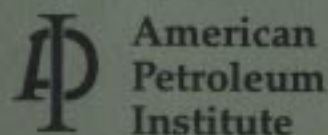


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Critical Review of Draft EPA Guidance on Assessment and Control of Bioconcentratable Contaminants in Surface Waters



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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

API PUBLICATION NUMBER 4610

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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 The EPA draft guidance does not provide a sound basis for identifying and predicting bioaccumulation of nonpolar organic chemicals of the types found in petroleum industry effluents.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 $\log K_{ow}/\log \text{BCF}$ model is very weak. Regression equations between $\log K_{ow}$ and $\log \text{BCF}$, 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 it 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 $\mu\text{g}/\text{kg}$ 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 ($\mu\text{g/L}$) 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 ($\text{Log } K_{ow} > 3.5$) Chemicals in Oil Industry Effluents and Span the Range of $\text{log } K_{ow}$ Values in the Three HPLC Fractions of the Proposed Fractionation Method.

<u>Chemical</u>	<u>Class</u>	<u>Log K_{ow}</u> ¹
<u>Fraction 1: Log K_{ow} 3.5 to 4.5</u>		
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
<u>Fraction 2: Log K_{ow} 4.5 to 5.7</u>		
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
<u>Fraction 3: Log K_{ow} 5.7 to 8.2</u>		
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 $0.1\mu\text{g/L}$ or $5\mu\text{g/kg}$, 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:

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

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 $\log \text{BCF}$ 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 $\log \text{BCF}$ 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:

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

There is a good correlation between $\log \text{BCF}$ 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 $\log K_{ow}/\log \text{BCF}$ 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.

Schüttürmann 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} (Schüttürmann 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; Schüttürmann 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:

	<u>Log K_{ow} Range</u>	<u>K_{ow} Range</u>
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