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EPA

Technical Basis for the Derivation of Equilibrium Partitioning Sediment Guidelines (ESGs) for the Protection of Benthic Organisms: Nonionic Organics

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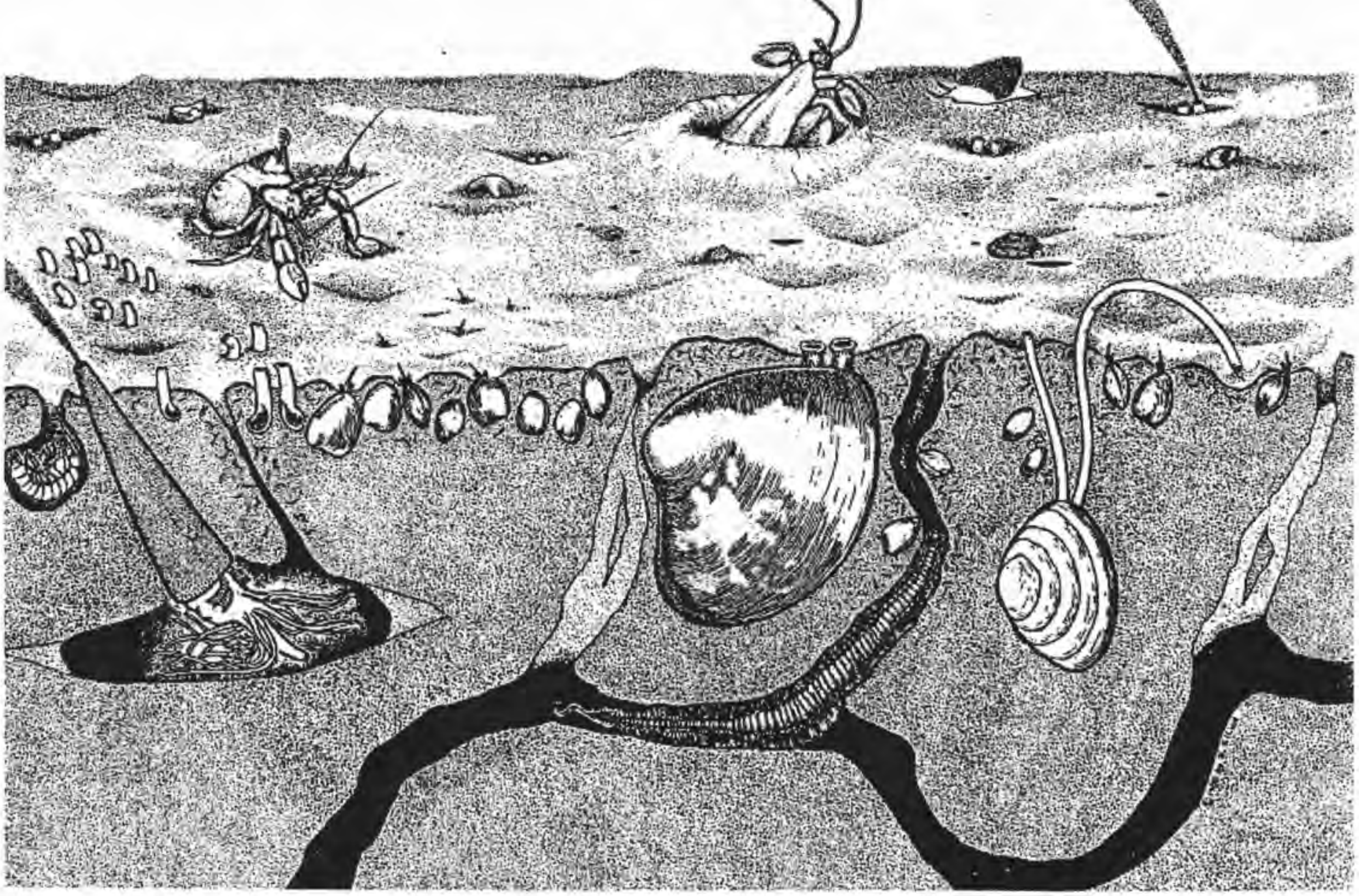

Foreword

Under the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) and the States develop programs for protecting the chemical, physical, and biological integrity of the nation's waters. To meet the objectives of the CWA, EPA has periodically issued ambient water quality criteria (WQC) beginning with the publication of "Water Quality Criteria, 1972" (NAS, 1973). The development of WQC is authorized by Section 304(a)(1) of the CWA, which directs the Administrator to develop and publish "criteria" reflecting the latest scientific knowledge on (1) the kind and extent of effects on human health and welfare, including effects on plankton, fish, shellfish, and wildlife, that may be expected from the presence of pollutants in any body of water, including ground water; and (2) the concentration and dispersal of pollutants on biological community diversity, productivity, and stability. All criteria guidance through late 1986 was summarized in an EPA document entitled "Quality Criteria for Water, 1986" (U.S. EPA, 1987). Updates on WQC documents for selected chemicals and new criteria recommendations for other pollutants have been more recently published as "National Recommended Water Quality Criteria-Correction" (U.S. EPA, 1999). EPA will continue to update the nationally recommended WQC as needed in the future.

In addition to the development of WQC and to continue to meet the objectives of the CWA, EPA has conducted efforts to develop and publish equilibrium partitioning sediment guidelines (ESGs) for some of the 65 toxic pollutants or toxic pollutant categories. Toxic contaminants in bottom sediments of the nation's lakes, rivers, wetlands, and coastal waters create the potential for continued environmental degradation even where water column contaminant levels meet applicable water quality standards. In addition, contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased. These guidelines are authorized under Section 304(a)(2) of the CWA, which directs the Administrator to develop and publish information on, among other things, the factors necessary to restore and maintain the chemical, physical, and biological integrity of all navigable waters.

The ESGs and associated methodology presented in this document are EPA's best recommendation as to the concentrations of a substance that may be present in sediment while still protecting benthic organisms from the effects of that substance. These guidelines are applicable to a variety of freshwater and marine sediments because they are based on the biologically available concentration of the substance in the sediments. These ESGs are intended to provide protection to benthic organisms from direct toxicity due to this substance. In some cases, the additive toxicity for specific classes of toxicants (e.g., metal mixtures or polycyclic aromatic hydrocarbon mixtures) is addressed. The ESGs do not protect against synergistic or antagonistic effects of contaminants or bioaccumulative effects to benthos. They are not protective of wildlife or human health endpoints.

EPA recommends that ESGs be used as a complement to existing sediment assessment tools, to help assess the extent of sediment contamination, to help identify chemicals causing toxicity, and to serve as targets for pollutant loading control measures. EPA is developing guidance to assist in the application of these guidelines in water-related programs of the States and this Agency. This document provides guidance to EPA Regions, States, the regulated community, and the public. It is designed to implement national policy concerning the matters addressed. It does not, however, substitute for the CWA or EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, States, or the regulated community. EPA and State decisionmakers retain the discretion to adopt approaches on a case-by-case basis that differ from this guidance where appropriate. EPA may change this guidance in the future.

Foreword

This document has been reviewed by EPA's Office of Science and Technology (Health and Ecological Criteria Division, Washington, DC) and Office of Research and Development (Mid-Continent Ecology Division, Duluth, MN; Atlantic Ecology Division, Narragansett, RI), and approved for publication.

Front cover image provided by Wayne R. Davis and Virginia Lee.

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Executive Summary

The purpose of this document is to present the technical basis for establishing sediment guidelines for nonionic organic chemicals using equilibrium partitioning (EqP). This approach is chosen because it addresses the two principal technical issues that must be resolved in deriving nationally applicable, scientifically defensible sediment guidelines: varying bioavailability of chemicals in sediment and selection of an appropriate biological effects concentration.

The data used to examine the question of varying bioavailability across sediments are from toxicity and bioaccumulation experiments using the same chemical and test organism but different sediments. It has been demonstrated that if the different sediments in each experiment are compared, there are only weak relationships between sediment chemical concentrations on a dry weight basis and biological effects. However, if the chemical concentrations in the interstitial water of the sediment are used (for chemicals that are not highly hydrophobic), or if the sediment chemical concentrations on an organic carbon basis are used, then the biological effects occur at similar concentrations for the different sediments (typically within a factor of two). Most importantly, the effects concentrations are the same as, or they can be predicted from, the effects concentration determined in water-only exposures.

The EqP methodology assumes that the partitioning of a chemical between sediment organic carbon and interstitial water is at or near equilibrium. For both of these phases, the fugacity or activity of the chemical is the same at equilibrium. As a result, the principal assumption is that the organism receives an equivalent exposure from the water-only phase or from any equilibrated phase: either from interstitial water via respiration, or from sediment carbon via ingestion, or from a mixture of exposure routes. Therefore, the pathway of exposure is not significant. For the data presented herein, the observed effects concentration for a chemical on an organic carbon basis can be predicted to within the uncertainty of the model.

Equilibrium partitioning sediment guidelines (ESGs) for nonionic organic chemicals are based on the organic carbon-normalized chemical concentration. The interstitial water concentration is the sum of the free chemical concentration, which is bioavailable and represents the chemical activity, and the concentration of chemical complexed to dissolved organic carbon, which is not bioavailable. For highly hydrophobic chemicals ($K_{\mathrm{OW}} > 5.5$), this is necessary because the interstitial water concentration is, for these chemicals, not necessarily a good estimate of the chemical activity; that is, the proportion of chemical bound to dissolved organic carbon is high. Use of the chemical concentration in sediment organic carbon eliminates this ambiguity.

ESGs also require that a chemical concentration be selected that is appropriately protective of benthic organisms. The final chronic value (FCV) from the U.S. Environmental Protection Agency (EPA) aquatic life water quality criteria (WQC) has been chosen. Analysis of the data compiled in the published or draft WQC documents demonstrates that benthic species, defined as either epibenthic or infaunal species, have a similar sensitivity to all water quality criteria species combined. This similarity is the case if the most sensitive species are compared and if all species are compared. The results of benthic colonization experiments also support use of the FCV. Therefore, if the effects concentrations in sediments can be accurately predicted using the partitioning of the chemical in organic carbon and data from water-only tests, the ESGs protecting benthic species can be predicted using the organic carbon partition coefficient, K_{OC}, and FCV. EqP cannot remove all the variation in the experimentally observed sediment-effects concentration and the concentration predicted from water-only exposures. Thus, a quantification of this uncertainty should accompany the ESG.

EPA has developed both Tier 1 and Tier 2 ESGs to reflect the differing degrees of data availability and uncertainty. The minimum requirements to derive a Tier 1 ESG include (1) an octanol-water partitioning coefficient (K_{OW}) of the chemical, measured with current experimental techniques; (2) derivation of the FCV which should also be updated to include the most recent toxicological information; and (3) sediment toxicity "check" tests to verify EqP predictions. As such, the ESGs derived for dieldrin, endrin, metal mixtures (Cd, Cu, Pb, Ni, Ag, Zn), and polycyclic aromatic hydrocarbon (PAH) mixtures would represent Tier 1 ESGs (U.S. EPA, 2000b,c,d,f). In comparison, the minimum requirements for a Tier 2 ESG include a K_{OW} for the chemical (as described above) and the use of either a FCV or secondary chronic value (SCV). The performance of sediment toxicity tests is recommended, but not required for the development of Tier 2 ESGs. Therefore, in comparison to Tier 1 ESGs, the level of protection provided by the Tier 2 ESGs would be associated with more uncertainty due to the use of the SCV and absence of sediment check tests. Examples of Tier 2 ESGs for nonionics are found in U.S. EPA (2000g).

Glossary of Abbreviations

ACR	Acute–chronic ratio
ANOVA	Analysis of variance
AR	Approximate randomization
ASTM	American Society for Testing and Materials
BAF	Bioaccumulation factor; partition coefficient between organism lipid and water
BSAF	Biota sediment accumulation factor; partition coefficient between organism lipid and sediment organic carbon
C_b	Chemical concentration per unit wet weight of the organism
$C_{b,L}$	Lipid-normalized organism concentration
C_d	Freely-dissolved interstitial water chemical concentration
C_{DOC}	DOC-complexed chemical concentration in interstitial water
C_{IW}	Total interstitial water chemical concentration (includes freely-dissolved and DOC-complexed)
C_{OCT}	Chemical concentration in octanol
C_S	Chemical concentration on sediment particles
$C_{S,OC}$	Chemical concentration on sediment particles normalized to organic carbon
C_T	Total chemical concentration in sediment (includes solid and interstitial water phases)
C_W	Chemical concentration in water
COE	U.S. Army Corps of Engineers
CV	Coefficient of variation
CWA	Clean Water Act
DOC	Dissolved organic carbon
EC50	Concentration estimated to cause effects to 50% of test organisms within a specified time period
EPA	United States Environmental Protection Agency
EqP	Equilibrium partitioning
ESG(s)	Equilibrium partitioning sediment guideline(s)
ESG_{OC}	Organic carbon–normalized equilibrium partitioning sediment guideline
f_{OC}	Fraction of organic carbon in sediment
f_L	Weight fraction of lipid
FACR	Final acute–chronic ratio
FAV	Final acute value
FCV	Final chronic value
HA	Humic acid
HECD	U.S. EPA, Health and Ecological Criteria Division

HPLC	High performance liquid chromatography
IUPAC	International Union of Pure and Applied Chemistry
IWTU	Interstitial water toxic unit
K_{DOC}	Dissolved organic carbon–water partition coefficient
K_L	Lipid–water partition coefficient
K_{OC}	Organic carbon–interstitial water partition coefficient
K_{OC}'	Apparent organic carbon–normalized partition coefficient
K_{OW}	Octanol–water partition coefficient
K_P	Sediment–water partition coefficient
$K_P{}^*$	Reversible component partition coefficient
K_p'	Apparent partition coefficient
LC50	Concentration estimated to be lethal to 50% of test organisms within a specified time period
$LC50_{S,OC}$	Organic carbon–normalized LC50 from sediment exposures
$LC50_W$	LC50 from water-only exposures
LOEC	Lowest observed effect concentration
m_{DOC}	Measured DOC concentration
NAS	National Academy of Sciences
NERL	U.S. EPA, National Exposure Research Laboratory
NHEERL	U.S. EPA, National Health and Environmental Effects Research Laboratory
NOAA	National Oceanographic and Atmospheric Administration
NOEC	No observed effect concentration
NTIS	National Technical Information Service
OST	U.S. EPA, Office of Science and Technology
PAH	Polycyclic aromatic hydrocarbon
PCB	Polychlorinated biphenyl
PIM	Particle interaction model
POC	Particulate organic carbon
PSTU	Predicted sediment toxic unit
SPARC	SPARC performs automated reasoning in chemistry
STORET	EPA's computerized database for STOrage and RETrieval of water-related data
TOC	Total organic carbon
TU	Toxic unit
WQC	Water quality criteria

Section 1

Introduction

1.1 General Information

Under the Clean Water Act (CWA), the U.S. Environmental Protection Agency (EPA) is responsible for protecting the chemical, physical, and biological integrity of the nation's waters. In keeping with this responsibility, EPA published water quality criteria (WQC) in 1980 for 64 of the 65 priority pollutants and pollutant categories listed as toxic in the CWA. Additional WQC documents that update criteria for selected consent decree and new chemicals have been published since 1980. These WQC are numerical concentration limits that are protective of aquatic organisms and their uses. Although these criteria play an important role in ensuring a healthy aquatic environment, they alone are not sufficient to ensure appropriate levels of environmental and human health protection.

Toxic contaminants in bottom sediments of the nation's lakes, rivers, wetlands, and coastal waters create potential for continued environmental degradation even where water column contaminant levels comply with established WQC. The absence of defensible sediment guidelines makes it difficult to assess the extent of sediment contamination, implement measures to limit or prevent additional contamination from occurring, or identify and implement appropriate remediation as needed.

As a result of the need to assist regulatory agencies in making decisions concerning contaminated sediment, the EPA Office of Science and Technology (OST), Health and Ecological Criteria Division (HECD), established a research team to review alternative approaches to assess sediment contamination. Sediment contamination and related problems were the subject of a conference (Dickson et al., 1987). Alternative approaches to establishing sediment guidelines (Pavlou and Weston, 1983a) and their merits and deficiencies were discussed (Chapman, 1987). Additional efforts were undertaken to identify the scope of national sediment contamination (Bolton et al., 1985) and to review proposed approaches for addressing contaminated sediments (Pavlou and Weston, 1983b; JRB Associates, 1984). The equilibrium partitioning (EqP) method was selected because it provides the most practical, scientifically defensible, and effective regulatory tool for addressing individual nonionic chemicals associated with contaminated sediments on a national basis (Battelle, 1984).

1.2 Rationale for Selecting the EqP Method

The principal reasons for selection of the EqP method include the following:

1. The EqP method was most likely to yield sediment guidelines predictive of biological effects in the field and defensible when used in a regulatory context. These guidelines address the issue of bioavailability and are founded on the extensive biological effects database used to establish national WQC.

2. Sediment guidelines can be readily incorporated into existing regulatory operations because a unique numerical sediment-specific guideline can be established for any chemical and compared with field measurements to assess the likelihood of significant adverse effects.

3. Sediment guidelines provide a simple and cost-effective means of screening measured sediment contaminant concentrations to identify areas of concern and provide information to regulators in a short period of time.

4. The method takes advantage of the data and expertise that led to the development of national WQC.

5. The methodology can be used as a regulatory tool to ensure that uncontaminated sites are protected from attaining unacceptable levels of contamination and can assist in restoring the beneficial uses at contaminated sites.

1.3 Relationship to WQC Methodology

At first glance, it might seem logical to use the WQC procedure for development of sediment guidelines. A detailed methodology has already been developed that presents the supporting logic, establishes the required minimum toxicological dataset, and specifies the numerical procedures to be used to calculate the WQC values (Stephan et al., 1985). Furthermore, WQC developed through this methodology are routinely used in regulation of effluent discharges. Therefore, it would seem natural to extend these methods directly to sediments.

The WQC are based on using the total chemical concentration as a measure of bioavailable chemical concentration. However, use of total sediment chemical concentration as a measure of the bioavailable—or even potentially bioavailable—chemical concentration is not supported by existing data (Luoma and Bryan, 1981). The results of recent experiments indicate that sediments can differ in toxicity by factors of 100 or more for the same total chemical concentration. This difference is a significant obstacle. Without a quantitative estimate of the bioavailable chemical concentration in a sediment, it is impossible to predict a sediment's toxicity on the basis of chemical measurements, regardless of the method used to assess biological impact—be it laboratory toxicity experiments or field datasets comprising benthic biological and chemical sampling (Chapman and Long, 1983; Long and Chapman, 1985; Barrick et al., 1985; Long and Morgan, 1990). Similarly, without a unique relationship between chemical measurements and biological endpoints that can be applied across the range of sediment properties and affect bioavailability, the cause and effect linkage is not supportable. For example, if the same total chemical concentration is 100 times more toxic in one sediment than it is in another, how can universal guidelines be set that depend only on the total sediment chemical concentration? Any sediment guideline based on total sediment concentration would reflect a potential uncertainty of at least this magnitude. Thus, bioavailability must be explicitly considered for any sediment evaluation methodology that depends on chemical measurements to establish defensible sediment guidelines.

1.4 Applications of Sediment Guidelines

Sediment guidelines that are reasonably accurate in their ability to predict the potential for biological impacts are useful for other applications (Cowan and Zarba, 1987). Sediment guidelines can play an important role in identification, monitoring, and cleanup of contaminated sediment sites on a national basis and also provide a basis to ensure that sites that are uncontaminated will remain so. They are particularly useful when used in conjunction with biological sampling and testing.

In many ways, sediment guidelines developed using the EqP methodology are similar to WQC. However, their application may be quite different. In most cases, contaminants exceeding WQC in the water column need only be controlled at the source to eliminate unacceptable adverse impacts. Contaminated sediments have often been in place for long periods of time, and controlling the source of the pollution (if the source still exists) may not be sufficient to alleviate the problem. The difficulty is compounded because safe removal and treatment or disposal of contaminated sediment can be laborious and expensive.

Application of equilibrium partitioning sediment guidelines (ESGs) in specific EPA regulatory programs is detailed in the "Implementation Framework for Use of Equilibrium Partitioning Sediment Guidelines" (U.S. EPA, 2000a). The range of potential uses is quite large because the need to evaluate potentially contaminated sediment arises in many contexts. ESGs are intended to complement existing sediment assessment tools such as whole sediment toxicity tests and benthic community analyses. They provide a chemical-by-chemical specification of what sediment concentrations are protective of benthic aquatic life. Therefore, they can be useful in identifying causative chemicals when toxicity is indicated by biological assessment tools. They can also be used to help prioritize sites for biological testing, and to serve as targets for load controls to help assure attainment of designated uses of water bodies. ESGs can also be useful screening tools in assessing dredged material and contaminated hazardous waste sites. The utility of EqP for a particular chemical will be verified in subsequent sections.

Sediment guidelines can be used as a means for predicting or identifying the degree and extent of contaminated areas such that more informed regulatory decisions can be made. Sediment guidelines will be particularly valuable in monitoring applications in which sediment contaminant concentrations are gradually approaching the guidelines. Comparison of field measurements with sediment guidelines will

provide reliable warning of potential problems. Such an early warning provides an opportunity to take corrective action before adverse impacts occur.

For the purposes of this and other related documents, EPA has developed both Tier 1 and Tier 2 ESGs to reflect the differing degrees of data availability and uncertainty. Examples of chemicals to which this methodology applies include dieldrin, endrin, metal mixtures (Cd, Cu, Pb, Ni, Ag, Zn), and polycyclic aromatic hydrocarbon (PAH) mixtures. The minimum requirements to derive a Tier 1 ESG include (1) an octanol-water partitioning coefficient (K_{OW}) of the chemical, measured with current experimental techniques, which appears to remove the large variation in reported values; (2) derivation of the FCV, which should also be updated to include the most recent toxicological information; and (3) sediment toxicity "check" tests to verify EqP predictions. Check experiments can be used to verify the utility of EqP for a particular chemical. As such, the ESGs derived for nonionic organics, such as dieldrin and endrin, metal mixtures, and PAH mixtures represent Tier 1 ESGs (U.S. EPA 2000b,c,d,f). In comparison, the minimum requirements for a Tier 2 ESG include a K_{ow} for the chemical (as described above) and the use of either a FCV or secondary chronic value (SCV). The performance of sediment toxicity tests is recommended, but not required for the development of Tier 2 ESGs. Therefore, in comparison to Tier 1 ESGs, the level of protection provided by the Tier 2 ESGs would be associated with more uncertainty due to the use of the SCV and absence of sediment toxicity tests. Examples of Tier 2 ESGs for nonionics are found in U.S. EPA (2000g). The minimum requirements to compute Tier 1 and 2 ESGs are further discussed in Section 6.5.

1.5 Overview

This document presents the technical basis for developing ESGs for nonionic organic chemicals. The term ESG, as used herein, refers to numerical concentrations for individual chemicals or groups of chemicals that are applicable across the range of sediments encountered in practice. ESGs are intended to be predictive of biological effects. As a consequence, they can be used in much the same way as final chronic values (FCVs) are used in WQC as the concentration of a chemical that is protective of benthic aquatic life.

Section 1 of this document reviews the background that led to the need for ESGs and also the selection of the EqP methodology. Section 2 summarizes the evidence and the major lines of reasoning of the EqP methodology, with supporting references cited in the body of the document. Section 3 reviews the development of concentration-response curves for interstitial water concentrations and sediment organic carbon–normalized concentrations to determine toxicity and bioavailability in contaminated sediments. It also presents analyses of sediment toxicity and bioaccumulation experiments. Section 4 reviews the partitioning of nonionic organic chemicals to sediments using laboratory and field studies. Section 5 reviews a comparison of benthic and water column species using aquatic toxicity data contained in EPA's WQC documents to show the applicability of WQC as effects levels for benthic organisms. Section 6 reviews the computation of an ESG and presents an analysis for quantifying uncertainty associated with the ESG. This section also presents minimum data requirements and example calculations and compares the ESG computed for two chemicals, endrin and dieldrin, with field data. The description of Tier 1 and Tier 2 ESGs is also provided. Section 7 presents conclusions and further research needs. Section 8 lists the references cited in this document.

Section 2

Partitioning of Nonionics in Sediments

2.1 Toxicity and Bioavailability of Chemicals in Sediments

Establishing ESGs requires determination of the extent of the bioavailability of chemicals associated with sediment. It has frequently been observed that similar concentrations of a chemical, in units of mass of chemical per mass of sediment dry weight (e.g., μg/g sediment), can exhibit a range in toxicity in different sediments. If the purpose of ESGs is to establish chemical concentrations that apply to sediments of differing types, it is essential that the reasons for this varying bioavailability be understood and explicitly included in the guidelines. Otherwise the guidelines cannot be presumed applicable across sediments of differing properties (Di Toro et al., 1991).

The importance of this issue cannot be overemphasized. For example, if 1 μg/g of kepone is the LC50 for an organism in one sediment and 35 μg/g is the LC50 in another sediment, then unless the cause of this difference can be associated with some explicit sediment properties, it is not possible to determine what the LC50 of a third sediment would be without performing a toxicity test. The results of toxicity tests used to establish the toxicity of chemicals in sediments could not be generalized to other sediments. Imagine the situation if the results of toxicity tests in water depended strongly on the particular water source, for example, Lake Superior versus well water. Until the source of the difference was understood, it would be fruitless to attempt to establish WQC. For instance, one source of uncertainty that has been identified in the WQC for metals in freshwater is hardness. Organic carbon may also effect toxicity in the water column. For this reason bioavailability is a principal focus of this document.

The key insight into the problem of quantifying the bioavailability of chemicals in sediments was that the concentration-response curve for the biological effect of concern can be correlated not to the total sediment chemical concentration (μg/g sediment), but to the interstitial water chemical concentration (μg chemical/L interstitial water) (Adams et al., 1985). In addition, the effects concentration found for the chemical in interstitial water is essentially equal to that found in water-only exposures. Organism mortality, growth rate, and bioaccumulation data are used to demonstrate this correlation, which is a critical part of the logic behind the EqP approach to developing ESGs. For nonionic organic chemicals, the concentration-response curves correlate equally well with the sediment chemical concentration on a sediment organic carbon basis.

These observations can be explained by assuming that the chemical concentration in interstitial water and sediment organic carbon are in equilibrium and that these two concentrations are related by the organic carbon partition coefficient, K_{OC}, as shown in Figure 2-1. The term equilibrium partitioning describes this assumption. The assumption for the equality of water-only and sediment exposure effects concentrations on an interstitial water basis is that the sediment–interstitial water equilibrium system (Figure 2-1, right) provides the same exposure as a water-only exposure (Figure 2-1, left). The chemical activity is the same in each system at equilibrium. It should be pointed out that the EqP assumptions are only approximately true; for example, not all organic carbon has exactly the same partitioning properties, and not all sediments are at complete equilibrium. Therefore, predictions from the model have an inherent uncertainty. The data presented below illustrate the degree to which EqP can explain the observations. For the data presented herein, the observed effects concentration for a chemical on an organic carbon basis can be predicted to within the uncertainty of the model.

Figure 2-2 presents mortality data for various chemicals and sediments compared with interstitial water concentrations when normalized on a toxic unit (TU) basis. Interstitial water TUs (IWTUs) are the ratio of the measured interstitial water concentration to the LC50 from water-only toxicity tests (Equation 2-1). Three

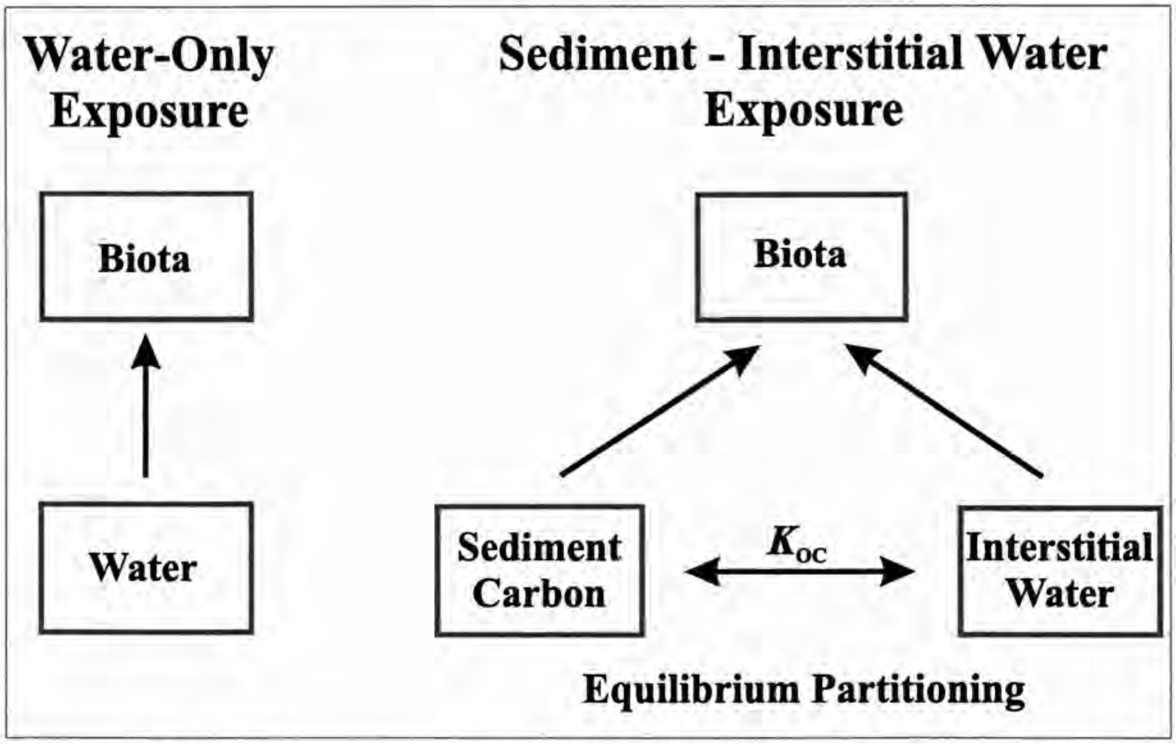

Figure 2-1. **Diagram of the organism exposure routes for a water-only exposure (left) and a sediment exposure (right). Equilibrium partitioning refers to the assumption that an equilibrium exists between the chemical sorbed to the particulate sediment organic carbon and the interstitial water. K_{oc} is the organic carbon partition coefficient.**

different sediments are tested for each chemical as indicated. The EqP model predicts that the interstitial water LC50 will equal the water-only LC50, which is obtained from a separate water-only exposure toxicity test

$$\text{IWTU} = \frac{\text{(interstitial water concentration)}}{\text{(water-only LC50)}} \qquad (2\text{-}1)$$

Therefore, an IWTU of 1 occurs when the interstitial water concentration equals the water-only LC50, at which point it would be predicted that 50% mortality would be observed. The correlation of observed mortality to predicted IWTUs in Figure 2-2 demonstrates (1) the efficacy of using interstitial water concentrations to remove sediment-to-sediment differences and (2) the applicability of the water-only effects concentration and, by implication, the validity of the EqP model. By contrast, the mortality versus sediment chemical concentration on a dry weight basis varies dramatically from sediment to sediment. This will be presented subsequently.

The equality of the effects concentration on an interstitial water basis could be taken to suggest that the route of exposure is via interstitial water. However, the equality of the effects concentration on a sediment organic carbon basis, which is demonstrated below, could similarly be taken to suggest that ingestion of sediment organic carbon is the primary route of exposure. It is important to realize that if the concentration of chemical in sediment and interstitial water are in equilibrium, then the effective exposure concentration is the same regardless of exposure route. Therefore, it is not possible or necessary to determine the primary route of exposure from equilibrated experiments.

Whatever the route of exposure, the correlation to interstitial water suggests that if it were possible to either measure the interstitial water chemical concentration or predict it from the total sediment concentration and the relevant sediment properties such as the sediment organic carbon concentration, then that concentration could be used to quantify the exposure concentration for an organism. Thus, partitioning of chemicals between the solid and the

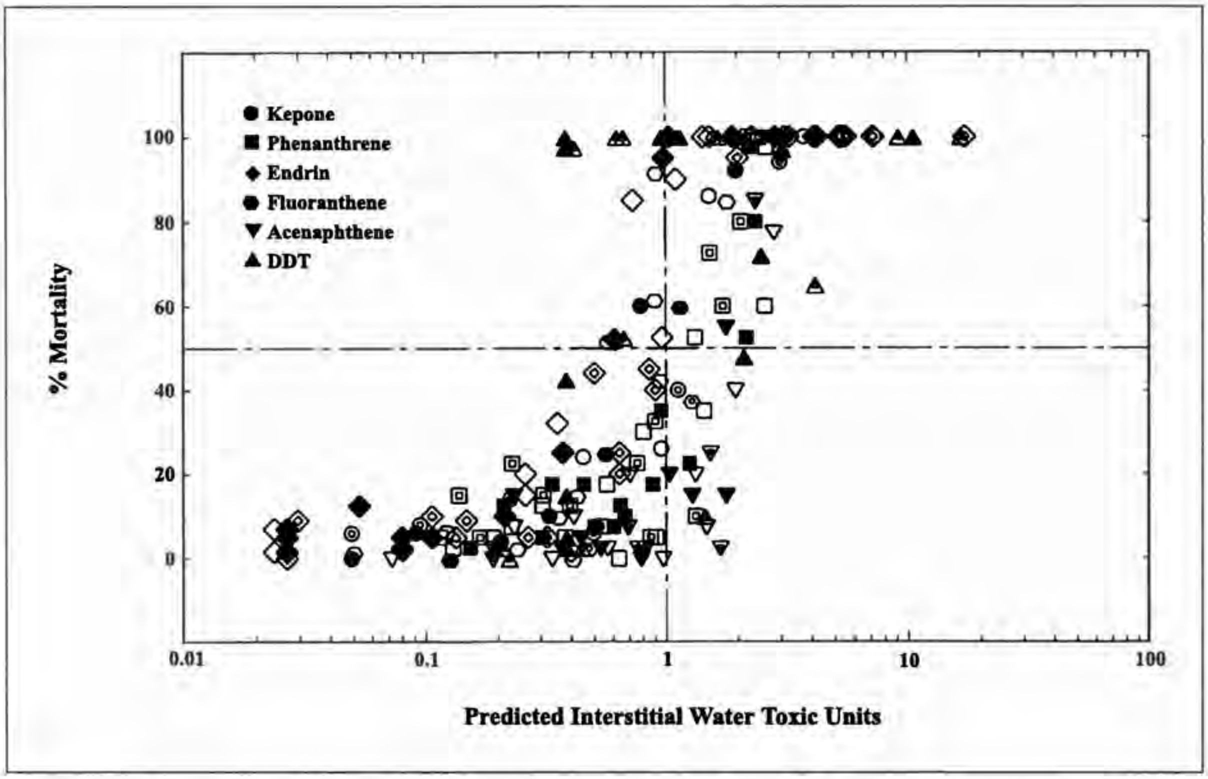

Figure 2-2. **Percent mortality versus predicted interstitial water toxic units for six chemicals and three sediments per chemical. Sediment types are indicated by the open symbols (lowest organic carbon content), double symbols (intermediate organic carbon content), and filled symbols (highest organic carbon content). See Tables 3-1 and 3-2 for data sources.**

liquid phase in a sediment becomes a necessary component for establishing ESGs.

In addition, if it is true that benthic organisms are as sensitive as water column organisms, and the evidence to be presented appears to support this supposition, then ESGs could be established using the FCV from WQC documents as the effects concentration for benthic organisms. The apparent equality between the effects concentration as measured in interstitial water and in water-only exposures (Figure 2-2) supports using an effects concentration derived from water-only exposures.

The calculation procedure for establishing ESGs is as follows. If the FCV (μg/L) is the final chronic value from the WQC for the chemical of interest, then the ESG (μg/g sediment) is computed as the product of the FCV and the partition coefficient, K_p (L/kg sediment), defined as the ratio of the chemical concentration in the sediment and in the interstitial water at equilibrium

$$\text{ESG} = K_p \text{FCV} \tag{2-2}$$

This is the fundamental equation from which the ESGs are generated.

2.2 Partitioning of Nonionic Organic Chemicals

Partitioning of nonionic organic chemicals to soil and sediment particles is reasonably well understood, and a standard model exists for describing the process. The hydrophobicity of the chemical is quantified by using the octanol–water partition coefficient, K_{OW}. The sorption capacity of the sediment is determined by the mass fraction of organic carbon for the sediment, f_{OC}. For sediments with $f_{OC} \geq 0.2\%$ by weight, the organic carbon appears to be the predominant phase for chemical sorption. The partition coefficient, K_p, the ratio of sediment concentration, C_s, to the concentration freely-dissolved in interstitial water, C_d, is given by

$$K_p = \frac{C_s}{C_d} = f_{OC} K_{OC} \tag{2-3}$$

where K_{OC} is the partition coefficient for sediment organic carbon.

The only other environmental variable that has a dramatic effect on partitioning appears to be the particle concentration in the suspension in which K_p is measured. There is considerable controversy regarding the mechanism responsible for the particle concentration effect, and a number of explanations have been offered. However, all the interpretations yield the same result for sediment–interstitial water partitioning, namely that $K_{OC} \approx K_{OW}$ for sediments. Using Equations 2-2 and 2-3, an ESG is calculated from

$$\mathrm{ESG} = f_{OC} K_{OC} \mathrm{FCV} \tag{2-4}$$

This equation is linear in the organic carbon fraction, f_{OC}. As a consequence, the relationship can be expressed as

$$\frac{\mathrm{ESG}}{f_{OC}} = K_{OC}\mathrm{FCV} \tag{2-5}$$

If we define

$$\mathrm{ESG}_{OC} = \frac{\mathrm{ESG}}{f_{OC}} \tag{2-6}$$

as the organic carbon–normalized ESG concentration (μg chemical/g organic carbon), then

$$\mathrm{ESG}_{OC} = K_{OC}\mathrm{FCV} \tag{2-7}$$

Thus, we arrive at the following important conclusion: for a specific chemical having a specific K_{OC}, the organic carbon–normalized sediment concentration, ESG_{OC}, is independent of sediment properties.

Hydrophobic chemicals also tend to partition to colloidal-sized organic carbon particles that are commonly referred to as dissolved organic carbon (DOC) (Gobas and Zhang, 1994). Although DOC affects the apparent interstitial water concentrations of highly hydrophobic chemicals, the DOC-bound fraction of the chemical appears not to be bioavailable and Equation 2-7 for ESG_{OC} still applies.

Therefore, we expect that toxicity in sediment can be predicted from the water-only effects concentration and the K_{OC} of the chemical. The utility of these ideas can be tested with the same mortality data as those in Figure 2-2. The concept of predicted sediment TUs (PSTUs) is useful in this regard. These units are computed as the ratio of the organic carbon–normalized sediment concentrations, C_S/f_{OC}, and the predicted sediment LC50 using K_{OC} and the water-only LC50 (PSTU). That is,

$$\mathrm{PSTU} = \frac{C_S / f_{OC}}{K_{OC}\,(\text{water-only LC50})} \tag{2-8}$$

Figure 2-3 presents the percent mortality versus PSTU for seven chemicals. The correlation is similar to that obtained using the interstitial water concentrations in Figure 2-2. The PSTUs for each chemical follow a similar concentration-response curve independent of sediment type. The data demonstrate that 50% mortality occurs at about 1 PSTU, independent of chemical, species of organism, or sediment type, as expected if the EqP assumptions are correct.

If the assumptions of EqP were exactly true, and there were no experimental variability or measurement error, then all data in Figures 2-2 and 2-3 should predict 50% mortality at 1 PSTU. There is an uncertainty of approximately ±2 in the results. This uncertainty is calculated in Section 6 of this document. The error bars computed from the uncertainty are shown in Figure 2-3 as $\pm 1.96 \times$ (ESG uncertainty). The value 1.96 is the t statistic. It is used to provide a 95% confidence interval around the ESG. This variation reflects inherent variability in these experiments and phenomena that have not been accounted for in the EqP model. It also appears to be the limit of the accuracy and precision that can be expected with this model.

2.3 Effects Concentration

Development of an ESG requires an effects concentration for benthic organisms. Because many of the organisms used to establish the WQC are benthic, perhaps the WQC are adequate estimates of the effects concentrations for benthic organisms. To examine this possibility, the acute toxicity database, which is used to establish the WQC, is segregated into benthic and water column species, and the relative sensitivities of each group are compared. Figure 2-4 compares the final acute values (FAVs) for the most sensitive benthic (epibenthic and infaunal) species with the most sensitive water column species. The data are from EPA's proposed and published water quality criteria, and are described further in Di Toro et al. (1991). Despite the scatter, these results, a more detailed analysis of all the acute toxicity data, and the results of benthic colonization experiments support the contention of equal sensitivity.

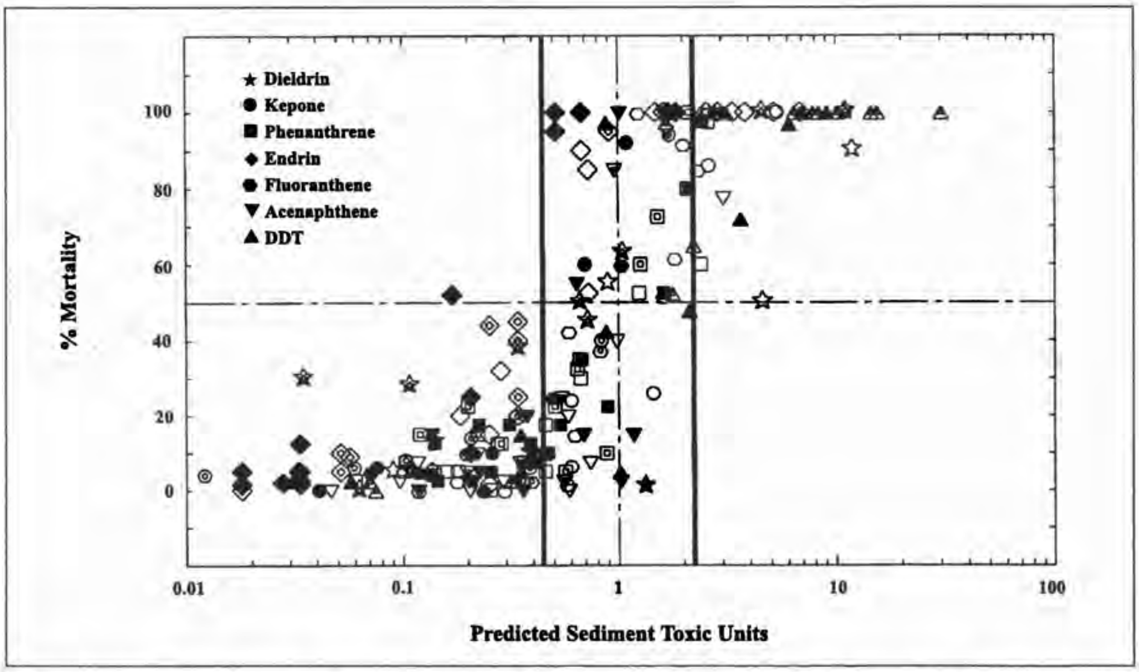

Figure 2-3. Percent mortality versus predicted sediment toxic units for seven chemicals and three sediments per chemical. Sediment types are indicated by the open symbols (lowest organic carbon content), double symbols (intermediate organic carbon content), and filled symbols (highest organic carbon content). See Tables 3-1 and 3-2 for data sources. Uncertainty error bars are represented by solid vertical lines.

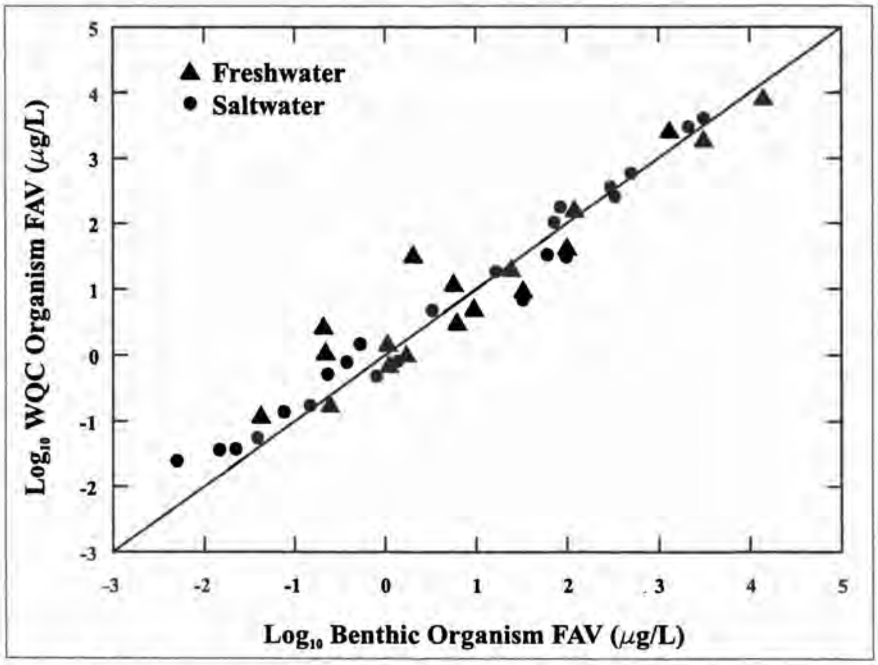

Figure 2-4. Comparison of the FAV for water column versus benthic organisms. Each data point represents an FAV for a particular chemical in either a freshwater or a saltwater exposure. The data are from the WQC or draft criteria documents. See Table 5-1 for data sources.

Section 3

Toxicity and Bioavailability of Chemicals in Sediments

3.1 Toxicity Experiments

As mentioned above, a key insight into the problem of quantifying the bioavailability of chemicals in sediments was that the concentration-response curve for the biological effect of concern could be correlated, not to the total sediment chemical concentration (μg chemical/g dry sediment), but to the interstitial water concentration (μg chemical/L interstitial water) (Adams et al., 1985). However, these results do not necessarily imply that interstitial water is the primary route of exposure, because all exposure pathways are at equal chemical activity in an equilibrium experiment (see Figure 2-1), and the route of exposure cannot be determined. Nevertheless, this observation is the critical first step in understanding bioavailability of chemicals in sediments.

A substantial amount of data has been assembled addressing the relationship between toxicity and interstitial water chemical concentrations. Table 3-1 lists the sources and characteristics of these experiments. Chemicals listed in Table 3-1 for which sediment toxicity experiments have been performed at EPA research laboratories as part of the development of ESGs include acenaphthene, dieldrin, fluoranthene, and phenanthrene. The remaining chemicals listed in Table 3-1 represent experiments in the literature that can be used to demonstrate EqP theory. Individual ESGs have been derived for endrin and dieldrin (U.S. EPA, 2000c, d). These derivations will be presented later in this document. The derivation of a polycyclic aromatic hydrocarbon (PAH) mixtures ESG will be presented in a separate document (U.S. EPA, 2000b). However, the experiments performed for the three individual PAHs will be used in this document along with the endrin and dieldrin data to demonstrate the applicability of EqP theory.

Some of the data listed in Table 3-1 are presented in Figures 3-1 through 3-4. The remaining data listed in Table 3-1 are presented elsewhere in this document. In Figures 3-1 through 3-3, the biological response—mortality or growth rate suppression—is plotted versus the total sediment concentration in the top panels, and versus the measured interstitial water concentration in the bottom panels. Table 3-2 summarizes the LC50 and EC50 estimates and 95% confidence limits for these data on a total sediment, interstitial water, and organic carbon basis, as well as the water-only values. The results from kepone experiments (Figure 3-1) illustrate the general trends in these data (Adams et al., 1985). For the low organic carbon sediment ($f_{OC} = 0.09\%$), the 50th percentile total kepone concentration for both *Chironomus tentans* mortality (LC50) and growth rate reduction from a life-cycle test (EC50) are <1 μg/g sediment dry weight. By contrast, the 1.5% organic carbon sediment LC50 and EC50 are approximately 7 and 10 μg/g sediment dry weight, respectively. The high organic carbon sediment (12%) exhibits still higher LC50 and EC50 values on a total sediment kepone concentration basis (35.2 and 37.3 μg/g sediment dry weight, respectively). However, as shown in the bottom panels of Figure 3-1, essentially all the mortality data collapse into a single curve and the variation in growth rate is significantly reduced when the interstitial water concentrations are used as the correlating concentrations. On an interstitial water basis the biological responses, as measured by LC50 or EC50, vary by approximately a factor of two, whereas when they are evaluated on a total sediment kepone basis, they exhibit a 40-fold range in kepone toxicity.

The comparison between the interstitial water effects concentrations and the water-only results for kepone indicates that they are similar. The interstitial water LC50 values are 18.6 to 31.3 μg/L, and the water-only exposure LC50 is 26.4 μg/L. The interstitial water EC50 values are 17.1 to 48.5 μg/L, and the water-only EC50 is 16.2 μg/L (Table 3-2).

Laboratory experiments have also been performed to characterize the toxicity of fluoranthene (Swartz et al., 1990) to the sediment-dwelling marine amphipod *Rhepoxynius abronius*. Figure 3-2 presents the *R. abronius* mortality data for the fluoranthene experiment. The results of the fluoranthene experiments parallel

those for kepone. The sediment with the lowest organic carbon content (0.2%) exhibits the lowest LC50 on a total sediment concentration basis (3.2 μg/g sediment dry weight), and as the organic carbon concentration increases (0.3% and 0.5%), the LC50 increases (6.4 and 10.7 μg/g sediment dry weight, respectively). On an interstitial water basis, the data again collapse to a single concentration-response curve and the LC50 values differ by less than 50%.

Table 3-1. Sediment toxicity and bioaccumulation data

Chemical	Organism	Sediment Source	Exposure Duration (days)	Biological Endpoint	Reference	Figure
Acenaphthene	*Eohaustorius estuarius*	South Beach, OR	10	Mortality	Swartz, 1991	4-18
Acenaphthene	*Leptocheirus plumulosus*	South Beach, OR	10	Mortality	Swartz, 1991	4-18
Cypermethrin	*Chironomus tentans*	River and pond	1	Body burden	Muir et al., 1985	3-4
DDT	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	Nebeker et al., 1989; Schuytema et al., 1989	3-3
Dieldrin	*Chironomus tentans*	Airport Pond, MN	10	Mortality	Hoke et al., 1995	4-18
Dieldrin	*Hyalella azteca*	West Bearskin and Pequaywan Lakes, MN	10	Mortality	Hoke et al., 1995	—
Dieldrin	*Hyalella azteca*	Airport Pond, MN	10	Mortality	Hoke and Ankley, 1992	4-19
Endrin	*Diporeia* sp.	Lake Michigan	10	Mortality	Stehly, 1991	4-18
Endrin	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	Nebeker et al., 1989; Schuytema et al., 1989	3-3
Fluoranthene	*Rhepoxynius abronius*	Amended Ona Beach, OR	10	Mortality	DeWitt et al., 1992	4-18
Fluoranthene	*Rhepoxynius abronius*	Yaquina Bay, OR	10	Mortality	Swartz et al., 1990	3-2, 4-18
Kepone	*Chironomus tentans*	Soil	14	Body burden	Adams et al., 1985; Adams, 1987	—
Kepone	*Chironomus tentans*	Soil	14	Growth	Adams et al., 1985	3-1, 4-21
Kepone	*Chironomus tentans*	Soil	14	Mortality	Adams et al., 1985	3-1, 4-21
Permethrin	*Chironomus tentans*	River and pond	1	Body burden	Muir et al., 1985	3-4
Phenanthrene	*Eohaustorius estaurius*	South Beach, OR	10	Mortality	Swartz, 1991	4-18
Phenanthrene	*Leptocheirus plumulosus*	South Beach, OR	10	Mortality	Swartz, 1991	4-18

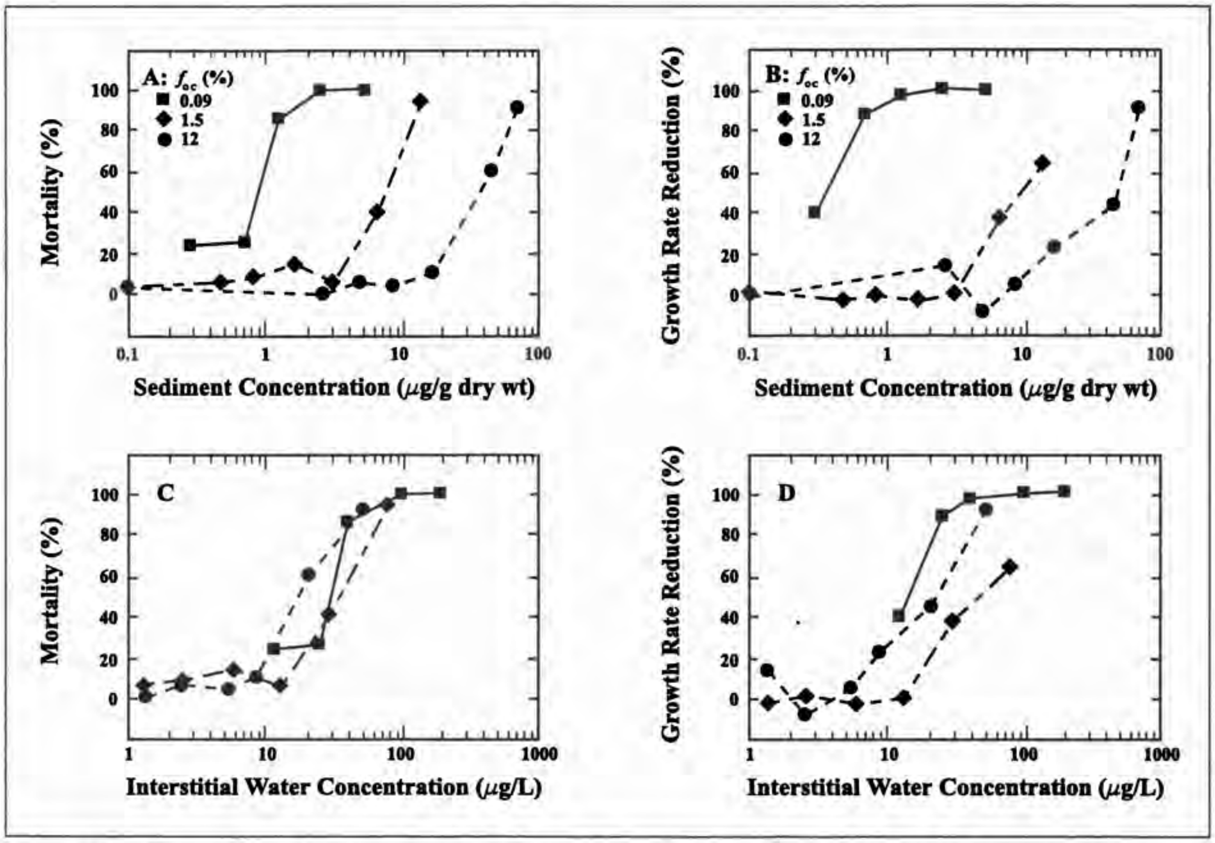

Figure 3-1. Comparison of percent mortality (left) and growth rate reduction (right) of *C. tentans* to kepone concentrations in bulk sediment (top) and interstitial water (bottom) for three sediments with varying organic carbon concentrations (data from Adams et al., 1985).

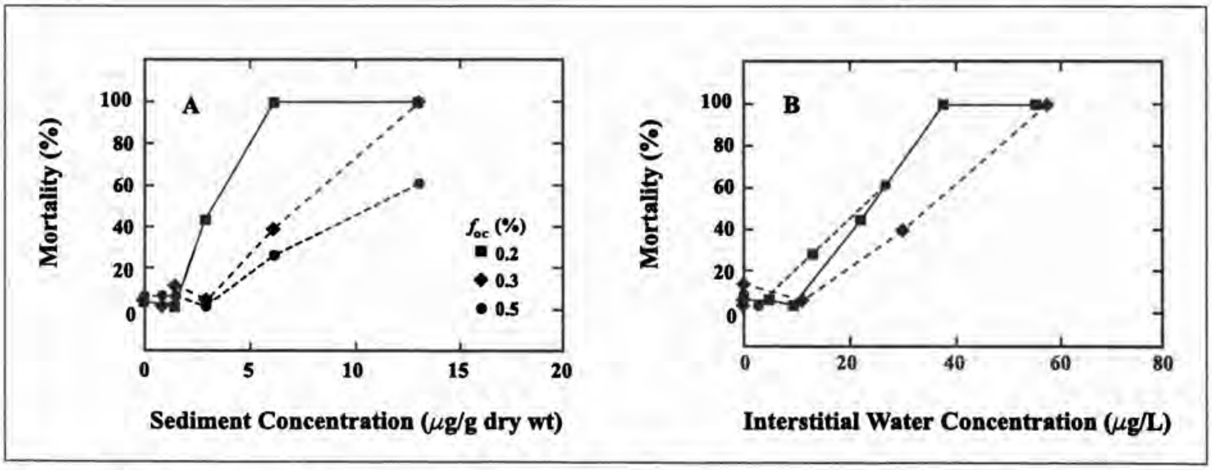

Figure 3-2. Comparison of percent mortality of *R. abronius* to fluoranthene concentrations in bulk sediment (left) and interstitial water (right) for sediments with varying organic carbon concentrations (data from Swartz et al., 1990).

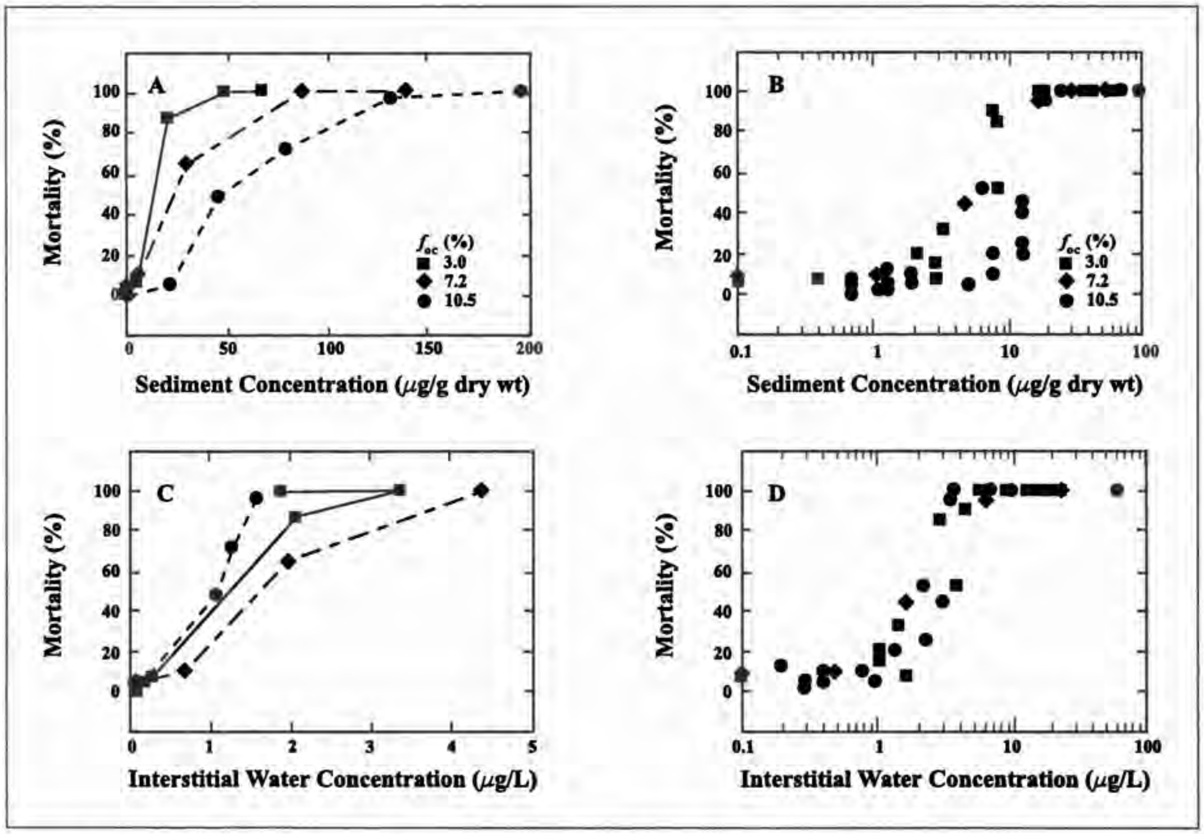

Figure 3-3. **Comparison of percent mortality of *H. azteca* with DDT (left) and endrin (right) concentrations in bulk sediment (top) and interstitial water (bottom) for three sediments with varying organic carbon concentrations (data from Nebeker et al., 1989; Schuytema et al., 1989).**

Figure 3-3 presents mortality data for DDT and endrin using the freshwater amphipod *Hyalella azteca* (Nebeker et al., 1989; Schuytema et al., 1989). The responses for DDT (Nebeker et al., 1989) are similar to those observed for kepone and fluoranthene. On a total sediment concentration basis, the organism responses differ for the various sediments (LC50 values are 10.3 to 44.9 µg/g sediment dry weight), but on an interstitial water basis the responses are again similar (LC50 values are 0.74 to 1.45 µg/L) and comparable to the water-only LC50 value of approximately 0.5 µg/L. The total sediment LC50 data for DDT reported by Schuytema et al. (1989) are more variable. Similarly, organism survival for endrin exposures on a sediment dry weight basis varies by a factor of almost six among the six sediment tests. The LC50 values are 3.39 to 18.9 µg/g sediment dry weight. The interstitial water LC50 values were less variable (1.74 to 3.75 µg/L) and comparable to the water-only exposure LC50 of approximately 4 µg/L (Table 3-2).

3.2 Bioaccumulation

One measure of bioavailability is the amount of chemical retained in organism tissues. Hence, tissue bioaccumulation data can be used to examine the extent of chemical bioavailability. *Chironomus tentans* was exposed to two synthetic pyrethroids, cypermethrin and permethrin, spiked into three sediments, one of which was laboratory-grade sand (Muir et al., 1985). The bioaccumulation from the sand was approximately an order of magnitude higher than it was from the organic carbon–containing sediments for both cypermethrin and permethrin (Figure 3-4A and B). On an interstitial water basis, the bioaccumulation appears to be approximately linear and independent of sediment type (Figure 3-4C and D). The mean bioaccumulation factor (BAF) for cypermethrin (and permethrin) varies from 6.21 to 0.50 (4.04 to 0.23) µg/g organism per µg/g sediment as sediment f_{OC} increases (Table 3-3). By contrast, the mean BAFs on an interstitial water basis vary by less than a factor of two.

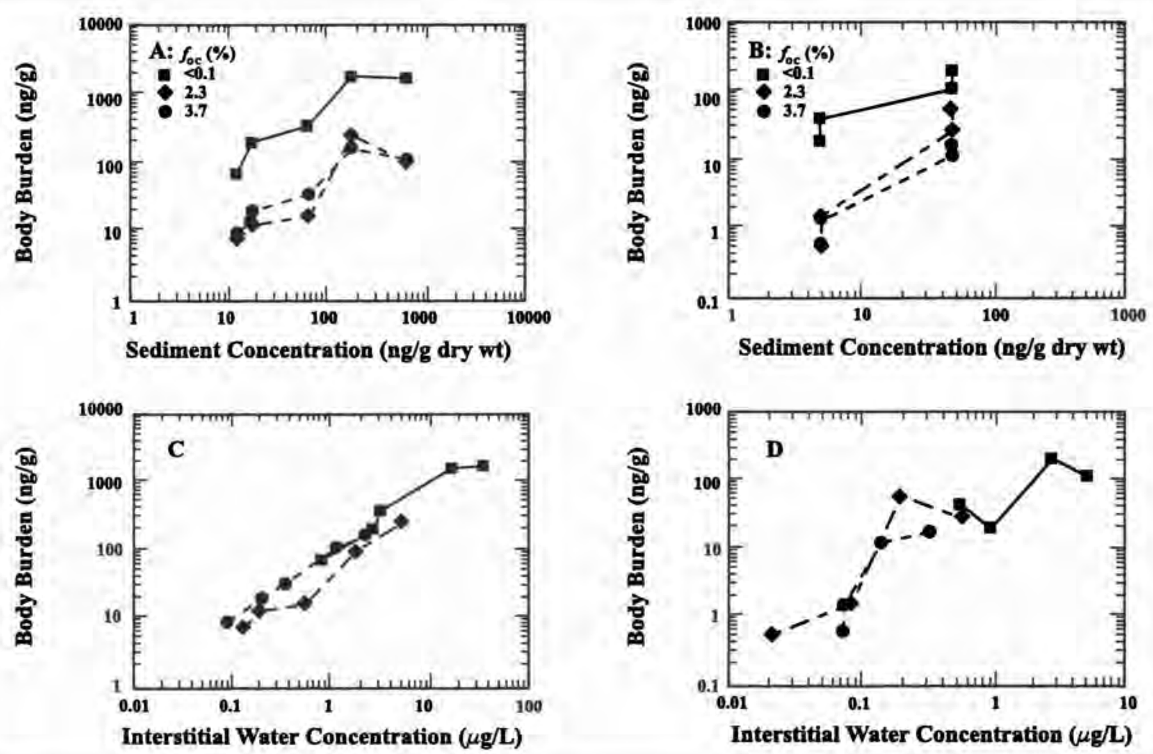

Figure 3-4. Comparison of body burden in *C. tentans* of cypermethrin (left) and permethrin (right) versus concentration in bulk sediment (top) and interstitial water (bottom) for sediments with varying organic carbon concentrations (data from Muir et al., 1985).

Bioaccumulation was also measured by Adams et al. (1983 and 1985) and Adams (1987) in the *C. tentans* kepone experiments presented previously (Table 3-3). The body burden variation on a total sediment basis is over two orders of magnitude (BAF = 3.3 to 600 µg/g organism per µg/g sediment), whereas the interstitial water BAF is within a factor of four (5,180 to 17,600 µg/kg organism per µg/L), with the very low organic carbon sediment exhibiting the largest deviation (Table 3-3).

3.3 Conclusions

There is more than one way to interpret the observation that organism concentration-response and bioaccumulation from different sediments can be reduced to one curve if interstitial water is considered as the concentration that quantifies exposure. First, these results do not necessarily imply that interstitial water is the primary route of exposure, because all exposure pathways are at equal chemical activity in an equilibrium experiment. Second, the route of exposure cannot be determined, as we can see by comparing the concentration-response correlations with interstitial water and organic carbon–normalized sediment concentrations. That both interstitial water and organic carbon–normalized sediment concentration are equally successful at correlating the data suggests that neither the interstitial water nor the sediment exposure pathway can be implicated as the primary exposure route.

In order to relate interstitial water exposure to sediment carbon exposure, it is necessary to establish the relationship between these two concentrations. Therefore, a method for predicting the partitioning of chemicals between the solid and the liquid phase is required. This method is described in the following section.

Table 3-2. Comparison of LC50 and EC50 values on a sediment dry weight– and sediment organic carbon–normalized basis to values calculated from interstitial water and water-only exposures

		LC50 and EC50 Values[a]				
Chemical (Endpoint)	f_{OC} (%)	Total Sediment (μg/g)	Interstitial Water (μg/L)	Organic Carbon (μg/g)	Water-only (μg/L)	Reference
Kepone (Mortality)	0.09	0.90 (0.73-1.10)	29.9 (25.3-35.6)	1,000 (811-1,220)	26.4 (22.7-30.6)	Adams et al., 1985
	1.50	6.9 (5.85-8.12)	31.3 (25.7-38.1)	460 (390-541)		
	12.0	35.2 (30.6-40.5)	18.6 (15.7-21.9)	293 (255-337)		
Kepone (Growth)	0.09	0.46 (0.42-0.51)	17.1 (15.7-18.7)	511 (467-567)	16.2 (15.0-17.5)	Adams et al., 1985
	1.50	9.93 (7.74-12.8)	48.5 (34.6-67.8)	662 (516-1,050)		
	12.0	37.3 (31.5-44.2)	20.1 (16.7-24.1)	311 (262-368)		
Fluoranthene (Mortality)	0.2	3.2 (2.85-3.59)	21.9 (19.6-24.4)	1,600 (1,430-1,800)		Swartz et al., 1990
	0.3	6.4 (5.56-727)	30.9 (27.0-35.4)	2,130 (1,850-2,420)		
	0.5	10.7 (8.34-13.7)	22.2 (17.5-29.3)	2,140 (1,670-2,740)		
DDT (Mortality)	3.0	10.3 (8.74-12.2)	0.74 (0.67-0.82)	344 (291-405)	0.45 (0.38-0.53)	Nebeker et al., 1989
	7.2	17.5 (12.5-24.3)	1.45 (1.20-1.75)	243 (174-338)	0.48 (0.42-0.55)	
	10.5	44.9 (36.7-55.0)	0.77 (0.67-0.89)	428 (350-524)	0.52 (0.45-0.60)	
DDT (Mortality)	3.0	1.54 (1.18-2.00)		51.3 (39.3-66.7)		Schuytema et al., 1989
	3.0	4.16 (3.91-4.42)		139 (130-147)		
	11.0	10.95 (9.34-12.9)		99.6 (84.9-117)		
Endrin (Mortality)	3.0	3.39 (2.61-4.41)	1.80 (1.44-2.24)	113 (87.0147)	4.81 (4.46-5.20)	Nebeker et al., 1989
	6.1	5.07 (4.05-6.36)	1.92 (1.55-2.36)	83.1 (66.4-104)	3.39 (3.10-4.98)	
	11.2	5.91 (4.73-7.37)	1.74 (1.37-2.20)	52.8 (42.2-65.8)	3.71 (3.11-4.44)	
Endrin (Mortality)	3.0	4.76 (3.70-6.13)	2.26 (1.67-3.05)	159 (123-204)		Schuytema et al., 1989
	11.0	18.9 (13.6-26.3)	3.75 (2.72-5.19)	172 (124-239)		
	11.0	10.5 (8.29-12.7)	2.81 (2.44-3.23)	95.8 (75.4-115)		

[a] The LC50 and EC50 values and the 95% confidence limits in parentheses are computed by the modified Spearman-Karber method (Hamilton et al., 1977).

Table 3-3. Bioaccumulation factors for *C. tentans*

		BAF[a]			
Chemical	f_{OC} (%)	Total Sediment[b]	Interstitial Water[c]	Organic Carbon–Normalized Sediment[d]	Reference
Kepone	0.09	600 (308-892)	17,600 (6,540-28,600)	0.54 (0.277-0.803)	Adams, 1987; Adams et al., 1983, 1985
	1.50	20 (4.8-35.2)	5,180 (1,970-8,390)	0.30 (0.072-0.528)	
	12	3.3 (0.3-6.3)	5,790 (2,890-8,700)	0.40 (0.036-0.756)	
Cypermethrin	<0.1	6.21 (4.41-8.01)	80.1 (73.5-86.7)	<0.006 (0.004-0.008)	Muir et al., 1985
	2.3	0.50 (0.30-0.71)	51.3 (43.8-58.8)	0.012 (0.008-0.016)	
	3.7	0.60 (0.37-0.83)	92.9 (87.0-98.8)	0.022 (0.012-0.032)	
Permethrin	<0.1	4.04 (2.89-5.20)	39.7 (25.0-54.3)	<0.004 (0.002-0.006)	Muir et al., 1985
	2.3	0.38 (0.17-0.59)	52.5 (22.6-82.4)	0.009 (0.005-0.013)	
	3.7	0.23 (0.18-0.28)	29.7 (15.6-43.7)	0.008 (0.006-0.010)	

[a] The 95% confidence limits are shown in parentheses.

[b] Values are in μg/g organism per μg/g sediment.

[c] Values are in μg/kg organism per μg/L.

[d] Values are in μg/kg organism per $\mu g/g_{OC}$ sediment.

Section 4

Sorption of Nonionic Organic Chemicals

4.1 Partitioning in Particle Suspensions

A number of empirical models have been suggested to explain the sorption of nonionic hydrophobic organic chemicals to natural soils and sediment particles (see Karickhoff, 1984). The chemical property that indexes hydrophobicity is the octanol–water partition coefficient, K_{OW}. The important particle property is the weight fraction of organic carbon, f_{OC}. Another important environmental variable appears to be the particle concentration itself.

In many experiments using particle suspensions, the partition coefficients have been observed to decrease as the particle concentration used in the experiment is increased (O'Connor and Connolly, 1980). Very few experiments have been done on settled or undisturbed sediments; therefore, the correct interpretation of particle suspension experiments is of critical importance. It is not uncommon for the partition coefficient to decrease by two to three orders of magnitude at high particle concentrations. If this partitioning behavior is characteristic of bedded sediments, then quite low partition coefficients would be appropriate, which would result in lower sediment chemical concentrations for ESGs. If, however, this phenomenon is an artifact or a result of a phenomenon that does not apply to bedded sediments, then a quite different partition coefficient would be used. The practical importance of this issue requires a detailed discussion of the particle concentration effect.

4.1.1 *Particle Concentration Effect*

For the reversible (or readily desorbable) component of sorption, a particle interaction model (PIM) has been proposed that accounts for the particle concentration effect and predicts the partition coefficient of nonionic hydrophobic chemicals over a range of nearly seven orders of magnitude with a $\log_{10}$ standard error of the estimate of 0.38 (Di Toro, 1985). The reversible component partition coefficient, $K_p{}^*$, is the ratio of reversibly bound sediment chemical concentration, C_S (μg/kg dry weight), to the freely-dissolved chemical concentration, C_d (μg/L)

$$C_S = K_p{}^* C_d \tag{4-1}$$

The PIM model for $K_P{}^*$ is

$$K_p{}^* = \frac{f_{oc} K_{oc}}{1 + m f_{oc} K_{oc} / \upsilon_x} \tag{4-2}$$

where

$K_p{}^*$ = reversible component partition coefficient (L/kg dry weight)

K_{OC} = particle organic carbon partition coefficient (L/kg organic carbon)

f_{OC} = particle organic carbon weight fraction (kg organic carbon/kg dry weight)

m = particle concentration in the suspension (kg dry weight/L)

υ_x = 1.4, an empirical constant (unitless)

The regression of K_{OC} to the octanol–water coefficient, K_{OW}, yields

$$\log_{10} K_{OC} = 0.00028 + 0.983 \log_{10} K_{OW} \tag{4-3}$$

or essentially that K_{OC} approximately equals K_{OW} (Di Toro, 1985). Figure 4-1 presents the observed versus predicted reversible component partition coefficients using this model (Di Toro, 1985). A substantial fraction of the data in the regression is at high particle concentrations ($m f_{OC} K_{OW} > 10$), where the partitioning is determined only by the solids concentration and υ_x. The low particle concentration data ($m f_{OC} K_{OW} < 1$) are presented in Figure 4-2 for the conventional adsorption (Figure 4-2A) and reversible component (Figure 4-2B) partition coefficient, $K_p{}^*$, normalized by f_{OC}, that is: $K_{OC} = K_p / f_{OC}$. The relationship $K_{OC} \approx K_{OW}$ is demonstrated from the agreement between the line of perfect equality and the data. It is important to note that although Equation 4-2 applies only to the

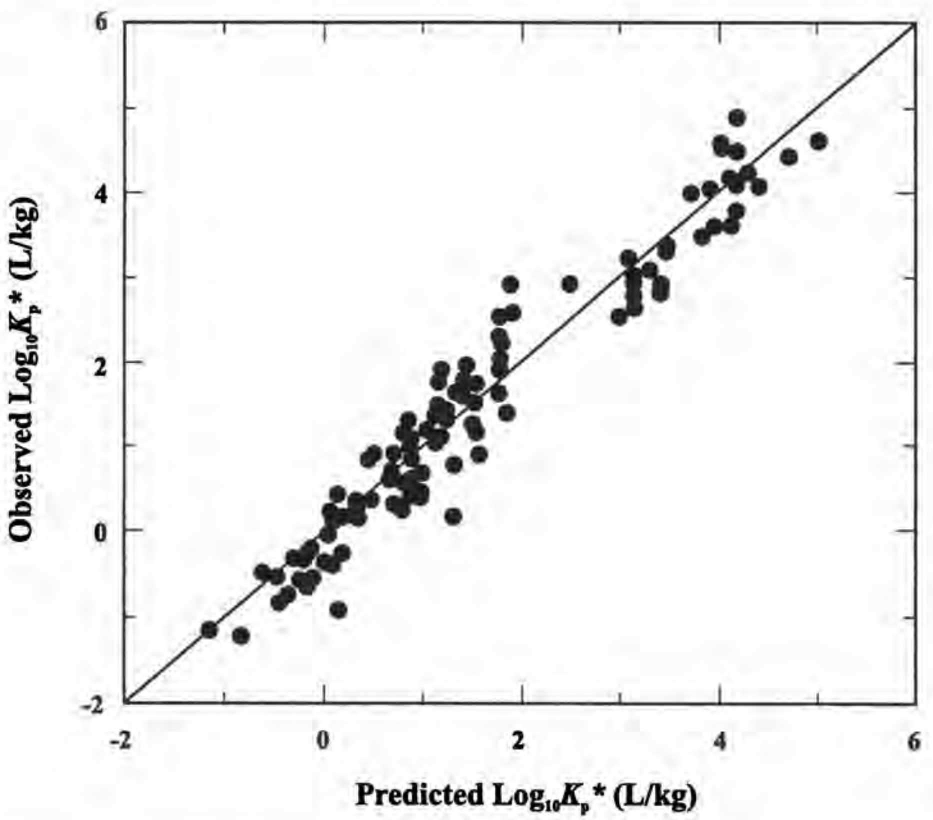

Figure 4-1. **Observed versus predicted reversible component partition coefficient for nonionic organic chemicals using Equation 4-2 (figure from Di Toro, 1985).**

reversible component partition coefficient, K_p*, the equation $K_p \approx f_{OC}\,K_{OW}$ applies to the conventional adsorption partition coefficient as well (Figure 4-2A).

A number of explanations have been offered for the particle concentration effect. The most popular is the existence of an additional third sorbing phase or complexing component that is associated with the particles, but is inadvertently measured as part of the dissolved chemical concentration because of experimental limitations. Colloidal particles that remain in solution after particle separation (Benes and Majer, 1980; Gschwend and Wu, 1985) and dissolved ligands or macromolecules that desorb from the particles and remain in solution (Carter and Suffett, 1983; Voice et al., 1983; Curl and Keolelan, 1984; Nelson et al., 1985) have been suggested. It has also been suggested that increasing particle concentration increases the degree of particle aggregation, decreasing the surface area, and hence, the partition coefficient (Karickhoff and Morris, 1985). The effect has also been attributed to kinetic effects (Karickhoff, 1984).

Sorption by nonseparated particles or complexing by DOC can produce an apparent decrease in partition coefficient with increasing particle concentration if the operational method of measuring dissolved chemical concentration does not properly discriminate the truly dissolved or free chemical concentration from the complexed or colloidally sorbed portion. However, the question is not whether improperly measured dissolved concentrations can lead to an apparent decrease in partition coefficient with increasing particle concentrations, but whether these third-phase models explain all (or most) of the observed partition coefficient–particle concentration relationships.

An alternative possibility is that the particle concentration effect is a distinct phenomenon that is a ubiquitous feature of aqueous-phase particle sorption. A number of experiments have been designed explicitly to exclude possible third-phase interferences. Particle concentration effects are displayed in the resuspension experiment for polychlorinated biphenyls (PCBs) and metals, in which particles are resuspended into a

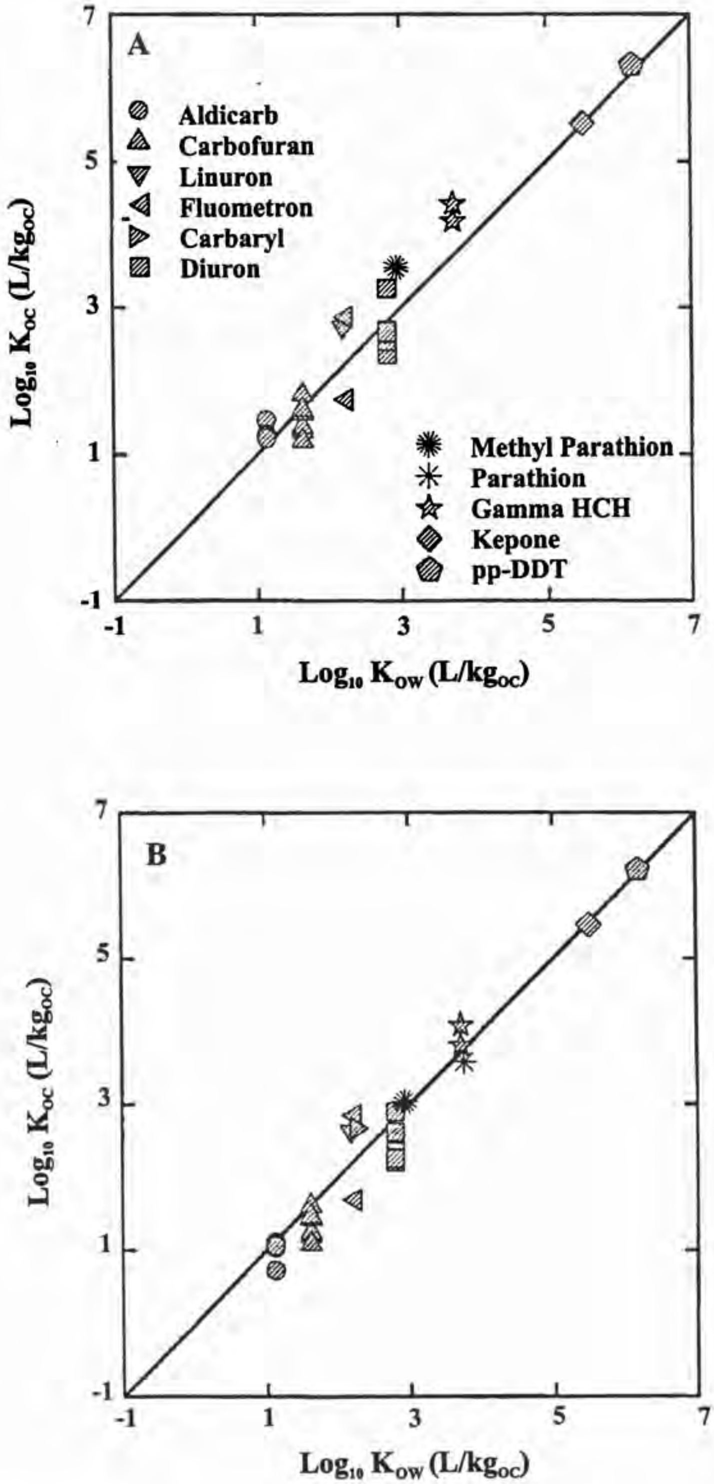

Figure 4-2. Comparison of the conventional adsorption (A) and reversible component (B) organic carbon-normalized partition coefficient, K_{OC}, to the octanol–water partition coefficient, K_{OW}, for experiments with low solids concentrations: $mf_{OC}K_{OW}<1$. The line represents equality (figure from Di Toro, 1985).

reduced volume of supernatant (Nelson et al., 1985; Karickoff and Morris, 1985; Di Toro and Horzempa, 1983), and in the dilution experiment in which the particle suspension is diluted with supernatant from a parallel vessel (Nelson et al., 1985). It is difficult to see how third-phase models can account for these results because the concentration of the colloidal particles is constant whereas the concentration of the sediment particles varies substantially.

The model (Equation 4-2) is based on the hypothesis that particle concentration effects result from an additional desorption reaction induced by particle–particle interactions (Di Toro, 1985). It has been suggested that actual particle collisions are responsible (Mackay and Powers, 1987). This interpretation relates υ_x to the collision efficiency for desorption and demonstrates that it is independent of the chemical and particle properties, a fact that has been experimentally observed (Di Toro, 1985; Di Toro et al., 1986).

It is not necessary to decide which of these mechanisms is responsible for the effect if all the possible interpretations yield the same result for sediment–interstitial water partitioning. Particle interaction models would predict that $K_{OC} \approx K_{OW}$ because the particles are stationary in sediments. Third-phase models would also relate the freely-dissolved (i.e., uncomplexed) chemical concentration to particulate concentration via the same equation. As for kinetic effects, the equilibrium concentration is again given by the relationship $K_{OC} \approx K_{OW}$. Thus, there is unanimity on the proper partition coefficient to be used in order to relate the freely-dissolved chemical concentration to the sediment concentration, $K_{OC} \approx K_{OW}$.

4.1.2 *Organic Carbon Fraction*

The unifying parameter that permits development of ESGs for nonionic hydrophobic organic chemicals applicable to a broad range of sediment types is the organic carbon content of the sediments. This development can be shown as follows. The sediment–interstitial water partition coefficient, K_p, is given by

$$K_P = f_{OC}\,K_{OC} \approx f_{OC}\,K_{OW} \tag{4-4}$$

and the solid phase concentration is given by

$$C_S = f_{OC}\,K_{OC}\,C_d \tag{4-5}$$

where C_S is the chemical concentration on sediment particles. An important observation can be made that leads to the idea of organic carbon normalization. Equation 4-4 indicates that the partition coefficient for any nonionic organic chemical is linear in the organic carbon fraction, f_{OC}. The partitioning data examined in Figure 4-2 can be used to examine the linearity of K_p to f_{OC}. Figure 4-3 compares K_p/K_{OW} to f_{OC} for both the adsorption and the reversible component partition coefficients. The data are restricted to $mf_{OC}\,K_{OW} < 1$ to suppress particle effects. The line indicates the expected linear relationship in Equation 4-4. These data and an analysis presented below appear to support the linearity of partitioning to a value of $f_{OC} = 0.2\%$. This result, and the toxicity experiments examined below, suggest that for $f_{OC} > 0.2\%$, organic carbon normalization is valid.

As a consequence of the linear relationship of C_S and f_{OC}, the relationship between sediment concentration, C_S, and freely-dissolved concentration, C_d, can be expressed as

$$\frac{C_S}{f_{OC}} = K_{OC}\,C_d \tag{4-6}$$

If we define

$$C_{S,OC} = \frac{C_S}{f_{OC}} \tag{4-7}$$

as the organic carbon–normalized sediment concentration (μg chemical/kg organic carbon), then from Equation 4-6

$$C_{S,OC} = K_{OC} C_d \tag{4-8}$$

Therefore, for a specific chemical with a specific K_{OC}, the organic carbon–normalized total sediment concentration, $C_{S,OC}$, is proportional to the freely-dissolved concentration, C_d, for any sediment with $f_{OC} \geq 0.2\%$. This latter qualification is judged necessary because at $f_{OC} < 0.2\%$, other factors that influence partitioning (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important (Karickhoff, 1984). Using the proportional relationship given by Equation 4-8, the concentration of freely-dissolved chemical can be predicted from the normalized sediment concentration and K_{OC}. The freely-dissolved concentration is of concern because it is the form that is bioavailable. The evidence is discussed in the next section.

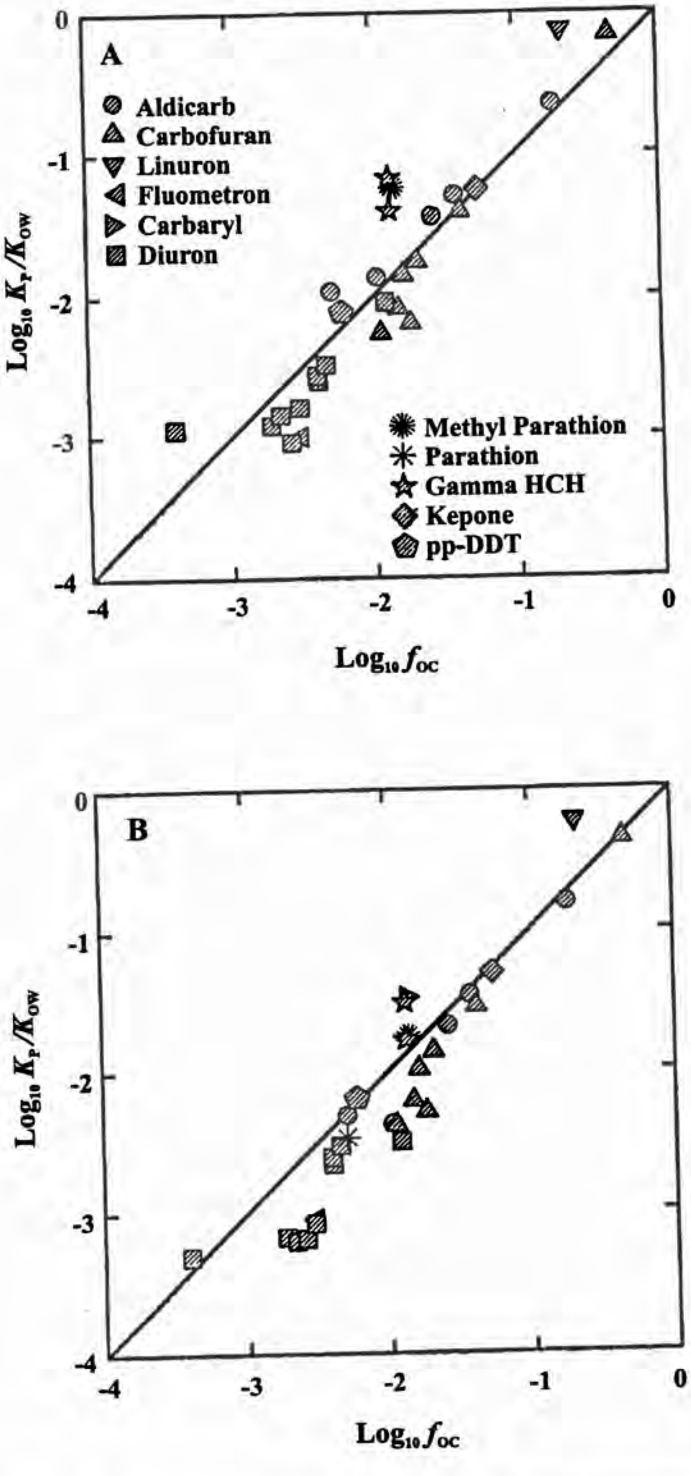

Figure 4-3. Comparison of the normalized partition coefficients for adsorption (A) and reversible component sorption (B) to sediment organic carbon. The data are restricted so that particle effects are not expected to be significant: $mf_{OC}K_{OW}<1$. The line represents equality (figure from Di Toro, 1985).

4.1.3 *Organic Carbon Composition*

The K_{OC} values used in the EqP calculations described in this document assume that the organic carbon in sediments is similar in partitioning properties to "natural" organic carbon found in most sediments. While this has proven true for most sediments EPA has studied, it is possible that some sites may have components of sediment organic carbon with different properties. This might be associated with sediments whose composition has been highly modified by industrial activity, resulting in high percentages of atypical organic carbon such as rubber, animal processing waste (e.g., hair or hide fragments), coal particles, or wood processing wastes (bark, wood fiber, or chips). Relatively undegraded woody debris or plant matter (e.g., roots, leaves) may also contribute organic carbon that partitions differently from typical organic carbon (e.g., Iglesias-Jimenez et al., 1997; Grathwohl, 1990; Xing et al., 1994). Sediments with substantial amounts of these materials may exhibit higher concentrations of chemicals in interstitial water than would be predicted using generic K_{OC} values, thereby making the ESG underprotective. If such a situation is encountered, the applicability of literature K_{OC} values can be evaluated by analyzing for the chemical of interest in both sediment and interstitial water. If the measured concentration in interstitial water is markedly greater (e.g., more than twofold) than that predicted using the K_{OC} values recommended herein (after accounting for DOC binding in the interstitial water), then the national ESGs would be underprotective and calculation of a site-specific ESG should be considered (see U.S. EPA, 2000e).

The presence of organic carbon in large particles may also influence the apparent partitioning. Large particles may artificially inflate the effect of the organic carbon because of their large mass, but comparatively small surface area; they also may increase variability in

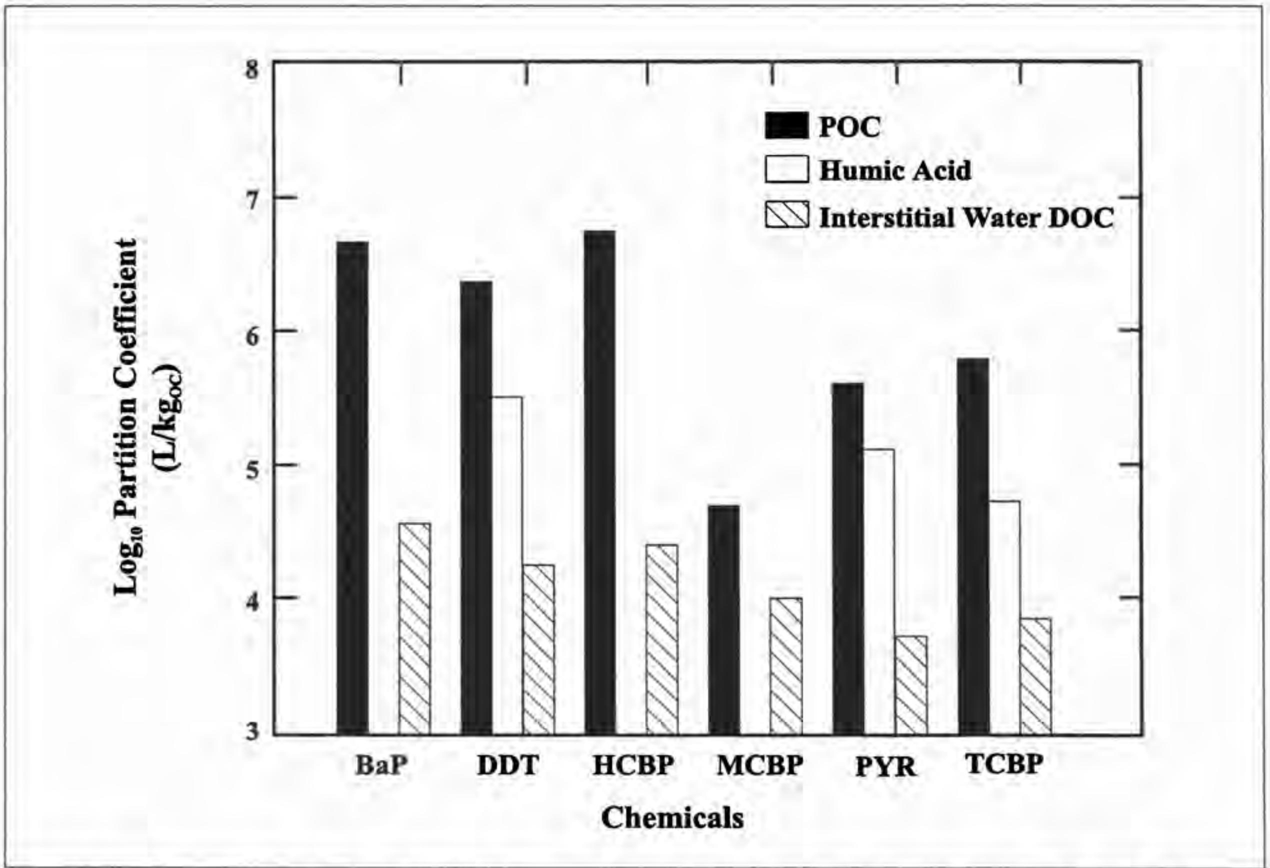

Figure 4-4. Partition coefficients of chemicals to particulate organic carbon (POC), Aldrich® humic acid, and natural DOC. Benzo[a]pyrene (BaP); DDT; 2,2',4,4',5,5'-hexachlorobiphenyl (HCBP); 4-monochlorobiphenyl (MCBP); pyrene (PYR); 2,2',5,5'-tetrachlorobiphenyl (TCBP) (data from Eadie et al., 1990).

TOC measurements by causing sample heterogeneity. The effect of these particles on partitioning can be evaluated by analysis of interstitial water as described above, and site-specific ESGs may be used if required. It may be possible to screen large particles from sediment prior to analysis to reduce their influence on the interpretation of sediment chemistry relative to ESGs.

4.2 Dissolved Organic Carbon Complexing

In addition to the partitioning of a chemical to the particulate organic carbon (POC) associated with sediment particles, hydrophobic chemicals can also partition to the organic carbon in colloidal-sized particles. These particles are too small to be removed by conventional filtration or centrifugation and are therefore operationally defined as dissolved organic carbon, or DOC. Sediment interstitial waters frequently contain significant levels of DOC and must be considered in evaluating the phase distribution of chemicals.

A distinction is made between the freely-dissolved chemical concentration, C_d, and the DOC-complexed chemical, C_{DOC}. The partition coefficient for DOC, K_{DOC}, is analogous to K_{OC}, as it quantifies the ratio of DOC-bound chemical, C_{DOC}, to the freely-dissolved concentration, C_d

$$C_{DOC} = m_{DOC} K_{DOC} C_d \tag{4-9}$$

where m_{DOC} is the measured DOC concentration. The magnitude of both K_{DOC} and DOC determine the extent of DOC complexation that takes place. Thus, it is important to have estimates of these quantities when calculating the level of freely-dissolved chemical in sediment interstitial waters.

A recent compilation of K_{DOC} together with additional experimental determinations is available (Eadie et al., 1990). A summary that compares the partitioning of six chemicals with POC, natural DOC, and Aldrich humic acid (HA) is shown on Figure 4-4. The magnitude of the partition coefficients follows the order: POC > HA > natural DOC. The upper bound on K_{DOC} would appear to be where $K_{DOC} = K_{OC}$, the POC partition coefficient.

4.3 Phase Distribution in Sediments

Chemicals in sediments are partitioned into three phases: freely-dissolved chemical, chemical sorbed to POC, and chemical sorbed to DOC. To evaluate the partitioning among these three phases, consider the mass balance for the total chemical concentration in sediment, C_T:

$$C_T = \varnothing\, C_d + m f_{OC} K_{OC} C_d + m_{DOC} K_{DOC} C_d \tag{4-10}$$

where $\varnothing$ is the sediment porosity (volume of water/volume of water plus solids) and m is the sediment solids concentration (mass of solids/volume of water plus solids). The three terms on the right side of the equation are the concentration of freely-dissolved chemical in the interstitial water, and that sorbed to the POC and DOC, respectively. Hence, from Equation 4-10, the freely-dissolved chemical concentration can be expressed as

$$C_d = \frac{C_T}{\varnothing + m f_{oc} K_{oc} + \varnothing m_{DOC} K_{DOC}} \tag{4-11}$$

The concentration associated with the particle carbon (Equation 4-8) and DOC (Equation 4-9) can then be calculated. The total interstitial water concentration, C_{IW}, is the sum of the freely-dissolved chemical and DOC-complexed chemical, so that

$$C_{IW} = C_d + C_{DOC} = C_d (1 + m_{DOC} K_{DOC}) \tag{4-12}$$

Figure 4-5 illustrates the phase partitioning behavior of a system for a unit concentration of a chemical with the following properties: $K_{OC} = K_{DOC} = 10^6$ L/kg, $f_{OC} = 2.0\%$, $m = 0.5$ kg solids/L sediment, and m_{DOC} varies from 0 to 50 mg/L, a reasonable range for interstitial waters (Thurman, 1985). With no DOC present, the interstitial water concentration equals the freely-dissolved concentration. As DOC increases, the interstitial water concentration increases because of the increase in complexed chemical, C_{DOC}. Accompanying this increase in C_{DOC} is a slight—in fact, insignificant—decrease in C_d (Equation 4-11) and a proportional decrease in C_S (Equation 4-8).

It is important to realize that the freely-dissolved chemical concentration, C_d, can be estimated directly from $C_{S,OC}$, the organic carbon–normalized sediment concentration, using Equation 4-8, and that the estimate is independent of the DOC concentration. However, to estimate C_d from the interstitial water concentration requires that the DOC concentration and K_{DOC} be known. The assumption $C_{IW} = C_d$ is clearly not warranted for very hydrophobic chemicals. For these cases, $C_{S,OC}$ gives a more direct estimate of the freely-dissolved bioavailable concentration, C_d, than does the interstitial water concentration.

4.4 Bioavailability of DOC-Complexed Chemicals

The proportion of a chemical in interstitial water that is complexed to DOC can be substantial (Figure 4-5). Hence, the question of bioavailability of DOC-complexed chemical can be important in assessing toxicity directly from measured interstitial water concentrations. Data indicate that DOC-complexed chemical is not bioavailable. Fish (McCarthy and Jimenez, 1985) and amphipod (Landrum et al., 1987) uptake of PAHs are significantly reduced by adding DOC. An example is shown in Figure 4-6 for a freshwater amphipod, *Pontoporeia hoyi* (Landrum et al., 1987). For a highly hydrophobic chemical such as benzo[a]pyrene (BaP), the effect is substantial, whereas for less hydrophobic chemicals (e.g., phenanthrene) the reduction in uptake rate is insignificant. This result was expected because, for a fixed amount of DOC, the quantity of DOC-complexed chemical decreases with decreasing K_{DOC} (Equation 4-9).

The quantitative demonstration that DOC-complexed chemicals are not bioavailable requires an independent determination of the concentration of complexed chemical. Landrum et al. (1987) have developed a C_{18} reverse-phase HPLC column technique that separates the complexed and freely-dissolved chemical. Thus it is possible to compare the measured DOC-complexed chemical with the quantity of complexed chemical inferred from the uptake experiments, assuming that all the complexed chemical is not bioavailable (Landrum et al., 1985, 1987). As shown in Figure 4-7, although the K_{DOC} inferred from uptake suppression is larger than that inferred from the reverse-phase separation for HA, these data support the assumption that the DOC-complexed fraction, C_{DOC}, is not bioavailable. Hence the bioavailable form of dissolved chemical is C_d, the free uncomplexed component. This is an important observation because it is C_d that is in equilibrium with $C_{S,OC}$, the organic carbon–normalized sediment concentration (Equation 4-7).

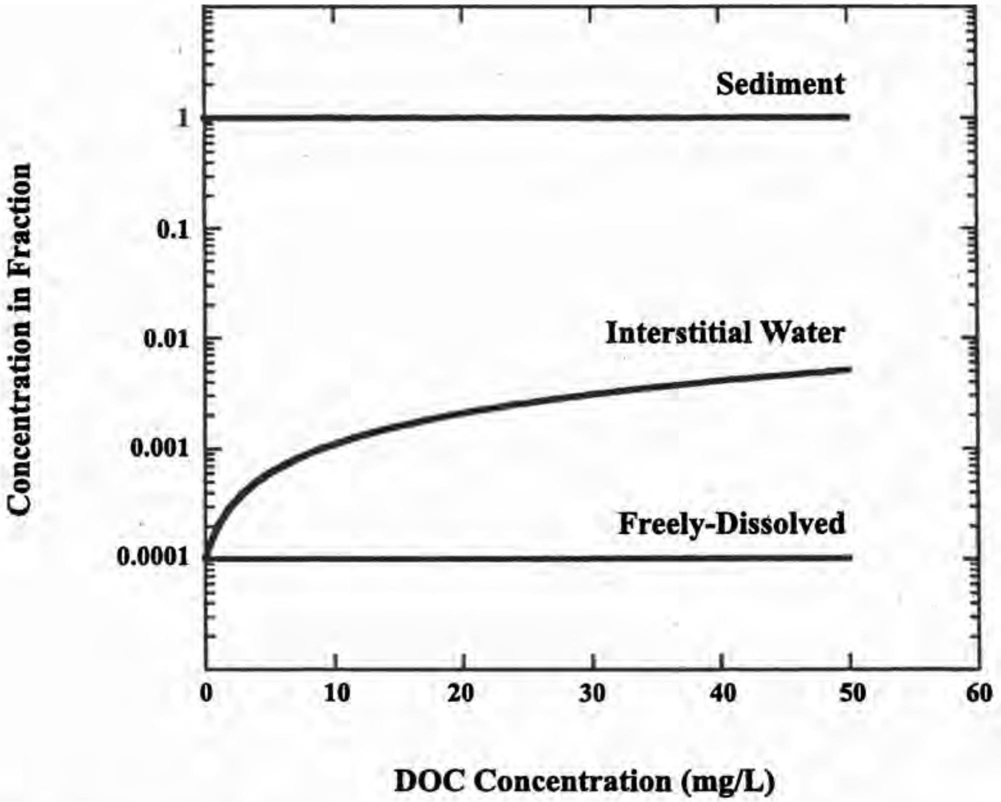

Figure 4-5. **Phase distribution of a chemical in the three-phase system: sediment, interstitial water (C_{IW}), and freely-dissolved (C_d) (Equations 4-10, 4-11, and 4-12). $K_{OC} = K_{OW} = K_{DOC} = 10^6$ L/kg, $f_{OC} = 2.0\%$, and $m = 0.5$ kg/L.**

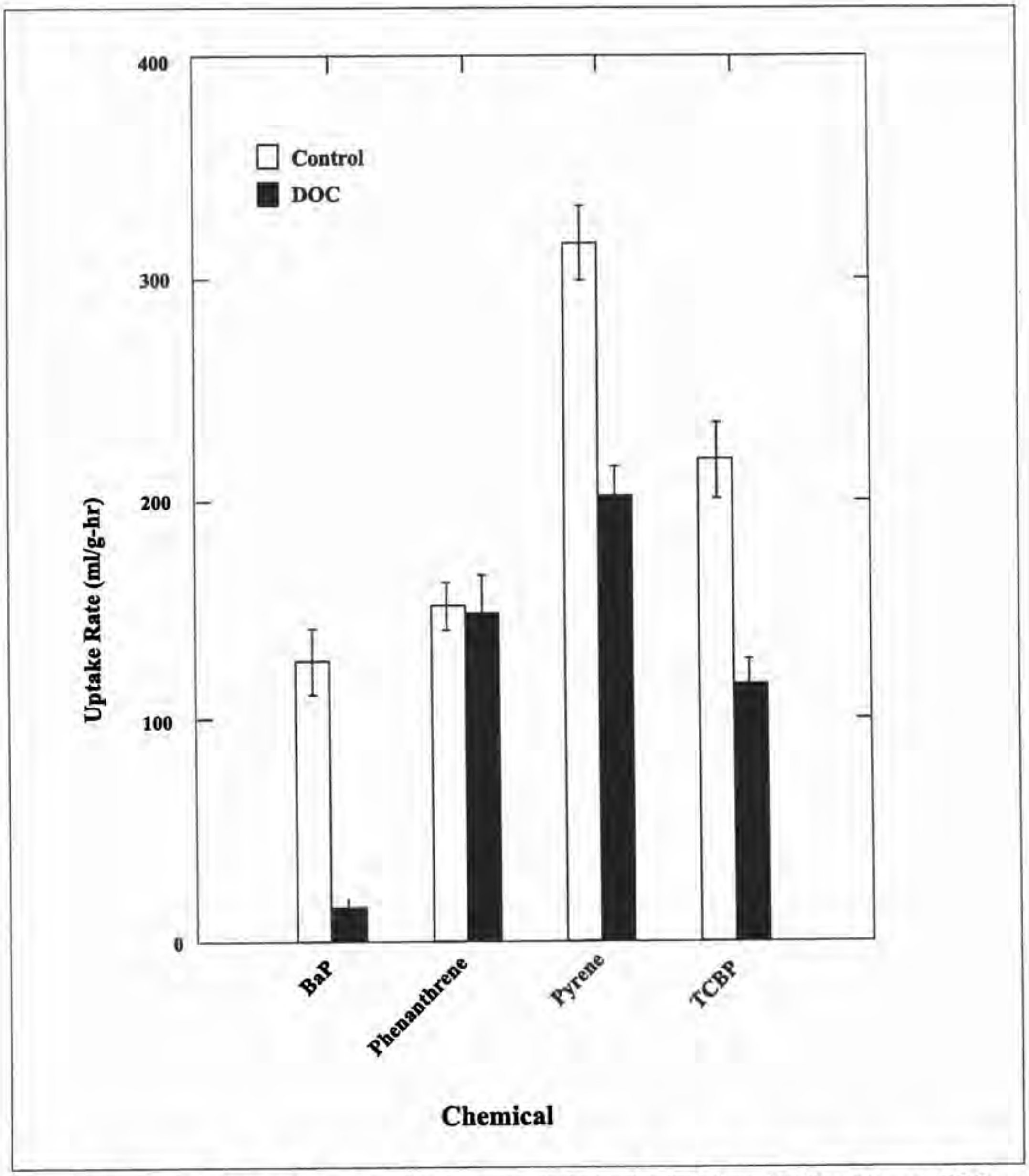

Figure 4-6. Average uptake rate of chemicals by *Pontoporeia hoyi* with (filled) and without (open) DOC present. Benzo[*a*]pyrene (BaP); phenanthrene; pyrene; 2,2',4,4'-tetrachlorobiphenyl (TCBP) (data from Landrum et al., 1987).

4.5 Field Observations of Partitioning in Sediments

An enormous quantity of laboratory data exists for partitioning in particle suspensions. However, interstitial water and sediment data from field samples are scarce. Two types of data from field samples are examined. The first is a direct test of the partitioning equation $C_{S,OC} = K_{OC}\, C_d$, which is independent of the DOC concentration. The second examines the sediment and interstitial water concentrations and accounts for the DOC that is present.

4.5.1 *Organic Carbon Normalization*

Consider a sediment sample that is segregated into various size classes after collection. The particles in each class were in contact with the interstitial water. If sorption equilibrium has been attained for each class, then, letting $C_S(j)$ be the particle chemical concentration of the j^{th} size class, it is true that

$$C_S(j) = f_{OC}(j) K_{OC} C_d \qquad (4\text{-}13)$$

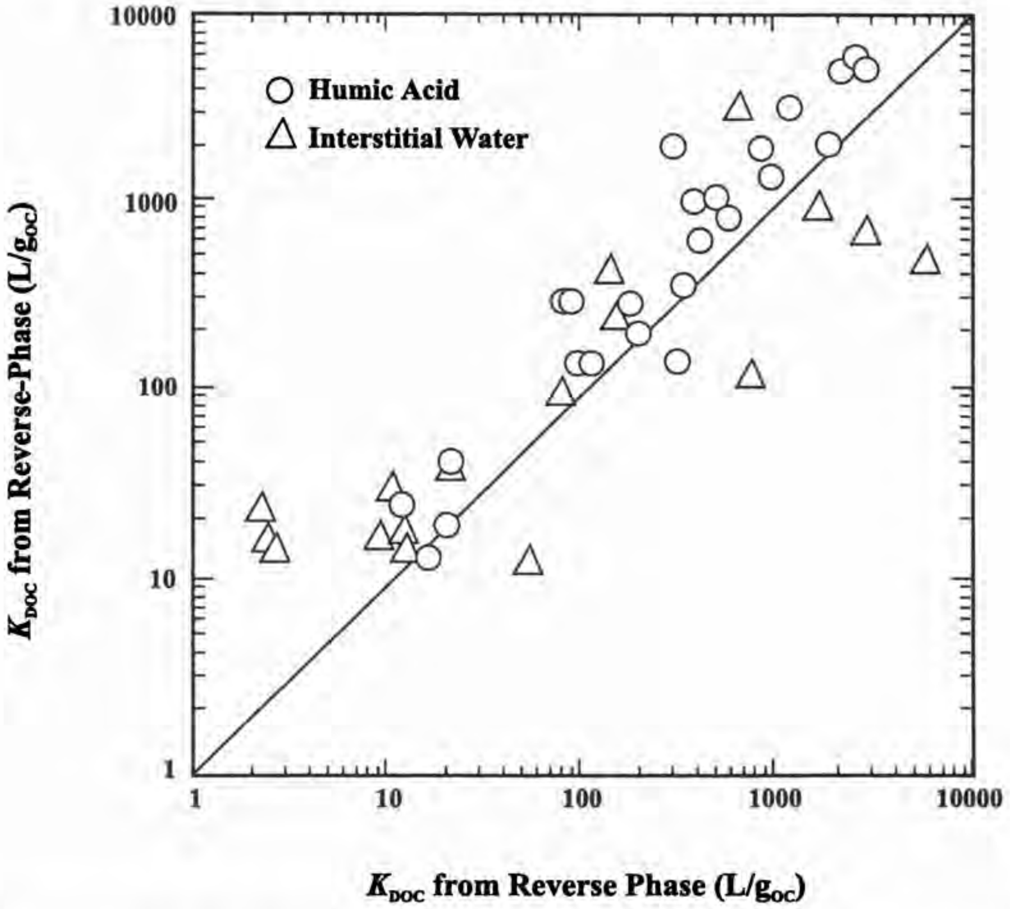

Figure 4-7. Comparison of the DOC partition coefficient calculated from the suppression of chemical uptake versus the C18 reverse-phase HPLC column estimate. Circles are Aldrich® humic acid; triangles are interstitial water DOC. Chemicals are listed in Figure 4-6 caption (also anthracene and benz[a]anthracene). The line represents equality.

where $f_{OC}(j)$ is the organic carbon fraction for each size class j. On an organic carbon–normalized basis this equation becomes

$$C_{S,OC}(j) = K_{OC}C_d \qquad (4\text{-}14)$$

where $C_{S,OC}(j) = C_S(j)/f_{OC}(j)$. This result indicates that the organic carbon–normalized sediment concentration of a chemical should be equal in each size class because K_{OC} and C_d are the same for each size class. Thus a direct test of the validity of both organic carbon normalization and EqP would be to examine whether $C_{S,OC}(j)$ is constant across size classes in a sediment sample.

A literature review was performed to identify studies where sediment chemical concentrations were reported along with sediment organic carbon for various size classes within a sediment sample. Five studies were identified that can be used to verify organic carbon normalization under field conditions. These studies represent data collected in estuaries, canals, and coastal areas. These studies were not specifically designed to test organic carbon normalization; nonetheless they provide useful data. Table 4-1 lists the five study areas, sediment sample depth, and chemicals analyzed in each study. Also included in Table 4-1 is a brief description of the sedimentation characteristics of the study area if they were given by the respective authors. These study areas represent areas of both deposition and resuspension.

Table 4-1. Summary information for studies used to verify field organic carbon normalization

Study Area	Author's Sedimentation Description	Sediment Sample Depth	Chemicals	Reference
Washington Coastal Basin Columbia River Basin	Resuspension, deposition No information given	4-8 cm	Phenanthrene Fluoranthene Anthracene Pyrene Retene Benz(a)anthracene Chrysene Benzofluoranthenes Benzo(e)pyrene Benzo(a)pyrene Perylene Indeno(c,d)pyrene Benzo(ghi)perylene	Prahl, 1982
River Derwent Derbyshire, U.K.	Predominantly eroding at stations C & Da; predominantly depositing at stations G, H, & K	0-10 cm	Total PAH	Evans et al., 1990
Belgian Continental Shelf (coastal region) & Scheldt Estuary	High turbidity, high sedimentation rates	0-1 cm	8 PCB congeners (IUPAC #s 28, 52, 101, 118, 138, 153, 170, 180)	Delbeke et al., 1990
Lazaret Bay near Toulon Harbor and Porquerolles Is., French Mediterranean Coast	No information given	0-5 cm	20 PCB congeners (IUPAC #s 8, 18, 28, 44, 52, 66, 87, 101, 105, 118, 128, 138, 153, 170, 180, 187, 195, 200, 206, 209)	Pierard et al., 1996
Bayou d'Inde, tributary of Calcasiew River near Lake Charles, Louisiana	No information given	0-15 cm	Hexachlorobenzene Hexachlorobutadiene Bentachlorobenzene Tetrachlorobenzene Trichlorobenzene Dichlorobenzene	Prytula and Pavlostathis, 1996

In Prahl (1982), sediment cores were collected at three stations near the Washington State coast (Stations 4, 5, and 7). These were sieved into a silt-and-clay–sized fraction (<64 μm) and a sand-sized fraction (>64 mm). This latter fraction was further separated into a low-density(<1.9 g/cm^3) and high-density fraction of sand-sized particles. The concentrations of 13 individual PAHs were measured in each size fraction. It is important to realize that the size fractions reported in this study, and in each of the following studies, are not pure clay, silt, or sand, but natural particles in the size classes denoted by clay, silt, and sand. The organic carbon fractions, shown in Figure 4-8A, range from 0.2% for the high-density sand-sized fraction to greater than 30% for the low-density fraction. This exceeds two orders of magnitude and essentially spans the range usually found in practice. For example, 90% of the estuarine and coastal sediments sampled for the National Status and Trends Program exceed 0.2% organic carbon (NOAA, 1991).

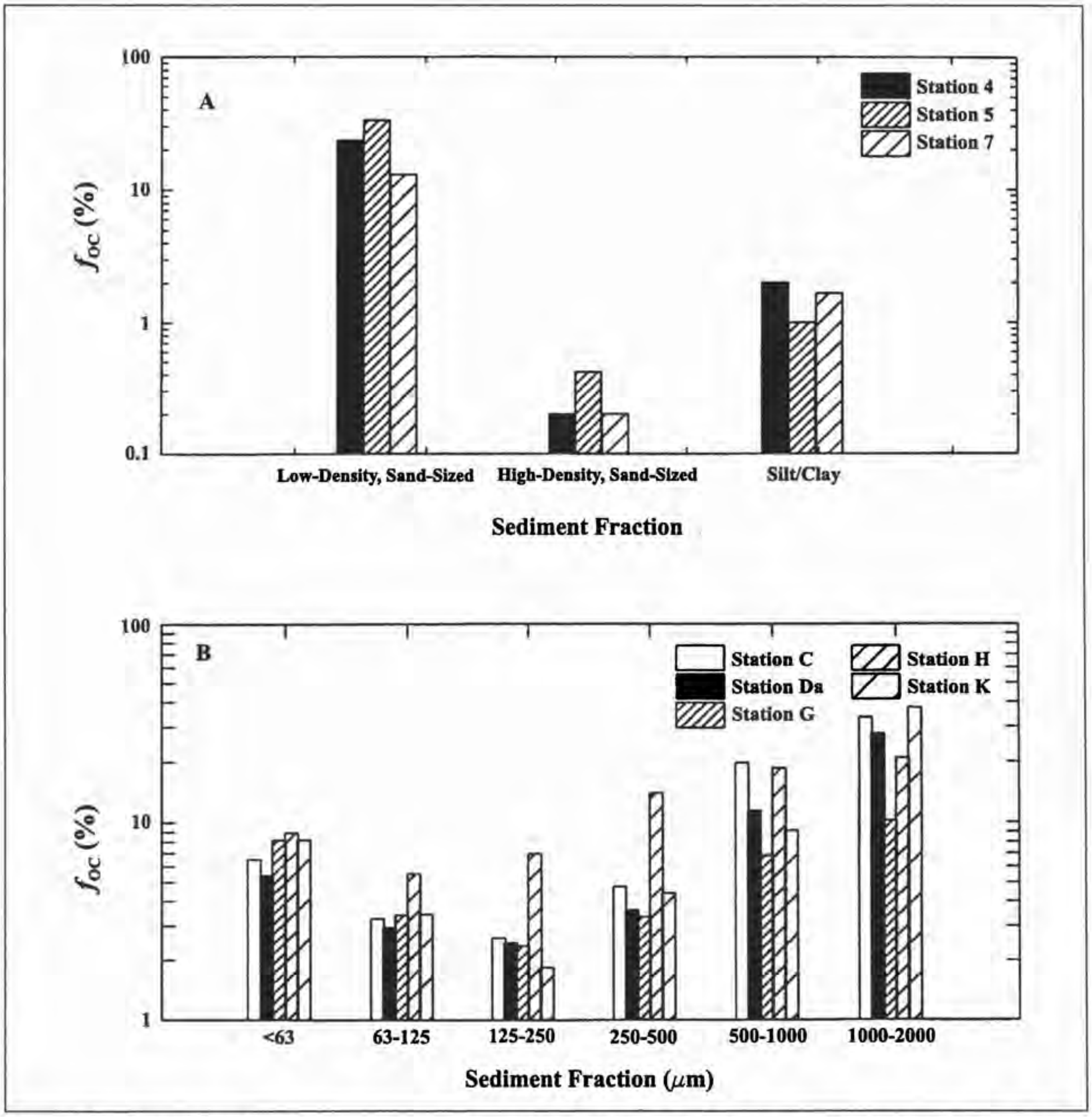

Figure 4-8. **Organic carbon fractions (percent dry weight) as indicated on the y-axis. The top panel shows the low-density sand-sized fraction (>64 μm, <1.9 g/cm^3), the high-density sand-sized fraction (>64 μm, >1.9 g/cm^3), and the silt/clay-sized fraction (<64 μm) (data from Prahl, 1982). The bottom panel shows the organic carbon fraction in the size classes as indicated (data from Evans et al., 1990).**

Figures 4-9A and B compare the dry weight–normalized clay/silt-sized fraction sediment PAH concentrations, C_S(j) (y-xis), with the sand-sized high- and low-density PAH concentrations on a dry weight basis. The dry weight–normalized data have distinctly different concentrations—the low-density high–organic carbon fraction is highly enriched, whereas the sand-sized fraction is substantially below the clay/silt fraction concentrations. Figures 4-9C and D present the same data but on an organic carbon–normalized basis, $C_{S,OC}$(j). In contrast to dry weight normalization, the PAH concentrations are essentially the same in each size class, as predicted by Equation 4-14. The lines in Figure 4-9 represent equality and have been

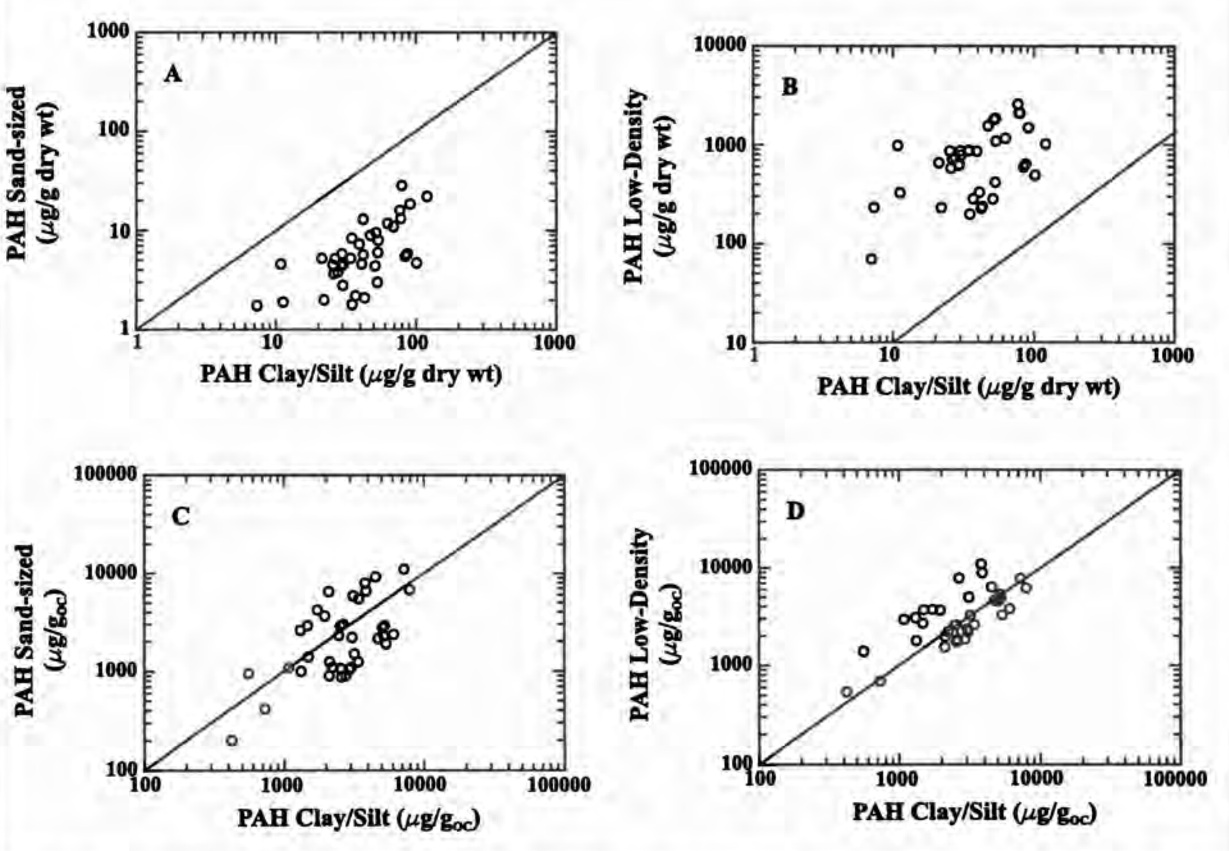

Figure 4-9. **Comparison of PAH concentrations of the sand-sized (left) and low-density (right) sediment particles to the clay/silt fraction (x-axis). PAH sediment concentrations are dry weight– (top) and organic carbon–normalized (bottom) for Stations 4, 5, and 7. The line represents equality (data from Prahl, 1982).**

added as a visual aid. These lines have also been used in Figures 4-10, 4-12, 4-13, and 4-14.

Evans et al. (1990) collected sediments at five sites along the River Derwent, Derbyshire, United Kingdom. Sediments were separated into six sediment size classes representative of clay and silt (<63 μm) to coarse sand (1.0 to 2.0 mm). Organic carbon content and total PAH were measured in each sediment size class. Figure 4-8B presents the different size classes and associated organic carbon contents. Evans et al. (1990) attributed the bimodal distribution of f_{OC} to two types of organic matter. Organic matter in the 1.0 to 2.0 mm size class may result from fragmentary plant material from organic carbon, whereas the size class less than 500 μm is the result of aging humic material. The organic content in this study ranged from 2.0% to 40%.

Figure 4-10 presents a comparison of PAH concentration for different sediment classes for dry weight normalization and organic carbon normalization. Figure 4-10A compares PAH concentrations on the sand fraction (63 to 500 μm) and the clay/silt fraction (<63 μm) on a dry weight basis. Figure 4-10B compares PAH concentrations on the coarse sand fraction (0.5 to 2.0 mm) and the clay/silt fraction (<63 μm) on a dry weight basis. The data indicate that the PAH concentration is higher in the coarse sand fraction of sediment. Recall from Figure 4-8A that the clay/silt and low-density sand fractions contain a higher fraction organic carbon content. The bottom panels of Figure 4-10 (C and D) present the organic carbon–normalized comparison of PAH concentrations by sediment class. For both panels, the organic carbon–normalized PAH concentrations are similar regardless of the sediment size class as predicted by Equation 4-14.

Delbeke et al. (1990) collected sediments from seven sites in the Belgian continental shelf and the Scheldt estuary. These sites were analyzed for eight PCB congeners and organic carbon in the bulk sediment and clay/silt (<63 μm) sediment fraction. In

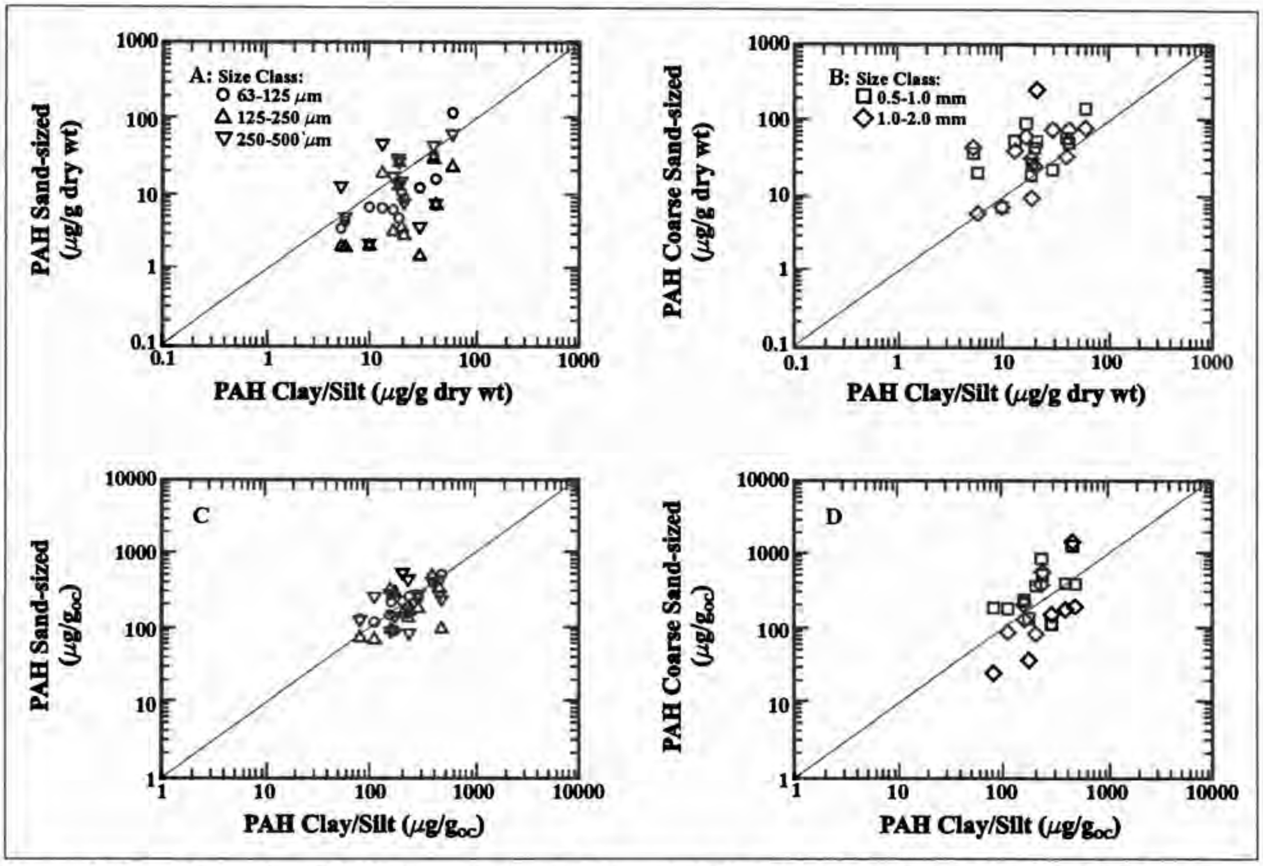

Figure 4-10. **Comparison of PAH concentrations of the sand-sized (left) and coarse sand–sized (right) sediment particles indicated by symbols to the clay/silt fraction (x-axis). PAH sediment concentrations are dry weight– (top) and organic carbon–normalized (bottom) for Stations C, Da, G, H, and K. The line represents equality (data from Evans et al., 1990).**

addition, analyses of the samples were done to determine the percentage of size fractions ranging from 3 to 500 μm that made up the sample. The PCB congeners measured in this study were IUPAC numbers 28, 52, 101, 118, 138, 153, 170, and 180 (Table 4-1). Using concentrations reported for bulk sediment samples and for clay/silt samples, and measurements of percent size fractions of each sample, calculations were done to estimate concentrations on the greater than (>) 63 μm portion of the sample. Similar calculations were done to determine organic carbon content on the less than (<) 63 μm portion of the sample. Organic content varied from 0.01% to 10% inclusive of both <63 μm and >63 μm portions of the sediment.

Figure 4-11A presents the percent organic carbon on the <63 μm portion of the sample (filled bar) and on the >63 μm portion of the sample (hatched bar). PCB congener concentrations on a dry weight basis (Figure 4-12A) and on an organic carbon basis (Figure 4-12B) are shown for comparison. Organic carbon content in the >63 μm class size at stations 2 and 4 is 0.01% and 0.06%, respectively, as indicated in Figure 4-11. The data for these stations are shown in Figure 4-12 using filled symbols. Although an f_{OC} > 0.2% has been presented as the value for which organic carbon normalization applies, normalization at these f_{OC} values seems appropriate for this dataset. Figure 4-12A indicates no evident relationship between PCBs in the <63 μm sample and PCBs in the >63 μm sample on a dry weight basis. When concentrations in either class size are normalized to organic carbon content, then concentrations are similar for both class sizes as shown in Figure 4-12B. This indicates that PCB concentrations are similar across sediment class sizes.

Pierard et al. (1996) collected sediment samples from three locations in the French Mediterranean Coast: Lazaret Bay near Toulon Harbor, Roquebrune Bay near Monaco, and Porquerolles Island, which is a marine natural park. Only data from the Lazaret Bay and Porquerolles Island areas are discussed here

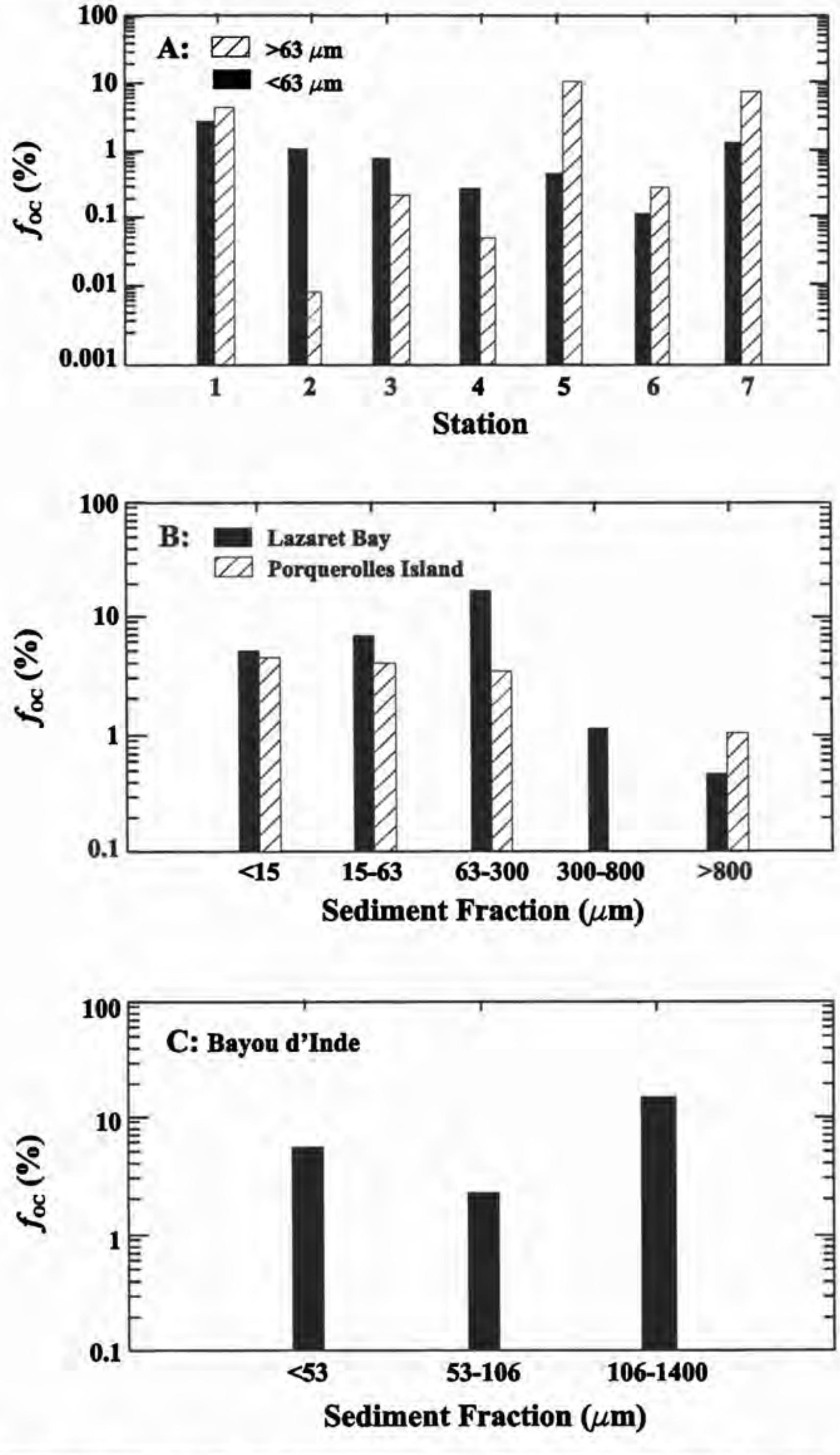

Figure 4-11. **Organic carbon fractions (percent dry weight) for (A) two sediment size classes (<63 μm and >63 μm) from seven sampling stations (data from Delbeke et al., 1990), (B) five sediment size classes (x-axis) from two sampling locations (data from Pierard et al., 1996), and (C) three sediment size classes as indicated on the x-axis (data from Prytula and Pavlostathis, 1996).**

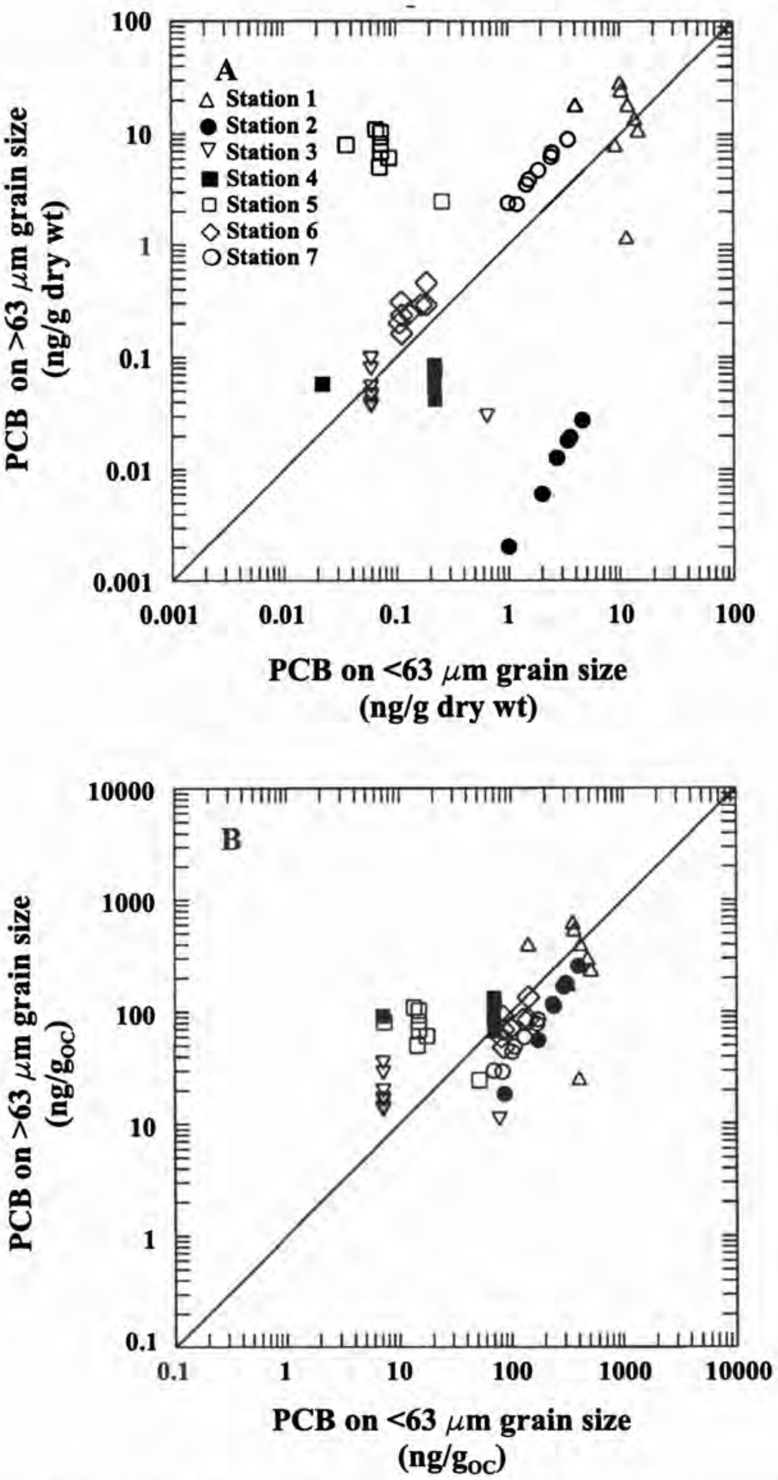

Figure 4-12. Comparison of eight PCB congener concentrations of >63 μm sized particles with <63 μm sized particles. Sediment concentrations plotted as dry weight– (A) and organic carbon–normalized (B) for Stations 1–7. The line represents equality (data from Delbeke et al., 1990).

because sediment organic carbon was reported for these two areas. Sediment samples were taken at 0 to 5 cm depths. Pierard et al. separated the sediment samples into five grain-size fractions defined as follows: fine silts/clays (<15 μm), medium silts (15 to 63 μm), medium to fine sands (63 to 300 μm), medium to coarse sands (300 to 800 μm), and very coarse sands (>800 μm). Fractions here are defined by sieve size, and no attempt to determine the amount of silt or sand in each defined class is made.

After sample separation, organic carbon content and PCB concentrations for 20 congeners (see Table 4-1) were measured for each size class. Figure 4-11B compares the organic carbon content within each of the size classes for the Lazaret and Porquerolles samples. Organic carbon ranges from 0.44% to 16.1%. Three samples for which both locations report organic carbon indicate that the organic carbon at the two locations is comparable. The 16.1% value for the 63 to 300 μm Lazaret sample appears high. However, the Porquerolles 63 to 300 μm organic carbon value of 3.24% is also applied to the Lazaret 63 to 300 μm size class sample for normalization. Organic carbon for the Porquerolles 300 to 800 μm size fraction was not reported. In order to use the data, and because three of the fractions show comparable organic carbon content between the two locations, the Lazaret 300 to 800 μm organic carbon content was used for the Porquerolles 300 to 800 μm sample for normalizing. Comparisons of bulk dry weight–normalized chemical (top panel) and organic carbon–normalized chemical (bottom panel) concentrations for the <15 μm size class with each of the other size classes are made in Figure 4-13. Comparisons of size classes with similar organic carbon contents do not change with organic carbon normalization (<15 μm vs. 15 to 63 μm and vs. 63 to 300 μm, panels A and B). Panels C and D indicate a somewhat improved relationship with normalization. Additional comparisons for each of the size classes versus the remaining size classes were done with similar results. These are not presented here.

Prytula and Pavlostathis (1996) reported sediment fractionation data for a sediment site in the Bayou d'Inde, a tributary of the Calcasieu River near Lake Charles, Louisiana. This site is part of an ongoing investigation and is located at the intersection of an industrial canal and Bayou d'Inde. Sediments were sieved into three particle sizes; <53 μm, 53 to 106 μm, and 106 to 1,400 μm. Fractions were analyzed for organic carbon and several chlorinated organic compounds which are listed in Table 4-1. Organic carbon contents for each size class are shown in Figure 4-11C. Organic carbon ranges from 2.1% to 14.5%.

Compound concentrations for each of the three size classes are compared for bulk dry weight–normalized (top panels) and organic carbon–normalized (bottom panels) data in Figure 4-14. Panels A and B compare the <53 μm size class with the 53 to 106 μm and 106 to 1,400 μm size classes, respectively. The panel A comparison does not improve the relationship of the two sizes with normalization. The panel B comparison indicates that normalization slightly improves the relationship of the two size classes. A comparison of the mid (53 to 106 μm) and larger size classes (106 to 1400 μm) is shown in panel C. The concentrations improve with normalization.

4.5.2 *Verification of Field Organic Carbon Normalization*

Analyses of the above datasets suggest that when sediment concentrations for different size classes within a bulk sediment sample are organic carbon–normalized, the concentrations between size classes become comparable. This conclusion also suggests that organic carbon is the predominant controlling factor in determining the partition coefficient of the differently sized particles in a sediment sample. A statistical evaluation to support this conclusion is as follows. An average coefficient of variation (CV) for each of the studies was computed for both dry weight– and organic carbon–normalized concentrations. To do this, the mean concentration and normalized variance for each chemical at a station were computed over the particle sizes. Then the CV was computed. The equations are as follows. Let

$$c_{ijk} = a_{ij} + e_{ijk} \qquad \begin{array}{l} i = 1,\ldots,N_c \\ j + 1,\ldots,N_S \\ k = 1,\ldots,N_p \end{array} \tag{4-15}$$

where c_{ijk} = ln of the concentration for the i^{th} chemical, j^{th} station, k^{th} particle size class; a_{ij} = ln mean concentration for the i^{th} chemical, j^{th} station; and e_{ijk} = ln concentration variation due to the k^{th} particle size class.

The average concentration across particle size is computed for each chemical–station pair as follows

$$\bar{\alpha}_{ij} = \sum_{k=1}^{N_p} c_{ijk} \,/\, N_p \tag{4-16}$$

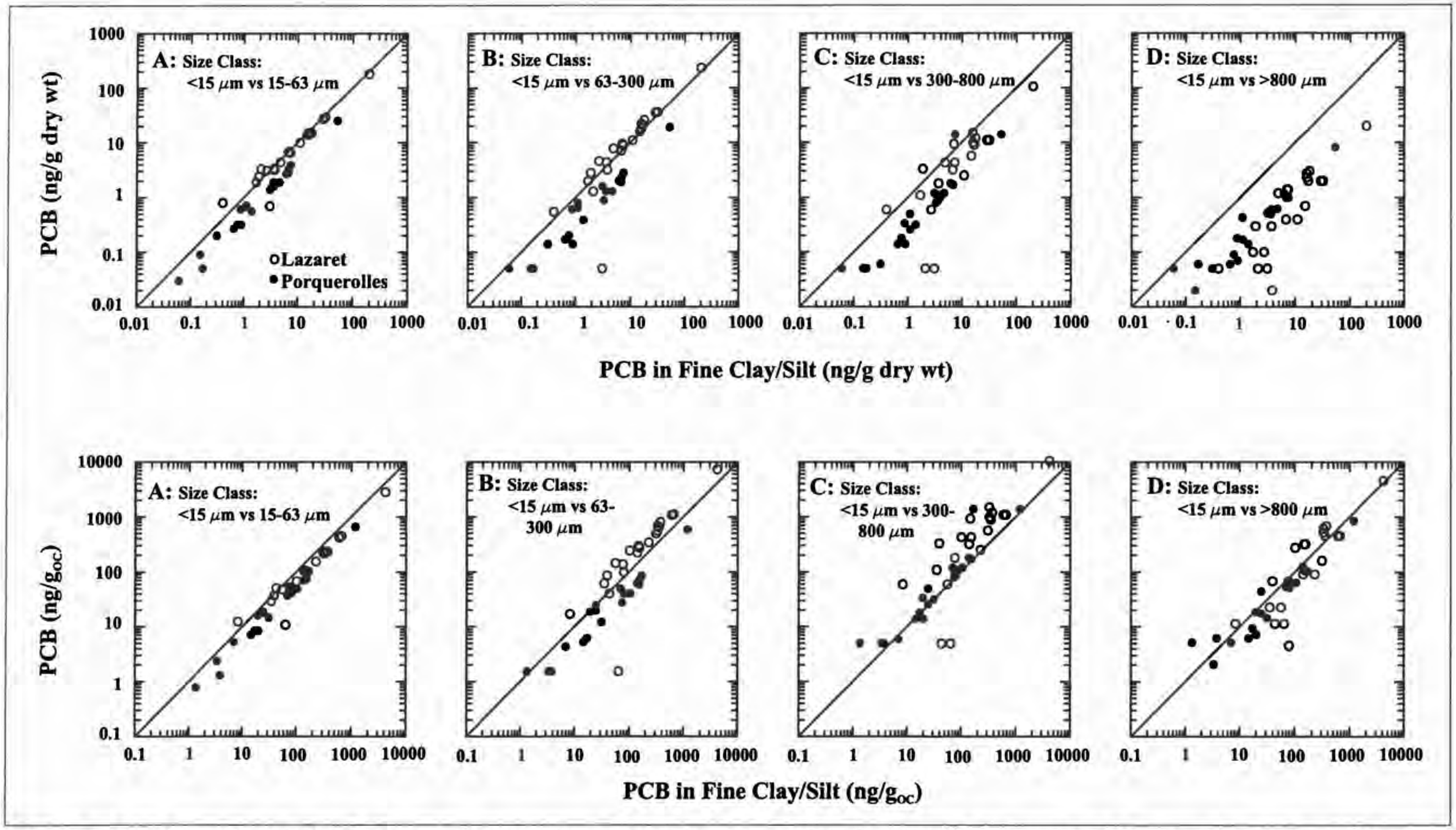

Figure 4-13. Comparison of 20 PCB congener concentrations on the <15 μm size particles (x-axis) with four larger size fractions (y-axis). Sediment concentrations plotted as dry weight- (top) and organic carbon-normalized (bottom) for grain size classes (A) <15 μm vs 15-63 μm, (B) <15 μm vs 63-300 μm, (C) <15 μm vs 300-800 μm, and (D) <15 μm vs >800 μm (data from Pierard et al., 1996).

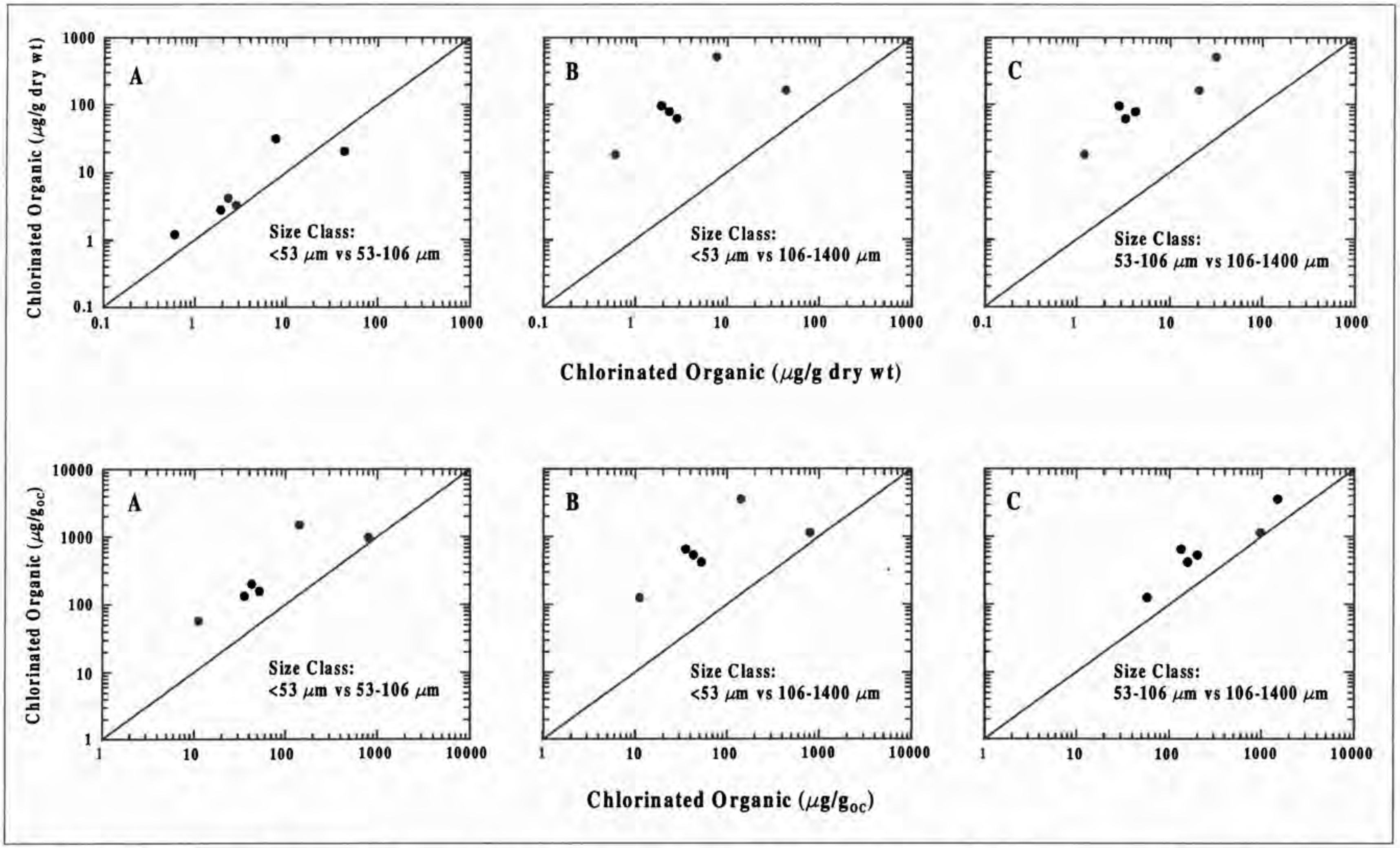

Figure 4-14. Comparison of six chlorinated organic chemical concentrations on three sediment size fractions. Sediment concentration plotted as dry weight– (top) and organic carbon–normalized (bottom) for grain size classes (A) <53 μm vs 53-106 μm, (B) <53 μm vs 106-1400 μm, and (C) 53-106 μm vs 106-1400 μm (data from Prytula and Pavlostathis, 1996).

The variance (σ) for a chemical at each station due to particle size effects can then be computed

$$\sigma\{\varepsilon_{ij}\} = \frac{1}{N_{p-1}} \sum_{k=1}^{N_p} (c_{ijk} - \bar{\alpha}_{ij})^2 \tag{4-17}$$

The variance for each chemical–station pair can then be normalized by the average for each chemical–station pair

$$\frac{\sigma\{\varepsilon_{ij}\}}{\bar{\alpha}_{ij}^{\,2}} = \frac{1}{N_{p-1}} \sum_{k=1}^{N_p} \left(\frac{c_{ijk}}{\bar{\alpha}_{ij}^{\,2}} - \frac{1}{\bar{\alpha}_{ij}} \right) \tag{4-18}$$

The CV over all chemicals and stations for each dataset is then computed by summing the normalized variances and dividing by the number of chemical station pairs

$$\begin{aligned} \overline{\mathrm{CV}} &= \sqrt{\overline{\mathrm{CV}}^2} \\ \overline{\mathrm{CV}}^2 &= \frac{1}{N_c N_s} \sum_{i=1}^{N_c} \sum_{j=1}^{N_s} \frac{\sigma\{\varepsilon_{ij}\}}{\bar{\alpha}_{ij}^{\,2}} \end{aligned} \tag{4-19}$$

The resulting CV for each study for both dry weight– and organic carbon–normalized concentrations is shown in Figure 4-15A. Table 4-2 presents CV values for both dry weight– and organic carbon–normalized concentrations for each study. Percent changes in CV due to organic carbon normalization were calculated. Percent reduction in CV due to organic carbon normalization is tabulated in Table 4-2 and shown graphically in Figure 4-15B. Reductions in variation range from 69.1% to 96.4%. These results indicate that large reductions in variation occur when sediments of varying class sizes are carbon-normalized.

The average organic carbon–normalized CV for the five datasets is 18.3%. The results of this statistical analysis verify the utility of organic carbon normalization for field-collected sediments.

4.5.2.1 *Sediment Equilibrium*

An important assumption in the ESG methodology is the assumption of sediment equilibrium. It is difficult to prove equilibrium in the field. A more realistic assumption is that sediments exist in near-equilibrium conditions. Information on specific sedimentation rates was not collected for the five studies; however, information given in Table 4-1 indicates that surface sediments are in flux. A reasonable generalization of sedimentation for coastal areas and rivers is 1.0 cm/year (Sadler, 1981). Therefore, bedded sediment contact times are long, and desorption would have to be very slow for nonequilibrium conditions to exist for the sample depths of 1 cm or greater. Sediment samples at the depths listed in Table 4-1 would be in place long enough for sediment equilibrium to be established for four of the five studies even though surface sediments may not be in equilibrium. Less confidence in this assumption should be given to Delbeke et al. (1990) where samples of 0-1 cm in depth were obtained. Verification of organic carbon normalization as presented in Figure 4-15 validates the assumption of sediment equilibrium. The above datasets indicate that organic carbon normalization is valid and the assumption of sediment equilibrium, as applied to ESGs, is also valid in areas under near-equilibrium conditions.

During resuspension of sediments or similar events (e.g., dredging and disposal), the equilibrium of sediments will likely be disturbed. In essence, this disequilibrium manifests itself as decreased concentrations of chemicals in the interstitial water caused by mixing of the sediment with additional water from the water column (assuming that concentrations of the chemical are comparatively low in the water column). Immediately following resettling of the sediment and allowing time for any particle interactions to subside, interstitial water may show lower chemical concentrations than would be predicted through EqP and, accordingly, EqP might predict greater toxicity than would be expected based on that instantaneous condition. However, in evaluating such sediments, it should be remembered that absent further disturbance, near-equilibrium conditions can be expected to be reestablished in the sediment within one to a few weeks, depending on the chemical (Schwarzenbach et al, 1993; Wu and Gschwend, 1986). For this reason, when near-equilibrium conditions are reestablished, the long-term toxicity of the sediment can be expected to be close to that predicted by EqP, even if the sediment is not in equilibrium when the solid-phase chemistry is measured. Based on these considerations, ESGs may be useful for predicting the long-term risk from nonpolar organic contaminants (with log $K_{OW} > 3$) in sediment even in cases where short-term disturbances occur. When equilibrium is lost due to disturbance, the resulting errors should be toward overpredicting toxicity (i.e., the guideline would be overprotective rather than underprotective), errors that may still be acceptable for certain assessment scenarios.

4.5.2.2 *Summary*

Field data from five studies were analyzed to confirm the utility of organic carbon normalization. For each of the five studies, both bulk concentrations and organic carbon–normalized concentrations were

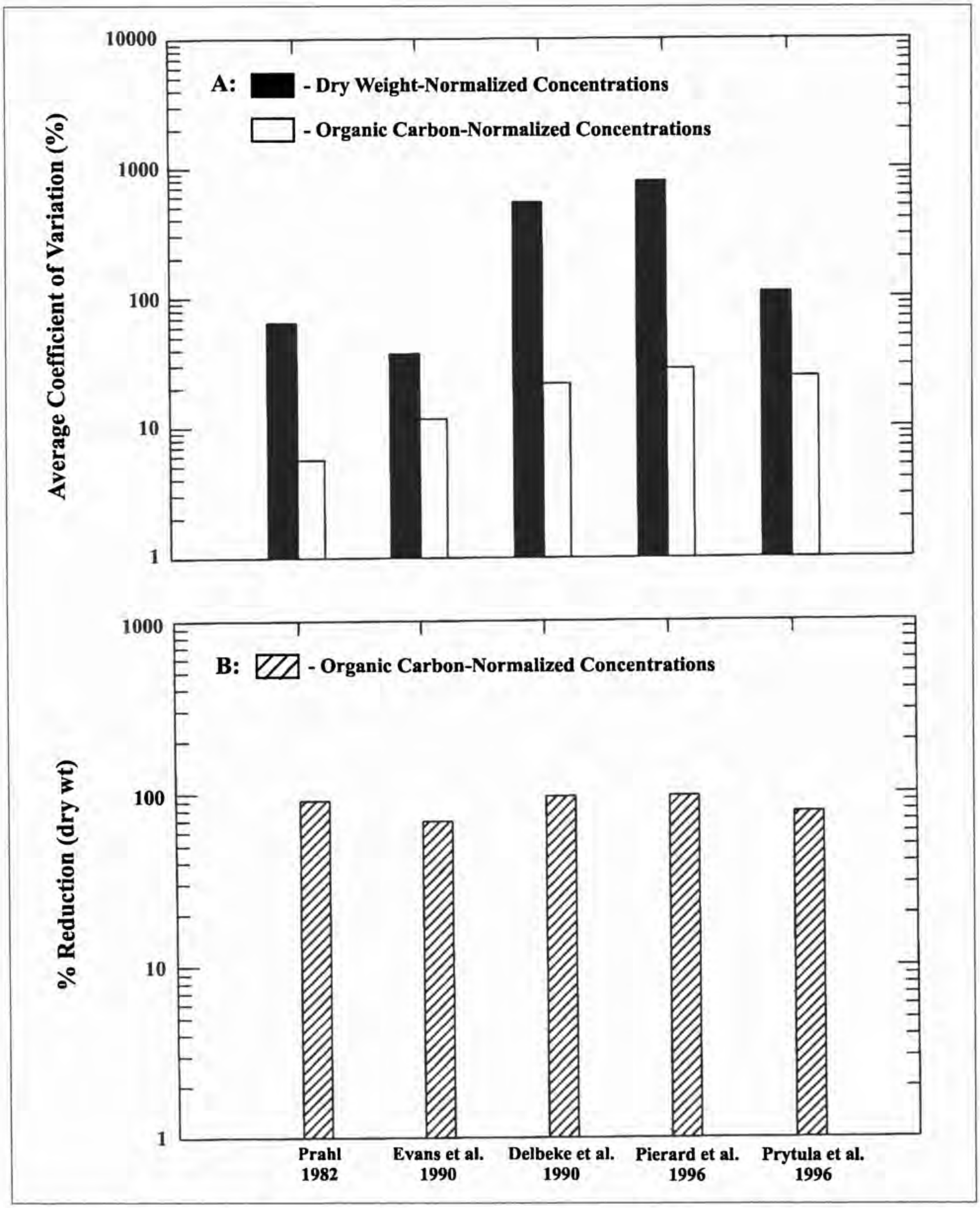

Figure 4-15. Comparison of the average coefficient of variation for dry weight–normalized (A) and organic carbon–normalized (B) concentrations and the percent reduction in the average coefficient of variation due to organic carbon normalization for each study.

Table 4-2. Comparison of average coefficient of variation using dry weight– or organic carbon–normalized concentrations

Average Coefficient of Variation (CV)			
Dry Weight-Normalized Concentrations (%)	Organic Carbon-Normalized Concentrations (%)	Percent Reduction in CV due to OC Normalization	Reference
65.1	5.62	91.4	Prahl, 1982
37.5	11.6	69.1	Evans et al., 1990
540	21.6	96.0	Delbeke et al., 1990
787	28.1	96.4	Pierard et al., 1996
110	24.6	77.7	Prytula et al., 1996

compared across particle size classes of a sample. In almost all cases, organic carbon normalization resulted in more comparable concentrations. The average CV was computed for each dataset for both bulk concentrations and organic carbon–normalized concentrations. In all cases, the CV was reduced with organic carbon normalization. Studies used here represent areas where surface sediments (upper cm) may not be in equilibrium due to hydrodynamic conditions. However, sample depths provide sediment samples that are in equilibrium or near equilibrium. Two important conclusions can be drawn from this analysis: (1) organic carbon normalization has been shown to be valid under field conditions and (2) the assumption of sediment equilibrium for the purpose of organic carbon normalization is valid in areas where typical sedimentation and resuspension may be occurring.

4.5.3 *Sediment/Interstitial Water Partitioning*

Normally, when measurements of sediment chemical concentration, C_S, and total interstitial water chemical concentrations, C_{IW}, are made, the value of the apparent partition coefficient is calculated directly from the ratio of these quantities. As a consequence of DOC complexation, the apparent partition coefficient, $K_p{'}$, defined as

$$K_p{'} = \frac{C_S}{C_{IW}} \tag{4-20}$$

is given by

$$K_p{'} = \frac{K_p}{1 + m_{DOC} K_{DOC}} = \frac{f_{OC} K_{OC}}{1 + m_{DOC} K_{DOC}} \tag{4-21}$$

As m_{DOC} (measured DOC) increases, the quantity of DOC-complexed chemical increases and the apparent partition coefficient approaches

$$K_p{'} = \frac{f_{OC} K_{OC}}{m_{DOC} K_{DOC}} \tag{4-22}$$

which is just the ratio of sorbed to complexed chemical. Because the solid-phase chemical concentration is proportional to the freely-dissolved portion of the interstitial water concentration, C_d, the actual partition coefficient, K_p, should be calculated using the freely-dissolved concentration. The freely-dissolved concentration will typically be lower than the total dissolved interstitial water chemical concentration in the presence of significant levels of interstitial water DOC (e.g., Figure 4-5). As a result, the actual partition coefficient calculated with the freely-dissolved concentration is higher than the apparent partition coefficient calculated with the total dissolved interstitial water concentration C_{IW}.

Direct observations of interstitial water partition coefficients are restricted to the apparent partition coefficient, $K_p{'}$ (Equation 4-20), because (1) total concentrations in the interstitial water are typically reported and (2) DOC complexing is expected to be significant at the DOC concentrations found in interstitial waters. Data reported by Brownawell and Farrington (1986) demonstrate the importance of DOC complexing in interstitial water. Figure 4-16 presents the apparent partition coefficient, measured for 10 PCB congeners at various depths in a sediment core, versus $f_{OC} K_{OW}$, the calculated partition coefficient The partition coefficients are computed for total (squares) and freely-dissolved PCB (circles) using Equation 4-23 and $K_{DOC} = K_{OW}$. The line corresponds to the relationship $K_{OC} = K_{OW}$, which is the expected result if

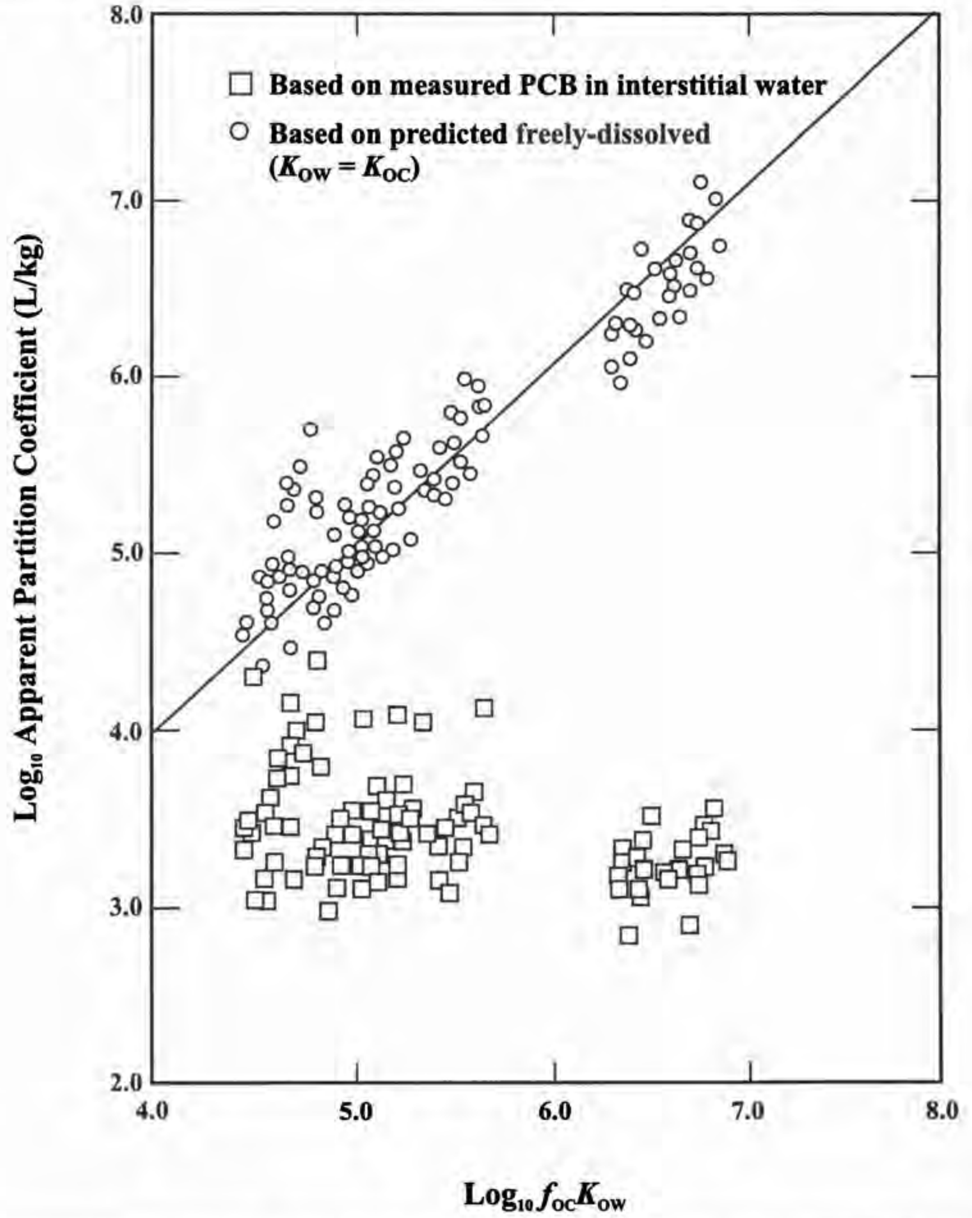

Figure 4-16. **Apparent partition coefficient versus the product of the organic carbon fraction and K_{OW}. The line represents equality (data from Brownawell and Farrington, 1986).**

DOC complexing were not significant. Because DOC concentrations were measured for these data, it is possible to estimate C_d with Equation 4-12 in the form

$$C_d = \frac{C_{IW}}{1 + m_{DOC} K_{DOC}} \quad (4\text{-}23)$$

and to compute the actual partition coefficient: $K_p = C_s/C_d$. The data indicate that if $K_{DOC} = K_{OW}$ is used, the results, shown on Figure 4-16, agree with the expected partition equation, namely that $K_p = f_{OC} K_{OW}$. A similar three-phase model was presented by Brownawell and Farrington (1985).

Other data with sediment–interstitial water partition coefficients for which the DOC concentrations have not been reported (Socha and Carpenter, 1987; Oliver, 1987) are available to assess the significance of DOC partitioning on the apparent sediment partition coefficient. Figure 4-17 presents these apparent organic carbon–normalized partition coefficients, that

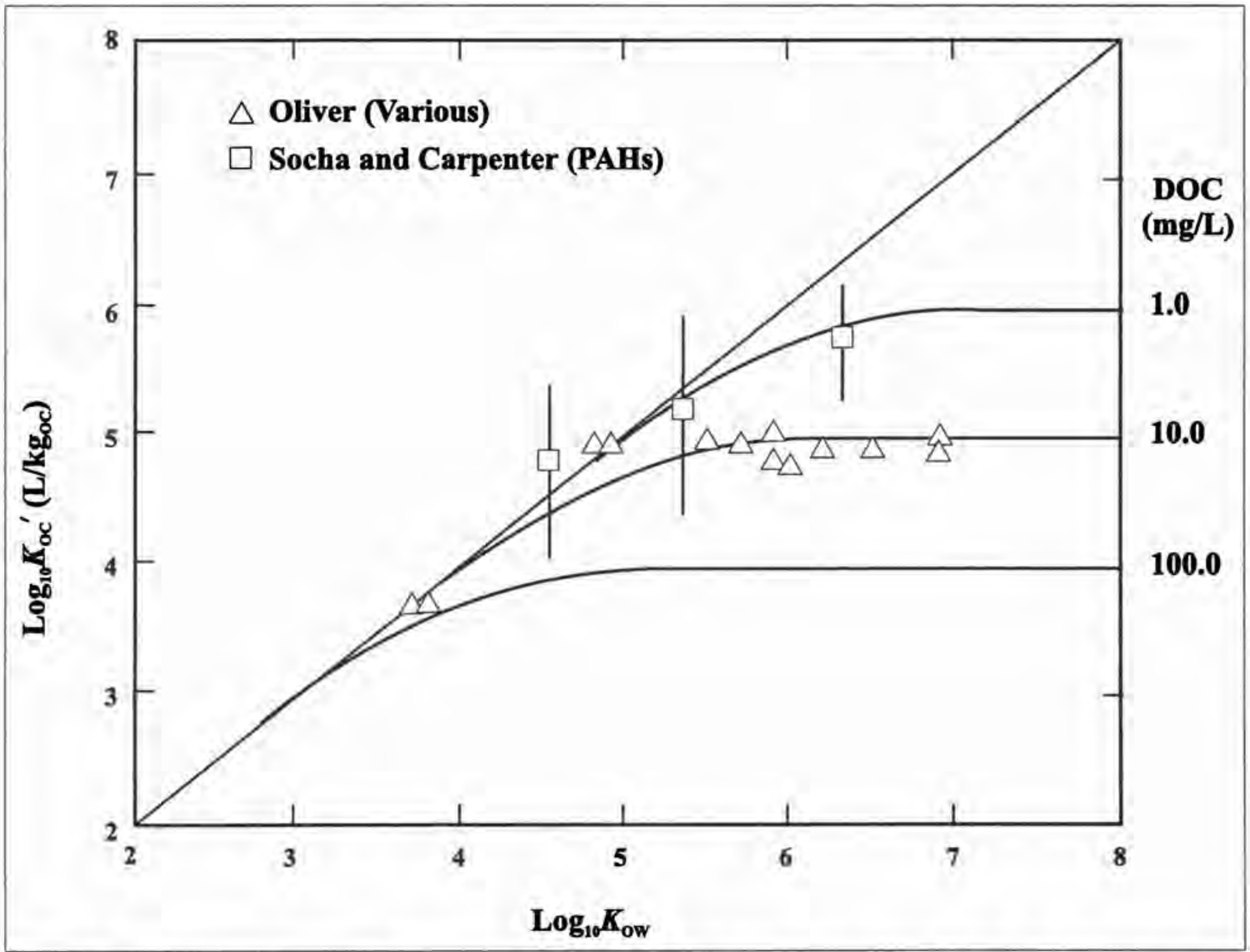

Figure 4-17. **Apparent organic carbon–normalized partition coefficient (K_{OC}') versus K_{OW}. The lines represent the expected relationship for DOC concentrations of 0, 1, 10, and 100 mg/L $K_{DOC} = K_{OW}$ (data from Oliver (1987) for PCB congeners and other chemicals, and from Socha and Carpenter (1987) for phenanthrene, fluoranthene, and perylene).**

is, $K_{OC}' = K_p'/f_{OC}$ versus K_{OW}. The expected relationship for DOC concentrations of 0, 1, 10, and 100 mg/L is also shown. Although substantial scatter in these data reflect the difficulty of measuring interstitial water concentrations, the data conform to DOC levels of 1.0 to 10 mg/L, which is well within the observed range for interstitial waters (Thurman, 1985; Brownawell and Farrington, 1986). Thus, these results do not refute the hypothesis that $K_{OC} \approx K_{OW}$ in sediments but show the need to account for DOC complexing in the analysis of interstitial water chemical concentrations.

4.5.4 *Laboratory Toxicity Tests*

Another way to verify Equation 4-14 is from data collected during sediment toxicity tests in the laboratory. These tests yield sediment ($C_{S,OC}$) and freely-dissolved interstitial water (C_d) chemical concentrations at several dosages bounding an experimentally estimated toxic concentration for the test organism. The organic content of the sediment must be measured also. Sediment toxicity tests are done under quiescent conditions when sediment and interstitial water are in equilibrium. The results of these tests can be used to compute the organic carbon partition coefficient, K_{OC}. To verify Equation 4-14, estimates of K_{OC} computed from Equation 4-3 and EPA-recommended K_{OW} values are compared with partitioning in sediment toxicity tests. Sediment toxicity tests and K_{OW} measurements are available for five chemicals: endrin (Nebeker et al, 1989; Schuytema et al., 1989; Stehly, 1991), dieldrin (Hoke and Ankley, 1992), acenaphthene (Swartz, 1991), phenanthrene

(Swartz, 1991), and fluoranthene (Swartz et al., 1990; DeWitt et al., 1992). Sediment toxicity tests for these chemicals were performed as part of the development of ESGs. Mortality results for these tests were presented in Figures 2-2 and 2-3. A discussion of K_{OW} selection follows.

Figure 4-18 shows organic carbon–normalized sorption isotherms for acenaphthene, endrin, phenanthrene, and fluoranthene, where the sediment concentration ($\mu g/g_{OC}$) is plotted versus interstitial water concentration (μg/L). These tests represent freshwater and marine sediments exhibiting a range of organic carbon content of 0.07% to 11%. In each panel, the line corresponds to Equation 4-8, where K_{OC} is derived from EPA-recommended K_{OW} values. In each of the panels, the toxicity test data are in agreement with the line computed from the calculated K_{OC}. For these chemicals, DOC measurements are unavailable, and partitioning to DOC in the interstitial water has not been considered. The figure indicates, however, that DOC complexing in these experiments appears to be negligible.

Partitioning in the dieldrin experiment indicates that DOC complexation may be significant. The partitioning isotherm for dieldrin represents organic carbon–normalized sediment concentrations versus total (Figure 4-19A) and computed dissolved (Figure 4-19B) interstitial water concentrations. Dissolved interstitial water concentrations are computed using Equation 4-23, DOC measurements, and an estimated $\log_{10}K_{DOC} = 5.28$. Log K_{DOC} is estimated from $\log_{10} K_{OC} = 5.28$ for dieldrin. Figure 4-19 represents data from Hoke and Ankley (1992) because Hoke et al. (1995) did not measure interstitial water. Adjusting for partitioning to DOC (Figure 4-19B) indicates better agreement with the recommended K_{OC}. These data represent one sediment

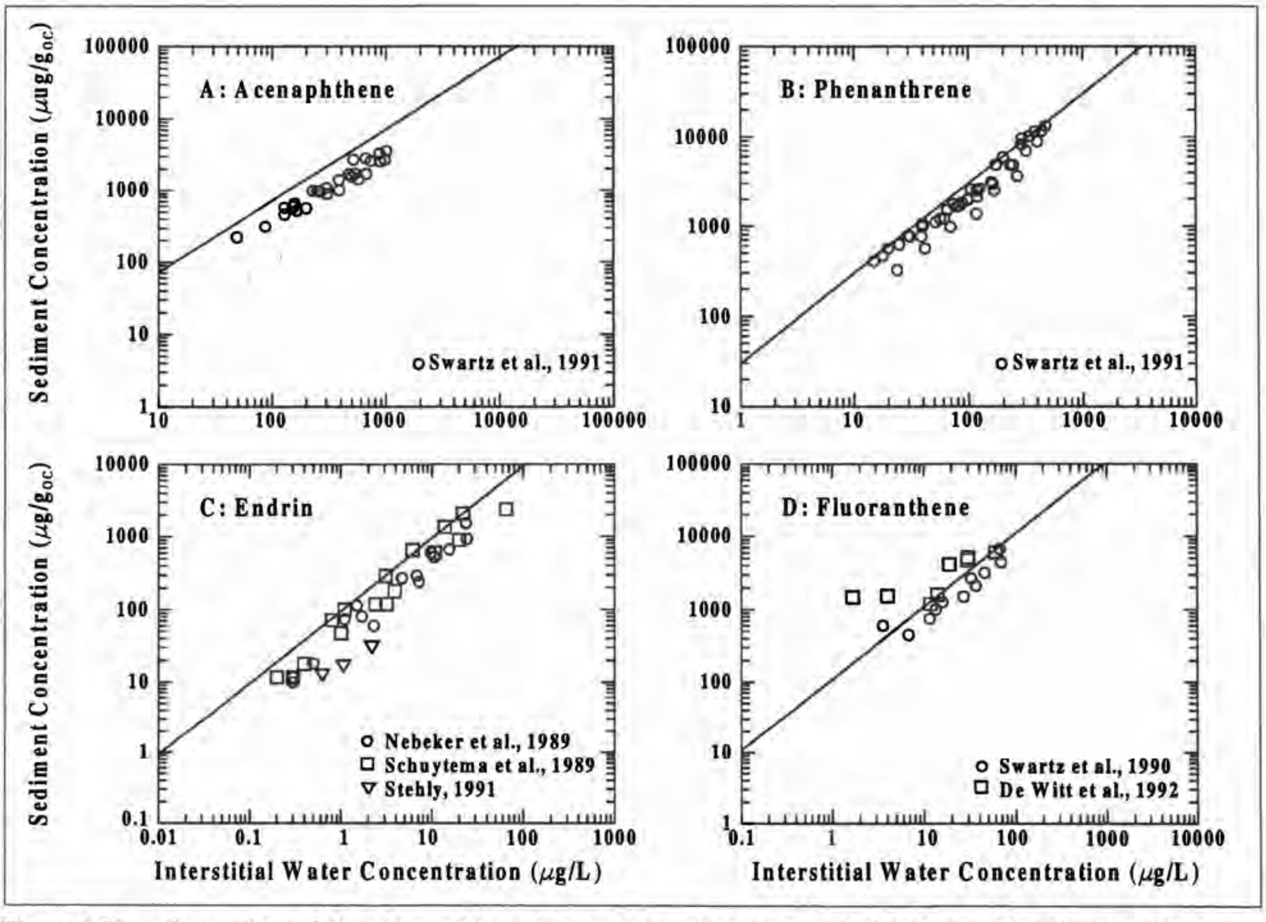

Figure 4-18. Comparison of K_{OC} observed in toxicity tests (symbols) to K_{OC} calculated using Equation 4-3 and K_{OW} values recommended by Karickhoff and Long (1995; solid line). Symbols are sediment concentration versus interstitial water concentration. Solid line is $C_{S,OC}=K_{OC}C_d$, where $\log_{10}K_{OC}$ is 3.85 for acenaphthene, 4.97 for endrin, 4.47 for phenanthrene, and 5.03 for fluoranthene.

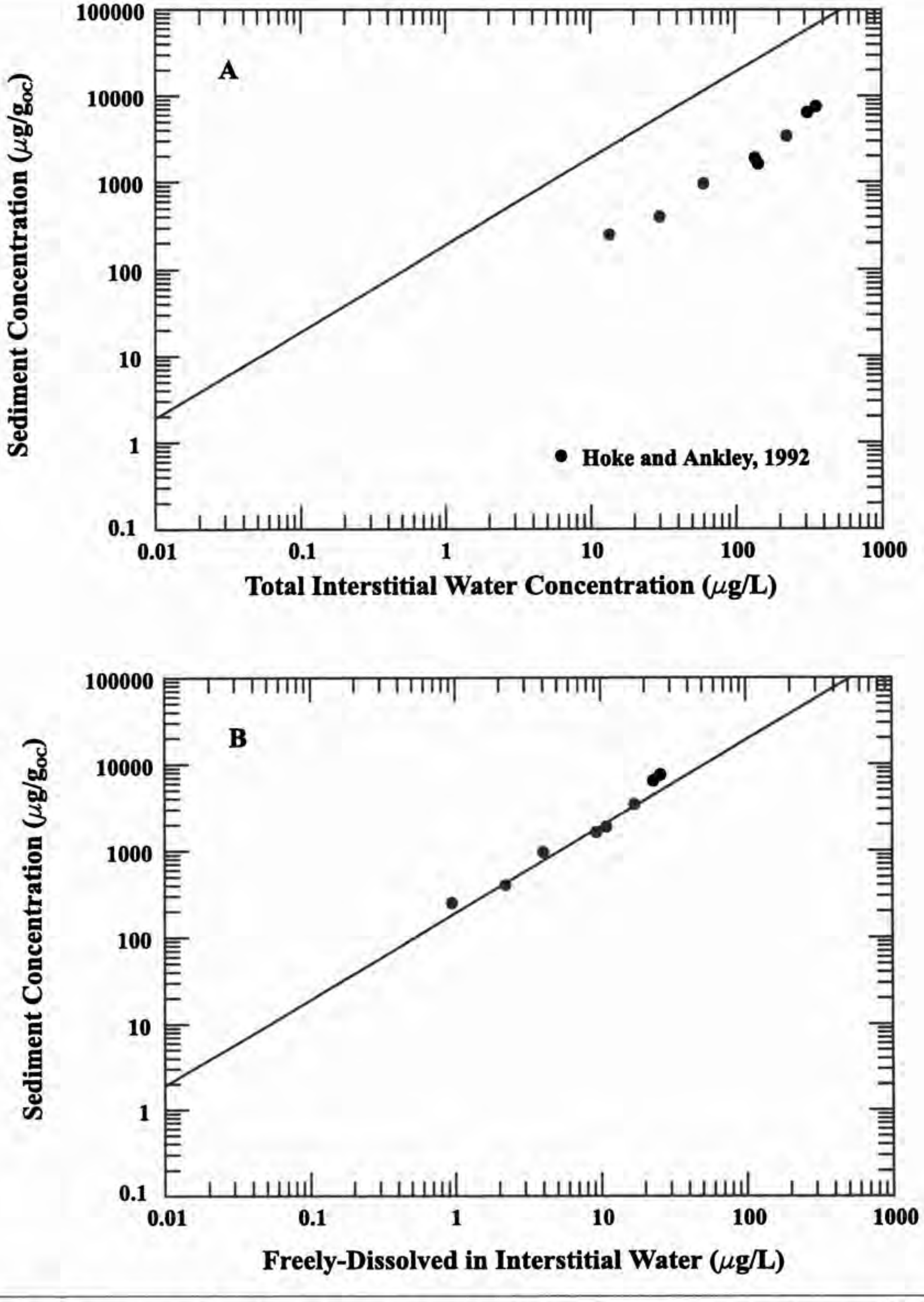

Figure 4-19. Comparison of K_{OC} observed in toxicity tests (symbols) to K_{OC} calculated using Equation 4-3 and K_{OW} values recommended by Karickhoff and Long (1995; solid line). Symbols are sediment concentration versus total (top) and freely-dissolved (bottom) interstitial water concentrations. Solid line is $C_{S,OC}=K_{OC}C_d$, where $\log_{10}K_{OC}$ is 5.28 for dieldrin.

with an organic carbon content of 1.6%. It is important to note that dieldrin has the highest K_{OC} of the five chemicals ($\log_{10}K_{OC}$ dieldrin = 5.28, acenaphthene = 3.85, endrin = 4.97, phenanthrene = 4.47, fluoranthene = 5.03). DOC complexing increases with an increasing partition coefficient, which explains why DOC complexing is significant for dieldrin.

A correlation of $\log_{10}K_{OC}$ from sediment toxicity tests to $\log_{10}K_{OC}$ calculated from selected K_{OW} is presented in Figure 4-20. The data yield a correlation coefficient of 0.843. Therefore, the calculated K_{OC} and the K_{OC} from sediment toxicity tests are in agreement.

4.6 Organic Carbon Normalization of Biological Responses

The results discussed above suggest that if a concentration-response curve correlates to interstitial water concentration, it should correlate equally well to organic carbon–normalized total chemical concentration, independent of sediment properties. This is based on the partitioning formula $C_{S,OC} = K_{OC}C_d$ (Equation 4-8), which relates the freely-dissolved concentration to the organic carbon–normalized particle concentration. This applies only to nonionic hydrophobic organic chemicals because the rationale is based on a partitioning theory for this class of chemicals.

4.6.1 *Toxicity and Bioaccumulation Experiments*

To demonstrate the relationship between organic carbon normalization and biological response concentration, concentration-response curves for the data presented in Figures 3-1 and 3-3 are used to compare results on a interstitial water–normalized and organic carbon–normalized chemical concentration basis. Figures 4-21 through 4-23 present these comparisons for kepone, DDT, endrin, and fluoranthene. The mean and 95% confidence limits of

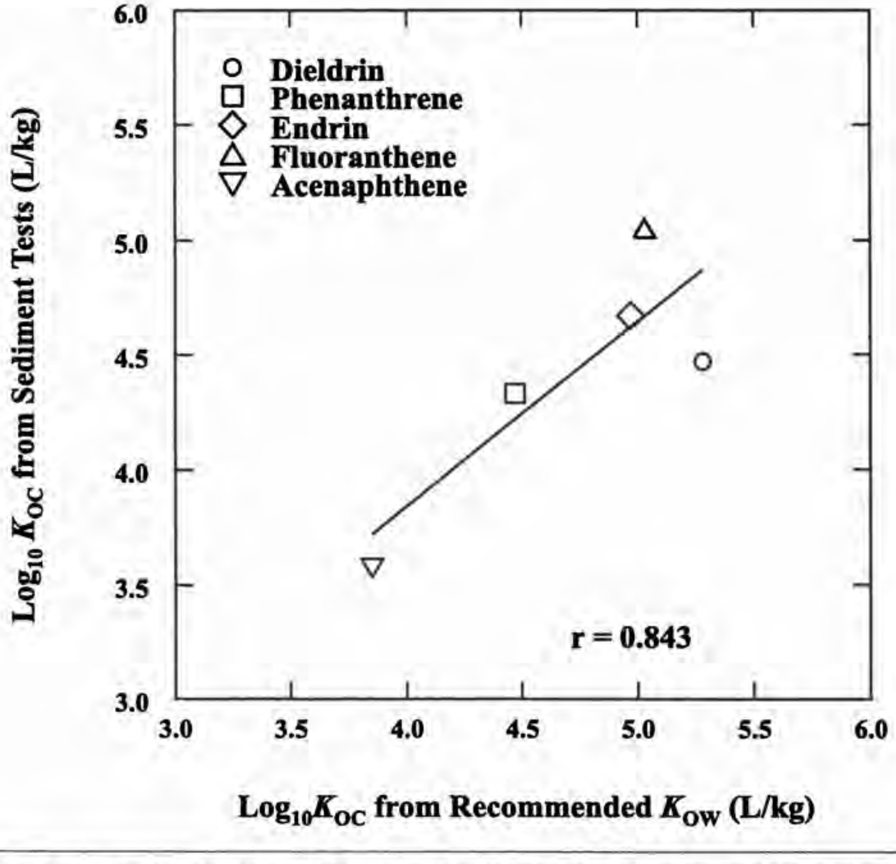

Figure 4-20. **Correlation of $\log_{10}K_{OC}$ from sediment toxicity tests to $\log_{10}K_{OC}$ estimated from EPA-recommended K_{OW} values for five chemicals.**

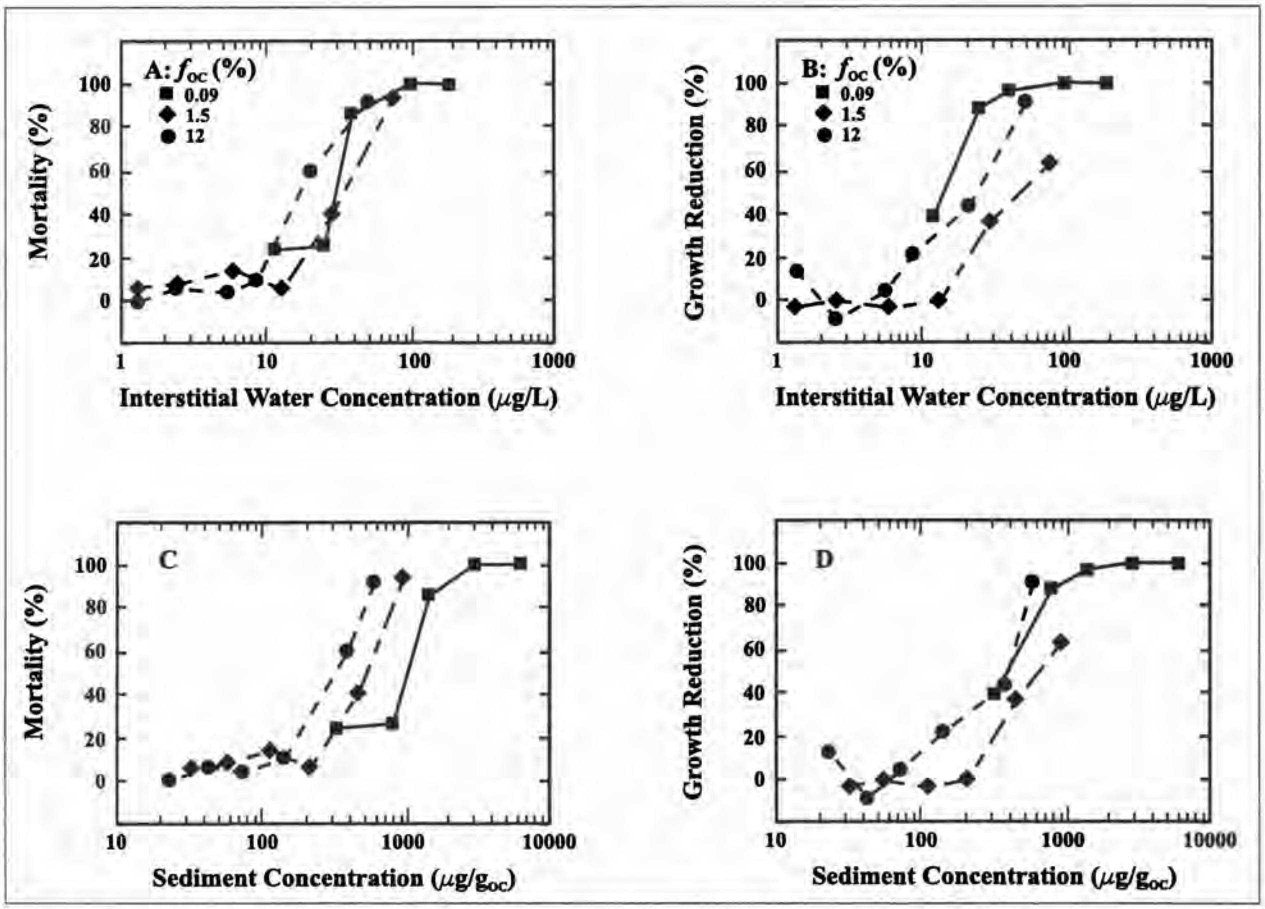

Figure 4-21. **Comparison of percent mortality (left) and growth rate reduction (right) of *C. tentans* to kepone concentrations in interstitial water (top) and in bulk sediment using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations (data from Adams et al., 1985).**

the LC50 and EC50 values for each set of data were listed in Table 3-2. The top panels repeat the response-interstitial water concentration plots shown previously in Figures 3-1 through 3-3, and the lower panels present the response versus the sediment concentration, which is organic carbon–normalized (µg chemical/g$_{OC}$).

The general impression of these data is that there is no reason to prefer interstitial water normalization over sediment organic carbon normalization. In some cases, interstitial water normalization is superior to organic carbon normalization, e.g., kepone-mortality data (Figure 4-21; left), whereas the converse sometimes occurs, e.g., kepone-growth rate (Figure 4-21; right). A more quantitative comparison can be made with the LC50 and EC50 values in Table 3-2. The variation of organic carbon–normalized LC50 and EC50 values between sediments is less than a factor of two to three and is comparable to the variation in interstitial water LC50 and EC50 values. A more comprehensive comparison was presented in Figures 2-2 and 2-3, which also examine the use of the water-only LC50 to predict the interstitial water and sediment organic carbon LC50 values.

Bioaccumulation factors calculated on the basis of organic carbon–normalized chemical concentrations are listed in Table 3-3, for permethrin, cypermethrin, and kepone. Again, the variation of organic carbon–normalized BAFs between sediments is less than a factor of two to three and is comparable to the variation in interstitial water BAFs.

4.6.2 *Bioaccumulation and Organic Carbon Normalization*

Laboratory and field data also exist for which no interstitial water or DOC measurements are available

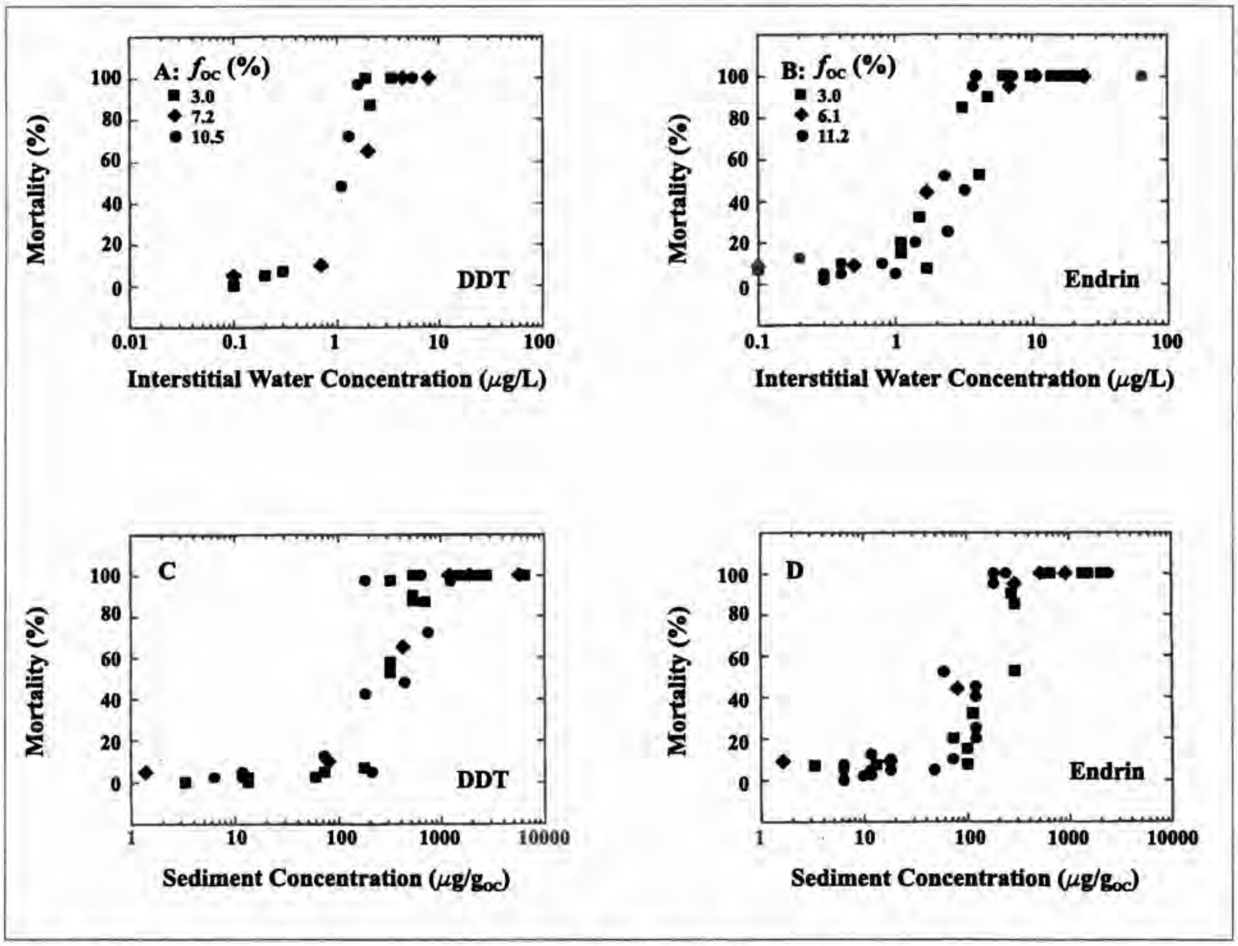

Figure 4-22. **Comparison of percent mortality of *H. azteca* with DDT (left) and endrin (right) concentrations in interstitial water (top) and in bulk sediment using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations (data from Nebeker et al., 1989; Schuytema et al., 1989).**

but for which sediment concentration, organic carbon fraction, and organism body burden have been determined. These data can be used to test organic carbon normalization for sediments and to examine organism normalization as well. It is conventional to use organism lipid fraction for this normalization (see references in Chiou, 1985). If C_b is the chemical concentration per unit wet weight of the organism, then the partitioning equation is

$$C_b = K_L f_L C_d \tag{4-24}$$

where K_L = lipid/water partition coefficient (L/kg lipid); f_L = weight fraction of lipid (kg lipid/kg organism); and C_d = freely-dissolved chemical concentration (µg/L).

The lipid-normalized organism concentration, $C_{b,L}$, is

$$C_{b,L} = \frac{C_b}{f_L} = K_L C_d \tag{4-25}$$

The lipid-normalized body burden and the organic carbon–normalized sediment concentration can be used to compute a biota-sediment accumulation factor, BSAF (Thomann et al., 1992)

$$\mathrm{BSAF} = \frac{C_{b,L}}{C_{s,oc}} = \frac{K_L}{K_{OC}} \cong \frac{K_L}{K_{OW}} \tag{4-26}$$

The second equality results from using partitioning Equations 4-8 and 4-25 and the third from the approximation that $K_{OC} \simeq K_{OW}$. The BSAF is the partition coefficient between organism lipid and sediment organic carbon. If the equilibrium assumptions are valid for both organisms and sediment particles, the BSAF should be independent of both particle and organism properties. In addition, if lipid

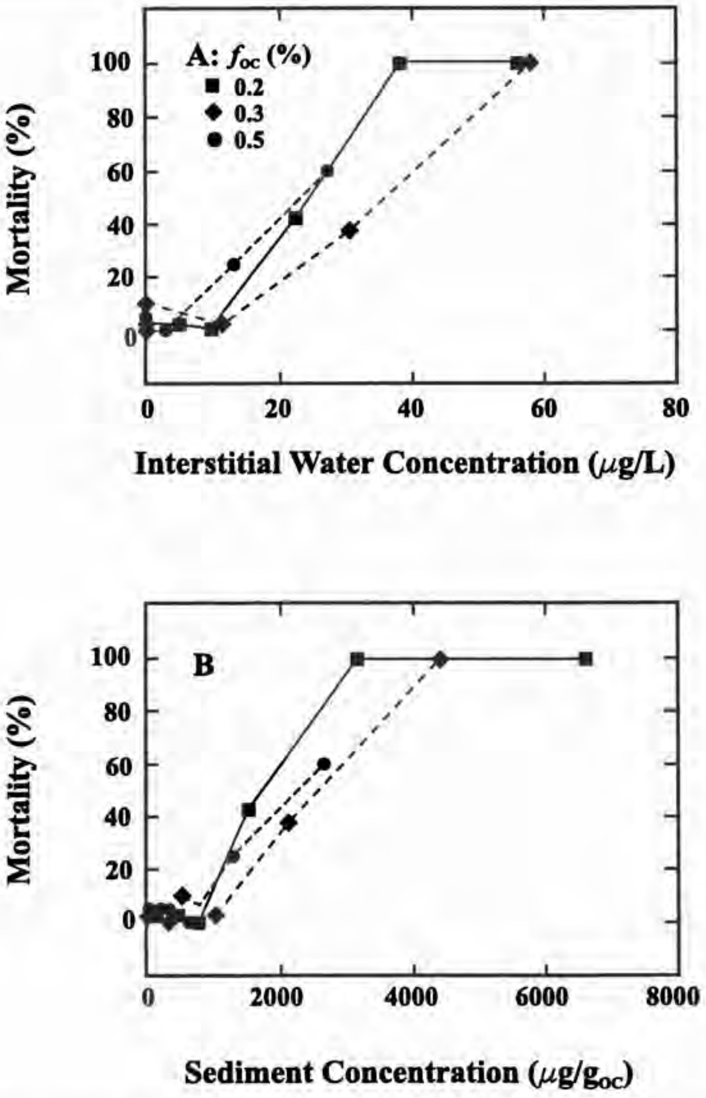

Figure 4-23. Comparison of percent mortality of *R. abronius* to fluoranthene concentrations in interstitial water (top) and bulk sediment using organic carbon normalization (bottom) for sediments with varying organic carbon concentrations (data from Swartz et al., 1990).

solubility of a chemical is proportional to its octanol solubility, $K_L \approx K_{OW}$, then the lipid-normalized, organic carbon–normalized BSAF should be a constant, independent of particles, organisms, and chemical properties (Thomann et al., 1992; McFarland, 1984; Lake et al., 1987). This result can be tested directly.

Representation of benthic organisms as passive encapsulations of lipid that equilibrate with external chemical concentrations is clearly only a first-order approximation. Biomagnification effects, which can occur via ingestion of contaminated food, and the dynamics of internal organic carbon metabolism can be included in a more comprehensive analysis (Thomann et al., 1992). It is, nevertheless, an appropriate initial assumption because deviations from the first-order representation will point to necessary refinements, and for many purposes this approximation may suffice.

A comprehensive experiment involving four benthic organisms (two species of deposit-feeding marine polychaetes, *Nereis* and *Nephtys*, and two species of deposit-feeding marine clams, *Yoldia* and *Macoma*) and five sediments was performed by

Rubinstein et al. (1988). The uptake of various PCB congeners was monitored until steady-state body burdens were reached. Sediment organic carbon and organism lipid content were measured. Figures 4-24 and 4-25 present the log mean of the replicates for the ratio of organism-to-sediment concentration for all measured congeners versus K_{OW} for each organism. Dry weight normalization for both organism and sediment (left panels), organic carbon normalization for the sediment (center panels), and both organic carbon and lipid normalization (right panels) are shown. The results for each sediment are connected by lines and separately identified. The BSAFs based on dry weight normalization (Figures 4-24A and 4-25A) are quite different for each of the sediments, with the low carbon sediment exhibiting the largest values. Organic carbon normalization (Figures 4-24B and 4-25B) markedly reduces the variability in the BSAFs from sediment to sediment. Lipid normalization usually further reduces the variability (Figures 4-24C and 4-25C). Note that the BSAFs are reasonably constant for the polychaetes (Figure 4-24), although some suppression is evident at $\log_{10}K_{ow} > 7$. The clams, however, exhibit a marked declining relationship (Figure 4-25).

Results of a similar although less extensive experiment using one sediment and oligochaete worms have been reported (Oliver, 1987). A plot of the organic carbon– and lipid-normalized BSAF versus K_{OW} from this experiment is shown on Figure 4-26, together with the averaged polychaete data (Figure 4-24). There appears to be a systematic variation with respect to K_{OW}, which suggests that the simple lipid equilibration model with a constant lipid-octanol solubility ratio is not descriptive for all chemicals. This suggests that a more detailed model of benthic organism uptake is required to describe chemical body burdens for all nonionic chemicals as a function of K_{OW} (Thomann et al., 1992). However, for a specific chemical and a specific organism, for example, *Nereis* and any PCB congener (Figure 4-24), organic carbon normalization reduces the effect of the varying sediments. This demonstrates the utility of organic carbon normalization and supports its use in generating ESGs.

A further conclusion can be reached from these results. Bierman (1990) pointed out that the lipid- and carbon-normalized BSAF is in the range of 0.1 to 10

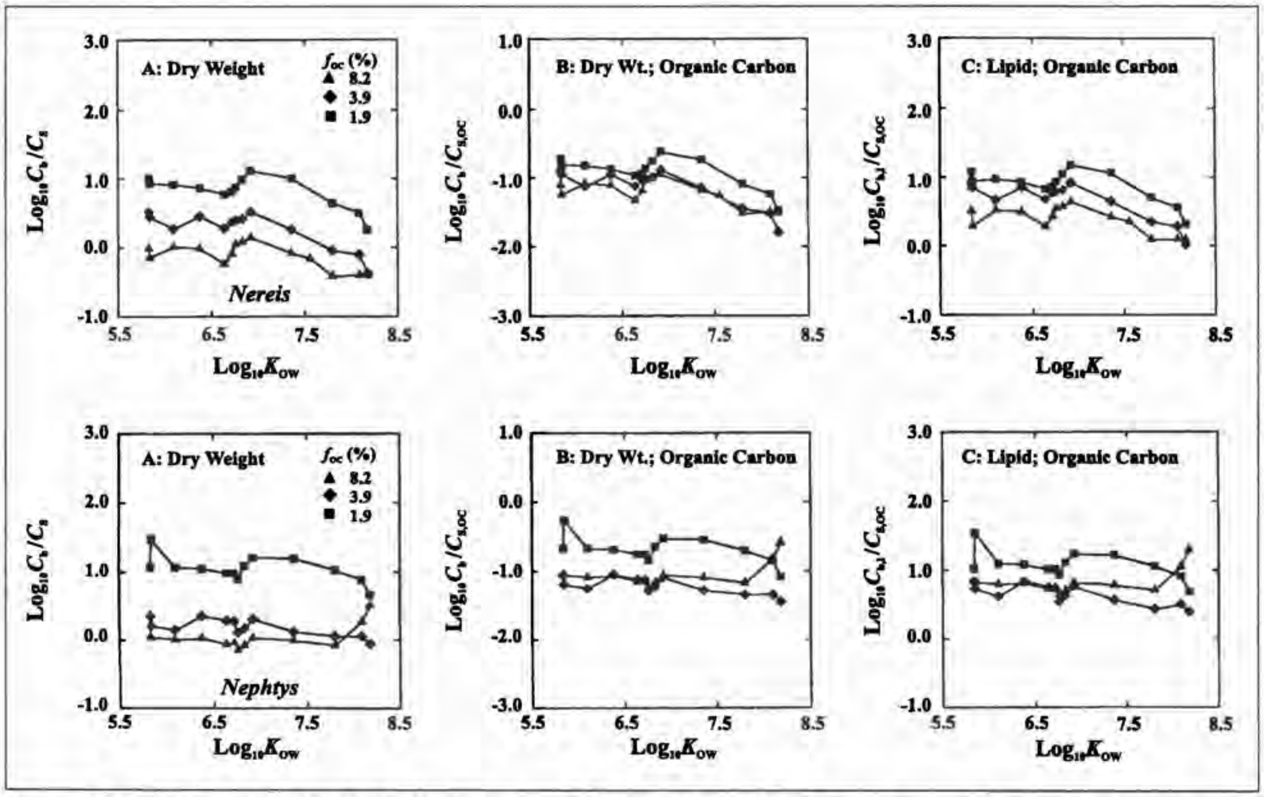

Figure 4-24. **Plots of the BSAFs for *Nereis* (top) and *Nephtys* (bottom) for three sediments for a series of PCB congeners versus the $\log_{10}K_{OW}$ for that congener: (A) dry weight–normalized for both organism and sediment, (B) organic carbon–normalized for the sediment, and (C) lipid- and organic carbon–normalized as indicated (data from Rubinstein et al., 1988).**

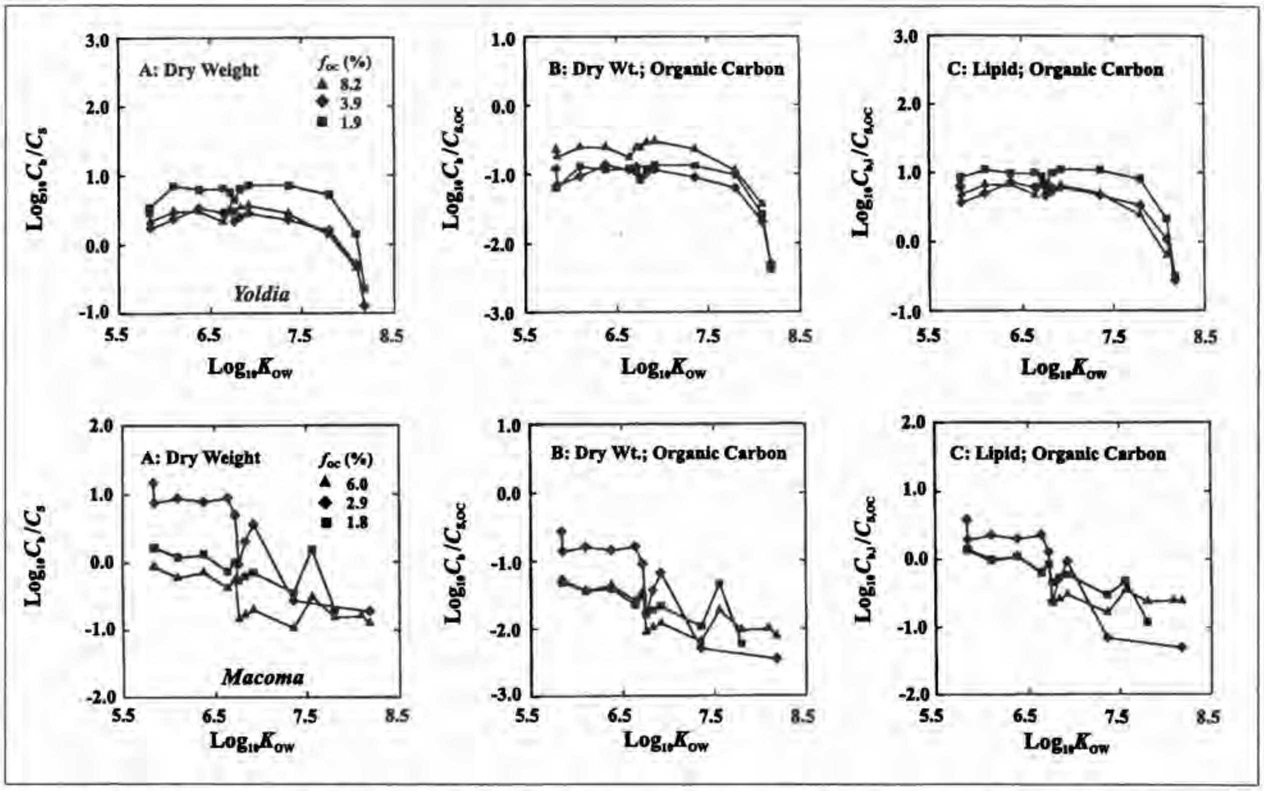

Figure 4-25. **Plots of the BSAFs for *Yoldia* (top) and *Macoma* (bottom) for three sediments for a series of PCB congeners versus the $\log_{10}K_{OW}$ for that congener: (A) dry weight–normalized for both organism and sediment; (B) organic carbon–normalized for the sediment; and (C) lipid and organic carbon–normalized as indicated (data from Rubinstein et al., 1988).**

(Figures 4-24 through 4-26), which supports the contention that the partition coefficient for sediments is $K_{OC} = K_{OW}$ and that the particle concentration effect does not appear to affect the free concentration in sediment interstitial water. The reason for this observation is that the lipid- and organic carbon–normalized BSAF is the ratio of the solubilities of the chemical in lipid and in particle carbon (Equation 4-26). Because the solubility of nonionic organic chemicals in various nonpolar solvents is similar (Leo, 1972), it would be expected that the lipid–organic carbon solubility ratio should be on the order of one. If this ratio is taken to be approximately one, then the conclusion from the BSAF data is that K_{OC} is approximately equal to K_{OW} for sediments (Bierman, 1990).

A final observation can be made. The data analyzed in this section demonstrate that organic carbon normalization accounts for much of the reported differences in bioavailability of chemicals in sediments for deposit-feeding polychaetes, oligochaetes, and clams. The data presented in previous sections are for amphipods and midges. Hence these data provide important additional support for organic carbon normalization as a determinant of bioavailability for different classes of organisms.

4.7 Determination of Route of Exposure

The exposure route by which organic chemicals are accumulated has been examined in some detail for water column organisms (e.g., by Thomann and Connolly, 1984). It might be supposed that the toxicity and bioaccumulation data presented above can be used to examine the question of the route of exposure. The initial observations were that biological effects appear to correlate to the interstitial water concentration, independent of sediment type. This has been interpreted to mean that exposure is primarily via interstitial water. However, the data correlate equally well with the organic carbon–normalized sediment concentration (see Figures 2-2 and 2-3). This observation could be taken to suggest that sediment organic carbon is the route of exposure. In fact, neither conclusion follows necessarily from these data because

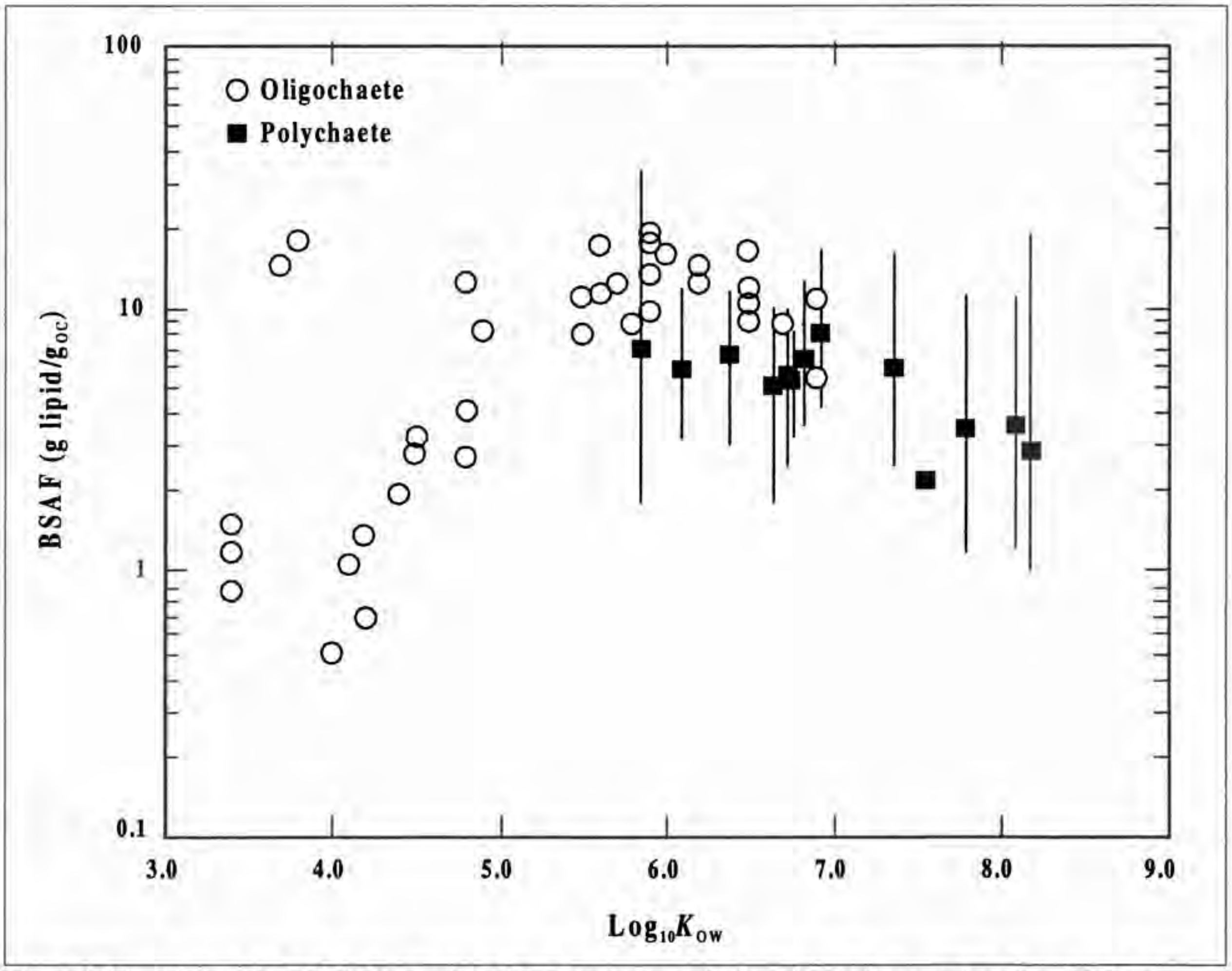

Figure 4-26. **Plots of the BSAFs for a series of PCB congeners and other chemicals versus $\log_{10}K_{OW}$. Data for oligochaetes from Oliver (1987). Data for polychaetes from Rubinstein et al. (1988).**

an alternative explanation is available that is independent of the exposure pathway.

Consider the hypothesis that the chemical potential, sometimes called fugacity (Mackay, 1979), of a chemical controls its biological activity. The chemical potential, μ_d, of the freely-dissolved concentration of chemical in interstitial water, C_d, is

$$\mu_d = \mu_O + RT \ln (C_d) \quad (4\text{-}27)$$

where μ_o is the standard state chemical potential and RT is the product of the universal gas constant and absolute temperature (Stumm and Morgan, 1970). For a chemical dissolved in organic carbon, assuming that particle organic carbon can be characterized as a homogeneous phase, its chemical potential is

$$\mu_{OC} = \mu_O + RT \ln (C_{S,OC}) \quad (4\text{-}28)$$

where $C_{S,OC}$ is the weight fraction of chemical in sediment organic carbon. If the interstitial water is in equilibrium with the sediment organic carbon, then

$$\mu_d = \mu_{OC} \quad (4\text{-}29)$$

The chemical potential that the organism experiences from either route of exposure (interstitial water or sediment) is the same. Hence, so long as the sediment is in equilibrium with the interstitial water, the route of exposure is immaterial. Equilibrium experiments cannot distinguish between different routes of exposure.

The data analysis presented above, which normalizes biological response to either interstitial water or organic carbon–normalized sediment concentration, suggests that biological effects are proportional to chemical potential or fugacity.

Section 5

Applicability of WQC as Effects Levels for Benthic Organisms

The EqP method for deriving ESGs utilizes partitioning theory to relate the sediment concentration to the equivalent freely-dissolved chemical concentration in interstitial water and in sediment organic carbon. The interstitial water concentration for ESGs should be the effects concentration for benthic species.

This section examines the validity of using EPA WQC concentrations to define the effects concentration for benthic organisms. This use of WQC assumes that (1) the sensitivities of benthic species and species tested to derive WQC, predominantly water column species, are similar; (2) the levels of protection afforded by WQC are appropriate for benthic organisms; and (3) exposures are similar regardless of feeding type or habitat. This section examines the assumption of similarity of sensitivity in two ways. First, a comparative toxicological examination is presented of the acute sensitivities of benthic and water column species using data compiled from the published and draft EPA WQC for nonionic organic chemicals as well as metals and ionic organic chemicals. Then a comparison of the FCVs and the chronic sensitivities of benthic saltwater species in a series of sediment colonization experiments is made.

5.1 Relative Acute Sensitivity of Benthic and Water Column Species

Relative acute sensitivities of benthic and water column species are examined by using LC50 values for freshwater and saltwater species from draft or published WQC documents that contain minimum database requirements for calculation of final acute values (FAVs) (Table 5-1). These datasets are selected because exposures were via water, durations were similar, and data and test conditions have been scrutinized by reviewing the original references. For each of the 2,887 tests conducted in freshwater, using 208 species with 40 chemicals, and the 1,046 tests conducted in saltwater, using 118 species with 30 chemicals, the chemical, species, life-stage, salinity, hardness, temperature, pH, acute value, and test condition (i.e., static, renewal, flow-through, nominal, or measured) were entered into a database. If necessary, original references were consulted to determine the tested life-stage and any other missing information. Each life-stage of the tested species was classified according to habitat (Table 5-2). Habitats were based on degree of association with sediment. A life-stage that occupied more than one habitat was assigned to both of the appropriate habitats.

For each chemical, if a life-stage was tested more than once or more than one life-stage was tested, data were systematically sorted in a three-step process to arrive at the acute value based on the most experimentally sound testing methodology and the most sensitive life-stages. First, if a life-stage for a species was tested more than once, flow-through tests with measured concentrations had precedence, and data from other tests were omitted. When there were no flow-through tests with measured concentrations, all acute values for that life-stage were given equal weight. If the remaining acute values for that life-stage differed by a factor greater than four, the higher values were omitted and the geometric mean of the lower acute values was calculated to derive the acute value for that life-stage. Second, life-stages were classified as either "benthic" (infaunal species [habitats 1 and 2] or infaunal and epibenthic species [habitats 1, 2, 3, and 4]) or "water column" (habitats 5 to 8) (Table 5-2). Third, if two or more life-stages were classified as either benthic or water column and their acute values differed by a factor of four, the higher values were omitted and the geometric mean of the lower acute values was calculated to derive the acute value for that life-stage of the benthic or water column species. This procedure is similar to that used for WQC (Stephan et al., 1985).

5.2 Comparison of Sensitivity of Benthic and Water Column Species

5.2.1 *Most Sensitive Species*

The relative acute sensitivities of the most sensitive benthic and water column species were

Table 5-1. **Draft or published WQC documents and number of infaunal (habitats 1 and 2), epibenthic (habitats 3 and 4), and water column (habitats 5 to 8) species tested acutely for each substance**

		Number of Saltwater Species				Number of Freshwater Species			
Chemical	Date of Publication	Total[a]	Infaunal	Epibenthic	Water Column	Total[a]	Infaunal	Epibenthic	Water Column
Acenaphthene	9/87[b]	—	—	—	—	10	—	3	7
Acrolein	9/87[b]	—	—	—	—	12	1	5	7
Aldrin	1980	16	0	11	12	21	2	10	15
Aluminum	1988	—	—	—	—	15	—	5	11
Ammonia	1985; 1989	20	2	7	16	48	2	17	33
Antimony (III)	9/87[b]	11	3	6	5	9	1	2	6
Arsenic (III)	1985	12	2	3	8	16	1	6	13
Cadmium	1985	38	10	18	18	56	13	16	31
Chlordane	1980	8	1	7	7	14	1	4	10
Chloride	1988	—	—	—	—	15	3	6	8
Chlorine	1985	23	2	9	15	33	1	9	26
Chlorpyrifos	1986	15	2	8	10	18	2	8	11
Chromium (III)	1985	—	—	—	—	17	3	8	12
Chromium (VI)	1985	23	8	9	9	33	1	10	21
Copper	1985	25	6	5	18	57	8	15	36
Cyanide	1985	9	1	4	5	17	1	6	12
DDT	1980	17	1	11	12	42	3	15	29
Dieldrin	1980	21	1	15	15	19	1	9	12
2,4-Dimethylphenol	6/88[b]	9	2	2	6	12	1	3	7
Endosulfan	1980	12	2	8	8	10	1	4	7
Endrin	1980	21	1	14	16	28	3	12	17
Heptachlor	1980	19	1	14	13	18	2	8	12
Hexachlorocy-clohexane	1980	19	2	14	12	22	1	4	18
Lead	1985	13	2	3	10	14	—	4	11
Mercury	1985	33	10	7	18	30	11	8	12
Nickel	1986	23	7	10	9	21	2	7	13
Parathion	1986	—	—	—	—	37	7	14	23
Parathion, Methyl	10/88[b]	—	—	—	—	36	1	9	25
Pentachlorophenol	1986	19	7	7	11	41	9	11	23
Phenanthrene	9/87[b]	10	4	6	4	9	2	1	6

Table 5-1. **Draft or published WQC documents and number of infaunal (habitats 1 and 2), epibenthic (habitats 3 and 4), and water column (habitats 5 to 8) species tested acutely for each substance (continued)**

		Number of Saltwater Species				Number of Freshwater Species			
Chemical	Date of Publication	Total[a]	Infaunal	Epibenthic	Water Column	Total[a]	Infaunal	Epibenthic	Water Column
Phenol	5/88[b]	—	—	—	—	32	6	9	20
Selenium (IV)	1987	16	1	5	13	23	2	6	19
Selenium (VI)	1987	—	—	—	—	12	1	4	10
Silver	9/87[b]	21	1	6	16	19	1	9	13
Thallium	11/88[b]	—	—	—	—	8	1	3	3
Toxaphene	1986	15	2	9	11	37	5	13	23
Tributyltin	9/87	19	1	8	15	9	1	1	6
1,2,4-Trichlorobenzene	9/88[b]	15	7	7	4	14	2	5	7
2,4,5-Trichlorophenol	9/87[b]	11	4	5	5	10	1	2	8
Zinc	1987	33	10	9	17	45	5	12	30

[a] The total numbers of tested species may not be the same as the sum of the number of species from each habitat type because a species may occupy more than one habitat.

[b] Aquatic life criteria document, U.S. Environmental Protection Agency, Office of Science & Technology, Health and Ecological Criteria Division, Washington, DC.

Table 5-2. **Habitat classification system for life-stages of organisms**

Habitat Type	Description
1	Life-stages that usually live in the sediment and whose food consists mostly of sediment or organisms living in the sediment: infaunal nonfilter feeders
2	Life-stages that usually live in the sediment and whose food consists mostly of plankton and/or suspended organic matter filtered from the water column: infaunal filter feeders
3	Life-stages that usually live on the surface of sediment and whose food consists mostly of organic matter in sediments and/or organisms living in or on the sediment: epibenthic bottom feeders
4	Life-stages that usually live on the surface of sediment and whose food is mostly from the water column, including suspended detritus, plankton, and larger prey: epibenthic water column feeders
5	Life-stages that usually live in the water column and whose food consists mostly of organisms that live on or in the sediment
6	Life-stages that usually live in and obtain their food from the water column but have slight interaction with sediment because they occasionally rest or sit on the sediment and/or occasionally consume organisms that live in or on the sediment
7	Life-stages that live in or on such inorganic substrates as sand, rock, and gravel, but have negligible contact with sediment containing organic carbon
8	Life-stages that have negligible interactions with sediment because they spend essentially all their time in the water column and rarely consume organisms in direct contact with the sediment; e.g., fouling organisms on pilings or ships and zooplankton, pelagic fish.

examined by comparing the FAVs for benthic and water column organisms from databases having eight or more acute values. These FAVs were derived from the acute LC50 concentrations from the 40 freshwater and the 30 saltwater WQC documents. When benthic species were defined as only infaunal organisms (habitat types 1 and 2) and water column species were defined as all others (habitat types 3 to 8), the water column species were typically the most sensitive. The results are cross-plotted on Figure 5-1A. The line represents perfect agreement.

Data on the sensitivities of benthic infaunal species are limited. Of the 40 chemicals for which published and draft WQC for freshwater organisms are available, 2 or fewer infaunal species were tested with 28 (70%) of the chemicals, and 5 or fewer species were tested with 34 (85%) of the chemicals. Of the 30 chemicals for which WQC for saltwater organisms are available, 2 or fewer infaunal species were tested with 19 (63%) of the chemicals, and 5 or fewer species were tested with 23 (77%) of the chemicals. Of these chemicals only zinc in saltwater has been tested using infaunal species from three or more phyla and eight or more families, the minimum acute toxicity database required for criteria derivation. As a result, FAVs could not be computed for several of the chemicals. Therefore, it is probably premature to conclude from the existing data that infaunal species are more tolerant than water column species.

A similar examination of the FAVs calculated for benthic and water column species, where the definition of benthic includes both infaunal and epibenthic species (habitat types 1 to 4), is based on more data and suggests a similarity in sensitivity (Figure 5-1B). In this comparison, the number of acute values for freshwater benthic species for each chemical averaged 9, with a range of 2 to 27; the number of acute values for saltwater benthic species for each chemical substance averaged 11, with a range of 4 to 26. The variability of these data is high, suggesting that for some chemicals, benthic and water column species may differ in sensitivity and that additional testing is desirable, or that this approach to examining species sensitivity is not sufficiently rigorous.

Examination of individual criteria documents in which benthic species were markedly less sensitive than water column species suggests that the major factor for this difference is that benthic species phylogenetically related to sensitive water column species have not been tested. Apparent differences in sensitivity, therefore, may reflect an absence of appropriate data. Data that are available suggest that, on the average, benthic and water column species are similarly sensitive and support the use of WQC to derive ESGs for the protection of infaunal and epibenthic species.

5.2.2 *All Species*

A more general comparison of the species sensitivities can be made if all the LC50 data are used. One approach examines the relative location of benthic species in the overall species sensitivity distribution. For each chemical in either fresh- or saltwater, one can examine the distribution of benthic species in a rank-ordering of all the species' LC50 values. If benthic species were relatively insensitive, then they would predominate in ranking among the higher LC50 concentrations. Equal sensitivity would be indicated by a uniform distribution of species within the overall ranking. Figure 5-2 presents the results for tests of nickel in saltwater. The LC50 values are plotted in rank order, and the benthic species are indicated. Infaunal species are among the most tolerant (Figure 5-2A), whereas infaunal and epibenthic species are uniformly distributed among the species (Figure 5-2B).

This comparison can be done chemical by chemical. However, to make the analysis more robust, the data for each chemical-water type can be normalized to zero log mean and unit log variance as follows

$$\mathrm{LC50}_{\mathrm{n,ij}} = \frac{\log(\mathrm{LC50}_{\mathrm{ij}}) - \mu_{\mathrm{i}}}{\sigma_{\mathrm{i}}} \qquad (5\text{-}1)$$

where i indexes the chemical-water type, μ_i is the log mean, and σ_i is the log standard deviation; j indexes the LC50 values within the ith class; and $\mathrm{LC50}_{\mathrm{n,ij}}$ is the normalized LC50. This places all the LC50 values from each set of chemical-water type on the same footing. Thus, the data can now be combined and the uniformity of representation of benthic species can be examined in the combined dataset.

The comparison is made in Figure 5-3. If the sensitivity of benthic species is not unique, then a constant percentage of benthic species–normalized LC50 values, indicated by the dashed line, should be represented in each 10-percentile (decile) interval of data for all species. That is, the 10 rectangles in each histogram should be identical in height. The infaunal species (Figure 5-3A and B) display a tendency to be

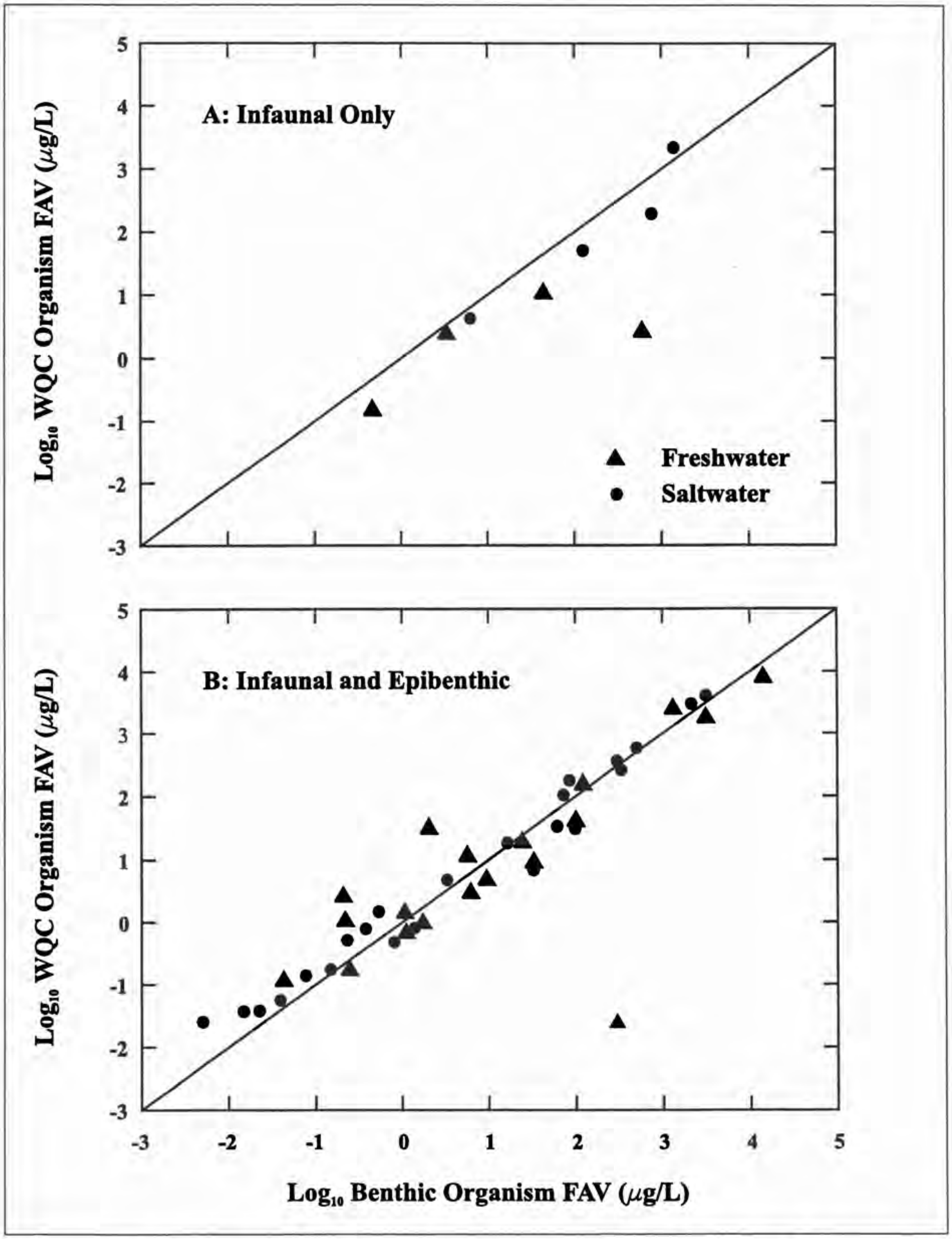

Figure 5-1. Comparison of the FAVs for water column versus benthic organisms for chemicals listed on Table 5-1. Benthic species are defined as (A) infaunal species (habitat types 1 and 2) or (B) infaunal and epibenthic species (habitat types 1–4). See Table 5-2 for habitat definitions.

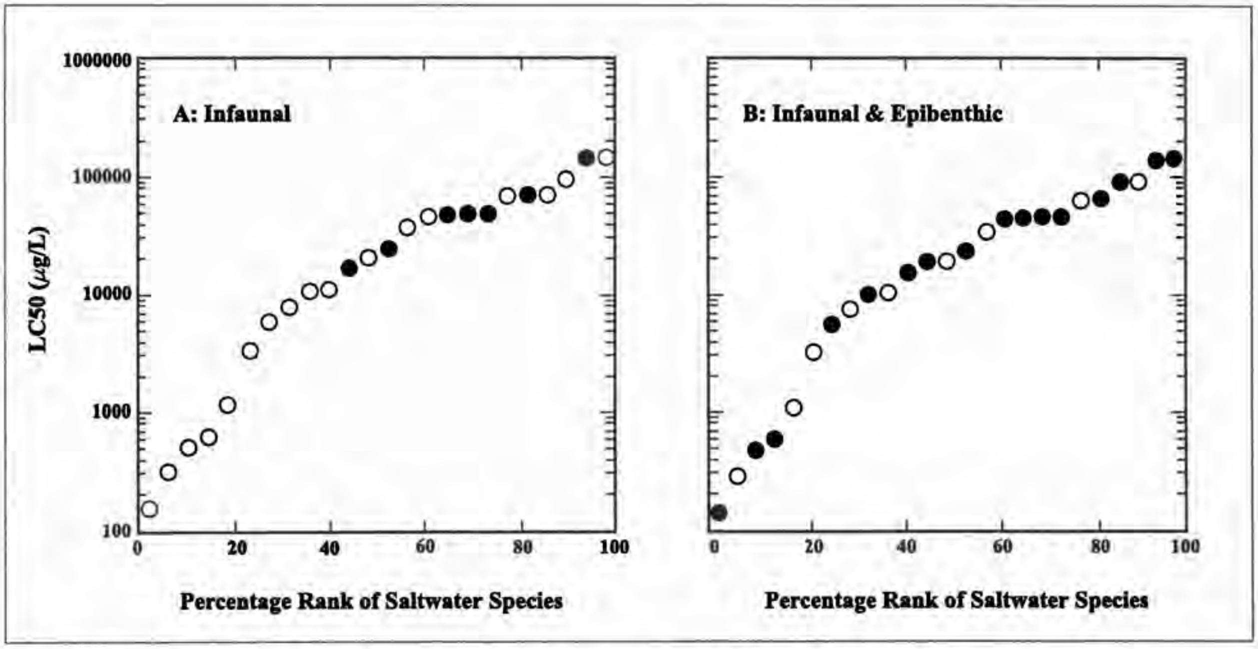

Figure 5-2. LC50 values versus percentage rank sensitivities for nickel in saltwater species. The closed symbols identify (A) infaunal and (B) infaunal and epibenthic organisms (figure from Di Toro et al., 1991). The open symbols identify water column organisms.

underrepresented in the lowest deciles. However, the infaunal and epibenthic species (Figure 5-3C and D) more closely follow this idealized distribution. Infaunal and epibenthic freshwater species are nearly uniformly distributed, whereas the saltwater benthic species are somewhat underrepresented in the lowest ranks.

Given the limitations of these data, they appear to indicate that, except for possibly freshwater infaunal species, benthic species are not uniquely sensitive or insensitive and that ESGs derived by using the FCV should protect benthic species.

5.3 Relating Acute to Chronic Sensitivities for Benthic Organisms

Thus far, comparisons of overall species sensitivities and benthic species sensitivities have used acute test results. Acute–chronic ratios (ACRs) extracted from draft or published EPA criteria documents (see Table 5-1) will be used to relate acute to chronic sensitivities for benthic species. The dataset of ACRs is made up of 295 data points of which 83 represent benthic organisms. A test of applying the idea of similar sensitivities, as indicated by analyses of acute data, to chronic sensitivities would be to determine if the distributions of ACRs for all species and for benthic species are similar.

If ACRs for benthic species were dissimilar, either much higher or much lower, then this would indicate that the relationship of acute to chronic toxicity is anomalous for benthic organisms. That is, the benthic organisms could be construed to be either more or less sensitive than the overall set of test species. However, similar distributions would indicate that sensitivity for benthic species is similar to overall species sensitivity. Rank distributions of ACRs for all species (open symbols) and ACRs for benthic species (closed symbols) are shown in Figure 5-4. Similarity of the distributions indicates that overall species sensitivity and benthic species sensitivity are the same for chronic data. This supports the use of the FCV in computing ESG.

5.4 Benthic Community Colonization Experiments

Toxicity tests that determine the effects of chemicals on the colonization of communities of benthic saltwater species (Hansen, 1974; Tagatz, 1977; Hansen and Tagatz, 1980; Tagatz and Ivey, 1981; Tagatz et al., 1982, 1983) appear particularly sensitive for measuring the impacts of chemicals on benthic organisms. This is probably because the experiment exposes the most sensitive life-stages of a wide variety of benthic saltwater species, and they are exposed for a

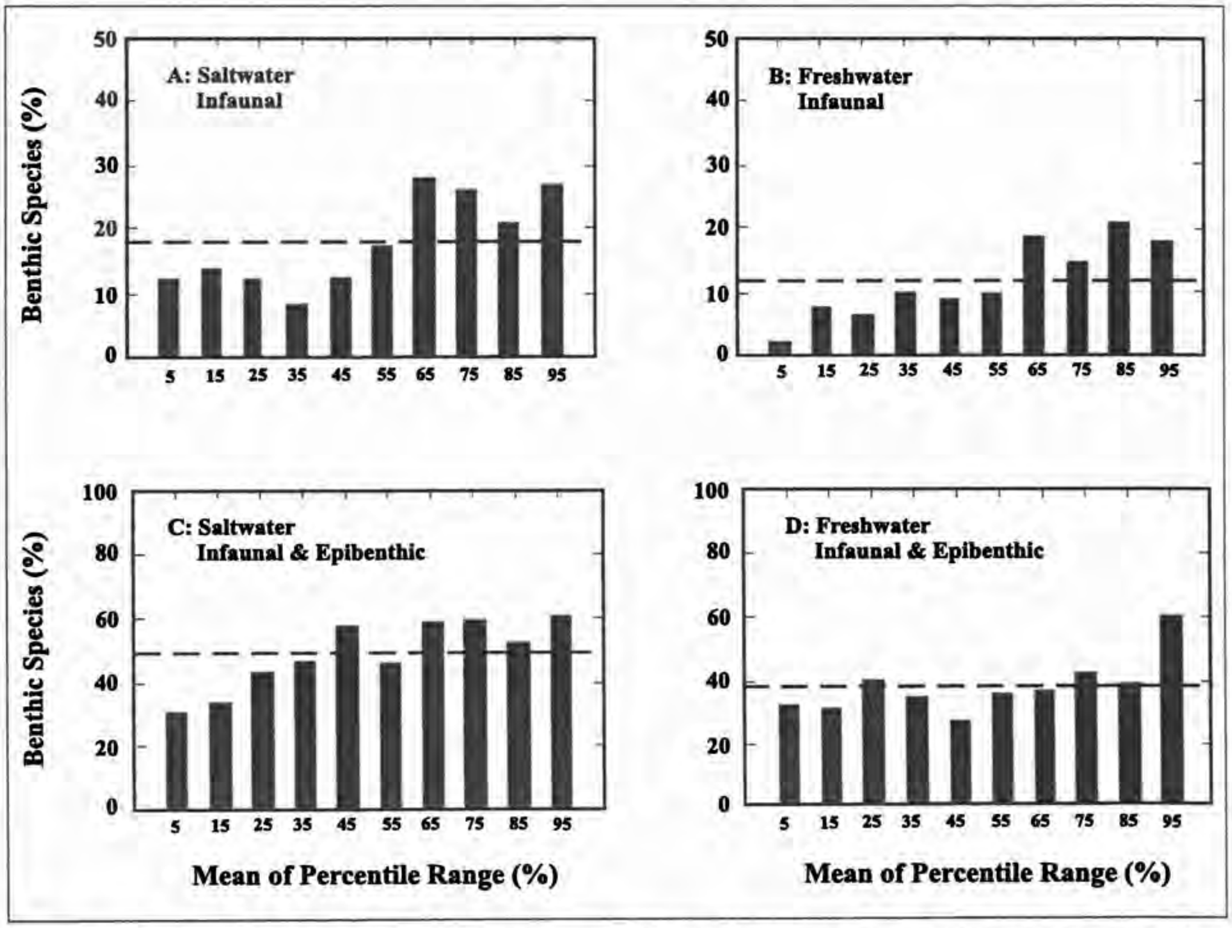

Figure 5-3. **Proportion of saltwater (left) and freshwater (right) benthic organisms in 10 percentile groups of all normalized LC50 values for infaunal (top) and infaunal and epibenthic (bottom) organisms as benthic. The dashed lines indicate the average sensitivities of the overall percentage of benthic species in the dataset.**

sufficient duration to maximize response. The test typically includes 3 concentrations of a chemical and a control, each with 6 to 10 replicates. The test chemical is added to inflowing ambient seawater containing planktonic larvae and other life-stages of marine organisms that can settle on clean sand in each replicate aquarium. The test typically lasts 2 to 4 months, and the numbers of species and individuals in aquaria receiving the chemical are enumerated and compared with controls.

If this test is extremely sensitive and if concentrations in interstitial water, overlying water, and the sediment particles reach equilibrium, then the effect and no-effect concentrations from this test can be compared with the FCV from the saltwater WQC documents to examine the applicability of WQC to protect benthic organisms. An FCV is the concentration, derived from acute and chronic toxicity data, that is predicted to protect 95% of the tested organisms from chronic effects of a chemical (Stephan et al., 1985). In addition, similarities in sensitivities of taxa tested as individual species and in the colonization experiment can indicate whether the conclusion of similarity of sensitivities of benthic and water column species is reasonable.

The benthic colonization experiment is consistent with the assumptions used to derive ESGs. The initially clean sandy sediment will rapidly equilibrate with the inflowing overlying water chemical concentration as the interstitial water concentrations reach the overlying water concentration. The production of sedimentary organic matter should be slow enough to permit its equilibration as well. As a consequence, the organisms will be exposed to an equilibrium system with a unique chemical potential. Thus, the assumption of the EqP is met by this design.

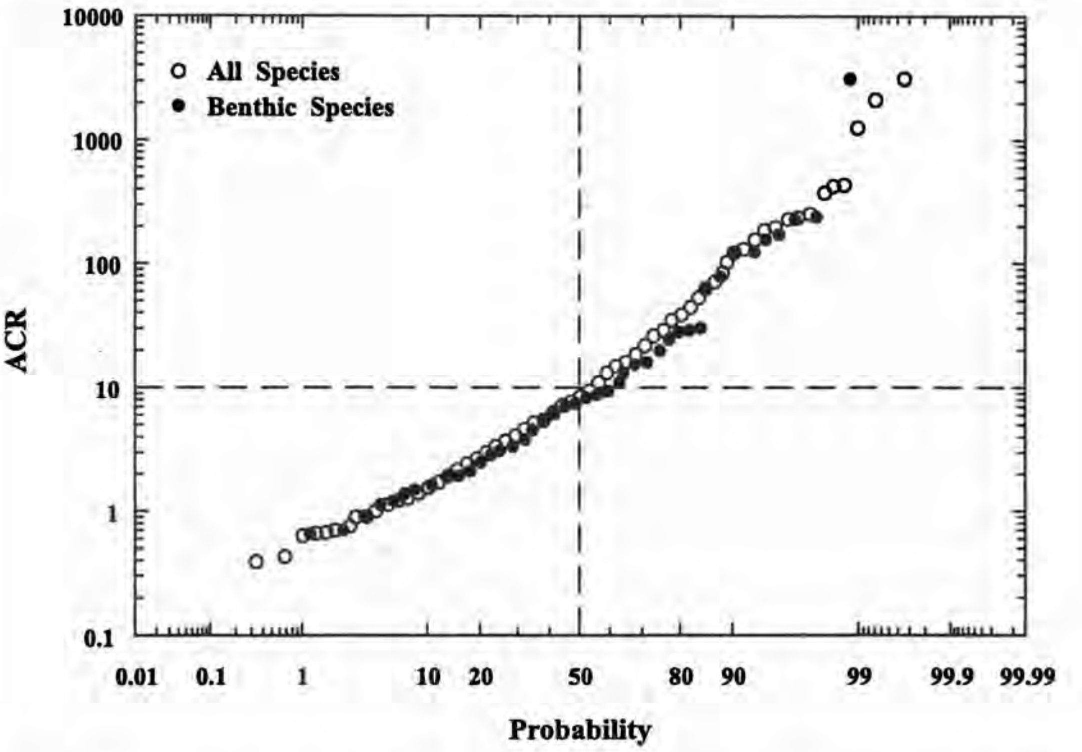

Figure 5-4. **Distribution of acute-chronic ratios showing all species (○) and benthic species only (●) (species from Table 5-1).**

In addition, the experimental design guarantees that the interstitial water–sediment–overlying water is at the chemical potential of the overlying water. Hence there is a direct correspondence between the exposure in the colonization experiment and the water-only exposures from which WQC are derived, namely, the overlying water chemical concentration. This allows a direct comparison.

5.5 WQC Concentrations Versus Colonization Experiments

Comparison of the concentrations of six chemicals that had the lowest-observable-effect concentration (LOEC) and the no-observable-effect concentration (NOEC) on benthic colonization with the FCVs either published in saltwater portions of WQC documents or estimated from available toxicity data (Table 5-3) suggests that the level of protection afforded by WQC to benthic organisms is appropriate. The FCV should be lower than the LOEC and larger than the NOEC. The FCV from the WQC document for pentachlorophenol of 7.9 μg/L is less than the LOEC for colonization of 16.0 μg/L. The NOEC of 7.0 μg/L is less than the FCV. Although no FCV is available for Aroclor 1254, the lowest concentration causing no effects on the sheepshead minnow (*Cyprinodon variegatus*) and pink shrimp (*Penaeus duorarum*) as cited in the WQC document is about 0.1 μg/L. This concentration is less than the LOEC of 0.6 μg/L and is the same as the NOEC of 0.1 μg/L based on a nominal concentration in a colonization experiment. The lowest concentration tested with chlorpyrifos (0.1 μg/L) and fenvalerate (0.01 μg/L) affected colonization of benthic species. Both values are greater than either the FCV estimated for chlorpyrifos (0.005 μg/L) or the FCV estimated from acute and chronic effects data for fenvalerate (0.002 μg/L). The draft WQC document for 1,2,4-trichlorobenzene suggests that the FCV should be 50.0 μg/L. This value is slightly above the LOEC from a colonization experiment (40.0 μg/L) suggesting that the criterion might be somewhat underprotective for benthic species. Finally, a colonization experiment with toxaphene provides the only evidence from these

Table 5-3. Comparison of WQC FCVs and concentrations affecting (LOEC) and not affecting (NOEC) benthic colonization

Substance	Colonization vs. FCV[a]	Concentration (μg/L)	Sensitive Taxa	References
Pentachlorophenol	Colonization LOEC[a]	16.0	Molluscs, abundance	Tagatz, 1977; Tagatz et al., 1983
	FCV	7.9	Molluscs, crustacea, fish	
	Colonization NOEC	7.0	—	
Aroclor 1254	Colonization LOEC	0.6	Crustacea	Hansen, 1974
	Estimated FCV	~0.1	Crustacea, fish	Hansen and Tagatz, 1980
	Colonization NOEC	0.1	—	
Chlorpyrifos	Colonization LOEC	0.1	Crustacea, molluscs, species richness	Tagatz et al., 1982
	Estimated FCV	0.005	Crustacea	
	Colonization NOEC	—	—	
Fenvalerate	Colonization LOEC	0.01	Crustacea, chordates	Tagatz and Ivey, 1981
	Estimated FCV	~0.002	Crustacea	
	Colonization NOEC	—	—	
1,2,4-Trichlorobenzene[a]	Estimated FCV	50	Crustacea, fish	Tagatz et al., 1985
	Colonization LOEC	40	Molluscs, abundance	
	Colonization NOEC	—	—	
Toxaphene	Colonization LOEC	11.0	Crustacea, species richness	Hansen and Tagatz, 1980
	Colonization NOEC	0.8	—	
	FCV	0.2	Crustacea, fish	

[a] Six-day exposure to established benthic community.

tests that the FCV might be overprotective for benthic species; the FCV is 0.2 μg/L versus the NOEC for colonization of 0.8 μg/L. The taxa most sensitive to chemicals, as indicated by their LC50s and the results of colonization experiments, are generally similar, although, as might be expected, differences occur. Both the WQC documents and the colonization experiments suggest that crustacea are most sensitive to Aroclor 1254, chlorpyrifos, fenvalerate, and toxaphene. Colonization experiments indicated that molluscs are particularly sensitive to three chemicals, an observation noted only for pentachlorophenol in WQC documents. Fish, which are not tested in colonization experiments, are particularly sensitive to four of the six chemicals.

5.6 Conclusions

Comparative toxicological data on the acute and chronic sensitivities of freshwater and saltwater benthic species in the ambient WQC documents are limited. Acute values are available for only 34 freshwater infaunal species from 4 phyla and only 28 saltwater infaunal species from 5 phyla. Only 7 freshwater infaunal species and 24 freshwater epibenthic species have been tested with 5 or more of the 40 WQC chemicals. Similarly, 9 saltwater infaunal species and 20 epibenthic species have been tested with 5 or more of the 30 substances for which saltwater criteria are available.

In spite of the paucity of acute toxicity data on benthic species, available data suggest that benthic species are not uniquely sensitive and that ESGs can be derived from WQC. The data suggest that the most sensitive infaunal species are typically less sensitive than the most sensitive water column (epibenthic and water column) species. When both infaunal and epibenthic species are classed as benthic, the sensitivities of benthic and water column species are similar, on average. Frequency distributions of the sensitivities of all species to all chemicals indicate that infaunal species may be relatively insensitive but that infaunal and epibenthic species appear almost evenly distributed among both sensitive and insensitive species overall. Distributions of ACRs indicate that chronic sensitivities of benthic organisms are similar to chronic sensitivities of all species.

Finally, in experiments to determine the effects of chemicals on colonization of benthic saltwater organisms, concentrations affecting colonization were generally greater, and concentrations not affecting colonization were generally lower than estimated or actual saltwater WQC FCVs.

Section 6

Generation of ESG

6.1 Parameter Values

The equation from which ESGs are calculated is

$$ESG_{OC} = K_{OC} FCV \quad (6\text{–}1)$$

(see Equations 2-2 to 2-7 and associated text). Hence, the ESG concentration depends only on these two parameters. The K_{OC} of the chemical is calculated from the K_{OW} of the chemical via the regression Equation 4-3. Reliability of ESG_{OC} depends directly on reliability of K_{OW}. For most chemicals of interest, the available K_{OW} values (e.g., Leo and Hansch, 1986) are highly variable; a range of two orders of magnitude is not unusual. Therefore, the measurement methods and/or estimation methodologies used to obtain each estimate must be critically evaluated to ensure their validity. The technology for measuring K_{OW} has improved in recent years. For example, the generator column method (Woodburn et al., 1984) and the slow stirring method (Tagatz and Ivey, 1981) appear to give comparable results, whereas earlier methods produced more variable results. Hence, it is recommended that literature values for K_{OW} not be used unless they have been measured using the newer techniques.

6.2 Selection of K_{OW}

The K_{OW} is defined as the ratio of the equilibrium concentrations of a dissolved substance in a system consisting of n-octanol and water and is ideally dependent only on temperature and pressure

$$K_{OW} = C_{OCT}/C_W \quad (6\text{-}2)$$

where C_{OCT} is the concentration of the substance in n-octanol and C_w is the concentration of the substance in water. The K_{OW} is frequently reported in the form of its logarithm to base 10 as log P.

The EPA Ecosystems Research Division at Athens, GA, has established a protocol for recommending the best K_{OW} value (U.S. EPA, 1996). The protocol includes assembling and evaluating all experimental and calculated data. Using this protocol, Karickoff and Long (1995) recommend $\log_{10}K_{OW}$ values for several chemicals. These recommended $\log_{10}K_{OW}$ values were used to compute $\log_{10}K_{OC}$ for five chemicals (Table 6-1).

6.2.1 K_{OC} *Determination*

The previous section discusses selecting the method for measuring K_{OW} for use in computing ESGs. It is widely accepted that K_{OC} can be estimated from K_{OW}. The K_{OC} used to calculate the ESGs is based on the regression of $\log_{10}K_{OC}$ to $\log_{10}K_{OW}$, Equation 4-3. Computed $\log_{10}K_{OC}$ values are given in Table 6-1. This equation is based on an analysis of an extensive body of experimental data for a wide range of compound types and experimental conditions, thus encompassing a wide range of K_{OW} and f_{OC} values (Di Toro, 1985).

Sediment toxicity tests provide a favorable environment for measuring K_{OW}. Figures 4-18 and 4-19 presented plots of the organic carbon–normalized sorption isotherm from sediment toxicity tests for the five chemicals where the sediment concentration ($\mu g/g_{OC}$) is plotted versus interstitial water

Table 6-1. Recommended $\log_{10}K_{OW}$ and their corresponding $\log_{10}K_{OC}$ values for five chemicals

Chemical	$\text{Log}_{10}K_{OW}$	$\text{Log}_{10}K_{OC}$ [a]
Endrin	5.06	4.97
Dieldrin	5.37	5.28
Acenaphthene	3.92	3.85
Phenanthrene	4.55	4.47
Fluoranthene	5.12	5.03

[a] $\text{Log}_{10}K_{OC}$ calculated using Equation 4-3.

concentration (μg/L). Also included in each panel is the line to the partition, Equation 4-8, where K_{OC} is computed from the recommended K_{OW} values. These plots can be used to compare the K_{OC} computed from the recommended K_{OW} and the regression equation with the partitioning behavior of the chemical in the sediment toxicity tests. For each of the chemicals, the K_{OC} line is in agreement with the data demonstrating the validity of the use of the recommended K_{OW} in the ESG computation.

6.3 Species Sensitivity

The FCV is used as the endpoint for the protection of benthic organisms. Although previous work has indicated that the FCV is applicable for all criteria chemicals, this assumption should be verified for each chemical. To test this assumption for a particular chemical, a statistical method known as the approximate randomization (AR) method (Noreen, 1989) can be used. The idea is to test whether the difference between the FAV derived from considering only benthic organisms is statistically different from the FAV contained in the WQC document.

The AR method tests the significance level of the test statistic by comparing it with the distribution of statistics generated from many random reorderings of the LC50 values from WQC documents. For example, the test statistic in this case is the difference between the FAV, computed from the WQC LC50 values, and the benthic FAV, computed from the benthic organism LC50 values. Note that the benthic organism LC50 values are a subset of the WQC LC50 values. In the AR method for this test, the number of data points coinciding with the number of benthic organisms is selected from the WQC dataset. A "benthic" FAV is computed. The original WQC FAV and the "benthic" FAV are then used to compute the difference statistics. This is done many times and the resulting distribution is representative of the population of FAV difference statistics. The test statistic is compared with this distribution to determine its level of significance.

For each chemical, an initial test of the difference between the freshwater and saltwater FAVs for all species (benthic and water column species combined, hereafter referred to as "WQC") is performed. The probability distribution of the FAV differences for dieldrin is shown in Figure 6-1A. The horizontal line that crosses the distribution is the test statistic computed from the original WQC and benthic FAVs. For dieldrin, the test statistic falls at the 16th percentile. Since the probability is less than 95%, the hypothesis of no significant difference in sensitivity is accepted.

Because freshwater and saltwater species show similar sensitivity, a test of difference in sensitivity for benthic and WQC organisms combining freshwater and saltwater species can be made. Figure 6-1B represents the AR analysis to test the hypothesis of no difference in sensitivity between benthic and WQC organisms for dieldrin. The test statistic for this analysis falls at the 68th percentile and the hypothesis of no difference in sensitivity is accepted.

Table 6-2 presents the AR analysis for endrin and dieldrin for which ESG documents have been developed. Dieldrin results indicate no difference in sensitivity for freshwater and saltwater species. The test for endrin fails at the 99th percentile, which indicates that FAVs for freshwater and saltwater are different. Therefore, separate analyses for the freshwater and saltwater organisms are performed.

Table 6-3 presents the results of the statistical analysis for each chemical for benthic organisms and WQC organisms. In all cases the hypothesis of no difference in sensitivity is accepted. Therefore, for each individual chemical the WQC are accepted as the appropriate effects concentrations for benthic organisms.

6.4 Quantification of Uncertainty Associated with ESGs

The uncertainty in the ESGs can be estimated from the degree to which the EqP model (which is the basis for the guidelines) predicts toxicity in sediment tests using the water-only LC50 data, K_{OC}, and the organic carbon–normalized sediment concentration. The EqP model asserts that (1) bioavailability of nonionic organic chemicals from sediments is equal on an organic carbon basis and (2) the effects concentration in sediment can be estimated from the product of the effects concentration from water-only exposures and the partition coefficient K_{OC}. The uncertainty associated with the ESGs can be obtained from a quantitative estimate of the degree to which the available data support these assertions.

The data used in the uncertainty analysis are from the water-only and sediment toxicity tests that were conducted in support of the sediment guidelines development effort. A listing of the data sources used

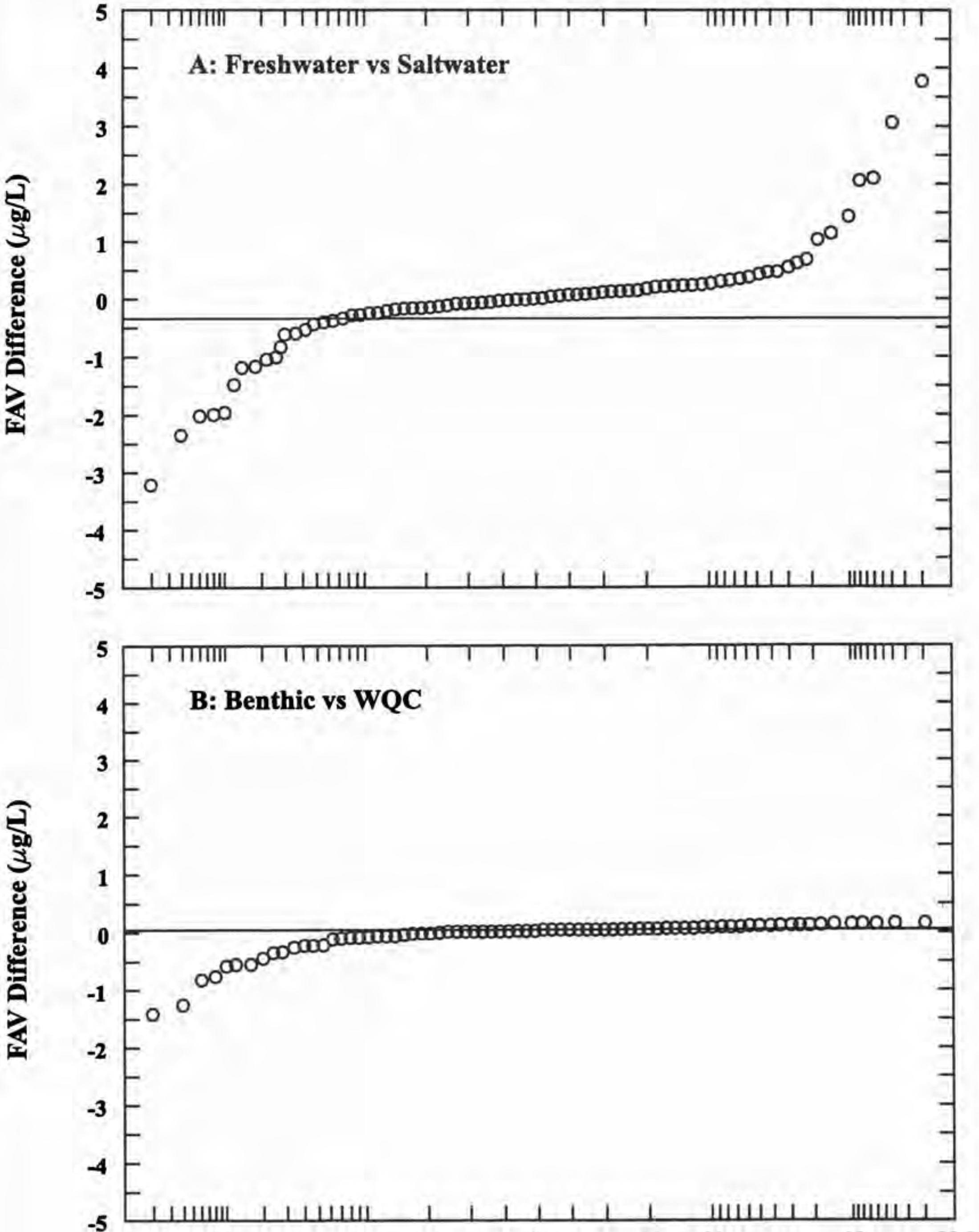

Figure 6-1. Probability distributions of randomly generated differences between freshwater FAVs and saltwater FAVs (A) and randomly generated differences between benthic FAVs and WQC FAVs (B) using the approximate randomization method for dieldrin. The horizontal lines in each panel indicate the test statistics, which are the FAV differences from the original LC50 datasets.

in the EqP uncertainty analysis is presented in Table 6-4. These freshwater and saltwater tests span a range of chemicals and organisms; they include both water-only and sediment exposures, and with the exception of the dieldrin water-only exposure test, they are replicated within each chemical-organism-exposure media treatment. These data are analyzed using an analysis of variance (ANOVA) to estimate the uncertainty (i.e., the variance) associated with varying the exposure media and the uncertainty associated with experimental error. If the EqP model were perfect, then there would be only experimental error. Therefore, the uncertainty associated with the use of EqP is the variance associated with varying exposure media. Sources of variation present in the EqP methodology are represented as one overall uncertainty calculated as the variance associated with varying exposure media.

Sediment and water-only LC50s are computed from the sediment and water-only toxicity tests. An LC50 is computed for each replicate using the Spearman-Karber calculation. The EqP model can be used to normalize the data in order to put it on a common basis. The LC50 from water-only exposures, $LC50_w$ (μg/L), is related to the LC50 for sediment on an organic carbon basis, $LC50_{S,OC}$ ($\mu g/g_{OC}$) via the partitioning equation

$$LC50_{S,OC} = K_{OC} LC50_W \qquad (6\text{-}3)$$

The EqP model asserts that the toxicity of sediments expressed on an organic carbon basis equals toxicity in water-only tests multiplied by the K_{OC}. Therefore, either $LC50_{S,OC}$ ($\mu g/g_{OC}$), from sediment toxicity experiments, or $K_{OC} \times LC50_W$ (μg/L) are estimates of the true LC50 for this chemical-organism pair. In this analysis, the accuracy of K_{OC} is not treated separately. Any error associated with K_{OC} will be reflected in the uncertainty attributed to varying the exposure media.

A model of the random variations is required to perform an ANOVA. As discussed above, experiments that seek to validate Equation 5-1 are subject to various sources of random variations. A number of chemicals and organisms have been tested. Each chemical–organism pair was tested in water-only exposures and in different sediments. Let α represent the random variation due to the varying exposure media. Also, each experiment was replicated. Let ε represent the random variation due to replication. If the model were perfect, there would be no random variation other than that resulting from the experimental error reflected in the replications. Thus, α represents the uncertainty due to the approximations inherent in the model, and ε represents the experimental error. Let σ_α^2 and σ_ε^2 be the variances of these random variables. Let i index a specific chemical–organism pair. Let j index the exposure media, water-only, or the individual

Table 6-2. Results of approximate randomization (AR) test for the equality of the freshwater and saltwater FAV distributions for endrin and dieldrin

	Number[a]		Final Acute Value (FAV)			
Chemical	Saltwater	Freshwater	Saltwater	Freshwater	Difference	%
Endrin	19	32	0.033	0.182	0.149	99
Dieldrin	19	21	0.621	0.287	-0.334	16

[a] Note that greater than (>) values were omitted. This resulted in one dieldrin saltwater benthic organism and two endrin freshwater benthic organisms being omitted from the AR analysis. Hence, these FAVs are slightly different from those reported in the original ESG. See individual guidelines documents for data listings (U.S. EPA, 2000c,d).

Table 6-3. Results of approximate randomization (AR) test for benthic and combined benthic and water column (WQC) FAV distributions for endrin and dieldrin

		Number[a]		Final Acute Value (FAV)			
Chemical	Water Type	WQC	Benthic	WQC	Benthic	Difference	%
Endrin	Freshwater	32	21	0.182	0.224	-0.042	7
Endrin	Saltwater	19	11	0.033	0.021	0.012	68
Dieldrin	Combined	40	26	0.543	0.491	0.052	68

[a] Note that greater than (>) values were omitted. This resulted in one dieldrin saltwater benthic organism and two endrin freshwater benthic organisms being omitted from the AR analysis. Hence, these FAVs are slightly different from those reported in the original ESG. See individual guidelines documents for data listings (U.S. EPA, 2000c,d).

Table 6-4. Data used in the equilibrium partitioning uncertainty analysis

Chemical	Organism	Test Type	No. of Replicates	Sediment (OC%)	Reference
Endrin	*Hyalella azteca*	Sediment	2	Soap Creek, soluble-cold exp. (3%)	Schuytema et al., 1989
Endrin	*Hyalella azteca*	Sediment	4	Mercer Lake, soluble-cold exp. (11%)	Schuytema et al., 1989
Endrin	*Hyalella azteca*	Sediment	3	Soap Creek (3%)	Nebeker et al., 1989
Endrin	*Hyalella azteca*	Sediment	3	Soap Creek & Mercer Lake (6.1%)	Nebeker et al., 1989
Endrin	*Hyalella azteca*	Sediment	3	Mercer Lake (11.1%)	Nebeker et al., 1989
Endrin	*Hyalella azteca*	Water-only	3		Nebeker et al., 1989
Endrin	*Hyalella azteca*	Water-only	3		Nebeker et al., 1989
Endrin	*Hyalella azteca*	Water-only	3		Nebeker et al., 1989
Dieldrin	*Hyalella azteca*	Water-only	1		Hoke et al., 1995
Dieldrin	*Chironomus tentans*	Sediment	4	Airport Pond (1.82-2.14%)	Hoke et al., 1995
Dieldrin	*Chironomus tentans*	Sediment	4	Airport Pond (1.42-1.69%)	Hoke et al., 1995
Dieldrin	*Hyalella azteca*	Sediment	4	West Bearskin (2.52-3.36%)	Hoke et al., 1995
Dieldrin	*Hyalella azteca*	Sediment	4	Pequaywan (6.68-10.9%)	Hoke et al., 1995
Fluoranthene	*Rhepoxynius abronius*	Sediment	2	Yaquina Bay (0.18%)	Swartz et al., 1990
Fluoranthene	*Rhepoxynius abronius*	Sediment	2	Yaquina Bay (0.31%)	Swartz et al., 1990
Fluoranthene	*Rhepoxynius abronius*	Sediment	2	Yaquina Bay (0.48%)	Swartz et al., 1990
Fluoranthene	*Rhepoxynius abronius*	Sediment	3	Suspended Solids (0.34%)	DeWitt et al., 1992
Fluoranthene	*Rhepoxynius abronius*	Sediment	2	McKinney Mud (0.40%)	DeWitt et al., 1992
Fluoranthene	*Rhepoxynius abronius*	Sediment	3	Shrimp feces (0.31%)	DeWitt et al., 1992
Acenaphthene	*Eohaustorius estuarius*	Sediment	2	South Beach (0.82%, 1.23%)	Swartz, 1991

Table 6-4. Data used in the equilibrium partitioning uncertainty analysis (continued)

Chemical	Organism	Test Type	No. of Replicates	Sediment (OC%)	Reference
Acenaphthene	*Eohaustorius estuarius*	Sediment	2	McKinney (2.49%)	Swartz, 1991
Acenaphthene	*Eohaustorius estuarius*	Sediment	2	Eckman (4.21)	Swartz, 1991
Acenaphthene	*Leptocheirus plumulosus*	Sediment	2	South Beach (0.82%, 1.62%)	Swartz, 1991
Acenaphthene	*Leptocheirus plumulosus*	Sediment	2	McKinney (2.36%, 2.52%)	Swartz, 1991
Acenaphthene	*Leptocheirus plumulosus*	Sediment	2	Eckman (2.97%, 3.66%)	Swartz, 1991
Acenaphthene	*Leptocheirus plumulosus*	Water-only	4		Swartz, 1991
Acenaphthene	*Leptocheirus plumulosus*	Water-only	4		Swartz, 1991
Phenanthrene	*Eohaustorius estuarius*	Sediment	2	South Beach (0.82%, 1.02%)	Swartz, 1991
Phenanthrene	*Eohaustorius estuarius*	Sediment	2	McKinney (2.36%, 2.47%)	Swartz, 1991
Phenanthrene	*Eohaustorius estuarius*	Sediment	2	Eckman (2.97%, 3.66%)	Swartz, 1991
Phenanthrene	*Leptocheirus plumulosus*	Sediment	2	South Beach (0.82%, 1.96%)	Swartz, 1991
Phenanthrene	*Leptocheirus plumulosus*	Sediment	2	McKinney (2.36%, 2.50%)	Swartz, 1991
Phenanthrene	*Leptocheirus plumulosus*	Sediment	2	Eckman (2.97%, 3.60%)	Swartz, 1991
Phenanthrene	*Leptocheirus plumulosus*	Water-only	4		Swartz, 1991
Phenanthrene	*Eohaustorius estuarius*	Water-only	4		Swartz, 1991

sediments. Let k index the replication of the experiment. Then the equation that describes this relationship is

$$\ln(\mathrm{LC50}_{ijk}) = \mu_i + \alpha_{ij} + \varepsilon_{ijk} \qquad (6\text{-}4)$$

where $\ln(\mathrm{LC50}_{ijk})$ are either $\ln(\mathrm{LC50}_w)$ or $\ln(\mathrm{LC50}_{S,OC})$ corresponding to a water-only or sediment exposure and μ_i are the population of ln(LC50) for chemical–organism pair i. The error structure is assumed to be lognormal, which corresponds to assuming that the errors are proportional to the means (e.g., 20%) rather than absolute quantities (e.g., 1 mg/L). The statistical problem is to estimate μ_i and the variances of the model error, σ_α^2, and the measurement error, σ_ε^2. The maximum likelihood method is used to make these estimates (El-Shaarawi and Dolan, 1989). In summary, LC50 values from water-only exposures and sediment toxicity tests were used to compute the variances resulting from varying the exposure media and those due to experimental error. The results are shown in Table 6-5.

Table 6-5. ANOVA for derivation of confidence limits of ESG values

Source of Uncertainty	Parameter	Value ($\mu g/g_{OC}$)
Exposure media	σ_α	0.41
Replication	σ_ε	0.29
ESG	σ_{ESG}[a]	0.41

[a] $\sigma_{ESG} = \sigma_\alpha$.

This ANOVA was computed using combined datasets shown in Table 6-4. Combining the datasets provides a more robust analysis with a wider range of organic carbon. The ANOVA were computed for individual chemicals for comparative purposes. The individual and combined error estimates for exposure media and replication along with the number of data points are tabulated in Table 6-6. Errors due to exposure media are shown in Figure 6-2. The solid line represents the combined error for comparison to the individual error. The differences between the mean errors of the individual chemicals and the error of the combined chemicals are minimal. Combining the datasets provides the best estimate of the uncertainty of the overall model. This uncertainty will be recomputed as additional ESGs are formulated.

The last line of Table 6-5 is the uncertainty associated with the ESG, that is, the variance associated with the exposure media variability. The confidence limits for the ESG are computed using this uncertainty. For the 95% confidence interval limits, the significance level is 1.96 for normally distributed errors. Thus

$$\ln(ESG_{OC})_{upper} = \ln(ESG_{OC}) + 1.96\sigma_{ESG} \qquad (6\text{-}5)$$

$$\ln(ESG_{OC})_{lower} = \ln(ESG_{OC}) - 1.96\sigma_{ESG} \qquad (6\text{-}6)$$

The ESG and 95% confidence limits for endrin and dieldrin are given in Table 6-7. Figure 2-3 reflects this uncertainty using solid vertical bars around 1 TU.

6.5 Minimum Requirements To Compute an ESG

It has been demonstrated that the computation of an ESG for a particular chemical requires key parameter values, as well as evidence that EqP is applicable for a particular chemical. Minimum requirements for these parameters are warranted so that they provide the level of protection intended by ESGs within the limits of uncertainty set forth in this document. This section outlines the minimum data requirements to compute ESGs and the necessary guidance for deriving them. This step is critical to the development of reliable parameters that are to be used to compute ESGs. The minimum requirements to compute an ESG are as follows:

- Octanol-water partition coefficient (K_{OW})
- Final chronic value (FCV)
- Sediment toxicity tests

Procedures to ensure that these data meet assumptions of the EqP approach will also be addressed.

Table 6-6. Comparison of individual and combined error estimates

Chemical	Number of Data Points	Variance Due to Exposure Media	Variance Due to Replication
Acenaphthene	20	0.38	0.15
Phenanthrene	20	0.12	0.14
Dieldrin	17	0.31	0.54
Endrin	24	0.65	0.29
Fluoranthene	14	0.34	0.056
Mean of Individual Chemicals		0.36	0.24

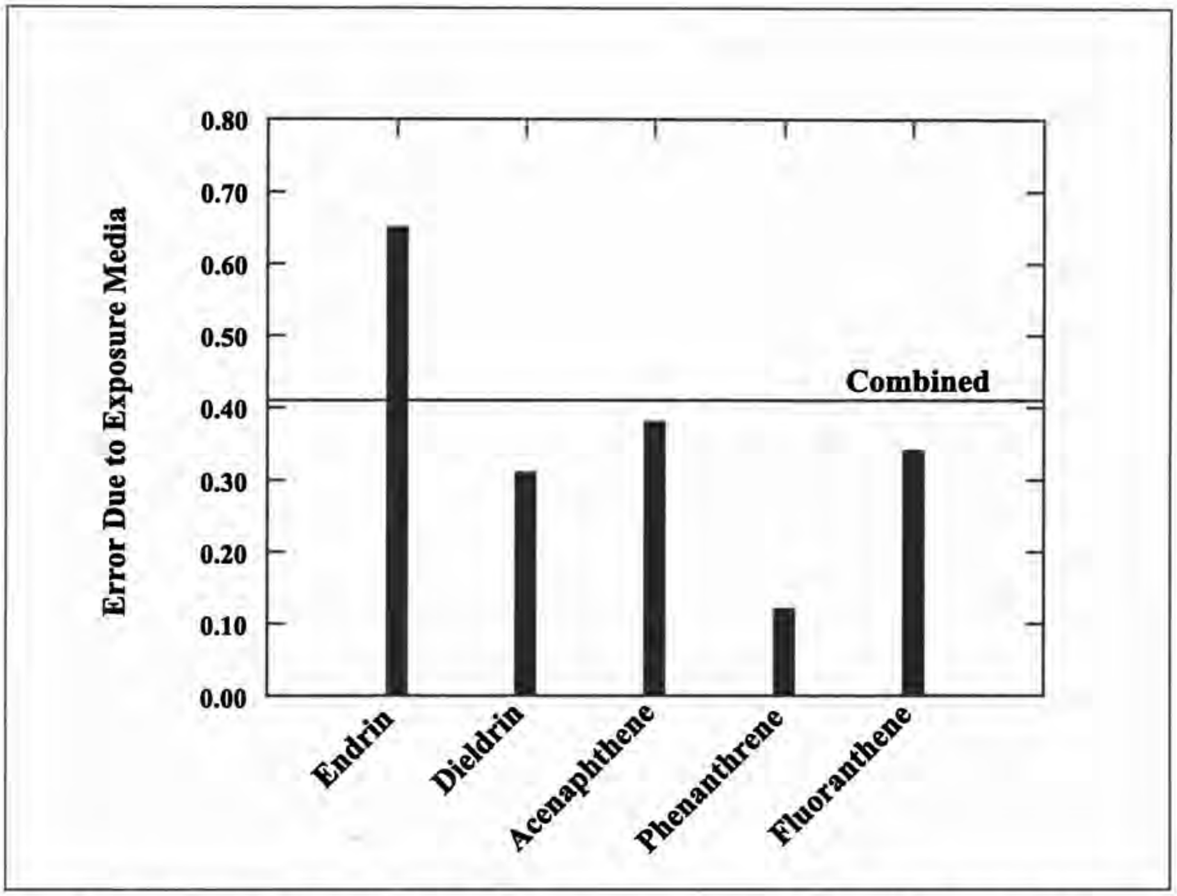

Figure 6-2. **Comparison of individual error due to exposure media (bars) and combined error due to exposure media (solid line).**

6.5.1 *Octanol–Water Partition Coefficient*

A K_{OW} value is required to compute the K_{OC}. EPA recommends using K_{OW} values from Karickhoff and Long (1995; Long and Karickhoff, 1996) when available.

6.5.2 *Final Chronic Value*

The FCV is computed as part of the derivation of the WQC for a compound, and is defined as the quotient of the FAV and the final acute–chronic ratio (FACR) (Stephan et al., 1985). The data required to compute the FCV are water-only toxicity tests for a variety of organisms meeting minimum database requirements. The FCV computation and minimum database requirements are presented in Stephan et al. (1985).

WQC are based on an assessment of a compound's acute and chronic toxicity for organisms representing a range of sensitivities, particularly the most sensitive organisms. This is appropriate because the objective of WQC is to set limits based on the best estimate of organism sensitivity. The toxicity database should therefore include all available data that meet requirements. That is, a complete search, retrieval, and review for any applicable data must be conducted, to locate all preexisting toxicity data. For some compounds, a WQC FCV may exist that would provide a significant amount of toxicity data. Literature searches are recommended to locate other sources of toxicity data.

Reevaluation of an already existing FCV is warranted because data postdating publication of the WQC can be incorporated into the FCV value. Also, minimum database requirements have changed since some WQC were published. For those compounds for which FCVs do not exist, compiled toxicity data are evaluated to see if minimum data requirements, as put forth by Stephan et al. (1985), are met. If so, an FCV could then be computed. If there are not enough water-only toxicity data to compute an FCV, additional water-

Table 6-7. Confidence limits of the ESGs for endrin and dieldrin

Chemical	Type of Water Body	ESG_{OC} ($\mu g/g_{OC}$)	95% Confidence Limits ($\mu g/g_{OC}$)	
			Lower	Upper
Endrin	Freshwater	5.4	2.4	12
	Saltwater	0.99	0.44	2.2
Dieldrin	Freshwater	12	5.4	27
	Saltwater	28	12	62

only tests should be conducted so that sufficient data are available to satisfy minimum database requirements.

6.5.3 *Sediment Toxicity Tests*

Verification of the applicability of EqP theory is required for each compound. Sediment toxicity tests can be used for this. These tests provide a sediment-based LC50. Comparison of the EqP-predicted LC50 with the sediment LC50 concentration is direct confirmation of the EqP approach. Validity of EqP is confirmed when the toxicity test results fall within the limits of uncertainty determined in this document.

Guidelines for conducting sediment toxicity tests ensure that the tests are uniform and are designed to incorporate the assumptions of EqP. These tests must represent a range of organic carbon content and include organisms that exhibit sensitivity to the chemical in question. The range of organic carbon should be at least a factor of 3. Minimum organic carbon content for test sediments should be 0.2%. Replicated toxicity tests for at least two sediments are required. Organisms to be used in the sediment toxicity tests are benthic animals, which are most sensitive to the compound in question. Guidelines on appropriate selection of benthic organisms is given in the American Society for Testing and Materials (ASTM) annual handbook (ASTM, 1992).

Several studies are required as part of the sediment toxicity testing. A water-only flow-through test is required to establish the water-only effect concentrations for the chemical and organism to be used in the sediment toxicity test. Water-only tests are run for multiple concentrations (e.g., five) of the compound in question and a control. The endpoint of interest is the 10-day mortality of the test species, if that matches the duration of the corresponding sediment test. Test concentrations should be selected to provide a range in organism mortality (e.g., 0% to 100%) and to characterize the range of partial mortality as effectively as possible. This value will be compared with the interstitial water and sediment mortality from the sediment spiking tests discussed next. Guidelines for conducting water-only tests are given by ASTM (1996).

Once water-only toxicity data have been collected, sediment toxicity tests with spiked sediments are conducted. In early sediment check tests, two sediment-spiking tests were often employed. In the first test, sediment concentrations were selected using the water-only LC50 ($\mu g/L$) and K_{OC} so that the interstitial water concentrations bracketed the LC50 from the water-only test. Three spiking treatments were typically used in the first test: low, medium, and high concentrations. The amount of compound to add to each treatment was calculated using the initial chemical weight, the % total organic carbon (TOC), the % dry weight, and the total volume of spiked sediment. Samples for chemical analyses in bulk sediment and interstitial water were collected at various time intervals. Nominal sediment-spiking concentrations, measured sediment TOC, and measured and EqP-predicted compound concentrations in sediments and interstitial waters were obtained for each sample period to establish time-to-equilibrium and to verify that spiking produced the appropriate concentrations in the interstitial water. Sorption equilibrium, an assumption of EqP theory, is essential for valid interstitial water and sediment concentrations. Guidelines for conducting sediment toxicity tests are given by ASTM (1992, 1994a,b), and EPA (U.S. EPA, 1994).

The second test was a definitive experiment that utilized three sediments with differing organic carbon concentrations that were spiked with a series of concentrations such that the chemical concentrations were similar on an organic carbon–normalized basis. Experience with these check-tests has shown that range-finding tests above are not required for selection of spiking concentrations in the definitive tests so long as the selected water-only LC50 value and K_{OC} values (derived from Karickhoff and Long, 1995; Long and Karickhoff, 1996) are within a factor of about two of the

sediment LC50 (Figure 2-3). Prior to testing, spiked sediments must be held for an appropriate time to ensure equilibrium is established. This can be demonstrated by measuring the interstitial water and sediment concentrations. The other requirement is that the benthic species selected for these toxicity tests must be sensitive at less than the chemical's solubility in water and preferably one of the species should be the most sensitive to the chemical. Although five sediment concentrations with dilution factors of about 0.5 have been used successfully to bracket the predicted sediment LC50, more treatments or different dilution factors may be useful. Organisms are placed in replicated beakers and 10-day sediment toxicity tests with the equilibrated spiked sediments are conducted. Biological and chemical replicates for each treatment are required. Chemical replicates should be sampled at the beginning and end of the tests for interstitial water and sediment analyses. Biological replicates are sampled at the end of the 10-day test.

The overall approach for conducting EqP check experiments is given by Hoke et al. (1995). These experiments provide data to compute IWTUs and PSTUs (Equations 2-1 and 2-8). The results of these equations serve as direct comparisons of the predicted toxicity (Equation 2-1 and 2-8 numerator) to the observed toxicity (Equation 2-1 and 2-8 denominator). That is, validity of EqP for a chemical is confirmed when the IWTUs and PSTUs fall within the limits of uncertainty determined in this document.

6.5.4 *Test of the Applicability to ESG Derivation*

The purpose of these procedures is to verify that

- The WQC FCV applies to benthic organisms
- The K_{OC} from the EPA-recommended K_{OW} is an accurate estimate of K_{OW}

A test for the WQC FCV, which is applicable to the most sensitive water column organisms and to the most sensitive benthic organisms, is needed for each chemical. In computing ESGs for endrin and dieldrin, the AR method was applied. This is a statistical test to compare the WQC toxicity database with benthic organism toxicity. The methodology is presented in Section 6-3. If it is found that benthic organisms exhibit similar or less sensitivity to a chemical than those organisms used to compute WQC, then the WQC FCV can be applied in computing an ESG. If benthic organisms exhibit a greater sensitivity than the WQC organisms, then toxicity experiments for benthic organisms are required.

A check on the computed K_{OC} from the recommended K_{OW} must be done by comparing it with the K_{OC} computed from sediment toxicity tests. Interstitial water and sediment concentrations from the sediment toxicity test provide data necessary to compute the K_{OC}. For chemicals with $\log K_{OW}$ substantially greater than 5.0, DOC binding must be considered when evaluating interstitial water data (see Section 4.3).

Finally, when a site's sediments are being studied, a check to show that the ESG applies to the site is needed. National ESGs may be under- or overprotective if (1) the species at the site are more or less sensitive than those included in the dataset used to derive the ESG or (2) the sediment quality characteristics of the site alter the bioavailability predicted by EqP and, ultimately, the predicted toxicity of the sediment bound chemical. Therefore, it is appropriate that site-specific guidelines procedures address each of these conditions separately, as well as jointly. Methods to determine the applicability of national ESGs to a site and to determine site-specific ESGs if needed are presented in "Methods for the Derivation of Site-Specific Equilibrium Partitioning Sediment Guidelines (ESGs) for the Protection of Benthic Organisms: Nonionic Organics" (U.S. EPA, 2000e).

6.5.5 *Tier 1 and Tier 2 ESGs*

Minimum database and analytical requirements must be set when deriving national sediment guidelines. The reasons for this are twofold. First, the requirements establish a level of protection intended by the guidelines. Second, they establish that the behavior and toxicity of the chemical in sediment adheres to the assumptions of EqP theory. The required parameters include a K_{OW} value (used to compute the K_{OC}), a FCV, and sediment toxicity tests. Procedures to verify that these values are appropriate to use in the ESG computation are also required. It must be shown that the FCV is protective of benthic organisms. Confidence in the K_{OC} must also be established by comparing the K_{OC} with the observed K_{OC} in sediment toxicity tests. Individual sites may exhibit greater or lesser toxicity of a chemical than that predicted by ESGs at an individual site. EPA procedures to test this assumption, as well as to compute site-specific ESGs, are available.

EPA has developed both Tier 1 and Tier 2 ESGs to reflect the differing degrees of data availability and

uncertainty. A Tier 1 ESG would meet all of the above requirements as previously described; these include K_{ow} and FCV values as well as sediment toxicity tests to verify EqP assumptions. As such, the ESGs derived for nonionic organics, such as dieldrin and endrin, metal mixtures, and PAH mixtures would represent Tier 1 ESGs (U.S. EPA, 2000b,c,d,f).

Comparatively, the derivation of a Tier 2 ESG requires a K_{ow} value and either a FCV or a secondary chronic value (SCV). The minimum requirement for deriving a SCV is toxicity data from a single taxonomic family (*Daphnidae*), provided the data are acceptable. The EPA methodology for deriving WQC SCVs is described further in "Water Quality Guidance for the Great Lakes System: Supplementary Information Document" (U.S. EPA, 1995). Performance of sediment toxicity "check" tests is recommended, but not required for a Tier 2 ESG. Therefore, in comparison to Tier 1 ESGs, the level of protection provided by the Tier 2 ESGs would be associated with more uncertainty due to the use of the SCV and absence of sediment check tests. Examples of Tier 2 ESGs for nonionics are found in U.S. EPA (2000g). Information on how EPA recommends ESGs be applied in specific regulatory programs is described in "Implementation Framework for the Use of Equilibrium Partitioning Sediment Guidelines (ESGs)" (EPA, 2000a).

6.5.6 *Summary*

Computation of ESGs for individual chemicals requires a number of key parameters. Minimum requirements for these parameters are warranted to provide the level of protection intended by ESGs within the limits of uncertainty set forth in this document. The following minimum data are required to compute Tier 1 and Tier 2 ESGs:

	Partitioning Coefficient	Aquatic Life Protection Level	Verification Requirements
Tier 1 ESGs	Octanol-water partitioning coefficient (K_{OW})	WQC final chronic value (FCV)	Sediment toxicity test
Tier 2 ESGs	Octanol-water partitioning coefficient (K_{OW})	WQC FCV or secondary chronic value (SCV)	

6.6 Example Calculations

Equation 2-7 can be used to compute an ESG_{OC} for a range of K_{OW} and FCV values. The results for several chemicals are shown in Figure 6-3 in the form of a nomograph. The diagonal lines are for constant FCV as indicated. The x-axis is $\log_{10} K_{OW}$. For example, for endrin the saltwater FCV is 0.01 μg/L and the $\log_{10} K_{OW}$ is 5.06, so that the $\log_{10}$ESG is approximately 10 to the zero = 0.99 μg endrin/g_{OC}.

As can be seen, the relationships between ESG_{OC} and the parameters that determine its magnitude, K_{OW} and FCV, are essentially linear on a log-log basis. For a constant FCV, a 10-fold increase in K_{OW} (1 log unit) increases the ESG_{OC} by approximately 10-fold (1 log unit) because K_{OC} also increases approximately 10-fold. Thus, chemicals with similar FCVs will have larger ESG_{OC} values if their K_{OW} values are larger.

The chemicals listed in Figure 6-3 have been chosen to illustrate the ESG_{OC} concentrations that result from applying the EqP method. The WQCs are the FCVs (not the final residue values) computed as part of the development of ESGs for endrin and dieldrin or from published and draft EPA WQC documents (see Table 5-1 for the remaining chemicals plotted). The K_{OW} values for endrin and dieldrin are from the EPA-recommended values in Table 6-1. The K_{OW} values for the remaining chemicals are the log averages of the values reported in the Log P database (Leo and Hansch, 1986). Although the ESGs for endrin and dieldrin meet the minimum database requirements presented in the previous section, ESGs for the remaining chemicals are illustrative only and should not be considered final ESG values. Final ESGs, when published, should reflect the best current information for both FCV and K_{OW}.

FCVs available for nonionic organic insecticides range from approximately 0.01 to 0.3 μg/L, a factor of 30 (Dave Hansen, Great Lakes Environmental Center, Traverse City, MI, personal communication). The ESG_{OC} values range from approximately 0.01 μg/g_{OC} to in excess of 10 μg/g_{OC}, a factor of over 1,000. This increased range in values occurs because the K_{OW} values of these chemicals span over two orders of magnitude. The most stringent ESG_{OC} in this example is for pesticide C, a chemical with one of the lowest K_{OW} values among the chemicals with an FCV of approximately 0.01 μg/L.

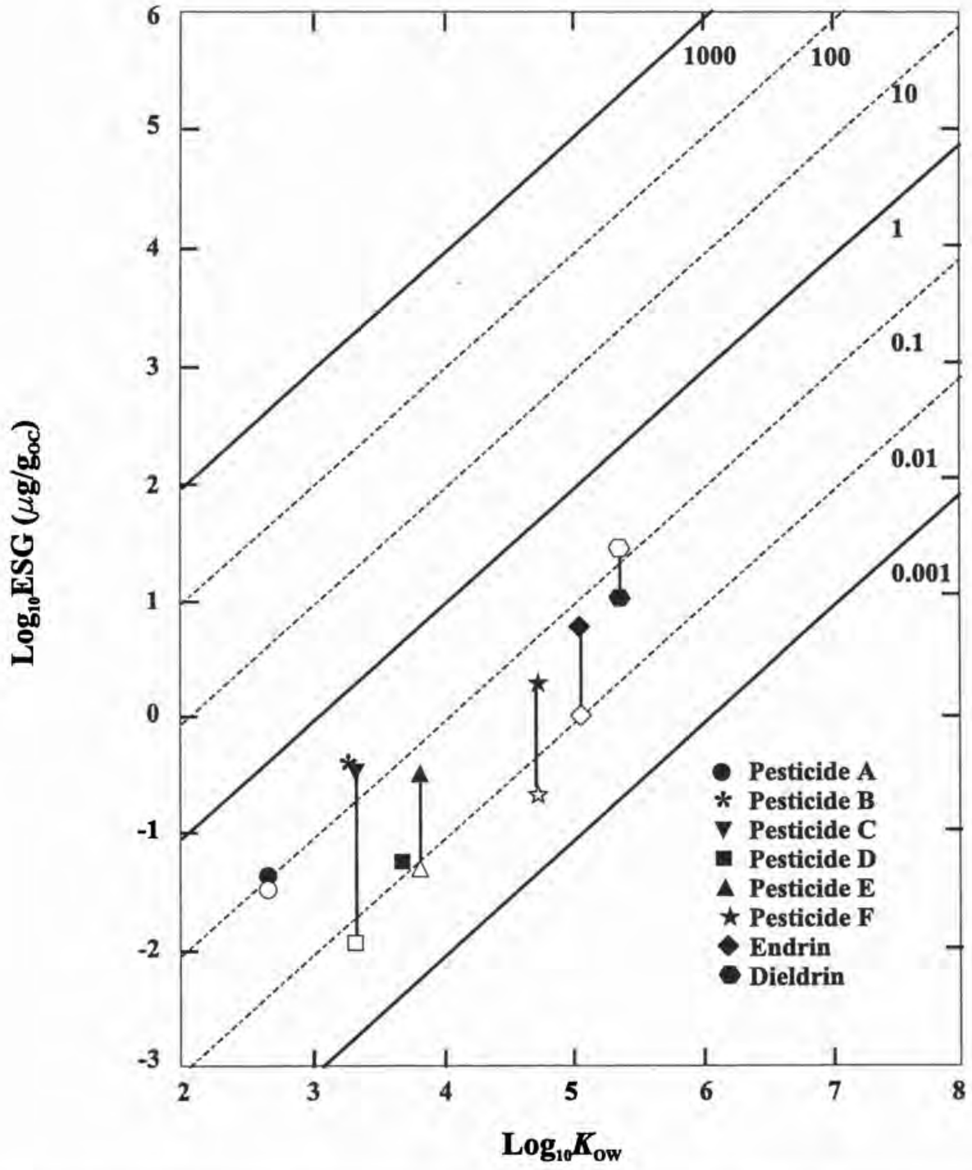

Figure 6-3. Log$_{10}$ESG versus log$_{10}K_{OW}$. Diagonal lines indicate the FCV values. ESG values are computed from Equation 6-1. K_{OC} is obtained from K_{OW} with Equation 4-3. The symbols indicate ESG$_{OC}$ for the freshwater (filled) and saltwater (open) criteria for the listed chemicals. Vertical lines connect symbols for the same chemical.

6.7 Field Data

Information on the actual levels of the guidelines chemicals in the environment was assembled to provide an indication of the relationship between ESG concentrations and the concentration levels observed in the sediments of U.S. surface water bodies. Three separate databases were examined:

- EPA's STORET database (U.S. EPA, 1989)
- NOAA's National Status and Trends database, which focused on water bodies in coastal areas (O'Connor, 1991)
- Corps of Engineers (COE) database for San Francisco Bay (U.S. Army Corps of Engineers, 1991)

Several of the guidelines chemicals are frequently measured when samples are taken to measure sediment contamination, and these values are frequently reported in databases on sediment contamination. This means that it is possible that many of the sediments from the nation's waterways might exceed the guidelines for these chemicals. In order to investigate this possibility, the guidelines for dieldrin and endrin were compared with data from several available databases of sediment chemistry.

The data that were retrieved have been summarized on probability graphs that are presented in the subsections that follow for each of the data sources. A large proportion of the observations are below detection limit values and indicate only that the actual concentration is unknown, but less than the concentration plotted. These data are plotted with a "less than" symbol. As a result, the probability plots should not be interpreted as representations of the actual probability distribution of the monitored samples. They do, however, provide a useful visual indication of the range of concentration levels of the study chemicals in natural sediments.

A suggestion of the probable extent to which problem sediments might be encountered is provided by the plot overlay showing the ESG concentration developed by this research. In the case of the STORET data, the ESG is shown as a band because the f_{OC} is not reported. The lines represent the ESG for f_{OC} between 1% and 10%. The other two databases provide the necessary information on sediment organic carbon levels, and the results have been properly normalized. Very few of the measured values from either of the databases for endrin and dieldrin exceeded the ESGs.

6.7.1 *STORET Data*

A STORET data retrieval was performed to obtain a preliminary assessment of the concentrations of the guidelines chemicals in the sediments of the nation's water bodies. The data retrieved were restricted to samples measured in the period 1986 to 1990. Selection of this period eliminated many older data with higher detection limits to more accurately indicate current conditions. Log probability plots concentrations are shown in Figure 6-4. Concentrations are shown on a dry weight basis, because sediment organic carbon is not reported. The ESGs are computed on the basis of a sediment organic carbon content (f_{OC}) of 1% and 10%, which is the typical range for inland sediments. The STORET data distinguish between type of water body, and separate displays are provided for stations in streams, lakes, and estuaries.

The data for endrin and dieldrin are shown in Figures 6-4 and 6-5, respectively. The total number of samples, and the number of detected samples, are indicated on the figures. The plotted points are restricted to a subset of the total number of samples, so that the plots are legible. A few samples with detected concentrations, the solid symbols, exceed the ESG for $f_{OC} = 1\%$, and fewer exceed the ESG for $f_{OC} = 10\%$. The nondetected data, plotted at the detection limit with "<", are below the value indicated on the plot. In fact, with nondetected data included in the probability plot, the actual plotting positions of the detected data are uncertain, because the nondetected data may occupy plotting positions further to the left, at lower probabilities. Thus the exceedence probabilities for the detected data are at least as large as indicated on the plots. Less than 3% of the detected dieldrin and endrin samples exceed the lower ESG.

6.7.2 *National Status and Trends Program Data*

NOAA's National Status and Trends Program developed a database on the quality of marine sediments focusing on estuarine and coastal sites that are not in close proximity to known sources of contamination (O'Connor, 1991). Figure 6-6 displays the distribution of sediment concentrations from the National Status and Trends Program sites for dieldrin (endrin concentrations were not measured). Sediment organic carbon concentrations were measured in this program and ranged from less than 0.20% to 16.2%. The availability of f_{OC} permits the plots to display both observed concentrations and the ESG value using organic carbon normalization.

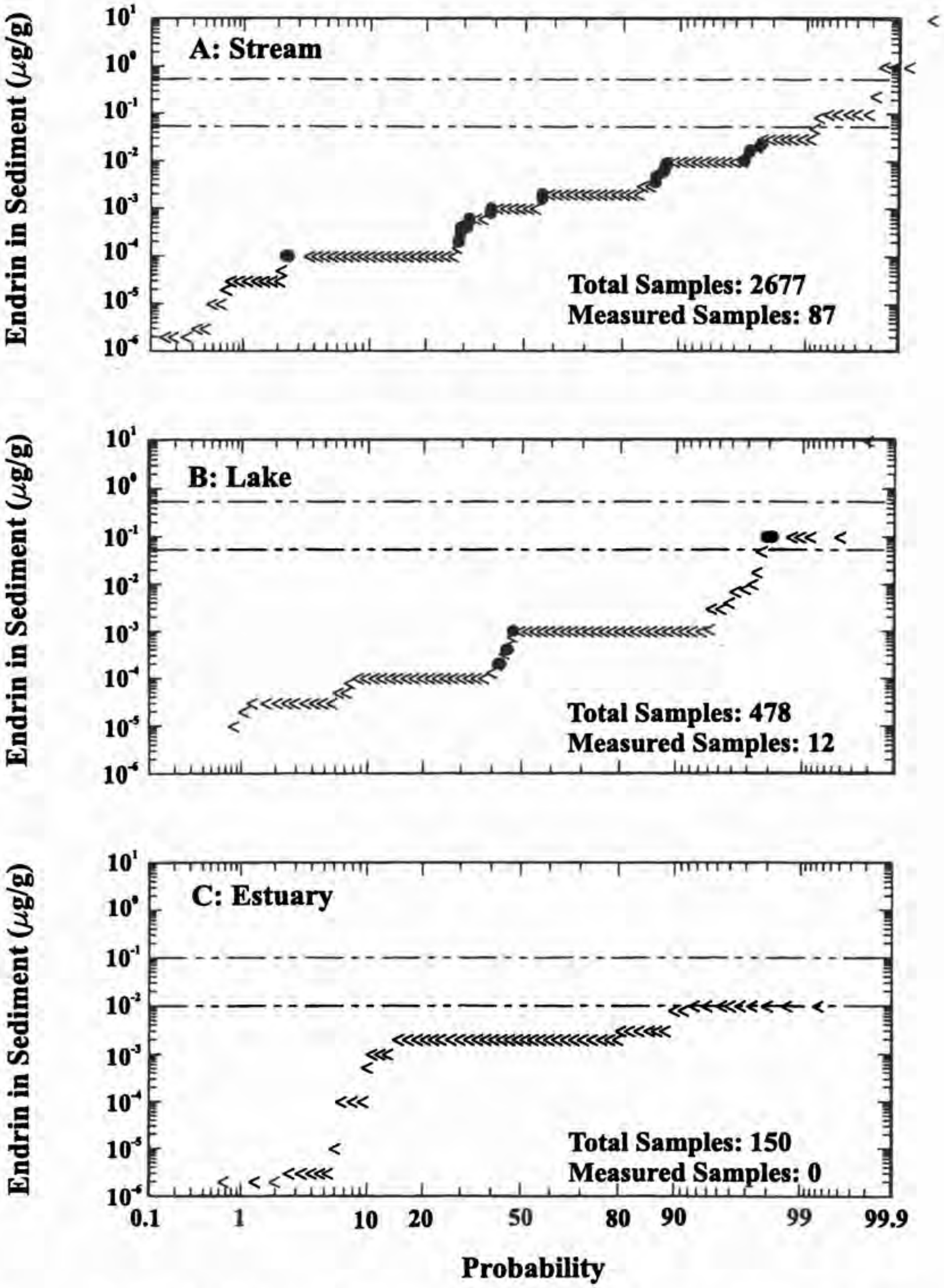

Figure 6-4. Probability distribution of concentrations of endrin in sediments from streams (A), lakes (B), and estuaries (C) in the United States from 1986 to 1990 from the STORET database compared with the endrin ESG values. Sediment endrin concentrations below the detection limits are shown as less than symbols (<); measured concentrations are shown as solid circles (●). The upper dashed line on each figure represents the ESG value when TOC =10%; the lower dashed line represents the ESG when TOC=1% (data from U.S. EPA, 1989).

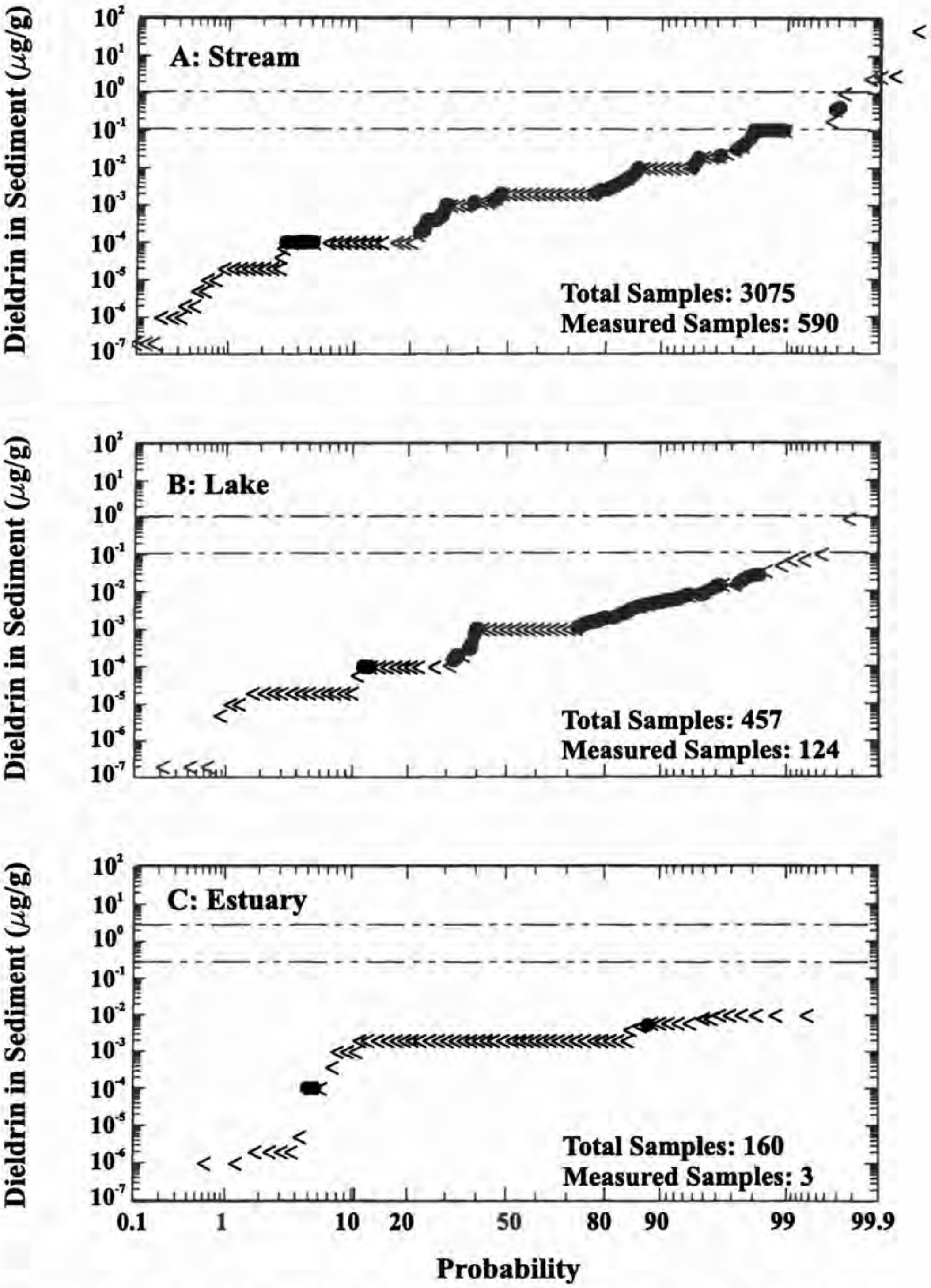

Figure 6-5. Probability distribution of concentrations of dieldrin in sediments from streams (A), lakes (B), and estuaries (C) in the United States from 1986 to 1990 from the STORET database compared to the dieldrin ESG values. Sediment dieldrin concentrations below the detection limits are shown as less than symbols (<); measured concentrations are shown as solid circles (●). The upper dashed line on each figure represents the ESG value when TOC=10%, the lower dashed line represents the ESG when TOC=1% (data from U.S. EPA, 1989).

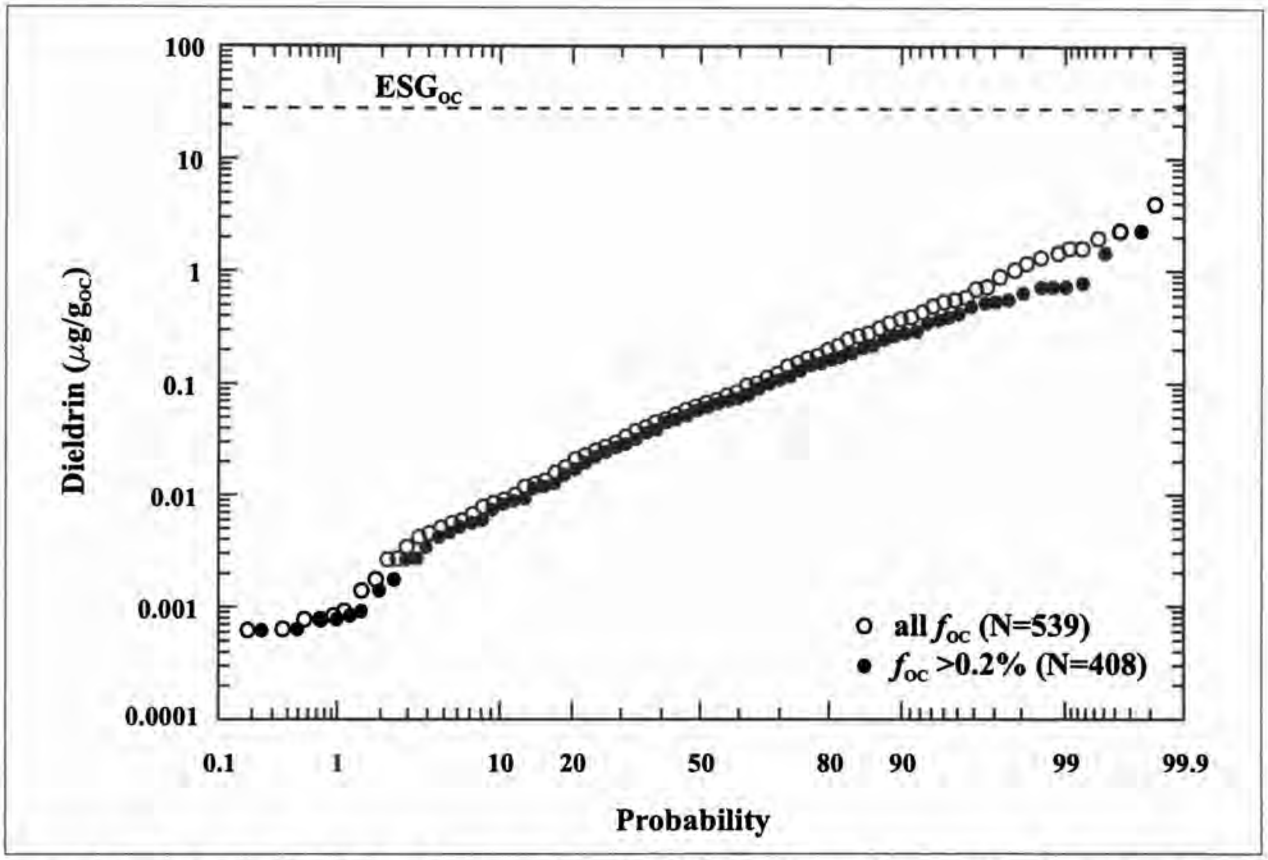

Figure 6-6. Probability distribution of concentrations of dieldrin in sediments from coastal and estuarine sites from 1984 to 1989 as measured by the National Status and Trends Program. The horizontal dashed line is the saltwater ESG value of 28 $\mu g/g_{oc}$. Samples with organic carbon greater than 0.2% (●) and samples for all organic carbon contents (○) are shown. Data from NOAA (O'Connor, 1991).

Results are displayed in the plots for all samples (open symbols) and for the subset that contained organic carbon fractions greater than 0.2%, the limit of applicability for the EqP-derived ESG (filled symbols). The ESG is applicable to the 75% to 85% of all sediment samples that have f_{OC} values greater than 0.2%. However, there is only a nominal effect on estimates of the percentage of the samples that exceed the ESG, depending on whether the full set, or the subset, of samples is considered. The dieldrin ESG is not exceeded.

6.7.3 *Corps of Engineers Data*

A set of data from the U.S. Army Corps of Engineers monitoring program for a number of locations in various parts of San Francisco Bay has been analyzed. Table 6-8 identifies the locations sampled, the number of observations at each site, and the period during which the results were obtained. These data were collected to examine the quality of dredged sediments in order to determine their suitability for open water disposal. The database did not indicate what determinations were made concerning their acceptability for this purpose.

Investigators compared the frequency of occurrence (in individual samples, not dredge sites) with the ESG developed using the EqP methodology. The major portion (93%) of the samples analyzed had organic carbon fractions greater than 0.2%, for which the ESG concentrations are applicable. The concentrations of each chemical measured in these sediments was normalized by the organic carbon content and the results are displayed (Figure 6-7) as probability plots to illustrate the frequency at which different levels are observed. Results are presented for the two guidelines chemicals: endrin and dieldrin. A horizontal line at the concentration value of the ESG provides a reference that indicates the relationship

Table 6-8. San Francisco Bay sediment samples

Location	No. of Samples Analyzed[a]	Years
Port of San Francisco: Piers 27-29, 35, 38, 48, 70, 80, and 94	23	1988 and 1990
Fisherman's Wharf and Islais Creek	2	1990
Suisun Channel	6	1991
West Richmond	11	1990
Pinole Shoal	44	1990
Carquinez Strait	10	1990
Mare Island Strait	6	1990
Richmond Harbor Channel	43	1990
Santa Fe Channel	6	1990
Outer and Inner Richmond Harbor Channel	6	1991
Port of Oakland Tier II: Berths 20-23, 25, 26-30, 31, 35-38, 60-63, and 82-84	41	1989-1990
Port of Oakland Outer and Inner Harbor	8	1990-1991
Treasure Island	5 composites	1990
San Leandro Bay	1 composite	1990
San Pablo Bay	6	1989-1990

[a] Samples were analyzed for endrin and dieldrin.

between observed range of quality and the ESG for each chemical. Virtually all of the samples were less than the varying detection limits of the analytical tests. Each of the samples for which actual measurements were obtained were at least an order of magnitude lower than the ESG. An estimate of the possible frequency distribution of sediment concentrations of dieldrin and endrin was developed by the application of an analysis technique that accounts for the varying detection limits and the presence of nondetected observations (U.S. EPA, 1989). The results are illustrated by the straight line, which suggests that no appreciable number of exceedences is expected. However, the virtual absence of detected concentrations makes the distribution estimates unreliable. They are presented only to suggest the probable relationship between the levels of these two pesticides in relation to sediment guidelines.

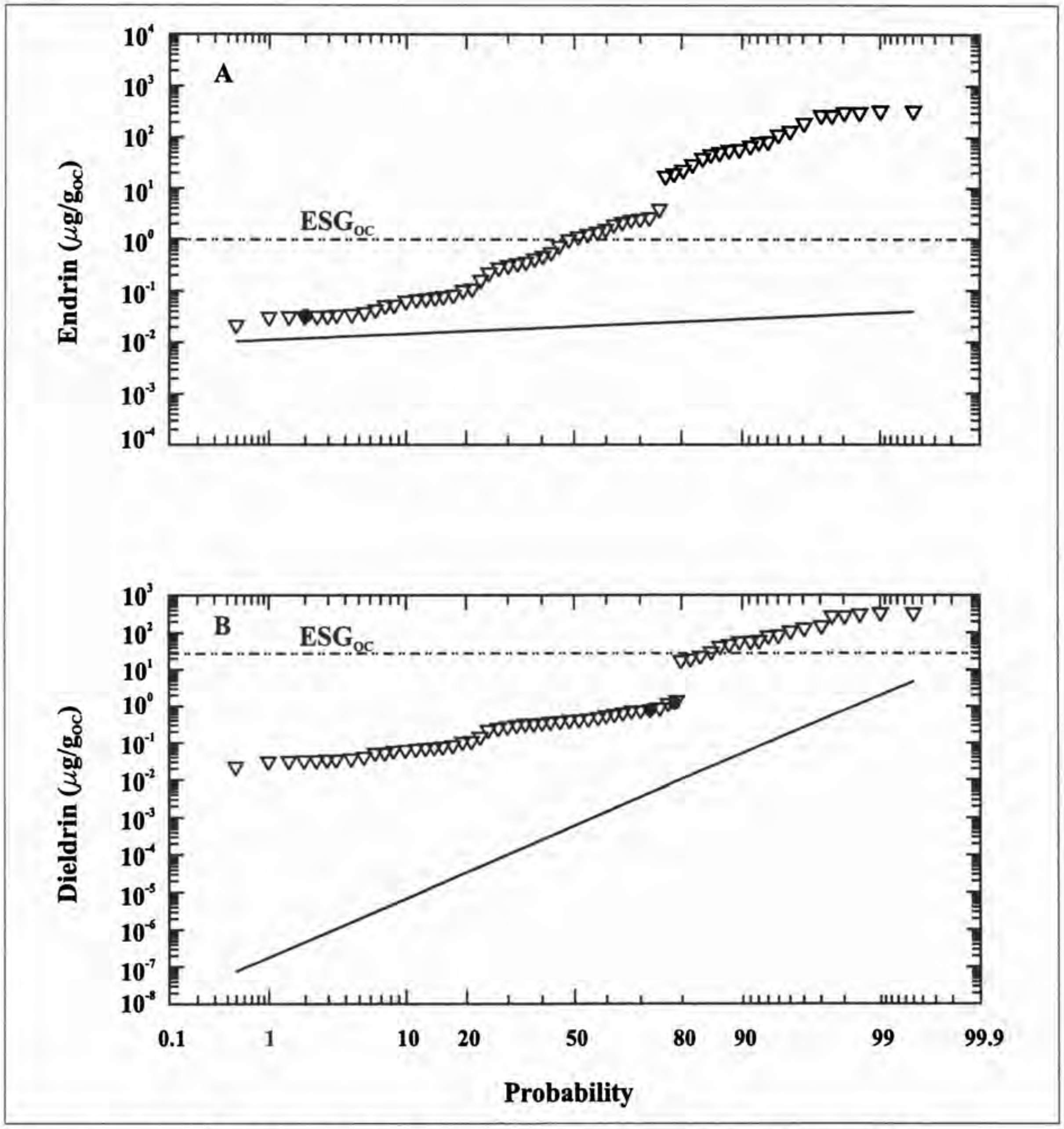

Figure 6-7. Probability distribution of organic carbon–normalized sediment endrin (A) and dieldrin (B) concentrations from the U.S. Army Corps of Engineers (1991) monitoring program of San Francisco Bay. Sediment concentrations less than the detection limits are shown as open triangles (∇); measured concentrations are shown as solid circles (•). The solid lines in each are an estimate of the distribution developed by accounting for nondetected observations. The dashed line represents the organic carbon–normalized ESG.

Section 7

Conclusions

The technical basis and data that support the use of the ESGs have been presented for nonionic organic chemicals. The use of organic carbon normalization is equivalent to using interstitial water normalization as a means of accounting for varying bioavailability (Figures 2-2, 2-3, 3-1 through 3-4, and 4-21 through 4-23). The variation in organism body burden across sediments is significantly reduced if organic carbon and lipid normalization are used (Figures 4-24 through 4-26). For contaminated sediments, particle size effects are removed if organic carbon–normalized concentrations are compared (Figures 4-9, 4-10, and 4-12 through 4-14). These data establish that organic carbon is an appropriate normalization for partitioning between freely-dissolved chemical and sediment-bound chemical (Figure 4-3).

Interpretation of interstitial water chemistry data for highly hydrophobic chemicals is complicated by chemical complexing to DOC (Figure 4-5). Partitioning between interstitial water and sediment organic carbon from field-collected sediments can be clarified if DOC complexing is taken into account (Figures 4-16 and 4-17). However, the complexed chemical appears not to be bioavailable (Figure 4-7).

These observations are consistent with the EqP model, which assumes the equivalence of water-only exposure and the exposure from interstitial water and/ or sediment organic carbon. ESGs are based on organic carbon normalization because interstitial water normalization is complicated by DOC complexing for highly hydrophobic chemicals.

The justification for using the FCV from the WQC to define the effects level for benthic organisms has also been discussed. Water column and benthic organisms appear to have similar sensitivities when both the FAVs are compared for individual chemicals (Figure 5-1) and when data from all chemicals are pooled (Figure 5-2). Benthic colonization experiments also demonstrate that WQC FCVs can be used to predict effects concentrations for benthic organisms. A direct statistical test of the equality of the distributions can be used to confirm or refute this assumption for individual chemicals (Figure 6-1).

Equilibrium partitioning cannot remove all of the observed variation from sediment-to- sediment. It does, however, reduce the much larger sediment-to-sediment variation that exists if no corrections for bioavailability are made (Figures 3-1 to 3-4). A variation factor of approximately two to three remains (Figures 2-2 and 2-3), which includes measurement and other sources of variability. This is not unexpected, because EqP is an idealization of the actual situation. Other factors that are not considered in the model have roles in determining biological effects. Hence, it is recognized that a quantification of the uncertainty should accompany the ESG that reflects these additional sources of variation.

7.1 Research Needs

Final validation of ESG will come from field studies designed to evaluate the extent to which biological effects can be predicted from ESG. The colonization experiments (Table 5-3) are a laboratory simulation of a field validation. ESGs may be easier to validate than WQC because determining the organism exposure is more straightforward (chemical concentrations are relatively stable in bedded sediments and many benthic organisms show relatively small home ranges, unlike many pelagic organisms). Benthic population exposure is quantified by the organic carbon–normalized sediment concentration.

It has been suggested that the kinetics of PAH desorption from sediments control the chemical body burden of a benthic amphipod (Landrum, 1989). The extent to which kinetics can be important in field situations is unknown at present, and field studies would be an important component in examining this question. In addition, more laboratory sediment toxicity tests, particularly chronic tests involving multiple sediments, would also be helpful. In a typical practical application of an ESG, mixtures of chemicals are involved. The extension of EqP methodology to mixtures would be of great practical value, and for these reasons EPA has also developed ESGs for mixtures of metals (cadmium, copper, lead, nickel, silver, and zinc) (U.S. EPA, 2000f), as well as for mixtures of PAHs (U.S. EPA, 2000b).

The EqP method is presently restricted to computing effects-based guidelines for the protection of benthic organisms. Direct extension of this methodology for computing sediment guidelines that are protective of human health, wildlife, and marketability of fish and shellfish requires that the equilibrium assumption be extended to the water column and to water column organisms. This assumption is, in general, untenable. Water column concentrations can be much lower than interstitial water concentrations if sufficient dilution flow is present. Conversely, upper-trophic-level organisms are at concentrations well above equilibrium values (Connolly and Pederson, 1988). Hence, the application of the final residue values from the WQC for the computation of ESGs, as was done for certain interim criteria (Cowan and Di Toro, 1988), is not technically justifiable. At present, organism lipid-to-sediment organic carbon ratios, that is, BSAFs (Equation 4-26), might be useful in estimating the concentration of contaminants in benthic species, for which the assumption of equilibrium is reasonable. EPA is currently refining methods for predicting chemical concentrations in tissues of organisms in upper trophic levels; see U.S. EPA (1998) for details. However, at this time, the ESGs do not protect against synergistic effects, or other interactions with non-ESG chemicals. Therefore, they do not address effects mediated through bioaccumulation and food-chain transfer, and thus are not protective of wildlife or human health endpoints.

Section 8

References

Adams WJ. 1987. Bioavailability of neutral lipophilic organic chemicals contained in sediments: A review. In Dickson KL, Maki AW, Brungs WA, eds, *Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems*. Pergamon Press, New York, NY, pp 219–244.

Adams WJ, Kimerle RA, Mosher RG. 1983. Aquatic safety assessment of chemicals sorbed to sediments. Special Study Report No. ES-EAG-83-1. Monsanto Company, Environmental Sciences Center, St. Louis, MO.

Adams WJ, Kimerle RA, Mosher RG. 1985. Aquatic safety assessment of chemicals sorbed to sediments. In Cardwell RD, Purdy R, Bahner RC, eds, *Aquatic Toxicology and Hazard Assessment: Seventh Symposium*. STP 854. American Society for Testing and Materials, Philadelphia, PA, pp 429–453.

American Society for Testing and Materials (ASTM). 1992. Standard guide for conducting 10-day static sediment toxicity tests with marine and estuarine amphipods. E 1367-92. *ASTM 1992 Annual Book of Standards*. Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1994a. Standard guide for designing biological tests with sediments. E 1525-94a. *ASTM 1994 Annual Book of Standards*. Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1994b. Standard guide for collection, storage, characterization, and manipulation of sediments for toxicological testing. E 1391-94. *ASTM 1994 Annual Book of Standards*. Philadelphia, PA.

American Society for Testing and Materials (ASTM). 1996. Standard guide for conducting acute toxicity tests on test materials with fishes, macroinvertebrates, and amphibians. E 729-96. *ASTM 1996 Annual Book of Standards*. West Conshohocken, PA.

Barrick RC, Becker DS, Weston DP, Ginn TC. 1985. Commencement Bay nearshore/tideflats remedial investigation. EPA 910/9-85-134b. Final Report. U.S. Environmental Protection Agency, Washington, DC.

Battelle. 1984. Sediment quality criteria development workshop. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Benes P, Majer V. 1980. *Trace Chemistry of Aqueous Solutions*. Elsevier, New York, NY.

Bierman VJ Jr. 1990. Equilibrium and biomagnification partitioning of organic chemicals in benthic animals. *Environ Sci Technol* 24:1407–1412.

Bolton SH, Breteler RJ, Vigon BW, Scanlon JA, Clark SL. 1985. National perspective on sediment quality. EPA 68-01-6986. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Brownawell BJ, Farrington JW. 1985. Partitioning of PCBs in marine sediments. In Sigleo AC, Hattori A, eds, *Marine and Estuarine Geochemistry*. Lewis Publishers, Chelsea, MI, pp 97–119.

Brownawell BJ, Farrington JW. 1986. Biogeochemistry of PCBs in interstitial waters of a coastal marine sediment. *Geochim Cosmochim Acta* 50:157–169.

Carter CW, Suffett IH. 1983. Interactions between dissolved humic and fulvic acids and pollutants in aquatic environments. In Swann RL, Eschenroeder A, eds, *Fate of Chemicals in the Environment*. ACS Symposium Series 225. American Chemical Society, Washington, DC, pp 215–230.

Chapman GA. 1987. Establishing sediment criteria for chemicals—regulatory perspective. In Dickson KL, Maki AW, Brungs WA, eds, *Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems*. Pergamon Press, New York, NY, pp 355–376.

Chapman PM, Long ER. 1983. The use of bioassays as part of a comprehensive approach to marine pollution assessment. *Mar Pollut Bull* 14:81–84.

Chiou CT. 1985. Partition coefficients of organic compounds in lipid-water systems and correlations with fish bioconcentration factors. *Environ Sci Technol* 19:57–62.

Connolly JP. 1991. Application of a food chain model to polychlorinated biphenyl contamination of the lobster and winter flounder food chains in New Bedford Harbor. *Environ Sci Technol* 25:760–770.

Connolly JP, Pederson CJ. 1988. A thermodynamic-based evaluation of organic chemical accumulation in aquatic organisms. *Environ Sci Technol* 22:99–103.

Cowan CE, Zarba CS. 1987. Regulatory applications of sediment quality criteria. EPA 68-01-6986. Final Report. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Cowan DE, Di Toro DM. 1988. Interim sediment criteria values for nonpolar hydrophobic compounds. Final Report. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Curl RL, Keolelan GA. 1984. Implicit-adsorbate model for apparent anomalies with organic adsorption on natural absorbents. *Environ Sci Technol* 18:916–922.

Delbeke K, Claude RJ, Bossicart M. 1990. Organochlorides in different fractions of sediments and different planktonic compartments of the Belgian Continental Shelf and Schelt Estuary. *Environ Pollut* 66:325–349.

DeWitt TH, Ozretich RJ, Swartz RC, Lamberson JO, Schults DW, Ditsworth GR, Jones JKP, Hoselton L, Smith LM. 1992. The influence of organic matter quality on the toxicity and partitioning of sediment-associated fluoranthene. *Environ Toxicol Chem* 11:197–208.

Dickson KL, Maki AW, Brungs WA, eds. 1987. *Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems*. Pergamon Press, New York, NY.

Di Toro DM. 1985. A particle interaction model of reversible organic chemical sorption. *Chemosphere* 14:1503–1538.

Di Toro DM, Horzempa L. 1983. Reversible and resistant component model of hexachlorobiphenyl adsorption-desorption: Resuspension and dilution. In Mackay D, Paterson S, Eisenreich SJ, Simmons MS, eds, *Physical Behavior of PCBs in the Great Lakes*. Ann Arbor Science, Ann Arbor, MI, pp 89–114.

Di Toro DM, Mahony JD, Kirchgraber PR, O'Byrne AL, Pasquale LR, Piccirilli DC. 1986. Effects of nonreversibility, particle concentration, and ionic strength on heavy metal sorption. *Environ Sci Technol* 20:55.

Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environ Toxicol Chem* 10:1541-1583.

Eadie BJ, Morehead NR, Landrum PF. 1990. Three-phase partitioning of hydrophobic organic compounds in Great Lakes waters. *Chemosphere* 20:161–178.

El-Shaarawi AH, Dolan DM. 1989. Maximum likelihood estimation of water quality concentrations from censored data. *Can J Fish Aquat Sci* 46:1033–1039.

Evans KM, Gill RA, Robotham PWJ. 1990. The PAH and organic content of sediment particle size fractions. *Water Air Soil Pollut* 51:13–31.

Gobas F, Zhang X. 1994. Interactions of organic chemicals with particulate and dissolved organic matter in the aquatic environment. In Hamelink et al. (eds), *Bioavailability: Physical, Chemical, and Biological Interactions*. Lewis Publishers, Boca Raton, FL, pp 83–92.

Grathwohl P. 1990. Influence of organic matter from soils and sediments from various origins on the sorption of some chlorinated aliphatic hydrocarbons: Implications on K_{oc} correlations. *Environ Sci Technol* 24:1687–1693.

Gschwend PM, Wu S. 1985. On the constancy of sediment-water partition coefficients of hydrophobic organic pollutants. *Environ Sci Technol* 19:90–96.

Hamilton MA, Russo RC, Thurston RV. 1977. Trimmed Spearman-Karber method of estimating median lethal concentrations in toxicity bioassays. *Environ Sci Technol* 11:714–19. Correction 12:417 (1978).

Hansen DJ. 1974. Aroclor 1254: Effect on composition of developing estuarine animal communities in the laboratory. *Contrib Mar Sci* 18:19–33.

Hansen DJ, Tagatz ME. 1980. A laboratory test for assessing the impacts of substances on developing communities of benthic estuarine organisms. In Eaton JG, Parrish PR, Hendricks AC, eds, *Aquatic Toxicology: Third Symposium*. STP 707. American Society for Testing and Materials, Philadelphia, PA, pp 40–57.

Hoke RA, Ankley GT. 1992. Results of Airport Pond dieldrin-spiked sediments. Memorandum to Hansen D and Di Toro D, HydroQual, Inc., Mahwah, NJ. January 27, 1992. 8 pp.

Hoke RA, Kosian PA, Ankley GT, Cotter AM, Vandermeiden FM, Phipps GL, Durhan EJ. 1995. Check studies with *Hyalella azteca* and *Chironomus tentans* in support of the development of a sediment quality criterion for dieldrin. *Environ Toxicol Chem* 14:435–443.

Iglesias-Jimenez E, Poveda E, Sanchez-Martin M.J, Sanchez-Camazano M. 1997. Effect of the nature of exogenous organic matter on pesticide sorption by the soil. *Arch Environ Contam Toxicol* 33:117–124.

JRB Associates. 1984. Background and review document on the development of sediment criteria. EPA 68-01-6388. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Karickhoff SW. 1984. Organic pollutant sorption in aquatic systems. *J Hydraul Div ASCE* 110:707–735.

Karickhoff SW, Long, JM. 1995. Internal report on summary of measured, calculated and recommended LogK_{OW} values. Internal Report. Environmental Research Laboratory, U.S. Environmental Protection Agency, Athens, GA.

Karickhoff SW, Morris KR. 1985. Sorption dynamics of hydrophobic pollutants in sediment suspensions. *Environ Toxicol Chem* 4:469–479.

Lake JL, Rubinstein N, Pavignano S. 1987. Predicting bioaccumulation: Development of a simple partitioning model for use as a screening tool for regulating ocean disposal of wastes. In Dickson KL, Maki AW, Brungs WA, eds, *Fate and Effects of Sediment-Bound Chemicals in Aquatic Systems*. Pergamon Press, Elmsford, NY, pp 151–166.

Landrum PF. 1989. Bioavailability and toxicokinetics of polycyclic aromatic hydrocarbons sorbed to sediments for the amphipod *Pontororeia hoyi*. *Environ Sci Technol* 23:588–595.

Landrum PF, Nihart SR, Eadie BJ, Herche LR. 1987. Reduction in bioavailability of organic contaminants to the amphipod *Pontoporeia hoyi* by dissolved organic matter of sediment interstitial waters. *Environ Toxicol Chem* 6:11–20.

Landrum PF, Reinhold MD, Nihart SR, Eadie BJ. 1985. Predicting the bioavailability of organic xenobiotics to *Pontoporeia hoyi* in the presence of humic and fulvic materials and natural dissolved organic matter. *Environ Toxicol Chem* 4:459–467.

Leo A, Hansch C, eds. 1986. *Log(P) Database and Related Parameters*. Pomona College, Claremont, CA.

Leo AJ. 1972. Relationships between partitioning solvent systems. In Gould RF, ed, *Biological Correlations—The Hansch Approach*. Advances in Chemistry Series 114. American Chemical Society, Washington, DC.

Long ER, Chapman PM. 1985. A sediment quality triad: Measures of sediment contamination, toxicity and infaunal community composition in Puget Sound. *Mar Pollut Bull* 16:405–415.

Long ER, Morgan LG. 1990. The potential for biological effects of sediment sorbed contaminants tested in the National Status and Trends Program. NOS OMA 52. Technical Memorandum. National Oceanic and Atmospheric Administration, Office of Oceanography and Marine Assessment, Seattle, WA.

Long JM, Karickhoff SW. 1996. Protocol for setting Kow values. Draft, September 5, 1996. U.S. Environmental Protection Agency, National Exposure Research Laboratory, Ecosystems Research Division. Athens, GA. 19pp.

Luoma SN, Bryan W. 1981. A statistical assessment of the form of trace metals in oxidized sediments employing chemical extractants. *Sci Total Environ* 17:165–196.

Mackay D. 1979. Finding fugacity feasible. *Environ Sci Technol* 13:1218.

Mackay D, Powers B. 1987. Sorption of hydrophobic chemicals from water: A hypothesis for the mechanism of the particle concentration effect. *Chemosphere* 16:745–757.

McCarthy JF, Jimenez BD. 1985. Reduction in bioavailability to bluegills of polycyclic aromatic hydrocarbons bound to dissolved humic material. *Environ Toxicol Chem* 4:511–521.

McFarland VA. 1984. Activity-based evaluation of potential bioaccumulation for sediments. In Montgomery RL, Leach JW, eds, *Dredging and Dredged Material Disposal*. Vol 1. American Society of Civil Engineers, New York, NY, pp 461–467.

Muir DCG, Rawn GP, Townsend BE, Lockhart WL, Greenhalgh R. 1985. Bioconcentration of cypermethrin, deltamethrin, fenvalerate, and permethrin by *Chironomus tentans* larvae in sediment and water. *Environ Toxicol Chem* 4:51–61.

National Academy of Sciences (NAS). 1973. Water quality criteria, 1972. EPA-R3-73-033. National Academy of Sciences, U.S. Environmental Protection Agency, Washington, DC.

National Oceanic and Atmospheric Administration (NOAA). 1991. Second summary of data on chemical contaminants in sediments from the National Status and Trends Program. NOS OMA 59. Technical Memorandum. Office of Oceanography and Marine Assessment, Rockville, MD.

Nebeker AV, Schuytema GS, Griffis WL, Barbitta JA, Carey LA. 1989. Effect of sediment organic carbon on survival of *Hyalella azteca* exposed to DDT and endrin. *Environ Toxicol Chem* 8:705–718.

Nelson DM, Penrose WR, Karttunen JO, Mehlhaff P. 1985. Effects of dissolved organic carbon on the adsorption properties of plutonium in natural waters. *Environ Sci Technol* 19:127–131.

Noreen EW. 1989. *Computer Intensive Methods for Testing Hypotheses: An Introduction*. John Wiley, New York, NY.

O'Connor DJ, Connolly J. 1980. The effect of concentration of adsorbing solids on the partition coefficient. *Water Resour* 14:1517–1523.

O'Connor TP. 1991. Concentrations of organic contaminants in mollusks and sediments at NOAA National Status and Trends sites in the coastal and estuarine United States. *Environ Health Perspect* 90:69–73.

Oliver BG. 1987. Biouptake of chlorinated hydrocarbons from laboratory-spiked and field sediments by oligochaete worms. *Environ Sci Technol* 21:785–790.

Pavlou SP, Weston DP. 1983a. Initial evaluation of alternatives for development of sediment related criteria for toxic contaminants in marine waters, Puget Sound. Phase I. Development of conceptual framework. Final Technical Report. JRB Associates, Bellevue, WA.

Pavlou SP, Weston DP. 1983b. Initial evaluation of alternatives for development of sediment related criteria for toxic contaminants in marine waters (Puget Sound) — Phase I and Phase II. EPA 68-01-6388. Office of Water Regulations and Standards, Criteria and Standards Division, U.S. Environmental Protection Agency, Washington, DC.

Pierard C, Budzinski H, Garrigues P. 1996. Grain-size distribution of polychlorobiphenyls in coastal sediments. *Environ Sci Technol* 30:2776–2783.

Prahl FG. 1982. The geochemistry of polycyclic aromatic hydrocarbons in Columbia River and Washington coastal sediments. PhD thesis. Washington State University, Pullman, WA.

Prytula TM, Pavlostathis SG. 1996. Extraction of sediment-bound chlorinated organic compounds: Implications on fate and hazard assessment. *Wat Sci Tech* 33:247–254.

Rubinstein NI, Lake JL, Pruell RJ, Lee H II, Taplin B, Heltshe J, Bowen R, Pavignano S. 1988. Predicting bioaccumulation of sediment-associated organic contaminants: Development of a regulatory tool for dredged material evaluation. Technical Report D-87-1. U.S. Environmental Protection Agency, Narragansett, RI, for the U.S. Army Corps of Engineers Waterway Experiment Station, Vicksburg, MS.

Sadler PM. 1981. Sediment accumulation rates and the completeness of stratigraphic sections. *J Geol* 89:569–584.

Schuytema GS, Nebeker AV, Griffis WL, Miller CE. 1989. Effects of freezing on toxicity of sediments contaminated with DDT and endrin. *Environ Toxicol Chem* 8:883–891.

Schwarzenbach RP, Gschwend PM, Imboden DM. 1993. Sorption: Solid-aqueous solution exchange. In *Environmental Organic Chemistry.* John Wiley, New York, NY. pp 255–341.

Socha SB, Carpenter R. 1987. Factors affecting pore water hydrocarbon concentrations in Puget Sound sediments. *Geochim Cosmochim Acta* 51:1237–1284.

Stehly GR. 1991. Memorandum to W. Berry, National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, Narragansett, RI, April 25, 1993. 1 pp.

Stephan CE, Mount DI, Hansen DJ, Gentile JH, Chapman GA, Brungs WA. 1985. Guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. PB85-227049. National Technical Information Service (NTIS), Springfield, VA.

Stumm W, Morgan JJ. 1970. *Aquatic Chemistry.* Wiley-Interscience, New York, NY.

Swartz RC. 1991. Acenaphthene and phenanthrene files. Memorandum to Hansen D, Great Lakes Environmental Center, Traverse City, MI. June 26, 1991. 160 pp.

Swartz RC, Schults DW, DeWitt TH, Ditsworth GR, Lamberson JO. 1990. Toxicity of fluoranthene in sediment to marine amphipods: A test of the equilibrium-partitioning approach to sediment quality criteria. *Environ Toxicol Chem* 9:1071–1080.

Tagatz ME. 1977. Effects of pentachlorophenol on the development of estuarine communities. *J Toxicol Environ Health* 3:501–506.

Tagatz ME, Ivey JM. 1981. Effects of fenvalerate on field- and laboratory-developed estuarine benthic communities. *Bull Environ Contam Toxicol* 27:256–267.

Tagatz ME, Deans CH, Plaia GR, Pool JD. 1983. Impact on and recovery of experimental macrobenthic communities exposed to pentachlorophenol. *Northeast Gulf Sci* 6:131–136.

Tagatz ME, Gregory NR, Plaia GR. 1982. Effects of chlorpyrifos on field- and laboratory-developed estuarine benthic communities. *J Toxicol Environ Health* 10:411–421.

Tagatz ME, Plaia GR, Deans CH. 1985. Effects of 1,2,4-trichlorobenzene on estuarine macrobenthic communities exposed via water and sediment. *Ecotoxicol Environ Saf* 10:351–360.

Thomann RV, Connolly JP. 1984. Model of PCB in the Lake Michigan lake trout food chain. *Environ Sci Technol* 18:65–71.

Thomann RV, Connolly JP, Parkerton TF. 1992. An equilibrium model of organic chemical accumulation in aquatic foodwebs with sediment interaction. *Environ Toxicol Chem* 11:615–629.

Thurman EM. 1985. *Organic Geochemistry of Natural Waters.* Martinus Nijhoff/Dr. W. Junk Publ., Dordrecht, The Netherlands.

U.S. Army Corps of Engineers (COE). 1991. Monitoring Program for San Francisco Bay Sediments. 1988 to 1990. Memorandum to D. Di Toro, HydroQual, Inc., Mahwah, NJ, 1991.

U.S. Environmental Protection Agency. 1987. Quality criteria for water, 1986. EPA 440/5-86-001. Office of Water Regulations and Standards, Washington, DC.

U.S. Environmental Protection Agency. 1989. Handbook: water quality control information systems, STORET. Office of Water and Hazardous Materials, Washington, DC.

U.S. Environmental Protection Agency. 1994. Methods for assessing the toxicity of sediment-associated contaminants with estuarine and marine amphipods. EPA/600/R-94/025. Office of Research and Development, Washington, DC.

U.S. Environmental Protection Agency. 1995. Water quality guidance for the Great Lakes System: Supplementary information document. EPA-820-B-95-001. Office of Water, Washington, DC.

U.S. Environmental Protection Agency. 1996. Draft protocol for setting K_{OW} values. National Exposure Research Laboratory, Ecosystems Research Division, Athens, GA.

U.S. Environmental Protection Agency. 1998. Ambient water quality criteria derivation methodology: Human health. Technical support document, final draft. EPA-822-B-98-005. Washington, DC.

U.S. Environmental Protection Agency. 1999. National recommended water quality criteria-correction. EPA-822-2-99-001. April 1999. Washington, DC.

U.S. Environmental Protection Agency. 2000a. Implementation framework for use of equilibrium partitioning sediment guidelines (ESGs). Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000b. Equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: PAH mixtures. Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000c. Equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: Dieldrin. EPA-822-R-00-003. Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000d. Equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: Endrin. EPA-822-R-00-004. Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000e. Methods for the derivation of site-specific equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: Nonionic organics. EPA-822-R-00-002. Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000f. Equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: Metal mixtures (cadmium, copper, lead, nickel, silver, and zinc). EPA-822-R-00-005. Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency. 2000g. Equilibrium partitioning sediment guidelines (ESGs) for the protection of benthic organisms: Nonionics compendium. EPA-822-R-00-06. Office of Science and Technology and Office of Research and Development, Washington, DC.

Voice TC, Rice CP, Weber WJ, Jr. 1983. Effect of solids concentration on the sorptive partitioning of hydrophobic pollutants in aquatic systems. *Environ Sci Technol* 17:513–518.

Woodburn KB, Doucette WJ, Andren AW. 1984. Generator column determination of octanol/water partition coefficients for selected polychlorinated biphenyl congeners. *Environ Sci Technol* 18:457–459.

Wu SC, Gschwend PM. 1986. Sorption kinetics of hydrophobic organic compounds to natural sediments and soils. *Environ Sci Technol* 20:717–725.

Xing B, McGill WB, Dudas MJ. 1994. Cross-correlation of polarity curves to predict partition coefficients of nonionic organic contaminants. *Environ Sci Technol* 28:1929–1933.