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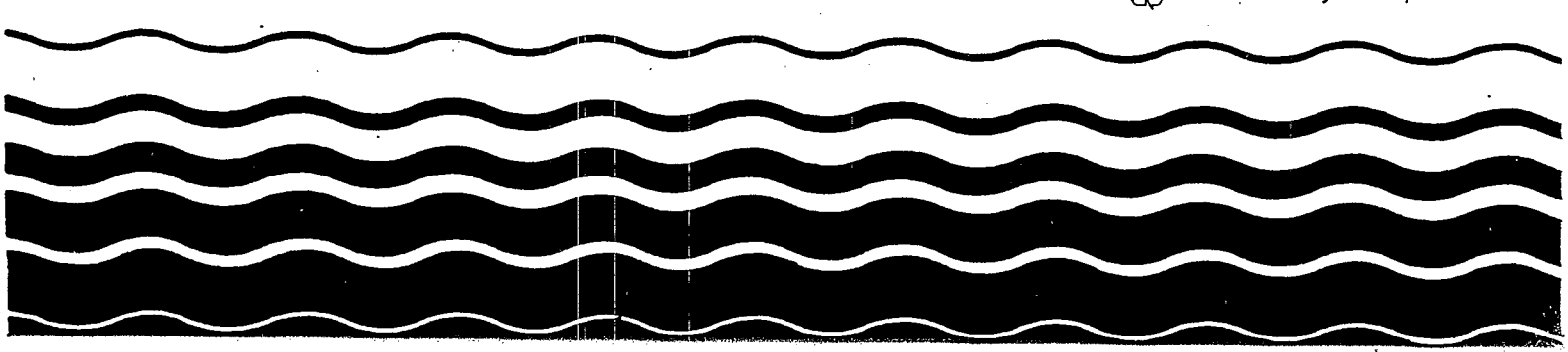
Technical Basis for Deriving Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic Organisms by Using Equilibrium Partitioning



This document presents the technical basis EPA has used in establishing the proposed methodology for deriving sediment quality criteria for the protection of benthic organisms from nonionic organic chemicals. It was issued in support of EPA regulations and policy initiatives involving the application of biological and chemical assessment techniques to control toxic pollution to surface waters and sediments. This document does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made applying the law and regulations on the basis of specific facts when permits are issued or regulations promulgated. This document is expected to be revised periodically to reflect advances in this rapidly evolving area.

This report has been reviewed by the Health and Ecological Criteria Division, Office of Science and Technology, U.S. Environmental Protection Agency, as well as other pertinent and interested offices in the Agency, and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendations for use.

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Abstract

The purpose of this report is to present the technical basis for establishing sediment quality criteria for nonionic organic chemicals, using equilibrium partitioning (EqP). Equilibrium partitioning is chosen because it addresses the two principal technical issues that must be resolved: the varying bioavailability of chemicals in sediments and the choice of the appropriate biological effects concentration.

The data that are 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 found that if the different sediments in each experiment are compared, there is essentially no relationship between sediment chemical concentrations on a dry weight basis and biological effects. However, if the chemical concentrations in the pore 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 (typically within a factor of two) for the different sediments. 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 rationalizes these results by assuming that the partitioning of the chemical between sediment-organic carbon and pore water is at equilibrium. In each of these phases, the fugacity or activity of the chemical is the same at equilibrium. As a consequence, it is assumed that the organism receives an equivalent exposure from a water only-exposure or from any equilibrated phase: either from pore water via respiration; or from sediment carbon, via ingestion; or from a mixture of the routes. Thus, the pathway of exposure is not significant. The biological effect is produced by the chemical activity of the single phase or the equilibrated system.

Sediment quality criteria (SQC) for nonionic organic chemicals are based on the chemical concentration in sediment organic carbon. For highly hydrophobic chemicals this is necessary because the pore water concentration is, for those chemicals, no longer a good estimate of the chemical activity. The pore 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. Using the chemical concentration in sediment organic carbon eliminates this ambiguity.

SQC also require that a chemical concentration be chosen that is sufficiently protective of benthic organisms. The final chronic value (FCV) from the U.S. Environmental Protection Agency (EPA) water quality criteria is proposed. An analysis of the data compiled in the water quality criteria documents demonstrates that benthic species, defined as either epibenthic or infaunal species, have a similar sensitivity to water column species. 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 the use of the FCV. Thus, if effects concentrations in sediments can be accurately predicted using the K_{oc} and data from water-only tests, the SQC protecting benthic species can be predicted using the K_{oc} and FCV.

Equilibrium partitioning cannot remove all the variation in the experimentally observed sediment-effects concentration and the concentration predicted from water-only exposures. A variation factor of approximately four to five remains. Thus, a quantification of this uncertainty should accompany the SQC.

The derivation of SQC requires that a minimum database be available. This includes: (1) the octanol/water partition coefficient of the chemical, which should be measured with modern experimental techniques, which appear to remove the large variation in reported values, (2) the derivation of the final chronic value, which should also be updated to include the most recent toxicological information, and (3) an SQC check test to establish variation of the EqP prediction. The SQC is then the FCV x K_{oc} with confidence limits based on SQC check tests.

OVERVIEW

This report presents the technical basis for establishing sediment quality criteria (SQC) for nonionic organic chemicals using the equilibrium partitioning (EqP) method. The term *sediment quality criteria*, as used herein, refers to numerical concentrations for individual chemicals that are applicable across the range of sediments encountered in practice. Sediment quality criteria are intended to be predictive of biological effects. As a consequence, they can be used in much the same way as final chronic values (FCV) are used in water quality criteria—as the concentration of a chemical that is protective of benthic aquatic life.

The specific regulatory uses of SQC have not been established. However, the range of potential applications is quite large because the need for the evaluation of potentially contaminated sediments arises in many contexts. SQC are meant to be used with direct toxicity testing of sediments as a method of evaluation. They provide a chemical by chemical specification of what sediment concentrations are protective of benthic aquatic life.

This overview (Section 1) summarizes the evidence and the major lines of reasoning of the EqP methodology, with supporting references cited in the body of the report. Section 2 reviews the background that led to the need for SQC and also the selection of the EqP methodology. Section 3 reviews the development of concentration-response curves for pore-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 Water Quality Criteria (WQC) documents to show the applicability of WQC as the effects levels for benthic organisms. Section 6 reviews the computation of an SQC and presents an analysis for quantifying the uncertainty associated with SQC. This section also presents minimum data requirements and example calculations and compares the SQC computed for five chemicals to field data. Section 7 presents conclusions and further research needs. Section 8 lists the references used in this document.

Toxicity and Bioavailability of Chemicals in Sediments

Establishing SQC requires a determination of the extent of the bioavailability of sediment associated chemicals. 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., micrograms chemical per gram sediment [μg/g]) can exhibit a range in toxicity in different sediments. If the purpose of SQC 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 criteria. Otherwise the criteria cannot be presumed to be applicable across sediments of differing properties.

The importance of this issue cannot be overemphasized. For example, if 1 μg/g of Kepone is the LC_{50} for an organism in one sediment and 35 μg/g is the LC_{50} in another sediment, then unless the cause of this difference can be associated with some explicit sediment properties it is not possible to decide what would be the LC_{50} of a third sediment without performing a toxicity test. The results of toxicity tests used to establish the toxicity of chemicals in sediments would not be generalizable 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 differences was understood, it would be fruitless to attempt to establish WQC. For this reason, bioavailability is a principal focus of this report.

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 (micrograms chemical per gram sediment), but to the interstitial water or pore water concentration (micrograms chemical per liter pore water). In addition, the effects concentration found for the pore 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 SQC. 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 rationalized by assuming that the pore water and sediment carbon are in equilibrium and that the concentrations are related by a partition coefficient, K_{OC}, as shown in Figure 1. The name *equilibrium partitioning* (EqP) describes this assumption. The rationalization for the equality of water-only and sediment-exposure-effects concentrations on a pore water basis is that the sediment-pore water equilibrium system (Fig. 1, right) provides the same exposure as a water-only exposure (Fig. 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; therefore, predictions from the model have an inherent uncertainty. The data presented below illustrate the degree to which EqP can rationalize the observations.

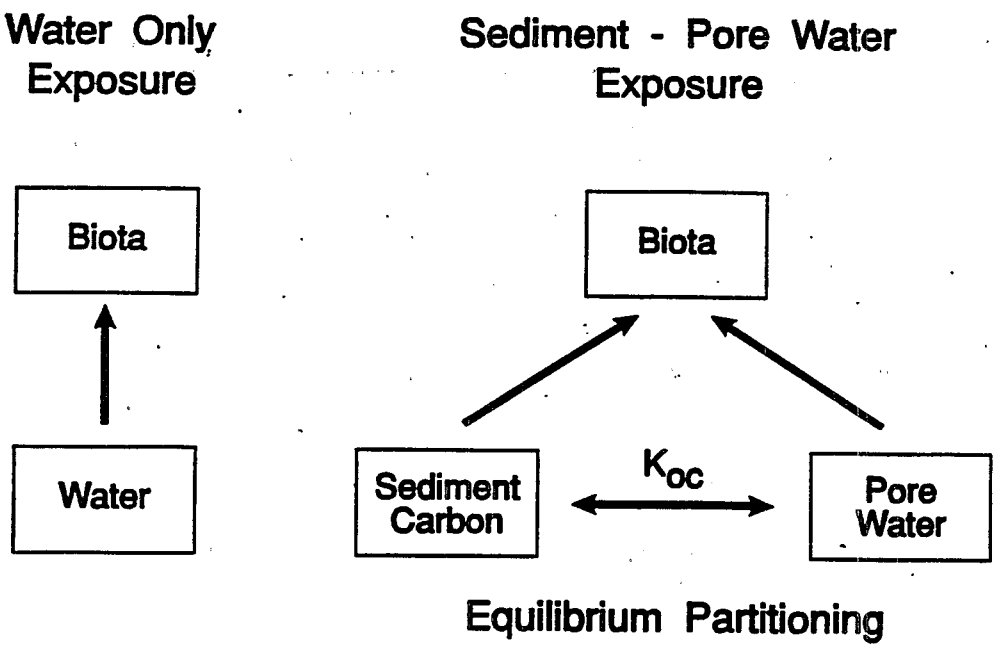


Figure 1.—Diagram of the organism exposure routes for a water-only exposure (left and a sediment exposure (right). *Equilibrium partitioning* refers to the assumption that an equilibrium exists between the chemical sorbed to the particulate sediment organic carbon and the pore water. K_{oc} is the organic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

Figure 2 presents mortality data for various chemicals and sediments compared to pore water concentrations when normalized on a toxic unit basis. Pore water toxic units are the ratio of the measured pore water concentration to the LC_{50} from water-only toxicity tests. Three different sediments are tested for each chemical as indicated. The EqP model predicts that the pore water LC_{50} will equal the water-only LC_{50} which is obtained from a separate water-only exposure toxicity test. Define:

pore water toxic unit

$$= \frac{\text{(pore water concentration)}}{\text{(water-only } LC_{50})} \qquad (1)$$

Therefore, a toxic unit of one occurs when the pore water concentration equals the water-only LC_{50}, at which point it would be predicted that 50 percent mortality would be observed. The correlation of observed mortality to predicted pore water toxic units in Figure 2 demonstrates (a) the efficacy of using pore water concentrations to remove sediment-to-sediment differences and (b) 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 a pore water basis suggests that the route of exposure is via pore water. However, the equality of the effects concentration on a sediment-organic carbon basis, which is demonstrated below, suggests that the ingestion of sediment-organic carbon is the primary route of exposure. It is important to realize that if the sediment and pore water are in equilibrium, then the effective exposure concentration is the same regardless of exposure route. Therefore, it is not possible to determine the primary route of exposure from equilibrated experiments.

Whatever the route of exposure, the correlation to pore water suggests that if it were possible to either measure the pore 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, the partitioning of chemicals between the solid and the liquid phase in a sediment becomes a necessary component for establishing SQC.

In addition, if it were true that benthic organisms are as sensitive as water column organisms—and the evidence to be presented appears to support this supposition—then SQC could be established using the FCV from WQC documents as the effects concentration for benthic organisms. The apparent equality between the effects concentration as meas-

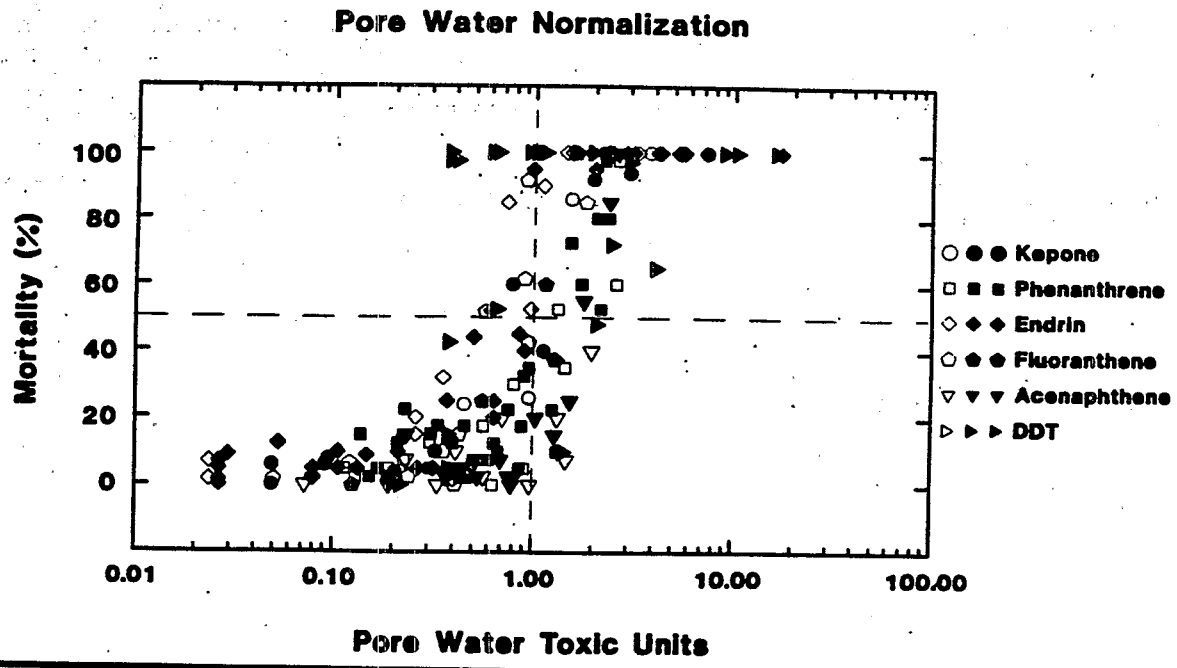


Figure 2.—Mortality versus predicted pore water toxic units for five chemicals and three sediments per chemical. Sediment types are indicated by the single hatching (lowest organic carbon content), cross-hatching (intermediate organic carbon content), and filled symbols (highest organic carbon content). See Tables 1 and 2 for data sources. Predicted pore water toxic units are the ratio of the pore water concentration to the water-only LC_{50} (Eqn. 1).

ured in pore water and in water-only exposures (Fig. 2) supports using an effects concentration derived from water-only exposures.

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

$$SQC = K_p FCV \times 0.001 \frac{kg}{g} \qquad (2)$$

This is the fundamental equation from which SQC are generated. Its utility depends on the existence of a methodology for quantifying partition coefficients.

Partitioning of Nonionic Organic Chemicals

The 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 $f_{oc} \geq 0.2$ percent 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 pore water concentration, C_d, is given by

$$K_p = \frac{C_s}{C_d} = f_{oc} K_{oc} \qquad (3)$$

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/pore water partitioning, namely that $K_{oc} \approx K_{ow}$ for sediments.

Using Equations 2 and 3, a SQC is calculated from

$$SQC = f_{oc} K_{oc} FCV. \qquad (4)$$

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

$$\frac{SQC}{f_{oc}} = K_{oc} FCV. \qquad (5)$$

If we define

$$SQC_{oc} = \frac{SQC}{f_{oc}} \quad (6)$$

as the organic carbon-normalized SQC concentration (microgram chemical per gram organic carbon), then

$$SQC_{oc} = K_{oc}FCV. \quad (7)$$

Thus, we arrive at the following important conclusion: For a specific chemical having a specific K_{oc}, the organic carbon-normalized sediment concentration, SQC_{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*, or *DOC*. Although DOC affects the apparent pore water concentrations of highly hydrophobic chemicals, the DOC-bound fraction of the chemical appears not to be bioavailable and Equation 7 for SQC_{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 but restricted to nonionic organic chemicals for which organic carbon normalization applies. The concept of sediment toxic units 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 LC_{50} using K_{oc} and the water-only LC_{50}. That is,

$$\begin{pmatrix}\text{predicted}\\ \text{sediment}\\ \text{toxic unit}\end{pmatrix} = \frac{C_s/f_{oc}}{K_{oc}\,(\text{water-only } LC_{50})} \quad (8)$$

Figure 3 presents the percent mortality versus predicted sediment toxic units. The correlation is similar to that obtained using the pore water concentrations in Figure 2. The cadmium data are not included because its partitioning is not determined by

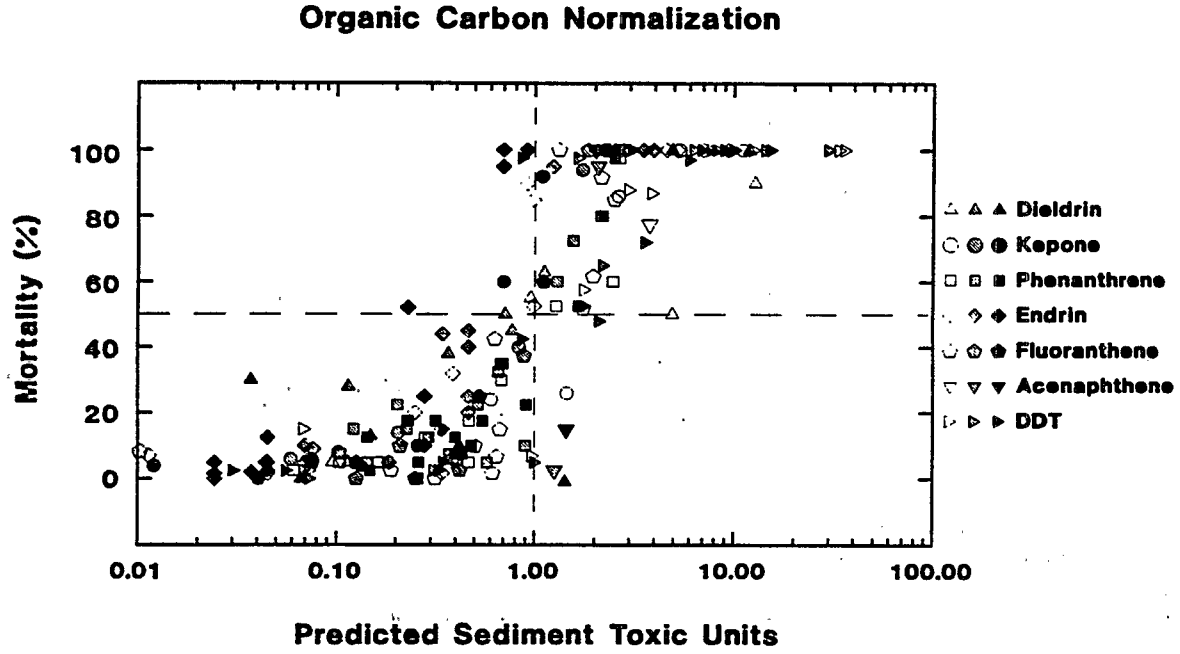


Figure 3.—Mortality versus predicted sediment toxic units. Predicted sediment toxic units are the ratio of the organic carbon-normalized sediment chemical concentration to the predicted sediment LC_{50} (Eqn. 8). Sediment types are indicated by the single hatching (lowest organic carbon content), cross-hatching (intermediate organic carbon content), and filled symbols (highest organic carbon content). See Tables 1 and 2 for data sources. K_{oc} values are computed from K_{ow} for DDT (5.84), endrin (4.84), fluoranthene (5.00), dieldrin (5.25), phenanthrene (4.46), and acenaphthene (3.76) with Equation 11. K_{ow} for DDT is the log average of the reported values in the Log P database [75]. The kepone K_{oc} is the log mean of the ratio of organic carbon-normalized kepone concentration to pore water-kepone concentration from the toxicity data set. K_{ow}s for the remaining compounds were computed by the U.S. EPA, Environmental Research Laboratory, Athens, Georgia. Methods are presented later in this document.

sediment organic carbon. The predicted sediment toxic units for each chemical follow a similar concentration-response curve independent of sediment type. The data demonstrate that 50 percent mortality occurs at about one sediment toxic unit, 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 and 3 should predict 50 percent mortality at one toxic unit. There is an uncertainty factor of approximately four to five in the results. 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.

Effects Concentration

The development of SQC 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 4 compares the acute values for the most sensitive benthic (epibenthic and infaunal) species to the most sensitive water column species. The data are from the 40 freshwater and 30 saltwater U.S. Environmental Protection Agency (EPA) criteria documents. Although there is considerable 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.

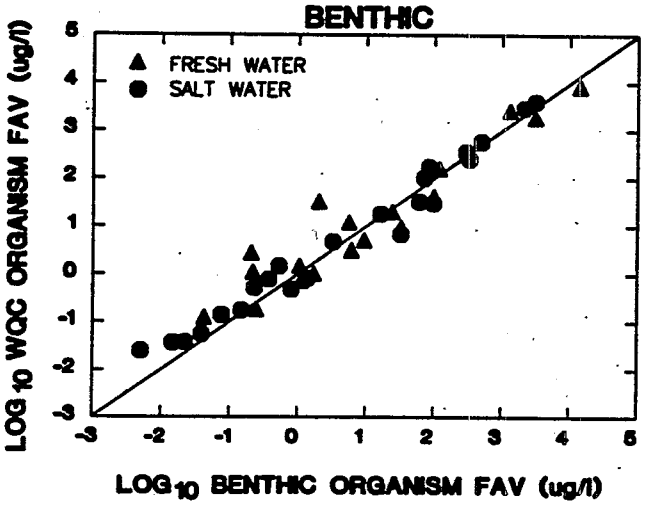


Figure 4.—A comparison of the final acute values (FAV) for water column versus benthic organisms. Each data point represents an FAV for a particular chemical in either a freshwater or a saltwater exposure. The data are from the WQC or draft criteria documents. See Table 4 for data sources.

Background

Under the Clean Water Act (CWA), the EPA is responsible for protecting the chemical, physical, and biological integrity of the nation's waters. In keeping with this responsibility, EPA published WQC in 1980 for 64 of the 65 priority pollutants and pollutant categories listed as toxic in the CWA. Additional water quality 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 human health and aquatic life. Although these criteria play an important role in assuring a healthy aquatic environment, they 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 the potential for continued environmental degradation even where water column contaminant levels comply with established WQC. The absence of defensible SQC makes it difficult to assess the extent of sediment contamination, implement measures to limit or prevent additional contamination from occurring, or to 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's Office of Science and Technology, Health and Ecological Criteria Division, established a research team to review alternative approaches to assess sediment contamination. Sediment contamination and related problems were the subject of a conference [1]. Alternative approaches to establishing SQC [2] and their merits and deficiencies were discussed [3]. Additional efforts were undertaken to identify the scope of national sediment contamination [4] and to review proposed approaches for addressing contaminated sediments [5, 6]. The 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 [7].

Rationale for Selecting the EqP Method

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

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

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

3. Sediment criteria provide a simple and cost-effective means of screening sediment measurements 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.

Relationship to WQC Methodology

The first question to be answered is this: Why not use the WQC procedure for the development of SQC? A detailed methodology has been developed that presents the supporting logic, establishes the required minimum toxicological data set, and specifies the numerical procedures to be used to calculate the criteria values [8]. Further, WQC developed through this methodology are routinely used in the regulation of effluent discharges. Therefore, it is only natural to extend these methods directly to sediments.

The WQC are based on total chemical concentration, so the transition to using dissolved chemical concentration for those chemicals that partition to a significant extent would not be difficult. The experience with site-specific modifications of the national WQC has demonstrated that the water-effect ratio, the ratio of chemical concentrations in site water to laboratory water that produces the same effect, has averaged 3.5 [9, 10]. The implication is that differences of this magnitude result from variations in site-specific water chemistry and are not an overwhelming impediment to nationally applicable numerical WQC.

The WQC are based on using the total chemical concentration as a measure of bioavailable chemical concentration. However, the use of total sediment chemical concentration as a measure of the bioavailable—or even potentially bioavailable—chemical concentration is not supported by the available data [11]. 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 data sets comprising benthic biological and chemical sampling [12-15].

Without a unique relationship between chemical measurements and biological end points that applies across the range of sediment properties that affect bioavailability, the cause and effect linkage is not supportable. If the same total chemical concentration is 100 times more toxic in one sediment than it is in another, how can we set universal SQC that depend only on the total sediment chemical concentration? Any SQC that are based on total sediment concentration have a potential uncertainty of this magnitude. Thus, bioavailability must be explicitly considered for any sediment evaluation methodology that depends on chemical measurements to establish defensible SQC.

Applications of SQC

SQC that are reasonably accurate in their ability to predict the potential for biological impacts are useful in many activities [16]. Sediment quality criteria can play a significant role in the identification, monitoring, and cleanup of contaminated sediment sites on a national basis and provide a basis to ensure that sites that are uncontaminated will remain so. In some cases, sediment criteria alone are sufficient to identify and establish cleanup levels for contaminated sediments. In other cases, they must be supplemented with biological sampling and testing before decisions are made.

In many ways, sediment criteria 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 quite some time, and controlling the source of that pollution (if the source still exists) may not be sufficient to alleviate the problem. The difficulty is compounded because the safe removal and treatment or disposal of contaminated sediments can be laborious and expensive.

Sediment criteria 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 criteria will be particularly valuable in monitoring applications in which sediment contaminant concentrations are gradually approaching the criteria. The comparison of field measurements to sediment criteria will provide reliable warning of potential problems. Such an early warning provides an opportunity to take corrective action before adverse impacts occur.

Toxicity and Bioavailability of Chemicals in Sediments

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 (micrograms chemical per gram dry sediment) but to the pore water concentration (micrograms chemical per liter pore water) [17]. However, these results do not necessarily imply that pore water is the primary route of exposure because all exposure pathways are at equal chemical activity in an equilibrium experiment (see Fig. 1) and the route of exposure cannot be determined. Nevertheless, this observation was the critical first step in understanding bioavailability of chemicals in sediments.

Toxicity Experiments

A substantial amount of data has been assembled that addresses the relationship between toxicity and pore water chemical concentrations. Table 1 lists the sources and characteristics of these experiments. Some of these data are presented in Figures 5 to 8. The remaining data are presented elewhere in this document. In Figures 5 to 8 the biological response—mortality or growth rate suppression—is plotted versus the total sediment concentration in the top panel, and versus the measured pore water concentration in the bottom panel. Table 2 summarizes the LC_{50} and EC_{50} estimates and 95 percent confidence limits for these data on a total sediment and pore water basis, as well as the water-only values.

The results from kepone experiments (Fig. 5) are illustrative of the general trends in these data [17, 18]. For the low organic carbon sediment (f_{oc} = 0.09 percent), the 50th percentile total kepone concentra-

Table 1.—Sediment toxicity data and bioaccumulation data.

CHEMICAL	ORGANISM	SEDIMENT SOURCE	EXPOSURE DURATION (DAYS)	BIOLOGICAL END POINT	REFERENCE	FIGURE
ACENAPHTHENE	*Eohaustorius estuarius*	South Beach, OR McKinney Slough, OR Eckman Slough, OR	10	Mortality	[56]	23
ACENAPHTHENE	*Leptocherius plumulosus*	South Beach, OR McKinney Slough, OR Eckman Slough, OR	10	Mortality	[56]	23
CYPERMETHRIN	*Chironomus tentans*	River and pond	1	Body burden	[22]	8
DDT	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	[20,21]	7
DIELDRIN	*Chironomus tentans*	Airport Pond, MN	10	Mortality	[55]	26
DIELDRIN	*Hyalella azteca*	West Bearskin Lake, MN Pequaywan Lake, MN	10	Mortality	[53]	–
DIELDRIN	*Hyalella azteca*	Airport Pond, MN	10	Mortality	[54]	24
ENDRIN	*Diporeia sp.*	Lake Michigan	10	Mortality	[52]	23
ENDRIN	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	[20,21]	7
FLUORANTHENE	*Rhepoxynius abronius*	Amended Ona Beach, OR	10	Mortality	[57]	23
FLUORANTHENE	*Rhepoxynius abronius*	Yaquina Bay, OR	10	Mortality	[19]	6
KEPONE	*Chironomus tentans*	Soil	14	Body burden	[17,24]	–
KEPONE	*Chironomus tentans*	Soil	14	Growth	[17]	5
KEPONE	*Chironomus tentans*	Soil	14	Mortality	[17]	5
PERMETHRIN	*Chironomus tentans*	River and pond	1	Body burden	[22]	8
PHENANTHRENE	*Eohaustorius estuarius*	South Beach, OR McKinney Slouth, OR Eckman Slough, OR	10	Mortality	[56]	23
PHENANTHRENE	*Leptocherius plumulosus*	South Beach, OR McKinney Slough, OR Eckman Slough, OR	10	Mortality	[56]	23

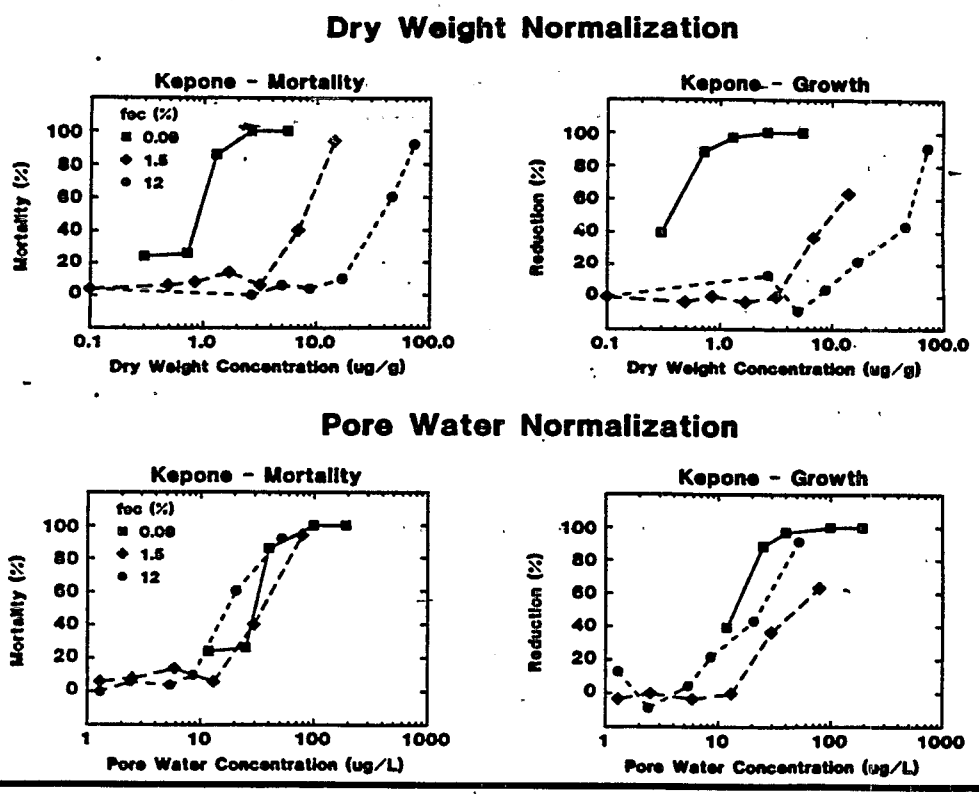


Figure 5.—Comparison of percent mortality (left) and growth rate reduction (right) of *C. tentans* to Kepone concentration in bulk sediment (top) and pore water (bottom) for three sediments with varying organic carbon concentrations [17].

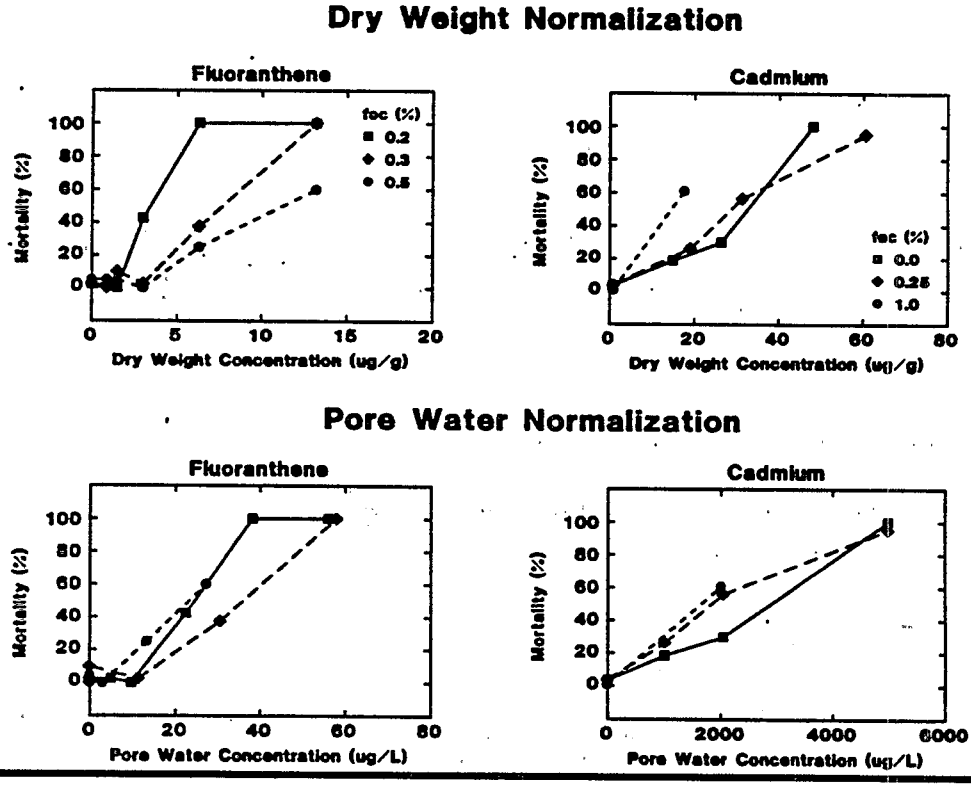


Figure 6.—Comparison of percent mortality of *R. abronium* to fluoranthene [19] concentrations in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations..

Table 2.—LC_{50} and EC_{50} for sediment dry weight and sediment-organic carbon normalization and for pore-water and water-only exposures.

		LC_{50} AND EC_{50}				
CHEMICAL (END POINT)	foc (%)	TOTAL SEDIMENT (μg/g)	PORE WATER (μg/L)	ORGANIC CARBON (μg/g)	WATER ONLY (μg/L)	REFERENCE
KEPONE (MORTALITY)	0.90	0.90 (0.73–1.10)	29.9 (25.3–35.6)	1,000 (811–1,220)	26.4 (22.7–30.6)	[17]
	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)	[17]
	1.5	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)		[19]
	0.3	6.4 (5.56–7.27)	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)	[20]
	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)		[21]
	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)	[20]
	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)		[21]
	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)		

The LC_{50}s and EC_{50}s and the 95% confidence limits in parentheses are computed by the modified Spearman–Karber method [123].

tion for both *Chironomus tentans* mortality (LC_{50}) and growth rate reduction from a life cycle test (EC_{50}) are <1 μg/g. By contrast, the 1.5 percent organic carbon sediment EC_{50} and LC_{50} are approximately 7 and 10 μg/g, respectively. The high organic carbon sediment (12 percent) exhibits still higher LC_{50} and EC_{50} values on a total sediment kepone concentration basis (35 and 37 μg/g, respectively).

However, as shown in the bottom panels, essentially all the mortality data collapse into a single curve and the variation in growth rate is significantly reduced when the pore water concentrations are used as the correlating concentrations. On a pore water basis, the biological responses as measured by LC_{50} or EC_{50} vary by approximately a factor of two, whereas when they are evaluated on a total sediment kepone basis, they exhibit an almost 40-fold range in kepone toxicity.

The comparison between the pore water effects concentrations and the water-only results indicates that they are similar. The pore water LC_{50}s are 19 to 30 μg/L, and the water-only exposure LC_{50} is 26 μg/L. The pore water EC_{50}s are 17 to 49 μg/L, and the water-only EC_{50} is 16 μg/L (Table 2).

Laboratory experiments have also been performed to characterize the toxicity of fluoranthene [19] to the sediment-dwelling marine amphipod *Rhepoxynius abronius*. Figure 6 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 percent) exhibits the lowest LC_{50} on a total sediment concentration basis (3.2 μg/g) and as the organic carbon concentration increases (0.3 and 0.5 percent) the LC_{50} increases (6.4 and 10.7 μg/g). On a pore water basis, the data again collapse to a single concentration-response curve and the LC_{50}s differ by less than 50 percent.

Figure 7 presents mortality data for DDT and endrin using the freshwater amphipod *Hyalella azteca* [20, 21]. The responses for DDT [20] are similar to those observed for kepone, cadmium, and fluoranthene. On a total sediment concentration basis the organism responses differ for the various sediments (LC_{50}s are 10.3 to 45 μg/L), but on a pore water basis the responses are again similar (LC_{50}s are 0.74 to 1.4 μg/L) and comparable to the water-only LC_{50}s of approximately 0.5 μg/L. The DDT data reported by Schuytema et al. [21] are more variable. By contrast,

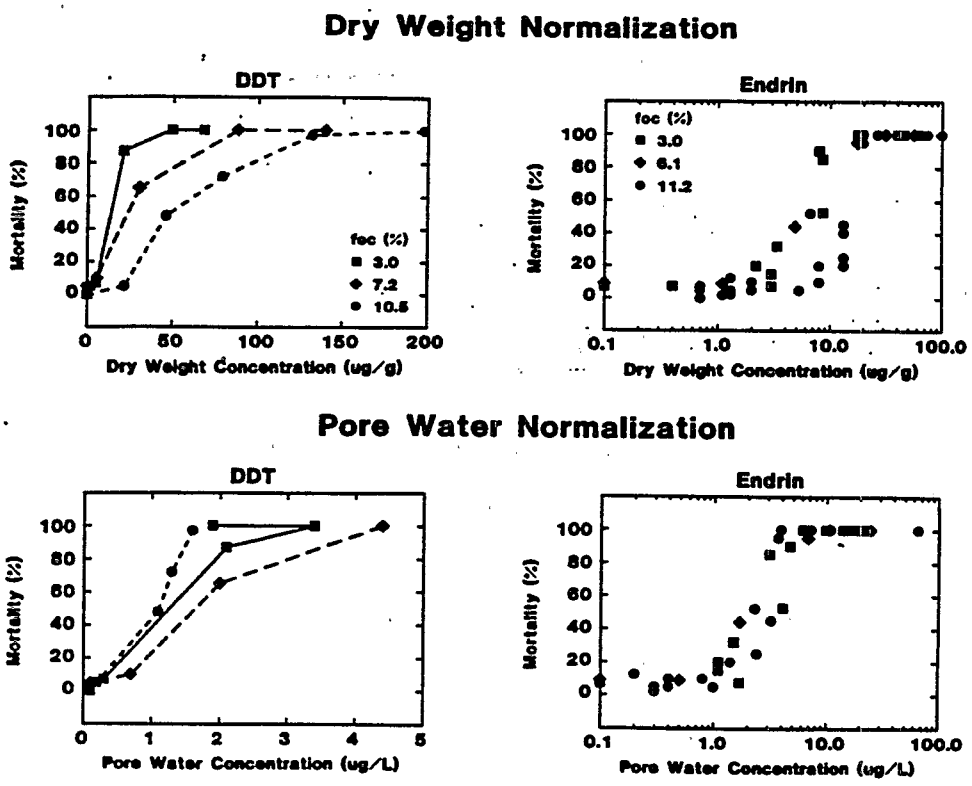


Figure 7.—Comparison of percent mortality of *H. azteca* to DDT (left) and endrin (right) concentrations in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations [20, 21].

the organism survival for endrin exposures on a dry weight basis varies by a factor of almost six among the six sediments. The LC_{50}s are 3.4 to 18.9 μg/g. The pore water LC_{50}s were less variable, 1.7 to 3.8 μg/L and comparable to the water-only exposure LC_{50} of approximately 4 μg/L (Table 2).

Bioaccumulation

A direct measure of chemical 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 [22]. 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 (Fig. 8, top panels).

On a pore water basis, the bioaccumulation appears to be approximately linear and independent of sediment type (bottom panels). The mean bioaccumulation factor (BAF) for cypermethrin (and permethrin) varies from 6.2 to 0.6 (4.0 to 0.23) (μg/g organism/μg/g sediment) as sediment f_{oc} increases (Table 3). By contrast the mean BAFs on a pore water basis vary by less than a factor of two.

Bioaccumulation was also measured by Adams et al. [17, 23] and Adams [24] in the *C. tentans*–kepone experiments presented previously (Figure 3). The body burden variation on a total sediment basis is over two orders of magnitude (BAF = 600 to 3.3 μg/g organism/μg/g sediment), whereas the pore water bioaccumulation factor is within a factor of four (5,200 to 17,600 μg/kg organism/μg/L), with the very low organic carbon sediment exhibiting the largest deviation (Table 3).

Conclusion

These observations—that organism concentration response and bioaccumulation from different sediments can be reduced to one curve if pore water is considered as the concentration that quantifies exposure—can be interpreted in a number of ways. However, these results do not necessarily imply that pore water is the primary route of exposure because all exposure pathways are at equal chemical activity in an

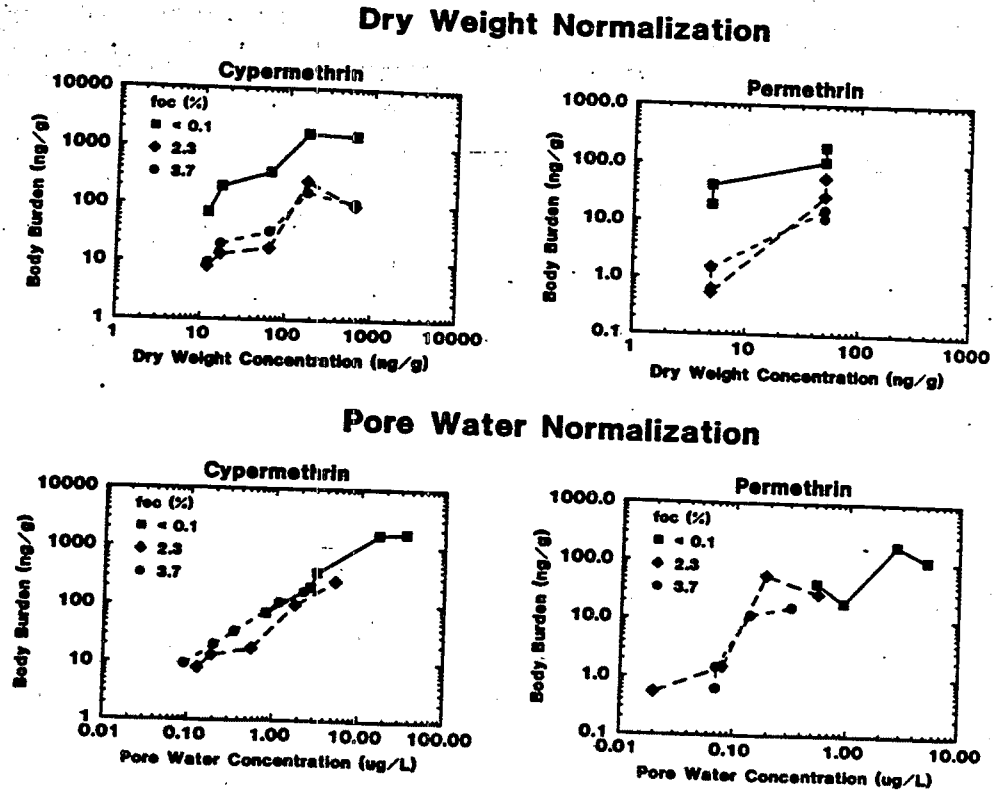


Figure 8.—Comparison of *C. tentans* body burden of cypermethrin (left) and permethrin (right) versus concentration in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations [22].

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

CHEMICAL	f_{oc} (%)	BIOACCUMULATION FACTORS[a] TOTAL SEDIMENT (μg/g ORGANISM / μg/g SEDIMENT)	BIOACCUMULATION FACTORS[a] PORE WATER (μg/kg ORGANISM / μg/L)	REFERENCE
CYPERMETHRIN	<0.1	6.21 (4.41–8.01)	80.1 (73.5–86.7)	[22]
	2.3	0.50 (0.30–0.71)	51.3 (43.8–58.8)	
	3.7	0.60 (0.37–0.83)	92.9 (87.0–98.8)	
PERMETHRIN	<0.1	4.04 (2.89–5.20)	39.7 (25.0–54.3)	[22]
	2.3	0.38 (0.17–0.59)	52.5 (22.6–82.4)	
	3.7	0.23 (0.18–0.28)	29.7 (15.6–43.7)	
KEPONE	0.09	600 (308–892)	17,600 (6,540–28,600)	[17,23,24]
	1.50	20 (4.8–35.2)	5,180 (1,970–8,390)	
	12	3.3 (0.3–6.3)	5,790 (2,890–8,700)	

[a]95% confidence limits shown in parentheses.

equilibrium experiment. The route of exposure cannot be determined, as we can see by comparing the concentration-response correlations to pore water and organic carbon-normalized sediment concentrations. That both are equally successful at correlating the data suggests that neither the pore water nor the sediment exposure pathway can be implicated as the primary exposure route.

In order to relate pore water exposure to sediment carbon exposure, it is necessary to establish the relationship between these two concentrations. Therefore, an examination of the state of the art of predicting the partitioning of chemicals between the solid and the liquid phase is required. This examination is described in the following section.

Sorption of Nonionic Organic Chemicals

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 [25] for an excellent review). 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 [26]. 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 SQC. 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.

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 $\log_{10}$ prediction standard error of 0.38 [27]. The reversible component partition coefficient, K_p^*, is the ratio of reversibly bound chemical concentration, C_s (μg/kg dry weight), to the dissolved chemical concentration, C_d (μg/L):

$$C_s = K_p^* C_d. \quad (9)$$

The PIM model for K_p^*, is

$$K_p^* = \frac{f_{oc} K_{oc}}{1 + m f_{oc} K_{oc}/\nu_x} \quad (10)$$

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)

ν_x = 1.4, an empirical constant (unitless).

The regression of K_{oc} to the octanol/water coefficient, K_{ow}, yields

$$\log_{10} K_{oc} = 0.00028 + 0.983 \log_{10} K_{ow} \quad (11)$$

which is that essentially K_{oc} approximately equals K_{ow}. Figure 9 presents the observed versus predicted reversible component partition coefficients using this model [27]. 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 ν_x. The low particle concentration data ($m f_{oc} K_{ow} < 1$) are presented in Figure 10 for the conventional adsorption (left) and reversible component (right) 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 while Equation 10 applies only to the reversible component partition coefficient, K_p, the equation: $K_p \approx f_{oc} K_{ow}$ applies to the conventional adsorption partition coefficient as well (Fig. 10, left).

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

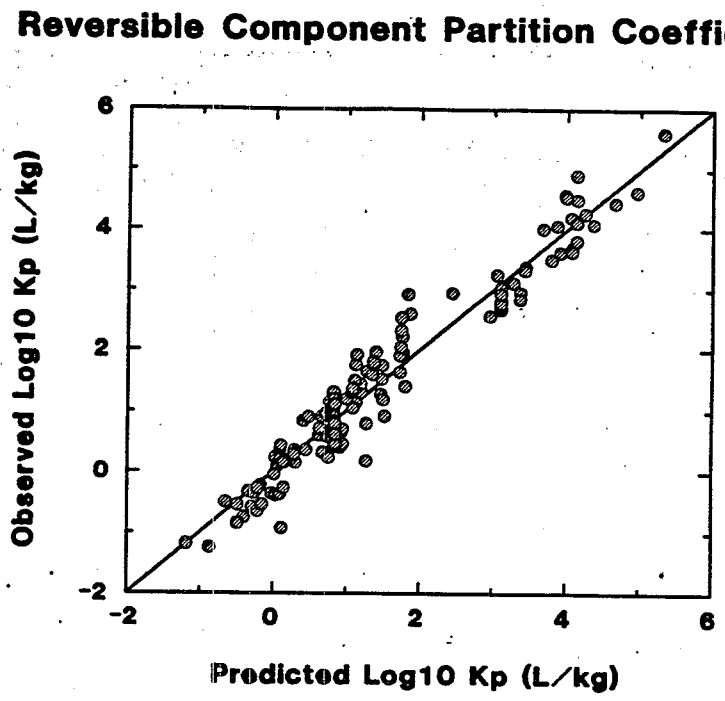


Figure 9.—Comparison of observed reversible component partition coefficient to calculated partition coefficient using Equation 10 [27].

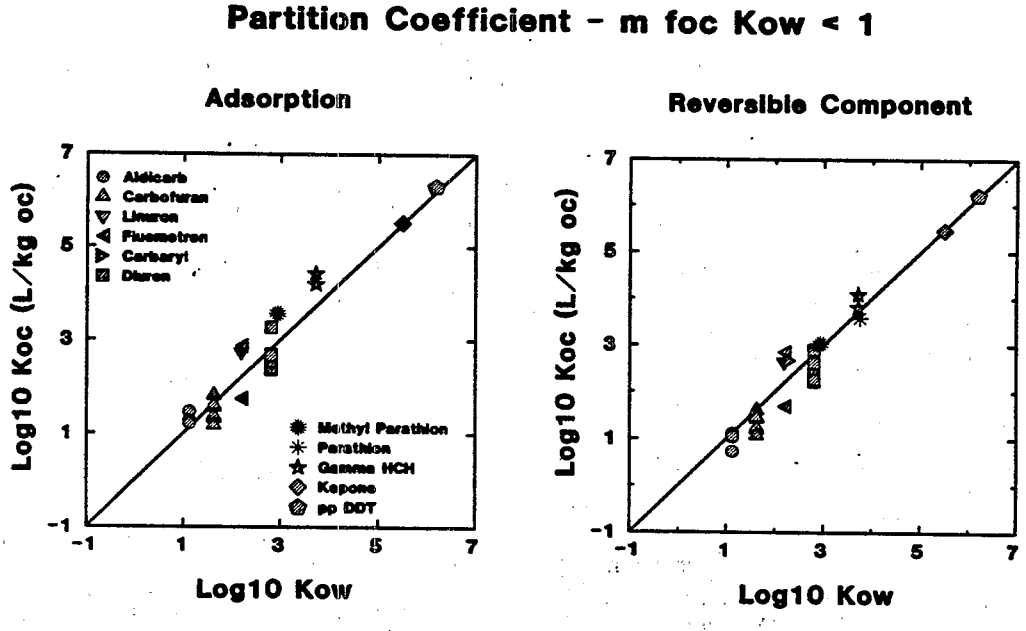


Figure 10.—Comparison of the adsorption (left) and reversible component (right) organic carbon-normalized partition coefficient, K_{oc}, to the octanol/water partition coefficient, K_{ow}, for experiments with low solids concentrations: $mf_{oc}K_{ow}<1$. The line represents equality [27].

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 [28, 29] and dissolved ligands or macromolecules that desorb from the particles and remain in solution [30-33] 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 [34]. The effect has also been attributed to kinetic effects [25].

Sorption by nonseparated particles or complexing by dissolved organic carbon 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. The question is whether these third-phase models explain all (or most) of the observed partition coefficient-particle concentration relationships.

An alternate possibility is that the particle concentration effect is a distinct phenomena 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 [35-37], in which particles are resuspended into a reduced volume of supernatant, and in the dilution experiment in which the particle suspension is diluted with supernatant from a parallel vessel [35]. It is difficult to see how third-phase models can account for these results because the concentration of the colloidal particles is constant while the concentration of the sediment particles varies substantially.

The model (Eqn. 10) is based on the hypothesis that particle concentration effects result from an additional desorption reaction induced by particle-particle interactions [27]. It has been suggested that actual particle collisions are responsible [38]. This interpretation relates ν_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 [27, 36].

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/pore water partitioning. Particle interaction models would predict that $K_{oc} = K_{ow}$ because the particles are stationary in sediments. Third-phase models would also relate the free (i.e., uncomplexed) dissolved chemical concentration to particulate concentration via the same equation. As for kinetic effects, the equilibrium concentration is again given by the relationship $K_{oc} = K_{ow}$. Thus there is unanimity on the proper partition coefficient to be used in order to relate the free dissolved chemical concentration to the sediment concentration: $K_{oc} = K_{ow}$.

Organic carbon fraction. The unifying parameter that permits the development of SQC for nonionic hydrophobic organic chemicals that are 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/pore water partition coefficient, K_p, is given by

$$K_p = f_{oc}K_{oc} = f_{oc}K_{ow} \qquad (12)$$

and the solid phase concentration is given by

$$C_s = f_{oc}K_{oc}C_d \qquad (13)$$

where C_s is the concentration on sediment particles. An important observation can be made that leads to the idea of organic carbon-normalization. Equation 12 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 10 can be used to examine the linearity of K_p to f_{oc}. Figure 11 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 12. These data and an analysis presented below appear to support the linearity of partitioning to a value of $f_{oc} = 0.2$ percent. This result and the toxicity experiments examined below suggest that for $f_{oc} > 0.2$ percent, 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 free dissolved concentration, C_d, can be expressed as

$$\frac{C_s}{f_{oc}} = K_{oc}C_d. \qquad (14)$$

If we define

$$C_{s,oc} = \frac{C_s}{f_{oc}} \qquad (15)$$

as the organic carbon normalized sediment concentration (μg chemical/kg organic carbon), then from Equation 14:

$$C_{s,oc} = K_{oc}C_d. \qquad (16)$$

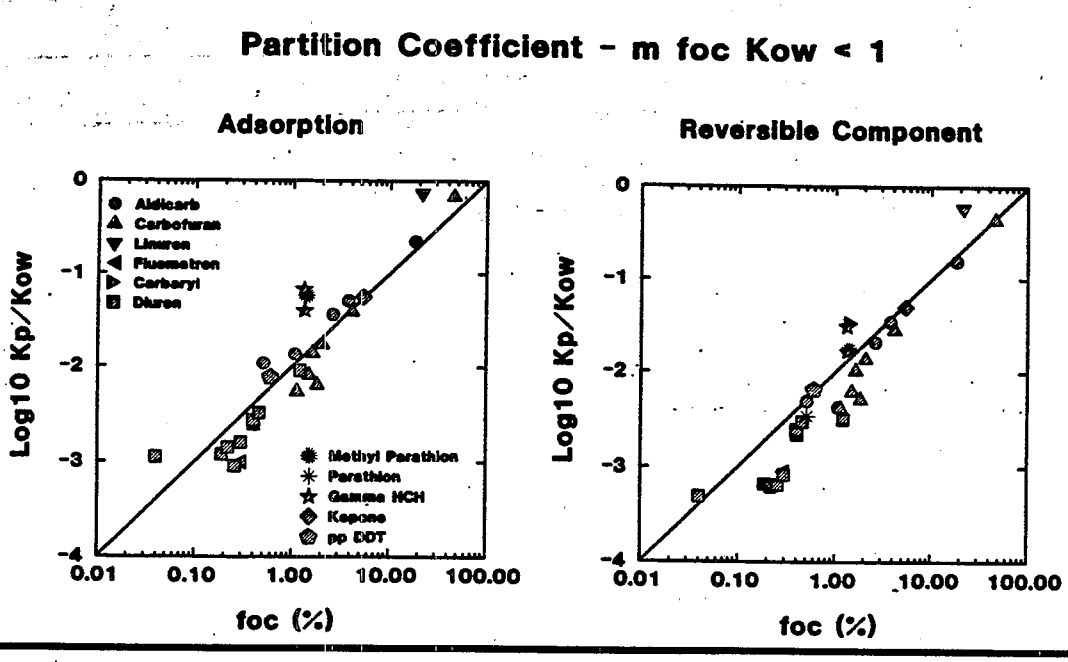


Figure 11.—Comparison of the normalized partition coefficients for adsorption (left) and reversible component sorption (right) to sediment organic carbon. The data are restricted so that particle effects are not expected to be significant: $mf_{OC}K_{OW} < 1$. The line represents perfect agreement [27].

Therefore, for a specific chemical with a specific K_{OC}, the organic carbon-normalized total sediment concentration, $C_{S,OC}$, is proportional to the dissolved free concentration, C_d, for any sediment with $f_{OC} > 0.2$ percent. This latter qualification is judged to be necessary because at $f_{OC} < 0.2$ percent the other factors that influence partitioning (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important [25]. Using the proportional relationship given by Equation 16, the concentration of free dissolved chemical can be predicted from the normalized sediment concentration and K_{OC}. The free concentration is of concern as it is the form that is bioavailable. The evidence is discussed in the next section.

Dissolved Organic Carbon (DOC) Complexing

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

A distinction is made between the free 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 free dissolved concentration, C_d:

$$C_{DOC} = m_{DOC}K_{DOC}C_d \quad (17)$$

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

A recent compilation of K_{DOC} together with additional experimental determinations is available [39]. A summary that compares the partitioning of six chemicals to POC, natural DOC, and Aldrich humic acid (HA) is shown on Figure 12. The magnitude of the partition coefficients follow the order: POC > HA > natural DOC. The upper bound on K_{DOC} would appear to be $K_{DOC} = K_{OC}$, the POC partition coefficient.

Phase Distribution in Sediments

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

$$C_T = \phi C_d + mf_{OC}K_{OC}C_d + \phi m_{DOC}K_{DOC}C_d \quad (18)$$

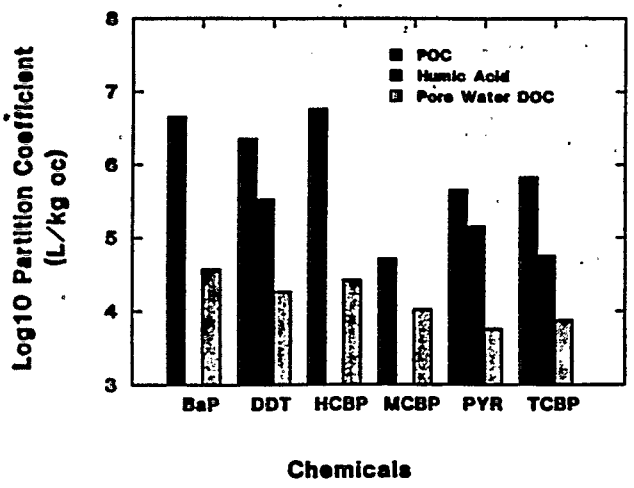


Figure 12.—Partition coefficients of chemicals to particulate organic carbon (POC), Aldrich humic acid, and natural DOC. Benzo[a]pyrene (BaP); 2,2',4,4',5,5' hexachlorobiphenyl (HCBP); DDT; 2,2',5,5'-tetrachlorobiphenyl (TCBP); pyreqe (PYR); 4-monochlorobiphenyl (MCBP). Data from Eadie et al. [39].

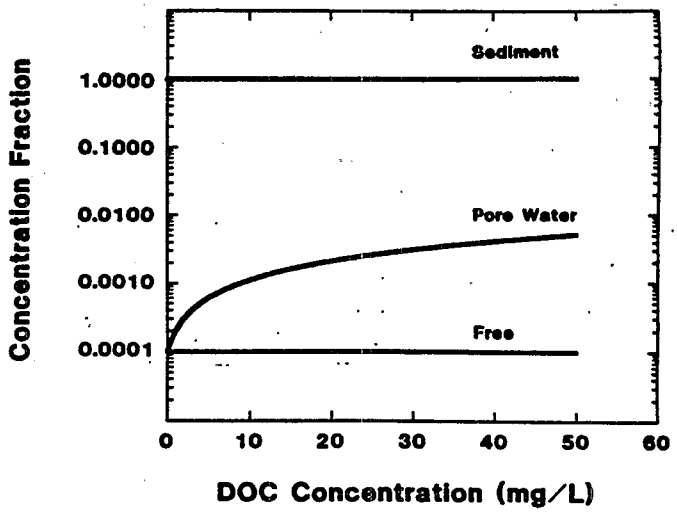


Figure 13.—Partition coefficients of chemicals to particulate organic carbon (POC), Aldrich humic acid, and natural DOC. Benzo[a]pyrene (BaP); 2,2',4,4',5,5' hexachlorobiphenyl (HCBP); DDT; 2,2',5,5'-tetrachlorobiphenyl (TCBP); pyrene (PYR); 4-monochlorobiphenyl (MCBP). Data from Eadie et al. [39].

where ø 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 free chemical in the interstitial water, and that sorbed to the POC and DOC, respectively. Hence, from Equation 18 the free dissolved concentration can be expressed as

$$C_d = \frac{C_T}{ø + mf_{oc}K_{oc} + øm_{DOC}K_{DOC}}. \quad (19)$$

The concentration associated with the particle carbon (Eqn. 16) and DOC (Eqn. 17) can then be calculated. The total pore water concentration is the sum of the free and DOC complexed chemical, so that

$$C_{pore} = C_d + C_{DOC} = C_d(1 + m_{DOC}K_{DOC}). \quad (20)$$

Figure 13 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 percent, m = 0.5 kg solids/L sediment, and m_{DOC} varies from 0 to 50 mg/L, a reasonable range for pore waters [40]. With no DOC present, the pore water concentration equals the free concentration. As DOC increases, the pore 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 (Eqn. 19) and a proportional decrease in C_s (Eqn. 16).

It is important to realize that the free chemical concentration, C_d, can be estimated directly from $C_{s,oc}$, the organic carbon-normalized sediment concentration, using Equation 16, and that the estimate is independent of the DOC concentration. However, to estimate C_d from the pore water concentration requires that the DOC concentration and K_{DOC} be known. The assumption $C_{pore} = C_d$ is clearly not warranted for very hydrophobic chemicals. For these cases $C_{s,oc}$ gives a more direct estimate of the free dissolved bioavailable concentration, C_d, than does the pore water concentration.

Bioavailability of DOC-Complexed Chemicals

The proportion of a chemical in pore water that is complexed to DOC can be substantial (Fig. 13). Hence, the question of bioavailability of DOC-complexed chemical can be important in assessing toxicity directly from measured pore water concentraions. A significant quantity of data indicates that DOC-complexed chemical is not bioavailable. Fish [41] and amphipod [42] uptake of polycyclic aromatic hydrocarbons (PAHs) are significantly reduced by adding DOC. An example is shown in Figure 14 for a freshwater amphipod [42]. 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} (Eqn. 17).

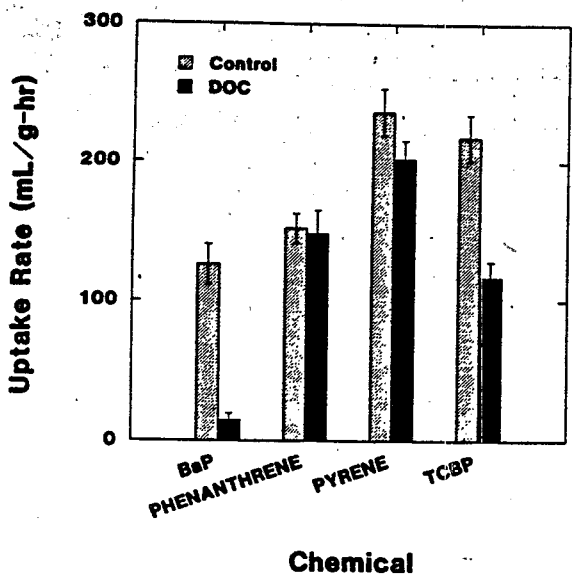


Figure 14.—Average uptake rate of chemicals by *Pontoporeia hoyi* with (filled) and without (hatched) DOC present. Benzo[*a*]pyrene (BaP); 2,2',4,4'-tetrachlorobiphenyl (TCBP); pyrene, phenanthrene. Data from Landrum et al. [42].

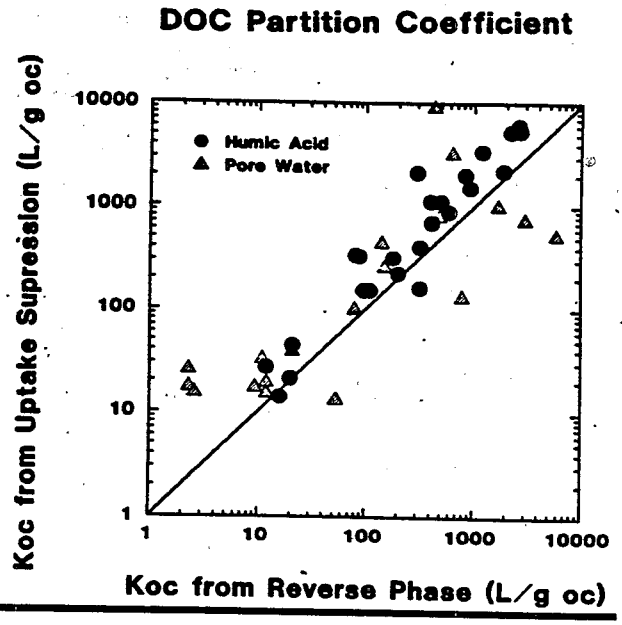


Figure 15.—Comparison of the DOC partition coefficient calculated from the suppression of chemical uptake versus the C_{18} reversed-phase HPLC column estimate. Circles are Aldrich humic acid; triangles are interstitial water DOC. Chemicals are listed in Figure 14 caption (also anthracene and benzo[*a*]anthracene).

The quantitative demonstration that DOC-complexed chemicals are not bioavailable requires an independent determination of the concentration of complexed chemical. Landrum et al. [42] have developed a C_{18} reverse-phase HPLC column technique that separates the complexed and free chemical. Thus it is possible to compare the measured DOC-complexed chemical to the quantity of complexed chemical inferred from the uptake experiments, assuming that all the complexed chemical is not bioavailable [42, 43]. As shown on Figure 15, 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 (Eqn. 15).

Field Observations of Partitioning in Sediments

An enormous quantity of laboratory data exists for partitioning in particle suspensions. However, pore 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 pore water concentrations and accounts for the DOC that is present.

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 pore water. If sorption equilibrium has been attained for each class, then, letting $C_s(j)$ be the particle chemical concentration of the jth size class, it is true that

$$C_s(j) = f_{oc}(j) K_{oc} C_d \qquad (21)$$

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

$$C_{s,oc}(j) = K_{oc} C_d \qquad (22)$$

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.

Data from three field studies, Prahl [44], Evans et al. [45], and Delbeke et al. [46], can be used to test this prediction. In Prahl's study, 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 fraction (<1.9 g/cm3) and the remaining higher density sand-sized particles. The concentrations of 13 individual PAHs were measured in each size fraction.

It is important to realize that these size fractions are not pure clay, silt, or sand but are natural particles in the size classes denoted by clay, silt, and sand. The organic carbon fractions, shown on Figure 16, range from 0.2 percent for the high-density sand-sized fraction to greater than 30 percent for the low-density fraction. This exceeds two orders of magnitude and essentially spans the range usually found in practice. For example, 90 percent of the estuarine and coastal sediments sampled for the National Status and Trends program exceed 0.2 percent organic carbon [47].

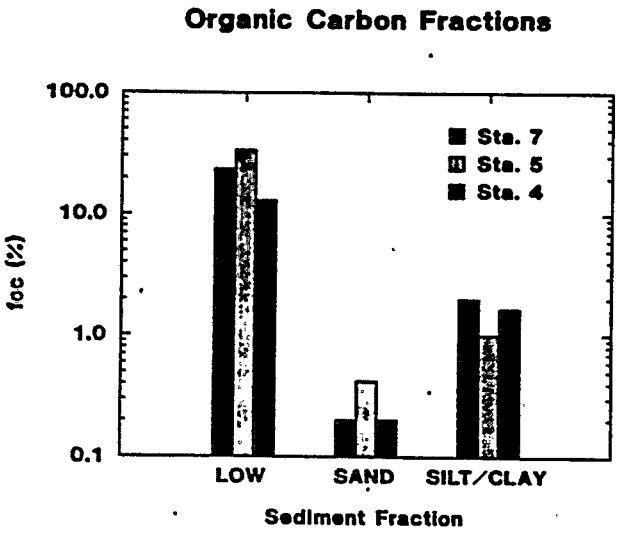


Figure 16.—The organic carbon fractions (% dry weight) in the low-density fraction .64 μm, <1.9 g/cm^3; the sand-sized fraction >64 μm, >1.9 g/cm^3; the silt/clay-sized fraction <64 μm. Numbered stations as indicated. Data from [44].

Figure 17 (top) compares the dry weight-normalized clay/silt sized fraction sediment PAH concentrations, $C_s(j)$, to 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. Figure 17 (bottom) presents 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 22.

In the field data from Evans et al. [45] sediments were collected at five sites along the River Derwent, Derbyshire, United Kingdom, and separated into six sediment size classes. The size classes were representative of clay and silt (<63 μm) to course sand (1.0 to 2.0 mm). Organic carbon content and total PAH were measured in each sediment size class. Figure 18 presents the size classes and associated organic carbon content. Evans et al. attribute 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 be from fragmentary plant material while the size classes less then 500 μm organic carbon content is the result of aging humic material. The organic content in this study ranges from 2.0 to 40 percent.

Figure 19 presents a comparison of PAH concentration for different sediment classes for dry weight normalization and organic carbon normalization. The top left panel compares PAH concentrations on sand (63 μm - 500 μm) and clay/silt (< 63 μm) on a dry weight basis. The top right panel compares PAH concentrations on course sand (0.5 μm - 2.0 μm) and clay/silt (< 63 μm) on a dry weight basis. The data indicates that the PAH concentration is higher in the course sand fraction of sediment. Recall from Figure 18 that the clay/silt and course sand fractions contain higher fraction organic carbon content. The bottom panels of Figure 19 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 22.

Lastly, Delbeke et al. [46] 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 addition, analyses of the samples were done to determine the percent of size fractions ranging from 500 μm to 3 μm which made up the sample. The PCB congeners tested for in this study were IUPAC numbers 28, 52, 101, 118, 153, 138, 170 and 180.

Using concentrations reported for bulk samples, concentrations for clay/silt samples, and 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 >63 μm portion of the sample. Organic content varied from 0.01 percent to 10 percent inclusive of both <63 μm and >63 μm portions of the sediment.

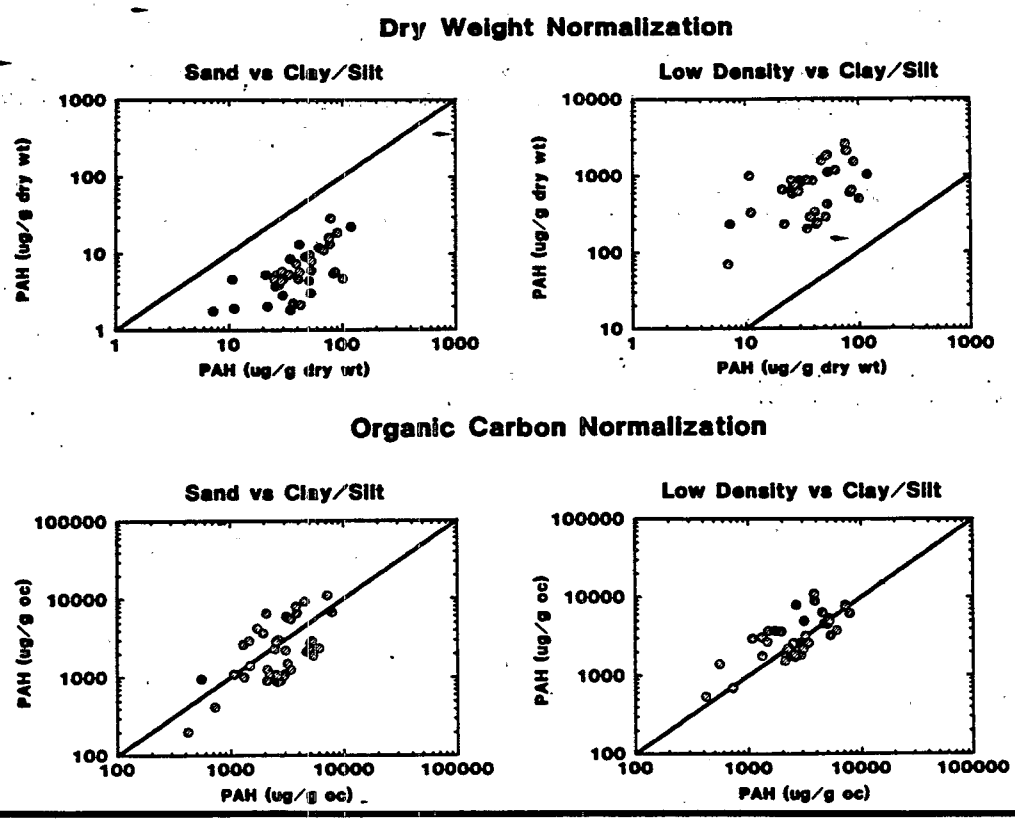


Figure 17.—Comparison of PAH concentrations of the sand-sized- and low-density-fraction sediment particles ordinate to the clay/silt fraction abscissa (Stations 4, 5, 7). Top panels are for dry weight normalization; bottom panels are for organic carbon normalization. Data from [44].

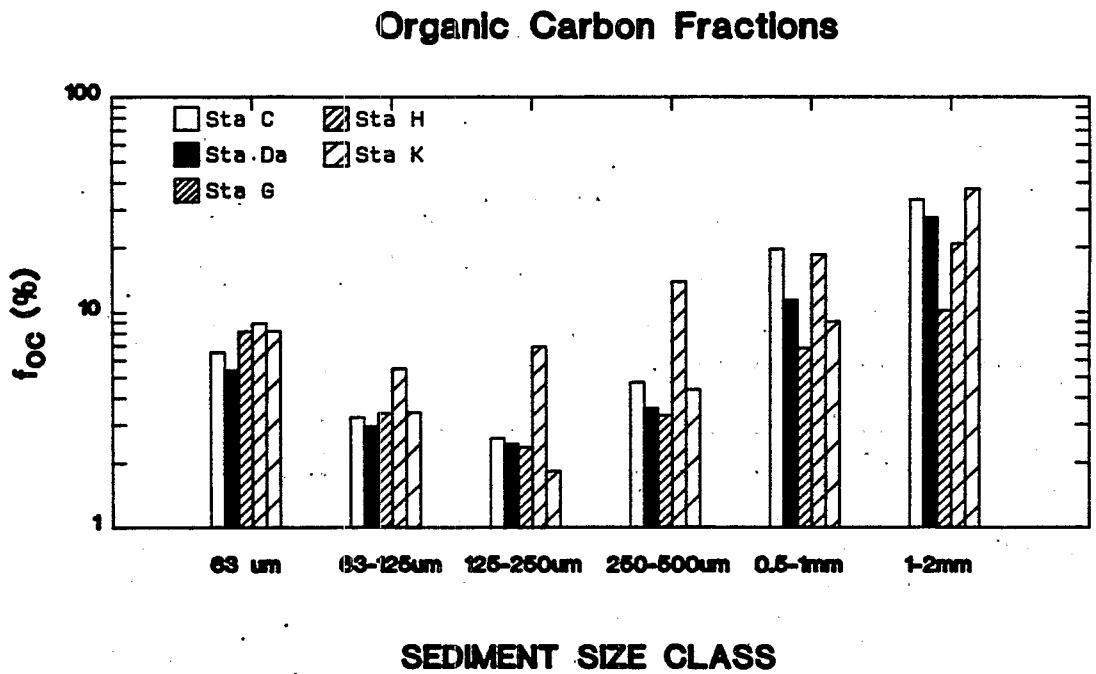


Figure 18.—The organic carbon fractions (% dry weight) in five sediment size classes ranging from clay and silt (<63 μm) to course sand (1.0 to 2.0 mm). Stations are indicated by hatch type. Data from [45].

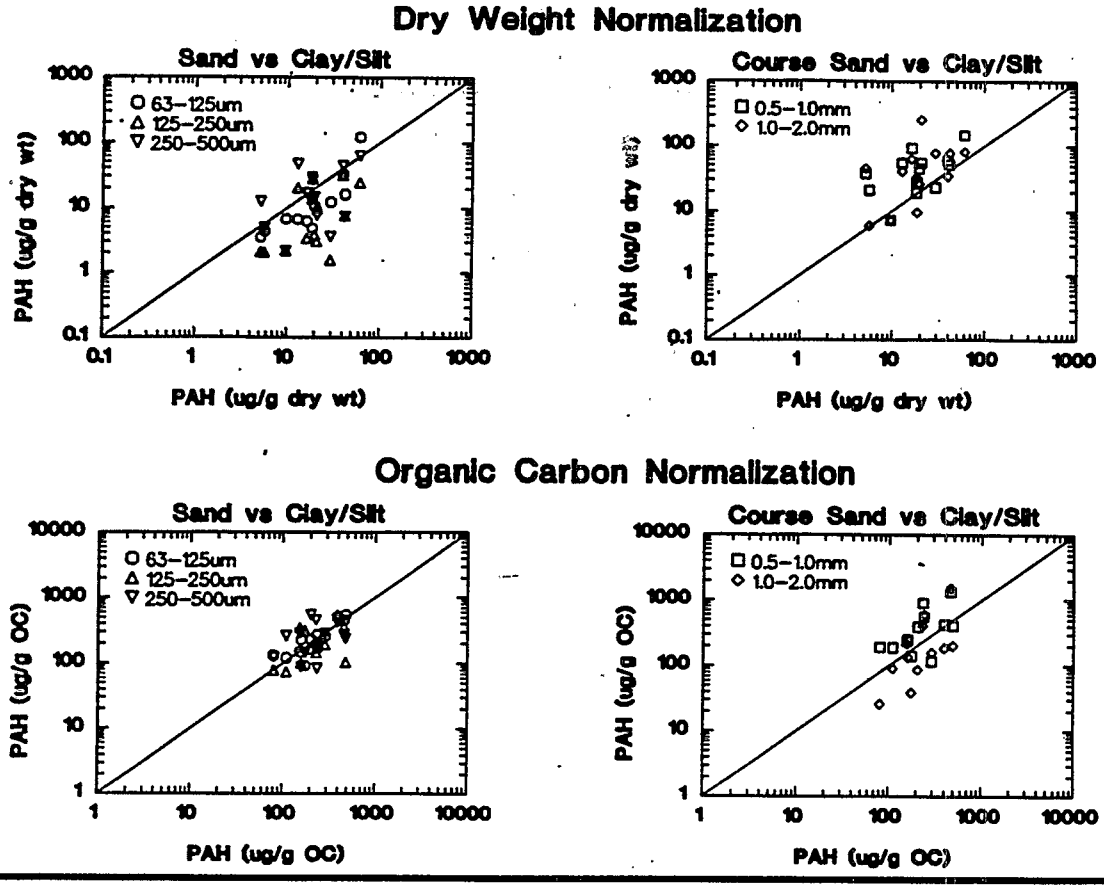


Figure 19.—Comparison of PAH concentrations of the sand-sized and course sand-sized fraction sediment particles indicated by symbols, ordinate, to the clay/silt fraction, abscissa (Stations C, Da, G, H, K). Top panels are for dry weight normalization; bottom panels are for organic carbon normalization. Data from [45].

Figure 20 presents the percent organic carbon on the <63 µm portion of the sample (filled bar) and on the >63 µm portion of the sample (shaded bar). A comparison of the PCB congener concentrations on a dry weight basis (top) and on an organic carbon basis (bottom) is shown in Figure 21. Organic carbon content in the >63 µm class size at stations 2 and 4 is 0.01 percent and 0.06 percent respectively, as indicated in Figure 20. The data for these stations are shown on Figure 21 using filled symbols. Though an f_{OC} > 0.2 percent has been presented as the value for which organic carbon normalization applies, normalization at these f_{OC} values seems appropriate for this data set.

The top panel of Figure 21 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 the concentrations are similar for both class sizes as shown in the bottom panel. This indicates that PCB concentrations are similar across sediment class sizes which supports organic carbon normalization.

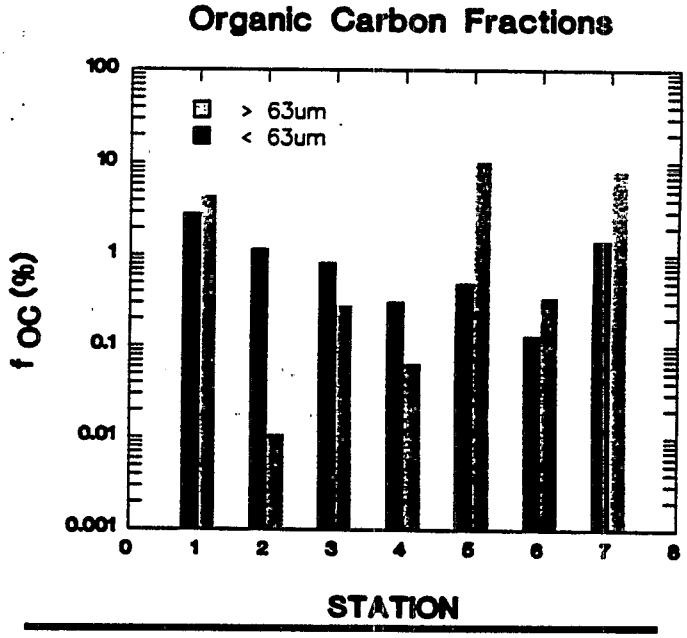


Figure 20.—The organic carbon fractions (% dry weight) in two sediment size classes, <63 µm and >63 µm. Seven stations are indicated. Data from [46].

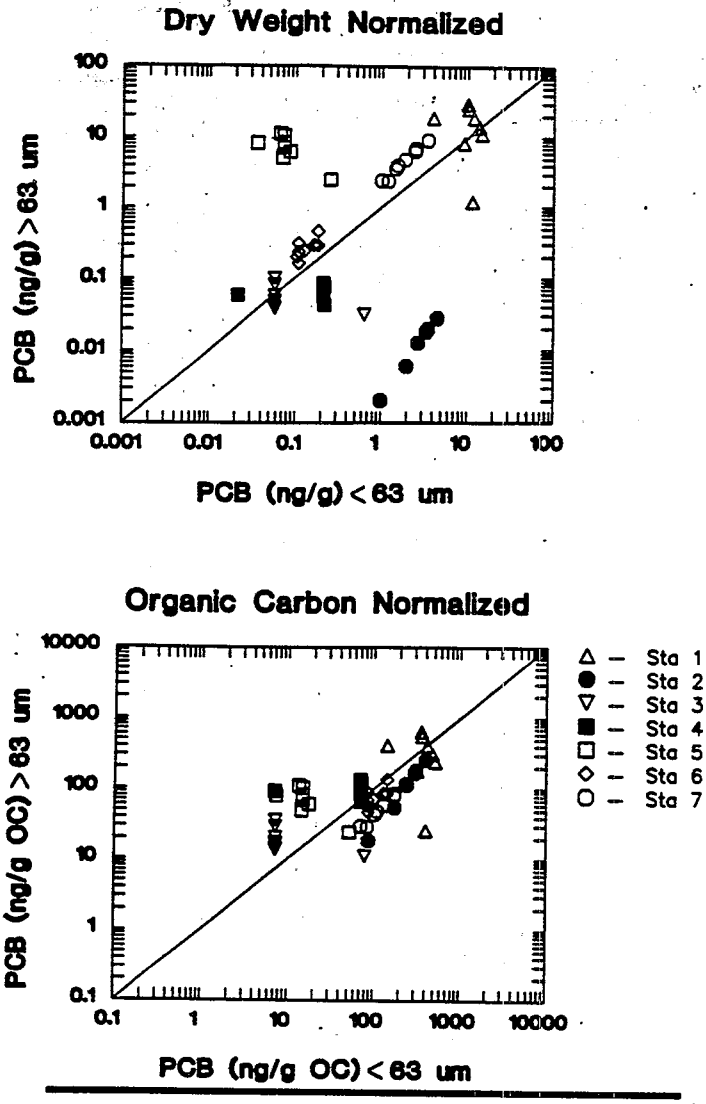


Figure 21.—Comparison of eight PCB congener concentrations of >63 μm sized particles, ordinate, to <63 μm sized particles, abscissa (Stations 1-7). Top panel is for dry weight normalization; bottom panel is for organic carbon normalization. PCB congeners are IUPAC Nos 28, 52, 101, 118, 138, 153, 179 and 180. Data from [47].

It can be concluded from the data of Prahl, Evans et al., and Delbeke et al., that the organic carbon-normalized PAH and PCB concentrations are relatively independent of particle size class and that organic carbon is the predominant controlling factor in determining the partition coefficient of the different sediment size particles in a sediment sample. The organic carbon concentration of the high-density sand-sized fraction in Prahl's data (0.2 to 0.3 percent) suggests that organic carbon normalization is appropriate at these low levels. The data from Evans et al. suggests that EqP can be applied to organic carbon originating from more than one source, that is, fragmentary plant matter and aging humic material.

Sediment/pore water partitioning. Normally when measurements of sediment chemical concentration, Cs, and total pore water chemical concentrations, Cpore, 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

$$K_p' = \frac{C_s}{C_{pore}} \qquad (23)$$

is given by

$$K_p' = \frac{K_p}{1 + m_{DOC}K_{DOC}} = \frac{f_{oc}K_{oc}}{1 + m_{DOC}K_{DOC}}. \qquad (24)$$

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

$$K_p' = \frac{f_{oc}K_{oc}}{m_{DOC}K_{DOC}} \qquad (25)$$

which is just the ratio of sorbed to complexed chemical. Because the solid-phase chemical concentration is proportional to the free dissolved portion of the pore water concentration, Cd, the actual partition coefficient, Kp, should be calculated using the free dissolved concentration. The free dissolved concentration will typically be lower than the total dissolved pore water chemical concentration in the presence of significant levels of pore water DOC (e.g., Fig. 13). As a result, the actual partition coefficient calculated with the free dissolved concentration is higher than the apparent partition coefficient calculated with the total dissolved pore water concentration.

Direct observations of pore water partition coefficients are restricted to the apparent partition coefficient, K_p' (Eqn. 23), because total concentrations in the pore water are reported and DOC complexing is expected to be significant at the DOC concentrations found in pore waters. Data reported by Brownawell and Farrington in 1986 [48] demonstrate the importance of DOC complexing in pore water. Figure 22 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 line corresponds to the relationship, $K_{oc} = K_{ow}$, which is the expected result if DOC complexing were not significant. Because DOC concentrations were measured for these data, it is possible to estimate C_d with Equation 20 in the form:

$$C_d = \frac{C_{pore}}{1 + m_{DOC}K_{DOC}} \qquad (26)$$

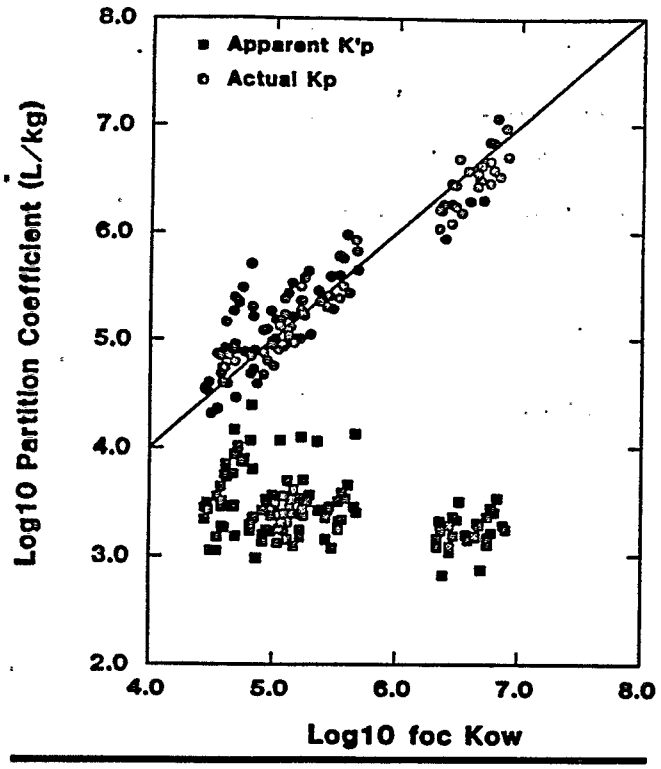


Figure 22.—Observed partition coefficient versus the product of organic carbon fraction and octanol/water partition coefficient. The line represents equality. The partition coefficients are computed by using total dissolved PCB (squares), and free PCB (circles) which is computed with Equation 26 with $K_{DOC} = K_{ow}$. Data from [48].

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 22, 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 in 1984 [49].

Other data with sediment/pore water partition coefficients for which the DOC concentrations have not been reported [50, 51] are available to assess the significance of DOC partitioning on the apparent sediment partition coefficient. Figure 23 presents these apparent organic carbon-normalized partition coefficients, that 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 there is substantial scatter in these data, reflecting the difficulty of measuring pore water concentrations, the data conform to DOC levels of 1.0 to 10 mg/L, which is well within the observed range for pore waters [40, 48]. Thus, these results do not refute the hypothesis that $K_{oc} = K_{ow}$ in sediments but show the need to account for DOC complexing in the analysis of pore water chemical concentrations.

Laboratory toxicity tests. Another way to verify Equation 22 is from data collected during sediment toxicity tests in the laboratory. These tests yield sediment ($C_{s,oc}$) and pore 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 and sediment and pore water are in equilibrium. The results of these tests can be used to

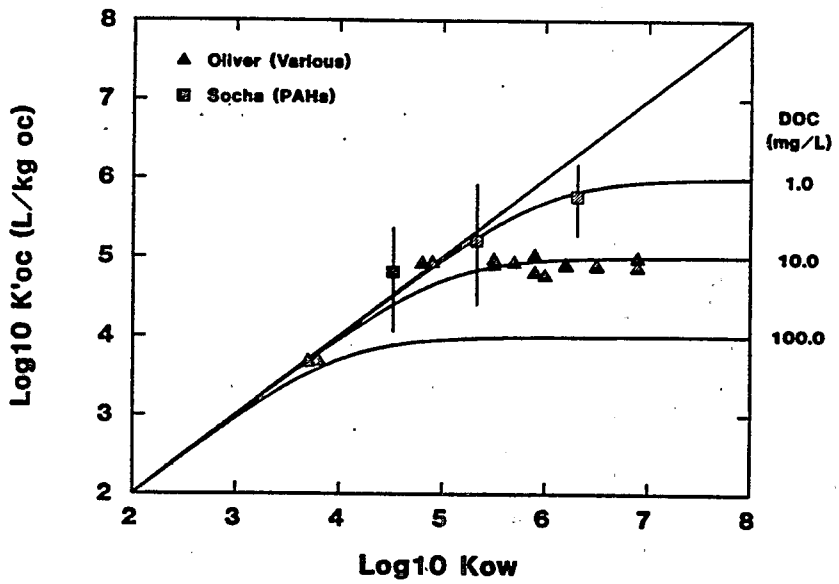


Figure 23.—Observed apparent partition coefficient to organic carbon versus the octanol/water partition coefficient. The lines represent the expected relationship for DOC concentrations of 0, 1, 10, and 100 mg/L $K_{DOC} = K_{ow}$. Data from [51] for PCB congeners and other chemicals and from [50] for phenanthrene, fluoranthene, and perylene.

compute the organic carbon partition coefficient K_{oc}. To verify Equation 22, estimates of K_{oc} computed from Equation 11 using laboratory measurements of K_{ow} are then compared to partitioning in the sediment toxicity test. Sediment toxicity tests and K_{ow} measurements are available for five chemicals: endrin [20, 21, 52], dieldrin [54, 55], acenaphthene [56], phenanthrene [56], and fluoranthene [19, 57]. Sediment toxicity tests for these chemicals were performed as part of the development of SQC. Mortality results for these tests were presented in Figures 2 and 3.

Figure 24 shows organic carbon normalized sorption isotherm for acenaphthene, endrin, phenanthrene and fluoranthene, where the sediment concentration (µg/g OC) is plotted versus pore water concentration (µg/L). These tests represent freshwater and marine sediments having a range of organic carbon content of 0.07 to 11.0 percent. In each panel, the line corresponds to Equation 16 where K_{oc} is derived from K_{ow} measurements in the laboratory. A full discussion of laboratory K_{ow} measurements is presented subsequently. In each of the panels the toxicity test data are in agreement with the line computed from experimentally determined K_{oc}. For these chemicals DOC measurements are unavailable and partitioning to DOC in the pore water has not been considered. The figure indicates, however, that DOC complexing in these experiments appears to be negligible.

Partitioning in the dieldrin experiment indicated that DOC complexation may have been significant. The partitioning isotherm for dieldrin, Figure 25), represents organic carbon normalized sediment concentration, versus total (top panel) and computed dissolved (bottom panel) pore water concentrations. Dissolved pore water concentrations are computed

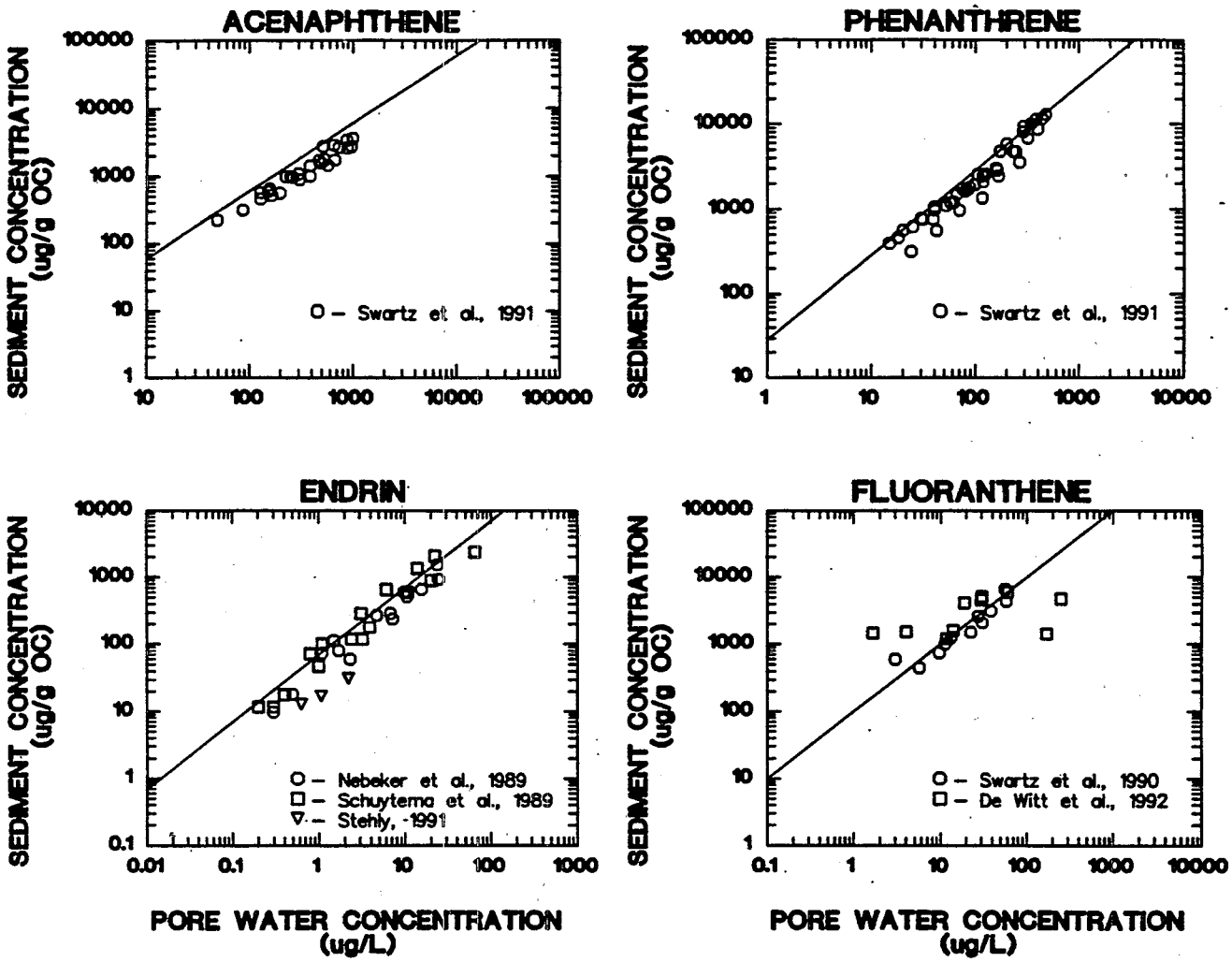


Figure 24.—Comparison of organic carbon partition coefficient (K_{oc}) observed in toxicity tests (symbols) to K_{oc} derived from laboratory K_{ow} and Equation 11 (solid line). Symbols are sediment concentration, ordinate, versus pore water concentration, abscissa. Solid line is $C_{s,oc} = K_{oc} * C_d$, where Log_{10} K_{oc} is 3.76 for acenaphthene, 4.84 for endrin, 4.46 for phenanthrene, and 5.00 for fluoranthene. These Log_{10} K_{oc} values are estimated from Log_{10} K_{ow} values measured at the U.S. EPA Environmental Research Laboratory at Athens, Georgia. Data sources as indicated.

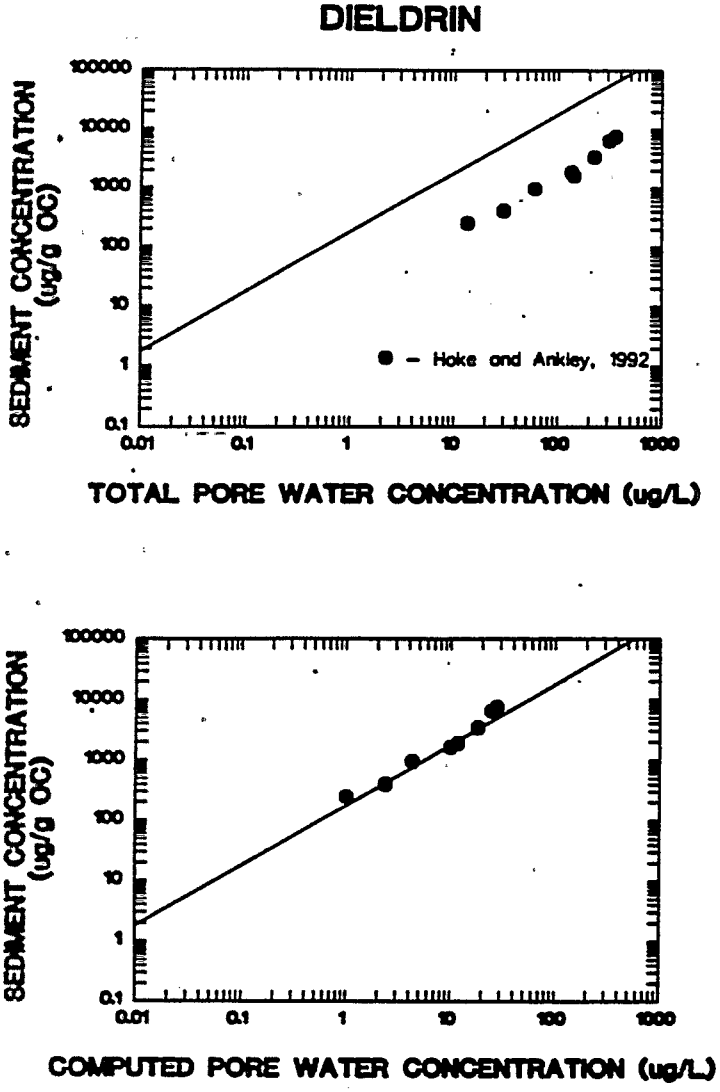


Figure 25.—Comparison of organic carbon partition coefficient (K_{oc}) observed in toxicity tests (symbols) to K_{oc} derived from laboratory K_{ow} and Equation 11 (solid line). Symbols are sediment concentration, ordinate, versus total (top panel) and free (bottom panel) pore water concentrations, abscissa. Solid line is $C_{s,oc} = K_{oc} * C_d$, where Log_{10} K_{oc} is 5.25 for dieldrin. The Log_{10} K_{oc} value is estimated from Log_{10} K_{ow} value measured at the U.S. EPA Environmental Research Laboratory at Athens, Georgia. Data source as indicated.

using Equation 26, DOC measurements and an estimated log K_{DOC} = 5.25. Log K_{DOC} is estimated from log K_{oc} = 5.25 for dieldrin. Figure 25 represents data from Hoke and Aukley [55] since Hoke [56] did not measure pore water. Adjusting for partitioning on to the DOC in the bottom panel results in better agreement with the experimentally determined K_{oc}. These data represent one sediment with an organic carbon content of 1.6 percent. It is important to note that dieldrin has the highest K_{oc} of the five chemicals ($Log_{10}K_{oc}$ dieldrin = 5.25, acenaphthene = 3.76, endrin = 4.84, phenanthrene = 4.46, fluoranthene = 5.00. DOC complexing increases with an increasing partition coefficient which explains why DOC complexing is significant for dieldrin.

Organic Carbon Normalization of Biological Responses

The results discussed above suggest that if a concentration-response curve correlates to pore 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 $C_{s,oc} = K_{oc}C_d$ (Eqn.16), which relates the free 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.

Toxicity and bioaccumulation experiments. To demonstrate this relationship, concentration-response curves for the data presented in Figures 5 and 7 are used to compare results on a pore water-normalized and organic carbon-normalized chemical concentration basis. Figures 26 to 28 present these comparisons for kepone, DDT, endrin, and fluoranthene. The mean and 95 percent confidence limits of the LC_{50} and EC_{50} values for each set of data are listed in Table 2. The top panels repeat the response-pore water concentration plots shown previously in Figures 5 to 7, while the lower panels present the response versus the sediment concentration, which is organic carbon-normalized (microgram chemical per gram organic carbon).

The general impression of these data is that there is no reason to prefer pore water normalization over sediment organic carbon normalization. In some cases, pore water normalization is superior to organic carbon normalization, for example, kepone-mortality data (Fig. 26) whereas the converse sometimes occurs, for example kepone-growth rate (Fig. 26). A more quantitative comparison can be made with the LC_{50}s and EC_{50}s in Table 2. The variation of organic carbon-normalized LC_{50}s and EC_{50}s between sediments is less than a factor of two to three and is comparable to the variation in pore water LC_{50}s and EC_{50}s. A more comprehensive comparison has been presented in Figures 2 and 3, which also examine the use of the water-only LC_{50} to predict the pore water and sediment organic carbon LC_{50}s.

Bioaccumulation factors calculated on the basis of organic carbon-normalized chemical concentrations are listed in Table 3, for permethrin, cypermethrin, and

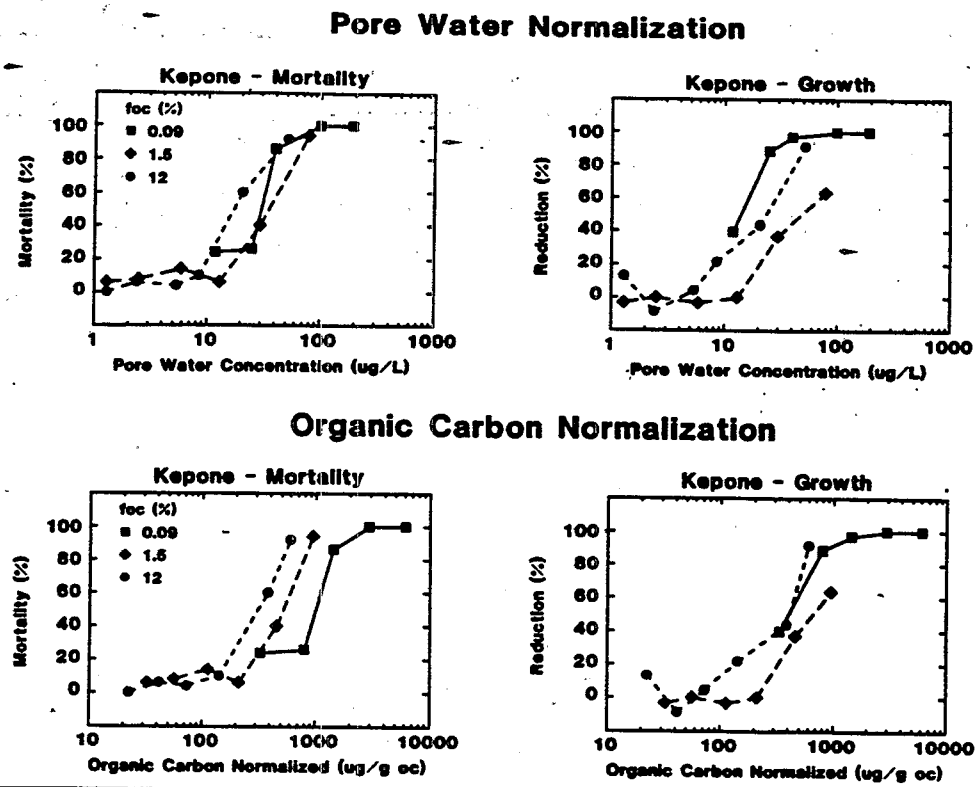


Figure 26.—Comparison of percent survival (left) and growth rate reduction (right) of C. tentans to kepone concentration in pore water (top) and in bulk sediment, using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations [17].

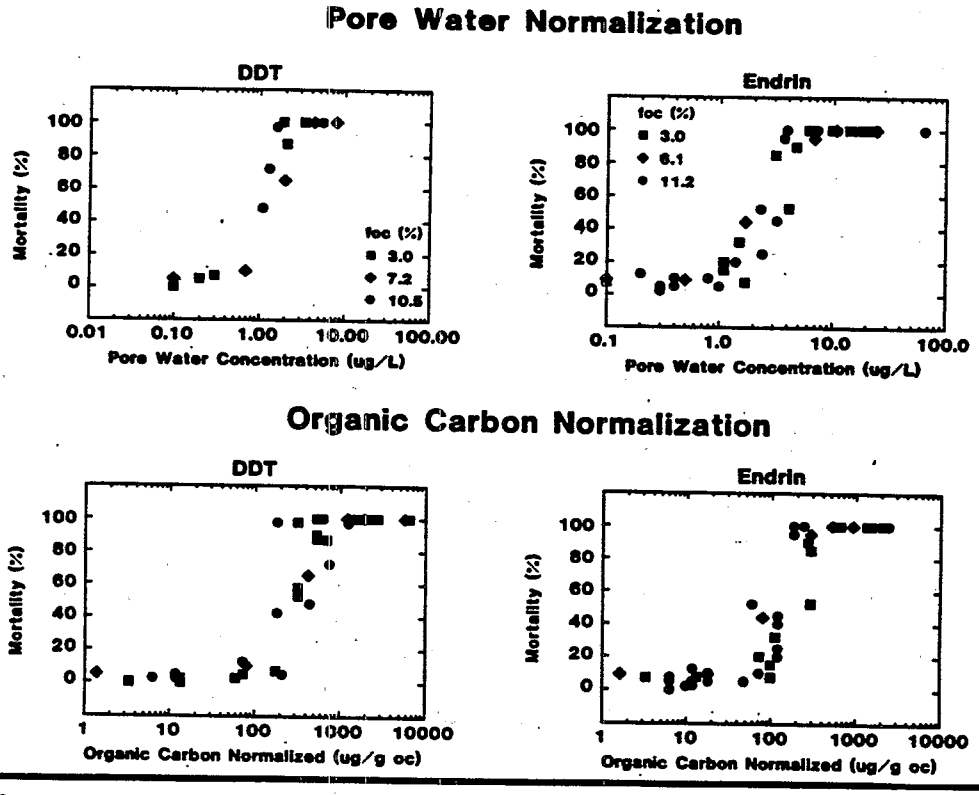


Figure 27.—Comparison of percent survival of *H. azteca* to DDT (left) and endrin (right) concentration in pore water (top) and in bulk sediment, using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations [20, 21].

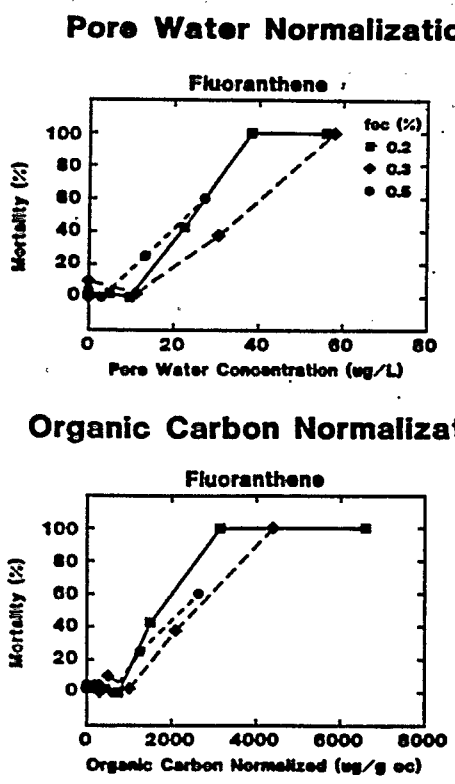


Figure 28.—Comparison of percent survival of *R. abronius* to fluoranthene concentration in pore water (top) and bulk sediment, using organic carbon normalization (bottom) for sediments with varying organic carbon concentrations [19].

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 pore water BAFs.

Bioaccumulation and organic carbon normalization. Laboratory and field data also exist for which no pore water or DOC measurements are available 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 [58]). If C_b is the chemical concentration per unit wet weight of the organism, then the partitioning equation is

$$C_b = K_L f_L C_d \qquad (27)$$

where

K_L = lipid/water partition coefficient (L/kg lipid)

f_L = weight fraction of lipid (kg lipid/kg organism)

C_d = free dissolved chemical concentration (μg/L)

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

$$C_{b,L} = \frac{C_b}{f_L} = K_L C_d. \qquad (28)$$

The lipid-normalized body burden and the organic carbon-normalized sediment concentration can be used to compute a bioaccumulation ratio, which can be termed the BSF [59]:

$$BSF = \frac{C_{b,L}}{C_{s,oc}} = \frac{K_L}{K_{oc}} \approx \frac{K_L}{K_{ow}} \qquad (29)$$

The second equality results from using the partitioning Equations 16 and 28 and the third from the approximation that $K_{oc} \approx K_{ow}$. The BSF is the partition coefficient between organism lipid and sediment organic carbon. If the equilibrium assumptions are valid for both organisms and sediment particles, the BSF should be independent of both particle and organism properties. In addition, if lipid solubility of a chemical is proportional to its octanol solubility, $K_L \propto K_{ow}$, then the lipid normalized-organic carbon normalized BSF should be a constant, independent of particles, organisms, and chemical properties [59, 60, 61]. This result can be tested directly.

The 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 [59]. 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 has been performed by Rubinstein et al. [62]. 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 29 and 30 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

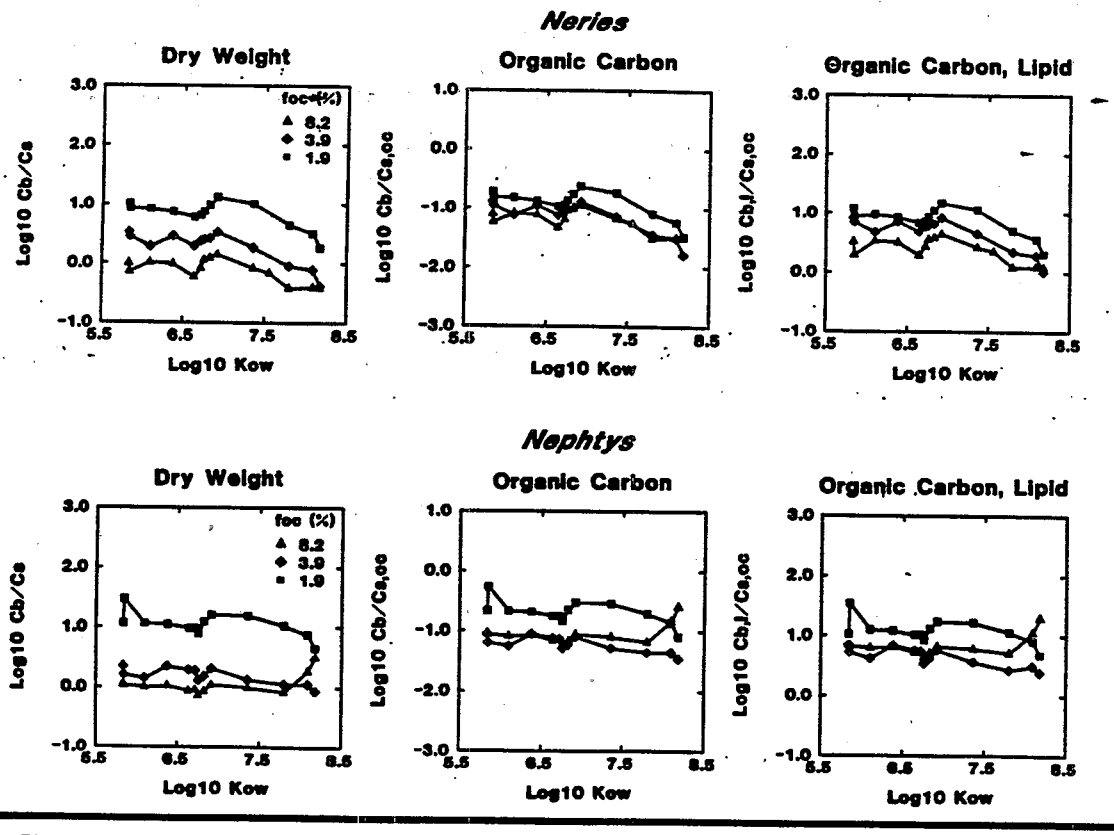


Figure 29.—Plots of the BSF (ratio of organism-to-sediment concentration) for three sediments for a series of PCB congeners versus the $\log_{10}K_{ow}$ for that congener. The dry weight normalization for both organism and sediment (left panels); organic carbon normalization for the sediment (middle panels); and organic and lipid normalization (right panels) as indicated. The organisms are *Nereis* (top) and *Nephtys* (bottom). Data from [62].

carbon and lipid normalization (right panels) are shown. The results for each sediment are connected by lines and separately identified.

The BSFs based on dry weight normalization are quite different for each of the sediments with the low carbon sediment exhibiting the largest values. Organic carbon normalization markedly reduces the variability in the BSFs from sediment to sediment (center panels). Lipid normalization usually further reduces the variability. Note that the BSFs are reasonably constant for the polychaetes, although some suppression is evident at $\log_{10}K_{ow} > 7$. The clams, however, exhibit a marked declining relationship.

Results of a similar though less extensive experiment using one sediment and oligochaete worms have been reported [52]. A plot of the organic carbon- and lipid-normalized BSF versus K_{ow} from this experiment is shown on Figure 31, together with the averaged polychaete data (Fig. 29). 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} [59]. However, for a specific chemical and a specific organism, for example *Nereis* and any PCB congener (Fig. 29) organic carbon normalization reduces the effect of the varying sediments. This demonstrates the utility of organic carbon normalization and supports its use in generating SQC.

A further conclusion can be reached from these results. It has been pointed out by Bierman [63] that the lipid- and carbon-normalized BSF is in the range of 0.1 to 10 (Figs. 29 to 31) supports the contention that the partition coefficient for sediments is $K_{oc} = K_{ow}$ and that the particle concentration effect does not appear to be affecting the free concentration in sediment pore water. The reason is that the lipid- and carbon-normalized BSF is the ratio of the solubilities of the chemical in lipid and in particle carbon (Eqn. 29). Because the solubility of nonionic organic chemicals in various nonpolar solvents is similar [64], 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 BSF data is that K_{oc} is approximately equal to K_{ow} for sediments [63].

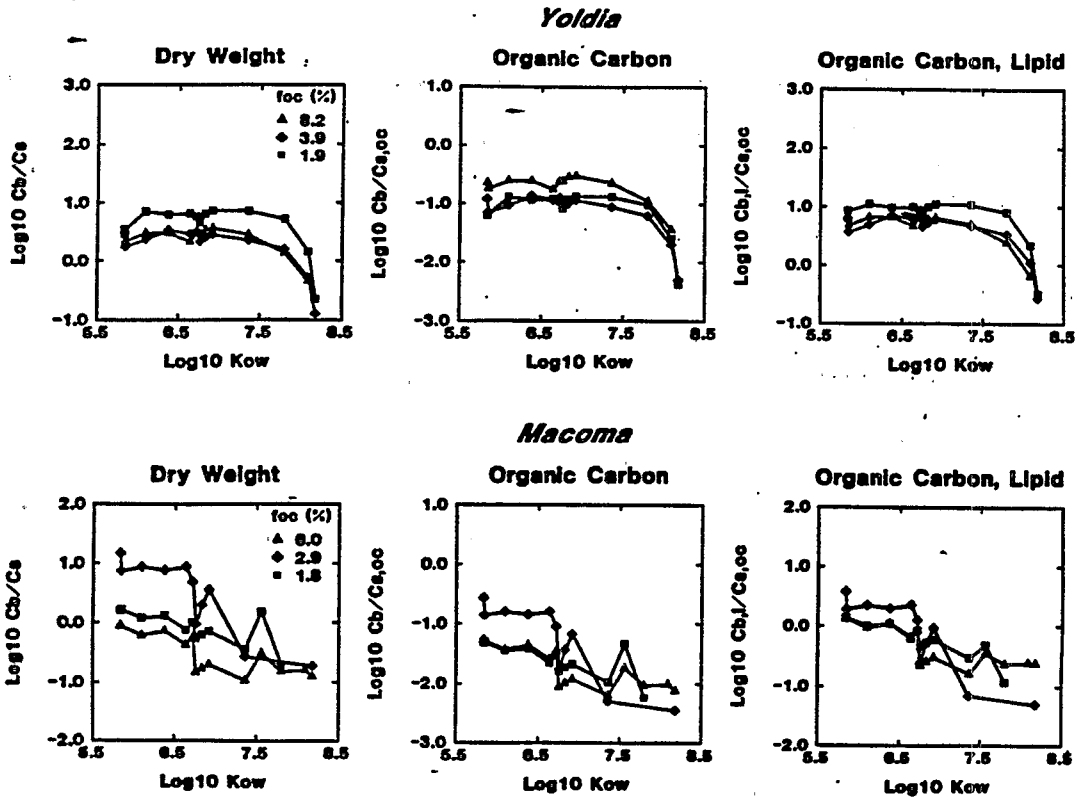


Figure 30.—Plots of the BSF (ratio of organism-to-sediment concentration) for three sediments for a series of PCB congeners versus the $\log_{10}K_{ow}$ for that congener. The dry weight normalization for both organism and sediment (left panels); organic carbon normalization for the sediment (middle panels); and organic and lipid normalization (right panels) as indicated. The organisms are *Yoldia* (top) and *Macoma* (bottom). Data from [62].

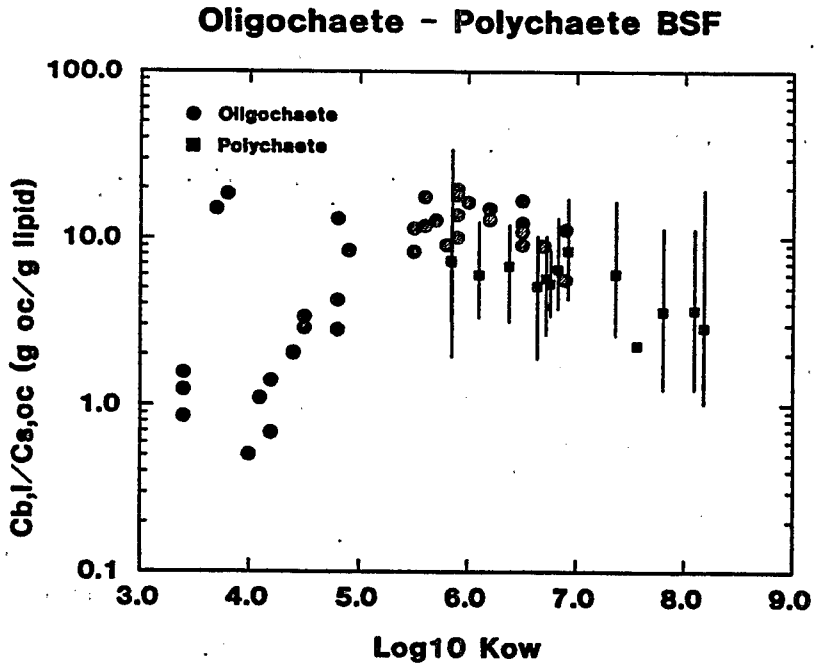


Figure 31.—Plots of the BSF (ratio of organism lipid to sediment organic carbon concentration) for a series of PCB congeners and other chemicals versus $\log_{10}K_{ow}$. Data for oligochaetes [51] and polychaetes [62].

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.

Determination of the 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 [65]). 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 pore water. However, the data correlate equally well with the organic carbon-normalized sediment concentration (see Figs. 2 and 3). This observation suggests that sediment organic carbon is the route of exposure. In fact, neither conclusion follows necessarily from these data because an alternate explanation is available that is independent of the exposure pathway.

Consider the hypothesis that the chemical potential or, as it is sometimes called, the fugacity [66] of a chemical controls its biological activity. The chemical potential, μ_d, of the free concentration of chemical in pore water, C_d, is

$$\mu_d = \mu_o + RT \ln(C_d) \quad (30)$$

where μ_o is the standard state chemical potential and RT is the product of the universal gas constant and absolute temperature [67]. For a chemical dissolved in organic carbon—assuming that particle organic carbon can be characterized as a homogeneous phase—its chemical potential is

$$\mu_{oc} = \mu_o' + RT \ln (C_{s,oc}) \quad (31)$$

where Cs,oc is the weight fraction of chemical in organic carbon. If the pore water is in equilibrium with the sediment organic carbon then

$$\mu_d = \mu_{oc}. \quad (32)$$

The chemical potential that the organism experiences from either route of exposure (pore water or sediment) is the same. Hence, so long as the sediment is in equilibrium with the pore 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 pore water or organic carbon-normalized sediment concentration, suggests that biological effects are proportional to chemical potential or fugacity.

The issue with respect to bioavailability is this: In which phase is μ most easily and reliably measured? Pore water concentration is one option.

However, it is necessary that the chemical complexed to DOC be a small fraction of the total measured concentration or that the free concentration be directly measured, perhaps by the C_{18} column technique [42]. Total sediment concentration normalized by sediment organic carbon fraction is a second option. This measurement is not affected by DOC complexing. The only requirement is that sediment organic carbon be the only sediment phase that contains significant amounts of the chemical. This appears to be a reasonable assumption for most aquatic sediments. Hence, SQC are based on organic carbon normalization because pore water normalization is complicated by DOC complexing for highly hydrophobic chemicals.

Applicability of WQC as the Effects Levels for Benthic Organisms

The EqP method for deriving SQC utilizes partitioning theory to relate the sediment concentration to the equivalent free chemical concentration in pore water and in sediment organic carbon. The pore water concentration for SQC should be the effects concentration for benthic species.

This section examines the validity of using the EPA WQC concentrations to define the effects concentration for benthic organisms. This use of WQC assumes that (a) the sensitivities of benthic species and species tested to derive WQC, predominantly water column species, are similar, (b) the levels of protection afforded by WQC are appropriate for benthic organisms, and c) 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 of the acute sensitivities of benthic and water column species, using data compiled from the published EPA WQC for nonionic organic chemicals as well as metals and ionic organic chemicals, is presented. Then a comparison of the FCVs and the chronic sensitivities of benthic saltwater species in a series of sediment colonization experiments is made.

Method-Relative Acute Sensitivity

The relative acute sensitivities of benthic and water column species are examined by using LC_{50}s for freshwater and saltwater species from draft or published WQC documents that contain minimum database requirements for calculation of final acute values (Table 4). These data sets 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 fresh water, using 208 species with 40 chemicals, and the 1,046 tests conducted in salt water, 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). 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 greater than 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. 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). 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 [8].

Comparison of the Sensitivity of Benthic and Water Column Species

Most Sensitive Species. The relative acute sensitivities of the most sensitive benthic and water column species were examined by comparing the final acute values (FAV) for benthic and water column organisms, using acute LC_{50} 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 32 (top). The line represents perfect agreement.

Data on the sensitivities of benthic infaunal species are limited. Of the 40 chemicals for which WQC for freshwater organisms are available, two or fewer infaunal species were tested with 28 (70 percent) of the chemicals, and five or fewer species were tested with 34 (85 percent) 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 percent) of the chemicals, and 5 or fewer species were tested with 23 (77 percent) of the chemicals. Of these chemicals only zinc in salt water 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 most sensitive 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 (Fig. 32, bottom). In this comparison, the number of acute values for freshwater benthic species for each chemical averaged nine, 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 SQC for the protection of infaunal and epibenthic species.

All species. A more general comparison of the species sensitivities can be made if all the LC_{50} data are used. One approach examines the relative loca-

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

		NO. OF SALTWATER SPECIES				NO. OF FRESHWATER SPECIES			
CHEMICAL	DATE OF PUBLICATION	TOTAL[a]	INFAUNAL	EPIBENTHIC	WATER COLUMN	TOTAL[a]	INFAUNAL	EPIBENTHIC	WATER COLUMN
ACENAPTHENE	9/87[b]	10	–	3	7				
ACROLEIN	9/87[b]	–	–	–	–	12	1	5	7
ADRIN	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
CHLORINE	1985	23	2	9	15	33	1	9	26
CHLORPYRIFOS	1986	15	2	8	10	18	2	8	11
CHROMIUM (III)	1984	–	–	–	–	17	3		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
HEXACHLOROCYCLOHEXANE	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
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	1	3
TOXAPHENE	1986	15	2	9	11	37	5	13	23
TRIBUTYLTIN	9/87[b]	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] Draft aquatic life criteria document, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards division, Washington, D.C.

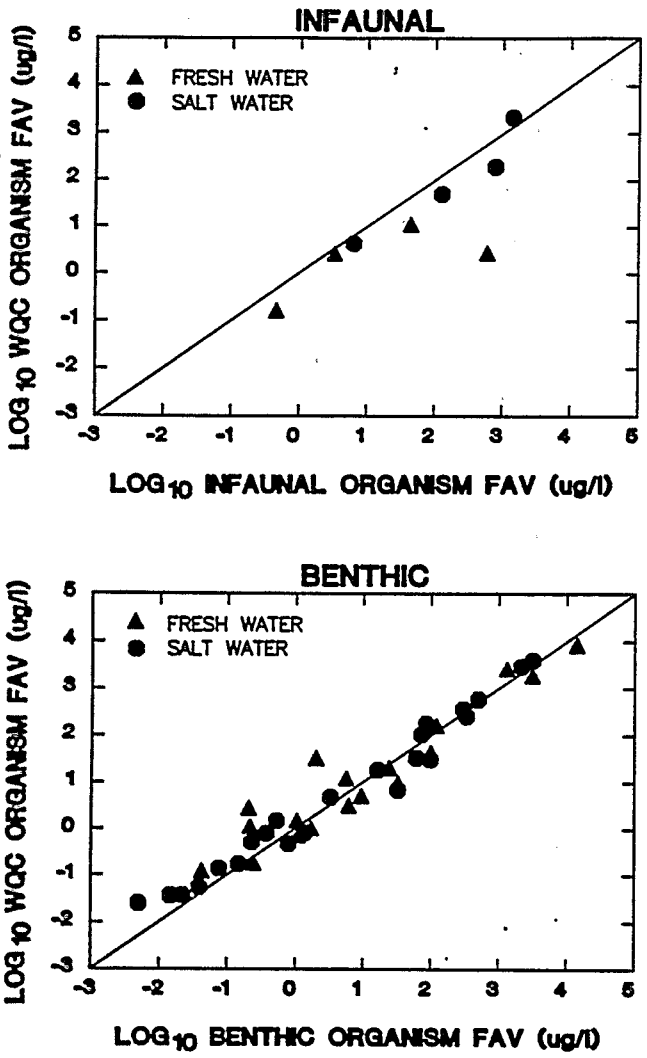


Figure 32.—Comparison of LC_{50} or EC_{50} acute values for the most sensitive benthic (abscissa) and water column (ordinate) species for chemicals listed in Table 5. Benthic species are defined as infaunal species (habitat types 1 and 2, left panel) or infaunal and epibenthic species (habitat types 1–4); see Table 6.

tion of benthic species in the overall species sensitivity distribution. For each chemical in either fresh or salt water, one can examine the distribution of benthic species in a rank-ordering of all the species' LC_{50}s. If benthic species were relatively insensitive, then they would predominate in ranking among the larger LC_{50} concentrations. Equal sensitivity would be indicated by a uniform distribution of species within the overall ranking. Figure 33 presents the results for tests of nickel in salt water. The LC_{50}s are plotted in rank order, and the benthic species are indicated. Infaunal species are among the most tolerant (left panel), whereas infaunal and epibenthic species are uniformly distributed among the species (right panel).

Table 5.—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; that is fouling organisms on pilings, ships, and so on, and zooplankton, pelagic fish, and so on.

This comparison can be done chemical by chemical. However, to make the analysis more robust, the LC_{50} data for each chemical-water type can be normalized to zero log mean and unit log variance as follows:

$$LC_{50n,ij} = \frac{\log(LC_{50ij}) - \mu_i}{\sigma_i} \qquad (33)$$

where i indexes the chemical-water type, μ_i is the log mean and si is the log standard deviation, j indexes the LC_{50}s within the ith class, and $LC_{50n,ij}$ is the normalized LC_{50}. This places all the LC_{50}s 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 data set.

The comparison is made in Figure 34. If the sensitivity of benthic species is not unique, then a constant percentage of benthic species-normalized LC_{50}s, indicated by the dashed line, should be repre-

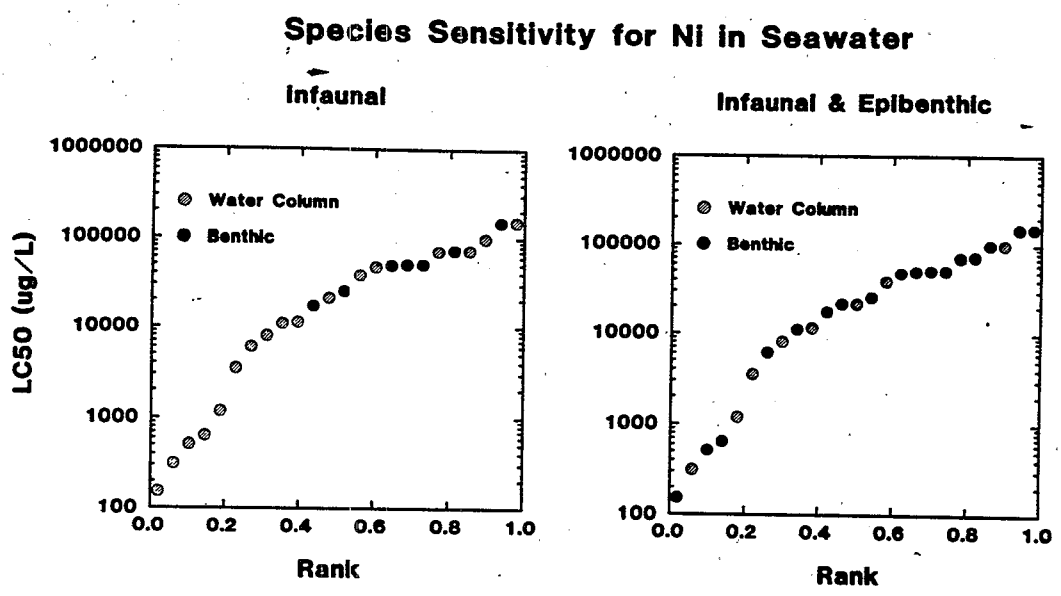


Figure 33.—LC_{50}s versus rank for nickel in seawater. Infaunal organisms (left) and infaunal and epibenthic (right) are identified by the solid symbols. The plot illustrates the distribution of benthic organisms in the overall species sensitivity distribution.

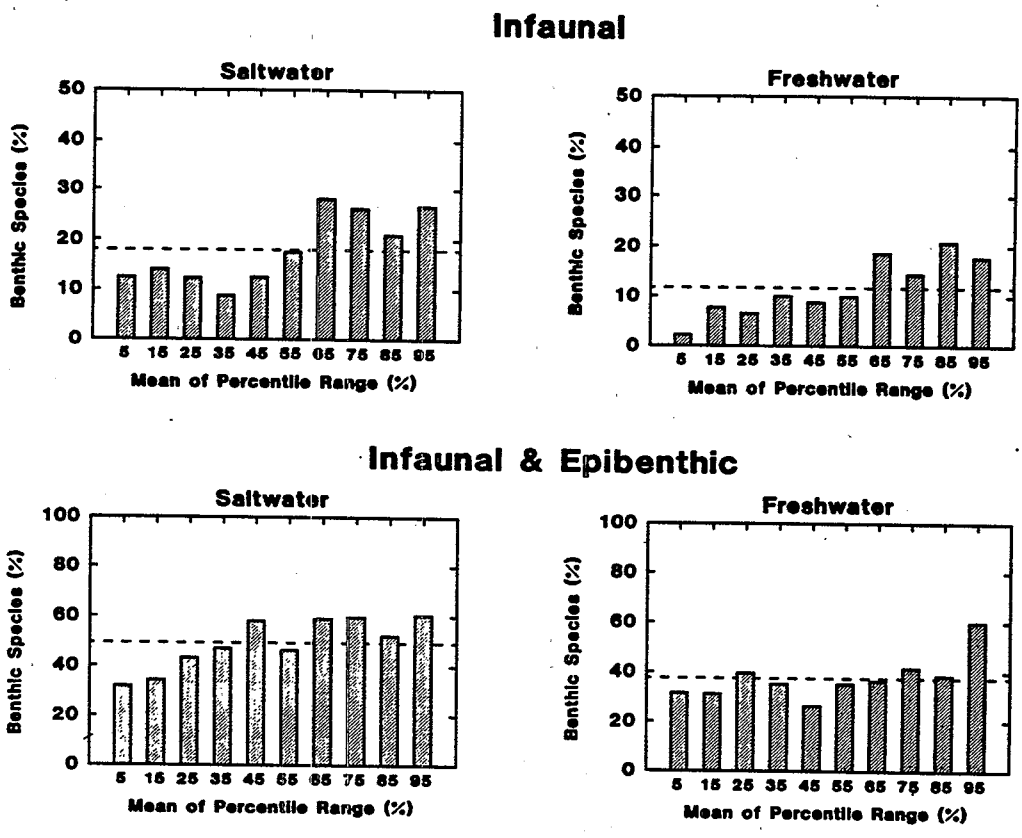


Figure 34.—Histograms of the proportion of saltwater and freshwater benthic organisms in 10 percentile groups of all normalized LC_{50}s. If benthic organisms were as equally sensitive as water column organisms, the histograms should be of uniform height as indicated by the dashed line, the overall percentage of benthic species in the data set. Top panels include only infaunal organisms as benthic. The bottom panel includes infaunal and epibenthic as benthic organisms.

sented 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 (top panel) display a tendency to be underrepresented in the lowest deciles. However, the infaunal and epibenthic species (bottom panels) 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 SQC derived by using the FCV should protect benthic species.

Benthic Community Colonization Experiments

Toxicity tests that determine the effects of chemicals on the colonization of communities of benthic saltwater species [68-74] appear to be particularly sensitive at 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 sufficient duration to maximize response. The test typically includes three 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 from two to four months, and the number of species and individuals in aquaria receiving the chemical are enumerated and compared to 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 organisms from chronic effects of a chemical [8]. 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 SQC. The initially clean sandy sediment will rapidly equilibrate with the inflowing overlying water chemical concentration as the pore 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. 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.

Water Quality Criteria (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 6) 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 similar to 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 water quality criteria 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 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 LC_{50}s and the results of colonization experiments, are generally similar, although, as

Table 6.—Comparison of WQC FCVs and concentrations affecting (LOEC) and not affecting (NOEC) benthic colonization.

SUBSTANCE	COLONIZATION VERSUS FCV[a]	CONC. µg/L	SENSITIVE TAXA	REFERENCE
PENTACHLOROPHENOL	Colonization LOEC	16.0	Molluscs, Abundance	[69,70]
	FCV	7.9	Molluscs, Crustacea, Fish	
	Colonization NOEC	7.0	–	
AROCLOR 1254	Colonization LOEC	0.6	Crustacea	[71]
	Estimated FCV	~0.1	Crustacea, Fish	[68]
	Colonization NOEC	0.1	–	
CHLORPYRIFOS	Colonization LOEC	0.1	Crustacea, Molluscs, species richness	[72]
	FCV	0.005	Crustacea	
	Colonization NOEC	–	–	
FENVALERATE	Colonization LOEC	0.01	Crustacea, Chordates	[73]
	Estimated FCV	~0.002	Crustacea	
	Colonization NOEC	–	–	
1,2,4-TRICHLOROBENZENE[a]	Estimated FCV	50.	Crustacea, Fish	[74]
	Colonization LOEC	40.	Molluscs, abundance	
	Colonization NOEC	–	–	
TOXAPHENE	Colonization LOEC	11.0	Crustacea, species richness	[68]
	Colonization NOEC	0.8	–	
	FCV	0.2	Crustacea, fish	

[a]Six day exposure to established benthic community

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.

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 four phyla and only 28 saltwater infaunal species from five phyla. Only seven freshwater infaunal species and 24 freshwater epibenthic species have been tested with five or more of the 40 WQC chemicals. Similarly, nine saltwater infaunal species and 20 epibenthic species have been tested with five 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 SQC 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.

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.

GENERATION OF SQC

Parameter Values

The equation from which SQC are calculated is

$$SQC_{oc} = K_{oc}FCV \quad (34)$$

(see Eqns. 2 to 7 and associated text). Hence, the SQC 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 11.

The reliability of SQC_{oc} depends directly on the reliability of K_{ow}. For most chemicals of interest, the available K_{ow}s (e.g., [75]) 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 [76] and the slow stirring [73] method appear to give comparable results, whereas earlier methods produced more variable results. Hence, it is recommended that literature values for K_{ow}s not be used unless they have been measured using the newer techniques.

Measurement 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:

$$K_{ow} = C_{OCT}/C_w \qquad (35)$$

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 ten as log P.

At the EPA Environmental Research Laboratory (ERL) at Athens, Georgia, three methods were selected for measurement and one for estimation of K_{ow} for the five chemicals for which SQC are being developed. The measurement methods were shake-centrifugation (SC), generator column (GC), and slow-stir-flask (SSF). The estimations were made using the computer expert system SPARC. The discussion of these methods is adapted from ERL at Athens research protocols.

The SC method [78] is routinely used to measure the partitioning of compounds with K_{ow} values on the order of 10^2 to 10^6. The method involves adding a layer of octanol containing the compound of interest onto the surface of the water contained in a centrifuge tube. Both phases were mutually presaturated before beginning the measurements. Equilibration is established by gentle agitation and any emulsions formed are broken by centrifugation. The concentration in each phase is determined, usually by a chromatographic method, and the K_{ow} value calculated using Equation 35.

The original GC method, limited to compounds with K_{ow} values of less than 10^6, was modified [76] and used to determine K_{ow} values up to 10^8. Briefly, the method requires the packing of a 24-cm length of tubing with silanized Chromosorb W. Octanol, containing the chemical in a known concentration, is then pulled through the dry support by gentle suction until the octanol appears at the exit of the column. Water is then pumped through the column at a rate of less than 2 mL per minute to allow equilibration of the chemical between the octanol and water. The first 100 mL are discarded followed by collection of an amount of water sufficient to determine the chemical concentration. The K_{ow} is calculated using Equation 35.

The SSF method [77] achieves equilibrium of the compound between octanol and water by a gentle stirring of the phases contained in a six-liter flask. One liter aliquots of the aqueous phase are withdrawn at two-day intervals and the concentration of the chemical determined. Equilibrium is considered to be established when the concentration of the chemical is constant in successive samples (usually after two to six days). The procedure is to set up three six-liter flasks in a constant temperature room. Five liters of water are added to each flask and the water is stirred with teflon-coated magnetic stir bars overnight to achieve temperature equilibration. The temperature equilibrated octanol is added very gently along the side wall to avoid mixing of the two phases. At the time of sampling, a one-liter aqueous sample is drained from a sampling port at the base of the flask without disturbing the octanol layer. The concentration in each phase is determined, usually by a chromatographic method, and the K_{ow} value calculated using Equation 35.

When repetitive measures were made in the Athens laboratory, a protocol was established to assure compatibility with future experiments. These protocols described the entire experimental scheme including planning, sample requirements, experimental set up and chemical analysis, handling of data, and quality assurance. Only established analytical methods for solute concentration measurement were applied and the purity and identity of the chemical was determined by spectroscopic means. The name on the label of the chemical's container was not proof of identity.

Standard reference compounds (SRCs) were tested with each experiment. SRCs are compounds that are used as quality assurance standards and as references in inter-laboratory generation of data. The value of the process constant(s) has been established by repetitive measurements for an SRC and serves as baseline information for evaluating all experimental techniques and all aspects of quality assurance. Because the SRC is taken through the entire experimental scheme, its acceptable result assures the experimenter that equipment and measurement methods are functioning satisfactorily. Table 7 shows the $\log_{10}K_{ow}$ values for endrin, dieldrin, acenaphthene, phenantherene, and fluoranthene and the

Table 7.—$Log_{10}K_{ow}$ values measured by shake-centrifugation (SC), Generator column (GC), and slow-stir-flask (SSF) for Endrin, Dieldrin, Acenapthene, Phenanthrene, Fluoranthene and Concurrently analyzed standard reference compounds.

CHEMICAL	SC	GC	SSF
ENDRIN	4.65	4.67	4.86
	4.91	5.01	4.59
	4.79	4.73	4.97
	4.76	4.62	4.95
	4.84	5.09	5.02
	4.83	5.28	4.82
	4.84		5.04
	4.83		4.91
			5.07
			4.93
			4.96
			4.78
DIELDRIN	5.04	4.89	5.33
	5.00	4.88	5.43
	5.04	5.18	5.38
	5.03	5.15	5.33
	5.04	5.26	5.43
	4.88	5.38	5.08
	4.99	5.67	5.28
	5.04		
ACENAPHTHENE	3.82	4.18	3.81
	3.84	4.17	3.84
	3.88	4.16	3.84
	3.84	4.17	
PHENANTHRENE	4.29	4.47	4.57
	4.25	4.41	4.53
	4.33	4.46	4.50
	4.33	4.24	
FLUORANTHENE	4.99	5.19	4.98
	5.00	5.35	5.02
	5.01	5.47	5.02
		5.48	5.10
			5.14
			5.23
BIPHENYL	4.06		
PYRENE	5.17		

Source: U.S. EPA Environmental Research Laboratory, Athens Georgia.

SRCs, biphenyl and pyrene, measured at the Athens laboratory by the SC methods. The SRCs were not measured by the GC or SSF methods.

The log_{10} of the average of eight previous measurements of K_{ow} by the shake-centrifugation method for biphenyl is 4.06. The log_{10} of the average of 13 previous measurements of K_{ow} by the shake-centrifugation method for pyrene is 5.17. These average K_{ow}s are in good agreement with the SQC shake-centrifugation measurements for biphenyl and pyrene made concurrently with the measurements for the five chemicals providing quality assurance for the experimental techniques (see Table 7).

Literature K_{ow}. An extensive literature search was performed for the five compounds and two standard reference compounds, biphenyl and pyrene. Generally, problems encountered in compiling and reporting fate constants from published data and from databases during a several years have ranged from retrieval of misquoted numbers to solution of nested citations [79]. Some citations were three or more authors removed from the original work or contained data referenced as unpublished data or as personal communication. The same problems were experienced during a ERL, Athens literature search. The largest difference in misquoting numbers was six orders of magnitude. For these reasons, ERL obtained data from the primary sources and released values only from these primary sources. Unpublished data or data that originated through personal communication were rejected as well as data that were insufficiently documented to determine their credibility and applicability or reliability.

Tables 8 and 9 show the measured and estimated $\log_{10}K_{ow}$ values, respectively, retrieved by this literature search. Each of the measured values was experimentally determined by the researcher using one of several laboratory methods. The individual experimental methods are not identified here. The estimated literature values were computed by the researchers by one of several published techniques. The individual computational techniques also are not identified here.

Estimated K_{ow}. A promising new computational method for predicting reactivity is the computer expert system SPARC (SPARC Performs Automated Reasoning in Chemistry) being developed by ERL's Samuel W. Karickhoff and scientists at the University of Georgia [106]. The system has the capability of crossing chemical boundaries to cover all organic chemicals and uses algorithms based on fundamental chemical structural theory to estimate parameters. Organic chemists have in the past established the types of structural groups or atomic arrays that impart certain types of reactivity and have described, in "mechanistic" terms, the effects on reactivity of the structural constituents appended to the site of reaction.

To encode this knowledge base, Karickhoff and his associates developed a classification scheme that defines the role of structural constituents in affecting or modifying reactivity. SPARC quantifies reactivity by classifying molecular structures and selecting appropriate "mechanistic" models. It uses an approach that combines principles of quantitative structure-activity relationships, linear free energy theory (LFET), and perturbed molecular orbital (PMO) or quantum chemistry theory. In general, SPARC uses LFET to compute thermal properties and PMO theory to describe quantum effects such as delocalization energies or polarizabilities of *pi* electrons.

Table 8.—Measured $\log_{10}K_{ow}$ values found in the literature.

CHEMICAL	LOG10KOW VALUE	REFERENCE
ENDRIN	4.40	[80]
	4.92	[81]
	5.01	[82]
	5.195	[77]
DIELDRIN	4.09	[81]
	4.54	[83]
	4.65	[84]
	5.401	[77]
	6.2	[85]
ACENAPTHENE	3.92	[86]
PHENANTHRENE	4.28	[87]
	4.46	[88]
	4.562	[77]
	4.57	[78]
	4.63	[89]
FLUORANTHENE	5.155	[77]
BIPHENYL	3.16	[90]
	3.63	[84]
	3.75	[91]
	3.76	[92]
	3.79	[80]
	3.89	[76]
	4.008	[77]
	4.01	[82]
	4.04	[86]
	4.09	[84]
	4.10	[89]
PYRENE	4.96	[80]
	5.05	[84]
	5.09	[93]
	5.18	[78]
	5.22	[89]
	5.52	[94]

SPARC computes K_{ow} values from activity coefficients in the octanol ($\sim 1_o$) and water ($\sim 1_w$) phases using Equation 36:

$$\text{Log}_{10}K_{ow} = \log_{10}(\sim 1_w / \sim 1_o) + \log_{10}(M_o/M_w) \quad \textbf{(36)}$$

where M_o and M_w are solvent molecularities of octanol and water, respectively. SPARC computes activity coefficients for any solvent/solute pair for which the structure parser can process the structure codes. Ultimately, any solvent/solute combination can be addressed. New solvents can be added as easily as solutes by simply providing a Simplified Molecular

Table 9.—Estimated $\log_{10}K_{ow}$ values found in the literature.

CHEMICAL	LOG10KOW VALUE	REFERENCE
ENDRIN	3.54	[95]
	5.6	[96]
DIELDRIN	3.54	[95]
ACENAPTHENE	3.70	[96]
	3.92	[97]
	3.98	[95]
	4.03	[98]
	4.15	[99]
	4.22	[100]
	4.33	[101]
	4.43	[102]
PHENANTHRENE	4.44	[100]
	4.45	[95]
	4.63	[99]
	4.64	[96]
FLUORANTHENE	4.90	[95]
	4.95	U.S. EPA, Graphical Exposure Modeling System [GEMS]*
	5.22	[96]
	5.29	[99]
	5.33	[101]
BIPHENYL	3.79	[96]
	3.95	[97]
	3.98	[100]
	4.14	[99]
	4.25	[102]
	4.42	[103]
PYRENE	4.50	[104]
	4.85	[100]
	4.88	[105]
	4.90	[95]
	5.12	[99]
	5.22	[96]
	5.32	[101]

* The Graphical Exposure Modeling System (GEMS) is an interactive computer system located on the VAX Cluster in the National Computer Center in Research Triangle Park, North Carolina, under management of EPA's Office of Toxic Substances. PC GEMS is the version for personal computers.

Interactive Linear Entry System (SMILES) string [107, 108]. Activity coefficients for either solvent or solute are computed by solvation models that are built from structural constituents requiring no data besides the structures.

A goal for SPARC is to compute a value that is as accurate as a value obtained experimentally for a fraction of the cost required to measure it. Because SPARC does not depend on laboratory operations conducted on compounds with structures closely related to that of the solute of interest, it does not have the inherent problems of phase separation encountered in measuring highly hydrophobic compounds ($\log_{10}K_{ow} > 5$). For these compounds, SPARC's computed value should, therefore, be more reliable than a measured one. Reliable experimental data with good documentation are still necessary, however, for further testing and validation of SPARC.

CLOGP [109] is a computerized program that estimates the $\log_{10}K_{ow}$, based on Leo's Fragment Constant Method [105]. CLOGP provides an estimate of $\log_{10}K_{ow}$ using fragment constants (f_i) and structural factors (F_i) that have been empirically derived for many molecular groups. The estimated $\log_{10}K_{ow}$ is obtained from the sum of constants and factors for each of the molecular subgroups comprising the molecule using Equation 37.

$$\text{Log}_{10}K_{ow} = \sum_{i=1}^{n} (f_i + F_i) \qquad (37)$$

The method assumes that $\log_{10}K_{ow}$ is a linear additive function of the structure of the solute and its constituent parts and that the most important structural effects are described by available factors. The structure of the compound is specified using the SMILES notation. The CLOGP algorithm is included in the database QSAR (see Table 10) located at EPA's Environmental Research Laboratory at Duluth, Minnesota. All CLOGP values reported here were obtained through QSAR. Table 10 shows the estimated $\log_{10}K_{ow}$ values that were computed with SPARC and CLOGP.

Table 10.—QSAR *obtained $\text{Log}_{10}K_{ow}$ values estimated by SPARC and CLOGP

CHEMICAL	SPARC	CLOGP
ENDRIN	5.40	–
DIELDRIN	5.40	–
ACENAPTHENE	3.88	4.07
PHENANTHRENE	4.58	4.49
FLUORANTHENE	5.21	4.95
BIPHENYL	4.25	4.03
PYRENE	5.13	4.95

*Quantitative Structure-Activity Relationships (QSAR) is an interactive chemical database and hazard assessment system designed to provide basic information for the evaluation of the fate and effects of chemicals in the environment. QSAR was developed jointly by the U.S. EPA Environmental Research Laboratory, Duluth, Minnesota, Montana State University Center for Data System and Analysis, and the Pomona College Medicinal Chemistry Project.

K_{ow} Selection. Investigators selected SSF derived K_{ow} values to derive the K_{oc} to calculate SQC concentrations because SSF is the superior method for chemicals with low and high K_{ow} values, has the least statistical bias, and is highly reproducible. Use of values from one method provides consistency across chemicals. This choice was made after an analysis of the K_{ow} values generated by the three measurement methods discussed above (GC, SC, and SSF) and the SPARC estimation method for the five chemicals for which SQC are currently being developed (acenaphthene, dieldrin, endrin, fluoranthene, and phenanthrene). K_{ow}s were measured with repeat experiments and a mean K_{ow} was computed for each method, for each chemical (Table 11).

The mean measured K_{ow}s and the SPARC estimation method provide similar K_{ow} estimates. To select a final K_{ow} for computing the SQC, the four methods were compared and the bias of each method were quantified. (Bias is defined as the mean difference between the best-fit estimate of K_{ow} using all four methods and the estimates from each method.) Figure 35 presents the mean measured K_{ow}s for each chemical and the range of values. SC tends to estimate lower values while the GC method estimates higher values. GC values exhibit greater variability than the SC and SSF values. SSF estimates of K_{ow}s were generally within the range of the SC and GC methods.

A statistical analysis of the three measurement methods and SPARC method was performed. The following linear model was used to compute estimates of K_{ow} for each chemical (represented by E1, E2, E3, E4, E5) and the biases contributed by each of the estimation methods (represented by B1, B2, B3, B4). The regression model is as follows:

$$\log_{10}K_{ow} = E1 * \text{Endrin} + E2 * \text{Dieldrin} + E3 * \text{Acenaphthene} + E5 * \text{Fluoranthene} + B1 * \text{Shake Centrifugation} + B2 * \text{Generator Column} + B3 * \text{Slow-Stir-Flask} + B4 * \text{SPARC}$$

To compute $\log_{10}K_{ow}$ the variables, ENDRIN, ... SPARC, are set to either 0 or 1 and the appropriate coefficient for the chemical and method that corresponds to the particular K_{ow} measurement or estimate is selected. Table 12 presents the model K_{ow} results and bias contributed by each method. Shake centrifugation and SPARC estimates provide the greatest bias, followed by the generator column method. Slow-stir-flask provides the least bias. Slow-stir-flask was chosen as the method to use to determine K_{ow} for use in computing SQC since it appears to have the least bias. In addition, it exhibits similar variability to the shake centrifugation method and less variability than the generator column method.

Table 12.—Model results to determine method bias

COEFFICIENT	ESTIMATE OF K_{ow} OR BIAS FOR	VALUE
E1	Endrin	4.88
E2	Dieldrin	5.17
E3	Acenaphthene	3.94
E4	Phenanthrene	4.40
E5	Fluoranthene	5.13
B1	Shake Centrifugation	-0.115
B2	Generator Column	0.091
B3	Slow-stir Flask	0.040
B4	SPARC	0.193

K_{oc} Determination. The previous section discusses selecting the method for measuring K_{ow}s for use in computing SQC. It is widely accepted that K_{oc}s can be estimated from K_{ow}. The K_{oc} used to calculate the sediment quality criteria is based on the regression of $\log_{10}K_{oc}$ to $\log_{10}K_{ow}$, Equation 11.

Table 11.—K_{ow} as measured by the EPA Environmental Laboratory at Athens, GA.

	$\text{Log}_{10}K_{ow}$ (NUMBER OF DETERMINATIONS)		
CHEMICAL	SHAKE CENTRIFICATION	GENERATOR COLUMN	SLOW STIR FLASK
ENDRIN	4.80 (8)	4.97 (6)	4.92 (12)
DIELDRIN	5.01 (8)	5.16 (7)	5.34 (7)
ACENAPHTHENE	3.85 (4)	4.17 (4)	3.83 (3)
PHENANTHRENE	4.30 (4)	4.40 (4)	4.54 (3)
FLUORANTHENE	5.00 (3)	5.39 (4)	5.09 (6)

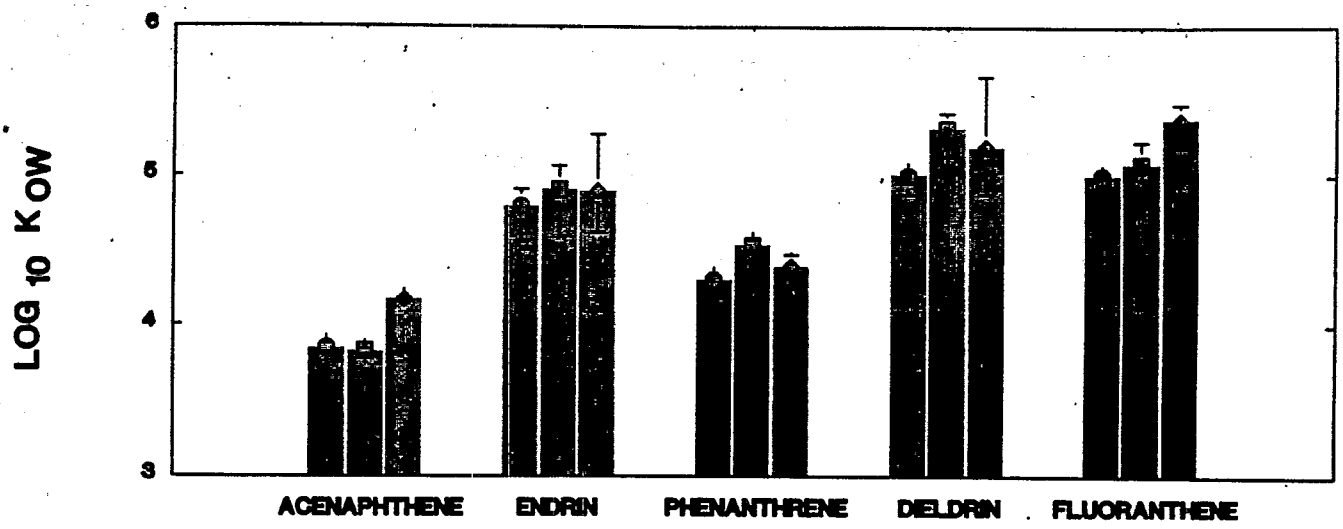


Figure 35.—Laboratory K_{ow} values for five chemicals using three experimental methods with replication. K_{ow} values were measured at the Environmental Research Laboratory, Athens, GA. For each chemical the average of the methods is indicated by O for shake centrifugation, □ for slow stir flask and <> for generator column. Ranges are indicated by ⊥.

This equation is based on any 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}s and f_{oc}s.

Sediment toxicity tests provide a favorable environment for measuring K_{ow}. Figures 24 and 25 presented plots of the organic carbon-normalized sorption isotherm from sediment toxicity tests for the five chemicals where the sediment concentration (μg/g oc) is plotted versus pore water concentration (μg/L). Also included in each panel is the line to the partition, Equation 16, where K_{oc} is computed from the slow-stir flask K_{ow} values. These plots can be used to compare the K_{oc} computed from laboratory determined 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 slow-stir flask K_{ow} in the SQC computation.

Species Sensitivity

The FCV is used as the appropriate end point for the protection of benthic organisms. Therefore, its applicability to benthic species for each chemical should be verified. The previous work has indicated that this is a reasonable assumption across all criteria chemicals. To test this assumption for a particular chemical a statistical method known as Approximate Randomization [110] is applied to each chemical. The idea is to test whether the difference between the final acute value (FAV) derived from considering only benthic organisms is statistically different from the FAV contained in the Water Quality Criteria (WQC).

The Approximate Randomization method tests the significance level of the test statistic by comparing it to the distribution of statistics generated from many random reorderings of the LC_{50} values. For example, the test statistic in this case is the difference between the WQC FAV, computed from the WQC LC_{50} values, and the benthic FAV, computed from the benthic organism LC_{50} values. Note that the benthic organism LC_{50} values are a subset of the WQC LC_{50} values. In the Approximate Randomization method for this test, the number of data points coinciding with the number of benthic organisms are selected from the WQC data set. 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 distribution that results is representative of the population of FAV difference statistics. The test statistic is compared to 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 (water column and benthic) is performed. The probability distribution of the FAV differences for fluoranthene are shown in the top panel of Figure 37. The horizontal line that crosses the distribution is the test statistic computed from the original WQC and benthic FAVS. For fluoranthene, the test statistic falls at the 78th percentile. Since the probability is less than 95 percent, the hypothesis of no significant difference in sensitivity is accepted.

Since 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. The bottom panel of Figure 36 represents the bootstrap analysis to test the hypothesis of no difference in sensitivity between benthic and WQC organisms for fluoranthene. The test statistic for this analysis falls at the 74th percentile and the hypothesis of no difference in sensitivity is accepted.

Table 13 presents the Approximate Randomization analysis for five chemicals for which SQC documents are being developed. Four chemicals, (acenaphthene, phenanthrene, fluoranthene and dieldrin) indicate that there is no difference in sensitivity for freshwater and saltwater species. The test for endrin fails at the 99 percentile which indicates that FAVs for freshwater and saltwater are different. Therefore, separate analyses for the freshwater and saltwater organisms are performed.

Table 14 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 is accepted as the appropriate effects concentrations for benthic organisms.

Quantification of Uncertainty Associated with SQC

The uncertainty in the SQC can be estimated from the degree to which the equilibrium partitioning model, which is the basis for the criteria, can rationalize the available sediment toxicity data. The EqP model asserts that (1) the bioavailability of nonionic organic chemicals from sediments is equal on an organic carbon basis; and (2) that 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 sediment quality criteria can be obtained from a quantitative estimate of the degree to which the available data support these assertions.

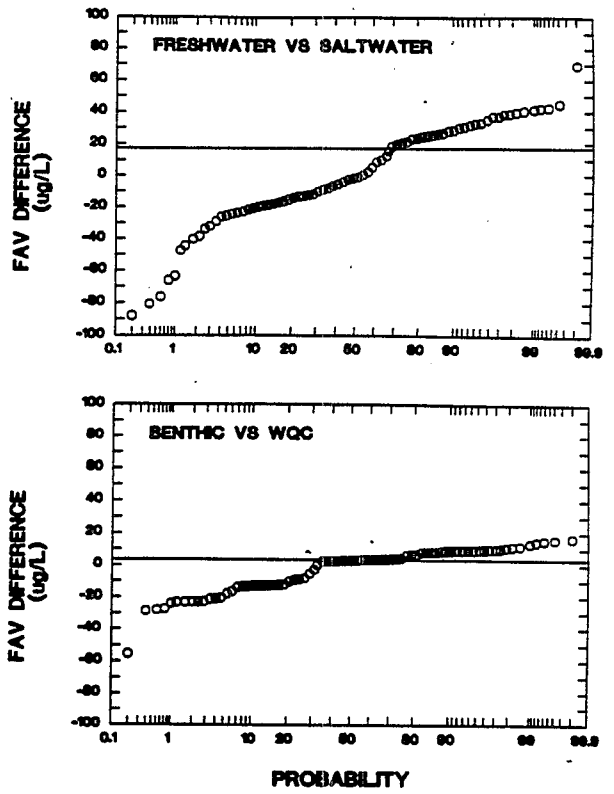


Figure 36.—Probability distributions of randomly generated differences between saltwater FAVs and freshwater FAVs (top panel) and randomly generated differences between WQC FAVs and benthic FAVs (bottom panel) using the Approximate Randomization method. Horizontal line in both panels indicates the test statistic which is the FAV difference from original LC_{50} data sets.

The data used in the uncertainty analysis are the water-only and sediment toxicity tests that have been conducted in support of the sediment criteria development effort. A listing of the data sources used in the EqP uncertainty analysis is presented in Table 15. These freshwater and saltwater tests span a range of chemicals and organisms; they include both water-only and sediment exposures, and they are replicated within each chemical-organism-exposure media

Table 13.—Approximate randomization analysis freshwater versus saltwater organisms.

	NUMBER		FINAL ACUTE VALUE (FAV)			
CHEMICAL	SALT WATER	FRESH WATER	SALT WATER	FRESH WATER	DIFF	%
ENDRIN	19	35	0.033	0.189	0.156	99
DIELDRIN	21	19	0.662	0.377	-0.305	31
ACENAPHTHENE	10	10	139.05	80.01	-59.04	33
PHENANTHRENE	11	8	16.6	59.63	43.02	73
FLUORANTHENE	8	12	16.13	33.58	17.45	78

Table 14.—Approximate randomization analysis benthic versus WQC organisms.

		NUMBER		FINAL ACUTE VALUE (FAV)			
CHEMICAL	WATER TYPE	WATER COL + BENTHIC	BENTHIC	WATER COL + BENTHIC	BENTHIC	DIFF	%
ENDRIN	Fresh	35	21	0.189	.234	-0.045	7
ENDRIN	Salt	19	12	0.033	0.023	0.010	66
DIELDRIN	Combined	40	26	0.621	0.532	0.090	72
ACENAPHTHENE	Combined	20	10	132.6	173.9	-38.34	31
PHENANTHRENE	Combined	19	13	26.62	19.27	7.35	80
FLUORANTHENE	Combined	20	14	37.91	34.27	3.64	74

Table 15.—Data for uncertainty analysis number of replicates/f_{oc}.

ENDRIN	DIELD	FLUOR	ACENAP	ACENAP	PHEN	PHEN
Hy	Hy	Re	Le	Eo	Le	Eo
3(3/-)	1/-	1/-	4/-	4/-	4/-	4/-
2/11%	2/1.7%	2/.18%	2/1.6%	2/1.2%	2/1.9%	2/1.0%
4/11%	4/2.9%	2/.30%	2/2.5%	2/2.5%	2/2.5%	2/2.5%
3/3.0%	4/8.7%	2/.48%	2/3.6%	2/3.6%	2/3.6%	2/3.3%
3/6.1%						
3/11.%						

Hy = Hyalella Re = Rhepoxynius Le = Leptocheirus Eo = Eohaustorius

Data sources: endrin [20, 21, 52], dieldrin [53] fluoranthene [19], acenaphthene [56] phenanthrene [56].

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.

Sediment and water only LC_{50s} are computed from the sediment and water-only toxicity tests. The EqP model can be used to normalize the data in order to put it on a common basis. The LC_{50} from water-only exposures, LC_{50w} (µg/L), is related to the LC_{50} for sediment on an organic carbon basis, $LC_{50s,oc}$ (µg/goc) via the partitioning equation:

$$LC_{50s,oc} = K_{oc}\, LC_{50w} \qquad \textbf{(38)}$$

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 $LC_{50s,oc}$ (µg/goc), from sediment toxicity experiments or K_{oc} x LC_{50w} (µg/goc), are estimates of the true LC_{50} 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.

In order to perform an analysis of variance, a model of the random variations is required. As discussed above, experiments that seek to validate Equation 38 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 which is 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 sediments. Let k-index the replication of the experiment. Then the equation that describes this relationship is

$$Ln(LC_{50i,j,k}) = \mu_i + \alpha_{i,j} + \varepsilon_{i,j,k} \quad (39)$$

where $Ln(LC_{50)i,j,k}$ are either $In(LC_{50w})$ or $In(LC_{50pw})$ corresponding to a water-only or sediment exposure; μ_i's are the population of $In(LC_{50})$ 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, for example, 20 percent; rather than absolute quantities, for example, 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 [109]. The results are shown in Table 16.

Table 16.—Analysis of variance for derivation of criteria confidence limits.

SOURCE OF UNCERTAINTY	PARAMETER	VALUE (μg/goc)
Exposure media	σ_α	0.39
Replication	σ_ε	0.21
Sediment Quality Criteria	σ_{SQC}	0.39

Note that $\sigma_{SQC} = \sigma_\alpha$ the variability due to EqP

The last line of Table 16 is the uncertainty associated with the SQC, that is, the variance associated with the exposure media variability. The confidence limits for the SQC are computed using this uncertainty for SQC. For the 95 percent confidence interval limits, the significance level is 1.96 for normally distributed errors. Thus

$$\ln(SQC_{oc})_{upper} = \ln(SQC_{oc}) + 1.96\sigma_{SQC} \quad (40)$$

$$\ln(SQC_{oc})_{lower} = \ln(SQC_{oc}) - 1.96\sigma_{SQC} \quad (41)$$

The confidence limits are given in Table 17.

Minimum Requirements to Compute SQC

It has been demonstrated that the computation of sediment quality criteria 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 SQC and that are within the limits of uncertainty set forth in this document. This section outlines minimum data requirements and guidance for deriving them. This is a necessary step to develop reliable parameters to be used in computing SQC. The minimum requirements for an EqP based SC 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.

Laboratory octanol-water partition coefficient. K_{ow} data developed by the slow stir flask measurement technique is required. This method has been shown to provide the least amount of variability and

Table 17.—Sediment quality criteria confidence limits for five chemicals.

		SEDIMENT QUALITY CRITERIA 95% CONFIDENCE LIMITS (μg/goc)		
CHEMICAL	TYPE OF WATER BODY	SQC_{oc} μg/goc	LOWER LIMIT	UPPER LIMIT
ACENAPTHENE	Fresh Water	132	61.5	283
	Salt Water	232	103	498
FLUORANTHENE	Fresh Water	616	290	1,300
	Salt Water	296	140	640
PHENANTHRENE	Fresh Water	182	85	391
	Salt Water	238	111	511
ENDRIN	Fresh Water	4.22	1.96	9.06
	Salt Water	0.76	0.354	1.63
DIELDRIN	Fresh Water	11.1	5.17	23.8
	Salt Water	20.4	9.50	43.8

the least bias when comparisons of K_{ow} estimation techniques were done for K_{ow}s derived for the five chemicals for which SQC have been developed. A minimum of three K_{ow} values are required. These values may be taken from the literature provided that methods followed yield a degree of confidence similar to that provided by the methodology used by EPA to derive K_{ow} values.

If slow stirk flask K_{ow} values do not exist then laboratory experiments must be conducted. Measurements of K_{ow} done at the EPA ERL, Athens, Georgia were presented. At a minimum, these procedures are recommended. EPA laboratory procedures include a quality assurance and control plan. The plan includes testing the compound by spectroscopic means to ensure its identity and purity as well as running concurrent K_{ow} measurements of reference compounds which have K_{ow}s that have been verified.

Final chronic value. The FCV is computed as part of the derivation of the water quality criteria for a compound, and is defined as the quotient of the Final Acute Value (FAV) and the Final Acute-Chronic Ratio (8). The data required to compute the WQC FCV are water-only toxicity tests for a variety of organisms meeting minimum data base requirements. The FCV computation and minimum database requirements are presented in the EPA document which describes methods to be used in deriving national ambient WQC (8).

WQC are based on an assessment of a compound's acute and chronic toxicity for organisms representing a range of sensitivities, most importantly most sensitive organisms. This is appropriate since the objective of WQC is to set limits based on the best estimate of organism sensitivity. The toxicity data base should therefore include all available data that meets 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 which would provide a significant amount of toxicity data. Literature searches are recommended to locate other sources of toxicity data.

A reevaluation of an already existing FCV is warranted because data post dating publication of the national FCV can be incorporated into the FCV value. Also minimum database requirements have changed since some WQC have been published. For those compounds for which WQC FCVs do not exist, compiled toxicity data are evaluated to see if minimum data requirements as put forth by EPA (8) are met. If so an FCV could then be computed. If there is not enough water only toxicity data to compute an FCV additional water only tests will be conducted so that there is enough data to satisfy minimum database requirements.

Sediment toxicity test. Verification of applicability of EqP theory is required for each compound. Sediment toxicity tests can be used for this. These tests provide a sediment based LC_{50}. Comparison of the EqP predicted LC_{50} with the sediment LC_{50} concentration is direct confirmation of the EqP approach. The 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 incorporae 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 must be no less than a factor of 3 and a factor of 10 is recommended. Organic carbon content shuld be no less than 0.2 percent. 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 appropriare selection of benthic organisms is given in the American Society for Testing and Materials annual handbook [111].

Several studies are required as part of sediment toxicity testing. A water-only flow through test is required. Water-only tests are run for five concentrations of the compound in question and a control. The endpoint of interest is the 10-day mortality of the test species. This value will be compared to the pore water and sediment mortality from the sediment spiking tests discussed next.

Two sediment spiking tests are required. The first test is for the purpose of identifying sediment spiking concentrations so that pore water concentrations in spiked sediments bracket the LC_{50} determined in the water-only test. In addition, this test is done to determine the time-to-equilibrium of the compound between the pore water and sediment. Sorption equilibrium, and assumption of EqP theory, is essential for valid porewater and sediment concentrations.

Three spiking treatments are recommended for this first test: low, medium and high concentration. The amount of compound to add to each treatment is calculated using the initial chemical weight, the % total organic carbon (TOC), % dry weight and total volume of spiked sediment. The results are sediment concentrations that bracket the predicted LC_{50}s estimated from the water-only LC_{50} ($\mu g/L$) andK_{oc}. Samples for chemical analyses in bulk sediment and pore water are collected at various time intervals. Nominal sediment spike concentrations, measured sediment TOC and measured and EqP-predicted compound concentrations in sediments and pore waters are obtained for each sample period to establish time-to-equilibrium and to verify that spiking produces the appropriate concentrations in the pore water.

In the second sediment spiking tests three sediments representing a range of organic carbon content are spiked to yield five estimated sediment concentrations to bracket the predicted sediment LC_{50}. The amount of compound for spiking is based on similar computations as in the first sediment spiking experiment. Each treatment (sediment by concentration) is held for the appropriate time based on time to equilibrium established in the first spiking test. Day 0 samples are taken for sediment and pore water analyses. Then organisms are placed in replicated beakers and 10-day sediment toxicity tests with the equilibrated spiked sediments are conducted. Eight replicates for each treatment are required. Four replicates are used for day 10 sediment and pore water analyses while the remaining four replicates are used to assess organism mortality.

These experiments provide data to compute pore water toxic units and sediment toxic units (Equations 1 and 8). The results of these equations serve as direct comparisons of the predicted toxicity (Equation 1 and 8 numerator) to the observed toxicity (Equation 1 and 8 denominator). That is, the validity of EqP for a chemical is confirmed when the pore water and sediment toxic units fall within the limits of uncertainty determined in this document.

Analytical procedures. The purpose of these procedures is to verify that:

- the WQC FCV applies to benthic organisms
- the K_{oc} from the slow stir flask K_{ow} is an accurate estimate of K_{ow}

A test that the WQC FCV, which is applicable to the most sensitive water column organisms, is applicable to the most sensitive benthic orgnaisms is needed for each chemical. In computing SQC for endrin, dieldrin, acenapthene, phenanthrene and fluoranthene, the Approximate Randomization test was applied. This is a statistical test to compare the WQC toxicity database to benthic organism toxicity. The methodology is presented previously. 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 SQC. If benthic organisms exhibit a greater sensitivity than the WQC orgnaisms then toxicity experiments for benthic organisms are required.

A check on the laboratory K_{oc} must be done by comparing it to the K_{oc} computed from sediment toxicity tests. Pore water and sediment concentrations from the sediment toxicity test provide data necessary to compute K_{oc}. This K_{oc} is then compared to the K_{oc} from the slow stir flask K_{ow}.

Lastly, when a site's sediments are being studied, a check to show that the SQC applies to the site is needed. National SQC may be under or over protective if 1) the species at the site are more or less sensitive than those included in the data set used to derive SQC 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 appropriare that site-specific guidelines procedures address each of these conditions separately, as well as jointly. Methods to determine the applicability of national SQC to a site and to determine site specific SQC if needed are presented in the EPA guidelines document for deriving site specific sediment criteria [112].

Conclusion. Minimum database and analytical requirements must be set when deriving national sediment criteria. The reasons for this is twofold. First, the requirements provide that a level of protection intended by the criteria are met. Secondly, the requirements provide that parameters used to compute the criteria satisfy assumptions underlying the EqP theory. The key required parameters are K_{ow} using the slow stir flask measurement method, the WQC FCV and sediment toxicity tests. Procedures to verify that these values are appropriate to use in the SQC 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_{ow} to the observed K_{oc} in sediment toxicity tests. Individual sites may exhibit greater or lesser toxicity to a chemical than that predicted by SQC to an individual site. EPA procedures to test this as well as to compute site specific SQC are available.

Example Calculations

Equation 34 can be used to compute SQC_{oc} for a range of K_{ow}s and FCVs. The results for several chemicals are shown in Figure 38 in the form of a nomograph. The diagonal lines are for constant FCVs as indicated. The abscissa is $\log_{10}K_{ow}$. For example, if a chemical has an FCV of 1.0 µg/L and a $\log_{10}K_{ow}$ of 4, so that $K_{ow} = 10^4$, the $\log_{10}$ SQC_{oc} is approximately 1 and the SQC $= 10^1 = 10.0$ µg chemical/g organic carbon.

As can be seen, the relationships between SQC_{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} (one log unit) increases the SQC_{oc} by approximately 10-fold (one log unit) because K_{oc} also increases approximately 10-fold. Thus, chemicals with similar FCVs will have larger SQC_{oc}s if their K_{ow}s are larger.

The chemicals listed in Figure 37 have been chosen to ilustrate the SQC_{oc} concentrations that result from applying the EqP method. The water quality concentrations are the FCVs (not the final residue values) computed as part of the development of SQC for acenaphthene, endrin, phenanthrene, dieldrin and fluoranthene or from draft or published EPA

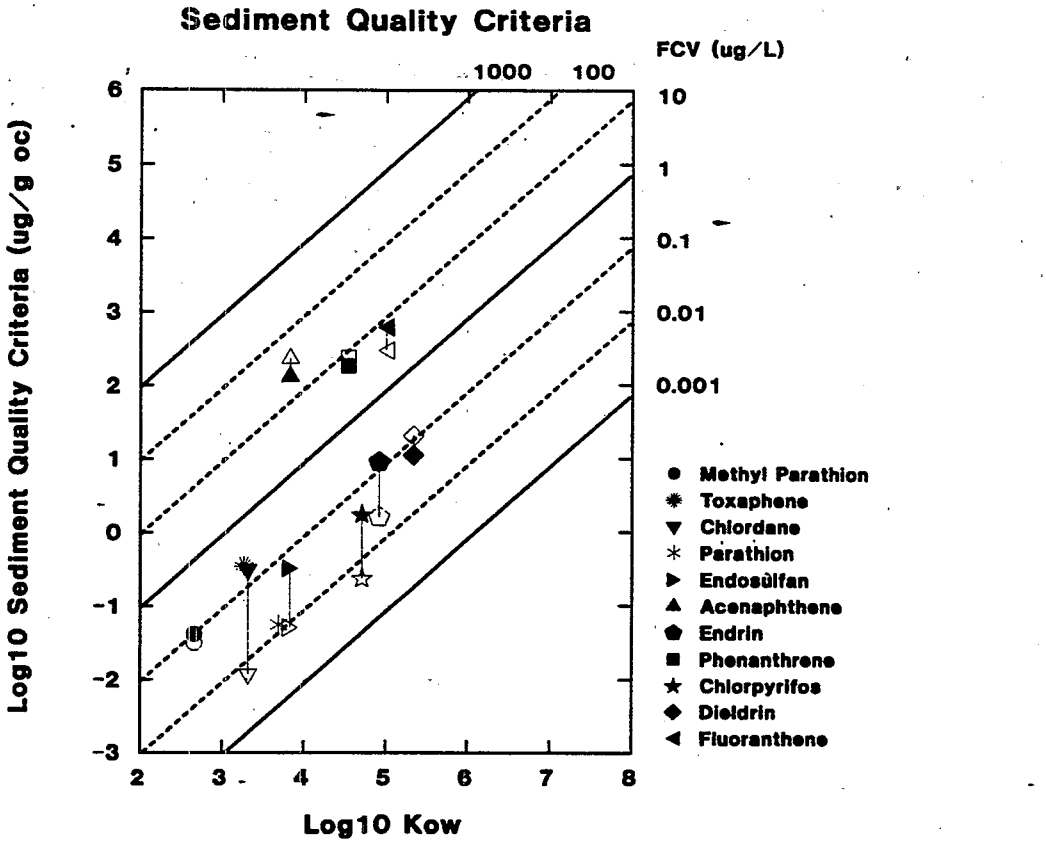


Figure 37.—Log_{10} SQC versus log_{10} K_{ow}. The diagonal lines indicate the FCV values. The criteria are computed from Equation 34. K_{oc} is obtained from K_{ow} with Equation 11. The symbols indicate SQC_{oc} for the freshwater (filled) and saltwater (hatched) criteria for the listed chemicals. The vertical line connects symbols for the same chemical. The FCVs for methyl parathion, toxaphene, chlordane, parathion are from WQC or draft documents, see Table 4. The FCVs for acenapthene, endrin, phenanthrene, fluoranthene and dieldrin are computed as part of the development of SQC. The octanol/water partition coefficients for methyl parathion, toxahene, chlordane, parathion, endosulfan and chlorpyrifos are the log mean of the values reported in the Log P database [75]. The K_{ow}s for acenaphthene, endrin, phenanthrene and dieldrin are those measured from the slow stir flask method.

WQC documents (see Table 4) for the remaining chemicals plotted. Measurement of K_{ow}s for acenaphthene, endrin, phenanthrene, dieldrin and fluoranthene are from the slow stir flask method as previously presented. The K_{ow}s for the remaining chemicals are the log averages of the values reported in the Log P database [75]. While the SQCs for acenapthene, endrin, phenanthrene, fluoranthene and dieldrin meet the minimum database requirements presented in the previous section, SQCs for the remaining chemicals are for illustrative purposes only and should not be considered final SQC values. Final SQC, when published, should reflect the best current information for both FCV and K_{ow}.

The FCVs that are available for nonionic organic insecticides range from approximately 0.01 µg/L to 0.3 µg/L, a factor of 30. The SQC_{ocs} range from approximately 0.01 µg/g organic carbon to in excess of 10 µg/g organic carbon, a factor of over 1,000. This increased range in values occurs because the K_{ow}s of these chemicals span over two orders of magnitude. The most stringent SQC_{oc} in this example is for chlordane, a chemical with one of the lowest K_{ow}s among the chemicals with an FCV of approximately 0.01 µg/L.

By contrast, the PAHs included in this example have a range of FCVs and K_{ow}s of approximately an order of magnitude. But these values vary inversely: The chemical with the larger FCV has a smaller K_{ow}. The result is that the SQC_{ocs} are approximately the same, 240 µg/g organic carbon. Classes of chemicals for which the effects concentrations decrease logarithmically with increasing K_{ow}s, for example, chemicals that are narcotics [113], will have SQC that are more nearly constant.

Field Data

Information on actual levels of the criteria chemicals in the environment was assembled in order to provide an indication of the relationship between the

SQC concentrations and the actual concentration levels observed in the sediments of U.S. surface water bodies. Three separate databases were examined:

- EPA's STORET database [114],
- NOAA's National Status and Trends database, which focused on water bodies in coastal areas [47], and the
- Corps of Engineers database for San Francisco Bay [116].

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 SQC concentration developed by this research. In the case of the STORET data, the SQC is shown as a band because the f_{oc} is not reported. The lines represent the SQC for between an f_{oc} = 1 to 10 percent. The other two data bases provide the necessary information on sediment organic carbon levels, and the results have been properly normalized.

Some salient features of the available field data displayed by the plots are summarized in Table 18. The SQC concentration is listed for each of the five criteria chemicals, together with the number of samples and the approximate percentage of the samples that exceed the SQC. The table also lists the sediment concentrations that are exceeded by 10, 5, and 1 percent of the measurements.

We recognize that the tabulated information represents only approximate estimates, because of the presence of large numbers of detection limit values. Nevertheless, it provides what we consider to be a reliable expectation that only a small percentage of sediment sites in the databases, less than 5 percent, will have concentrations that exceed the SQC levels.

We did not attempt a more rigorous analysis to provide a more definitive characterization of the spatial and temporal features of the database. Some of the recorded data clearly represent multiple samples at a particular site. The very high observed concentrations are relatively few in absolute number and may reflect multiple samples at one or a few particularly contaminated sites. Some of the probability plots also show a discontinuity at the high end. This is particularly true of the Corps of Engineers data that pool results from a limited number of stations in San Francisco Bay. Until a more detailed analysis is performed, the results of the preliminary screening should be considered approximate, upper bound estimates of the probable prevalence of sediment sites that may exceed the SQC.

STORET data. A STORET data retrieval was performed to obtain a preliminary assessment of the concentrations of the criteria chemicals in the sediments of the nation's waterbodies. The data retrieved was restricted to samples measured in the period 1986 to 1990. The selection of this recent period eliminated much of the older data with the higher detection limits to provide a more accurate indication of current conditions. Log probability plots concentrations are shown in Figures 38 and 39. Concentrations are shown on a dry weight basis, because sediment organic carbon is not reported. The SQCs are computed on the basis of a sediment organic carbon content (f_{oc}) of 1 percent and 10 percent, which is the typical range for inland sediments. The STORET data distinguishes between the type of waterbody, and separate displays are provided for stations on streams, lakes, and estuaries.

The PAH data are shown in Figure 38. 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 SQC for f_{oc} = 1 percent, and fewer exceed the SQC for f_{oc} = 10 percent. 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 is uncertain, since the nondetected data may in fact occupy plotting positions further to the left, at lower probabilities. Thus the exceedence probabilities for the detected data are at least as large as is indicated on the plots. Approximately 5 percent or less of the detected samples exceed the f_{oc} = 1 percent SQC.

The data for endrin and dieldrin are shown in Figure 39. Similar results are obtained. Less than 3 percent of the detected dieldrin and endrin samples exceed the lower SQC.

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 [116]. Figure 40 displays the distribution of sediment concentrations from the National Status and Trends Program sites for four of the five criteria chemicals

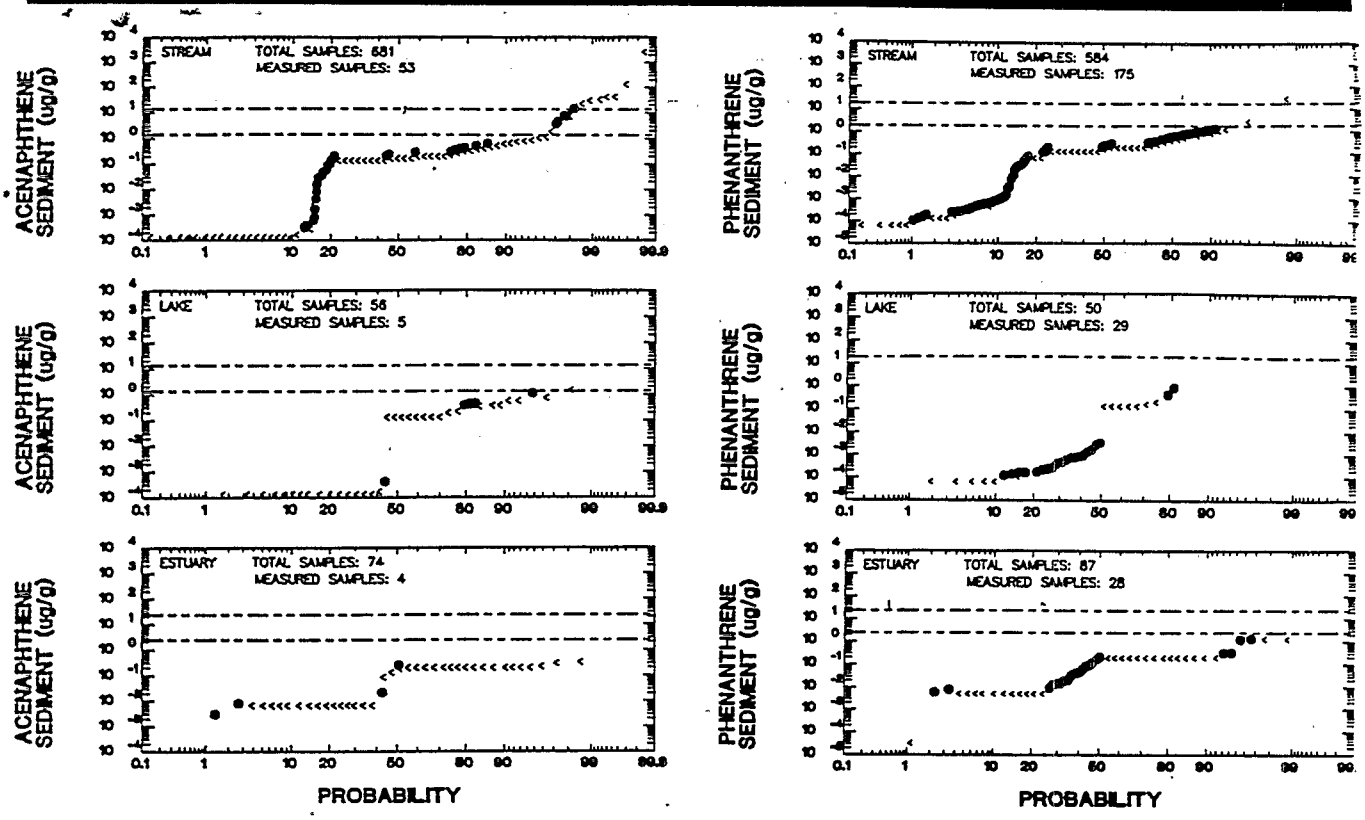
Table 18.—Observed quality of natural sediments.

		FLUORANTHENE	PHENANTHRENE	ACENAPTHENE	ENDRIN	DIELDRIN
SALT WATER	SQC (µg/g oc)	296	238	232	0.744	20.40
CORPS OF ENGINEERS	NO. OF SAMPLES	231	231	130	260	282
	% that exceed SQC	3%	4%	5%	0%	0%
	10% exceed - conoc	40	60	30	60	40
	5% exceed - conoc	300	300	200	150	80
	1% exceed - conc	40,000	25,000	3,000	700	600
NOAA	NO. OF SAMPLES	797	736	245	–	408
NATIONAL STATUS AND TRENDS PROGRAM	% THAT EXCEED SQC	0.2%	0.1%	0%	–	0%
	10% exceed - conc	4	25	4	–	0.3
	5% exceed - conc	7	40	7	–	0.5
	1% exceed - conc	40	90	40	–	1.0
EPA STORET ESTUARIES	SQC (µg/g) for sediment OC: 1–10%	3.0–30	2.4–24	2.3–23	.007–0.07	0.02–0.2
	NO. OF SAMPLES	88	87	74	150	160
	% THAT EXCEED SQC	1%	< 1%	0%	< 10%	0%
	10% exceed - conc	4	0.1	0.3	all	157/160
	5% exceed - conc	7	0.8	0.3	data are	data are
	1% exceed - conc	40	1.0	0.5	< DL	< DL
FRESH WATER	SQC (µg/g) for sediment OC: 1–10%	6.2–62	1.8–18	1.3–13	0.04–0.42	0.1–1
EPA STORET STREAMS	NO. OF SAMPLES	786	584	681	2677	3075
	% THAT EXCEED SQC	2%	7%	< 4%	1%	< 3%
	10% exceed - conc	4	1	1	0.01	0.005
	5% exceed - conc	7	2	1.5	0.01	0.01
	1% exceed - conc	40	?	40	0.04	0.05
EPA STORET LAKES	NO. OF SAMPLES	57	50	56	478	457
	% THAT EXCEED SQC	5%	< 0%	2%	2%	< 1%
	10% exceed - conc	4	1 (?)	0.7	0.001	0.005
	5 exceed - conc	7	2 (?)	1	0.005	0.01
	1% exceed - conc	40	10 (?)	3	0.100	0.08

(endrin concentrations were not measured). Sediment organic carbon concentrations were measured in this program, and ranged from less than 0.20 to 16.2 percent. The availability of f_{oc} permits the plots to display both observed concentrations and the SQC value using organic carbon normalization.

Results are displayed in the plots for all samples (open symbols) and for the subset that contained organic carbon fractions greater than 0.2 percent, the limit of applicability for the EqP derived SQC (filled symbols). The EqP derived SQC is applicable to the 75 to 85 percent of all sediment samples that have f_{oc}s greater than 0.2 percent. However, there is only a nominal effect on estimates of the percentage of the samples that exceed the SQC, depending on whether the full set, or the subset of samples is considered. Approximately one half a percent of subset samples exceed the phenanthrene and fluoranthene SQC, whereas none of the other SQC are exceeded. The fractions are not greatly increased if the SQC are applied to all samples.

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 19 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



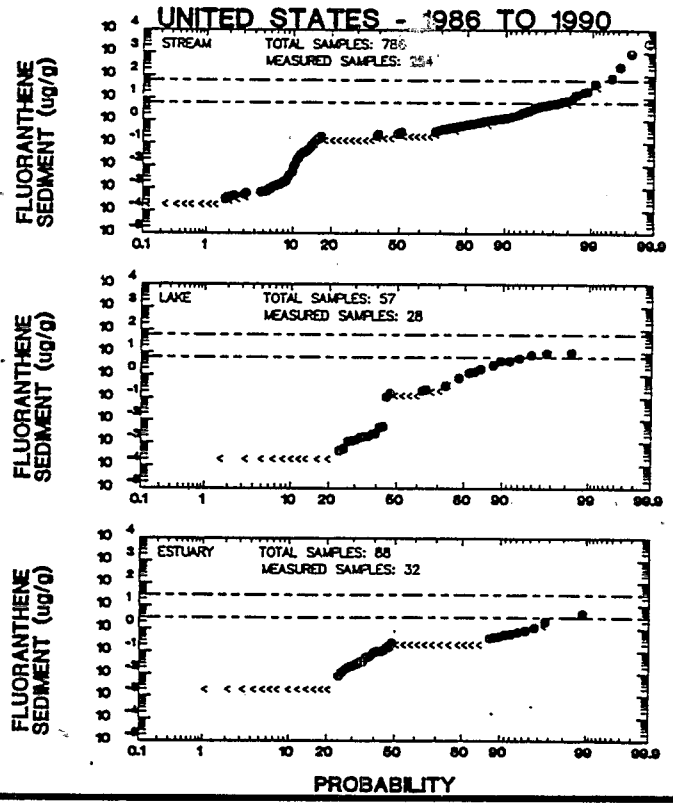


Figure 38.—Comparison of sediment quality criteria for sediments containing 1 percent and 10 percent organic carbon to the distributions of three sediment PAH concentrations from the U.S. EPA STORET database from 1986 to 1990. Samples above the detection limit (filled symbols) and samples less than the detection limit (less than symbols) are shown. Data from U.S. EPA [114].

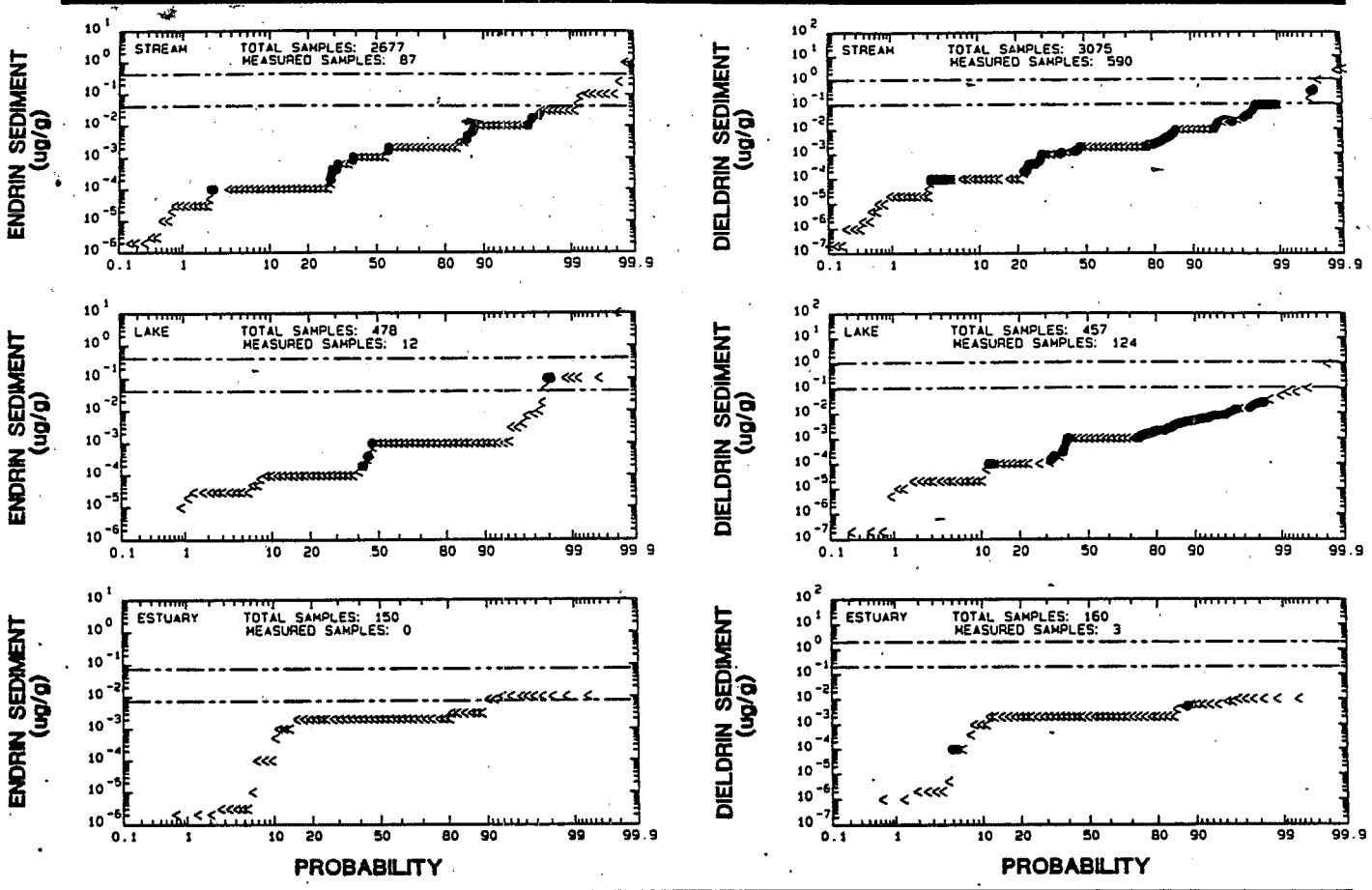


Figure 39.—Comparison of sediment quality criteria for sediments containing 1 percent and 10 percent organic carbon to the distributions of two sediment pesticide concentrations from the U.S. EPA STORET Database. Data are from 1986 to 1990. Samples above the detection limit (filled symbols) and samples less than the detection limit (less than symbols) are shown. Data from U.S. EPA [114].

Table 19.—San Francisco Bay sediment samples.

LOCATION	NO. OF SAMPLES PAHs & PESTICIDES	YEARS
Port of San Francisco: Piers 27-29, 35, 38, 48, 70, 80 and 94	21	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	48	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	40	1989-1990
Port of Oakland Outer and Inner Harbor	27	1990-1991
Treasure Island	5 composites	1990
San Leandro Bay	1 composite	1990
San Pablo Bay	6	1989-1990

Note: PAHs = Fluoranthene, Phenanthrene, Acenapthene; Pesticides = Dieldrin, Endrin.

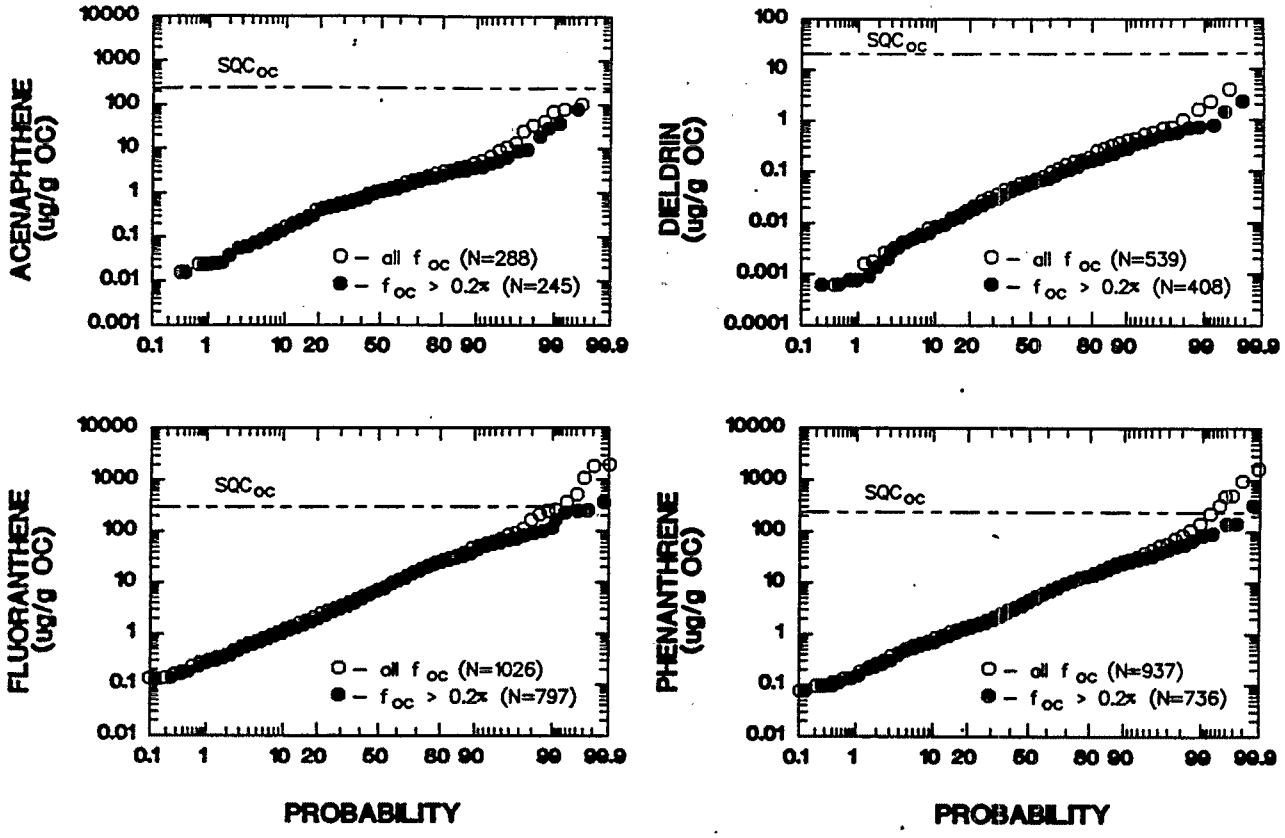


Figure 40.—Comparison of sediment quality criteria to the distributions of acenaphthene, fluoranthene, dieldrin, and phenanthrene organic carbon normalized sediment concentrations from NOAA's National Status and Trends Program. Data are from 1984 to 1989. Samples with organic carbon greater than 0.2 percent (filled symbols) and samples for all organic carbon contents (open symbols) are shown. Data from NOAA [47].

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 SQC criteria developed using the EqP methodology. The major portion (93 percent) of the samples analyzed had organic carbon fractions greater than 0.2 percent, for which the SQC concentrations are applicable. The concentrations of each chemical measured in these sediments was normalized by the organic carbon content and the results are displayed below as probability plots to illustrate the frequency at which different levels are observed. Results are presented for the five criteria chemicals. A horizontal line at the concentration value of the SQC provides a reference that indicates the relationship between observed range of quality and the SQC for each chemical.

PAH results are summarized in Figure 41. Less than 5 percent of the individual samples contained concentrations in excess of the sediment quality. It is informative to note that the small set of very high concentrations are nearly all from one sample site (Treasure Island). These samples are responsible for the discontinuous pattern of the frequency distribution.

Figure 42 presents the monitoring program results for the two pesticides in the same format. In this case, 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 SQC. 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 [117]. 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

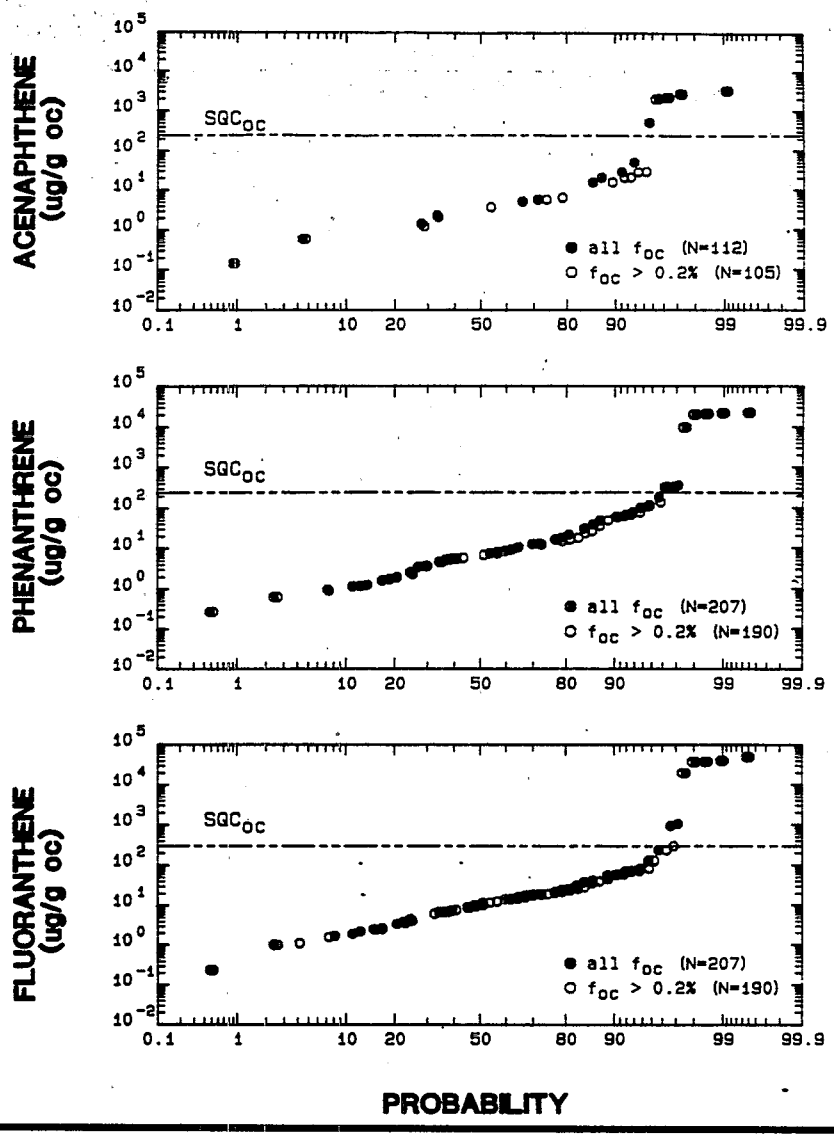


Figure 41.—Comparison of sediment quality criteria to the distributions of acenapthene, fluoranthene, and phenanthrene organic carbon normalized sediment concentrations from the U.S. Army Corps of Engineers monitoring program of San Francisco Bay. Samples with organic carbon greater than 0.2 percent (filled symbols) and samples for all organic carbon contents (open symbols) are shown. See Table 19 for description of location, number of samples, and sample period. Data from U.S. Army COE [115].

distribution estimates unreliable. They are presented only to suggest the probable relationship between the levels of these two pesticides in relation to sediment quality criteria.

CONCLUSIONS

The technical basis and data that support the use of the EqP method to generate SQC have been presented for nonionic organic chemicals. The use of organic carbon normalization is equivalent to using pore water normalization as a means of accounting for varying bioavailability (Figs. 2, 3, 5-8, 26-28). The variation in organism body burden across sediments can also be significantly reduced if organic carbon and lipid normalization are used (Figs. 29-31). For contaminated sediments, particle size effects are removed if organic carbon-normalized concentrations are compared (Figs. 17, 19, 21). The reason is that organic carbon is the proper normalization for partitioning between free dissolved chemical and sediment-bound chemical (Fig. 11).

Using pore water normalization for highly hydrophobic chemicals is complicated by chemical complexing to DOC (Fig. 13). Partitioning between

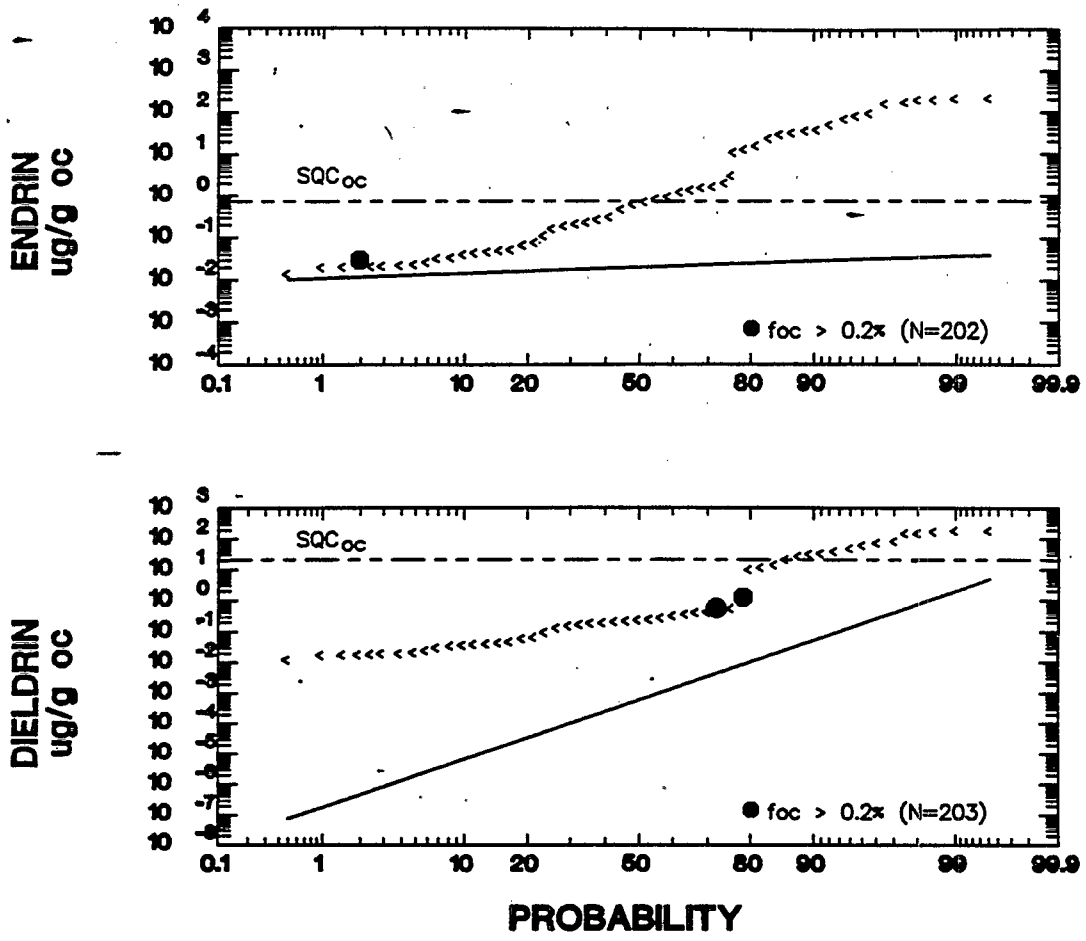


Figure 42.—Comparison of sediment quality criteria to the distributions of endrin and dieldrin organic carbon normalized sediment concentrations from the U.S. Army Corps of Engineers monitoring program of San Francisco Bay. See Table 19 for description of location, number of samples and sample period. Samples with organic carbon greater than 0.2 percent (filled symbols) and samples less than the detection limit (less than symbols) are shown. Also shown is an estimate of the distribution developed by accounting for nondetected observations (solid line). Data from U.S. Army COE [115].

pore water and sediment organic carbon from field-collected sediments can be rationalized if DOC complexing is taken into account (Figs. 22 and 23). However, the complexed chemical appears not to be bioavailable (Fig. 15).

These observations are consistent with the EqP model, which assumes the equivalence of water-only exposure and the exposure from pore water and/or sediment organic carbon. Sediment quality criteria are based on organic carbon normalization because pore 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 for both the most sensitive species tested (Fig. 32) and all tested species (Fig. 34). Benthic colonization experiments also demonstrate that WQC 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 (Fig. 36).

Equilibrium partitioning cannot remove all of the observed variation from sediment to sediment. It does reduce the much larger sediment-to-sediment variation that exists if no corrections for bioavailability are made (Figs. 5-8). A variation factor of approximately two to three remains (Figs. 2 and 3), which includes measurement and other sources of variability. This is not unexpected as EqP is an idealization of the actual situation. Other factors that are not considered in the model play roles in determining biological effects. Hence, it is recognized that a quantification of the uncertainty should accompany the SQC that reflect these additional sources of variation.

Research Needs

The final validation of SQC will come from field studies that are designed to evaluate the extent to which biological effects can be predicted from SQC. The colonization experiments (Table 6) are a laboratory simulation of a field validation. Sediment quality criteria can possibly be validated more easily than WQC because determining the organism exposure is more straightforward. The 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 [118]. 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 SQC, mixtures of chemicals are involved. The extension of EqP methodology to mixtures would be of great practical value. Initial experiments indicate that it should be possible [119].

The EqP method is presently restricted to computing effects-based criteria for the protection of benthic organisms. The direct extension of this methodology for computing sediment criteria 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 pore water concentrations if sufficient dilution flow is present. Conversely, upper-trophic-level organisms are at concentrations well above equilibrium values [120]. Hence, the application of the final residue values from the WQC for the computation of SQC, as was done for certain interim criteria [121], is not technically justifiable. At present, organism lipid-to-sediment organic carbon ratios, that is, BSFs (Eqn. 29), might be useful in estimating the concentration of contaminants in benthic species, for which the assumption of equilibrium is reasonable. However, a site-specific investigation (e.g., Connolly [122]) appears to be the only available method for performing an evaluation of the effect of contaminated sediments on the body burdens of upper-trophic-level organisms.

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