg/L	mM/L		
Polycyclic Aromatic Hydrocarbons (continued)					
1,3-Dimethyl naphthalene	156.2	8.00	0.0512	4.42	
1,4-Dimethyl naphthalene	156.2	11.40	0.073	4.37	
1,5-Dimethyl naphthalene	156.2	3.37	0.0216	4.38	
2,6-Dimethyl naphthalene	156.2	2.00	0.0128	4.31	0.0065
1,5-Dimethyl naphthalene	156.2	3.37	0.0216	4.38	
2,3-Dimethyl naphthalene	156.2	3.00	0.0192	4.40	0.0063
Fluorene	166.2	1.84	0.0111	4.18	0.0036
4-Methylbiphenyl	168.2	4.05	0.0241		
1,4,5-Trimethyl naphthalene	176.2	2.10	0.0119	4.90	0.0095
Phenanthrene	178.2	1.18	0.0066	4.57	0.0014
Anthracene	178.2	0.0731	0.0004	4.54	6.63-04
1-Methylfluorene	180.0	1.09	0.0061	4.97	
4,4'-Dimethyl biphenyl	183.2	0.176	0.000959		
2-Methyl anthracene	192.3	0.023	1.20-04	5.15	
9-Methyl anthracene	192.3	0.261	0.00136	5.07	0.0428
1-Methyl phenanthrene	192.3	0.269	0.00140	5.08	
2-Methyl anthracene	196.3	0.039	0.0002	5.15	
Pyrene	202.3	0.135	0.0007	5.18	3.47-04
Fluoranthene	202.3	0.263	0.0013	5.22	3.51-04
2-Ethylanthracene	206.3	0.027	0.00013	5.85	
9,10-Dimethyl anthracene	206.3	0.0557	0.0003	5.69	
Diisopropyl naphthalene	212	0.11	5.19-04	4.90	

(continued)

Table B-1. Physical/Chemical Properties of Non-Polar Organic Chemicals with K_{ow}>3.5 in Refinery, Marketing Terminal, and Produced Water Effluents (continued).

Compound	Molecular Weight	Aqueous Solubility		Log K_{ow}	Henry's Law Const.
		mg/L	mM/L		
Polycyclic Aromatic Hydrocarbons (continued)					
Dimethyl dibenzothiophenes	212.3			5.50	
2,3-Benzofluorene	216.3	0.002	9.2-06	5.75	
1,2-Benzofluorene	216.3	0.0454	2.1-04	5.32	
benzo(ghi) Fluoranthene	226.3			6.9	
Trimethyl dibenzothiophenes	226.4			5.73	
Chrysene	228.3	0.002	8.8-06	5.79	1.80-04
2,3-Benz anthracene	228.3	0.000571	2.5-06	5.90	
1,2-Benz anthracene	228.3	0.0140	6.1-05	5.91	1.68-04
Triphenylene	228.3	0.0066	2.89-05		
2,6-Diphenyl pyridine	232.3			4.82	
5-Methylchrysene	242.1	0.0629	2.6-04	6.42	
6-Methylchrysene	242.1	0.0654	2.7-04	6.42	
Benzo(b) Fluoranthene	252.3	0.0012	4.8-06		
Benzo(k) Fluoranthene	252.3	0.00055	2.2-06	6.4	
Benzo(e)pyrene	252.3	0.00630	2.5-05		6.4
Benzo(a)pyrene	252.3	0.00404	1.6-05	5.98	2.27-05
Perylene	252.3	0.000404	1.6-06	6.50	
7,12-Dimethyl benz(a)anthracene	256.1	0.0538	2.1-04	6.93	
3-Methyl cholanthrene	268.4	0.00295	1.1-05	7.11	
Indeno(1,2,3-cd) pyrene	276.3	0.0620	2.24-04	7.0	
Benzo(ghi) Perylene	276.3	0.00026	9.0-07	7.10	5.86-06
Picene	278.3	0.00038	1.34-07	7.19	
1,2,5,6-Dibenz anthracene	278.4	0.000501	1.8-06	7.19	3.07-06

(continued)

Table B-1. Physical/Chemical Properties of Non-Polar Organic Chemicals with K_{ow}>3.5 in Refinery, Marketing Terminal, and Produced Water Effluents (continued).

Compound	Molecular Weight	Aqueous Solubility		Log K_{ow}	Henry's Law Const.
		mg/L	mM/L		
Polycyclic Aromatic Hydrocarbons (continued)					
Coronene	300.4	0.000140	5.0-07	7.64	
Saturates					
2,2-Dimenthybutane	86.2	21.2	0.246	3.82	69.9
2,3-Dimethylbutane	86.2	19.1	0.222	3.85	57.0
n-Heptane	100.0	2.96	0.0306	3.50	80.6
2,2-Dimethylpentane	100.2	4.40	0.0439	3.10	129.0
2,4-Dimethylpentane	100.2	4.41	0.0440	3.10	120.0
3,3-Dimethylpentane	100.2	5.94	0.0593		74.9
2,3-Dimethylpentane	100.2	5.25	0.0524		70.7
3-Methylhexane	100.2	2.64	0.0263		126.0
1,1,3-Trimethyl cyclopentane	112.2	3.73	0.0332		64.3
1,4-Dimethyl cyclohexane	112.2	3.84	0.0342		35.6
1,2-Dimethyl cyclohexane	112.2	6.00	0.0535		14.6
Propylcyclopentane	112.2	2.04	0.0182		36.4
2,3,4-Trimethyl pentane	114.2	2.30	0.0201		72.1
2,2,4-Trimethyl pentane	114.2	2.44			
3-Methylheptane	114.2	0.792	0.00693		151.0
n-Octane	114.2	0.660	0.00577	4.00	
4-Methyloctane	128.3	0.115	8.97-04		406.0
Pentylcyclopentane	140.3	0.115	8.20-04		74.8
n-Nonane	128.2	0.22	1.7-03	4.51	
n-Decane	142.2	0.020	1.4-04	5.01	
n-Undecane	156.2	0.014	9.0-05	5.58	
n-Dodecane	170.3	0.0035	2.1-05	6.10	
n-Tridecane	184.3	0.0047	2.6-05	6.65	
n-Tetradecane	198.3	0.00033	1.7-06	7.20	
n-Pentadecane	212.4	0.000076	4.0-07	7.72	
n-Hexadecane	226.4	0.000021	9.3-08	8.25	
n-Heptodecane	240.4	0.0000055	2.3-08	8.79	
n-Octadecane	254.4	0.0000014	5.5-09	9.32	
n-Nonodecane	268.5	0.0000004	1.5-09	9.86	

(continued)

Table B-1. Physical/Chemical Properties of Non-Polar Organic Chemicals with K_{ow}>3.5 in Refinery, Marketing Terminal, and Produced Water Effluents (continued).

Compound	Molecular Weight	Aqueous Solubility		Log K_{ow}	Henry's Law Const.
		mg/L	mM/L		
Saturates (continued)					
n-Eicosane	282.5	0.0000001	3.5-10	10.39	
n-Heneicosane	296.6	0.00000003	1.0-10	10.93	
n-Docasane	310.6	0.000000008	2.6-11	11.46	
n-Tricosane	324.6	0.000000002	6.2-12	12.0	
n-Tetracosane	338.6	0.0000000006	1.8-12	12.53	
n-Pentacosane	352.6	0.0000000002	5.7-13	13.07	
n-Hexacosane	366.7	0.0000000001	2.7-13		
Olefins (alkenes)					
1-Octene	112.2	3.6	0.0321	4.57	38.9
1-Nonene	126.2	1.12	0.00885	5.15	
1-Decene	140.3			5.70	
Heterocyclic Compounds					
Methylindan	132.1				
Methyl benzothiophenes	147.2				
Carbazole	167.2	1.0	0.0060	3.84	
Dibenzofuran	168.2	4.22	0.0251	4.21	
Acridine	179.2	46.2	0.258	3.45	
Methylcarbazoles	180.2				
Dibenzo(1,4)dioxin	183.2	0.0267	0.000146	4.19	
Dibenzothiophene	184.3	1.47	0.0080	4.49	
Methyl dibenzothiophenes	198.3			4.86	
Benzo(b)naphtho (2,3d)thiophene	234.3			5.07	
13H-Dibenzo(a,i) carbazole	267.3	0.010	0.000039	5.89	
Chlorinated Compounds					
2-Chloronaphthalene	162.61			4.08	

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