Environmental Toxicology and Chemistry, Vol. 10, pp. 1541–1583, 1991
Printed in the USA. Pergamon Press plc

0730-7268/91 $3.00 + .00

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Annual Review

TECHNICAL BASIS FOR ESTABLISHING SEDIMENT QUALITY CRITERIA FOR NONIONIC ORGANIC CHEMICALS USING EQUILIBRIUM PARTITIONING

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(*Received* 18 *June* 1989; *Accepted* 26 *June* 1991)

Abstract—The purpose of this review paper is to present the technical basis for establishing sediment quality criteria 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 utilizing 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 (within a factor of two) for the different sediments. In addition, the effects concen-

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trations 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; 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 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, as the data presented below illustrate, is not bioavailable. Using the chemical concentration in sediment organic carbon eliminates this ambiguity.

Sediment quality criteria 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 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.

Equilibrium partitioning cannot remove all the variation in the experimentally observed sediment-effects concentration and the concentration predicted from water-only exposures. A variation of approximately a factor of two to three remains. Hence, it is recognized that a quantification of this uncertainty should accompany the sediment quality criteria.

The derivation of sediment quality criteria requires the octanol/water partition coefficient of the chemical. It should be measured with modern experimental techniques, which appear to remove the large variation in reported values. The derivation of the final chronic value should also be updated to include the most recent toxicological information.

Keywords—Equilibrium partitioning Sediment quality criteria
Organic carbon normalization

OVERVIEW

This paper presents the technical basis for establishing sediment quality criteria (SQC) for nonionic organic chemicals using the equilibrium partitioning (EqP) method. An overview is presented first that summarizes the evidence and the major lines of reasoning. The references are cited in the body of the paper. *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 could be used in much the same way as the final chronic value 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 as the need for the evaluation of potentially contaminated sediments arises in many contexts. Sediment quality criteria 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 would be protective of benthic aquatic life.

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), 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 be 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 LC50 for an organism in one sediment and 35 μg/g

is the LC50 in another sediment, then unless the cause of this difference can be associated with some explicit sediment properties it is not possible to decide what would be the LC50 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 water quality criteria (WQC). It is for this reason that the issue of bioavailability is a principal focus of this paper.

The observations that provided the key insight to the problem of quantifying the bioavailability of chemicals in sediments were 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 sediment), but to the interstitial water (i.e., 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, it is shown that 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 (right). The name *equilibrium partitioning* (EqP) describes this assumption of partitioning equilibrium. 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 (right) provides the same exposure as a water-only exposure (left). The reason is that the chemical activity is the same in each system at equilibrium. It should be pointed out that the EqP assumptions are only approximately true, and, therefore, the predictions from the model have an inherent uncertainty. The data presented below illustrate the degree to which EqP can rationalize the observations.

Figure 2 presents mortality data for various chemicals and sediments compared to pore water concentrations when normalized on a toxic unit basis. Three different sediments are tested for each chemical as indicated. Predicted pore water toxic units are the ratio of the measured pore water concentration to the LC50 from water-only toxicity tests. The EqP model predicts that the pore water

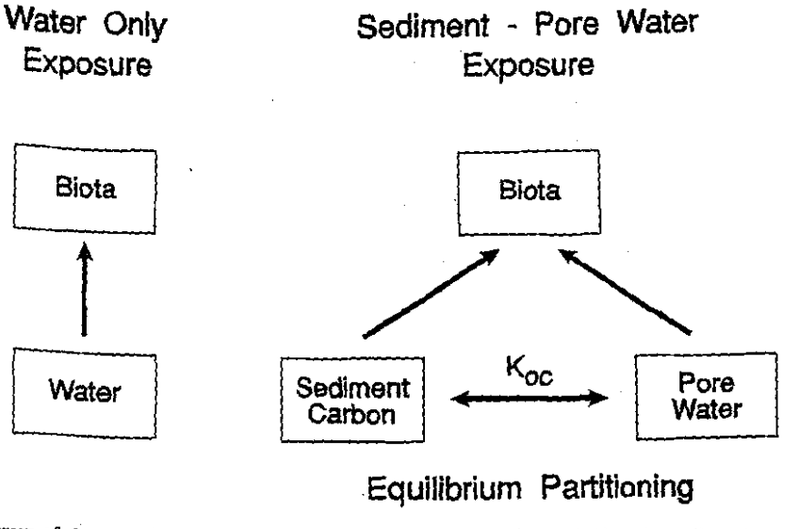

Fig. 1. Diagram of the organism exposure routes for a water-only exposure (left) and a sediment exposure (right). *Equilibrium partitioning* refers to the assumption that an equilibrium exists between the chemical sorbed to the particulate sediment organic carbon and the pore water. The partition coefficient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

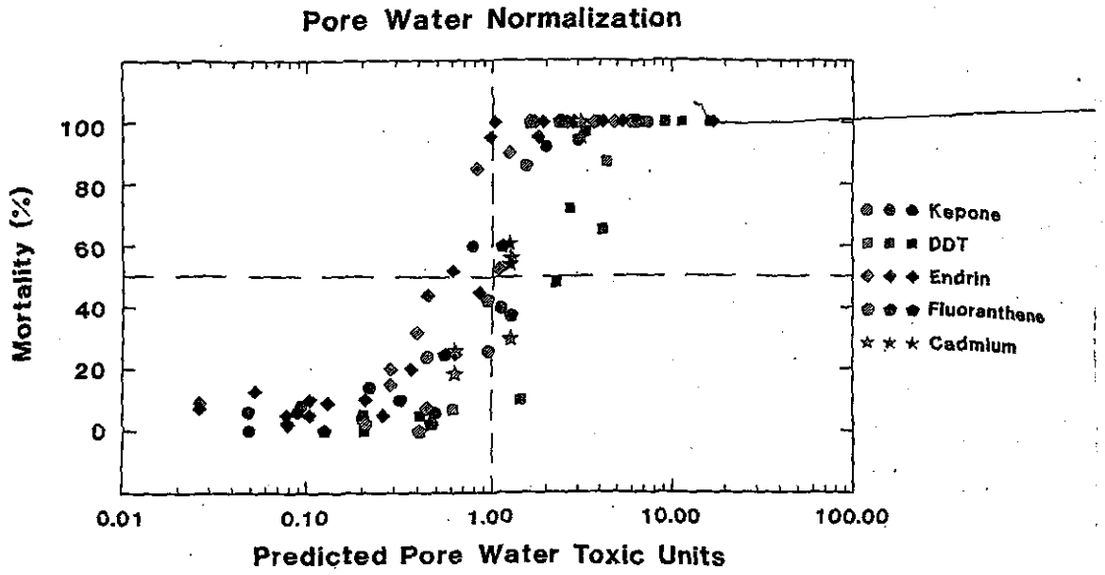

Fig. 2. Mortality versus predicted pore water toxic units for five chemicals and three sediments per chemical. Sediment types are indicated by the single hatching (lowest organic carbon content), cross-hatching (intermediate organic carbon content), and filled symbols (highest organic carbon content). 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 LC50 (Eqn. 1).

LC50 will equal the water-only LC50, which is obtained from a separate water-only exposure toxicity test. Define:

$$\text{predicted pore water toxic unit} = \frac{\text{(pore water concentration)}}{\text{(water-only LC50)}}. \quad (1)$$

Therefore a toxic unit of one occurs when the pore water concentration equals the water-only LC50, at which point it would be predicted that 50% mortality would be observed. The correlation of observed mortality to predicted 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, as shown below, the mortality versus sediment–chemical concentration on a dry weight basis varies dramatically from sediment to sediment.

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 final chronic value (FCV) from WQC documents as the effects concentration for benthic organisms. The apparent equality between the effects concentration as measured 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/kg sediment) are computed using the partition coefficient K_p (L/kg sediment) between sediment and pore water:

$$SQC = K_p\,FCV. \tag{2}$$

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 $f_{oc} > 0.2\%$ by weight, the organic carbon appears to be the predominant phase for chemical sorption. The partition coefficient, K_p (the ratio of sediment concentration, C_s, to pore water concentration, C_d) is given by

$$K_p = \frac{C_s}{C_d} = f_{oc}K_{oc}, \tag{3}$$

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 $K_{oc} \simeq K_{ow}$ for sediments. A detailed review of the arguments is presented below.

Using Equations 2 and 3, an SQC is calculated from

$$SQC = f_{oc}K_{oc}\,FCV. \tag{4}$$

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

$$\frac{SQC}{f_{oc}} = K_{oc}\,FCV. \tag{5}$$

If we define

$$SQC_{oc} = \frac{SQC}{f_{oc}} \tag{6}$$

as the organic carbon–normalized SQC concentration (microgram chemical per kilogram organic carbon), then

$$SQC_{oc} = K_{oc}\,FCV. \tag{7}$$

Hence 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 sediments 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 are computed as the ratio of the organic carbon–normalized sediment concentrations, C_s/f_{oc}, and the predicted sediment LC50 using K_{oc} and the water-only LC50. That is:

$$\begin{pmatrix}\text{predicted}\\ \text{sediment}\\ \text{toxic unit}\end{pmatrix} = \frac{C_s/f_{oc}}{K_{oc}\,(\text{water-only LC50})}. \tag{8}$$

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 sediment organic carbon. The predicted sediment toxic units for each chemical follow a similar concentration–response curve independent of sediment type. These data demonstrate that 50%

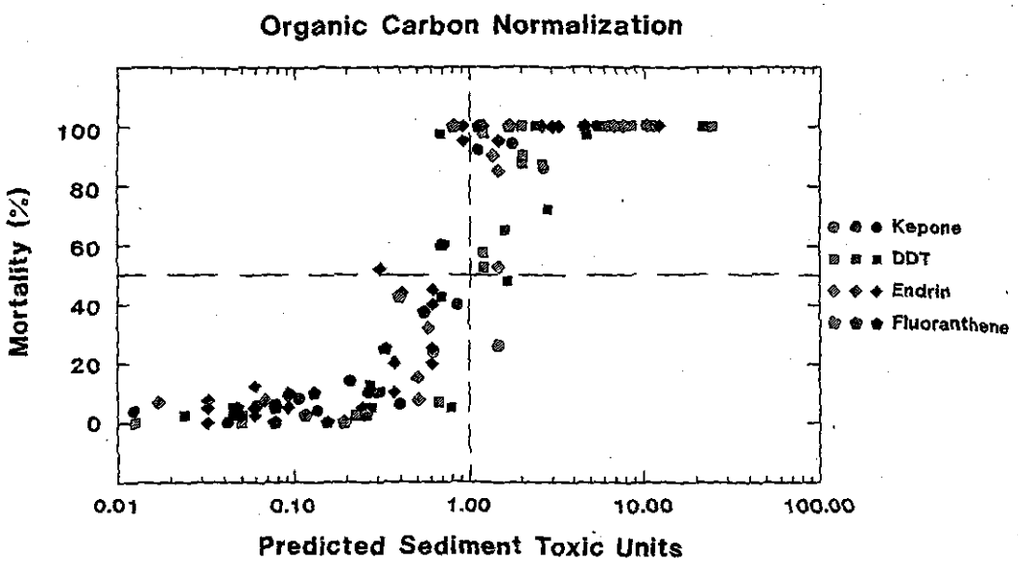

Fig. 3. Mortality versus predicted sediment toxic units. Predicted sediment toxic units are the ratio of the organic carbon-normalized sediment chemical concentration to the predicted sediment LC50 (Eqn. 8). Sediment types are indicated by the single hatching (lowest organic carbon content), cross-hatching (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 (4.80), and fluoranthene (5.30) with Equation 11. These are log averages of the reported values in the Log$P$ data base [71]. 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.

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 the data in Figures 2 and 3 should all predict 50% mortality at one toxic unit. There is an uncertainty of approximately a factor of two in the results (also see Table 2 below). This variation reflects inherent variability in these experiments as well as phenomena that have not been accounted for in the EqP model. This appears to be the limit of the accuracy and precision to 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 data base, 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, presented below, support the contention of equal sensitivity.

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 ambient 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 alone

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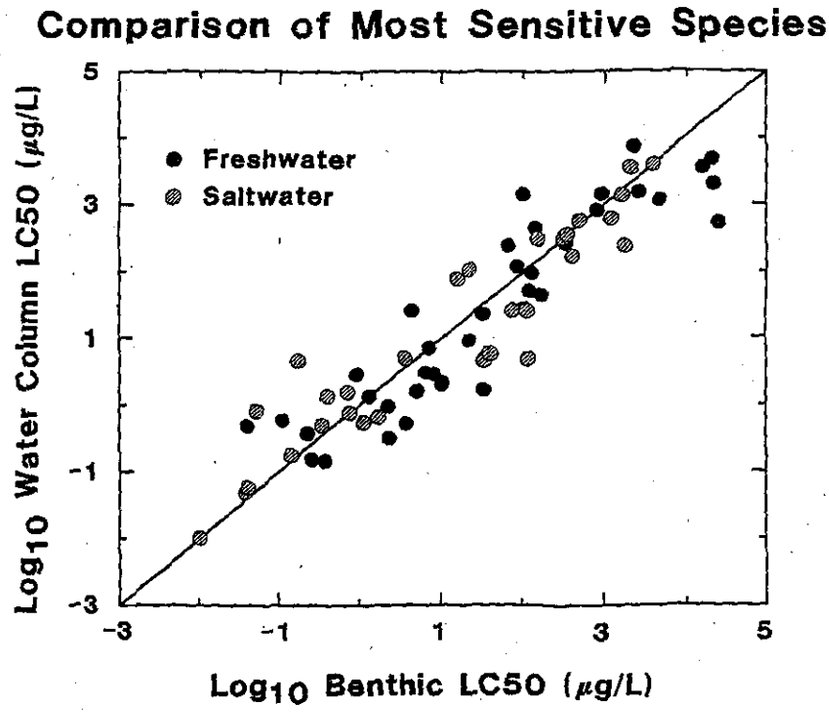


Fig. 4. A comparison of the minimum LC50 for water column versus benthic organisms. Each data point represents a particular chemical in either a freshwater or a saltwater exposure. The data are from the WQC or draft criteria documents. See Table 4 for data sources.

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 accurately assess the extent of sediment contamination, implement measures to limit or prevent additional contamination from occurring, and identify and implement appropriate remediation when needed.

As a result of the need to assist regulatory agencies in making decisions concerning contaminated sediment, the EPA's Office of Water Regulations and Standards, Criteria and Standards Division, established a research team to review alternative approaches to assess sediment contamination. These 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 to identify the scope of national sediment contamination [4] and to review proposed approaches for addressing contaminated sediments [5,6] were undertaken. The EqP method was selected because it appeared to provide the most practical, scientifically defensible, and effective regulatory tool for addressing individual 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 were:

1. It was likely that the EqP method would yield sediment criteria that were predictive of biological effects in the field and would be defensible when used in a regulatory context. These criteria directly address the issue of bioavailability and are founded on the extensive biological effects data base used to establish national WQC.
2. Sediment criteria could 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 could provide a simple and cost-effective means of screening sediment measurements to identify areas of concern and could provide regulators with information in a short period of time.
4. The method takes advantage of the large amount of data and expertise that went into the development of the national WQC.
5. The methodology could be used as a regulatory predictive tool to ensure uncontaminated sites would be protected from attaining unacceptable levels of contamination.

Relationship to WQC methodology

Perhaps the first question to be answered is: Why not use the already existing procedure for the development of WQC to develop 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]. Furthermore, WQC developed with this methodology are routinely used in the regulation of effluent discharges. A natural extension would be to apply these methods directly to sediments.

The WQC are based on total chemical concentration, and 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 due to variations in site-specific water chemistry 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 bioavailable—or even potentially bioavailable—chemical concentration is not supported by the available data [11]. A summary of recent experiments is presented in the two sections that follow. The results of these experiments indicate that sediments can differ in toxicity by factors of 100 or more for the same total chemical concentration. This 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. This is true regardless of the methodology 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 does one 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 order of magnitude. Thus, it appears that bioavailability must be explicitly considered for any sediment evaluation methodology that depends on chemical measurements and, in particular, in establishing defensible SQC.

Applications of SQC

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

In many ways sediment criteria developed with the EqP methodology are similar to existing 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 often have 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 spatial extent of contaminated areas such that more informed regulatory decisions can be made. Sediment criteria will be particularly valuable in site-monitoring

applications where sediment contaminant concentrations are gradually approaching the criteria over time. Comparison of field measurements to sediment criteria will be a reliable method for providing an early warning of potential problems. Such an early warning would provide an opportunity to take corrective action before adverse impacts occur.

TOXICITY AND BIOAVAILABILITY OF CHEMICALS IN SEDIMENTS

The observation that provided 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]. In retrospect it has become clear that these results do not necessarily imply that pore water is the primary route of exposure. This is 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 concentration. Table 1 lists the sources and characteristics of these experiments. The data are presented in a uniform fashion on 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 LC50 and EC50 estimates and 95% 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 particularly dramatic [17,18]. For the low organic carbon sediment (f_{oc} = 0.09%), the 50th percentile total Kepone concentration for both *Chironomus tentans* mortality (LC50) and growth rate reduction from a life cycle test (EC50) are <1 μg/g. By contrast, the 1.5% organic carbon sediment EC50 and LC50 are approximately 7 and 10 μg/g, respectively. The high organic carbon sediment (12%) exhibits still higher LC50 and EC50 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 data 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 LC50 or EC50 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 LC50s are 19 to 30 μg/L, and the water-only exposure LC50 is 26 μg/L. The pore water EC50s are 17 to 49 μg/L, and the water-only EC50 is 16 μg/L (Table 2).

Laboratory experiments have also been performed to characterize the toxicity of fluoranthene [19] and cadmium [20] to the sediment-dwelling

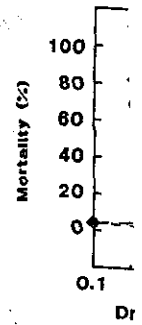
Table 1. Sediment toxicity data and bioaccumulation data

Chemical	Organism	Sediment source	Exposure duration (days)	Biological end point	Reference	Figure
Kepone	*Chironomus tentans*	Soil	14	Mortality	[17]	5
Kepone	*Chironomus tentans*	Soil	14	Growth	[17]	5
Cadmium	*Rhepoxynius abronius*	Yaquina Bay, OR	4	Mortality	[20]	6
Fluoranthene	*Rhepoxynius abronius*	Yaquina Bay, OR	10	Mortality	[19]	6
DDT	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	[21,22]	7
Endrin	*Hyalella azteca*	Soap Creek, Mercer Lake	10	Mortality	[21,22]	7
Cadmium	*Rhepoxynius abronius*	Yaquina Bay, OR	4	Mortality	[23]	8
Cadmium	*Ampelisca abdita*	Long Island Sound	10	Mortality	[24]	8
Cypermethrin	*Chironomus tentans*	River and pond	1	Body burden	[26]	9
Permethrin	*Chironomus tentans*	River and pond	1	Body burden	[26]	9
Kepone	*Chironomus tentans*	Soil	14	Body burden	[17,28]	–

Table 2. LC50 and EC50 for sediment dry weight and sediment-organic carbon normalization and for pore-water and water-only exposures

Chemical (end point)	f_{oc} (%)	LC50 and EC50 Total sediment (μg/g)	Pore water (μg/L)	Organic carbon (μg/g)	Water only (μg/L)	Reference
Kepone (mortality)	0.09	0.90 (0.73–1.10)	29.9 (25.3–35.6)	1,000 (811–1,220)	26.4 (22.7–30.6)	[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]
	1.50	9.93 (7.74–12.8)	48.5 (34.6–67.8)	662 (516–1,050)		
	12.0	37.3 (31.5–44.2)	20.1 (16.7–24.1)	311 (262–368)		
Fluoranthene (mortality)	0.2	3.2 (2.85–3.59)	21.9 (19.6–24.4)	1,600 (1,430–1,800)		[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)	[21]
	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)		[22]
	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 (87.0–147)	4.81 (4.46–5.20)	[21]
	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)		[22]
	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)		
Cadmium (mortality)	0.0	22.5 (18.7–27.1)	2.50 (2.19–2.87)		1.6 (1.4–1.8)	[23]
	0.25	20.8 (16.7–26.0)	1.76 (1.48–2.09)			
	1.0	10.2 (7.02–14.7)				

The LC50s and EC50s and the 95% confidence limits in parentheses are computed by the modified Spearman–Karber method [81].



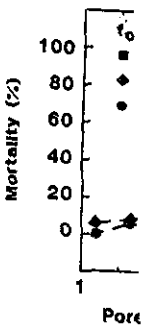


Fig. 5. Comparis
in bulk sediment

marine amphipod *Rhepoxynius abronius*. Figure 6 presents the *R. abronius* mortality data for the fluoranthene and cadmium experiments. The results of the fluoranthene experiments parallel those for Kepone. The sediment with the lowest organic carbon content (0.2%) exhibits the lowest LC50 on a total sediment concentration basis (3.2 μg/g), and as the organic carbon concentration increases (0.3 and 0.5%) the LC50 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 LC50s differ by less than 50%.

The cadmium experiments [20] were done with constant pore water concentrations and a sediment amended with varying quantities of organic carbon. The unamended and 0.25% additional organic carbon exhibit essentially similar responses. However, the 1% amended sediment had a much different LC50, based on the total sediment concentration. Using the pore water concentrations as the correlating variable again collapses the data into one concentration-response curve.

Figure 7 presents mortality data for DDT and endrin using the freshwater amphipod *Hyalella azteca* [21,22]. The responses for DDT [21] are similar to those observed for Kepone, cadmium, and fluoranthene. On a total sediment concentration basis the organism responses differ for the various sediments (LC50s are 10.3–45 μg/L), but on a pore water basis the responses are again similar (LC50s are 0.74–1.4 μg/L) and comparable to the water-only LC50s of approximately 0.5 μg/L. The DDT data in [22] are more variable. By contrast, the organism survival for endrin exposures varies by a factor of almost six among the six sediments. The LC50s are 3.4 to 18.9 μg/g. The pore water LC50s were less variable—1.7 to 3.8 μg/L—and comparable to the water-only exposure LC50 of approximately 4 μg/L (Table 2).

Additional cadmium toxicity data are compared

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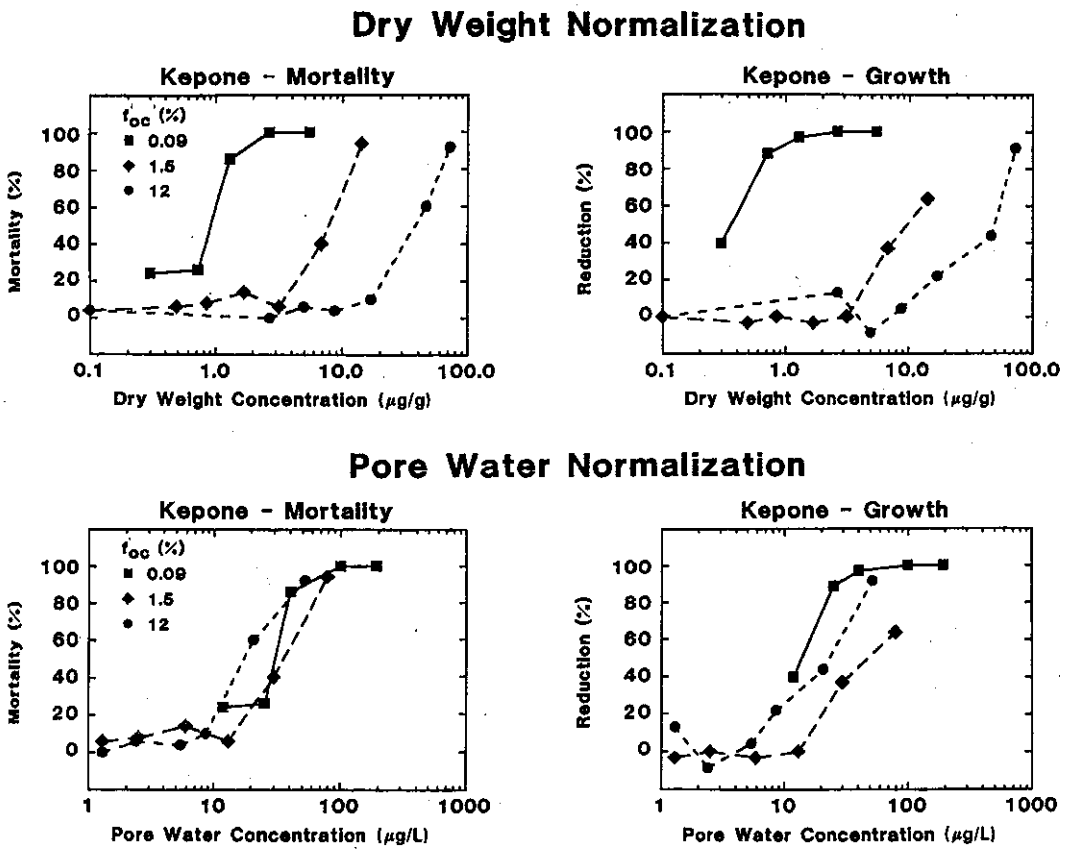


Fig. 5. Comparison of percent mortality (left) and growth rate reduction (right) of *C. tentans* to Kepone concentration in bulk sediment (top) and pore water (bottom) for three sediments with varying organic carbon concentrations [17].

on Figure 8. The responses of *R. abronius* [23] and *Ampelisca abdita* [24] to cadmium in seawater exposures without sediment and to the measured pore water concentrations in sediment exposures (lower panels) demonstrate again that the survival responses are similar with or without the sediment. The concentration–response curves using total cadmium concentrations are also shown (top panels). It is interesting to note that these two organisms exhibit similar sensitivity to cadmium in water-only exposures (0.34 mg/L for *A. abdita* and 1.6 mg/L for *R. abronius*—bottom panels), yet the total sediment cadmium LC50s differ by almost two orders of magnitude (25 and 2,000 μg/g, respectively) for the different sediments. These dramatic differences demonstrate the need to explicitly consider bioavailability of sediment cadmium and, by implication, any toxicant of concern in developing SQC. It has been demonstrated that the variation in bioavailability of cadmium and nickel in various freshwater and marine sediments can be related to the acid-volatile sulfide concentration of the sediment [24,25].

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—that were added to three sediments, one of which was laboratory-grade sand [26]. 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. 9, top panels). On a pore water basis, the bioaccumulation ap-

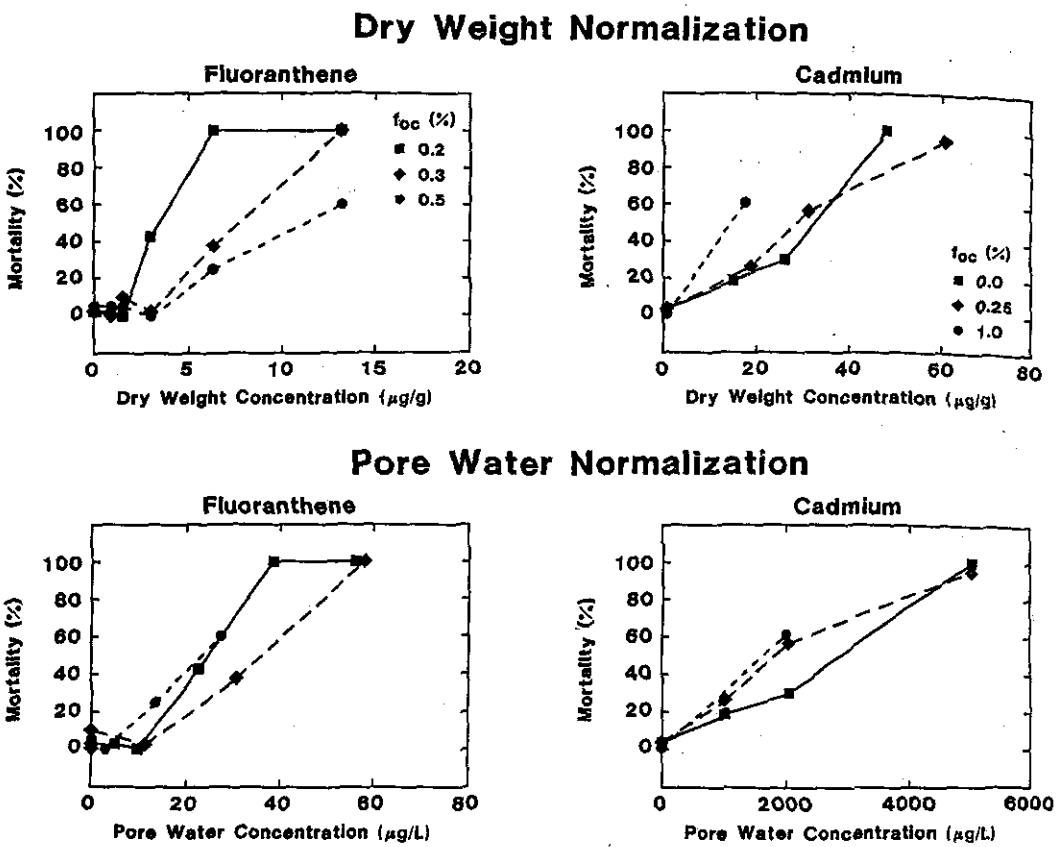


Fig. 6. Comparison of percent mortality of *R. abronius* to fluoranthene [19] (left) and cadmium [20] (right) concentrations in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations.

pears 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 (4.0–0.23) (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 2.

Bioaccumulation was also measured by Adams et al. [17,27,28] in the *C. tentans*-Kepone experiments presented previously (Fig. 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 4 (5,200–17,600 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 essentially one curve if pore water is considered as the concentration that quantifies exposure—can be interpreted in a number of ways. However, it has become clear that these results do not necessarily imply that pore water is the primary route of exposure. This is because all exposure pathways are at equal chemical activity in an equilibrium experiment. Hence the route of exposure cannot be determined. This can be seen by comparing the concentration–response correlations to pore water and organic carbon–normalized sediment concentrations. As shown below, both are equally successful at correlating the data. This suggests that neither the pore water nor the sediment exposure pathway can be implicated as the primary exposure route.

However, in order to relate pore water exposure to sediment carbon exposure, it is necessary that the relationship between these two concentrations be established. Thus, an examination of the state of the art of predicting the partitioning of chemi-

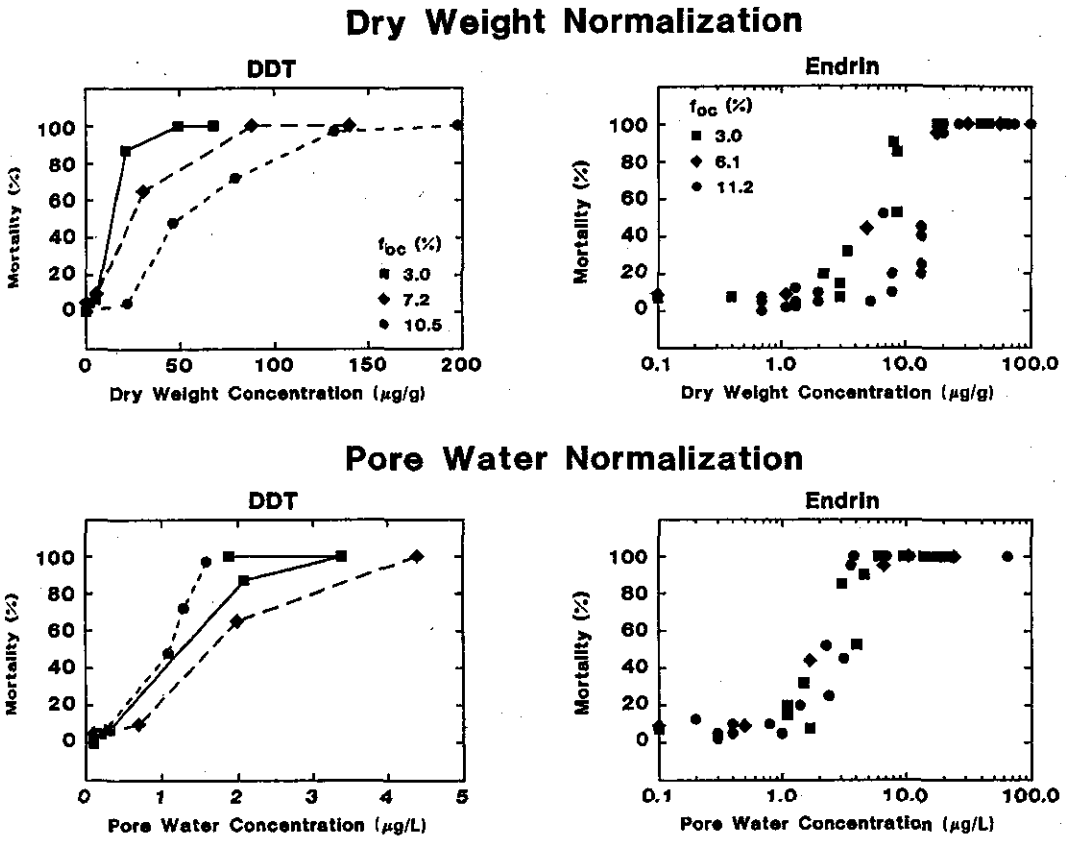


Fig. 7. Comparison of percent mortality of *H. azteca* to DDT (left) and endrin (right) concentrations in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations [21,22].

cals between the solid and the liquid phase is required. This is examined in the following section.

SORPTION OF NONIONIC ORGANIC CHEMICALS

Partitioning in particle suspensions

For nonionic hydrophobic organic chemicals sorbing to natural soils and sediment particles, a number of empirical models have been suggested (see Karickhoff [29] 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 [30].

In many experiments using particle suspensions, the partition coefficients have been observed to decrease as the particle concentration used in the experiment is increased [30]. Unfortunately 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. This would result in lower sediment chemical concentrations for SQC. However, if this phenomenon is an artifact or is due to 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

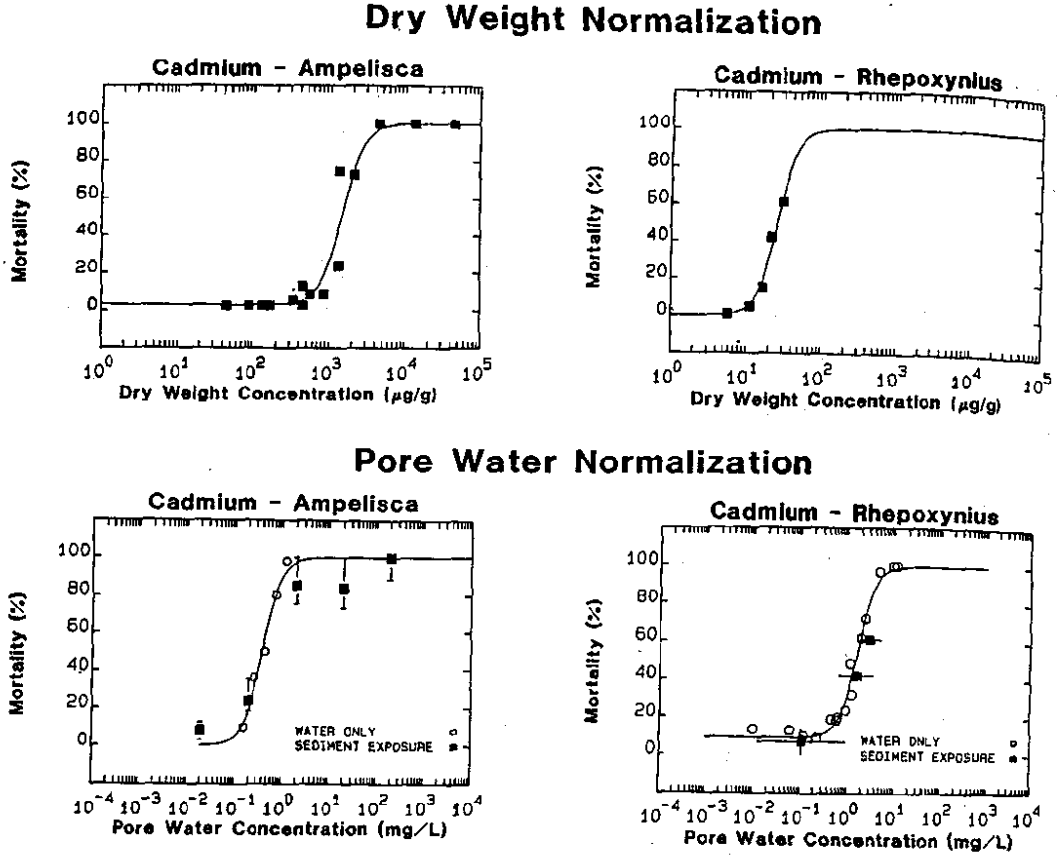
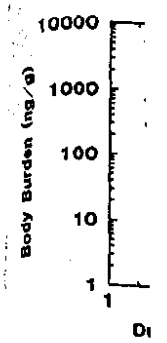


Fig. 8. Comparison of percent mortality of *A. abdita* [24] (left) and *R. abronius* [23] (right) to concentrations of cadmium in bulk sediment (top) and pore water (bottom). Also presented is water-only exposure data, identified with open circles.



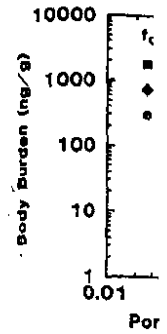


Fig. 9. Compari
in bulk sediment

seven orders of magnitude with a $\log_{10}$ prediction standard error of 0.38 [31]. 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):

$$C_s = K_p^* C_d. \tag{9}$$

The PIM model for K_p^* is

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

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/L)
ν_x = 1.4, an empirical constant (unitless).

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

$$\log_{10} K_{oc} = 0.00028 + 0.983 \log_{10} K_{ow} \tag{11}$$

which is essentially K_{oc} approximately equals K_{ow}. Figure 10 presents the observed versus predicted reversible component partition coefficients using this model [31]. 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 ($m f_{oc} K_{ow} < 1$)

Chemical	
Cypermethrin	
Permethrin	
Kepone	

[a]95% confidence li

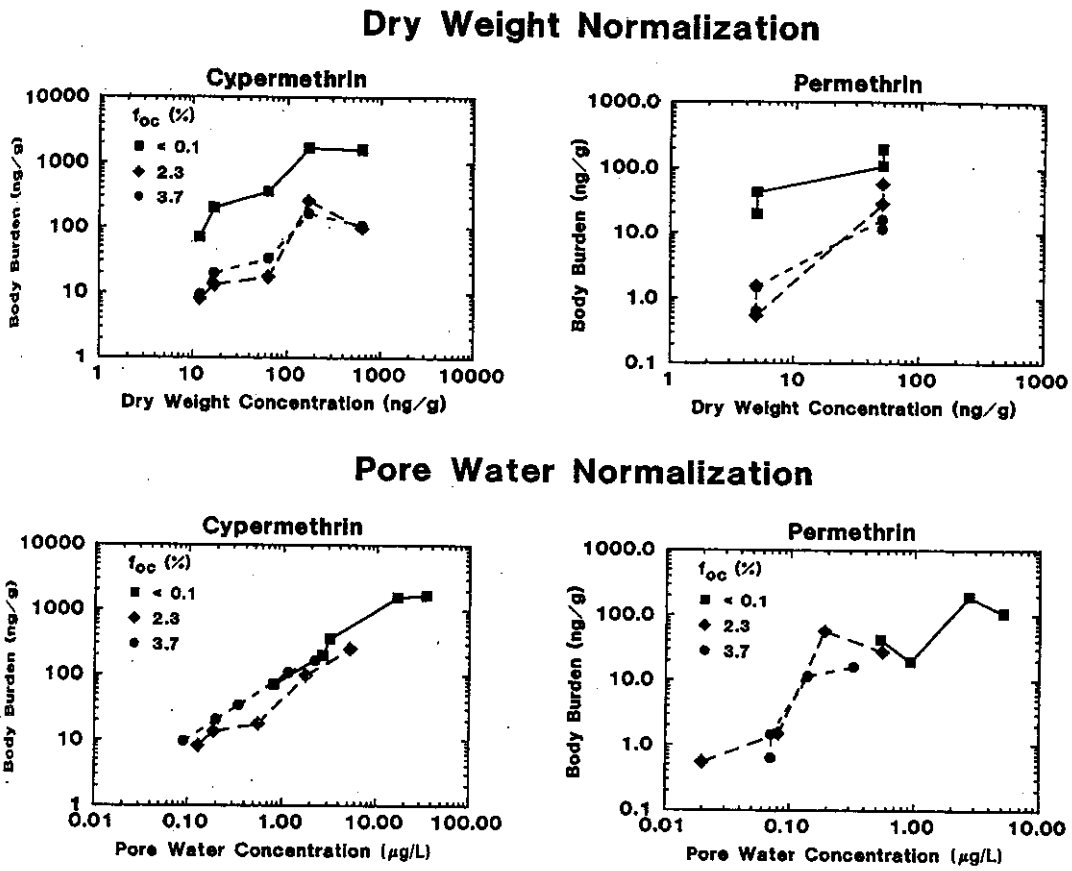


Fig. 9. Comparison of *C. tentans* body burden of cypermethrin (left) and permethrin (right) versus concentration in bulk sediment (top) and pore water (bottom) for sediments with varying organic carbon concentrations [26].

Table 3. Bioaccumulation factors for *C. tentans*

Chemical	f_{oc} (%)	Bioaccumulation factors[a]: Total sediment ($\frac{\mu g/g \text{ organism}}{\mu g/g \text{ sediment}}$)	Bioaccumulation factors[a]: Pore water ($\frac{\mu g/kg \text{ organism}}{\mu g/L}$)	Reference
Cypermethrin	<0.1	6.21 (4.41–8.01)	80.1 (73.5–86.7)	[26]
	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)	[26]
	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)	[17,27,28]
	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.

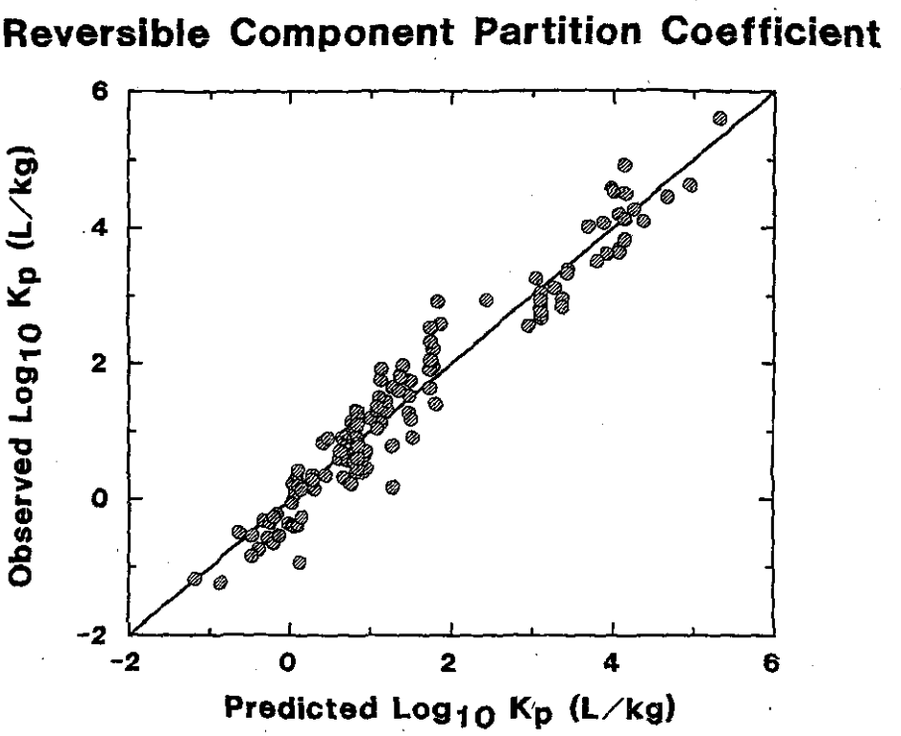


Fig. 10. Comparison of observed reversible component partition coefficient to calculated partition coefficient using Equation 10 [31].

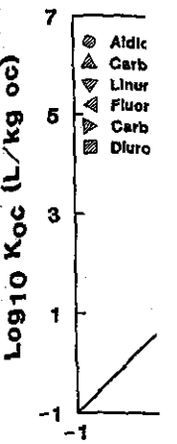


Fig. 11. Comparis
coefficient, K_{oc}, t
$mf_{oc}K_{ow} < 1$. The

are presented on Figure 11 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 $K_{oc} \simeq K_{ow}$ 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 $K_p \simeq f_{oc}K_{ow}$ applies to the conventional adsorption partition coefficient as well (Fig. 11, left).

A number of explanations have been offered for the particle concentration effect. The most popular is to posit the existence of an additional third sorbing phase or complexing component that is associated with the particles but is inadvertently measured as part of the dissolved chemical concentration due to experimental limitations. Colloidal particles that remain in solution after particle separation [32,33] and dissolved ligands or macromolecules that desorb from the particles and remain in solution [34–37] 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 [38]. The effect has also been attributed to kinetic effects [29].

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 to explicitly exclude possible third-phase interferences. Both the resuspension experiment for poly-

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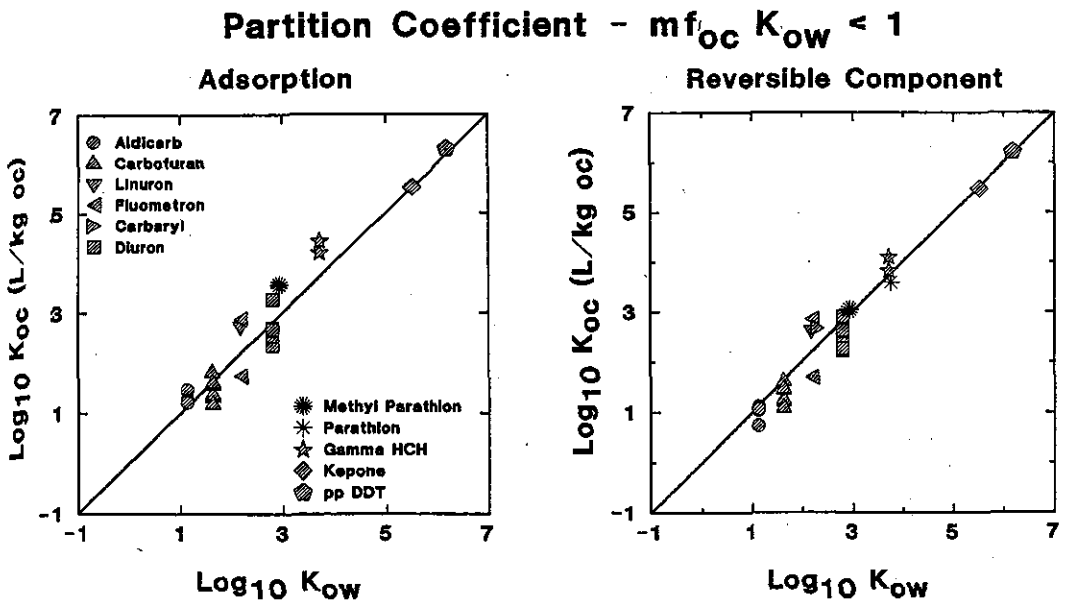

Fig. 11. Comparison of the adsorption (left) and reversible component (right) organic carbon–normalized partition coefficient, K_{oc}, to the octanol/water partition coefficient, K_{ow}, for experiments with low solids concentrations: $mf_{oc}K_{ow} < 1$. The line represents equality [31].

chlorinated biphenyls (PCBs) [39] and metals [40,41] in which particles are resuspended into a reduced volume of supernatant and the dilution experiment [39] in which the particle suspension is diluted with supernatant from a parallel vessel display particle concentration effects. 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 are due to an additional desorption reaction induced by particle-particle interactions [31]. It has been suggested that actual particle collisions are responsible [42]. 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 [31,40].

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 $K_{oc} \simeq K_{ow}$ 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 $K_{oc} \simeq K_{ow}$. 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, that is, $K_{oc} \simeq K_{ow}$.

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 can be shown as follows: The sediment/pore water partition coefficient, K_p is given by

$$K_p = f_{oc}K_{oc} \simeq f_{oc}K_{ow} \tag{12}$$

and the solid-phase concentration is given by

$$C_s = f_{oc}K_{oc}C_d \tag{13}$$

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 11 can be used to examine the linearity of K_p to f_{oc}. Figure 12 compares K_p/K_{ow}

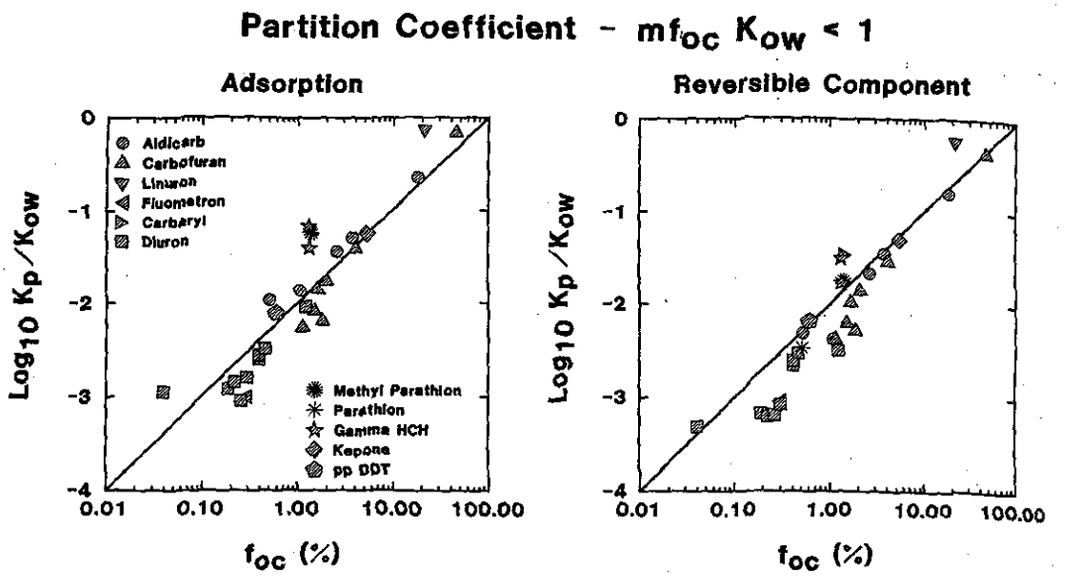

Fig. 12. Comparison of the normalized partition coefficients for adsorption (left) and reversible component sorption (right) to sediment organic carbon. The data are restricted so that particle effects are not expected to be significant: $mf_{oc}K_{ow} < 1$. The line represents perfect agreement [31].

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 $f_{oc} = 0.2\%$. This result and the toxicity experiments examined below suggest that for $f_{oc} > 0.2\%$, organic carbon normalization is valid.

As a consequence of the linear relationship of C_s and f_{oc}, the relationship between sediment concentration, C_s, and free dissolved concentration, C_d, can be expressed as

$$\frac{C_s}{f_{oc}} = K_{oc}C_d. \tag{14}$$

If we define

$$C_{s,oc} = \frac{C_s}{f_{oc}} \tag{15}$$

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

$$C_{s,oc} = K_{oc}C_d. \tag{16}$$

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 $f_{oc} > 0.2\%$. This latter qualification is judged to be necessary because at $f_{oc} < 0.2\%$ the other factors that influence partitioning (e.g., particle size and sorption to nonorganic mineral fractions) become relatively more important [29]. 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-com-

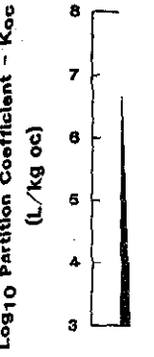

Fig. 13. Partiti
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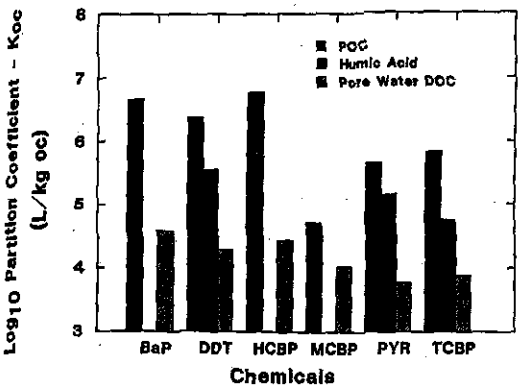

Fig. 13. Partition coefficients of chemicals to particulate organic carbon (POC), Aldrich humic acid, and natural DOC. Benzo[*a*]pyrene (BaP); 2,2′,4,4′,5,5′ hexachlorobiphenyl (HCBP); DDT; 2,2′,5,5′-tetrachlorobiphenyl (TCBP); pyrene (PYR); 4-monochlorobiphenyl (MCBP). Data from Eadie et al. [43].

plexed 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:

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

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. Hence 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 [43]. A summary that compares the partitioning of six chemicals to POC, natural DOC, and Aldrich humic acid (HA) is shown on Figure 13. The magnitudes 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:

$$C_T = \phi C_d + m f_{oc} K_{oc} C_d + \phi m_{DOC} K_{DOC} C_d \qquad (18)$$

where ϕ 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

$$C_d = \frac{C_T}{\phi + m f_{oc} K_{oc} + \phi m_{DOC} K_{DOC}}. \qquad (19)$$

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

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

Figure 14 illustrates the phase-partitioning behavior of a system for a unit concentration of a chemical with the following properties: $K_{oc} = K_{DOC} = 10^6$ L/kg, $f_{oc} = 2.0\%$, $m = 0.5$ kg solids/L sediment, and m_{DOC} varies from 0 to 50 mg/L, a reasonable range for pore waters [44]. With no DOC present, the pore water concentration equals the free concentration. As DOC increases, the pore water concentration increases due to the increase in complexed chemical, C_{DOC}. Accompanying this increase in C_{DOC} is a slight—in

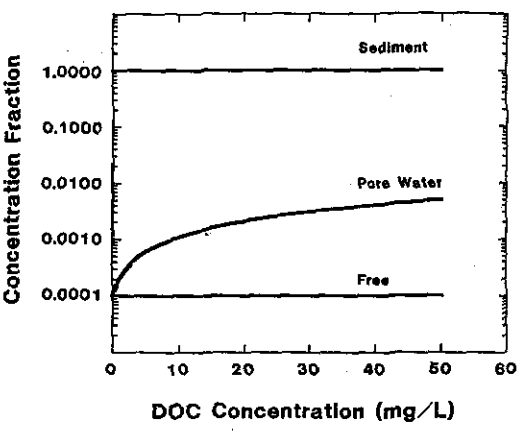

Fig. 14. Phase distribution of a chemical in the three-phase system: water, sediment, and DOC (Eqns. 18, 19, and 20). $K_{oc} = K_{DOC} = K_{ow} = 10^6$ L/kg, $f_{oc} = 2.0\%$, and $m = 0.5$ kg/L.

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. 14). Hence, the question of bioavailability of DOC-complexed chemical can be important in assessing toxicity directly from measured pore water concentrations. A significant quantity of data indicates that DOC-complexed chemical is not bioavailable. Fish [45] and amphipod [46] uptake of polycyclic aromatic hydrocarbons (PAHs) are significantly reduced by adding DOC. An example is shown in Figure 15 for a freshwater amphipod [46]. 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 is the expected result because, for a fixed amount of DOC, the quantity of DOC-complexed chemical decreases with decreasing K_{DOC} (Eqn. 17).

The quantitative demonstration that DOC-complexed chemicals are not bioavailable requires an independent determination of the concentration of complexed chemical. Landrum et al. [46] have developed a C_{18} reversed-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 [46,47]. As shown on Figure 16, although the K_{DOC} inferred from uptake suppression is larger than that inferred from the reversed-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).

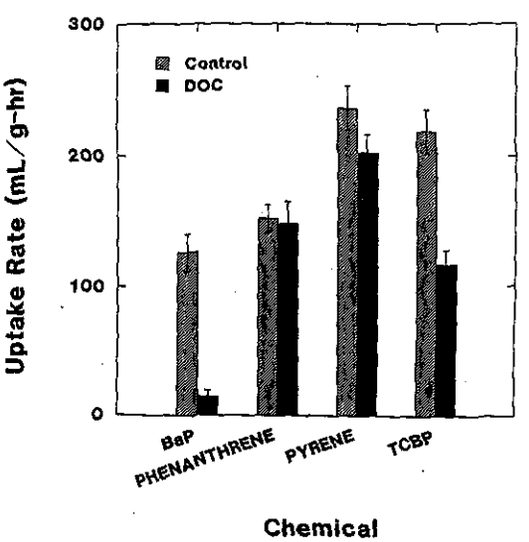

Fig. 15. Average uptake rate of chemicals by *Pontoporeia hoyi* with (filled) and without (hatched) DOC present. Benzo[*a*]pyrene (BaP); 2,2′,4,4′-tetrachlorobiphenyl (TCBP); pyrene; phenanthrene. Data from Landrum et al. [46].

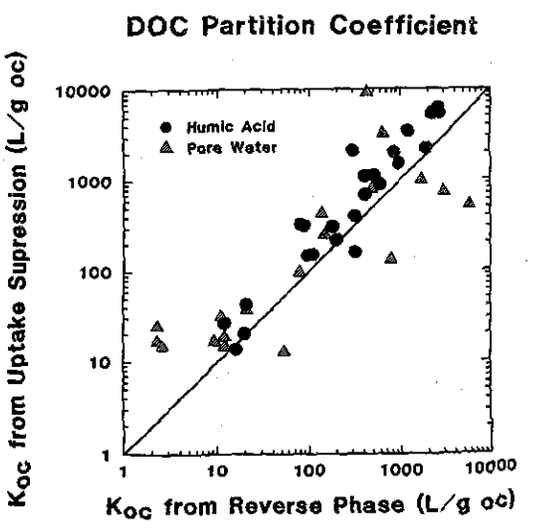

Fig. 16. Comparison of the DOC partition coefficient calculated from the suppression of chemical uptake versus the C_{18} reversed-phase HPLC column estimate. Circles are Aldrich humic acid; triangles are interstitial water DOC. Chemicals are listed in Figure 15 caption (also anthracene and benzo[*a*]anthracene).

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Field observations of partitioning in sediments

There exists an enormous quantity of laboratory data 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

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

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

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

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 Prahl [48] can be used to test this prediction. 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 μm). 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 17, range from 0.2% for the high-density sand-sized fraction to greater than 30% for the low-density fraction. This exceeds two orders of magnitude and essentially spans the range usually found

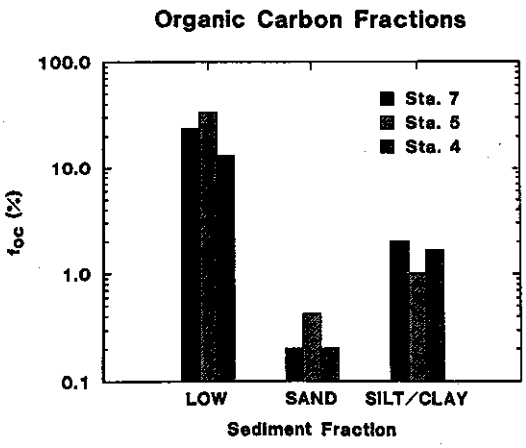


Fig. 17. The organic carbon fractions (% dry weight) in the low-density fraction >64 μm, <1.9 g/cm³; the sand-sized fraction >64 μm, >1.9 g/cm³; the silt/clay-sized fraction <64 μm. Numbered stations as indicated. Data from Prahl [48].

in practice. For example, 90% of the estuarine and coastal sediments sampled for the National Status and Trends program exceed 0.2% organic carbon [49].

Figure 18 (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 18 (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.

It is concluded from these data that the organic carbon–normalized PAH 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 (0.2–0.3%) suggests that organic carbon normalization is appropriate at these low levels.

Sediment/pore water partitioning. Normally when measurements of sediment chemical concentration, C_s, and total pore water chemical concentrations, C_{pore}, are made, the value of the apparent

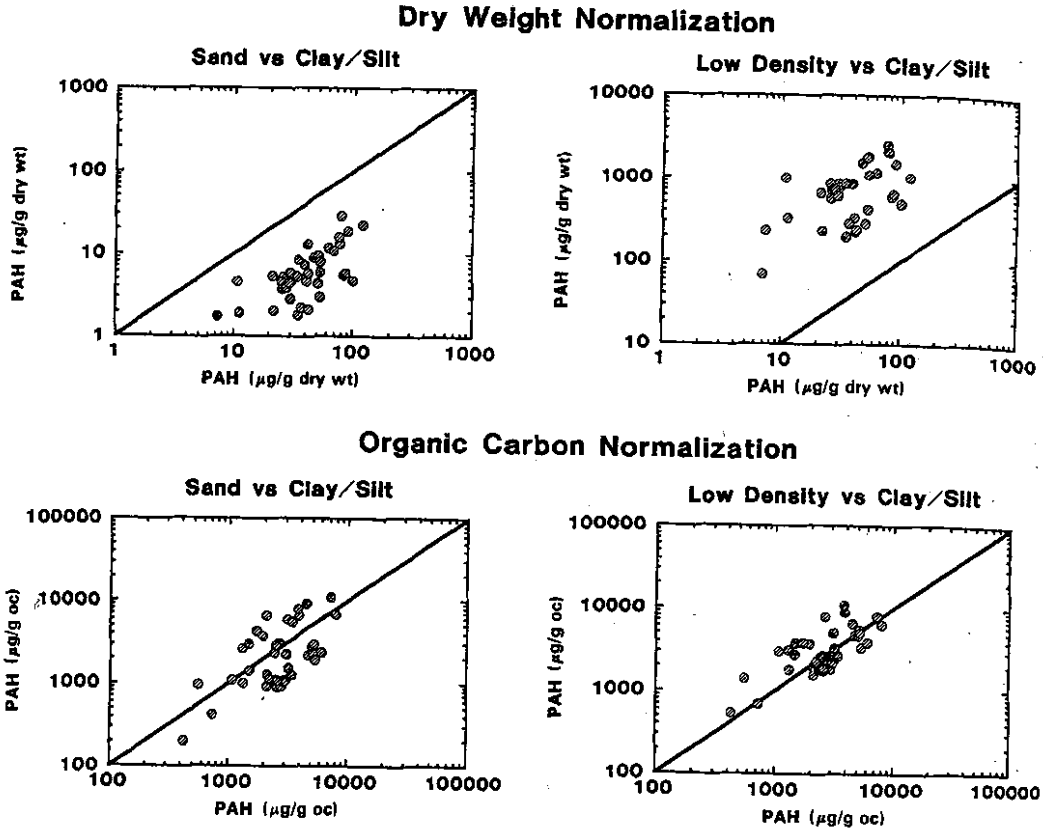


Fig. 18. Comparison of PAH concentrations of the sand-sized- and low-density-fraction sediment particles ordinate to the clay/silt fraction abscissa (Stations 4, 5, 7). Top panels are for dry weight normalization; bottom panels are for organic carbon normalization. Data from Prahl [48].

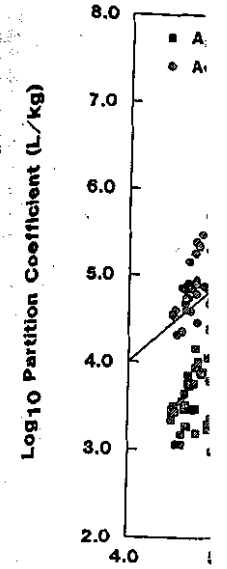


Fig. 19. Observed pa uct of organic carbon tion coefficient. Th partition coefficients solved PCB (squares) computed with Equa from [50].

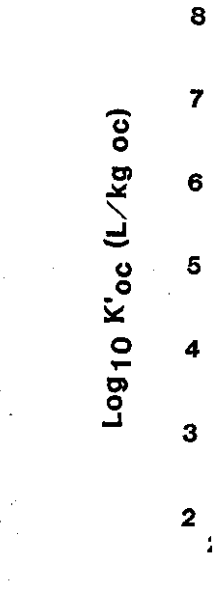


Fig. 20. Observed appar lines represent the expec from [53] for PCB cong

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

$$K_p' = \frac{C_s}{C_{pore}} \tag{23}$$

is given by

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

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

$$K_p' = \frac{f_{oc}K_{oc}}{m_{DOC}K_{DOC}} \tag{25}$$

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, C_d, the actual partition coefficient, K_p, 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. 14). 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 re-

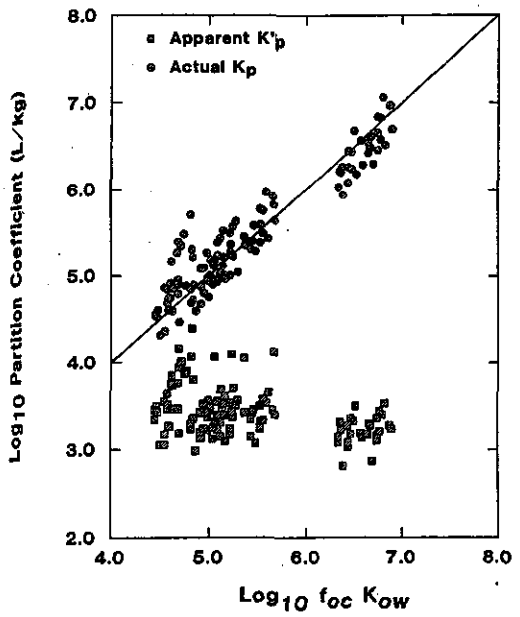


Fig. 19. Observed partition coefficient versus the product of organic carbon fraction and octanol/water partition coefficient. The line represents equality. The partition coefficients are computed by using total dissolved PCB (squares), and free PCB (circles) which is computed with Equation 26 with $K_{DOC} = K_{ow}$. Data from [50].

ported by Brownawell and Farrington [50] demonstrate the importance of DOC complexing in pore water. Figure 19 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:

$$C_d = \frac{C_{pore}}{1 + m_{DOC}K_{DOC}} \tag{26}$$

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 19, agree with the expected partition equation, namely that $K_p = f_{oc}K_{ow}$. A similar three-phase model has been presented by Brownawell and Farrington [51].

Other data with sediment/pore water partition coefficients for which the DOC concentrations have not been reported [52,53] are available to assess the significance of DOC partitioning on the apparent sediment partition coefficient. Figure 20 presents these apparent organic carbon-normalized

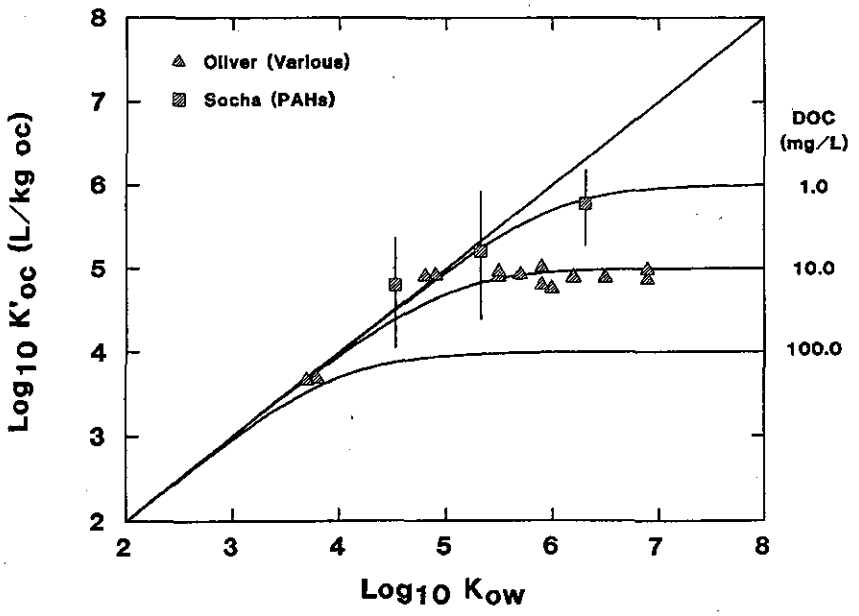


Fig. 20. Observed apparent partition coefficient to organic carbon versus the octanol/water partition coefficient. The lines represent the expected relationship for DOC concentrations of 0, 1, 10, and 100 mg/L and $K_{DOC} = K_{ow}$. Data from [53] for PCB congeners and other chemicals and from [52] for phenanthrene, fluoranthene, and perylene.

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 [44,50]. Thus these results do not refute the hypothesis that $K_{oc} \simeq K_{ow}$ in sediments but show the need to account for DOC complexing in the analysis of pore water chemical concentrations.

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 to 7 are used to compare results on a pore water–normalized and organic carbon–normalized chemical concentration basis. Figures 21 to 23 present these comparisons for Kepone, DDT, endrin, and fluoranthene. The mean and 95% confidence limits of the LC50 and EC50 values for each set of data are listed in Table 2. The top panels repeat the re-

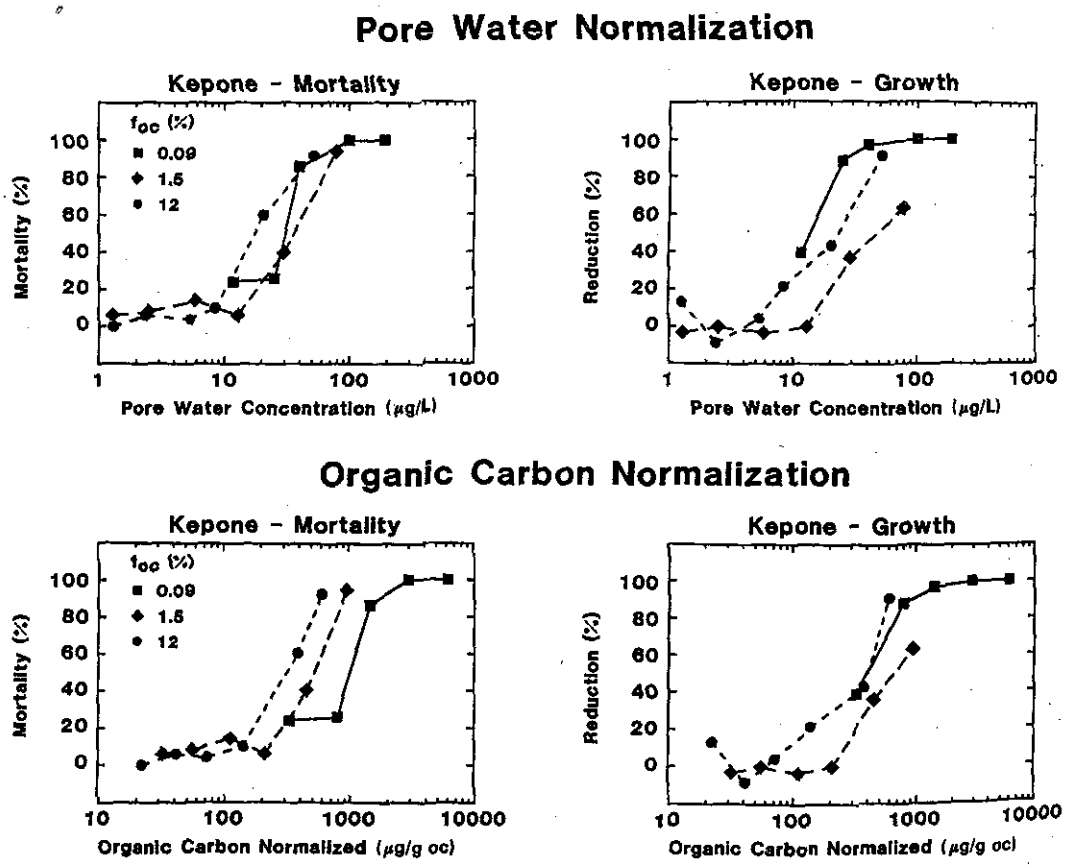
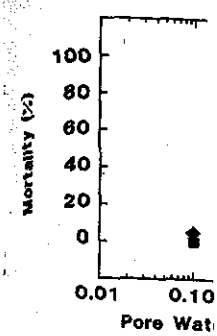


Fig. 21. Comparison of percent survival (left) and growth rate reduction (right) of *C. tentans* to Kepone concentration in pore water (top) and in bulk sediment, using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations [17].



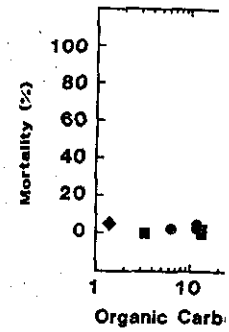


Fig. 22. Comparison o
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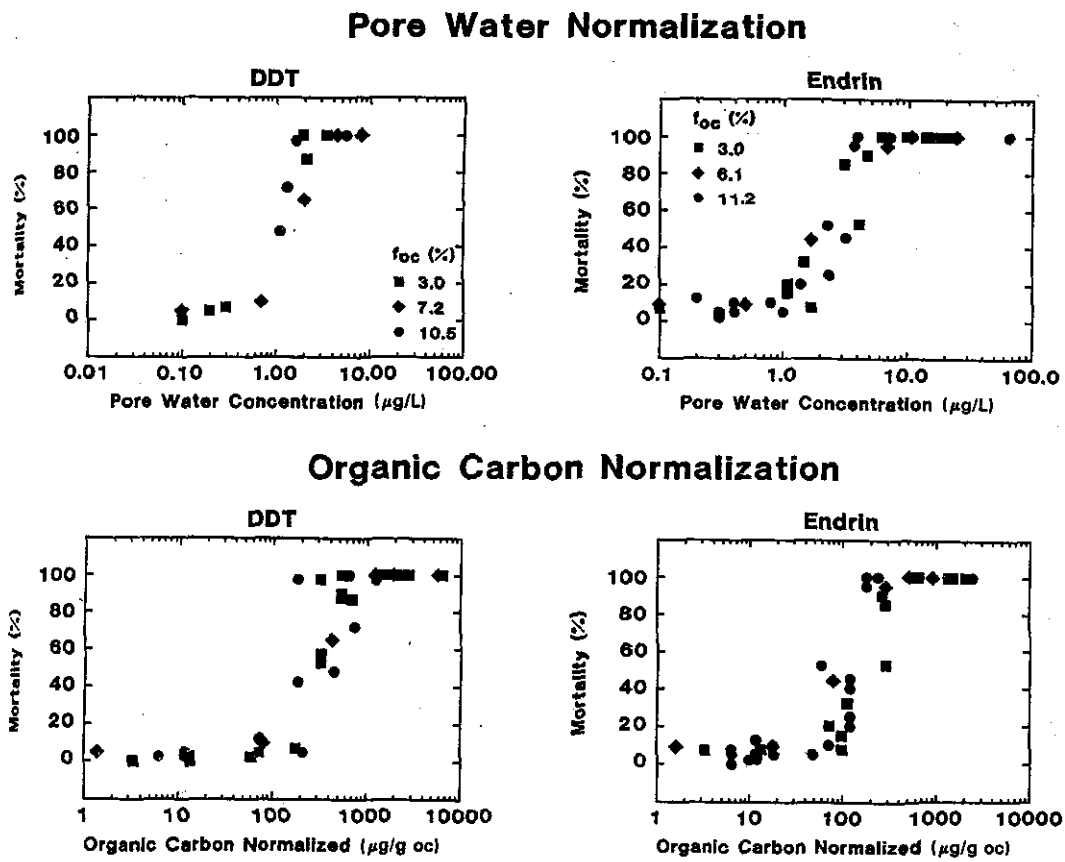


Fig. 22. Comparison of percent survival of *H. azteca* to DDT (left) and endrin (right) concentration in pore water (top) and in bulk sediment, using organic carbon normalization (bottom) for three sediments with varying organic carbon concentrations [21,22].

sponse–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 (micrograms 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. 21) – whereas the converse sometimes occurs – for example, Kepone–growth rate (Fig. 21). A more quantitative comparison can be made with the LC50s and EC50s in Table 2. The variation of organic carbon–normalized LC50s and EC50s between sediments is less than a factor of two to three and is comparable to the variation in pore water LC50s and EC50s. A more comprehensive comparison has been presented in Figures 2 and 3, which also examine the use of the water-only LC50 to predict the pore water and sediment organic carbon LC50s.

Bioaccumulation factors calculated on the basis of organic carbon–normalized chemical concentrations are listed in Table 3, for permethrin, cypermethrin, and Kepone. Again, the variation of organic carbon–normalized BAFs between sediments is less than a factor of two to three and is comparable to the variation in 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. The use of organism lipid fraction for this normal-

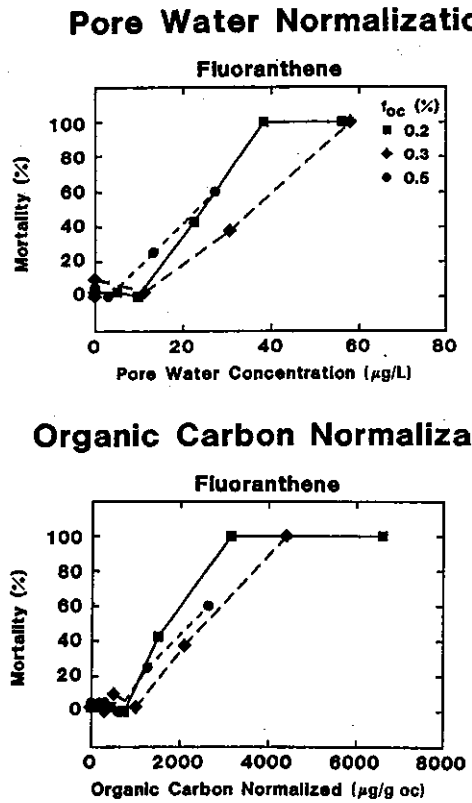


Fig. 23. Comparison of percent survival of *R. abronius* to fluoranthene concentration in pore water (top) and bulk sediment, using organic carbon normalization (bottom) for sediments with varying organic carbon concentrations [19].

ization has become conventional (see references in Chiou [54]). If C_b is the chemical concentration per unit wet weight of the organism, then the partitioning equation is

$$C_b = K_L f_L C_d \tag{27}$$

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

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

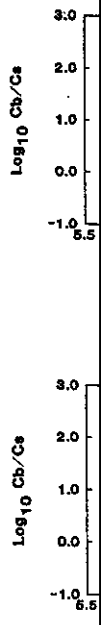
The lipid-normalized body burden and the organic carbon–normalized sediment concentration can be used to compute a bioaccumulation ratio, which can be termed the *BSF* [55]:

$$\text{BSF} = \frac{C_{b,L}}{C_{s,oc}} = \frac{K_L}{K_{oc}} \simeq \frac{K_L}{K_{ow}}. \tag{29}$$

The second equality results from using the partitioning Equations 16 and 28 and the third from the approximation that $K_{oc} \simeq K_{ow}$. 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 [54,56,57]. 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 [55]. Nevertheless it is 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, *Yolda* and *Macoma*—and five sediments has been performed by Rubinstein and co-workers [58]. 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 24 and 25 present the log mean of the replicates for the ratio of organism-to-sediment concentration for all measured congeners versus K_{ow} for each organism. Dry weight normalization for both organism and sediment (left panels), organic carbon normalization for the sediment (center panels), and both organic carbon and lipid normalization (right panels) are shown. The results for each sediment are connected by lines and separately identified.



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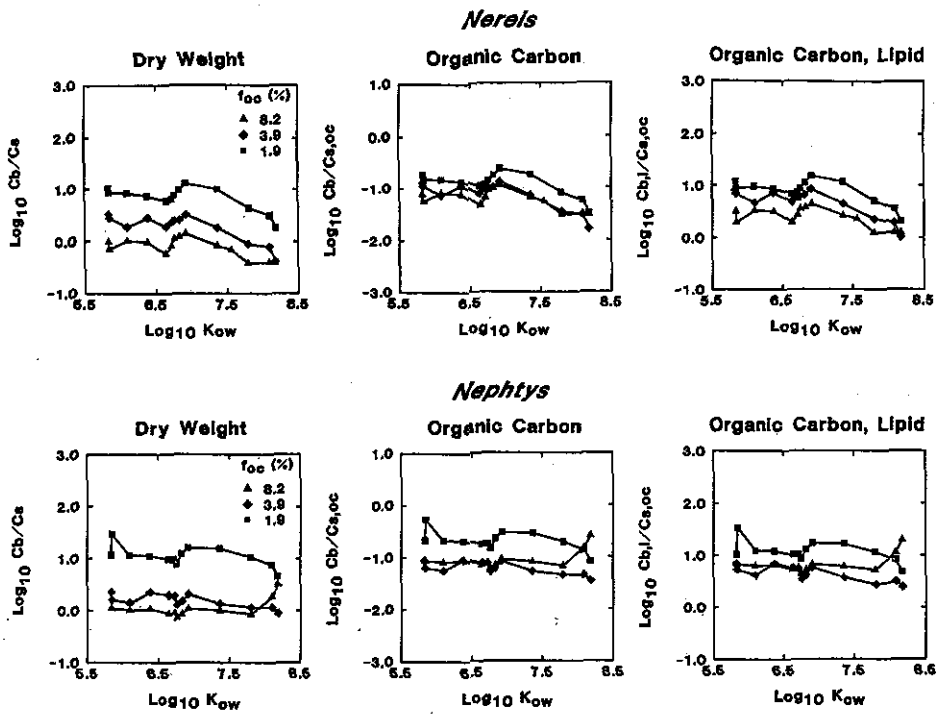

Fig. 24. Plots of the BSF (ratio of organism-to-sediment concentration) for three sediments for a series of PCB congeners versus the $\log_{10} K_{ow}$ for that congener. The dry weight normalization for both organism and sediment (left panels); organic carbon normalization for the sediment (middle panels); and organic carbon and lipid normalization (right panels) as indicated. The organisms are *Nereis* (top) and *Nephtys* (bottom). Data from [58].

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 at $\log_{10} K_{ow} > 7$ is evident. 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 [53]. A plot of the organic carbon- and lipid-normalized BSF versus K_{ow} from this experiment is shown on Figure 26, together with the averaged polychaete data (Fig. 24). There appears to be a systematic variation with respect to K_{ow}, which suggests that the simple lipid equilibration model with a constant lipid–octanol solubility ratio is not descriptive for all chemicals. This suggests that a more detailed model of benthic organism uptake is required to describe chemical body burdens for all nonionic chemicals as a function of K_{ow} [55]. However, for a specific chemical and a specific organism—for example, *Nereis* and any PCB congener (Fig. 24)—organic carbon normalization reduces the effect of the varying sediments. This demonstrates the utility of organic carbon normalization and supports its use in generating SQC.

A further conclusion can be reached from these results. It has been pointed out by Bierman [59] that the fact that the lipid- and carbon-normalized BSF is in the range of 0.1 to 10 (Figs. 24–26) 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 [60], it would be expected that the lipid–organic carbon solubility ratio should be of order one. If this ratio is taken

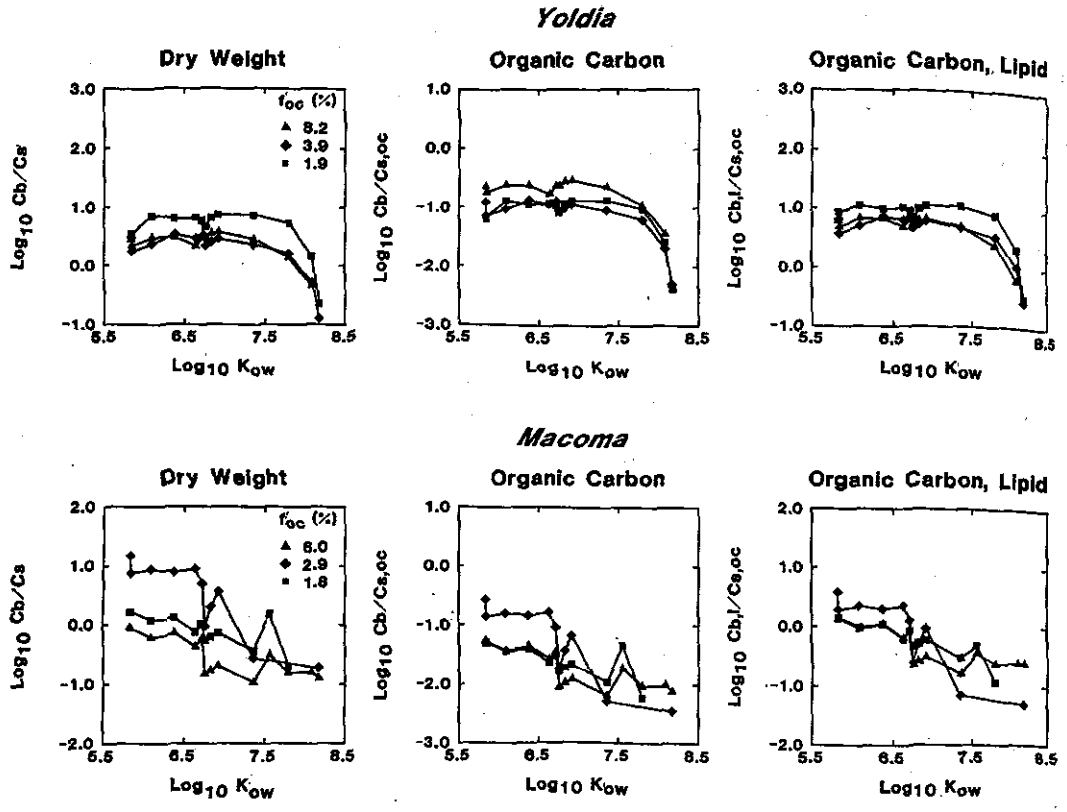

Fig. 25. Plots of the BSF (ratio of organism-to-sediment concentration) for three sediments for a series of PCB congeners versus the $\log_{10} K_{ow}$ for that congener. The dry weight normalization for both organism and sediment (left panels); organic carbon normalization for the sediment (middle panels); and organic carbon and lipid normalization (right panels) as indicated. The organisms are *Yoldia* (top) and *Macoma* (bottom). Data from [58].

to be approximately one, then the conclusion from the BSF data is that, indeed, K_{oc} is approximately equal to K_{ow} for sediments [59].

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. [61]). 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 suggests that the sediment organic carbon is the route of exposure. In fact, neither of these conclusions necessarily follow from these data. The reason is that 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 [62], of a chemical controls its biological activity. The chemical potential, μ_d, of the free concentration of chemical in pore water, C_d, is

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

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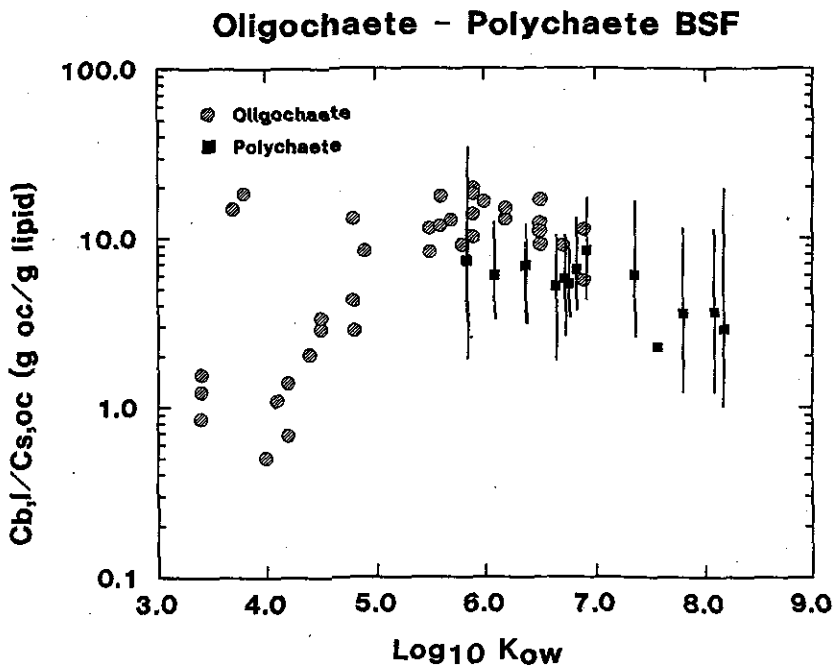

Fig. 26. Plots of the BSF (ratio of organism lipid to sediment organic carbon concentration) for a series of PCB congeners and other chemicals versus $\log_{10} K_{ow}$. Data for oligochaetes [53] and polychaetes [58].

where μ_o is the standard state chemical potential and RT is the product of the universal gas constant and absolute temperature [63]. 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 $C_{s,oc}$ 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 becomes: 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 [46]. 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 and (b) the levels of protection afforded by WQC are appropriate for benthic organisms. 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.

Table 4. Draft or published WQC documents and number of infaunal (habaitats 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
Acenaphthene	9/87[b]	–	–	–	–	10	–	3	7
Acrolein	9/87[b]	–	–	–	–	12	1	5	7
Aldrin	1980	16	0	11	12	21	2	10	15
Aluminum	1988	–	–	–	–	15	–	5	11
Ammonia	1985; 1989	20	2	7	16	48	2	17	33
Antimony(III)	9/87[b]	11	3	6	5	9	1	2	6
Arsenic(III)	1985	12	2	3	8	16	1	6	13
Cadmium	1985	38	10	18	18	56	13	16	31
Chlordane	1980	8	1	7	7	14	1	4	10
Chloride	1988	–	–	–	–	15	3	6	8
Chlorine	1985	23	2	9	15	33	1	9	26
Chlorpyrifos	1986	15	2	8	10	18	2	8	11
Chromium(III)	1985	–	–	–	–	17	3	8	12
Chromium(VI)	1985	23	8	9	9	33	1	10	21
Copper	1985	25	6	5	18	57	8	15	36
Cyanide	1985	9	1	4	5	17	1	6	12
DDT	1980	17	1	11	12	42	3	15	29
Dieldrin	1980	21	1	15	15	19	1	9	12
2,4,-Dimethylphenol	6/88[b]	9	2	2	6	12	1	3	7
Endosulfan	1980	12	2	8	8	10	1	4	7
Endrin	1980	21	1	14	16	28	3	12	17
Heptachlor	1980	19	1	14	13	18	2	8	12
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	3	3
Toxaphene	1986	15	2	9	11	37	5	13	23
Tributyltin	9/87	19	1	8	15	9	1	1	6
1,2,4-Trichlorobenzene	9/88[b]	15	7	7	4	14	2	5	7
2,4,5-Trichlorophenol	9/87[b]	11	4	5	5	10	1	2	8
Zinc	1987	33	10	9	17	45	5	12	30

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

[b]Draft aquatic life criteria document, U.S. Environmental Protection Agency, Office of Water Regulations and Standards, Criteria and Standards Division, Washington, DC.

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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 LC50s for freshwater and saltwater species from draft or published WQC documents that contain minimum data base 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 data base. 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].

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.

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 lowest acute LC50 concentration for the benthic and water column organisms, using acute values 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 3–8), the water column species were typically the most sensitive. The results are cross-plotted on Figure 27 (left). The line represents perfect agreement. In most instances where acute values for saltwater benthic and water column species are identical, it is because penaeid shrimp are most sensitive to insecticides and are classified as both infaunal (benthic) and epibenthic (water column).

Unfortunately 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%) of the chemicals, and five or fewer species were tested with 34 (85%) of the chemicals. Of the 30 chemicals for which WQC for saltwater organisms are available, two or fewer infaunal species were tested with 19 (63%) of the chemicals, and five or fewer species were tested with 23 (77%) 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 data base required for criteria derivation. 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 1–4), is based on more data and suggests a similarity in sensitivity (Fig. 27, right). 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, that additional testing would be 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 LC50

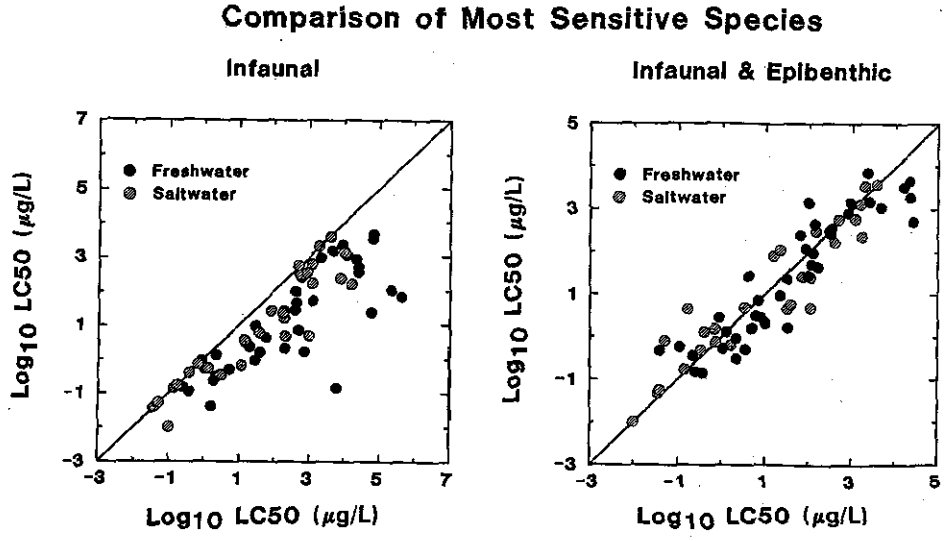

Fig. 27. Comparison of LC50 or EC50 acute values for the most sensitive benthic (abscissa) and water column (ordinate) species for chemicals listed in Table 5. Benthic species are defined as infaunal species (habitat types 1 and 2, left panel) or infaunal and epibenthic species (habitat types 1–4); see Table 6.

data are used. One approach examines the relative location of benthic species in the overall species sensitivity distribution. For each chemical in either fresh or salt water, one can examine the distribution of benthic species in a rank-ordering of all the species' LC50s. If benthic species were relatively insensitive, then they would predominate in ranking among the larger LC50 concentrations. Equal sensitivity would be indicated by a uniform distribution of species within the overall ranking. Figure 28 presents the results for tests of nickel in salt water. The LC50s 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).

This comparison can be done chemical by chemical. However, in order to make the analysis more robust, the LC50 data for each chemical–water type can be normalized to zero log mean and unit log variance as follows:

$$\mathrm{LC50}_{n,ij} = \frac{\log(\mathrm{LC50}_{ij}) - \mu_i}{\sigma_i} \qquad (33)$$

where i indexes the chemical–water type, μ_i is the log mean and σ_i is the log standard deviation, j indexes the LC50s within the ith class, and $\mathrm{LC50}_{n,ij}$ is the normalized LC50. This places all the LC50s 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 29. If the sensitivity of benthic species is not unique, then a constant percentage of benthic species–normalized LC50s, indicated by the dashed line, should be represented in each 10-percentile (decile) interval of data for all species. That is, the 10 rectangles in each histogram should be identical in height. The infaunal species (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

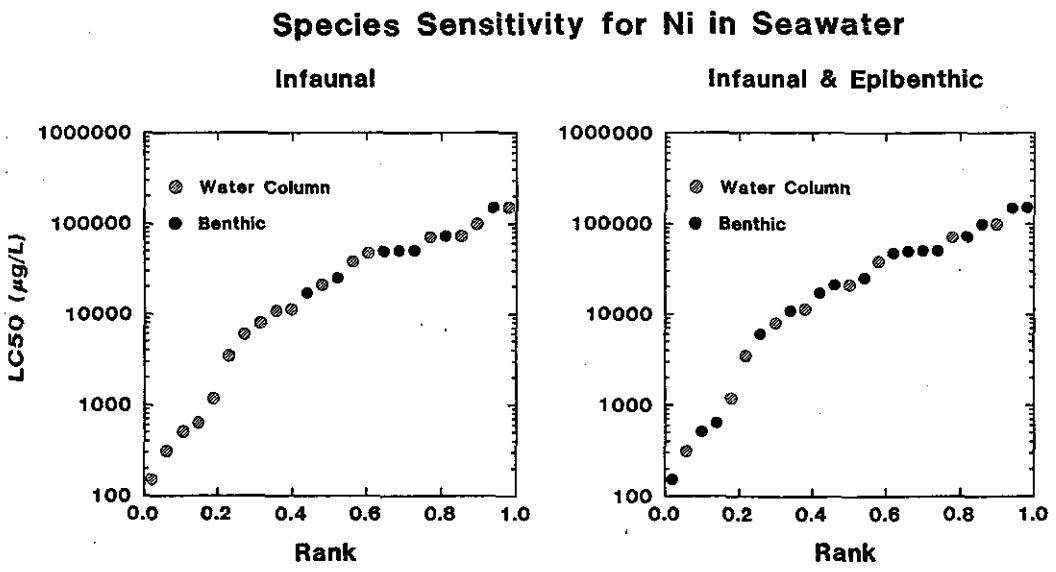

Fig. 28. LC50s versus rank for nickel in seawater. Infaunal organisms (left) and infaunal and epibenthic (right) are identified by the solid symbols. The plot illustrates the distribution of benthic organisms in the overall species sensitivity distribution.

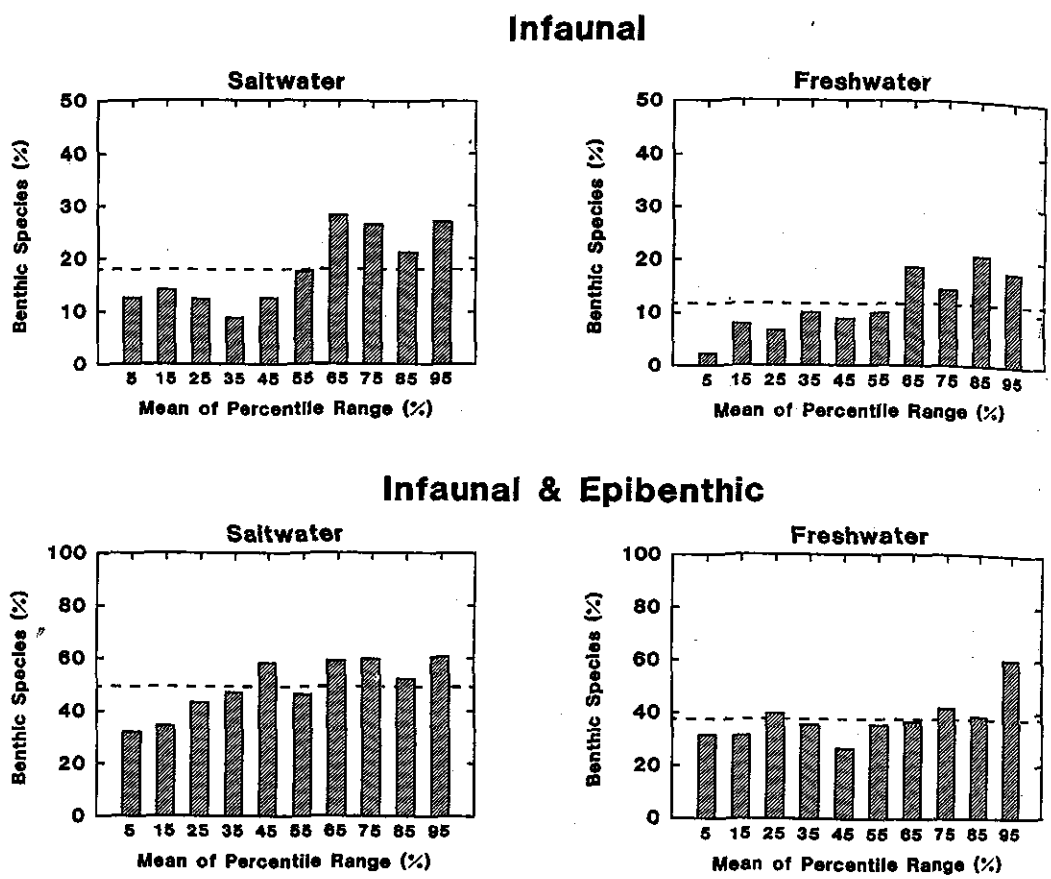

Fig. 29. Histograms of the proportion of saltwater and freshwater benthic organisms in 10 percentile groups of all normalized LC50s. If benthic organisms were as equally sensitive as water column organisms, the histograms should be of uniform height as indicated by the dashed line, the overall percentage 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.

benthic saltwater species [64–70] 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 20 replicates. The test chemical is added to inflowing ambient seawater containing planktonic larvae and other life stages of marine organisms that can settle onto 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.

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Table

Substance
Pentachlorophenol
Arochlor 1254
Chlorpyrifos
Fenvalerate
1,2,4-Trichlorobenzene[a]
Toxaphene

[a]Six-day exposure to estal

ent 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 WQC document for 1,2,4-trichlorobenzene suggests that the FCV should be 50.0 μg/L. This value is slightly above the LOEC from a colonization experiment (40.0 μg/L) suggesting that the criterion might be somewhat underprotective for benthic species. Finally, a colonization experiment with toxaphene

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

Substance	Colonization vs. FCV	Concn. (μg/L)	Sensitive taxa	Reference
Pentachlorophenol	Colonization LOEC	16.0	Molluscs, abundance	[65,66]
	FCV	7.9	Molluscs, crustacea, fish	
	Colonization NOEC	7.0	–	
Arochlor 1254	Colonization LOEC	0.6	Crustacea	[67]
	Estimated FCV	~0.1	Crustacea, fish	[64]
	Colonization NOEC	<0.1	–	
Chlorpyrifos	Colonization LOEC	0.1	Crustacea, molluscs, species richness	[68]
	FCV	0.005	Crustacea	
	Colonization NOEC	–	–	
Fenvalerate	Colonization LOEC	0.01	Crustacea, chordates	[69]
	Estimated FCV	~0.002	Crustacea	
	Colonization NOEC	–	–	
1,2,4-Trichlorobenzene[a]	Estimated FCV	50	Crustacea, fish	[70]
	Colonization LOEC	40	Molluscs, abundance	
	Colonization NOEC	–	–	
Toxaphene	Colonization LOEC	11.0	Crustacea, species richness	[64]
	Colonization NOEC	0.8	–	
	FCV	0.2	Crustacea, fish	

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

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 LC50s and the results of colonization experiments, are generally similar, although, as might be expected, differences occur. Both the WQC documents and the colonization experiments suggest that crustacea are most sensitive to Aroclor 1254, chlorpyrifos, fenvalerate, and toxaphene. Colonization experiments indicated that molluscs are particularly sensitive to three chemicals, an observation noted only for pentachlorophenol in WQC documents. Fish, which are not tested in colonization experiments, are particularly sensitive to four of the six chemicals.

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

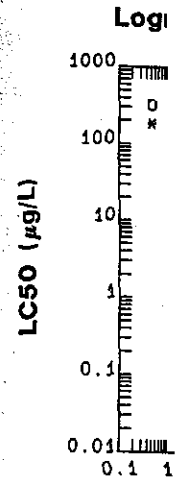
The equation from which SQC are calculated is

$$SQC_{oc} = K_{oc}FCV \tag{34}$$

(see Eqns. 2–7 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. [71]) 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 [72] 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 by these newer techniques.

The FCV is used as the appropriate end point for the protection of benthic organisms. Similarly, its applicability to benthic species for each chemical should be verified. The analysis presented in the previous section indicated that this is not an unreasonable assumption across all the criteria chemicals. To test this assumption for a particular chemical, the Kolmogorov–Smirnov test [74], which tests whether two samples came from the same population, can be applied to the distribution of LC50s for the water column and benthic species.

The Kolmogorov–Smirnov test is based on the maximum difference between the two empirical cumulative probability distributions. The test will reject the hypothesis that the samples come from the same probability distribution if the difference is so large, given the number of samples in each of the two distributions, that chance alone cannot account for the difference. An example for endrin is shown in Figure 30, which presents the probability distributions of the freshwater species' LC50s for the water column and benthic species. The left panel is a log probability plot of the two distributions. It presents the LC50s on a log scale versus the rank order on a normal probability scale. The natural way to judge the equality of these distribu-



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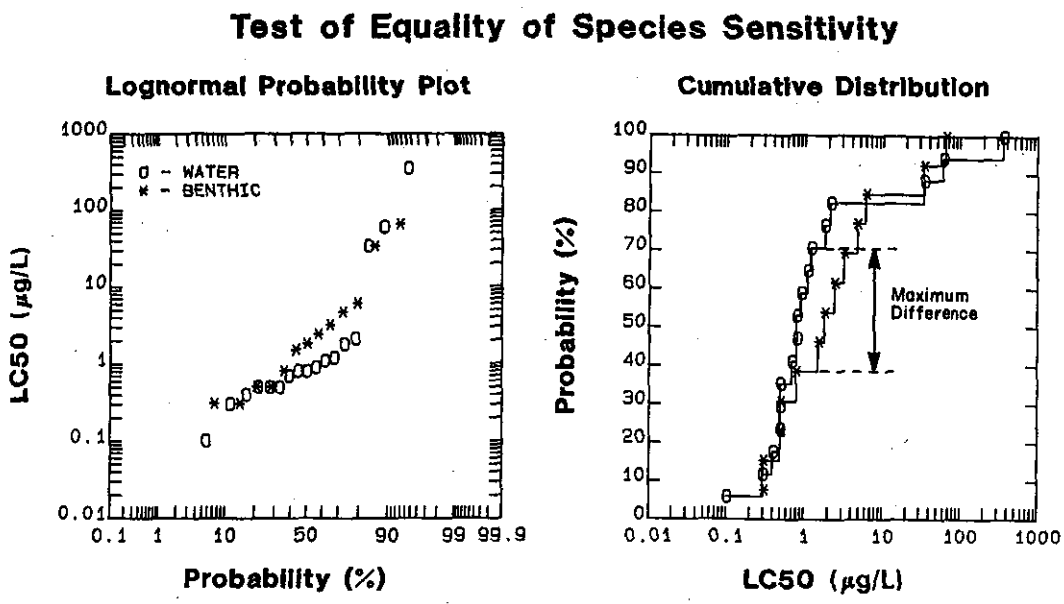

Fig. 30. Comparison of the endrin LC50 probability distributions for water column and benthic freshwater species. Lognormal probability plot (left panel) and the empirical cumulative distribution functions (right panel) with the maximum difference used in the Kolmogorov–Smirnov test indicated.

tions is to compare the LC50s at a particular probability, for example at 50% probability, which is a comparison of the medians.

The Kolmogorov–Smirnov test compares another difference. This is illustrated in the right panel, which presents the same data but in a slightly different way. The rank order, as a percentage, is plotted versus the LC50s. The points are connected with straight lines to form the empirical cumulative distribution functions for the two data sets. The Kolmogorov–Smirnov test is based on the maximum difference in probability between these two distributions, as indicated in the figure. Note that this difference is the horizontal distance on the log probability plot in Figure 30 if the probability scale were linear. The test depends on the number of LC50s in each distribution (17, 13) and the maximum difference in probability (0.321). The probability that a value of this magnitude or less can occur, given that these two samples came from the same distribution (0.677), can be calculated [74]. Because this probability is less than 0.95, the hypothesis that the samples came from the same distribution is accepted at a 95% confidence level. A similar test for the saltwater species yields a probability of 0.318, a value that is much less than 0.95, which would cause the hypothesis of equality to be rejected.

The conclusion from this analysis is that the benthic and water column species that have been tested with endrin come from the same probability distribution of LC50s for both freshwater and saltwater organisms. Therefore they have the same distribution of acute sensitivity. This suggests that the freshwater and saltwater FCVs for endrin are appropriate effects concentrations for benthic species and should provide a similar level of protection for benthic organisms and water column organisms. This analysis should be performed for any chemical for which SQC are developed.

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 31 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

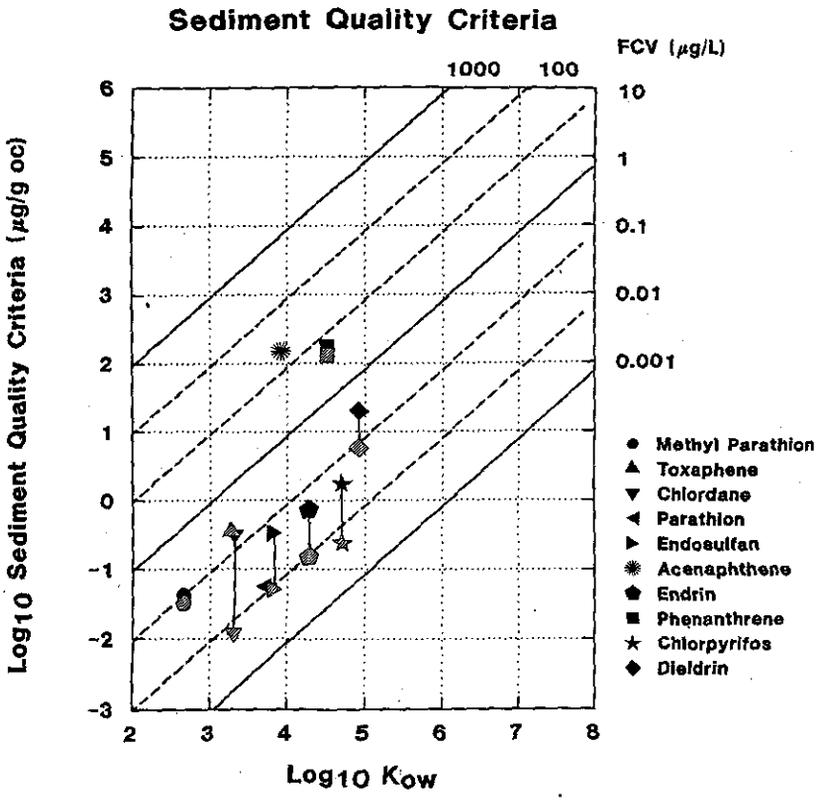

Fig. 31. $Log_{10}SQC$ versus $\log_{10}K_{ow}$. The diagonal lines indicated the FCV values. The criteria are computed from Equation 34. K_{oc} is obtained from K_{ow} with Equation 11. The symbols indicate SQC_{oc} for the freshwater (filled) and saltwater (hatched) criteria for the listed chemicals. The vertical line connects symbols for the same chemical. The FCVs are from the WQC or draft criteria documents (Table 4). The octanol/water partition coefficients are the log mean of the values reported in the Log P data base [71].

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 31 have been chosen to illustrate the SQC_{oc} concentrations that result from applying the EqP method. The water quality concentrations are the FCVs (not the final residue values) from draft or published EPA WQC documents (see Table 4). The K_{ow}s are the log averages of the values reported in the Log P data base [71]. These values are used for illustrative purposes only because final SQC, when published, should reflect the best current information for both FCV and K_{ow}, as discussed above.

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_{oc}s 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. Hence the most stringent SQC_{oc} in this example is for chlordane, a chemical with the lowest K_{ow} 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 one-half 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_{oc}s are approximately the same, 200 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 [75], will have SQC that are more nearly constant.

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Sediment quality criteria (SQC) uncertainty

The SQC methodology relies on an empirical partitioning model to relate the pore water exposure concentration (actually the chemical potential) to the equivalent sediment organic carbon exposure concentration. As a consequence there is an uncertainty associated with the use of the model. The assumption of equilibrium and the similarity of all sources of organic carbon are reflected in the model uncertainty. The organic carbon concentrations used to estimate the regression coefficients span the range from 0.2 to 40% from soils, sediments, and sewage sludges. The experiments from which those data were derived were typically equilibrated for a few hours to a few days at most [31], whereas in nature a sediment–interstitial water system would have a much longer equilibration time. In addition, there is uncertainty with respect to the K_{ow} associated with the specific chemical because it is an experimentally determined quantity.

It is anticipated that when final SQC are generated, confidence limits that are intended to quantify the uncertainty will also be determined. The method for estimating the range of uncertainty is currently under development and will be reported subsequently. It is likely that it will be based on an analysis of the data in the form presented in Figures 2 and 3. The initial impressions are that an uncertainty of a factor of two to three seems likely.

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, 5–9, 21–23). The variation in organism body burden across sediments can also be significantly reduced if organic carbon and lipid normalization are used (Figs. 24–26). For naturally contaminated sediments, particle size effects are removed if organic carbon–normalized concentrations are compared (Fig. 18). The reason is that organic carbon is the proper normalization for partitioning between free dissolved chemical and sediment-bound chemical (Fig. 12).

Using pore water normalization for highly hydrophobic chemicals is complicated by chemical complexing to DOC (Fig. 14). Partitioning between pore water and sediment organic carbon from field-collected sediments can be rationalized if DOC complexing is taken into account (Figs. 19 and 20). However, the complexed chemical appears not to be bioavailable (Fig. 16).

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. 27) and all tested species (Fig. 29). 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. 30).

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. 5–9). A variation of approximately a factor of two to three remains (Figs. 2 and 3), which includes measurement 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 [76]. 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 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 [77].

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 is, in general, an untenable assumption. 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 [78]. Hence, the application of the final residue values from the WQC for the computation of SQC, as was done for certain interim criteria [79], 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. [80]) 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.

Acknowledgement—This study was sponsored by the U.S. Environmental Protection Agency, Office of Water, Office of Water Regulation and Standards. The data, obtained from numerous sources, included both published and yet to be published data provided by the original researchers. We particularly appreciate the generosity and helpfulness of those researchers. Special thanks to Laurie Davanzo and John Connolly for their assistance, to our colleagues and critics for their many conversations and helpful observations, and to the reviewers for their thoughtful comments.

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