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BIOACCUMULATION:
ASSESSMENT AND REGULATION

Camp Dresser & McKee

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SECTION 1

INTRODUCTION

Aquatic organisms are capable of accumulating concentrations of toxic chemicals in their tissues that may be detrimental to themselves or to animals which feed upon them, including man. Sources of contaminants for biological uptake include water, sediment, and biota. A variety of methods have been developed for estimating the extent of biological uptake. These include empirical steady-state exposure, kinetic modeling, and methods based on thermodynamic equilibrium partitioning.

Predicting biological uptake from contaminated sediment is complicated because only a fraction of the total (bulk) concentration of contaminants in sediment may be bioavailable. The bioavailability of a sediment-associated contaminant can be defined as the degree to which the contaminant is biologically active or accumulated by aquatic biota (Adams, 1984). Sediment contamination has become a matter of concern in part because negative biological effects have been observed in aquatic ecosystems where water column contaminant concentrations do not exceed EPA water quality criteria. It has been suggested that the occurrence of adverse effects in the absence of water quality criteria violations may be due to sediment contamination, but that is difficult to prove.

An example of such a situation is the New York Bight Apex. Average water column concentrations of toxic chemicals in Apex waters are substantially lower than the average value saltwater quality criteria, while the benthic community is severely degraded in some areas of the Bight (Wang et al., 1984). Pavlou and Weston (1983) have suggested a similar scenario for Puget Sound. Dredged material and sewage sludge are discharged into the New York Bight Apex, representing two sources of contaminated sediment whose biological consequences need to be evaluated. The regulatory process requires that bioavailability be evaluated for dredged material proposed for discharge into ocean waters.

The objectives of this report are:

(1) to review the currently available methods for assessing biological uptake, with specific emphasis on uptake from sediment, and

(2) to review the regulatory application of bioaccumulation data, with specific emphasis on dredged material disposal in the marine environment.

SECTION 2

BIOACCUMULATION THEORY AND MODELING

BACKGROUND

Aquatic organisms can accumulate chemicals from their environment via at least three different pathways (Swartz and Lee, 1980):

- o direct adsorption to the body wall or exoskeleton;
- o direct absorption through the integument, gills, or other respiratory surfaces; or
- o ingestion of contaminated sediment, food, or water followed by absorption through the gut.

Three terms are frequently used in describing biological uptake of chemicals: bioconcentration, bioaccumulation and biomagnification. These terms are used inconsistently in the literature. Their meaning in this paper is consistent with the terminology of Brungs and Mount (1978):

- o Bioconcentration is the process by which toxic substances present in solution enter aquatic organisms directly through the gills or epithelial tissue.
- o Bioaccumulation includes bioconcentration and the uptake of toxic substances from dietary sources such as contaminated particles or prey organisms.
- o Biomagnification is the process by which the tissue concentration of a bioaccumulated toxic substance increases as the material passes up through two or more trophic levels.

In general, aqueous-phase contaminants are bioavailable and are readily bioconcentrated. For most chemicals, direct uptake from water is the primary route of exposure, while dietary uptake is relatively insignificant (Macek et al., 1979; Bruggeman et al., 1981). However, uptake from dietary sources may be an important route of exposure for very lipophilic chemicals. Macek et al. (1979) reported that dietary uptake by fish was

insignificant compared to bioconcentration for seven of eight chemicals studied of varying lipophilicity, but that dietary uptake of DDT contributed significantly to the total body burden (Jarvinen et al., 1977). DDT was the most lipophilic chemical in the data reviewed by Macek et al. and, consequently, exhibited the slowest depuration rates of residues from fish. Likewise, the models of Weininger (1978) and Thomann and Connolly (1984) have predicted that food chain transfer of PCBs in Lake Michigan accounts for nearly 100% of the total PCB residues in adult lake trout. Bruggeman et al. (1981) stated that biomagnification factors (ratio between concentration in fish and in food) greater than one can be expected only for very lipophilic chemicals having octanol/water partition coefficients greater than 5, and that under natural conditions a biomagnification factor of one or greater may indicate a significant contribution of dietary uptake to the total body burden.

Chapman (1984) presented a simple model of the relative importance of food and water as the route of contaminant uptake by fish. Respiratory exposure was computed as the product of ventilation rate and water concentration, and dietary exposure was computed as the product of feeding rate and contaminant concentration in food. Assuming that the relative efficiency of uptake via the two routes of exposure is equivalent, the relative importance of each route was estimated as a function of relative contaminant concentrations in food and water as shown in Table 1. Chapman's (1984) calculations (Table 1) indicate that dietary uptake is insignificant until contaminant concentrations in food exceed concentrations in water by more than 1,000-fold, and that dietary uptake is the dominant route of exposure when food concentrations are greater than 10,000 times aqueous concentrations.

It is clear that contaminated sediments can be an important source of contaminants for biological uptake. Uptake from sediment can occur via two potential avenues: desorption to interstitial and interfacial water followed by bioconcentration, or bioaccumulation through ingestion of contaminated sediment particles. The relative contribution of those two mechanisms has not been elucidated, but it will depend upon the feeding and respiratory strategies of the organism. Deposit-feeding infauna and epibenthos are of primary interest with respect to uptake from sediment.

TABLE 1

RELATIVE IMPORTANCE OF FOOD AND WATER AS THE ROUTE OF UPTAKE FOR FISH AS A FUNCTION OF THE RATIO OF CONTAMINATION BETWEEN FOOD AND WATER

Contaminant in Food (mg/kg):Water (mg/l)	Percent Uptake[a] from Food
1:1	< 1
10:1	< 1
100:1	1
1,000:1	9
10,000:1	50
100,000:1	91
1,000,000:1	99

[a]Calculations based on respiratory volume of 200 l/kg/day, food consumption of 0.02 kg/kg/day, and uptake/depuration rates independent of route of exposure.

Source: Chapman, 1984.

Hydrophobic organic compounds and some toxic metals have a strong affinity for particulate matter; consequently, those contaminants are commonly associated with the bottom sediments in aquatic systems. Toxic metals associated with sediments generally are not readily bioavailable. Thus, the water column appears to be the predominant source for biological uptake of many toxic metals (Fowler et al., 1978). In contrast, contaminated sediments can be an important source of hydrophobic organic compounds for biological uptake (Halter and Johnson, 1977; Fowler et al., 1978; Courtney and Langston, 1978; Rubinstein et al., 1983; Rubinstein et al., 1984). Although hydrophobic organic substances are readily taken up from water, they have low solubilities and are highly associated with particulate material. Consequently, relatively little of those substances is available for aqueous uptake compared to the amount associated with sediments. For example, Fowler et al. (1978) measured concentration factors for PCBs in a polychaete worm (Nereis diversicolor) of 800-fold from water and 3.5-fold from sediment, but because sediment concentrations of PCBs are typically so much greater than aqueous concentrations, the authors concluded that 85-99 percent of the worm's body burden could be attributed to uptake from sediment.

A number of recent studies have shown dietary uptake to be a major source of biological residues of hydrophobic organic compounds (Thomann, 1981; Jensen et al., 1982; Pizza and O'Connor, 1983; Thomann and Connolly, 1984; Rubinstein et al., 1984). Those substances are predominantly associated with particulate organic material in sediments, which can serve as a food source for infaunal and epibenthic organisms. Such species can accumulate synthetic organic compounds from contaminated sediments (Roesijadi et al., 1978; Fowler et al., 1978; Courtney and Langston, 1978; McLeese et al., 1980; Wyman and O'Connors, 1980; Lynch and Johnson, 1982; Rubinstein et al., 1983; Adams et al., 1983; Rubinstein et al., 1984), and many of those organisms are important prey species for organisms at higher trophic levels. Rubinstein et al. (1984) demonstrated that contaminated sediment can serve as a source of PCBs for uptake and trophic transfer in marine systems. Fish (Leiostomus xanthurus) exposed to PCB-contaminated sediments and fed a daily diet of polychaetes (Nereis virens) from the same sediment accumulated more than twice the PCB whole-body residues than fish exposed

to PCB-contaminated sediment but fed uncontaminated polychaetes (Rubinstein et al., 1984).

EMPIRICAL STEADY-STATE EXPOSURE METHOD

Chemicals can be taken up from the environment by aquatic organisms. In turn, animals may be capable of eliminating contaminants from their bodies. When the environmental concentration of a contaminant is constant, a theoretical equilibrium level exists where the amount of chemical entering an animal is equal to the amount leaving the animal. The condition under which a contaminant concentration is an animal is constant is defined as steady state, and is often recognized as a plateau in the observed tissue concentration (Figure 1). In laboratory tests aquatic organisms commonly require days to months of exposure to acquire steady state tissue concentrations of toxic organic compounds or toxic metals.

Equilibrium residue concentrations can be determined directly by exposing a large number of animals to a constant concentration of a chemical, periodically sampling the chemical concentration in the animals, until steady-state conditions are reached. This method can be used to measure uptake from water, sediment, food, or combinations of these sources.

The aqueous exposure system permits the most accurate measurement of bioconcentration factor (BCF), which is defined as the ratio of the equilibrium concentration of a chemical in aquatic organisms to the concentration in water:

$$BCF = \frac{C_b^{SS}}{C_w} \qquad (1)$$

where

C_b^{SS} = steady-state concentration of the chemical in biota

C_w = concentration of the chemical in water (which is kept constant during the test)

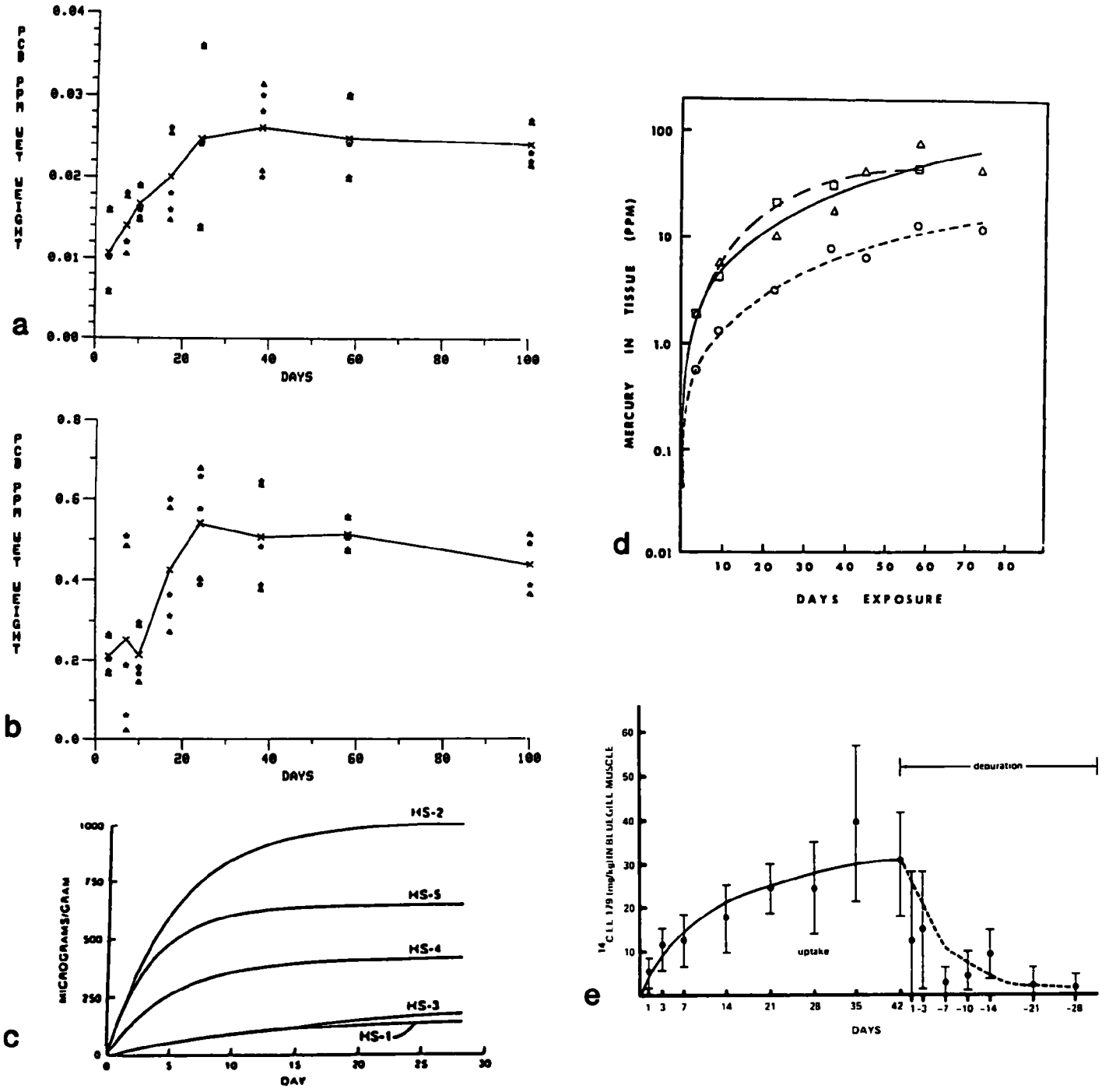


Figure 1. Typical uptake curves. Uptake of PCBs from contaminated sediments by (a) grass shrimp, (b) polychaete worm, and (c) Asiatic clam. Uptake from contaminated water of (d) mercury by eastern oyster and (e) isopropalin by bluegill. Sources: Rubinstein et al., 1983b; McFarland et al., 1984; Kopfler, 1974; Hamelink, 1977.

Uptake from the water column has been measured for many chemicals and many species. For example, in the Ambient Water Quality Criteria Documents (EPA, 1980, 1983), BCFs are reported for a variety of freshwater and saltwater organisms for cadmium, mercury, chlordane, DDT, dieldrin, heptachlor, PCBs, toxaphene, and other toxic chemicals.

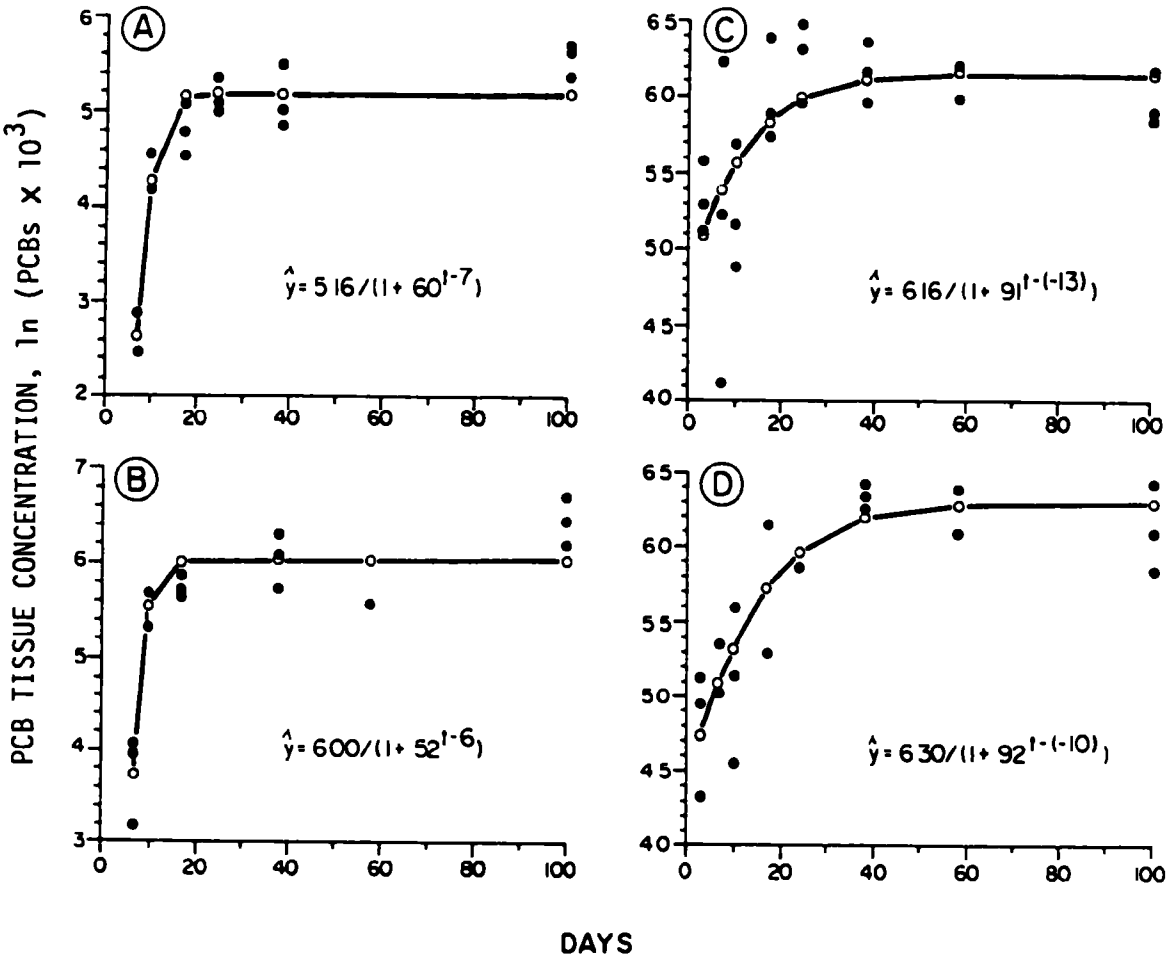
Since BCFs consider only uptake from water and ingnore ingestion of contaminated food and/or sediment, the term bioaccumulation factor (BAF) has been used to describe uptake from sediment or uptake from all sources.

The empirical steady-state exposure approach has the advantages of conceptual simplicity and a high degree of biological certainty (Hamelink, 1977), but the disadvantages of long test durations and the associated difficulty of maintaining constant test conditions. For example, Rubinstein et al. (1983) found that 30 to 40 days of exposure were required for Nereis worms to accumulate steady-state PCB concentrations. Another disadvantage is the inherent variability of tissue concentrations about the mean which makes it inappropriate to represent the equilibrium concentration as the observed body burden at the end of the test period. To resolve that problem, Rubinstein et al. (1983) used a nonlinear regression program to fit their data to the 3-parameter uptake model of Bahner and Oglesby (1981) to produce smooth uptake curves and yield an estimate of the steady-state concentration (Figure 2).

KINETIC METHODS

UPTAKE FROM WATER

The process of bioconcentration frequently has been described as the balance between two competing kinetic processes: uptake and depuration (e.g., Branson et al., 1975; Hamelink, 1977; Ernst, 1977; Veith et al., 1979; McLeese et al., 1980; Mackay, 1982). The simpliest kinetic model of biological uptake consists of a medium (water) compartment (C_w) and a biotic compartment (C_b):



Bahner and Oglesby Model

$$Y = \frac{P1}{1 + P2^{(t-P3)}}$$

Where $Y = \ln C_B$ at time t

$P1 = \ln C_B$, maximum

P2 = rising slope

P3 = t when Y = P1/2

Figure 2. Bioaccumulation of PCBs to steady-state by N. Virens exposed to four different sediments. The uptake curves were constructed using the non-linear regression model of Bahner and Oglesby (1981). Source: Rubinstein et al., 1983.

$$C_w \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_b \qquad (2)$$

where k_1 and k_2 are the rate constants for movement of the chemical into (uptake) and out of (depuration) the animal, respectively. Assuming first order kinetics for uptake and depuration, the following relationship has been derived:

$$dC_b/dt = k_1C_w - k_2C_b \qquad (3)$$

Integration of this differential equation, when C_w is constant and for initial conditions of t and C_b equal to zero, gives:

$$C_b = (k_1/k_2)\ C_w\ (1-e^{-k_2t}) \qquad (4)$$

As time approaches infinity, equilibrium is reached, i.e., $dC_b/dt = 0$, and the above equation becomes:

$$C_b^{SS} = (k_1/k_2)\ C_w^{SS} \qquad (5)$$

or

$$C_b^{SS}/C_w^{SS} = k_1/k_2 = BCF \qquad (6)$$

Thus, BCF can be estimated as the ratio between the uptake and depuration rate constants, which can be determined experimentally. Test conditions employed to determine the uptake rate constant are essentially the same as those used in the empirical steady-state exposure approach except that animals are sampled more frequently during a brief exposure period. After the uptake period, animals are transferred to aquaria containing clean water (and sediment) and periodically sampled until the depuration rate (k_2) is established. Then, k_1 can be calculated. Branson et al. (1975)

used this kinetic model to calculate a BCF for 2,2',4,4'-tetrachlorobiphenyl in rainbow trout muscle, and found that a 5-day uptake period plus a clearance time of one half-life (i.e., the time required to eliminate 50 percent of the accumulated contaminant residue) was sufficient to characterize uptake and depuration. The validity of the method was demonstrated when the BCF thus obtained compared favorably to that determined experimentally during 42 days of exposure.

McFarland et al. (1984) described an alternative method for estimating steady-state body burdens of hydrophobic organic compounds from residues measured after a short exposure period in which steady-state was not reached. Combining Equations 4 and 5 and rearranging the resulting expression yields:

$$C_b^{ss} = C_b/(1-e^{-k_2 t}) \qquad (7)$$

Equation 7 implies that under conditions of constant exposure a steady-state tissue concentration (C_b^{ss}) can be estimated from a tissue concentration (C_b) at any time (t), provided the elimination rate constant (k_2) is known or can be estimated for that chemical. The actual exposure concentration need not be known, but must be assumed to be constant (McFarland et al., 1984).

Spacie and Hamelink (1982) demonstrated that the kinetic elimination rate constant, k_2, for a particular chemical can be predicted from its octanol-water partition coefficient (K_{ow}). Using the data of Neely et al. (1974) and Konemann and van Leeuwen (1980), Spacie and Hamelink derived the regression:

$$\log k_2 = 1.47 - 0.414 \log K_{ow} \qquad (8)$$

$$r = 0.95$$

McFarland et al. (1984) used k_2 values estimated in this way along with residues of di- and tri-chlorobiphenyl in asiatic clams and fathead minnows

measured after seven days of exposure to estimate steady-state body burdens using Equation 7. Steady-state residues predicted from single-time-point observations did not differ significantly from tissue concentrations measured at a time corresponding to 99 percent of steady-state (McFarland et al., 1984).

A number of more complex kinetic models have been proposed for evaluating residue accumulation. Figure 3A schematically represents the simple two-compartment model described above. Figure 3B and 3C are three-compartment models (one water compartment and two biotic compartments) presented by Blau et al. (1975); the only difference being that Figure 3C includes a rate constant for elimination from compartment 3 back to the water. Blau and co-workers suggested that a three-compartment model may be appropriate in cases where the chemical is preferentially accumulated in a particular tissue or where the metabolization rate constant (k_{23}) is substantially different than the rate of uptake from the medium (k_{12}). Notice that in the model shown as Figure 3B when k_{32} is much greater than k_{23} the model reduces to the two-compartment model shown as Figure 3A. Krzeminski et al. (1977) presented the model shown diagramatically in Figure 3D and mathematically below, which includes a rapid exchange compartment (viscera) and a slow exchange compartment (tissue) for both the parent compound and metabolites.

$$\frac{dV}{dt} = k_1W + k_4T - (k_2 + k_3 + k_5)\,V \qquad (9)$$

$$\frac{dV_M}{dt} = k_5V + k_7T_M - (k_6 + k_8)\,V_M$$

$$\frac{dT}{dt} = k_3V - k_4T$$

$$\frac{dT_M}{dt} = k_6V_M - k_7T_M$$

where

W = the nominal exposure level during the exposure phase, and zero during the withdrawal phase

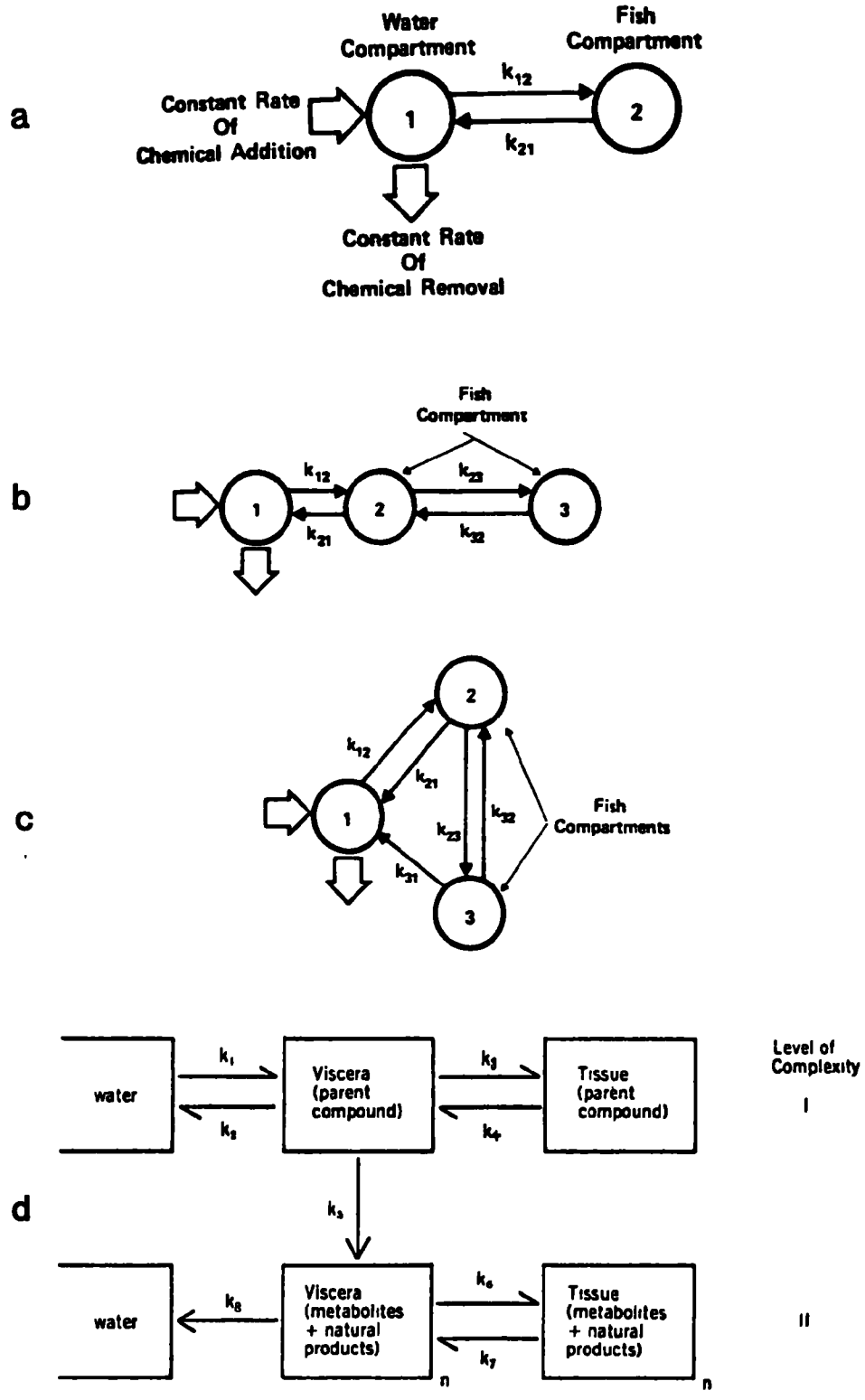


Figure 3. Kinetic compartment models of biological uptake. Sources: Blau et al., 1975; Krzeminski et al., 1977.

V = the concentration of the parent compound in the viscera at time t

V_M = the concentration of the metabolites in the viscera at time t

T = the concentration of the parent compound in the tissue at time t

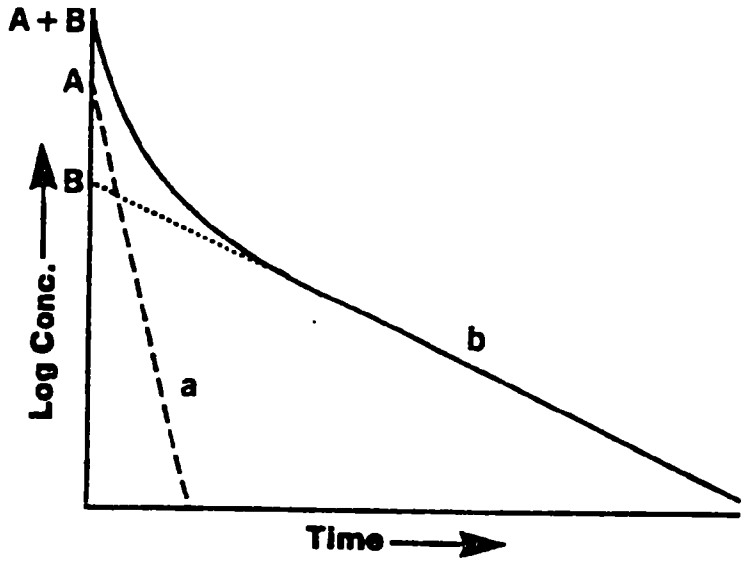
T_M = the concentration of the metabolites in the tissue at time t

k = the rate constants for the reactions shown in Figure 3D above

For refractory substances that resist metabolization such as PCBs, DDT, or toxic metals, this model would reduce to level one complexity, that is, the three-compartment model shown as Figure 3B.

Although first order kinetics are usually assumed in kinetic studies of bioaccumulation, they are rarely verified. While simple first order kinetics are apparently appropriate for describing initial uptake rates regardless of the mechanism or number of compartments used to model subsequent distribution in the animal, Spacie and Hamelink (1982) suggest that models with biphasic, second order, or Michaelis-Menten kinetics may better describe depuration, depending on exposure level and mode of elimination. For example, often an initial rapid loss phase is followed by a slower elimination rate, forming a biphasic pattern that can be resolved into two linear components (Figure 4). The initial rapid phase represents elimination from a fast or central compartment, while the slower phase represents redistribution from a peripheral compartment within the animal to the central one before elimination occurs. Figure 3B represents this type of model, and the rate constants can be determined using graphical constants as shown in Figure 4.

The major advantage of using kinetic models for assessing bioaccumulation is that shorter test durations are required for some chemicals compared to the empirical steady-state exposure method. Kinetic models can also provide insight into the routes and rates functioning in the bioaccumulation process. Use of kinetic models has the disadvantage of requiring



$$k_{32} = \frac{Ab + Ba}{A + B}$$

$$k_{23} = a + b - k_{32} - k_{21}$$

$$k_{21} = \frac{ab}{k_{32}}$$

Figure 4. Graphical representation of results obtained from a depuration experiment for which the first-order, three-compartment model (e.g., Figure 3b) would apply. Source: Spacie and Hamelink, 1982.

nonlinear regression parameter estimation techniques to estimate rate constants, and multicompartment models may require separate analysis of multiple anatomical compartments and/or analysis of parent compounds and metabolites.

UPTAKE FROM SEDIMENT

McLeese et al. (1980) used the first order, two compartment kinetic model described by Equation 4 to estimate steady-state PCB concentrations accumulated by Neveris virens exposed to contaminated sediment. The authors modified Equation 4 by substituting the ambient sediment concentration, C_s, for the aqueous concentration term, C_w:

$$C_b = (k_1/k_2)\ C_s\ (1-e^{-k_2 t}) \qquad (4)$$

where: C_s = concentration of PCB in sediment (ug/g dry weight)

The uptake rate constant (k_1) was determined from whole-body residue data measured over 32 days of exposure to contaminated sediment during which steady-state was not approached, and the depuration rate constant was determined from residue measurements after the worms were transferred to aquaria containing clean sand. Bioaccumulation factors, defined as the ratio of wet weight tissue concentration to the dry weight sediment concentration at steady state, were calculated mathematically as k_1/k_2. A schematic representation of the bioaccumulation model used by McLeese et al. (1980) is shown as Figure 5a.

McFarland et al. (1984) also applied the first order kinetic model to biological uptake of PCBs from contaminated sediment, but their exposure system was designed to ensure that the aqueous phase was an intermediate step between sediment and biota (Figure 5b). Indeed, it has been suggested that water is the probable medium of exchange for all pathways of bioaccumulation (Rubinstein et al. 1984). Fathead minnows (Pimephales promelas) and Asiatic clams (Corbicula fluminea) were, except for one series of exposures in which clams were allowed to burrow into sediment, restrained from contacting the contaminated sediments in the exposure tanks. Equation

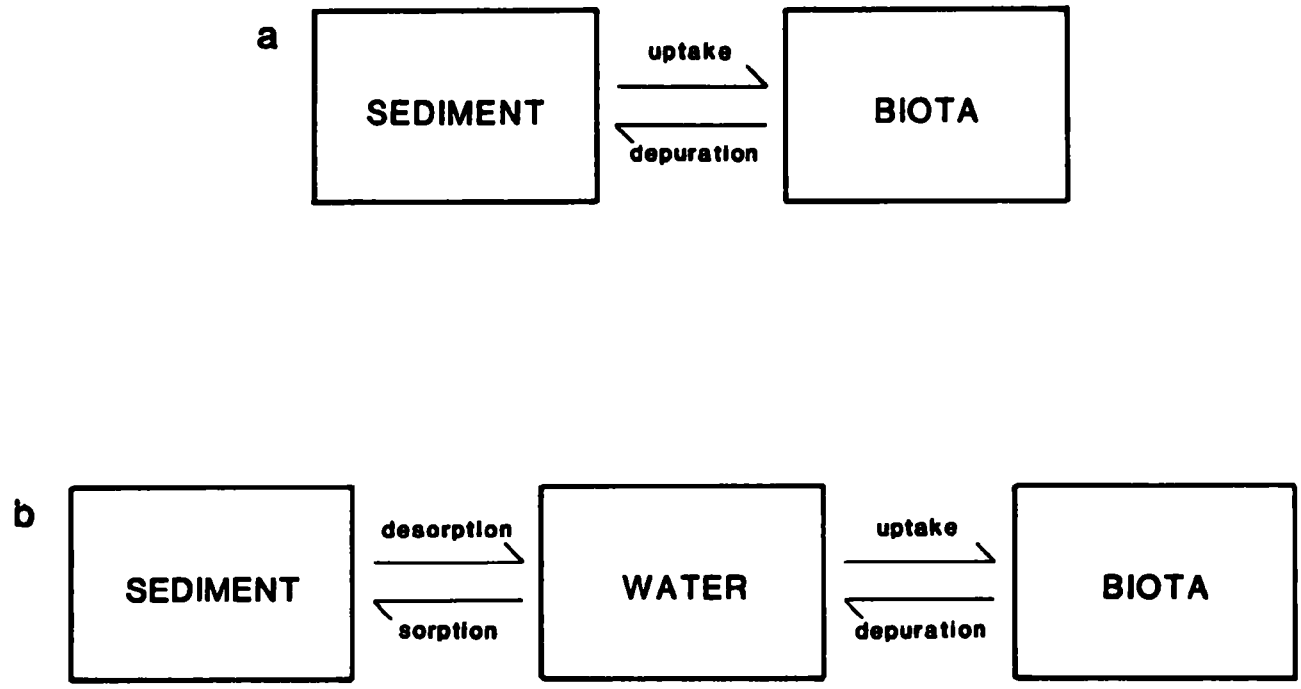


Figure 5. Schematic of kinetic uptake models used by: (a) McLeese et al. (1980) and (b) McFarland et al. (1984).

4 (without modification) was used to predict steady-state body burdens and BCFs.

THERMODYNAMIC EQUILIBRIUM METHODS

The thermodynamic equilibrium approach allows the prediction of equilibrium tissue concentrations of contaminants in biota based on physico-chemical equilibrium properties of the contaminant. The method is invalid for chemicals that are significantly transformed in the biotic phase (Mackay, 1982). However, many toxic compounds which are of greater environmental concern are fairly persistent, and this method shows great promise in predicting equilibrium contaminant concentrations in biota.

The theoretical basis behind the thermodynamic equilibrium approach was discussed by Mackay (1979). Mackay introduced the concept of fugacity by considering the environment as several compartments--including atmosphere, water, sediment, soil, and biota--some of which are contiguous (e.g., water and sediment) while others are not (e.g., atmosphere and aquatic sediment). If it is assumed that each compartment is completely mixed and at thermodynamic equilibrium, then a contaminant in the environment will be distributed such that the chemical potential (or fugacity) of the substance in each phase is equal (Mackay, 1979). The distribution of a substance between source and sink at equilibrium is independent of pathways of chemical exchange and can be described by a distribution or partition coefficient (K):

$$C^e_{sink}/C^e_{source} = K_{source,\ sink} \qquad (10)$$

where C^e is the concentration of a substance in a particular phase at equilibrium (equal chemical potential).

UPTAKE FROM WATER

Simple relationships have been established between equilibrium properties of organic chemicals and their ability to accumulate in aquatic biota. Several structure-activity correlations have been presented by which

bioconcentration factors of hydrophobic organic chemicals can be predicted from n-octanol/water partition coefficient (K_{ow}) or aqueous solubility (S).

BCF - K_{ow} Relationship

Bioconcentration can be viewed simply as the partitioning of a chemical between biota and water. n-Octanol is a good medium for simulating natural fatty tissues of plants and animals; therefore, the octanol/water partition coefficient,

$$K_{ow} = \frac{C^e_{\text{n-octanol}}}{C^e_{\text{water}}} \qquad (11)$$

is a good predictor of the partitioning of lipophilic organic chemicals between biota and water (BCF). Table 2 lists BCF-K_{ow} regression equations published in the literature. Those regressions were developed from fish (rainbow trout, fathead minnow, bluegill, guppy, mosquitofish) bioconcentration data.

Even though all researchers obtained a good linear relationship between log BCF and log K_{ow}, the values of the coefficients in the regression equations vary a great deal. Figure 6 is a comparison of the nine regressions listed in Table 2. The difference between the lowest and highest BCF predicted from a given K_{ow} by the lines in Figure 6 ranges between 30 to 10^3. The disparity among the regression equations may be due to at least three sources of variation: the chemical compounds used in developing the regression, the test species (and/or their lipid content) used in deriving BCFs, and the method used to measure or estimate K_{ow}'s. The variation among the regression lines calls for a closer examination of the biological- chemical meaning of the parameter values.

Applying the fugacity approach and assuming that the chemicals are not appreciably transformed, Mackay (1982) proposed that BCF is proportional to K_{ow}:

TABLE 2

PUBLISHED REGRESSION EQUATIONS BETWEEN BCF AND K_{ow}

	Equation	Number of Chemicals (n)	Correlation Coefficient (r)	Reference
1	$\log BCF = 0.124 + 0.542 \log K_{ow}$	8	0.97	Neely et al., 1974
2	$\log BCF = -0.7504 + 1.1587 \log K_{ow}$	9	0.98	Metcalf et al., 1975
3	$\log BCF = 0.7285 + 0.635 \log K_{ow}$	11	0.79	Kenaga & Goring, 1980
4	$\log BCF = -1.495 + 0.935 \log K_{ow}$	26	0.87	Kenaga & Goring, 1980
5	$\log BCF = -0.70 + 0.85 \log K_{ow}$	55	0.95	Veith et al., 1979
6	$\log BCF = -0.23 + 0.76 \log K_{ow}$	84	0.91	Veith et al., 1980
7	$\log BCF = -1.32 + \log K_{ow}$	44	0.97	Mackay 1982
8	$\log BCF = -0.063 + 0.980 \log K_{ow}$	6	0.99	Konemann & van Leeuwen, 1980
9	$\log BCF = -0.075 + 0.74 \log K_{ow}$	36	0.88	Pavlou & Weston, 1983

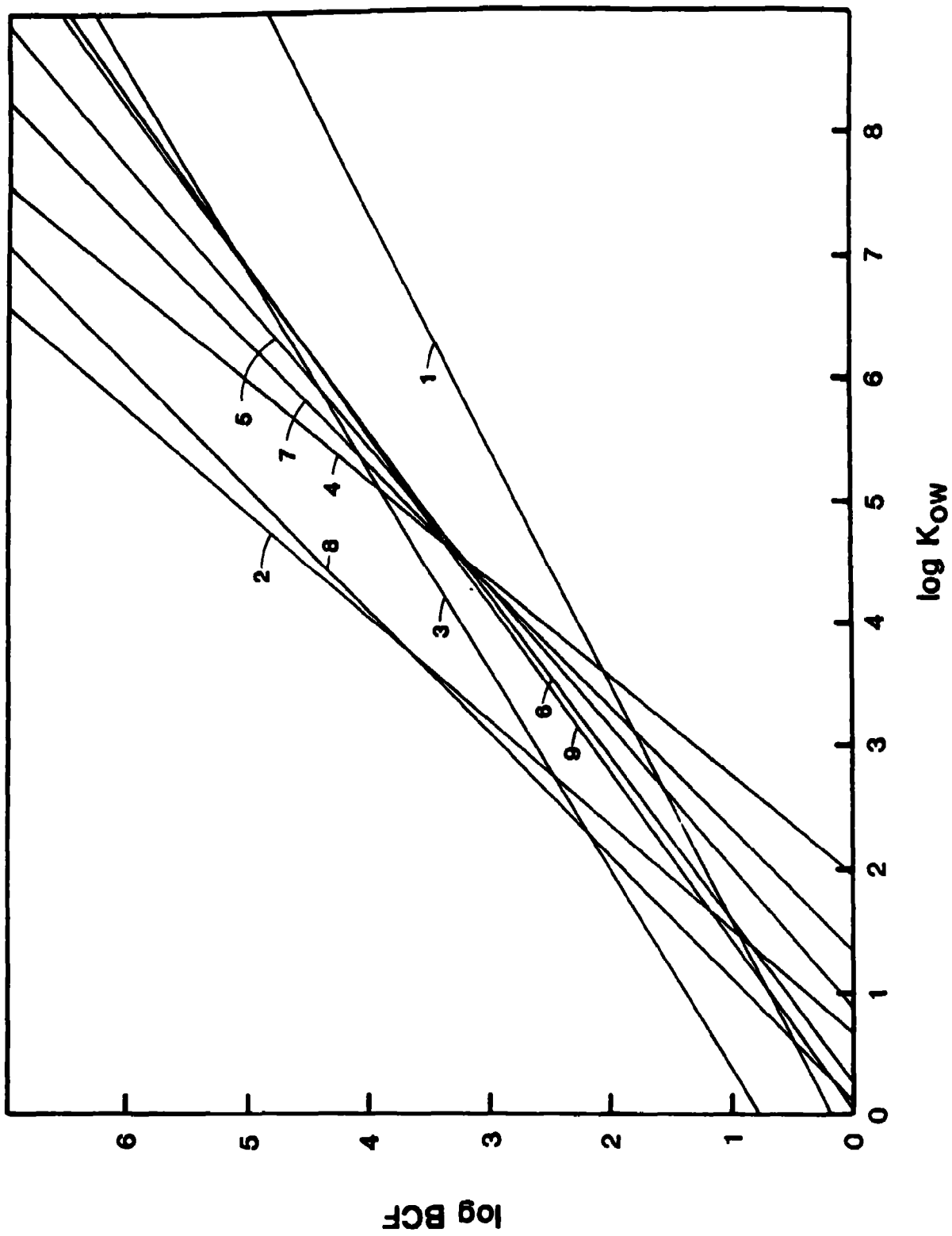


Figure 6. Plot of BCF-K_{OC} regression equations listed in Table 1.

$$BCF/K_{ow} = A \quad (12)$$

where A is a constant. In other words, in the general linear relationship between log BCF and log K_{ow}:

$$\log BCF = a + b \log K_{ow}$$

the coefficient b should be 1 and the value of a is a function of lipid content (y_L) and the relative activity coefficient (γ_i) and molar volume (ν_i) in lipid (L) or octanol (O):

$$a = \log A = \log \frac{y_L \gamma_O \nu_O}{\gamma_L \nu_L} \quad (13)$$

Mackay (1982) tested his hypothesis using the data of Veith et al. (1979). Some of those data were eliminated because of suspected error in measurement or discrepancies between K_{ow} values used by Veith et al. and those reported elsewhere in the literature. Data for chemicals with log K_{ow} greater than 6 and for compounds which are surfactants or may ionize were also discarded. The equation that resulted is:

$$\log BCF = -1.32 + \log K_{ow} \quad (14)$$

$$r = 0.97$$

This approach makes fuller use of the available theory and provides insight into the variables that affect the slope and intercept of BCF-K_{ow} relationships. For example, the lipid content of the test organisms is an important variable which is often neglected by researchers.

Mackay (1982) suggested that other BCF-K_{ow} correlations have often exhibited b values less than unity primarily due to the tendency to overestimate K_{ow} for high molecular weight compounds. Mackay further cautioned the use of the correlations when membrane permeability limits bioconcentration and for chemicals that bind to proteins causing an underestimation of the biotic concentration.

Published BCF-K_{OW} regressions have been developed from BCF data for a very limited group of organisms, primarily nektonic fish. For example, 90 percent of the data points included in Mackay's (1982) analysis (Equation 14) incorporated BCF values obtained using fathead minnows. The ability of such a regression to accurately predict bioconcentration in other species is uncertain. Veith et al. (1979) investigated the effect of species difference on bioconcentration and found that fathead minnow and green sunfish accumulated three times more PCB residues than rainbow trout.

It is possible that variability in lipid content is the primary cause of the different bioconcentration potential among species. McFarland et al. (1984) reported that bioconcentration is activity specific rather than species specific. McFarland and co-workers found that, when normalized by the lipid content of the test species, BCFs of PCBs were similar for Asiatic clams (2.03 percent lipid) and fathead minnnows (5.03 percent lipid). Based on their results, McFarland et al. (1984) suggested that expression of residue data on a lipid basis may enable comparisons among unrelated organisms. If this is true, it could greatly increase the utility of BCF-K_{OW} regression equations, and, therefore, further investigation is warranted to verify that suggestion.

BCF - Water Solubility Relationship

The aqueous solubility of organic chemicals can be used to predict bioconcentration in a manner similar to K_{OW}. Several authors have shown that solubility is related to K_{OW} (Hansch et al., 1967; Chiou et al., 1977; Tulp and Hutzinger, 1978; Kenaga and Goring, 1980; Mackay et al., 1980). Consequently, solubility correlates satisfactorily with BCF, as shown by the regression equations listed in Table 3 and plotted in Figure 7. Figure 7 shows that, for a given solubility, a BCF predicted by the plotted equations will be within a difference of 10 to 50. This variation is considerably less than that associated with BCF-K_{OW} regressions.

The BCF-K_{OW} and BCF-S correlations are useful because they allow prediction of contaminant residues from aqueous concentrations and physio-chemical properties that are more readily available or more easily measureable than

TABLE 3

PUBLISHED REGRESSION EQUATIONS BETWEEN BCF AND WATER SOLUBILITY(S)

	Equation	Units of S	Number of Chemicals (n)	Correlation Coefficient (r)	Reference
1	log BCF = 3.9950 - 0.3891 log S	ppb	11	0.92	Lu & Metcalf, 1975
2	log BCF = 3.41 - 0.508 log S	umole/l	8	0.96	Chiou et al., 1977
3	log BCF = 2.791 - 0.564 log S	ppm	36	0.72	Kenaga & Goring, 1980
4	log BCF = 2.183 - 0.629 log S	ppm	50	0.66	Kenaga & Goring, 1980
5	log BCF = 3.71 - 0.316 log S	ppb	25	0.57	Davies & Dobbs, 1984 (Recalculated from Veith et al., 1980)
6	log BCF = 5.09 - 0.85 log S	ppb	11	0.87	Metcalf et al., 1973
7	log BCF = 2.83 - 0.55 log S	ppm	42	-	Davies & Dobbs, 1984 (Extrapolation from Kobayashi, 1981)

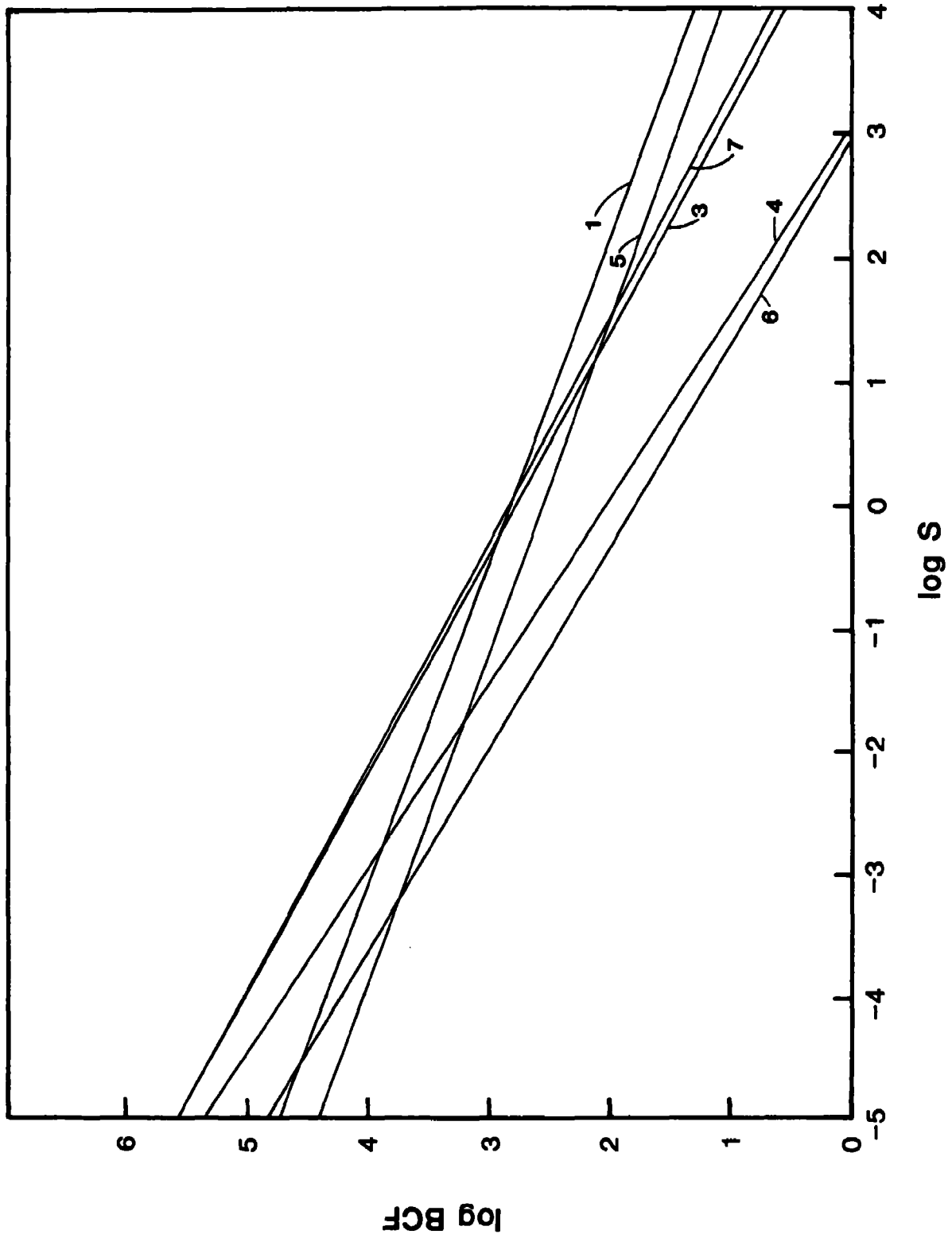


Figure 7. Plot of BCF-water solubility regression equations listed in Table 2 (S = ppm).

BCFs. However, they must be used discriminately. They may not accurately predict BCF for: compounds with log K_{ow} outside the range of 1 to 6; compounds with short half-lifes (high k_2); compounds that differ in chemical nature from those used in the regression development; or compounds with steric hinderances to accumulation (Tulp and Hutzinger, 1978; Mackay, 1982). Furthermore, these bioconcentration models do not account for changes in chemical forms resulting from the presence of suspended solids or sediments or for the effect of ingestion of contaminated food organisms or particles on total body burdens.

Bruggeman et al. (1981) developed an equilibrium partitioning model for directly estimating bioconcentration of lipophilic chemicals. Since lipophilic chemicals accumulate primarily in the lipid tissue of biota, the BCF can be estimated as:

$$BCF = \frac{k_1}{k_2} = \frac{\gamma_w}{\gamma_l} X_l = K_{wl} X_l \qquad (15)$$

where

γ = activity coefficient of the chemical in water (w) or lipid (l)

X_l = lipid content of the organism (g lipid/g organism weight)

K_{wl} = lipid/water partition coefficient

Bruggeman et al. (1981) reported that K_{wl} is relatively organism independent.

UPTAKE FROM SEDIMENT

Recently, biological uptake from contaminated sediments has generated much concern, especially since negative biological effects, including bioaccumulation, have been observed in areas where water column contaminant concentrations do not exceed ambient water quality criteria. Thermodynamic

methods have been proposed for predicting residue accumulation by benthic organisms from contaminated sediments.

Karickhoff et al. (1979), Means et al. (1980), and Karickhoff (1981) studied the equilibrium sorption behavior of hydrophobic organic chemicals and found that at low pollutant concentrations ($C_w < 0.5\ S$) sorption isotherms were linear, reversible, and characterized by a partition coefficient,

$$C^e_s = K_{ws}\, C^e_w \tag{16}$$

where C^e_s and C^e_w are the equilibrium concentrations of the substance in the sediment and water, respectively, and K_{ws} is the sediment/water partition coefficient. K_{ws} is directly related to the organic carbon content of sediments; consequently, K_{ws} is frequently normalized for organic carbon:

$$K_{ws}/X_{oc} = \frac{C^e_s/X_{oc}}{C^e_w} = K_{oc} \tag{17}$$

where X_{oc} is the fractional mass of organic carbon in the sediment and K_{oc} is the sediment-organic-carbon/water partition coefficient, commonly called the soil sorption coefficient. K_{oc}'s are relatively consistent over a wide variety of sediments (Means et al., 1980; Karickhoff, 1981). Regression equations have been developed for estimating K_{oc} from octanol/water partitioning or aqueous solubility, and are presented in Tables 4 and 5 and Figures 8 and 9.

Once the partition coefficients between sediment and water (K_{ws}) and between biota and water (BCF) have been determined or estimated by methods described above, the contaminant residues that are expected to occur in benthic biota exposed to interstitial or interfacial (water at the sedient/water interface) waters can be approximated as follows:

TABLE 4

PUBLISHED REGRESSION EQUATIONS BETWEEN K_{OC} AND K_{OW}

	Equation	Number of Chemicals (n)	Correlation Coefficient (r)	Reference
1	$\log K_{OC} = 0.885 + 0.524 \log K_{OW}$	30	0.96	Briggs, 1973
2	$\log K_{OC} = - 0.21 + 1.00 \log K_{OW}$	10	1.00	Karickhoff et al., 1979
	$K_{OC} = 0.63 K_{OW}$	10	0.98	
3	$\log K_{OC} = 1.377 + 0.544 \log K_{OW}$	45	0.86	Kenaga & Goring, 1980
4	$\log K_{OC} = - 0.317 + \log K_{OW}$	22	0.99	Means et al., 1980
5	$\log K_{OC} = - 0.346 + 0.989 \log K_{OW}$	5	1.00	Karickhoff, 1981
	$K_{OC} = 0.411 K_{OW}$	5	1.00	
6	$\log K_{OC} = -0.006 + 0.937 \log K_{OW}$	19	0.97	Pavlou & Weston, 1984 (From Brown et al., in prep.)
7	$\log K_{OC} = 0.02 + 0.94 \log K_{OW}$	9	-	Lyman et al., 1982
8	$\log K_{OC} = - 0.18 + 1.029 \log K_{OW}$	13	0.95	Rao & Davidson, 1980
9	$\log K_{OC} = 0.158 + 0.843 \log K_{OW}$	19	0.96	Pavlou & Weston, 1984

TABLE 5

PUBLISHED REGRESSION EQUATIONS BETWEEN K_{oc} AND WATER SOLUBILITY(S)

	Equation	Units of S	Number of Chemicals (n)	Correlation Coefficient (r)	Reference
1	$\log K_{oc} = 0.44 - 0.54 \log S$	mole fraction	10	0.97	Karickhoff et al., 1979
2	$\log K_{oc} = 4.040 - 0.557 \log S$	umole/l	15	0.99	Chiou et al., 1977
3	$\log K_{oc} = 3.64 - 0.55 \log S$	ppm	106	0.84	Kenaga & Goring, 1980
4	$\log K_{oc} = 4.273 - 0.686 \log S$	ppm	22	0.97	Hassett et al., 1980
5	$\log K_{oc} = 4.070 - 0.82 \log S$	ppm	4	1.00	Means et al., 1980
6	$\log K_{oc} = 3.933 - 0.642 \log S$	ppm	5	0.97	Calculated from data given in Karickhoff, 1981

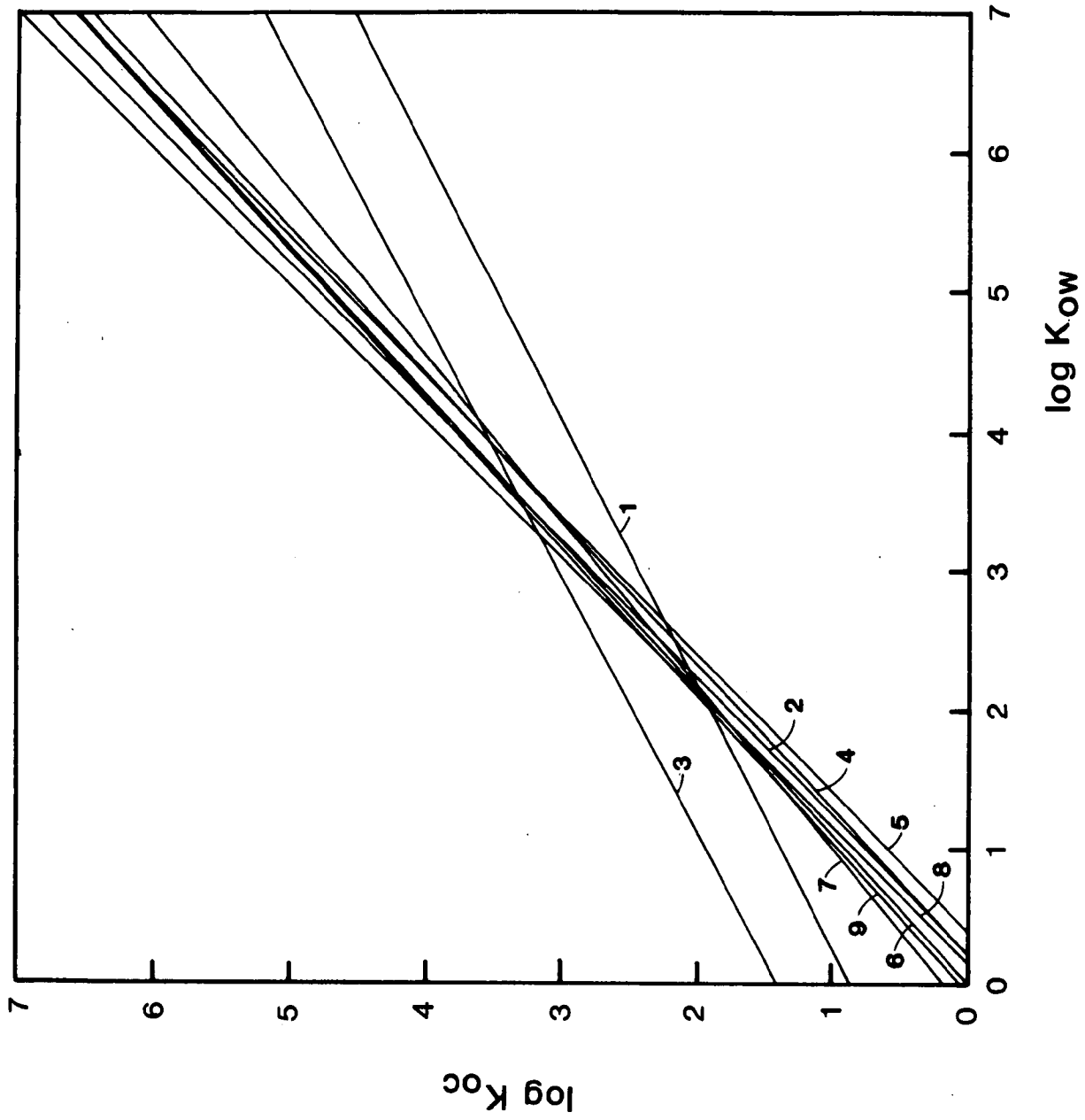


Figure 8. Plot of K_{oc}-K_{ow} regression equations listed in Table 3.

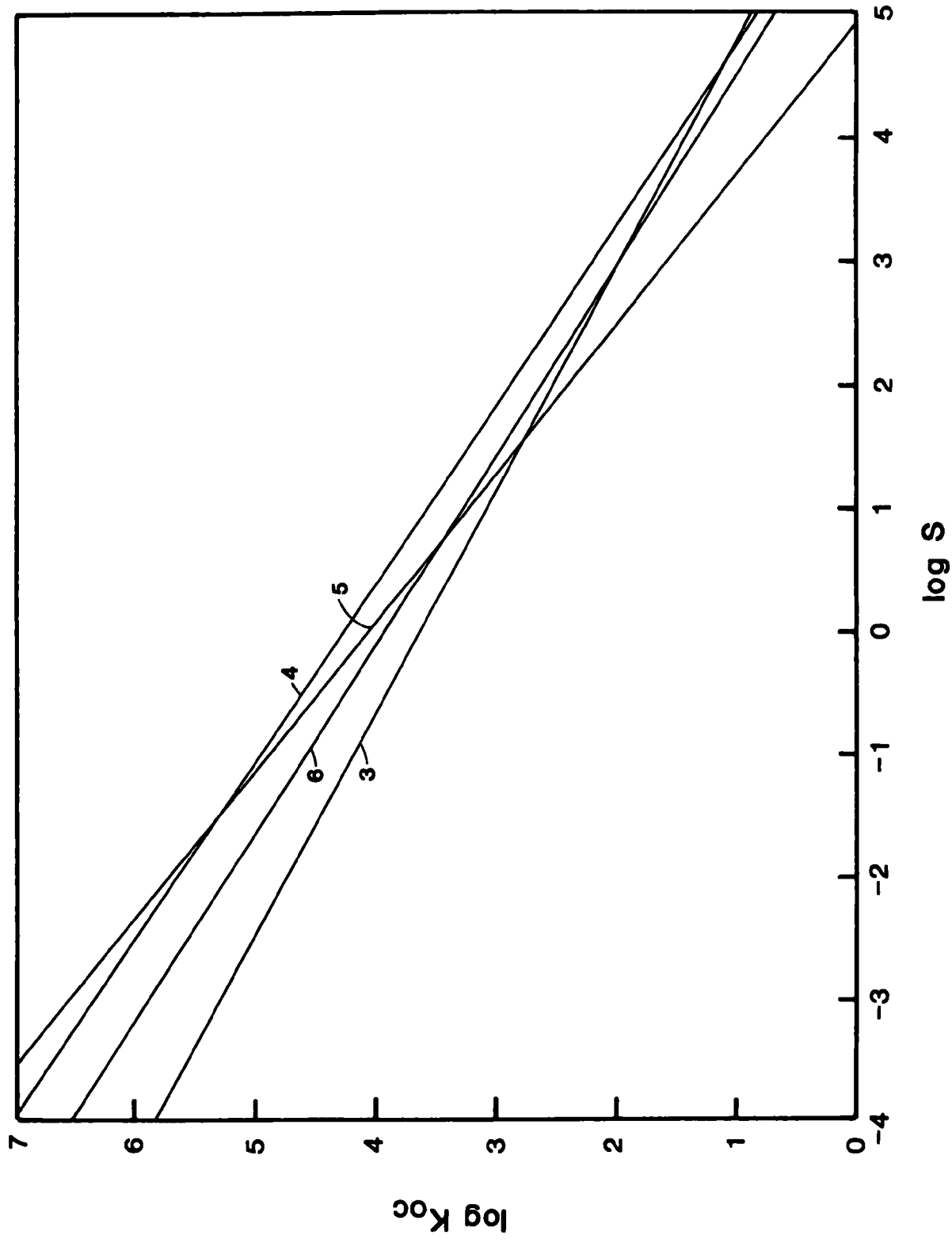


Figure 9. Plot of K_{OC}-water solubility regression equations listed in Table 4 (S^{OC}= ppm).

$$BCF/K_{ws} = K_{sb} \quad (18)$$

and

$$C^e_b = K_{sb}\, C^e_s \quad (19)$$

where K_{sb} is the biota/sediment partition coefficient. Using this relationship, Connor (1984) derived an equation for estimating K_{sb} by combining two regression equations of Kenaga and Goring (1980) along with the relationship between K_{oc} and K_{ws} (Equation 17):

$$\log BCF = -1.495 + 0.935 \log K_{ow}$$
$$\log K_{oc} = 1.377 + 0.544 \log K_{ow}$$
$$K_{oc} = K_{ws}/X_{oc}$$

$$\log K_{sb} = \log (BCF/K_{ws}) = -2.872 + 0.391 \log K_{ow} - \log X_{oc} \quad (20)$$

Karickhoff (1984) has proposed a more direct method of determining the potential for bioaccumulation of hydrophibic organics from contaminated sediments. This method is based on the assumption that the predominant pools for hydrophobic organic chemicals are lipid tissue in biota and organic carbon in sediments. At a state of equi-chemical potential, the distribution of a substance should be equal to the ratio of the chemical's affinity for lipid and organic carbon, which should be highly chemical independent. Thus, the thermodynamic potential for biological uptake of hydrophobic organics from a sediment source should depend only on the organic carbon content of the sediment, the lipid content of the organism, and the lipid/organic carbon partition coefficient ($K_{oc,l}$):

$$K_{sb} = \frac{X_l}{X_{oc}} K_{oc,l} \quad (21)$$

The value of $K_{oc,l}$ must be determined experimentally but should be on the order of unity, i.e.,

$$K_{sb} = \frac{X_1}{X_{oc}} \qquad (22)$$

The pollutant concentration in an aquatic organism at a state of equi-chemical potential with the source defines the maximal chemical uptake from purely thermodynamic considerations (Karickhoff, 1984). Unfortunately, no analogous method currently exists for determining the potential for bioaccumulation of metals or water soluble organics.

OTHER BIOACCUMULATION MODELS

Several other models capable of predicting bioaccumulation have been developed which do not fit precisely into the above sections. These are discussed briefly below.

Norstrom et al. (1976) developed a kinetic bioconcentration model based on fish bioenergetics. In general, their model can be described by (Neely, 1979):

$$\frac{dC_f}{dt} = \frac{EC_w R_v}{F} \qquad (23)$$

where

E = efficiency of chemical transfer across the gill membrane

C = chemical concentration in fish (f) or in water (w)

R_v = volume of water flowing past the gills per unit time (ventilation rate)

F = weight of fish

Bruggeman et al. (1981) also used bioenergetics terms in a kinetic model of bioaccumulation from contaminated food. Their model of uptake due to constant dietary exposure is given by:

$$C_f(t) = \frac{ef}{k_2} C_{fd} (1-e^{-k_2 t}) \quad (24)$$

where

C = chemical concentration in fish (f) and in food (fd)
e = adsorption efficiency for ingested chemical
f = feeding rate (food weight per fish weight per time)
k_2 = depuration rate
t = time

It follows from Equation 24 that the steady-state fish/food partition coefficient ($K_{fd,f}$), termed the biomagnification factor by the authors, can be determined by:

$$K_{fd,f} = \frac{C_f^{ss}}{C_{fd}^{ss}} = \frac{ef}{k_2} \quad (25)$$

The above equation was further modified by substituting an approximation for the depuration rate constant (k_2):

$$K_{fd,f} = \frac{efFK_{w1}X_1}{ER_v} \quad (26)$$

where all variables are as previously defined. The above expression for uptake from contaminated food incorporates a combination of kinetic-bioenergetics terms and an equilibrium term, K_{w1}. Total bioaccumulation (uptake from both food and water) can be determined by:

$$C_f = K_{fd,f} C_{fd} + BCF\ C_w \quad (27)$$

More complex food chain models have been developed (Weininger, 1978; Thomann, 1981; Thomann and Connolly, 1984). Although these models are more complex due to the number of auxiliary terms, Lake et al. (1984) reported

that, in general, these models predict contaminant residues in fish by applying the following differential equation:

$$\frac{dC_f}{dt} = k_1 C_w + k_{fd} C_{fd} \epsilon_{fd} - k_2 C_f \quad (28)$$

where

k_{fd} = rate constant for uptake from food
ϵ = uptake efficiency term from food

Fugacity models have been developed to predict the distribution of chemicals in idealized environments (Mackay, 1979; Mackay and Peterson, 1981, 1982). At thermodynamic equilibrium, the fugacity (f), or escaping tendency of a chemical substance from a phase, in all environmental compartments is equal, e.g.:

$$f_{air} = f_{water} = f_{sediment} = f_{biota} \quad (29)$$

Model assumptions are that: environmental compartments are completely mixed (i.e., homogeneous); there is no inflow or outflow from the system; and sufficient time has elapsed so that all compartments are in equilibrium.

DISCUSSION

Two basic types of models have been proposed to describe the concentration in the biota: kinetic and equilibrium. The first model considers the biota concentration as a balance between the kinetic processes of uptake and depuration. The second model considers the biotic phase as an inanimate volume of material that is approaching thermodynamic equilibrium. When first order kinetics are used to describe the uptake and depuration rates of the first model and the rate to approach equilibrium of the second model, the biota concentration (C_b) at any time (t) can be expressed as (Mackay, 1982):

Model I: $$C_b = (k_1/k_2)\, C_w\, [1-\exp(-k_2 t)] \quad (30)$$

Model II: $$C_b = (BCF)\, C_w\, [1-\exp(-\frac{k_3}{BCF}\, t)] \quad (31)$$

It is apparent that Equations 30 and 31 are of the same form, only their coefficients are different. Thus, uptake measurements are inherently incapable of differentiating between the two models. However, an important conceptual difference is that Model I is dependent on the kinetic rates and therefore the steady state concentration may not be the thermodynamic equilibrium concentration, while Model II is based on thermodynamic equilibrium partitioning and does not consider kinetic processes (routes and rates).

Thermodynamic equilibrium concentrations in the biotic phase will seldom be reached by steady-state concentrations in the environment (Peddicord and McFarland, personal communciation). However, steady-state concentrations estimated by kinetic modeling generally have not been compared in the literature to thermodynamic equilibrium concentrations. Comparisons between steady state concentrations (estimated from kinetic rates) and equilibrium concentrations (estimated from structure-activity relationships) might be misleading due to the large variation in the published thermodynamic equilibrium regression equations (e.g., see Figures 6 and 7). BCFs predicted using those relationships may vary as much as 10^3; consequently, the outcome of such a comparison greatly depends on the equation chosen to estimate the thermodynamic equilibrium concentration.

In the absence of biological transformation of bioaccumulated contaminants, the steady state concentration in an organism should be equal to the thermodynamic equilibrium concentration for the biotic phase. If chemical transformation occurs, however, the steady-state body burden will deviate from the thermodynamic equilibrium concentration. An important objective of a kinetic study should be to investigate and quantify this rate of biotransformation. However, depuration rates are commonly estimated by transferring test organisms to clean water. This measured depuration rate may be the cumulative result of exchange processes at the gill, excretion

via the kidney or bile, and biotransformation. If exchange and excretion processes are solely responsible for movement of a chemical from biological tissue to water and the chemical is not metabolized, the kinetic steady-state residue should be equivalent to the thermodynamic equilibrium concentration. Thus, the net depuration rate, k_2, provides little information on the deviation from equilibrium concentrations. In some instances, it is suspected that the metabolism rate is much smaller than the rate of elimination due to exchange or excretion, or there is a significant lag period for the metabolism rate; in such cases, the cumulative depuration rate is truly representative of the rate of chemical exchange between the biotic compartment and the environment. For example, the k_2 rates reported by Neely et al. (1974) have been found to correlate well with the thermodynamic equilibrium property K_{ow} (Spacie and Hamelink, 1982).

SECTION 3

REGULATORY APPLICATION OF BIOACCUMULATION DATA

IMPLEMENTATION MANUAL

The "Implementation Manual" (EPA and COE, 1977) specifies evaluations to be performed on dredged material proposed for discharge into marine waters. The bioavailability of sediment-associated contaminants is assessed via a 10-day solid phase bioassay followed by bioaccumulation analyses (whole-body residues) on surviving organisms. The procedure for assessing bioaccumulation potential described in the Implementation Manual is summarized in Figure 10 and the accompanying text below.

1. The Manual (EPA and COE, 1977) expresses a preference for assessing bioaccumulation potential in the field, when possible, rather than using laboratory bioassays, because the field method integrates influencing factors such as mixing zone, sediment transport, and long exposure times. Caged animals may also be used, although for those animals with no history of exposure long periods of time in situ will be necessary.

2. Conditions required for field assessment. The use of the field approach for assessing bioaccumulation potential is "technically valid only where there exists a true historical precedent for the proposed operation being evaluated. That is, it can be used only in the case of maintenance dredging where the quality of the sediment to be dredged is considered not to have deteriorated or become more contaminated since the last dredging and disposal operation. In addition, the disposal must be proposed for the site at which the dredged material in question has been previously disposed or for a site of similar sediment type supporting a similar biological community."

3a. Species selection for field assessment. Organisms must occur in sufficient numbers at all stations for collection of an adequate sample (several grams of tissue) to permit measurement of chemical concentrations. It is desirable to collect large organisms but they must be relatively immobile--bivalves, some gastropods, and large polychaetes are recommended.

3b. Species selection for laboratory assessment. Section 227.27(d) of the Federal Register (42 FR 2481) defines "appropriate sensitive benthic marine organisms" as at least three species consisting of a filter-feeding, a deposit-feeding, and a burrowing species. It is

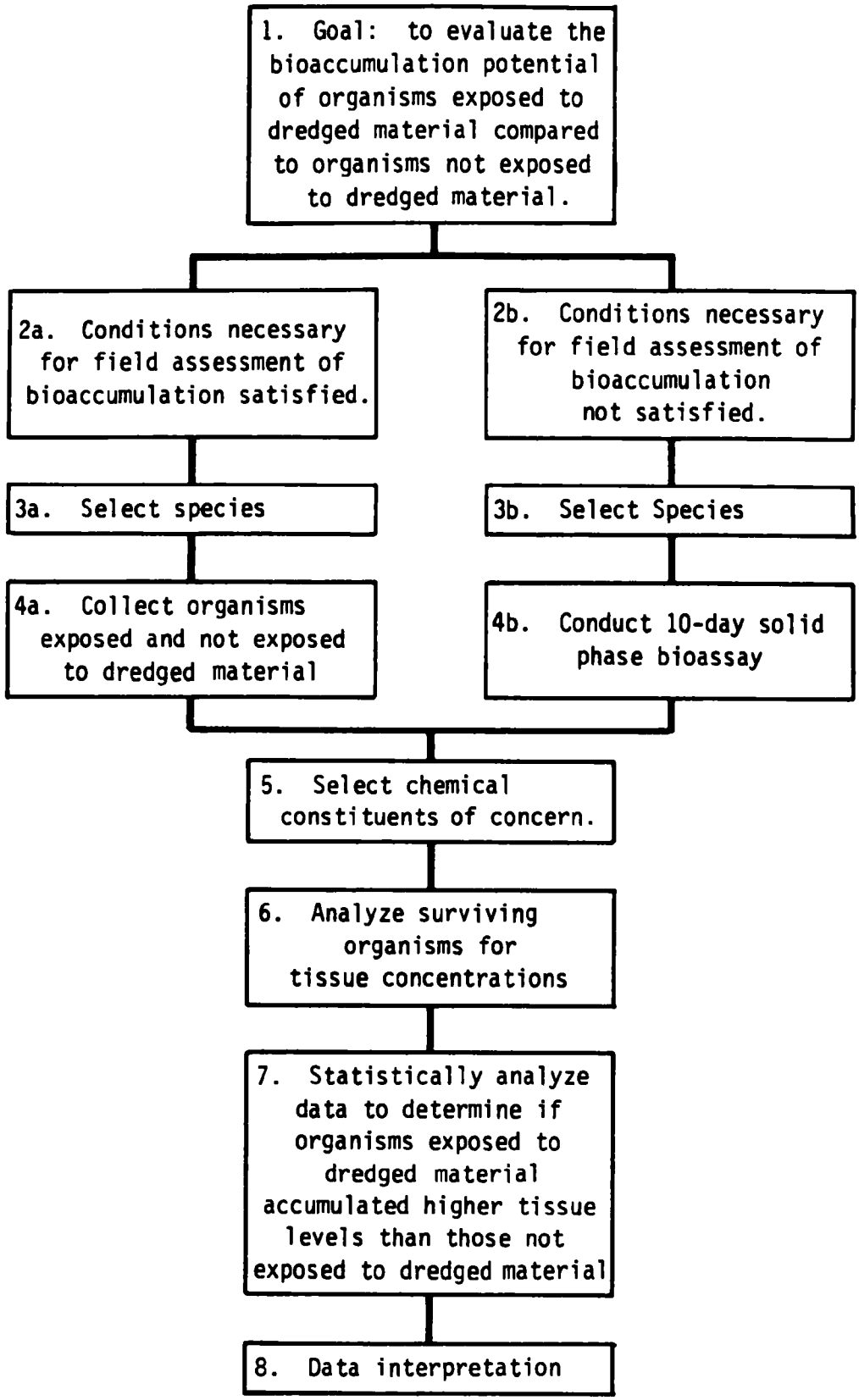


Figure 10. Flow chart of bioaccumulation potential assessment prescribed in the Implementation Manual.

recommended to include a crustacean, an infaunal bivalve, and an infaunal polychaete. The Manual lists recommended species for use in solid phase bioassays in Table F1. The guidance manual for the New York District (COE and EPA, 1982) specifies the use of Palaemonetes sp., Mercenaria mercenaria, and Nereis sp. or Neanthes sp. in bioaccumulation tests conducted on dredged materials proposed for disposal in the New York Bight.

4a. Field method design and conduct. Organisms are collected from at least three stations within disposal site boundaries and from at least six stations outside the disposal site with substrate that is sedimentologically similar to that within the disposal site. Of the six outside-site stations, three should be "downstream" from the site (in the direction of net bottom transport) and three or more must be located in an uncontaminated sediment in a direction opposite that of the net bottom transport (data from the latter will provide a reference level of tissue concentrations). After collection, organisms are held in clean water in the lab to allow voiding of digestive tracts (2-3 days). Also, shells are not included in the chemical analyses.

4b. Lab method design and conduct. Organisms are collected (preferably from the reference stations) and used in the 10-day solid phase bioassay described in the Manual (Appendix F). Reference aquaria contain a 45 mm layer of reference sediment. The New York District COE has identified specific locations for the collection of reference and control sediments for use in laboratory solid phase bioaccumulation tests (COE and EPA, 1982). Test organisms are allowed to establish themselves in a 30 mm layer of reference sediment in exposure aquaria and then a 15 mm layer of dredged material is added. Seawater may be added as a continuous flow-thru system or as a static system with periodic replacement. After ten days of exposure, the surviving organisms are removed and held in clean seawater to void digestive tracts as in the field method.

5. Selection of chemical constituents for analysis. Chemical constituents to be assessed in the tissues of test organisms are those deemed critical by the District Engineer and Regional Administrator after consideration of known inputs to the dredged material. Section 227.6 of the Federal Register cites the following constituents of particular concern:

   a. Organohalogen compounds,
   b. Mercury and its compounds,
   c. Cadmium and its compounds,
   d. Petroleum hydrocarbons,
   e. Known or suspected carcinogens, mutagens, or teratogens.

   In the New York District, bioaccumulation analyses are to be performed for cadmium, mercury, PCBs, and petroleum hydrocarbons, or other material as determined necessary under the above categories (COE and EPA, 1982).

6. Analysis of tissue concentrations. Tissue concentrations of the selected constituents are analyzed according to standard methods described in references cited in the Manual (Table G1).

7. Statistical analysis of data. Data is tabulated for each constituent and species. Tissue concentrations in exposed animals are compared to those in reference animals to determine if the former show statistically significant higher levels--indicating bioaccumulation potential of the dredged material. Statistical methods include:

   - Cochrane test--to see if variances of the data sets are homogeneous and if data transformation is necessary.
   - Analysis of variance
   - F-test--to see if there is any statistical difference between exposed and reference tissue concentrations.
   - Student-Newman-Keuls Multiple range test--to determine which exposed tissue concentration means are significantly different (higher) than reference tissue concentration means.

8. Data interpretation. The Implementation Manual recommends the environmentally protective approach of assuming that any statistically significant differences in tissue concentrations between reference and exposed organisms are a potential cause for concern. The "Decision Guidelines" are an attempt at interpreting laboratory bioaccumulation data for regulatory purposes.

DECISION GUIDELINES

BACKGROUND

The Decision Guideline documents (COE and EPA, 1980, undated a-c) provide a method for interpreting contaminant residues acquired by organisms exposed to dredged material in accordance with the Implementation Manual (EPA and COE, 1977) laboratory procedure. In developing the Decision Guidelines, average tissue levels in biota of the New York Bight were estimated from the available data for PCBs, cadmium, mercury, total naphthalenes, and DDT and its metabolites. Those levels were adopted as maximum values for each of three test species which, if not exceeded, should prevent significant undesirable effects from occurring in areas contiguous with the dredged material disposal site in the New York Bight Apex. The Decision Guidelines

were developed on an interim basis under the philosophy of maintaining the status quo and thereby preventing further degradation of the Bight.

The Decision Guidelines are regulatory tools, based on the available bioaccumulation data and the short-term administrative goal of no-further-degradation; they are not scientifically defensible because they do not consider the environmental significance or biological effects of contaminant residues. The long-range goals of bioaccumulation interpretation are effects-based regulation and mitigation of the environmental stress on the New York Bight due to dredged material disposal.

APPLICATION

The Decision Guidelines for the New York Bight and their method of derivation are summarized in Table 6. Figure 11 illustrates the use of the Decision Guidelines to interpret bioaccumulation data generated by the 10-day solid phase bioaccumulation test (EPA and COE, 1977). Figure 11 is actually a continuation of Figure 10 and together they represent the overall procedure for assessing the bioavailability of contaminants in dredged material proposed for disposal in the New York Bight Apex.

DISCUSSION

A major criticism of the Decision Guidelines interpretive approach is that, for some chemicals, non-steady-state residues acquired over ten days of laboratory exposure are compared to steady-state residues obtained from field data. The House Committee on Merchant Marine and Fisheries (1980) voiced that criticism in a question posed to the Corps of Engineers at a Congressional hearing on dredge spoil disposal and PCB contamination (p. 685):

> QUESTION 5: The Corps stated at the May 21 hearings that "it is equally clear that different species have different uptake rates for different contaminants and that within this ten-day exposure period, it is not possible to predict right now what the ultimate level in a particular organism might be." If this is the case, what validity do the matrix values have if the test data do not

TABLE 6

DECISION GUIDELINES FOR THE NEW YORK BIGHT

Chemical	Test Organism	Decision Guideline Level Wet Weight Tissue Concentration (mg/kg)	Derivation Method
Polychlorinated biphenyls	Mercenaria mercenaria	0.1	1
	Palaemonetes sp.	0.1	1
	Nereis sp.	0.4	2
Cadmium	all 3 species[a]	0.3	3,2
Mercury	all 3 species	0.2	3,2
Total naphthalenes	all 3 species	0.02	3
DDT + metabolites	all 3 species	0.04	2

1. Red Book (EPA, 1976; AFS, 1979) criteria level in fish for protection of freshwater and marine life and consumers thereof including fish-eating birds and mammals.

2. (NYB representative water column concentration) x (selected BCF) = (estimated average tissue concentration in NYB biota)

3. Grand mean of available tissue concentration data for invertebrates from the NYB.

[a]Mercenaria, Palaemonetes, and Nereis

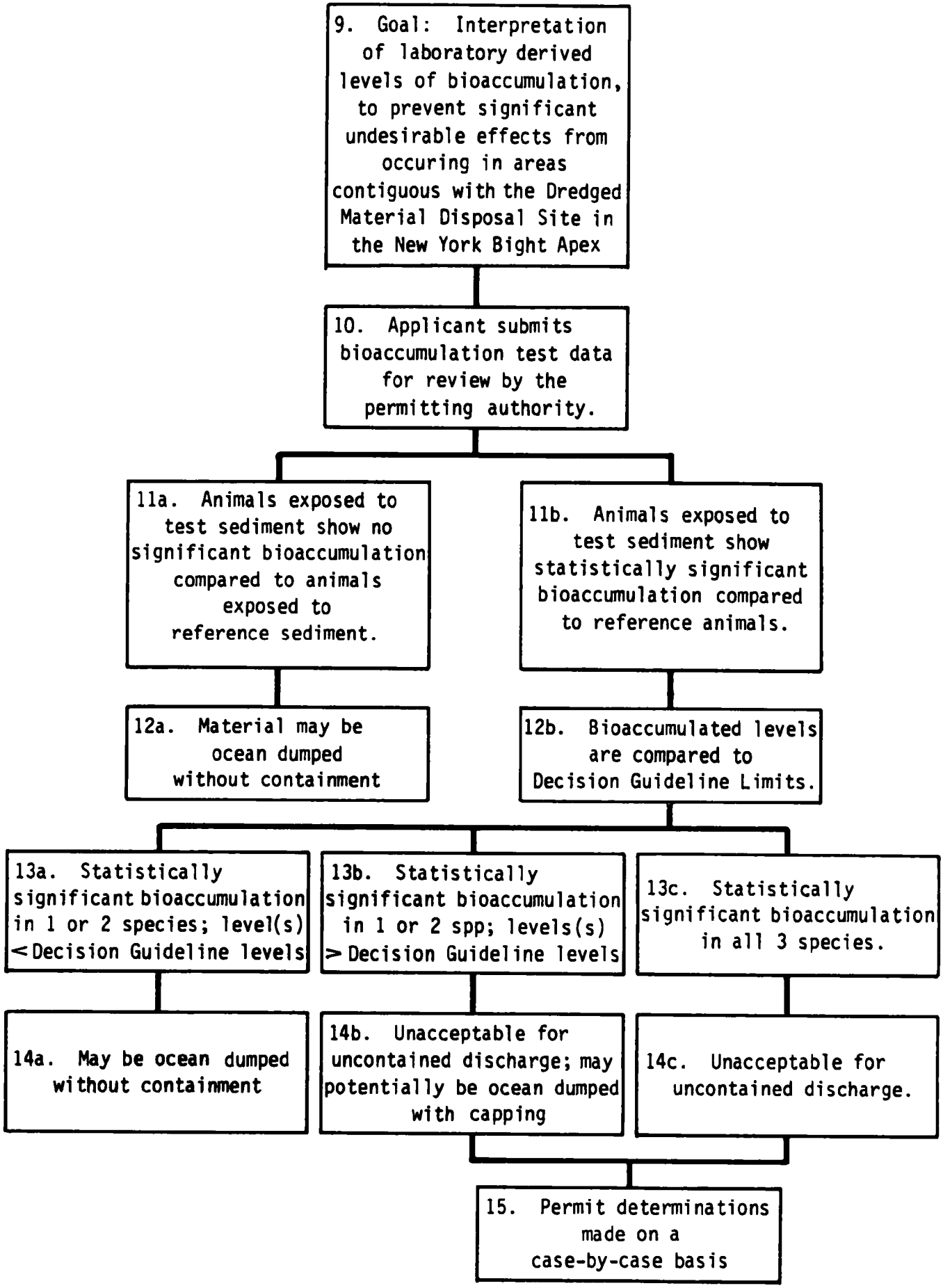


Figure 11. Flow chart of bioaccumulation data interpretation using the Decision Guidelines.

represent the ultimate concentration level to be reached in the organism?

The Corps' response, while answering the question, did not fully address the issue of data incomparability.

> RESPONSE 5: The matrix considers the variation in uptake by different species by considering the uptake of three species of very different ecological and taxonomic groupings. It also is based on actual uptake demonstrated upon exposure to the intact mixture of all contaminants in the dredged material.
>
> The matrix is clearly viewed by all involved parties as nothing more than an interpretive tool which will be revised on a regular basis as interpretive abilities improve. The use of such interim tools is necessary since Congress mandated that bioaccumulation be evaluated at a time when the state-of-the-art for the environmental interpretation of such data is far from fully developed. Without the use of some sort of interim tool, the only two approaches to interpretation are to consider any indication of potential bioaccumulation unacceptable or to consider all bioaccumulation acceptable, unless it is at a grossly high level where damage is obvious. Neither of these extremes represents a socially or environmentally acceptable view. The Ocean Dumping Implementation Manual gives preference to bioaccumulation studies done in the field over laboratory studies. In this manner, it is posible to assess bioaccumulation by animals that have spent major portions of their lives in and on sediments very similar to the dredged material in question. These organisms exist under the physical and chemical conditions actually occurring at the disposal site. The tissue concentrations in such animals are in equilibrium with their environment and can be compared directly to tissue levels in organisms from areas unaffected by the dumping. This approach is the most desirable, but until appropriate field studies designed specifically for the New York Bight have developed an adequate data base for intrepretation, laboratory studies must be used. However, the interpretive difficulties posed by laboratory bioaccumulation investigations require some sort of interpretive tool and the matrix is the best currently available attempt in devising such a tool. ...

The 10-day bioaccumulation test (EPA and COE, 1977) was designed to indicate whether there is a potential for contaminant uptake from dredged material (Peddicord, 1980, p. 587). Rubinstein et al. (1983) found that ten days of exposure is sufficient to demonstrate the potential for PCB bioaccumulation, but that there is no clear relationship between 10-day whole-body concentrations and steady-state concentrations. Steady-state

concentrations are clearly more meaningful than levels reported without reference to kinetic processes (McFarland et al., 1984). From their experimental data, Rubinstein et al. (1983) concluded that since 10-day residues do not reflect steady-state concentrations they cannot be compared directly to a value intended to represent concentrations in indigenous biota at the disposal site (i.e., the Decision Guideline values).

If a 10-day exposure period is to have predictive value, its relationship to long-term exposure must be determined. McFarland et al. (1984) have described a method by which a steady-state contaminant residue can be estimated from a single time-point measurement of the contaminant concentration in tissue and an elimination rate constant (k_2) estimated from the octanol/water partition coefficient of the chemical. This procedure, which is outlined in the Section 2, allows estimation of steady-state body burdens from 10-day bioaccumulation data. Conceptually, the Decision Guideline levels are more appropriately compared to steady-state residues than to 10-day, non-steady-state concentrations.

The Decision Guidelines can also be criticized over the inconsistency of methods used in their development. In spite of that inconsistency, however, the concentrations adopted to represent average contaminant residues in New York Bight macroinvertebrates appear to be fairly well supported by the currently-available data (as illustrated in the next section). Some arguable points pertaining to the derivation of the Guideline values are outlined below:

- The EPA Red Book value of 0.1 mg/kg adopted as the PCB Decision Guideline limit in Mercenaria and Palaemonetes is not based on recent or site-specific data.

- The approach wherein a water column concentration is multiplied by a BCF to estimate an average tissue concentration (Method 2 in Table 6) assumes that bioaccumulation of contaminants is via the water column. That assumption may not be valid for infaunal worms or deposit-feeding species which may accumulate contaminants primarily from sediment.

- Using the method described above in the derivation of the PCB Decision level for worms, the highest value of the range of reported water column concentrations was selected (44 ng/L), representing the least conservative choice.

- The Decision Guideline levels for cadmium and mercury were established based on the grand mean of body burdens measured in invertebrates from the New York Bight. The accuracy of those values was "tested" using Method 2 (Table 6). However, the range of BCFs reported for cadmium and mercury are wide, and whether or not the grand mean value fell within the range of values calculated by Method 2 depended on the arbitrary selection of BCF. For example, "the lowest bivalue BCF" (750 reported for quahog) was selected as the most conservative BCF for cadmium, whereas for mercury a conservative BCF of 1,000 was selected which is the value "intermediate between that of lobsters and oysters exposed to inorganic mercury"; while for PCBs the BCF chosen for setting the Guideline limit for worms was an approximate median value (10^4 selected from a range of 10^3-10^5).

REVIEW OF DECISION GUIDELINE LEVELS

The Decision Guidelines were viewed by their authors as "a dynamic tool which will be frequently reviewed and modified as additional data and more detailed analyses become available" (COE and EPA, 1980). According to Murphy (1980, p. 46), EPA expected the PCB Interim Decision Matrix to be usable for only about a year. Nevertheless, the Decision Guideline values have not been revised since their development, and the New York District Corps of Engineers continues to use the Decision Guidelines in their original form.

The currently-available data on residues of cadmium, mercury, PCBs, and DDT and its metabolites (quantitative data for total naphthalenes were scarce) in New York Bight biota were assembled for the purpose of comparing the Decision Guideline levels to our best estimate of actual average contaminant body burdens (Appendix A). To be consistent with the Decision Guidelines, only invertebrate species were included in the analysis. The grand mean of existing invertebrate body burdens was calculated for each contaminant, and the mean values are recorded in Table 7 along with the Decision Guideline levels. Separate mean PCBs concentrations were calculated for polychaete worms and for all other invertebrates for comparison to the two corresponding Decision Guideline concentrations. Also, since DDT residues measured in blue mussels (Mytilus edulis) were anomolously high compared to levels reported in other species, a mean DDTs concentration was calculated for all invertebrates except blue mussel.

TABLE 7

COMPARISON OF DECISION GUIDELINE LEVELS
WITH AVERAGE CONTAMINANT RESIDUES
IN NEW YORK BIGHT INVERTEBRATES

Chemical	Decision Guideline Concentration (mg/kg, wet)	Mean Concentration in all NYB Invertebrates (mg/kg, wet)	Mean Concentration in other NYB Invertebrate Groups (mg/kg, wet)
Total PCBs	0.1[a] 0.4[b]	0.193 (n=325)	0.17[d] (n=304) 0.528[e,c] (n=21)
Cadmium	0.3	0.337[c] (n=281)	
Mercury	0.2	0.099 (n=124)	
Total Naphthalenes	0.02	--	
DDT + Metabolites	0.04	0.073 (n=106)	0.033[f] (n=87)

[a]Decision Guideline level for PCBs in Palaemonetes sp. or Mercenaria mercenaria.

[b]Decision Guideline level for PCBs in Nereis sp. or Neanthes sp. The Decision Guideline concentrations for contaminants other than PCBs are applicable for all test species.

[c]No statistical difference ($\alpha = 0.05$) between the mean residue and the Decision Guideline level. All other computed mean residues are statistically different from the Decision Guideline concentrations.

[d]Mean concentration of PCBs in NYB invertebrates other than polychaete worms.

[e]Mean concentration of PCBs in NYB polychaete worms.

[f]Mean concentration of DDTs in NYB invertebrates excluding blue mussel.

The computed mean contaminant concentrations in New York Bight biota were statistically compared to the Decision Guideline levels using the t-test. At the 5 percent significance level, the residue means were statistically different from the Decision Guideline concentrations in every case except two: the mean cadmium concentration for all invertebrates and the mean PCBs concentration in polychaete worms only. However, the differences between calculated mean tissue concentrations of contaminants in New York Bight biota and the Decision Guideline levels are not large, and, in general, the Decision Guidelines are well supported by the present analysis of the literature data.

SEDIMENT QUALITY CRITERIA

The Decision Guidelines were developed with the interim goal of preventing further degradation of the New York Bight, but the ultimate goal of regulation is to effect improvement of the Bight ecosystem by mitigating the environmental stress caused by dredged material disposal. Preferable to the Decision Guidelines approach is to base regulation of contaminated sediments on biological effects.

EPA has published water quality criteria for many toxic chemicals, based on an extensive data base that relates biological effects to aqueous contaminant concentrations (EPA, 1980, 1983). Analogous sediment quality criteria have not been established.

A number of problems hinder the development of sediment quality criteria. Because a significant portion of sediment-associated contaminants may not be bioavailable and, therefore, not contribute to biological effects, it is inappropriate to base sediment quality criteria on total (bulk) concentrations of contaminants in sediments. Consequently, the bioavailability of sediment-associated contaminants needs to be evaluated. Bioaccumulation is currently the only reliable measure of the bioavailability of contaminants in sediments. Unfortunately, at the present, scientists do not know the precise relationship between tissue concentrations of contaminants and their biological consequences, although the relationships between contaminant body burdens and biological effects are beginning to be investigated.

The lack of residue/effects data makes it difficult to identify threshold concentrations which discriminate between acceptable and unacceptable levels of sediment contamination.

A number of alternatives for establishing sediment quality criteria have been proposed. Pavlou and Weston (1983) summarized several methods for the establishment of sediment criteria, including options based on: (1) background levels, (2) water quality criteria, (3) biological response, and (4) equilibrium partitioning.

BACKGROUND LEVELS

This approach considers any increase in contaminant concentrations above background levels undesirable. Background levels are determined from surficial sediments from areas isolated from known pollutional sources or from pre-anthropogenically contaminated strata of deep sediment cores. Implementation of sediment criteria based on background levels would require either (1) prohibiting any increase in contaminant concentrations over background levels or (2) allowing some increment of contamination above background levels. The former alternative would be unnecessarily restrictive for some chemicals and the latter alternative would require identification of threshold levels of sediment contamination--i.e., require the existence of some other type of sediment criterion, making the use of background levels superfluous (Chapman, 1984).

WATER QUALITY CRITERIA

This approach applies EPA ambient water quality criteria to interstitial and elutriate waters. The approach is appealing because it makes use of the extensive data base on biological effects underlying the water quality criteria. The application of water quality criteria to interstitial/interfacial waters is supported by the findings of Adams et al. (1983) who concluded that "[t]oxic effects can be expected to occur in benthic invertebrates only if the chemical concentration is high enough in the sediments such that the equilibrium interstitial water concentration

reached by desorption is equal to or higher than the concentration demonstrated to cause an effect in a water exposure test."

However, this approach assumes that the predominant route of exposure is via the interstitial water and water at the sediment/water interface, and neglects exposure following ingestion of sediment particles as an important exposure route. Consequently, direct application of water quality criteria to interstitial/interfacial waters is not appropriate for any chemical for which dietary uptake from sediment is a significant avenue of exposure. Chapman (1984) suggested that a simple model similar to the one described in Section 2 (Table 1) can be developed for sediment-dwelling organisms. Such a model could qualitatively indicate the relative significance of uptake from ingested sediment particles.

In addition, the water quality criteria approach is hampered by the difficulties of sampling and analyzing contaminants in interstitial water and by the unavailability of water quality criteria for a myriad of organic chemicals.

BIOLOGICAL RESPONSE

This approach involves the use of laboratory bioassays and biological field surveys to assess the biological response to contaminated sediments. Solid phase bioassays (e.g., EPA and COE, 1977) are valuable in assessing the toxicity of a particular sediment, but they do not indicate the contaminant(s) responsible for toxicity and, therefore, provide no guidance for setting regulatory criteria. Bioassays conducted with otherwise clean sediments spiked with a known contaminant concentration could be used to develop sediment quality criteria just as aqueous bioassay data were used to develop water quality criteria. However, because of the general paucity of this type of data and the wide variety of possible sediment characteristics, development of sediment criteria using this approach is unlikely to be possible in the near future. The utility of biological field surveys in sediment criteria development is limited because: they are site specific, natural biological variability can obscure pollutional effects, and negative environmental effects are observable only after the fact.

EQUILIBRIUM PARTITIONING

The equilibrium approaches discussed by Pavlou and Weston (1983) use equilibrium partitioning constants, which can be derived theoretically or empirically, to determine contaminant concentrations in various environmental compartments (water, sediment, and biota). Water quality criteria or FDA action levels are used to identify threshold levels of contaminants in those environmental compartments. Pavlou and Weston (1983) discussed four potential approaches for establishing sediment criteria based on equilibrium partitioning (Figure 12):

Approach #1, uses K_D and the existing EPA water quality criteria (applied to interfacial water) to compute a sediment threshold concentration. This calculated value is then compared to the actual measured contaminant concentration in the ambient sediment of a designated site to estimate the extent of violation. Conversely, using the ambient sediment burden and K_D the interfacial water concentration can be computed and compared directly to the appropriate EPA water criteria value.

Approach #2, is based on the application of water quality criteria to interfacial waters and the use of the BCF to compute a biota burden. The sediment threshold value can then be calculated by using the ARS constant. Indirectly, the computed biota burden may be compared to an existing body burden level known to induce a toxic effect.

Approach #3, uses the ARS quantity with either a measured body burden which induces a toxic effect (e.g., pathologic, behavioral or metabolic effect) or a federally established tissue concentration (if public health risks are the prime consideration) to compute a sediment threshold level.

Approach #4, is a combination of the above. It establishes a biological threshold concentration and determines a corresponding sediment threshold value via contaminant transfer through the aqueous phase.

Pavlou and Weston (1983) noted several limitations to the establishment of sediment criteria based on the equilibrium partitioning approaches described:

- Threshold levels based on water quality criteria do not consider direct transfer of contaminants from sediment to biota (e.g., following ingestion of sediment particles);

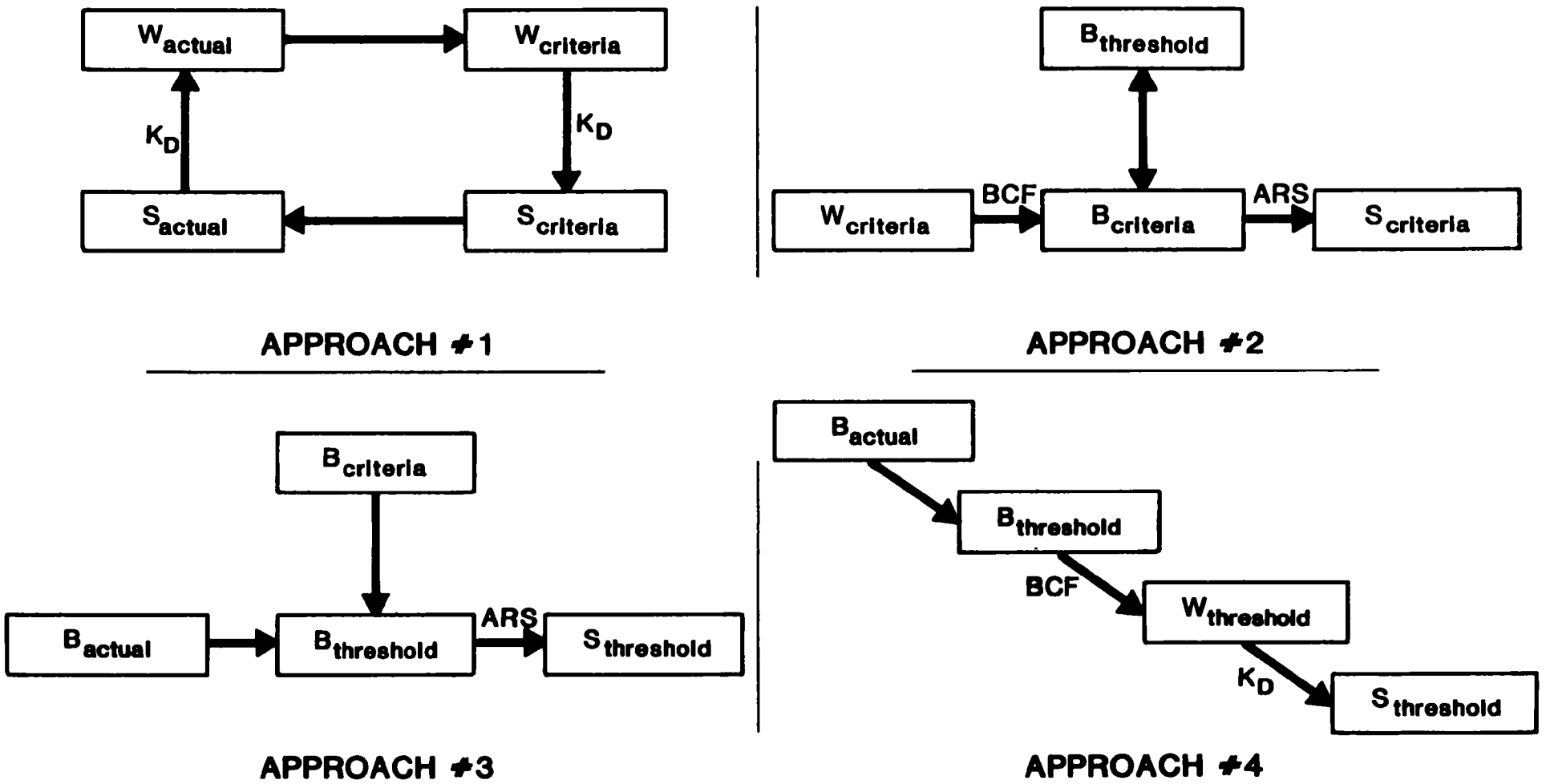


Figure 12. Schematic representation of sediment criteria development using equilibrium partitioning constants. Source: Pavlou and Weston, 1983.

- The use of multiple partition coefficients increases the potential for error;
- The sediment/water partition coefficients (K_D) determined empirically from partitioning between suspended particulate matter and water (and tabulated by Pavlou and Weston, 1983) are probably not applicable to partitioning between sediment and interstitial water because of the different physico-chemical conditions in sediments; and
- The biota/sediment partition coefficient (ARS) does not address the bioaccumulation mechanism.

Also, appropriate biota criteria are generally unavailable. Insufficient data exists to relate toxic effects to residue concentrations. FDA action levels are one type of biota criteria, but they have been established for only a few chemicals and they are designed to protect only human consumers of fish and shellfish, not the health of the aquatic community.

Pavlou and Weston (1984) used sediment/water partitioning (Approach #1) to develop sediment criteria for toxic contaminants in marine waters (Puget Sound). A sediment criterion was defined as the concentration of a contaminant in a sediment which insures that its concentration in interstitial water does not exceed the EPA water quality criterion. The expression for the sediment/water partition coefficient normalized for organic carbon (K_{OC}),

$$K_{oc} = \frac{C_{s/oc}}{C_{IW}} = \frac{K_D}{TOC} \tag{32}$$

where

$C_{s/oc}$ = contaminant concentration expressed in units of mass of contaminant/mass of organic carbon,

C_{IW} = contaminant concentration in interstitial water,

K_D = sediment/water partition coefficient (K_{ws}),

TOC = total organic carbon content of the sediment expressed as fractional mass on a dry weight basis.

was rearranged and modified by substituting the EPA water quality criterion ($C_{w/cr}$) for C_{IW}. Sediment criteria ($C_{s/cr/oc}$) were derived by the resulting equation:

$$C_{s/cr/oc} = K_{oc} C_{w/cr} \quad (33)$$

The general sediment criteria are applied to a specific site by multiplying $C_{s/cr/oc}$ by the organic carbon content of the sediment of concern, to obtain criteria that can be directly compared to contaminant concentrations in the sediment ($C_{s/cr}$):

$$C_{s/cr} = C_{s/cr/oc} \, TOC \quad (34)$$

The method described above can be used to develop sediment criteria for both organic and inorganic contaminants, providing that a water quality criterion is available. Pavlou and Weston (1984) estimated K_{oc} values for organic contaminants theoretically using a K_{oc}-K_{ow} regression equation developed for organic contaminants of concern in Puget Sound. K_{oc} values for trace metals were derived empirically by taking the mean of K_{oc} values calculated for a variety of sediments from measurements of trace metal concentrations measured in bulk sediments and interstitial water reported in the literature (Brannon et al., 1980).

The use of K_{oc} instead of the unnormalized sediment/water partition coefficient is based on the assumption that the organic carbon content of sediment is a major environmental variable affecting the sediment/water partitioning of contaminants. While that is clearly the case for synthetic organic chemicals, for trace metals it is not so evident. Pavlou and Weston (1984) evaluated the relationship between the sediment/water partition coefficient (K_D) and sediment organic carbon content for six trace metals. Three of the metals evaluated (Cu, Cd, Pb) exhibited statistically significant (albeit weakly so) correlations between K_D and sediment organic carbon, while three metals (Zn, As, Hg) did not show significant relationships.

Pavlou and Weston (1984) derived sediment criteria from both acute and chronic water quality criteria, where available. However, acute sediment criteria are generally considered to be inappropriate because of the reasons cited by the authors:

- Sediment contaminant concentrations reflect long-term conditions and do not demonstrate the extreme temporal variability of water column concentrations.
- Benthic organisms often lack the mobility required to escape a contaminated environment and therefore are susceptible to impacts resulting from long-term chronic exposure.

Thermodynamic estimation of the movement of hydrophobic organics from sediment to water may create an unnecessarily high potential for error due to environmental variability (Peddicord and McFarland, personal communication). Hydrophobic organic compounds are predominantly associated with organic carbon in sediments. The solubility of hydrophobic organics in sediment organic carbon is much greater (orders of magnitude) than their solubility in water. Chemical solubility in any environmental compartment is affected by a variety of environmental factors, including pH, redox potential, temperature, salinity, suspended particulates, organic matter content, etc. Consequently, the effect of environmental variability on the solubility of hydrophobic organics is low compared to their solubility in organic carbon, but is very high compared to their aqueous solubility. Thus, there is a relatively high probability of significant error propagation associated with partitioning between sediment and water.

In contrast, the solubility of hydrophobic organic compounds in organic carbon is comparable to their solubility in lipid tissue. Hence, the probability of error associated with thermodynamic estimation of the movement of chemicals between sediment and tissue is relatively low. Karickhoff (1984) described a method by which the potential for bioaccumulation of hydrophobic organics can be estimated directly from sediment concentrations without using the aqueous phase as an intermediate step (see Section 2). Since hydrophobic organics in the sediment are primarily associated with organic carbon and those chemicals in biota are primarily

associated with lipid tissue, the thermodynamic potential for bioaccumulation can be estimated from the organic carbon content of the sediment (X_{oc}) the lipid content of the animal (X_l) and the lipid/organic carbon partition coefficient ($K_{oc,l}$):

$$K_{sb} = \frac{X_l}{X_{oc}} K_{oc,l} \tag{21}$$

EPA and the Corps of Engineers are working toward the development of sediment quality criteria, using the theory behind Equation 21.

Workers at the U.S. EPA Environmental Research Laboratory--Narragansett are developing a thermodynamic equilibrium model for predicting maximum residues of organic compounds accumulated by aquatic organisms exposed to dissolved and suspended particulate-bound contaminants (Lake et al., 1984). Based on the fugacity model described by Mackay (1979), Lake et al. (1984) suggest that the bioaccumulation factor (BAF), at thermodynamic equilibrium, may be defined as:

$$BAF = C_l^e/(C_w^e + C_{oc}^e) \tag{35}$$

where

C^e = equilibrium contaminant concentration in lipid (l), water (w), or organic carbon (oc)

Or, since the fugacity (escaping tendency) of a chemical in any phase is given by:

$$f_{phase} = x_{phase} \gamma_{phase} f_R \tag{36}$$

where

f = fugacity
x = mole fraction
γ = activity coefficient
f_R = reference fugacity

the concentration terms in Equation 35 can be converted to mole fractions and the expression for BAF can be rewritten as:

$$BAF = (\gamma_w + \gamma_{oc})/\gamma_l \tag{37}$$

For conditions in which the aqueous phase is not an important storage compartment, as with hydrophobic oranic chemicals, the BAF will depend only on the contaminant concentration in the organic carbon of suspended particulate material and in the lipids of biota. Thus, the thermodynamic maximum whole-body tissue concentration can be predicted by (Lake et al., 1984):

$$C_b^e = \frac{X_l}{X_{oc}} C_{SPM}^e \tag{38}$$

or, if the lipid/organic carbon partition coefficient ($K_{oc,l}$) were determined rather than being assumed approximately equal to one (Karickhoff, 1984):

$$C_b^e = \frac{X_l}{X_{oc}} K_{oc,l} C_{SPM}^e \tag{39}$$

where

C_b^e = contaminant concentration in the organism at equilibrium
C_{SPM}^e = contaminant concentration in the SPM at equilibrium
X_l = lipid weight of the organism

X_{oc} = organic carbon weight of the suspended solids

$K_{oc,l}$ = lipid/organic carbon partition coefficient

Karickhoff (1984) suggested that this model can be referenced to the sediment, for hydrophobic organics, by:

$$C_b^e = \frac{X_l}{X_{oc}} K_{oc,l} \frac{C_s^e}{1 + 1/\alpha_{SPM} K_{oc} X_{oc}} \tag{40}$$

where

C_s^e = contaminant concentration in sediment at equilibrium

α_{SPM} = suspended solids concentration

K_{oc} = sediment-organic-carbon/water partition coefficient

The simple partitioning model described by Lake et al. (Equation 38) is designed to estimate maximum concentrations of organic chemicals in biota. After the model is tested, the authors propose to use the model as a first level screen to assess the advisability of ocean disposal of a given waste (e.g., dredged material, sewage sludge). If the theory is correct, predicted maximum concentrations should be greater than, or at least equal to, residues accumulated in the environment, thereby providing a conservative estimate for environmental protection regulatory purposes.

Workers at the U.S. Army Engineer Waterways Experiment Station similarly are developing a method for establishing sediment quality criteria for hydrophobic and neutral organic compounds based on thermodynamic equilibrium (maximum) residues (Peddicord, 1984). Thermodynamic equilibrium concentrations are limited by the basic laws of thermodynamics and therefore cannot be exceeded in the environment. Thus, sediment quality criteria set as concentrations of contaminants in sediment which, at thermodynamic equilibirum, will not result in unacceptable residues in biota will insure that any sediment with chemical concentrations below the criteria is environmentally acceptable. Sediments with chemical concentrations above such criteria are potentially unacceptable, but because

thermodynamic equilibrium concentrations are seldom reached in the environment, more detailed investigation of bioaccumulation is necessary to assess their impact potential. Sediment quality criteria based on equilibrium partitioning can be expressed mathematically as (Peddicord, 1984):

$$\log SQC = (\log C_T - 2.28) + \log TOC \quad (41)$$

where

SQC = sediment quality criterion for the particular compound on total sediment, dry weight basis, in same units as C_T,

C_T = acceptable tissue concentration for the particular compound, expressed on a lipid basis,

TOC = percent (not decimal fraction) total organic carbon in the sediment in question,

2.28 = factor accounting for the relative activities of hydrophobic or neutral compounds in TOC and in lipid, and for expressing sediment concentrations on a % TOC basis.

As noted earlier, appropriate, acceptable tissue concentrations have not been established, and insufficient data are presently available to relate biological effects to contaminant residues. In the absense of an adequate data base on residue/effects, the COE has elected to use the product of an EPA chronic water quality criterion and an estimated BCF to calculate an acceptable tissue concentration (C_T) for a given chemical. Peddicord (1984) used the BCF - K_{OW} regression equation of Konemann and van Leeuwen (1980) to estimate BCF:

$$\log BCF = 0.980 \log K_{OW} - 0.063 \quad (42)$$

Thus, C_T can be estimated as:

$$\log C_T = 0.980 \log K_{OW} - 0.063 + \log WQC - 3.0 \quad (43)$$

where

C_T = acceptable tissue concentration for the compound expressed on a lipid basis in units of ug/kg,

K_{ow} = octanol-water partition coefficient for the compound of concern,

WQC = chronic water quality criterion for the compound in units of ug/l,

3.0 = factor to convert the equation to units of ug/l.

Combining Equations 41 and 43, a sediment quality criterion for a contaminant in a particular sediment can be calculated from the knowledge of the chronic water quality criterion and the octanol/water partition coefficient for the given chemical and the organic carbon content of the given sediment as follows:

$$\log SQC = (\log WQC + 0.980 \log K_{ow} - 5.346) + \log TOC \qquad (44)$$

where

SQC = sediment quality criterion for the compound of concern, dry weight basis, units of ug/kg,

WQC = water quality criterion for the compound of concern, units of ug/l,

K_{ow} = octanol/water partition coefficient for the compound of concern

TOC = total organic carbon content of the sediment, dry weight basis, units of % (not decimal fraction).

This procedure is part of a tiered approach to sediment assessment recommended by the COE (Peddicord and McFarland, personal communication) in which the thermodynamic equilibrium method expressed in Equation 44 is applied as the first tier screening level. If the contaminant concentration in the sediment of interest is lower than the concentration computed by Equation 44, the sediment is considered environmentally acceptable; if the ambient concentration is higher than the computed level, the sediment may or may not be acceptable. When the latter case exists, the sediment

must undergo tier 2 testing in which bioaccumulation potential is assessed via empirical steady-state exposure or kinetic modeling.

Peddicord (1984) noted that the weakest scientific point of the COE approach is the present need to use water quality criteria to estimate C_T, based on the assumption that chronic water quality criteria are comprehensively protective of all aspects of aquatic ecology. In addition, chronic criteria have only been established for a few hydrophobic or neutral organic chemicals.

It is important to note that the COE thermodynamic equilibrium approach can be used to develop sediment quality criteria only for hydrophobic or neutral organic compounds and cannot be used for inorganics, water soluble organics, or compounds which associate with sediment primarily via electrostatic interactions.

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APPENDIX A

ANALYSIS OF MEAN CONTAMINANT RESIDUES IN AQUATIC INVERTEBRATES OF THE NEW YORK BIGHT

TABLE A-1

CONTAMINANT RESIDUES IN NEW YORK BIGHT BIOTA

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
Clam, Butter (Saxidomus gigantea)	5	0.178	6	0.036	6				
Clam, Hard [Quahog] (Mercenaria mercenaria)	5	0.567	6	0.052	6				
	11					0.230	36		
	4	0.800	1						
Clam, Surf (Spisula solidissima)	7					0.020	1	0.018	1
	7					0.010	1	0.008	1
	7					0.010	1	0.015	1
	7					0.020	1	0.026	1
	7					0.040	1	0.055	1
	7					0.020	1	0.069	1
	7					0.040	1	0.090	1
	7					0.040	1	0.015	1
	7					0.020	1	0.025	1
	7					0.030	1	0.018	1
	7					0.070	1	0.053	1
	7					0.070	1	0.036	1
	12	0.130	6						
	12	0.130	11						
	12	0.150	11						
	11					0.360	6		
	3					0.004	1		
	3					0.033	3		
	3					0.030	2		
	3					0.025	2		
	3					0.049	1		
	3					0.030	6		
	3					0.070	2		
	4	0.100	1						
	4	0.130	1						
	9							0.012	1
	9							0.004	1
	13	0.040	1						
	13	0.050	1						
	13	0.060	1						
Crab (Cancer sp.)	2					0.002	4	0.000	4
Crab, Blue (Callinectes sapidus)	11					0.320	14		
Crab, Dungeness (Cancer magister)	5	0.175	2	0.375	2				
Crab, King (Paralithodes camschatica)	5	0.242	9	0.128	9				
Crab, Rock (Cancer irroratus)	5	0.140	1	0.330	1				
	5	0.210	1	0.240	1				
	5	0.550	1	0.140	1				
	7					0.030	1	0.094	1
	7					0.070	1	0.051	1
	7					0.060	1	0.051	1
	7					0.040	1	0.047	1
	7					0.040	1	0.039	1
	7					0.060	1	0.073	1
	7					0.040	1	0.039	1

TABLE A-1 (Continued)

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
	7					0.020	1	0.017	1
	7					0.000	1	0.009	1
	2					0.043	12	0.025	12
	6	0.120	1			0.203	1		
	6	0.130	1			0.229	1		
	6	0.080	1	0.100	1	0.385	1		
	6	0.130	1	0.190	1	0.287	1		
	6	0.010	1			0.546	1		
	10					0.410	1	0.041	1
	10					0.500	1	0.047	1
	3					0.340	1		
	3					0.003	1		
	3					1.813	1		
	3					0.793	1		
	3					0.050	2		
	3					0.418	4		
	3					0.041	1		
	3					0.030	1		
	3					0.460	1		
	3					0.003	1		
	3					0.019	1		
	3					0.047	1		
	4	0.640	1						
	4			0.190	1				
	4			0.030	1				
	13	0.080	1						
	13	0.100	1						
	13	0.080	1						
Lobster, American (Homarus americanus)	7					0.040	1	0.050	1
	7					0.040	1	0.100	1
	7					0.040	1	0.060	1
	7					0.040	1	0.035	1
	7					0.001	1	0.002	1
	7					0.020	1	0.044	1
	2					0.095	6	0.024	6
	2					0.150	3	0.050	3
	11					0.130	1		
	11					0.150	1		
	8	0.014	1	0.190	1	0.070	1		
	8	0.024	1	0.120	1	0.120	1		
	8	0.018	1	0.180	1	0.200	1		
	8	0.015	1	0.130	1	0.230	1		
	8	0.017	1	0.080	1	0.120	1		
	8	0.015	1	0.080	1	0.160	1		
	8	0.023	1	0.170	1	0.130	1		
	8	0.024	1	0.310	1	0.070	1		
	8	0.011	1	0.130	1	0.094	1		
	8	0.017	1	0.140	1	0.083	1		

TABLE A-1 (Continued)

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
	8	0.018	1	0.200	1	0.100	1		
	8	0.017	1	0.130	1	0.079	1		
	8	0.018	1	0.340	1	0.220	1		
	8	0.021	1	0.160	1	0.095	1		
	8	0.023	1	0.150	1	0.260	1		
	8	0.016	1	0.260	1	0.210	1		
	8	0.017	1	0.230	1	0.140	1		
	8	0.012	1	0.260	1	0.150	1		
	8	0.012	1	0.150	1	0.062	1		
	8	0.020	1	0.370	1	0.190	1		
	3					0.040	1		
	3					0.151	10		
	3					0.145	10		
	4	0.140	1						
	4	1.080	1						
	4			0.034	1				
	4			0.320	1				
	9					0.030	1		
	9							0.007	1
	13	0.160	1						
	13	0.140	1						
	13	0.070	1						
	13	0.070	1						
	13	0.120	1						
	13	0.090	1						
	13	0.080	1						
	13	0.150	1						
	13	0.080	1						
	13	0.070	1						
Lobster, Spiny [Alt.] (Panulirus argus)	5	0.058	10	0.061	10				
Mussel, Blue (Mytilus edulis)	7					0.050	1	0.232	1
	7					0.200	1	0.240	1
	7					0.200	1	0.510	1
	7					0.090	1	0.150	1
	7					0.200	1	0.000	1
	7					0.400	1	0.070	1
	7					0.030	1	0.170	1
	7					0.200	1	0.260	1
	7					0.100	1	0.290	1
	7					0.070	1	0.270	1
	7					0.800	1	0.600	1
	7					0.300	1	0.230	1
	7					0.400	1	0.340	1
	7					0.400	1	0.370	1
	7					0.400	1	0.310	1
	7					0.100	1	0.211	1
	7					0.200	1	0.190	1
	7					0.200	1	0.110	1

TABLE A-1 (Continued)

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
	7					0.320	1	0.246	1
	11					0.000	36		
	3					0.130	1		
	3					0.210	1		
	3					0.050	2		
	3					0.210	1		
	3					0.140	2		
	3					0.450	1		
	3					0.447	3		
Oyster, American (Crassostrea virginica)	11					0.340	36		
	4	2.900	1						
Oyster, Giant [Pac.] (Crassostrea gigas)	5	2.812	10	0.038	10				
Polychaete worm	7					0.200	1	0.032	1
Polychaete worm (Ceriantheopsis americanus)	10					0.300	1	0.041	1
Polychaete worm (Glycera dibranchiata)	10	0.260	1						
Polychaete worm (Haplosoloplos robustus)	10	0.070	1	0.142	1				
Polychaete worm (Lumbrinereis fragilis)	10					0.201	1	0.029	1
	10					0.710	1	0.083	1
	10					0.188	1	0.007	1
	10	0.130	1	0.077	1				
Polychaete worm (Lumbrinereis tenuis)	10					0.188	1	0.007	1
Polychaete worm (Nepthys bucera)	10	0.290	1	0.073	1				
	10	0.100	1	0.052	1				
Polychaete worm (Nepthys incisa)	10	0.290	1	0.073	1				
	10	0.180	1						
	10					0.830	1	0.093	1
	10					0.760	1	0.024	1
	10					1.970	1	0.074	1
	10					1.020	1	0.112	1
	10	0.130	1	0.058	1				
Polychaete worm (Nepthys picta)	10	0.100	1	0.052	1				
Polychaete worm (Nereis virens)	10	0.710	1	0.021	1				
Polychaete worm (Ninoe nigripes)	10	0.060	1	0.660	1				
	10					1.230	1	0.143	1
Polychaete worm (Ophioglycera gigantea)	10					1.270	1	0.039	1
Polychaete worm (Pherusa affinis)	10	0.060	1						
	10	0.190	1						
	10	0.060	1	0.032	1				
	10	0.250	1	0.086	1				
	10	0.180	1						
	10	0.380	1	0.154	1				
	10	0.300	1	0.070	1				
Polychaete worm (Travisia carnea)	10	0.070	1						
Polychaete worm(Nepthys sp.+Pherusa affinis)	1					0.099	1	0.018	1
	1					0.214	1	0.019	1
	1					0.134	1	0.005	1
	1					0.216	1	0.009	1
	1					0.185	1	0.009	1

TABLE A-1 (Continued)

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
	1					0.254	1	0.016	1
	1					0.263	1	0.013	1
	1					0.712	1	0.016	1
	1					0.145	1		
Quahogs, Ocean (Artica islandica)	12	0.540	8						
	12	0.420	15						
	12	0.420	9						
	12	0.390	9						
	4	0.540	1						
	13	0.250	1						
	13	0.160	1						
	13	0.470	1						
	13	0.220	1						
	13	0.230	1						
	13	0.170	1						
	13	0.320	1						
	13	0.210	1						
	13	0.220	1						
	13	0.160	1						
	13	0.210	1						
	13	0.300	1						
	13	0.220	1						
	13	0.240	1						
	13	0.160	1						
	13	0.200	1						
	13	0.090	1						
	13	0.040	1						
	13	0.380	1						
	13	0.240	1						
	13	0.400	1						
	13	0.230	1						
	13	0.140	1						
	13	0.580	1						
	13	0.080	1						
	13	0.060	1						
	13	0.470	1						
	13	0.820	1						
	13	0.340	1						
	13	0.350	1						
	13	0.490	1						
	13	0.370	1						
	13	0.460	1						
	13	0.450	1						
	13	0.480	1						
	13	0.280	1						
	13	0.610	1						
	13	0.290	1						
	13	0.800	1						

TABLE A-1 (Continued)

SPECIES	REF	CADMIUM		MERCURY		PCBs		DDTs	
		mean	n	mean	n	mean	n	mean	n
	13	0.500	1						
	13	0.260	1						
	13	0.710	1						
	13	0.620	1						
	13	0.620	1						
	13	0.450	1						
	13	0.220	1						
	13	0.180	1						
	13	0.440	1						
	13	0.330	1						
	13	0.310	1						
Scallop, Sea (Palctopecten magillanicus)	7					0.030	1	0.060	1
	7					0.020	1	0.050	1
	7					0.010	1	0.004	1
	7					0.020	1	0.050	1
	2					0.001	5	0.000	5
	13	0.320	1						
	13	0.360	1						
	13	0.070	1						
	13	0.180	1						
	13	0.130	1						
	13	0.090	1						
	13	0.210	1						
	13	0.190	1						
	13	0.080	1						
Shrimp, Alaskan (Pandalopsis dispar)	5	0.085	10	0.040	10				
Shrimp, Grass (Palaemonetes pugio)	7					0.190	1	0.094	1
Squid, Longfinned [Alt.] (Loligo pealii)	5	0.145	2	0.000	2				
	5	0.155	3	0.030	3				
	5	0.158	13	0.048	13				
	5	0.168	5	0.023	5				
Squid, Shortfinned (Illex illecebrosus)	5	0.150	2	0.120	2				
	5	0.179	4	0.135	4				
Average Concentration		0.337		0.099		0.193		0.073	

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