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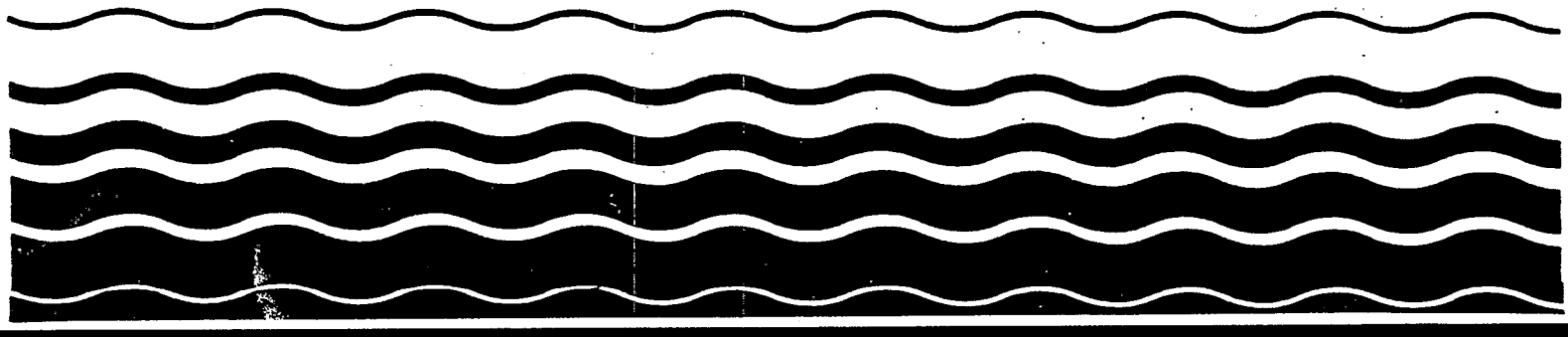
Sediment Quality Criteria for the Protection of Benthic Organisms:

PHENANTHRENE



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FOREWORD

Under the Clean Water Act (CWA) the U.S. Environmental Protection Agency (U.S. EPA) and the States develop programs for protecting the chemical, physical, and biological integrity of the nation's waters. Section 304(a)(1) directs the Administrator to develop and publish "criteria" reflecting the latest scientific knowledge on: (1) the kind and extent of effects on human health and welfare, including effects on plankton, fish, shellfish, and wildlife, which may be expected from the presence of pollutants in any body of water, including ground water, (2) the concentration and dispersal of pollutants, or their byproducts, through biological, physical and chemical processes, and (3) the effects of pollutants on biological community diversity, productivity, and stability. Section 304(a)(2) directs the Administrator to develop and publish information on, among other things, the factors necessary for the protection and propagation of shellfish, fish, and wildlife for classes and categories of receiving waters.

To meet this objective, U.S. EPA has periodically issued ambient water quality criteria (WQC) guidance beginning with the publication of "Water Quality Criteria 1972" (NAS/NAE, 1973). All criteria guidance through late 1986 was summarized in an U.S. EPA document entitled "Quality Criteria for Water, 1986" (U.S. EPA, 1987). Additional WQC documents that update criteria for selected chemicals and provide new criteria for other pollutants have also been published. In addition to the development of WQC and to continue to comply with the mandate of the CWA, U.S. EPA has conducted efforts to develop and publish sediment quality criteria (SQC) for some of the 65 toxic pollutants or toxic pollutant categories. Section 104 of the CWA authorizes the administrator to conduct and promote research into the causes, effects, extent, prevention, reduction and elimination of pollution, and to publish relevant information. Section 104(n)(1) in particular provides for study of the effects of pollution, including sedimentation in estuaries, on aquatic life, wildlife, and recreation. U.S. EPA's efforts with respect to sediment criteria are also authorized under CWA Section 304(a).

Toxic contaminants in bottom sediments of the nations's lakes, rivers, wetlands, and coastal waters create the potential for continued environmental degradation even where water column contaminant levels meet established WQC. In addition, contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased. EPA intends SQC be used to assess the extent of sediment contamination, to aid in implementing measures to limit or prevent additional contamination, and to identify and implement appropriate remediation activities when needed.

The criteria presented in this document are the U.S. EPA's best recommendation of the concentrations of a substance that may be present in sediment while still protecting benthic organisms from the effects of that substance. These criteria are applicable to a variety of freshwater and marine sediments because they are based on the biologically available concentration of the substance in sediments. These criteria do not protect against additive, synergistic or antagonistic effects of contaminants or bioaccumulative effects to aquatic life, wildlife or human health.

The criteria derivation methods outlined in this document are proposed to provide protection of benthic organisms from biological impacts from chemicals present in sediments. Guidelines and guidance are being developed by U.S. EPA to assist in the application of criteria presented in this document, in the development of sediment quality standards, and in other water-related programs of this Agency.

These criteria are being issued in support of U.S. EPA'S regulations and policy initiatives. This document is Agency guidance only. It does not establish or affect legal rights or obligations. It does not establish a binding norm and is not finally determinative of the issues addressed. Agency decisions in any particular case will be made by applying the law and regulations on the basis of the specific facts.

ACKNOWLEDGEMENTS

Principal Author

David J. Hansen	U.S. EPA, Environmental Research Laboratory, Narragansett, RI

Coauthors

Walter J. Berry	Science Applications International Corporation, Narragansett, RI
Dominic M. Di Toro	Manhattan College, Bronx, NY; HydroQual, Inc., Mahwah, NJ
Paul R.Paquin	HydroQual, Inc., Mahwah, NJ
Laurie D. De Rosa	HydroQual, Inc., Mahwah, NJ
Frank E. Stancil, Jr.	U.S. Environmental Research Laboratory, Athens, GA
Christopher S. Zarba	U.S. EPA Headquarters, Office of Water, Washington, DC

Technical and Clerical Support

Heinz P. Kollig	U.S. Environmental Research Laboratory, Athens, GA
Glen B. Thursby	Science Applications International Corporation Narragansett, RI
Maria R. Paruta	NCSC Senior Environmental Employment Program Narragansett, RI
Dinalyn Spears	Computer Science Corporation, Narragansett, RI
BettyAnne Rogers	Science Applications International Corporation Narragansett, RI

Persons who have made significant contributions to the development of the approach and supporting science used in the derivation of sediment criteria for non-ionic organic contaminants are as follows:

Herbert E. Allen	University of Delaware, Newark, DE
Gerald T. Ankley	U.S. EPA, Environmental Research Laboratory, Duluth, MN
Christina E. Cowan	Battelle, Richland, WA
Dominic M. Di Toro	HydroQual, Inc., Mahwah, NJ; Manhattan College, Bronx, NY
David J. Hansen	U.S. EPA, Environmental Research Laboratory, Narragansett, RI
Paul R. Paquin	HydroQual, Inc., Mahwah, NJ
Spyros P. Pavlou	Ebasco Environmental, Bellevue, WA
Richard C. Swartz	U.S. EPA, Environmental Research Laboratory, Newport,OR
Nelson A. Thomas	U.S. EPA, Environmental Research Laboratory, Duluth, MN
Christopher S. Zarba	U.S. EPA Headquarters, Office of Water, Washington, DC

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DISCLAIMER

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

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SECTION 1

INTRODUCTION

1.1 GENERAL INFORMATION:

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

Toxic pollutants in bottom sediments of the nation's lakes, rivers, wetlands, estuaries and marine coastal waters create the potential for continued environmental degradation even where water-column concentrations comply with established WQC. In addition, contaminated sediments can be a significant pollutant source that may cause water quality degradation to persist, even when other pollutant sources are stopped. The absence of defensible sediment quality criteria (SQC) makes it difficult to accurately assess the extent of the ecological risks of contaminated sediments and to identify, prioritize and implement appropriate clean up activities

and source controls. As a result of the need for a procedure to assist regulatory agencies in making decisions concerning contaminated sediment problems, a U.S. EPA Office of Science and Technology, Health and Ecological Criteria Division (OST/HEC) research team was established to review alternative approaches (Chapman, 1987). All of the approaches reviewed had both strengths and weaknesses and no single approach was found to be applicable for SQC derivation in all situations (U.S. EPA, 1989a). The equilibrium partitioning (EqP) approach was selected for non-ionic organic chemicals because it presented the greatest promise for generating defensible national numerical chemical-specific SQC applicable across a broad range of sediment types. The three principal observations that underlie the EqP method of establishing SQC are:

1. The concentrations of non-ionic organic chemicals in sediments, expressed on an organic carbon basis, and in pore waters correlate to observed biological effects on sediment dwelling organisms across a range of sediments.
2. Partitioning models can relate sediment concentrations for non-ionic organic chemicals on an organic carbon basis to freely dissolved concentrations in pore water.
3. The distribution of sensitivities of benthic and water column organisms to chemicals are similar; thus, the currently established WQC final chronic values (FCV) can be used to define the acceptable effects concentration of a chemical freely-dissolved in pore water.

The EqP approach, therefore, assumes that: (1) the partitioning of the chemical between sediment organic carbon and interstitial water is at equilibrium; (2) the concentration in either phase can be predicted using appropriate partition coefficients and the measured concentration

in the other phase; (3) organisms receive equivalent exposure from water-only exposures or from any equilibrated phase: either from pore water via respiration, sediment via ingestion, sediment-integument exchange, or from a mixture of exposure routes; (4) for non-ionic chemicals, effect concentrations in sediments on an organic carbon basis can be predicted using the organic carbon partition coefficient (K_{oc}) and effects concentrations in water; (5) the FCV concentration is an appropriate effects concentration for freely-dissolved chemical in interstitial water; and (6) the SQC ($\mu g/g_{oc}$) derived as the product of the K_{oc} and FCV is protective of benthic organisms. SQC concentrations presented in this document are expressed as μg chemical/g sediment organic carbon and not on an interstitial water basis because: (1) pore water is difficult to adequately sample; and (2) significant amounts of the dissolved chemical may be associated with dissolved organic carbon; thus, total chemical concentrations in interstitial water may overestimate exposure.

The data that support the EqP approach for deriving SQC for non-ionic organic chemicals are reviewed by Di Toro et al. (1991) and in the SQC guidelines (U.S. EPA, 1993a). Data supporting these observations for phenanthrene are presented in this document.

SQC generated using the EqP method are suitable for use in providing guidance to regulatory agencies because they are:

1. numerical values;
2. chemical specific;
3. applicable to most sediments;
4. predictive of biological effects; and
5. protective of benthic organisms.

As is the case with WQC, the SQC reflect the use of available scientific data to: (1) assess the likelihood of significant environmental effects to benthic organisms from chemicals in sediments; and (2) to derive regulatory requirements which will protect against these effects.

It should be emphasized that these criteria are intended to protect benthic organisms from the effects of chemicals associated with sediments. SQC are intended to apply to sediments permanently inundated with water, intertidal sediment and to sediments inundated periodically for durations sufficient to permit development of benthic assemblages. They do not apply to occasionally inundated soils containing terrestrial organisms. These criteria do not address the question of possible contamination of upper trophic level organisms or the synergistic, additive or antagonistic effects of multiple chemicals. SQC addressing these issues may result in values lower or higher than those presented in this document. The SQC presented in this document represent the U.S. EPA's best recommendation at this time of the concentration of a chemical in sediment that will not adversely affect most benthic organisms. SQC values may be adjusted to account for future data or site specific considerations.

SQC values may also need to be adjusted because of site specific considerations. In spill situations, where chemical equilibrium between water and sediments has not yet been reached, sediment chemical concentrations less than SQC may pose risks to benthic organisms. This is because for spills, disequilibrium concentrations in interstitial and overlying water may be proportionally higher relative to sediment concentrations. Research has shown that the source or "quality" of TOC in the sediment does not effect chemical binding (De Witt et al., 1992). However, the physical form of the chemical in the sediment may have an effect. At some sites concentrations in excess of the SQC may not pose risks to benthic organisms, because the

compound may be a component of a particulate, such as coal or soot, or exceed solubility such as undissolved oil. In these situations, the national SQC would be overly protective of benthic organisms and should not be used unless modified using the procedures outlined in the "Guidelines for Deriving Site-specific Sediment Quality Criteria for the Protection of Benthic Organisms" (U.S. EPA, 1993b). The SQC may be underprotective where the toxicity of other chemicals are additive with the SQC chemical or species of unusual sensitivity occur at the site.

This document presents the theoretical basis and the supporting data relevant to the derivation of the SQC for phenanthrene. An understanding of the "Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and Their Uses" (Stephan et al., 1985), response to public comment (U.S. EPA, 1985) and "Technical Basis for Deriving Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic Organisms by Using Equilibrium Partitioning " (U.S. EPA, 1993a) is necessary in order to understand the following text, tables and calculations. Guidance into the acceptable use of SQC values is contained in "Guide for the Use and Application of Sediment Quality Criteria for Nonionic Organic Chemicals" (U.S. EPA, 1993c).

1.2 GENERAL INFORMATION: PHENANTHRENE

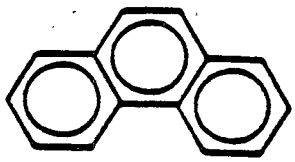
Phenanthrene is a member of the polycyclic aromatic hydrocarbon (PAH) group of organic compounds. Phenanthrene is produced by fractional distillation of high-boiling coal-tar oil and the subsequent purification of the crystalline solid (Hawley, 1981). Some uses of phenanthrene are in the manufacturing of dyestuffs and explosives, in the synthesis of drugs and in biochemical research (Verschueren, 1983). Some PAHs are of environmental concern because

they are known to be carcinogens and/or mutagens (Brookes, 1977). With an increase in fossil fuel consumption in the United States an increase in emissions of PAHs to the environment can be expected over the next several decades (Eadie et al., 1982).

Phenanthrene has a three ring structure and exists as colorless leaflets (Figure 1-1). It has a solubility in water at 25°C of 1.18 mg/L and is a solid at room temperature (melting point of 100.85°C) (Miller et al., 1985). Phenanthrene has a reported vapor pressure of 69.3 - 110.6 mPa at 25°C (Bidleman, 1984). Two significant processes which can influence the fate of phenanthrene in the sediment are sorption and biodegradation (U.S. EPA, 1980). Sorption of phenathrene onto solids in the water column and subsequent settling, as well as partitioning onto organics in the sediment, can significantly affect phenanthrene transport. Bioaccumulated PAHs with 4 rings or less are rapidly metabolized. Therefore, long-term partitioning into biota is not considered a significant fate process (U.S. EPA, 1980). Other processes found to have little or no effect on the fate of phenanthrene in the sediment are oxidation, hydrolysis and volatilization (U.S. EPA, 1980).

The acute toxicity of phenanthrene ranges from 96 to > 1150 ug/L for freshwater and 21.9 to 600 μg/L for saltwater organisms (Appendix A). Differences between phenanthrene concentrations causing acute lethality and chronic toxicity in invertebrates are small; acute-chronic ratios range from 1.2 to 3.3 for two species. The only available acute-chronic ratio for a fish, rainbow trout, is 59 (Table 3-3). Although phenanthrene bioaccumulates in aquatic biota, the associated health or ecological risks are unknown.

1.3 OVERVIEW OF DOCUMENT:



MOLECULAR FORMULA	$C_{14}H_{10}$
MOLECULAR WEIGHT	178.22
DENSITY	1.179 g/cc (25°C)
MELTING POINT	100.85°C
PHYSICAL FORM	Colorless leaflets
VAPOR PRESSURE	69.3 - 110.6 mPa (25°C)
CAS NUMBER:	85-01-8
CHEMICAL NAME:	Phenanthrene

FIGURE 1-1. Chemical structure and physical-chemical properties of phenanthrene.

1.3 OVERVIEW OF DOCUMENT:

Section 1 provides a brief review of the EqP methodology, and a summary of the physical-chemical properties and aquatic toxicity of phenanthrene. Section 2 reviews a variety of methods and data useful in deriving partition coefficients for phenanthrene and includes the K_{OC} recommended for use in the derivation of the phenanthrene SQC. Section 3 reviews aquatic toxicity data contained in the phenanthrene WQC document (U.S. EPA, 1980) and new data that were used to derive the FCV used in this document to derive the SQC concentration. In addition, the comparative sensitivity of benthic and water column species is examined as the justification for the use of the FCV for phenanthrene in the derivation of the SQC. Section 4 reviews data on the toxicity of phenanthrene in sediments, the need for organic carbon normalization of phenanthrene sediment concentrations and the accuracy of the EqP prediction of sediment toxicity using K_{OC} and an effect concentration in water. Data from Sections 2, 3 and 4 are used in Section 5 as the basis for the derivation of the SQC for phenanthrene and its uncertainty. The SQC for phenanthrene is then compared to STORET (U.S. EPA, 1989b) and National Status and Trends (NOAA, 1991) data on phenanthrene's environmental occurrence in sediments. Section 6 concludes with the criteria statement for phenanthrene. The references used in this document are listed in Section 7.

SECTION 2

PARTITIONING

2.1 DESCRIPTION OF THE EQUILIBRIUM PARTITIONING METHODOLOGY:

Sediment quality criteria (SQC) are the numerical concentrations of individual chemicals which are intended to be predictive of biological effects, protective of the presence of benthic organisms and applicable to the range of natural sediments from lakes, streams, estuaries and near coastal marine waters. As a consequence, they can be used in much the same way as water quality criteria (WQC); ie., the concentration of a chemical which is protective of the intended use such as aquatic life protection. For non-ionic organic chemicals, SQC are expressed as μg chemical/g organic carbon and apply to sediments having $\geq$ 0.2% organic carbon by dry weight. A brief overview follows of the concepts which underlie the equilibrium partitioning (EqP) methodology for deriving SQC. The methodology is discussed in detail in the "Technical Basis for Deriving Numerical Sediment Quality Criteria for Non-ionic Organic Contaminants for the protection of Benthic Organisms by Using Equilibrium Partitioning" (U.S. EPA, 1993a), hereafter referred to as the SQC Technical Basis Document.

Bioavailability of a chemical at a particular sediment concentration often differs from one sediment type to another. Therefore, a method is necessary for determining a SQC based on the bioavailable chemical fraction in a sediment. For non-ionic organic chemicals, the concentration-response relationship for the biological effect of concern can most often be correlated with the interstitial water (i.e., pore water) concentration (μg chemical/liter pore water) and not to the sediment chemical concentration (μg chemical/g sediment) (Di Toro et al.,

1991). From a purely practical point of view, this correlation suggests that if it were possible to measure the pore water chemical concentration, or predict it from the total sediment concentration and the relevant sediment properties, then that concentration could be used to quantify the exposure concentration for an organism. Thus, knowledge of the partitioning of chemicals between the solid and liquid phases in a sediment is a necessary component for establishing SQC. It is for this reason that the methodology described below is called the equilibrium partitioning (EqP) method.

It is shown in the SQC Technical Basis Document (U.S. EPA, 1993a) that the final acute values (FAVs) in the WQC documents are appropriate for benthic species for a wide range of chemicals. (The data showing this for phenanthrene are presented in Section 3). Thus, a SQC can be established using the final chronic value (FCV) derived using the WQC Guidelines (Stephan et al., 1985) as the acceptable effect concentration in pore or overlying water (see Section 5), and the partition coefficient can be used to relate the pore water concentration to the sediment concentration via the partitioning equation. This acceptable concentration in sediment is the SQC.

The calculation is as follows: Let FCV (μg/L) be the acceptable concentration in water for the chemical of interest; then compute the SQC using the partition coefficient, (K_p) ($L/Kg_{sediment}$), between sediment and water:

$$SQC = K_p FCV \qquad (2\text{-}1)$$

This is the fundamental equation used to generate the SQC. Its utility depends upon the existence of a methodology for quantifying the partition coefficient, K_p.

Organic carbon appears to be the dominant sorption phase for nonionic organic chemicals

in naturally occurring sediments and thus controls the bioavailability of these compounds in sediments. Evidence for this can be found in numerous toxicity tests, bioaccumulation studies and chemical analyses of pore water and sediments (Di Toro et al., 1991). The evidence for phenanthrene is discussed in this section and section 4. The organic carbon binding of a chemical in sediment is a function of that chemical's organic carbon partition coefficient (K_{oc}) and the weight fraction of organic carbon in the sediment (f_{oc}). The relationship is as follows:

$$K_P = f_{oc} K_{oc} \qquad (2\text{-}2)$$

It follows that:

$$SQC_{oc} = K_{oc} FCV \qquad (2\text{-}3)$$

where SQC_{oc} is the sediment quality criterion on a sediment organic carbon basis.

K_{oc} is not usually measured directly (although it can be done, see section 2.3). Fortunately, K_{oc} is closely related to the octanol-water partition coefficient (K_{ow}) (equation 2-5) which has been measured for many compounds, and can be measured very accurately. The next section reviews the available information on the K_{ow} for phenanthrene.

2.2 DETERMINATION OF K_{ow} FOR PHENANTHRENE:

Several approaches have been used to determine K_{ow} for the derivation of SQC, as discussed in the SQC Technical Basis Document. At the U.S. EPA, Environmental Research Laboratory at Athens, GA (ERL,A) two methods were selected for measurement and two for estimation of K_{ow}. The measurement methods were shake-centrifugation (SC), generator column

(GCol) and the estimation methods were SPARC (SPARC Performs Automated Reasoning in Chemistry; Karickhoff et al., 1989) and CLOGP (Chou and Jurs, 1979). Data were also extracted from the literature. The SC method is a standard procedure in the Organization for Economic Cooperation and Development (OECD) guidelines for testing chemicals, therefore it has regulatory precedence.

In the examination of the literature data primary references were found listing measured $\log_{10}K_{ow}$ values for phenanthrene ranging from 4.28 to 4.63 (Table 2-1). Primary references were found in the literature for estimated $\log_{10}K_{ow}$ values ranging from 4.44 to 4.64 (Table 2-1). Although the range of reported values for phenanthrene is significantly lower than the range of values for some other compounds, it is relatively large, and we were not able to determine from studying the primary articles that any value was more likely to be accurate than any other.

TABLE 2-1. PHENANTHRENE MEASURED AND ESTIMATED $LOG_{10}K_{ow}$ VALUES.

METHOD	$LOG_{10}K_{ow}$	REFERENCE
Measured	4.28	Haky and Young, 1984
Measured	4.46	Hansch and Fujita, 1964
Measured	4.56	De Bruijn et al., 1989
Measured	4.57	Karickhoff et al., 1979
Measured	4.63	Bruggeman et al., 1989
Estimated	4.44	Kamlet et al., 1988
Estimated	4.45	Mabey et al., 1982
Estimated	4.49	CLOGP[a]
Estimated	4.58	SPARC[b]
Estimated	4.63	Mackay et al., 1980
Estimated	4.64	Yalkowsky et al., 1983

aCLOGP is an algorithm that is included in the database QSAR located at the U.S. EPA, Environmental Research Lab., Duluth, MN (Chou and Jurs, 1979).
bSPARC is from SPARC Performs Automated Reasoning in Chemistry, (Karickhoff et al., 1989).

K_{ow} values for SPARC and CLOGP are also included in Table 2-1. SPARC is a computer expert system under development at ERL,A, and the University of Georgia, at Athens. The CLOGP algorithm is included in the database QSAR located at EPA's Environmental Research Laboratory (ERL,D) at Duluth, Minnesota. For more information on SPARC and CLOGP see U.S. EPA (1993a). The SPARC estimated $\log_{10}K_{ow}$ value for phenanthrene is 4.58. The CLOGP program estimate of the $\log_{10}K_{ow}$ value for phenanthrene using structure activity relationships is 4.49. We had little confidence in the available measured or estimated values for K_{ow}, therefore the SC, GCol, SSF methods were used to provide additional data from which to define K_{ow} for phenanthrene (Table 2-2). The SC method yielded a $\log_{10}K_{ow} = 4.30$ (n=4), the GCol method yielded a $\log_{10}K_{ow} = 4.40$ (n=4), and the SSF method yielded a $\log_{10}K_{ow} = 4.54$ (n=3). Comparison of the results from the SC, GCol, SSF and SPARC K_{ow} determination methods for the five chemicals for which SQC are currently being developed (acenaphthene, dieldrin, endrin, fluoranthene and phenanthrene) indicate that the SSF method provides the best estimate of K_{ow} (U.S. EPA, 1993a). The SSF method had less variability, less experimental bias (Bias is defined as the mean difference between the best-fit estimate of K_{ow} using all four methods and the estimates from each method.) and was generally in the range of the SC, GCol, and SPARC methods (U.S. EPA, 1993a). Therefore, the SSF value of 4.54 is the value for $\log_{10}K_{ow}$ recommended for SQC derivation. This value agrees with the SPARC estimated value and the average of the values measured by the three methods under carefully controlled conditions at ERL,A. This K_{ow} is the logarithm of the mean of three K_{ow} measurements made by SSF. The logs of the K_{ow} values measured by SSF range from 4.50 to 4.57.

TABLE 2-2. SUMMARY OF $LOG_{10}K_{ow}$ VALUES FOR PHENANTHRENE MEASURED BY THE U.S. EPA, ENVIRONMENTAL RESEARCH LABORATORY, ATHENS, GA.

SHAKE-CENTRIFUGATION	GENERATOR COLUMN	SLOW STIR FLASK
4.29	4.47	4.57
4.25	4.41	4.53
4.33	4.46	4.50
4.33	4.24	
4.30[a]	4.40[a]	4.54[a]

[a] Log_{10} of mean of measured values.

2.3 DERIVATION OF K_{oc} FROM ADSORPTION STUDIES:

Several types of experimental measurement of the K_{oc} are available. The first type involves experiments which were designed to measure the partition coefficient in particle suspensions. The second type of measurement is from sediment toxicity tests in which measurements of sediment phenanthrene, sediment organic carbon (OC), and non-dissolved organic carbon (DOC) associated phenanthrene dissolved in pore were used to compute K_{oc}.

2.3.1 K_{oc} FROM PARTICLE SUSPENSION STUDIES:

Laboratory studies to characterize adsorption are generally conducted using particle suspensions. The high concentrations of solids and turbulent conditions necessary to keep the mixture in suspension make data interpretation difficult as a result of a particle interaction effect. This effect suppresses the partition coefficient relative to that observed for undisturbed sediments (Di Toro, 1985; Mackay and Powers, 1987).

Based on analysis of an extensive body of experimental data for a wide range of

compound types and experimental conditions, the particle interaction model (Di Toro, 1985) yields the following relationship for estimating K_P:

$$K_P = \frac{f_{OC} K_{OC}}{1 + m f_{OC} K_{OC} / \upsilon_X} \qquad (2\text{-}4)$$

where m is the particle concentration in the suspension (kg/L), and $\upsilon_X = 1.4$, an empirical constant.

In this expression the KOC is given by:

$$\log_{10} K_{OC} = 0.00028 + 0.983 \log_{10} K_{OW} \qquad (2\text{-}5)$$

A sorption isotherm experiment that demonstrates the effect of particle suspensions was found in a comprehensive literature search for partitioning information for phenanthrene (Table 2-2) (Magee et al., 1991). The experiment showed an observed K_P of 12.9 L/kg for a phenanthrene solution and sand with 0.11% organic carbon content. Calculated K_P using K_{OC} (Equation 2-5) and f_{OC} is 21 L/kg. The difference between the observed and calculated K_P can be explained by particle interaction effects. Particle interaction results in a lower observed partition coefficient. The particle interaction model (Equation 2-4) predicts K_P of 8.29 L/kg, which is in agreement with the observed K_P. $Log_{10}K_{OC}$ computed from observed K_P and f_{OC} is 4.07. This value is lower than K_{OC} from laboratory measurements due to particle interaction effects. This data is presented as an example of particle interaction effects only, as 100 percent reversibility is assumed in the absence of a desorption study and an actual K_{OC} can not be computed.

In the absence of particle effects, K_{OC} is related to K_{OW} via Equation 2-5. For $\log_{10}K_{OW}$ = 4.36 (ERL,A, mean measured value), this expression results in an estimate of $\log_{10}K_{OC}$ =

4.29.

TABLE 2-3. SUMMARY OF K_{OC} VALUES FOR PHENANTHRENE DERIVED FROM LITERATURE SORPTION ISOTHERM DATA.

Observed $Log_{10}K_{OC}$	n	Solids (g/L)	References
4.07	1	100	Magee et al., 1991

2.3.2 K_{OC} FROM SEDIMENT TOXICITY TESTS:

Measurements of K_{OC} are available from sediment toxicity tests using phenanthrene (Swartz, 1991). These tests are from three marine sediments having a range of organic carbon contents of 0.82 to 3.6 percent (Table 4-1; Appendix B). Phenanthrene concentrations were measured in the sediment and pore waters providing the data necessary to calculate the partition coefficient for an undisturbed bedded sediment.

The upper panel or Figure 2-1 is a plot of the organic carbon-normalized sorption isotherm for phenanthrene, where the sediment phenanthrene concentration ($\mu g/g_{OC}$) is plotted versus pore water concentration ($\mu g/L$). The data used to make this plot are included in Appendix B. The line of unity slope corresponding to the $\log_{10}K_{OC} = 4.46$ derived from SSF is compared to the data. A probability plot of the observed experimental $\log_{10}K_{OC}$ values is shown in lower panel of Figure 2-1. The $\log_{10}K_{OC}$ values are approximately normally distributed with a mean of $\log_{10}K_{OC} = 4.33$ and a standard error of the mean of 0.016. This value agrees with the $\log_{10}K_{OC}$ of 4.46, which was computed from the SSF determined phenanthrene $\log_{10}K_{OW}$

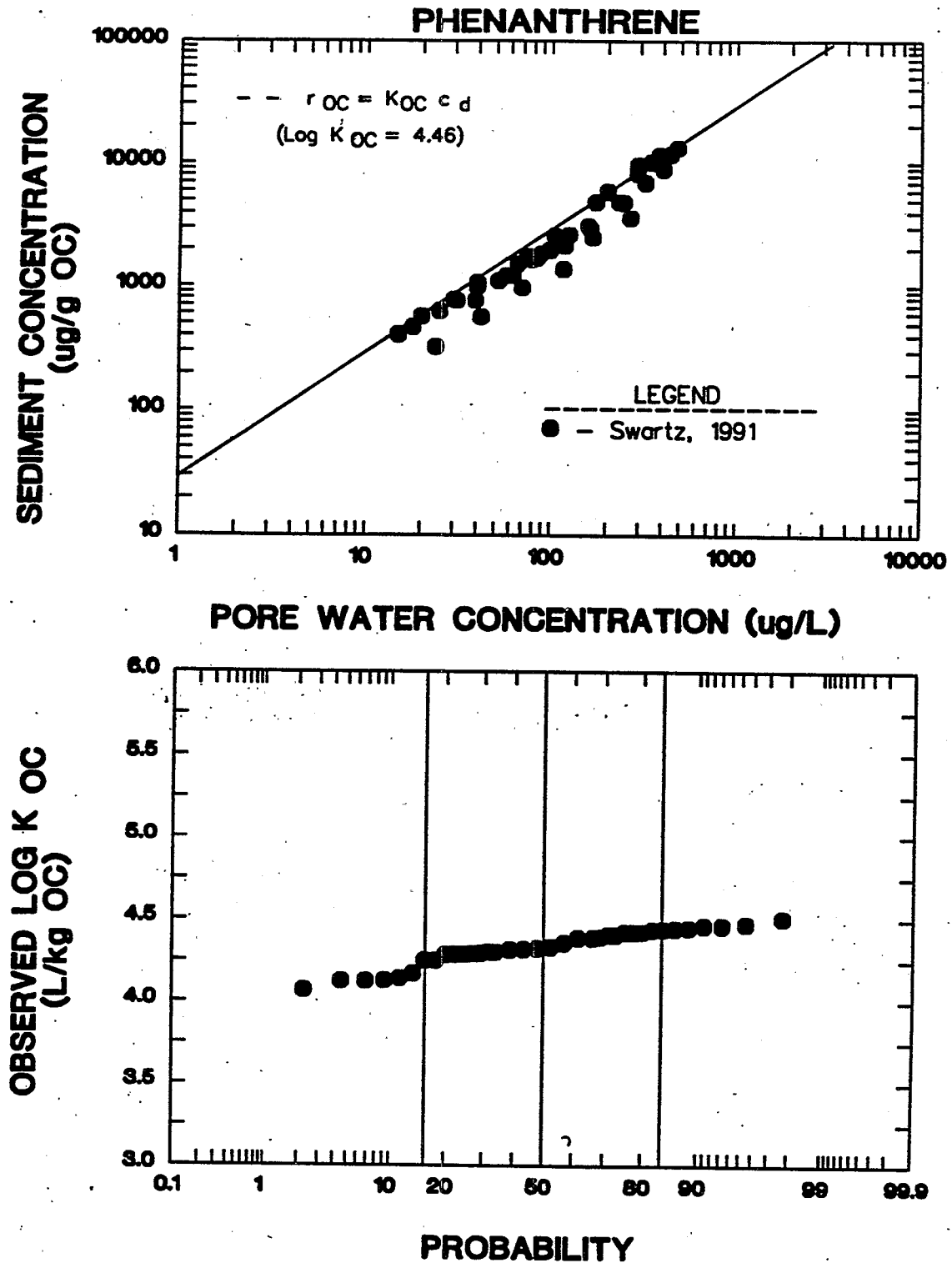


Figure 2-1. Organic carbon-normalized sorption isotherm for phenanthrene (top) and probability plot of K_{OC} (bottom) from sediment toxicity tests conducted by Swartz (1991). The line in the top panel represents the relationship predicted with a log K_{OC} of 4.46, that is $C_{s,oc} = K_{OC} \bullet C_D$.

of 4.54 using Equation 2-5.

2.4 SUMMARY OF DERIVATION OF K_{OC} FOR PHENANTHRENE:

The K_{OC} selected to calculate the sediment quality criteria for phenanthrene is based on the regression of $\log_{10}K_{OC}$ to $\log_{10}K_{OW}$ (Equation 2-5), using the phenanthrene $\log_{10}K_{OW}$ of 4.54 recently measured by ERL,A. This approach rather than the use of the K_{OC} from the toxicity test was adopted because the regression equation is based on the most robust data set available that spans a broad range of chemicals and particle types, thus encompassing a wide range of K_{OW} and f_{OC}. The regression equation yields a $\log_{10}K_{OC}$ of 4.46. This value is in agreement with the $\log_{10}K_{OC}$ of 4.33 measured in the sediment toxicity tests.

SECTION 3

TOXICITY OF PHENANTHRENE: WATER EXPOSURES

3.1 TOXICITY OF PHENANTHRENE IN WATER: DERIVATION OF PHENANTHRENE WATER QUALITY CRITERIA:

The equilibrium partitioning (EqP) method for derivation of sediment quality criteria (SQC) uses the phenanthrene water quality criterion (WQC) Final Chronic Value (FCV) and partition coefficients (K_{oc}) to estimate the maximum concentrations of nonionic organic chemicals in sediments, expressed on an organic carbon basis, that will not cause adverse effects to benthic organisms. For this document, life stages of species classed as benthic are either species that live in the sediment (infauna) or on the sediment surface (epibenthic) and obtain their food from either the sediment or water column (U.S. EPA, 1989c). In this section (1) the FCV from the phenanthrene WQC document (U.S. EPA, 1980) is revised using new aquatic toxicity test data; and (2) the use of this FCV is justified as the effects concentration for SQC derivation.

3.2 ACUTE TOXICITY - WATER EXPOSURES:

Fourteen standard acute toxicity tests with phenanthrene have been conducted on 9 freshwater species from 8 genera (Appendix A). Overall genus mean acute values (GMAVs) range from 96 to > 1,150 μg/L. The acute values for all species tested, except for fathead minnows, differed by only a factor of 5; 96 to 490 μg/L. Three tests on three benthic species from three genera are contained in this database (Figure 3-1; Appendix A). Benthic organisms were similar to water column species in sensitivity to phenanthrene; GMAVs range from 126

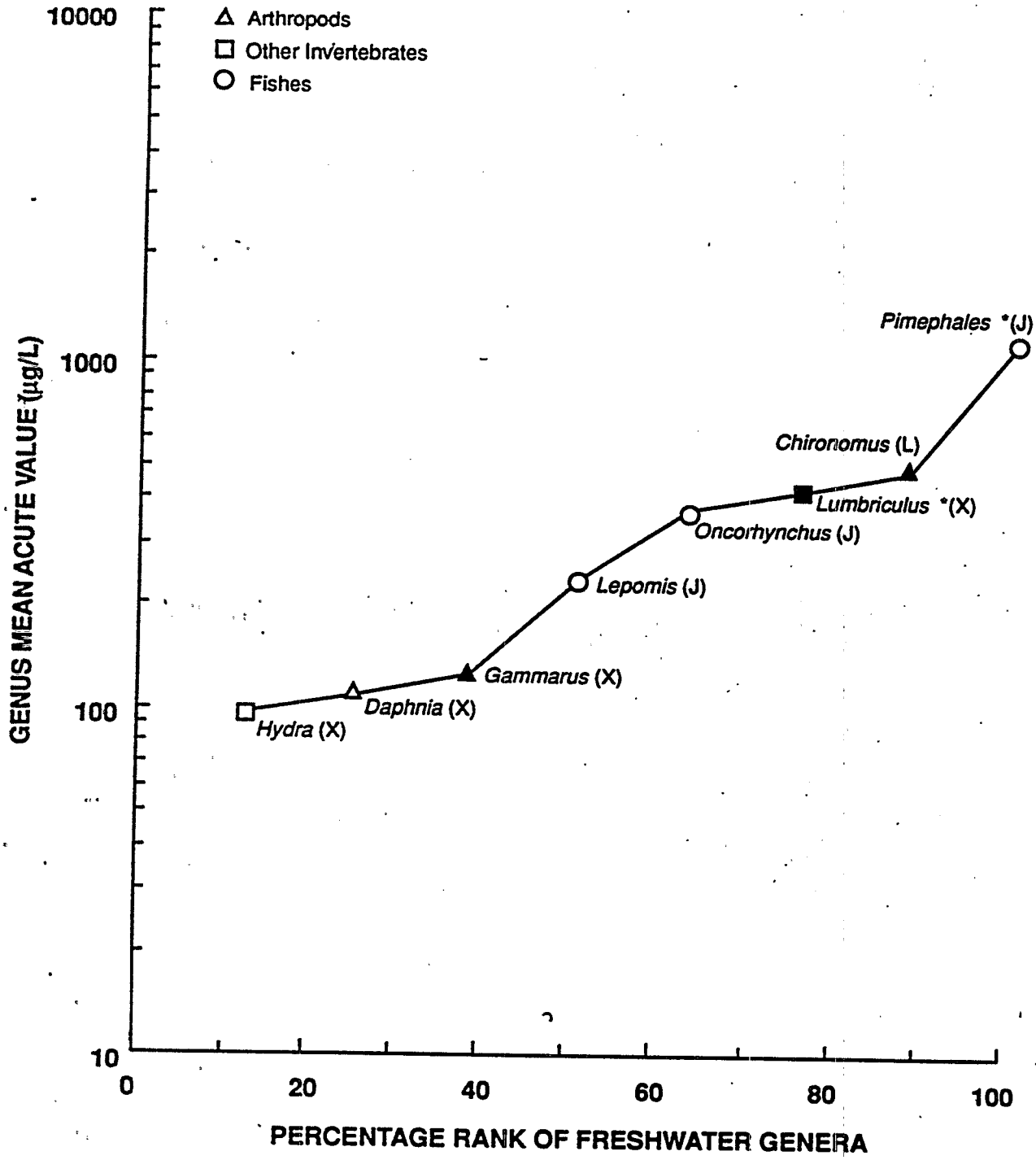


Figure 3-1. Genus mean acute values from water-only acute toxicity tests using freshwater species vs. percentage rank of their sensitivity. Symbols representing benthic species are solid, those representing water column species are open. Asterisks indicate greater than values. J = juvenile, L = larvae, X = unspecified life stage.

to 490 μg/L. One epibenthic species was tested, the amphipod, Gammarus pseudolimnaeus (LC50 = 126 μg/L). Infaunal species tested included the annelid, Lumbriculus variegatus (LC50 = >419 μg/L) and the midge, Chironomus tentans (LC50 = 490 μg/L). The Final Acute Value (FAV) derived from the overall GMAVs (Stephan et al., 1985) for freshwater organisms is 59.63 μg/L (Table 3-2).

Fourteen acute tests have been conducted on 11 saltwater species from 11 genera (Appendix A). Overall (GMAVs) range from 21.9 to 600 μg/L, similar to the range for freshwater genera. Fish and crustaceans were the most sensitive. Within this database there are results from thirteen tests on benthic life-stages of nine species from nine genera (Figure 3-2; Appendix A). Benthic organisms were among both the most sensitive, and most resistant, saltwater genera to phenanthrene. The most sensitive benthic species is the mysid, Mysidopsis bahia, with an average flow-through 96 hour LC50 of 21.9 μg/L based on two tests with measured concentrations. Other benthic species for which there are data appear less sensitive; GMAVs range from 145 to 600 μg/L. The FAV derived from the overall GMAVs (Stephan et al., 1985) for saltwater organisms is 16.61 μg/L (Table 3-2).

3.3 CHRONIC TOXICITY - WATER EXPOSURES:

Chronic toxicity tests have been conducted with phenanthrene using a freshwater cladoceran (Daphnia magna) and rainbow trout (Oncorhynchus mykiss) and a saltwater mysid (Mysidopsis bahia), (Table 3-1). The D. magna and O. mykiss were tested in life-cycle exposures. O. mykiss embryos, sac fry and swim-up benthic (intergravel) stages were tested in an early life-stage toxicity test.

Call et al. (1986) conducted both freshwater tests. D. magna exposed 21 days to a mean

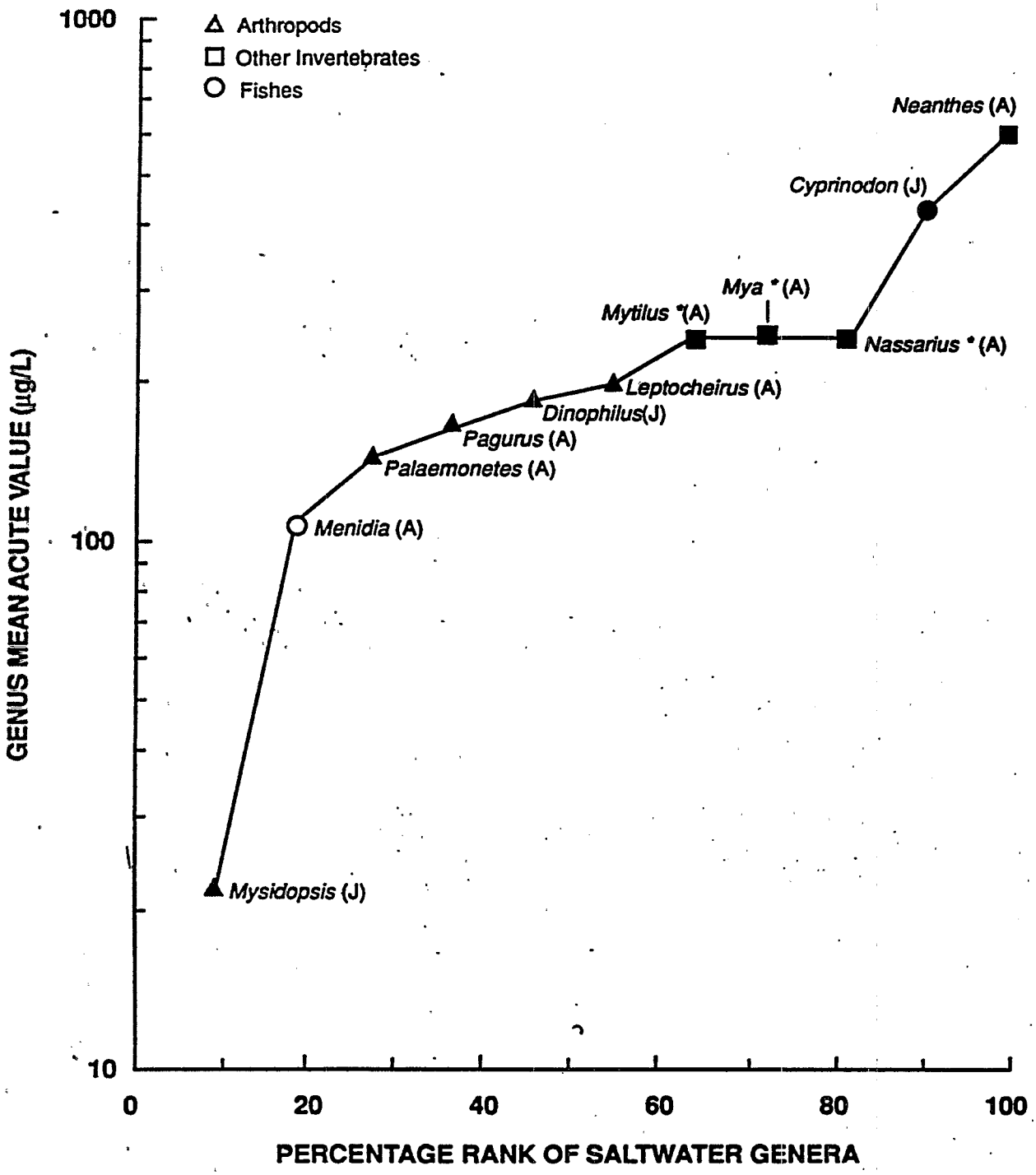


Figure 3-2. Genus mean acute values from water-only acute toxicity tests using saltwater species vs. percentage rank of their sensitivity. Symbols representing benthic species are solid, those representing water column species are open. Asterisks indicate greater than values. A = adult, J = juvenile.

TABLE 3-1. - CHRONIC SENSITIVITY OF FRESHWATER AND SALTWATER ORGANISMS TO PHENANTHRENE. TEST SPECIFIC DATA.

Common Name, Scientific Name	Test[a]	Habitat[b] (Life stage)	NOEC[c]	Parental LOEC[c]	Parental Effect[d]	Progeny LOEC[c]	Progeny Effect[d]	References
			µg/L	µg/L		µg/L		
FRESHWATER SPECIES								
Cladoceran, *Daphnia magna*	LC	W(J,A)	46,57	163	98% R 83% M	-	-	Call et al., 1986
Rainbow trout, *Oncorhynchus mykiss*	ELS	I(E,L)	5	8	33% G 41% M	-	-	Call et al., 1986
SALTWATER SPECIES								
Mysid, *Mysidopsis bahia*	LC	E(J,A)	1.50-5.55	11.9	100% R 100% M	-	-	Kuhn and Lussier, 1987

[a]TEST: LC = lifecycle, PLC = partial lifecycle, ELS = early lifestage.

[b]HABITAT: I = infauna, E = epibenthic, W = water column
LIFESTAGE: E = embryo, L = larval, J = Juvenile, A = Adult

[c]NOEC = No observed effect concentration(s); LOEC = lowest observed effect concentration(s).

[d]EFFECT: Percentage decrease relative to controls. M = mortality, G = growth, R = reproduction.

phenanthrene concentration of 163 μg/L experienced 98% reduction in reproduction and 83% reduction in survival relative to controls (Table 3-1). There was no statistically significant effect on survival or reproduction of daphnids in phenanthrene concentrations from 46 to 57 μg/L. O. mykiss exposed to phenanthrene for 90 days in an early life-stage toxicity test were not affected in 5 μg/L. Duration of incubation and hatching success were not affected in any treatment. However, the percentage of abnormal and dead fry at hatch was significantly increased at the highest exposure (66 μg/L). Sac fry were underdeveloped from hatching until test termination and swim-up delayed in $\geq$ 14 μg/L. At test termination, wet weights and standard lengths were reduced in $\geq$ 32 μg/L. Survival was reduced in $\geq$ 8 μg/L.

M. bahia exposed to phenanthrene in a life-cycle toxicity test (Kuhn and Lussier, 1987) were affected at phenanthrene concentrations similar to those affecting the O. mykiss (Table 3-1). Survival, growth and reproduction were not affected in $\leq$ 5.5 μg/L. At the highest concentration of phenanthrene (11.9 μg/L) all mysids died.

Derivation of the FCV for phenanthrene is complicated because Acute-Chronic Ratios (ACR) differ in the three species tested by a factor of almost 50 (Table 3-2). The final ACR, therefore, can not be the mean of these three values (Stephan et al., 1985). The difference between concentrations of phenanthrene acutely and chronically toxic to invertebrates is small. ACRs are 1.214 for the freshwater (D. magna) and 3.333 for the saltwater M. bahia, mean ratio of 2.012. The ACR of 59.29 for O. mykiss (Call et al., 1986) probably should not be used to derive the final ACR or chronic values for untested fishes because (1) it is over 10 x the ratio for tested invertebrates, (2) the O. mykiss 96 hr LC50 of 375 μg/L would be 50 μg/L if based on immobilization (Call et al., 1986), thus the ACR would be 7.905 and (3) the chronic value

TABLE 3-2. - SUMMARY OF FRESHWATER AND SALTWATER ACUTE AND CHRONIC VALUES, ACUTE-CHRONIC RATIOS AND DERIVATION OF FINAL ACUTE VALUES, FINAL ACUTE-CHRONIC RATIOS, AND FINAL CHRONIC VALUES FOR PHENANTHRENE.

Common Name, Scientific Name	Acute Value (µg/L)	Chronic Value (µg/L)	Acute-Chronic Ratio
		FRESHWATER SPECIES	
Cladoceran, *Daphnia magna*	117	96.39	1.214
Rainbow trout, *Oncorhynchus mykiss*	375	6.325	59.29
		SALTWATER SPECIES	
Mysid, *Mysidopsis bahia*	27.10	8.129	3.333

Freshwater:

Final Acute Value = 59.63 µg/L
Invertebrate Acute-Chronic Ratio = 2.012
Initial Final Chronic Value = 29.64 µg/L
Chronic Value for rainbow trout = 6.325 µg/L
Final Chronic Value = 6.325 µg/L

Saltwater:

Final Acute Value = 16.61 µg/L
Invertebrate Acute-Chronic Ratio = 2.012
Final Chronic Value = 8.255 µg/L

may be conservative based on tests with other fish species. In non-standard chronic exposures, sensitivities of early life-stages of largemouth bass (Micropterus salmoides) and O. mykiss (Black et al., 1983; Milleman et al., 1984) were less than observed by Call et al. (1986). These chronic exposures lasted from fertilization to four days after hatching, about 7 days for bass and 27 days for trout. Hatching and survival of O. mykiss were reduced in 38 μg/L but not in 31 μg/L; in contrast to the effect concentration of 8 μg/L was observed by Call et al. (1986). The LC50 for these tests was 40 μg/L for O. mykiss and 180 μg/L for bass (Black et al., 1983; Milleman et al., 1984). Because the most acutely sensitive species to phenanthrene were invertebrates, the FAV, 59.63 μg/L for freshwater and 16.61 μg/L for saltwater, was divided by the invertebrate mean ACR of 2.012 to derive an initial estimate of the FCV. These initial FCVs were 29.64 μg/L for freshwater and 8.255 μg/L for saltwater aquatic life. The initial freshwater FCV was lowered to 6.325 μg/L the chronic value from the O. mykiss early life-stage test with intergravel benthic embryonic and sac-fry life stages of this important species. The initial saltwater FCV of 8.255 μg/L was not lowered because the chronic sensitivities of saltwater fishes is not known and should not be estimated using the ACR for trout which may not be appropriate for other fish species. The initial FCV for saltwater aquatic life is used as the FCV because it is 13 to 52 times lower than acute values for tested saltwater fishes and approximately equal to the chronic value of 8.129 μg/L for the M. bahia. Although this procedure to derive the FCV is complicated and does not follow exactly the WQC Guidelines (Stephan et al.,1985) for idealized databases, the procedure is consistent with the guidelines requirement that the criterion be consistent with sound scientific evidence.

3.4 APPLICABILITY OF THE WATER QUALITY CRITERION AS THE EFFECTS CONCENTRATION FOR DERIVATION OF THE PHENANTHRENE SEDIMENT QUALITY CRITERION:

The use of the FCV (the chronic effects-based WQC concentration) as the effects concentration for calculation of the EqP-based SQC assumes that benthic (infaunal and epibenthic) species, taken as a group, have sensitivities similar to all benthic and water column species tested to derive the WQC concentration. Data supporting the reasonableness of this assumption over all chemicals for which there are published or draft WQC documents are presented in Di Toro et al. (1991), and the SQC Technical Basis Document (U.S. EPA, 1993a). The conclusion of similarity of sensitivity is supported by comparisons between (1) acute values for the most sensitive benthic and acute values for the most sensitive water column species for all chemicals; (2) acute values for all benthic species and acute values for all species in the WQC documents across all chemicals after standardizing the LC50 values; (3) FAVs calculated for benthic species alone and FAVs calculated for all species in the WQC documents; and (4) individual chemical comparisons of benthic species vs. all species. Only in this last comparison are phenanthrene-specific comparisons in sensitivity of benthic and all (benthic and water-column) species conducted. The following paragraphs examine the data on the similarity of sensitivity of benthic and all species for phenanthrene.

For phenanthrene, benthic species account for 3 out of 8 genera tested in freshwater, and 10 out of 11 genera tested in saltwater (Figures 3-1, 3-2). An initial test of the difference between the freshwater and saltwater FAVs for all species (water column and benthic) exposed to phenanthrene was performed using the Approximate Randomization method (Noreen, 1989). The Approximate Randomization method tests the significance level of a test statistic when

TABLE 3-3. RESULTS OF APPROXIMATE RANDOMIZATION TEST FOR THE EQUALITY OF THE FRESHWATER AND SALTWATER LC50 DISTRIBUTIONS FOR PHENANTHRENE AND APPROXIMATE RANDOMIZATION TEST FOR THE EQUALITY OF BENTHIC AND COMBINED BENTHIC AND WATER COLUMN (WQC) LC50 DISTRIBUTIONS.

Comparison	Habitat or Water Type[a]		AR Statistic[b]	Probability[c]
Fresh vs Salt	Fresh (8)	Salt (11)	43.03	72
Benthic vs Water Column + Benthic (WQC)	Benthic (13)	WQC (19)	7.35	80

[a]Values in parentheses are the number of LC50 values used in the comparison.
[b]AR statistic = FAV difference between original compared groups.
[c]Probability that the theoretical AR statistic ≤ the observed AR statistic given that the samples came from the same population.

compared to a distribution of statistics generated from many random subsamples. The test statistic in this case is the difference between the freshwater FAV, computed from the freshwater (combined water column and benthic) species LC50 values, and the saltwater FAV, computed from the saltwater (combined water column and benthic) species LC50 values (Table 3-1). In the Approximate Randomization method, the freshwater LC50 values and the saltwater LC50 values are combined into one data set. The data set is shuffled, then separated back so that randomly generated "freshwater" and "saltwater" FAVs can be computed. The LC50 values are separated back such that the number of LC50 values used to calculate the sample FAVs are the same as the number used to calculate the original FAVs. These two FAVs are subtracted

and the difference used as the sample statistic. This is done many times so that the sample statistics make up a distribution that is representative of the population of FAV differences (Figure 3-3). The test statistic is compared to this distribution to determine it's level of significance. The null hypothesis is that the LC50 values that comprise the saltwater and freshwater data bases are not different. If this is true, the difference between the actual freshwater and saltwater FAVs should be common to the majority of randomly generated FAV differences. For phenanthrene, the test-statistic falls at the 73 percentile of the generated FAV differences. Since the probability is less than 95%, the hypothesis of no significant difference in sensitivity for freshwater and saltwater species is accepted (Table 3-3).

Since freshwater and saltwater species showed similar sensitivity, a test of difference in sensitivity for benthic and all (benthic and water column species combined, hereafter referred to as "WQC") organisms combining freshwater and saltwater species using the Approximate Randomization method was performed. The test statistic in this case is the difference between the WQC FAV, computed from the WQC LC_{50} values, and the benthic FAV, computed from the benthic organism LC_{50} values. This is slightly different then the previous test for saltwater and freshwater species. The difference is that saltwater and freshwater species represent two separate groups. In this test the benthic organisms are a subset of the WQC organisms set. In the Approximate Randomization method for this test, the number of data points coinciding with the number of benthic organisms are selected from the WQC data set. A "benthic" FAV is computed. The original WQC FAV and the "benthic" FAV are then used to compute the difference statistic. This is done many times and the distribution that results is representative of the population of FAV difference statistics. The test statistic is compared to this distribution

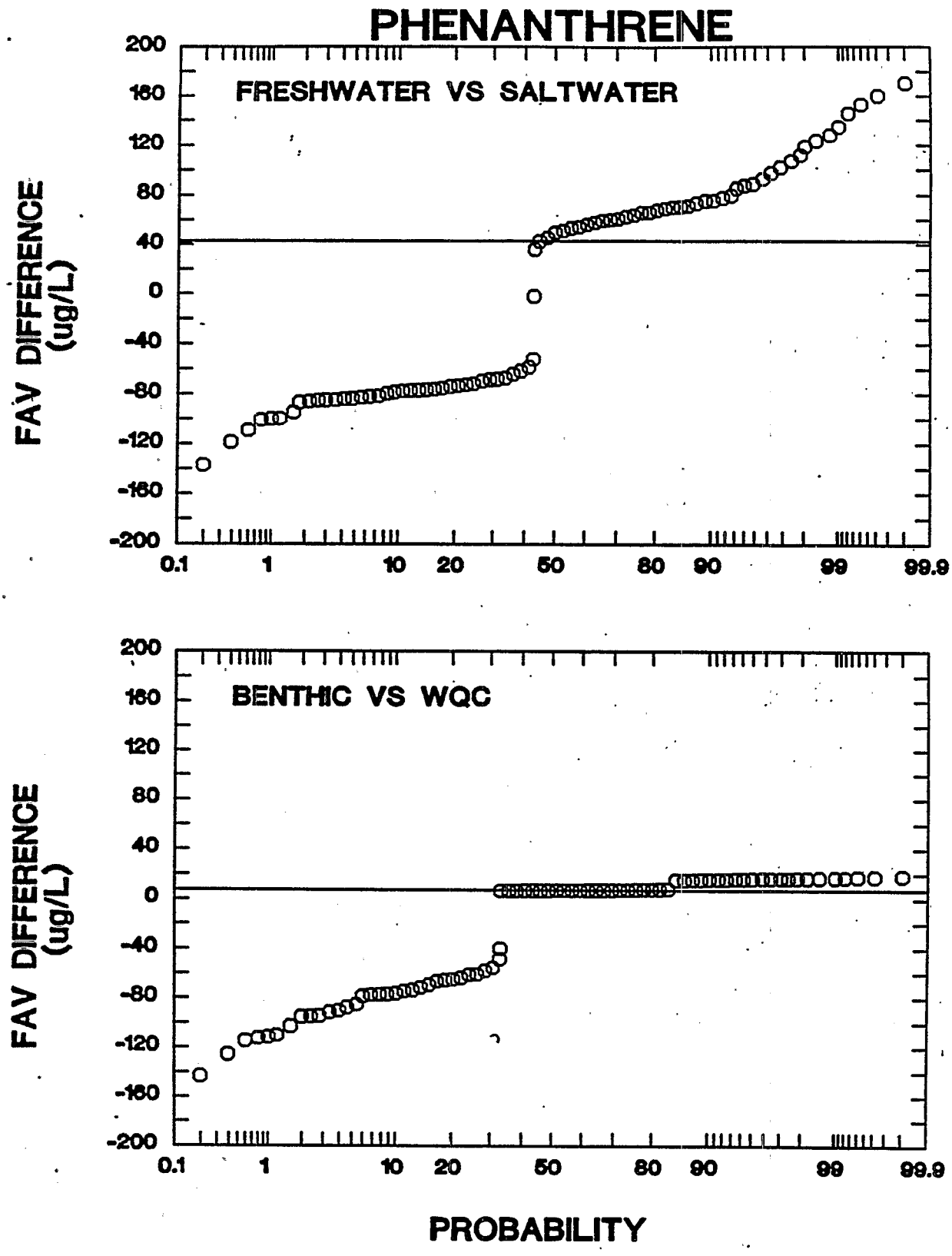


Figure 3-3. Probability distribution of FAV difference statistics to compare water-only data from freshwater vs saltwater (upper panel) and benthic vs. WQC (lower panel) data.

to determine its level of significance. The probability distribution of the computed FAV differences are shown in the bottom panel of Figure 3-3. The test statistic for this analysis falls at the 80 percentile and the hypothesis of no difference in sensitivity is accepted (Table 3-3). This analysis suggests that the FCV for phenanthrene based on data from all tested species is an appropriate effects concentration for benthic organisms.

SECTION 4

TOXICITY OF PHENANTHRENE (ACTUAL AND PREDICTED): SEDIMENT EXPOSURES

4.1 TOXICITY OF PHENANTHRENE IN SEDIMENTS:

The toxicity of phenanthrene spiked into sediments has been tested with two saltwater amphipod species. Freshwater benthic species have not been tested in phenanthrene-spiked sediments. All concentrations of phenanthrene in sediments or interstitial water where effects were observed in benthic species (Table 4-1) are greater than SQC or FCV concentrations reported in this document. Details about exposure methodology are provided because, unlike aquatic toxicity tests, sediment testing methodologies have not been standardized. Generalizations across species or sediments are limited because of the limited number of experiments. Therefore, insights into relative sensitivities of aquatic species to phenanthrene can only be obtained from results of water-only tests (Section 3). Data are available from many experiments using both field and laboratory sediments contaminated with mixtures of PAHs and other compounds which include phenanthrene. Data from these studies have not been included here because it is not possible to determine the contribution of phenanthrene to the observed toxicity.

Swartz (1991) exposed the amphipods Eohaustorius estuarius and Leptocheirus plumulosus to three phenanthrene-spiked sediments with total organic carbon contents (TOC) ranging from 0.82 to 3.6%. Sediments were rolled (1) for two hours in phenanthrene-coated bottles; (2) stored at 4°C for 72 hours; (3) rolled for an additional two hours, and (4) then

TABLE 4-1: SUMMARY OF TESTS WITH PHENANTHRENE-SPIKED SEDIMENT.

Common/Sci. Name	Sediment Source; Description	TOC (%)	Method[a]/ Duration (Days)	Response	Sediment Phenanthrene EC50 - LC50, µg/g Dry wt.	Sediment Phenanthrene EC50 - LC50, µg/g Org. Car.[a]	Pore Water EC50-LC50, µg/L	References
			SALTWATER SPECIES					
Amphipod, Rohaustorius estuarius	South Beach, OR	1.02 0.82[b]	S,M/10	LC50	39.2	4,050	138	Swartz, 1991
Amphipod, Rohaustorius estuarius	McKinney Slough, OR	2.47	S,M/10	LC50	97.2	3,920	139	Swartz, 1991
Amphipod, Rohaustorius estuarius	Eckman Slough, OR	3.33 2.97[b]	S,M/10	LC50	122	3,820	146	Swartz, 1991
Amphipod, Leptocheirus plumulosus	South Beach, OR	1.96 0.82[b]	S,M/10	LC50	92.4	8,200	387	Swartz, 1991
Amphipod, Leptocheirus plumulosus	McKinney Slough, OR	2.50	S,M/10	LC50	162	6,490	306	Swartz, 1991
Amphipod, Leptocheirus plumulosus	Eckman Slough, OR	3.60 2.97[b]	S,M/10	LC50	255	8,200	360	Swartz, 1991

[a]S = Static; M = Measured.

[a]Treatment-specific TOC concentrations were used in LC50 calculations.

[b]TOC of sediment used in highest concentration(s).

stored for 7 days at 4°C. In some of these experiments the concentration of phenanthrene was not sufficient to cause 50% mortality in any of the concentrations tested. In these cases additional experiments were performed with sediments from the same locations with similar TOC concentrations as were used in the original experiments, but with one or two treatments with higher phenanthrene concentrations and the appropriate controls (Table 4-1). When there was a difference between the control mortality in one of the original experiments and in the follow up experiment with the corresponding sediment and species, Abbott's correction was performed on the data for each treatment separately using the appropriate control mortality. Then the data for both experiments were pooled. The pooling of the data appears justified by the similarity of the dose-response relationships in the original and the follow up experiments (Appendix B). The 10-day LC50's for both species increased with increasing organic carbon concentration when the phenanthrene concentration was expressed on a dry weight basis, but decreased when concentration was expressed on an organic carbon basis. LC50's normalized to dry weight differed by a factor of 3.1 (39.2 to 122 $\mu g/g$) for E. estuarius over a 3.3-fold range of TOC and a factor of 2.8 (92.4 to 255 $\mu g/g$) for L. plumulosus over a 1.8-fold range of TOC. The organic carbon normalized LC50's for E. estuarius differed by a factor of 1.1 (3,820 to 4,050 $\mu g/g_{oc}$) while for L. plumulosus they differed by a factor of 1.3 (6,490 to 8,200 $\mu g/g_{oc}$).

Overall, the need for organic carbon normalization of the concentration of non-ionic organic chemicals in sediments is presented in the SQC Technical Basis Document (U.S. EPA, 1993a). The need for organic carbon normalization for phenanthrene is also supported by the results of spiked-sediment toxicity tests described above. Although it is important to demonstrate that organic carbon normalization is necessary if SQC are to be derived using the

EqP approach, it is fundamentally more important to demonstrate that K_{oc} and water only effects concentrations can be used to predict effects concentrations for phenanthrene and other non-ionic organic chemicals on an organic carbon basis for a range of sediments. Evidence supporting this prediction for phenanthrene and all other nonionic organic chemicals follows in Section 4.3.

4.2 CORRELATION BETWEEN ORGANISM RESPONSE AND PORE WATER CONCENTRATION:

One corollary of the EqP theory is that pore-water LC50's for a given organism should be constant across sediments of varying organic carbon content (U.S. EPA, 1993a). Appropriate pore-water LC50 values are available for two benthic species (Table 4-2). Swartz (1991) found 10-day LC50 values based on pore-water concentrations varied by a factor of 1.1 (138 to 146 μg/L) for E. estuarius and by a factor of 1.3 (306 to 387 μg/L) for L. plumulosus. This variability is somewhat less than that shown when dry weight (factors of 3.1 and 2.8) normalization is used to determine LC50s based on phenanthrene concentration in sediments, but similar to that shown when organic carbon (factors of 1.1 and 1.3) normalization is used.

A more detailed evaluation of the degree to which the response of benthic organisms can be predicted from toxic units of substances in pore water can be made utilizing results from toxicity tests with sediments spiked with other substances, including acenanphthene and phenanthrene (Swartz, 1991), endrin (Nebeker et al., 1989; Schuytema et al., 1989), dieldrin (Hoke 1992), fluoranthene (Swartz et al., 1990, De Witt et al., 1992), or kepone (Adams et al., 1985) (Figure 4-1; Appendix B). The data included in this analysis come from tests conducted at EPA laboratories or from tests which utilized designs at least as rigorous as those conducted at the EPA laboratories. Tests with acenaphthene and phenanthrene used two saltwater

TABLE 4-2: WATER-ONLY AND SEDIMENT LC50S USED TO TEST THE APPLICABILITY OF THE EQUILIBRIUM PARTITIONING THEORY FOR PHENANTHRENE.

Common/Sci. Name	Method[a] Duration (days)	Water Only LC50	Pore Water LC50	TOC (%)	Sediment Phenanthrene LC50 mg/g Dry Wt.	Sediment Phenanthrene LC50 µg/g[b] OC	Predicted[c] LC50 µg/g OC	Ratio: Actual LC50 Predicted	Reference
		µg/L	µg/L						
Amphipod, Rohaustorius estuarius	FT,M/10	131	138	1.02[d] 0.82	39.2	4,050	3,778	1.07	Swartz, 1991
Amphipod, Rohaustorius estuarius	FT,M/10	131	139	2.47	97.2	3,920	3,778	1.04	Swartz, 1991
Amphipod, Rohaustorius estuarius	FT,M/10	131	146	3.33[d] 2.97	122	3,820	3,778	1.04	Swartz, 1991
Amphipod, Leptocheirus plumulosus	FT,M/10	185	387	1.96[d] 0.82	92.4	8,200	5,335	1.54	Swartz, 1991
Amphipod, Leptocheirus plumulosus	FT,M/10	185	306	2.50	162	6,490	5,335	1.22	Swartz, 1991
Amphipod, Leptocheirus plumulosus	FT,M/10	185	360	3.60[d] 2.97	255	8,200	5,335	1.54	Swartz, 1991

[a] FT = Flow through, M = measured concentration.

[b] Treatment-specific TOC concentrations were used in LC50 calculations.

[c] Predicted LC50 ($\mu g/g_{oc}$) = water-only LC50 ($\mu g/L$) x K_{oc} (L/Kg_{oc}) x 1 $Kg_{oc}/1000g_{oc}$; Where $K_{oc} = 10^{4.46}$

[d] TOC of sediment used in highest concentration(s).

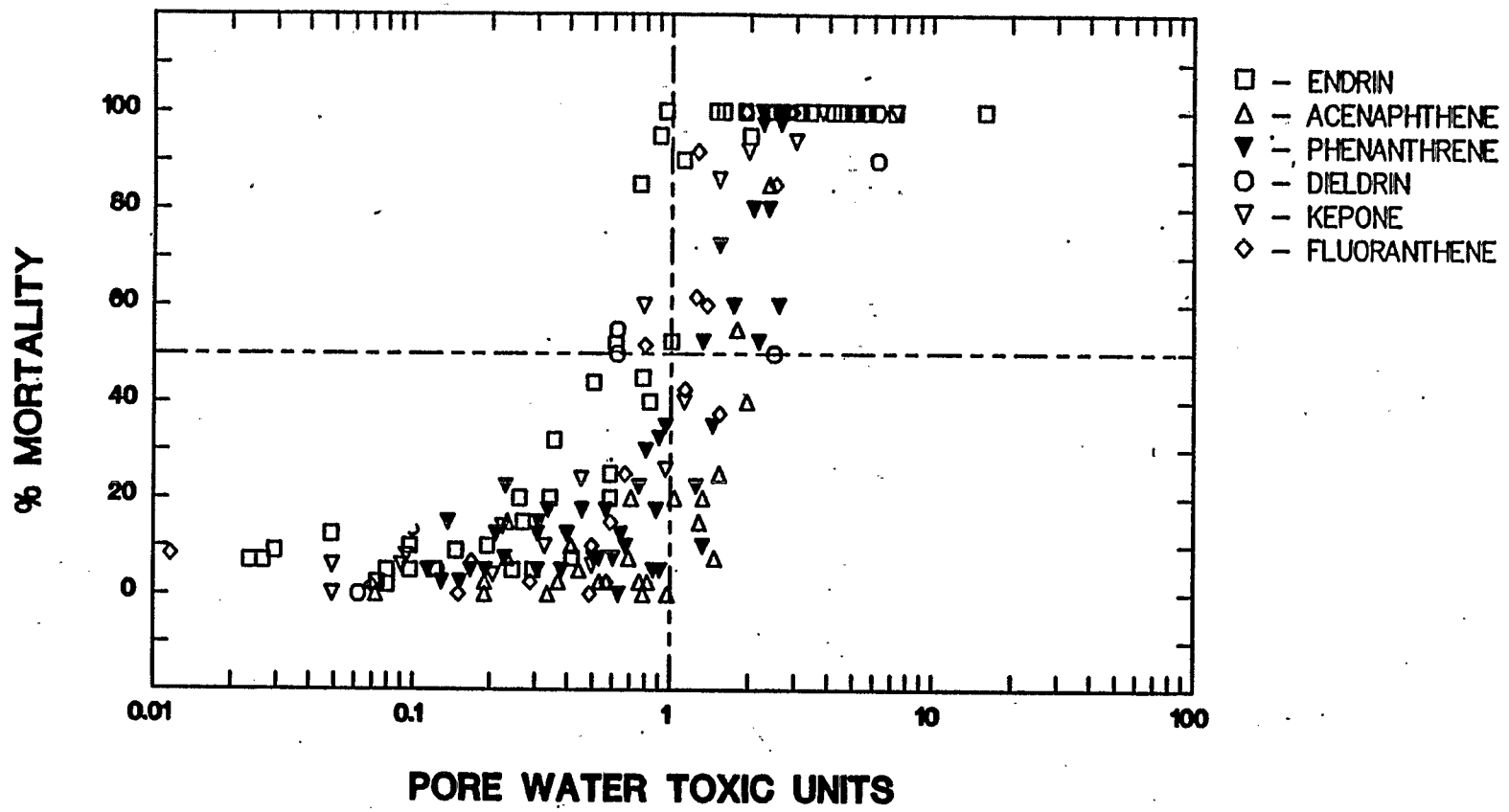


Figure 4-1. Percent mortality of amphipods in sediments spiked with acenaphthene or phenanthrene (Swartz, 1991), endrin (Nebeker et al., 1989; Schuytema et al., 1989), or fluoranthene (Swartz et al., 1990; De Witt et al., 1992) and midge in sediments spiked with dieldrin (Hoke, 1992) or kepone (Adams et al., 1985) relative to pore water toxic units. Pore water toxic units are ratios of concentrations of chemicals measured in individual treatments divided by the water-only LC50 value from water-only tests. (See Appendix B in this SQC document, Appendix B in the endrin, dieldrin, fluoranthene and acenaphthene SQC documents, and original references for raw data.)

amphipods (L. plumulosus and E. estuarius) and marine sediments. Tests with fluoranthene used the saltwater amphipod (Rhepoxynius abronius) and marine sediments. Freshwater sediments spiked with endrin were tested using the amphipod Hyalella azteca; while the midge, Chironomus tentans, was tested using kepone-spiked sediments. Figure 4-1 presents the percentage mortalities of the benthic species tested in individual treatments for each chemical versus "pore water toxic units" (PWTUs) for all sediments tested. PWTUs are the concentration of the chemical in pore water (μg/L) divided by the water only LC50 (μg/L). Theoretically, 50% mortality should occur at one interstitial water toxic unit. At concentrations below one PWTU there should be less than 50% mortality, and at concentrations above one PWTU there should be greater than 50% mortality. Figure 4-1 shows that at concentrations below one PWTU mortality was generally low, and increased sharply at approximately one PWTU. Therefore, this comparison supports the concept that interstitial water concentrations can be used to predict the response of an organism to a chemical that is not sediment-specific. This pore water normalization was not used to derive SQC in this document because of the complexation of nonionic organic chemicals with pore water DOC (Section 2) and the difficulties of adequately sampling pore waters.

4.3 TESTS OF THE EQUILIBRIUM PARTITIONING PREDICTION OF SEDIMENT TOXICITY:

SQC derived using the equilibrium partitioning approach utilize partition coefficients and FCV from WQC documents to derive the SQC concentration for protection of benthic organisms. The partition coefficient (K_{oc}) is used to normalize sediment concentrations and predict biologically available concentrations across sediment types. The data required to test the

organic carbon normalization for phenanthrene in sediments are available for two benthic species. Data from tests with water column species were not included in this analysis. Testing of this component of SQC derivation requires three elements: (1) a water-only effect concentration, such as a 10-day LC50 value in $\mu g/L$, (2) an identical sediment effect concentration on an organic carbon basis, such as a 10-day LC50 value in $\mu g/g_{oc}$, and (3) a partition coefficient for the chemical, K_{oc} in L/kg_{oc}. This section presents evidence that the observed effect concentration in sediments (2) can be predicted utilizing the water effect concentration (1) and the partition coefficient (3).

Predicted 10-day LC50 values from phenanthrene-spiked sediment with E. estuarius and L. plumulosus were calculated (Table 4-2) using the $\log_{10}K_{oc}$ value of 4.46 from Section 2 of this document and the sediment LC50's in Swartz (1991). Ratios of actual to predicted LC50s for phenanthrene averaged 1.05 (range 1.04 to 1.07) for E. estuarius and 1.42 (range 1.22 to 1.54) for L. plumulosus. The overall mean for both species was 1.22.

A more detailed evaluation of the accuracy and precision of the EqP prediction of the response of benthic organisms can be made using the results of toxicity tests with amphipods exposed to sediments spiked with acenaphthene, phenanthrene, dieldrin , endrin, or fluoranthene. The data included in this analysis come from tests conducted at EPA laboratories or from tests which utilized designs at least as rigorous as those conducted at the EPA laboratories. Data from the kepone experiments are not included because a measured K_{ow} obtained using the slow-stir flask method is not available. Swartz (1991) exposed the saltwater amphipods E. estuarius and L. plumulosus to acenaphthene in three marine sediments having organic carbon contents ranging from 0.82 to 4.2% and to phenanthrene in three marine sediments having organic carbon

contents ranging from 0.82 to 3.6%. Swartz et al. (1990) exposed the saltwater amphipod R. abronius to fluoranthene in three marine sediments having 0.18, 0.31 and 0.48% organic carbon. Hoke and Ankley (1991) exposed the amphipod H. azteca to three dieldrin-spiked freshwater sediments having 1.7, 3.0 and 8.5% organic carbon, and Hoke (1992) exposed the midge C. tentans to freshwater dieldrin spiked sediments having 2.0 and 1.5% organic carbon. Nebeker et al. (1989) and Schuytema et al. (1989) exposed H. azteca to three endrin-spiked sediments having 3.0, 6.1 and 11.2% organic carbon. Figure 4-2 presents the percentage mortalities of amphipods in individual treatments of each chemical versus "predicted sediment toxic units" for each sediment treatment. PSTUs are the concentration of the chemical in sediments ($\mu g/g_{oc}$) divided by the predicted LC50 ($\mu g/g_{oc}$) in sediments (the product of K_{oc} and the 10-day water-only LC50). In this normalization, 50% mortality should occur at one PSTU. At concentrations below one PSTU mortality was generally low, and increased sharply at one PSTU. The means of the LC50s for these tests calculated on a PSTU basis were 1.90 for acenaphthene, 1.16 for dieldrin, 0.44 for endrin, 0.80 for fluoranthene and 1.22 for phenanthrene. The mean value for the five chemicals is 0.99. This illustrates that the EqP method can account for the effects of different sediment properties and properly predict the effects concentration in sediments using the effects concentration from water only exposures.

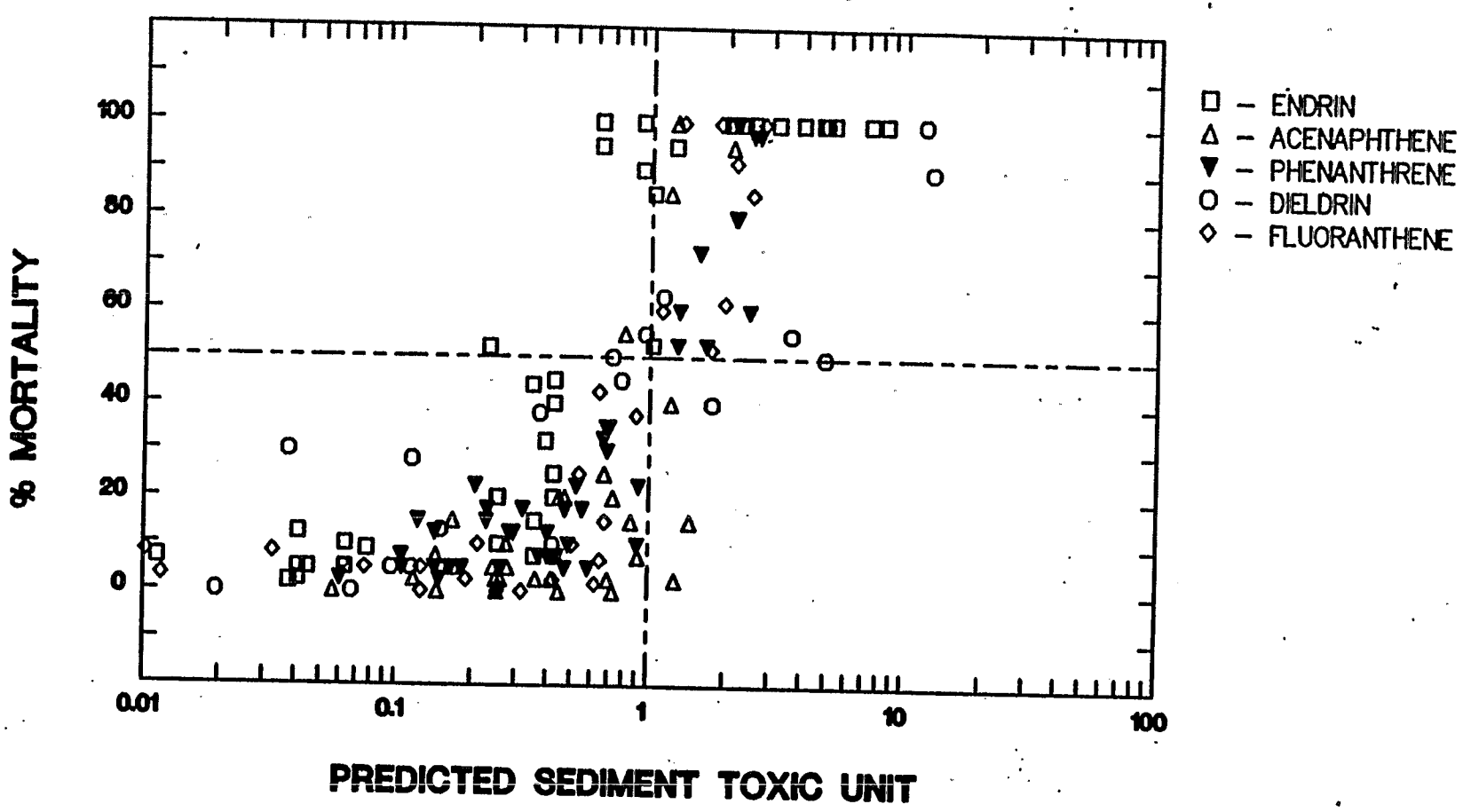


Figure 4-2. Percent mortality of amphipods in sediments spiked with acenaphthene or phenanthrene (Swartz, 1991), dieldrin (Hoke and Ankley, 1991), endrin (Nebeker et al., 1989; Schuytema et al., 1989) or fluoranthene (Swartz et al., 1990; De Witt et al., 1992) and midge in dieldrin spiked sediments (Hoke, 1992) relative to "predicted sediment toxic units." Predicted sediment toxic units are the ratios of measured treatment concentrations for each chemical in sediments ($\mu g/g_{oc}$) divided by the predicted LC50 ($\mu g/g_{oc}$) in sediments (K_{oc} x Water-only LC50 ($\mu g/L$) x 1 $Kg_{oc}/1{,}000g_{oc}$). (See Appendix B in this document and Appendix B in the dieldrin, endrin, fluoranthene, and acenaphthene SQC documents for raw data).

SECTION 5

CRITERIA DERIVATION FOR PHENANTHRENE

5.1 CRITERIA DERIVATION:

The water quality criteria (WQC) Final Chronic Value (FCV), without an averaging period or return frequency (See section 3), is used to calculate the sediment quality criteria (SQC) because it is probable that the concentration of contaminants in sediments are relatively stable over time, thus exposure to sedentary benthic species should be chronic and relatively constant. This is in contrast to the situation in the water column, where a rapid change in exposure and exposures of limited durations can occur due to fluctuations in effluent concentrations dilutions in receiving waters or the free-swimming or planktonic nature of water column organisms. For some particular uses of the SQC it may be appropriate to use the areal extent and vertical stratification of contamination of a sediment at a site in much the same way that averaging periods or mixing zones are used with WQC.

The FCV is the value that should protect 95% of the tested species included in the calculation of the WQC from chronic effects of the substance. The FCV is the quotient of the Final Acute Value (FAV), and the final Acute Chronic Ratio (ACR) for the substance. The FAV is an estimate of the acute LC50 or EC50 concentration of the substance corresponding to a cumulative probability of 0.05 for the genera from eight or more families for which acceptable acute tests have been conducted on the substance. The ACR is the mean ratio of acute to

chronic toxicity for three or more species exposed to the substance that meets minimum database requirements. For more information on the calculation of ACRs, FAVs, and FCVs see the National Water Quality Criteria Guidelines (Stephan et al., 1985). The FCV used in this document differs from the FCV in the phenanthrene WQC document (U.S. EPA, 1980) because it incorporates recent data not included in that document, and omits some data which does not meet the data requirements established in the WQC Guidelines (Stephan et al., 1985).

The equilibrium partitioning (EqP) method for calculating SQC is based on the following procedure. If FCV (μg/L) is the chronic concentration from the WQC for the chemical of interest, then the SQC (μg/g sediment), is computed using the partition coefficient, K_p (L/g sediment), between sediment and pore water:

$$SQC = K_p \, FCV \qquad (5\text{-}1)$$

Since organic carbon is the predominant sorption phase for nonionic organic chemicals in naturally occurring sediments, (salinity, grainsize and other sediment parameters have inconsequential roles in sorption, see sections 2.1 and 4.3) the organic carbon partition coefficient, (K_{oc}) can be substituted for K_p. Therefore, on a sediment organic carbon basis, the SQC_{oc} ($\mu g/g_{oc}$), is:

$$SQC_{oc} = K_{oc} \, FCV \qquad (5\text{-}2)$$

Since (K_{oc}) is presumably independent of sediment type for non-ionic organic chemicals, so also is SQC_{oc}. Table 5-1 contains the calculation of the phenanthrene SQC.

The organic carbon normalized SQC is applicable to sediments with an organic carbon fraction of $f_{oc} \geq 0.2\%$. For sediments with $f_{oc} < 0.2\%$, organic carbon normalization and SQC may not apply.

TABLE 5-1. SEDIMENT QUALITY CRITERIA FOR PHENANTHRENE

Type of Water Body	$Log_{10}K_{ow}$ (L/kg)	$Log_{10}K_{oc}$ (L/kg)	FCV ($\mu g/L$)	SQC_{oc} ($\mu g/g_{oc}$)
Fresh Water	4.54	4.46	6.32	180[a]
Salt Water	4.54	4.46	8.26	240[b]

[a] $SQC_{oc} = (10^{4.46}\ L/kg_{oc}) \bullet (10^{-3}\ kg_{oc}/g_{oc}) \bullet (6.32\ \mu g\ phenanthrene/L) = 180\ \mu g\ phenanthrene/g_{oc}$

[b] $SQC_{oc} = (10^{4.46}\ L/kg_{oc}) \bullet (10^{-3}\ kg_{oc}/g_{oc}) \bullet (8.26\ \mu g\ phenanthrene/L) = 240\ \mu g\ phenanthrene/g_{oc}$

Since organic carbon is the factor controlling the bioavailability of nonionic organic compounds in sediments, SQC have been developed on an organic carbon basis, not on a dry weight basis. When the chemical concentrations in sediments are reported as dry weight concentration and organic carbon data are available, it is best to convert the sediment concentration to μg chemical/gram organic carbon. These concentrations can then be directly compared to the SQC value. This facilitates comparisons between the SQC and field concentrations relative to identification of hot spots and the degree to which sediment concentrations do or do not exceed SQC values. The conversion from dry weight to organic carbon normalized concentration can be done using the following formula:

$$\mu g\ Chemical/g_{oc} = \mu g\ Chemical/g_{DRY\ WT} \div (\%\ TOC \div 100)$$

$$= \mu g\ Chemical/g_{DRY\ WT} \bullet 100 \div \%\ TOC$$

For example, a freshwater sediment with a concentration of 6.00 μg chemical/$g_{DRY\ WT}$ and 0.5 % TOC has an organic carbon-normalized concentration of 1,200 $\mu g/g_{oc}$ (6.00 $\mu g/g_{DRYWT}$ $\bullet$ 100 $\div$ 0.5 = 1,200 $\mu g/g_{oc}$) which exceeds the SQC of 180 $\mu g/g_{oc}$. Another freshwater

sediment with the same concentration of phenanthrene (6.00 $\mu g/g_{DRY\ WT}$) but a TOC concentration of 5.0% would have an organic carbon normalized concentration of 120 $\mu g/g_{OC}$ (6.00 $\mu g/g_{DRY\ WT}$ • 100 ÷ 5.0 = 120 $\mu g/g_{OC}$), which is below the SQC for phenanthrene.

In situations where TOC values for particular sediments are not available, a range of TOC values may be used in a "worst case" or "best case" analysis. In this case, the organic carbon-normalized SQC values (SQC_{OC}) may be "converted" to dry weight-normalized SQC values ($SQC_{DRY\ WT}$). This "conversion" must be done for each level of TOC of interest:

$$SQC_{DRY\ WT} = SQC_{OC}\ (\mu g/g_{OC}) \bullet (\%\ TOC \div 100)$$

where $SQC_{DRY\ WT}$ is the dry weight normalized SQC value. For example, the SQC value for freshwater sediments with 1% organic carbon is 1.8 $\mu g/g$:

$$SQC_{DRY\ WT} = 180\ \mu g/g_{OC} \bullet 1\%\ TOC \div 100 = 1.8\ \mu g/g_{DRY\ WT}$$

This method is used in the analysis of the STORET data in section 5.4.

5.2 UNCERTAINTY ANALYSIS:

Some of the uncertainty in the calculation of the phenanthrene SQC can be estimated from the degree to which the EqP model, which is the basis for the criteria, can rationalize the available sediment toxicity data. The EqP model asserts that (1) the bioavailability of nonionic organic chemicals from sediments is equal on an organic carbon basis, and (2) that the effects concentration in sediment ($\mu g/g_{OC}$) can be estimated from the product of the effects concentration from water only exposures ($\mu g/L$) and the partition coefficient K_{OC} (L/kg). The uncertainty associated with the SQC can be obtained from a quantitative estimate of the degree to which the available data support these assertions.

The data used in the uncertainty analysis are from the water-only and sediment toxicity tests that have been conducted to fulfill minimum database requirements for the development of SQC (see Section 4.3 and Technical Basis Document, U.S. EPA, 1993a). These freshwater and saltwater tests span a range of chemicals and organisms; they include both water-only and sediment exposures and they are replicated within each chemical-organism-exposure media treatment. These data were analyzed using an analysis of variance (ANOVA) to estimate the uncertainty (i.e. the variance) associated with varying the exposure media and that associated with experimental error. If the EqP model were perfect, then there would be only experimental error. Therefore, the uncertainty associated with the use of EqP is the variance associated with varying exposure media.

The data used in the uncertainty analysis are illustrated in Figure 4-2. The data for phenanthrene are summarized in Appendix B. LC50s for sediment and water-only tests were computed from these data. The EqP model can be used to normalize the data in order to put it on a common basis. The LC50s from water-only exposures ($LC50_w$; $\mu g/L$) are related to the organic carbon-normalized LC50s from sediment exposures ($LC50_{s,oc}$; $\mu g/g_{oc}$) via the partitioning equation:

$$LC50_{s,oc} = K_{oc}LC50_w \qquad (5\text{-}3)$$

The EqP model asserts that the toxicity of sediments expressed on an organic carbon basis equals the toxicity in water tests multiplied by the K_{oc}. Therefore, both $LC50_{s,oc}$ and $K_{oc} \bullet LC50_w$ are estimates of the true $LC50_{oc}$ for each chemical-organism pair. In this analysis, the

uncertainty of K_{OC} is not treated separately. Any error associated with K_{OC} will be reflected in the uncertainty attributed to varying the exposure media.

In order to perform an analysis of variance, a model of the random variations is required. As discussed above, experiments that seek to validate equation 5-3 are subject to various sources of random variations. A number of chemicals and organisms have been tested. Each chemical - organism pair was tested in water-only exposures and in different sediments. Let α represent the random variation due to this source. Also, each experiment is replicated. Let $\in$ represent the random variation due to this source. If the model were perfect, there would be no random variations other than that due to experimental error which is reflected in the replications. Hence α represents the uncertainty due to the approximations inherent in the model and $\in$ represents the experimental error. Let $(\sigma_\alpha)^2$ and $(\sigma_\in)^2$ be the variances of these random variables. Let i index a specific chemical-organism pair. Let j index the exposure media, water-only, or the individual sediments. Let k index the replication of the experiment. Then the equation that describes this relationship:

$$\ln(LC50_{i,j,k}) = \mu_i + \alpha_{i,j} + \in_{i,j,k} \qquad (5\text{-}4)$$

where $\ln(LC50)_{i,j,k}$, are either $\ln(LC50_w)$ or $\ln(LC50_{s,oc})$ corresponding to a water-only or sediment exposure; μ_i are the population of ln(LC50) for chemical-organism pair i. The error structure is assumed to be lognormal which corresponds to assuming that the errors are proportional to the means, e.g. 20%, rather than absolute quantities, e.g. 1 $\mu g/g_{OC}$. The statistical problem is to estimate μ_i, $(\sigma_A)^2$, and $(\sigma_\in)^2$. The maximum likelihood method is used to make these estimates (U.S. EPA, 1993a). The results are shown in Table 5-2.

TABLE 5-2: ANALYSIS OF VARIANCE FOR DERIVATION OF SEDIMENT QUALITY CRITERIA CONFIDENCE LIMITS FOR PHENANTHRENE.

Source of Uncertainty	Parameter	Value ($\mu g/g_{OC}$)
Exposure media	σ_α	0.39
Replication	σ_ϵ	0.21
Sediment Quality Criteria	σ_{SQC} [a]	0.39

[a] $\sigma_{SQC} = \sigma_A$

The last line of Table 5-2 is the uncertainty associated with the SQC i.e., the variance associated with the exposure media variability.

The confidence limits for the SQC are computed using this estimate of uncertainty for SQC. For the 95% confidence interval limits, the significance level is 1.96 for normally distributed errors.

Hence:

$$\ln(SQC_{OC})_{UPPER} = \ln(SQC_{OC}) + 1.96\sigma_{SQC} \quad (5\text{-}5)$$

$$\ln(SQC_{OC})_{LOWER} = \ln(SQC_{OC}) - 1.96\sigma_{SQC} \quad (5\text{-}6)$$

The confidence limits are given in Table 5-3.

The organic carbon normalized SQC is applicable to sediments with an organic carbon fraction of $f_{OC} \geq 0.2\%$. For sediments with $f_{OC} < 0.2\%$, organic carbon normalization and SQC do not apply.

TABLE 5-3. SEDIMENT QUALITY CRITERIA CONFIDENCE LIMITS FOR PHENANTHRENE

Type of Water Body	Sediment Quality Criteria 95% Confidence Limits ($\mu g/g_{oc}$) SQC_{oc} $\mu g/g_{oc}$	Lower	Upper
Fresh Water	180	85	390
Salt Water	240	110	510

5.3 COMPARISON OF PHENANTHRENE SQC AND UNCERTAINTY CONCENTRATIONS TO SEDIMENT CONCENTRATIONS THAT ARE TOXIC OR PREDICTED TO BE CHRONICALLY ACCEPTABLE.

Insight into the magnitude of protection afforded to benthic species by SQC concentrations and 95% confidence intervals can be determined from effect concentrations from toxicity tests with benthic species exposed to sediments spiked with phenanthrene and sediment concentrations predicted to be chronically safe to organisms tested in water-only exposures (Figure 5-1). This is because, effect concentrations in sediments can be predicted from water-only toxicity data and K_{oc} values (See Section 4). Chronically acceptable concentrations are extrapolated from genus mean acute values (GMAV) from water-only, 96-hour lethality tests using acute-chronic ratios (ACR). Therefore, it may be reasonable to combine these two predictive procedures to estimate for phenanthrene, chronically acceptable sediment concentrations (Predicted Genus Mean Chronic Value, PGMCV) from GMAVs (Appendix A), ACRs (Table 3-2) and the K_{oc} (Table 5-1):

$$PGMCV = (GMAV \div ACR)K_{oc}. \qquad (5\text{-}7)$$

In Figures 5-1 and 5-2, each PGMCV for fishes, arthropods or other invertebrates tested

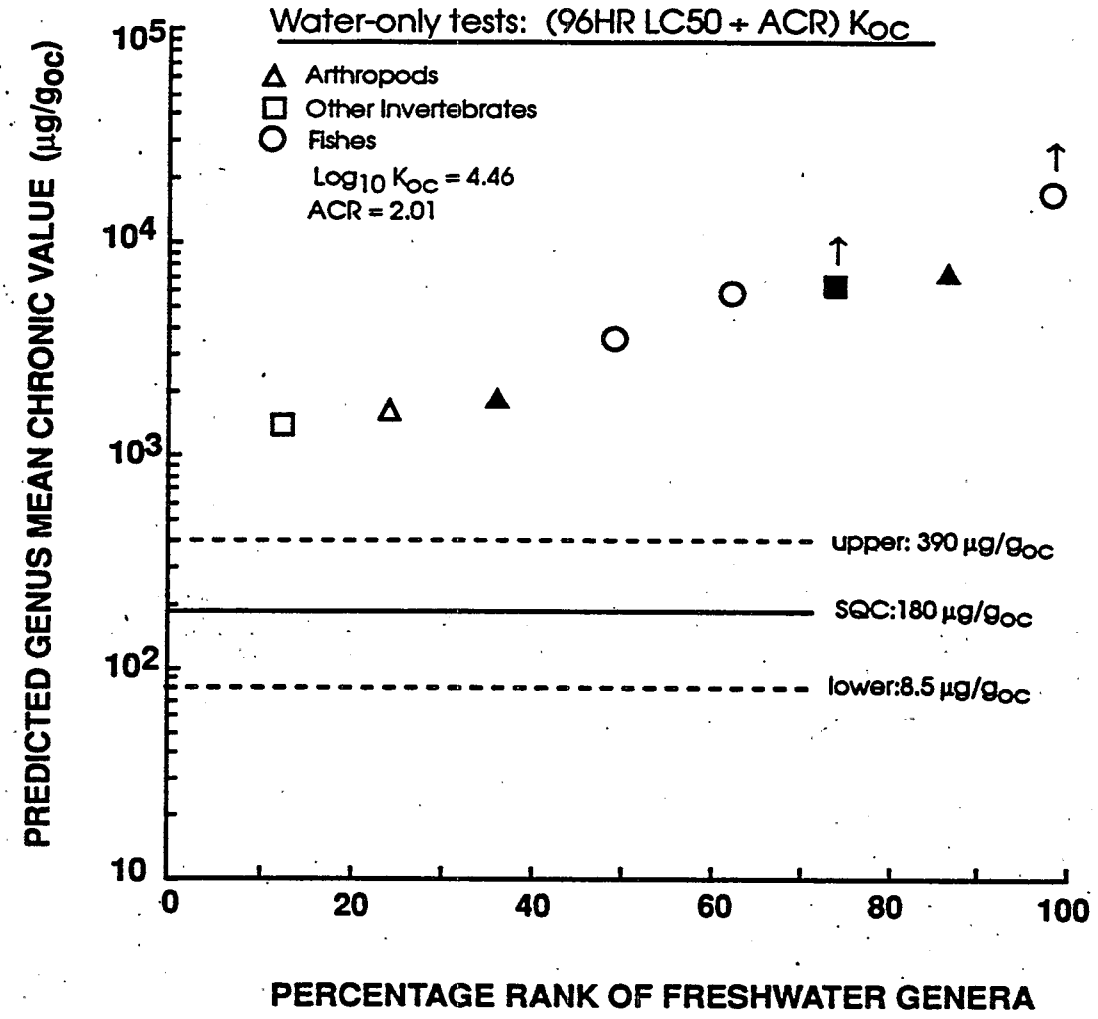


Figure 5-1. Comparison between SQC concentrations and 95% confidence intervals, effect concentrations from benthic organisms exposed to phenanthrene-spiked sediments and sediment concentrations predicted to be chronically safe in fresh water sediments. Concentrations predicted to be chronically safe (Predicted Genus Mean Chronic Values, PGMCV) are derived from the Genus Mean Acute Values (GMAV) from water-only 96-hour lethality tests, Acute Chronic Ratios (ACR) and K_{OC} values. PGMCV = (GMAV ÷ ACR)K_{OC}. Symbols for PGMCVs are Δ for arthropods, ○ for fishes and □ for other invertebrates. Solid symbols are benthic genera; open symbols water column genera. Arrows indicate greater than values. Error bars around sediment LC50 values indicate observed range of LC50s.

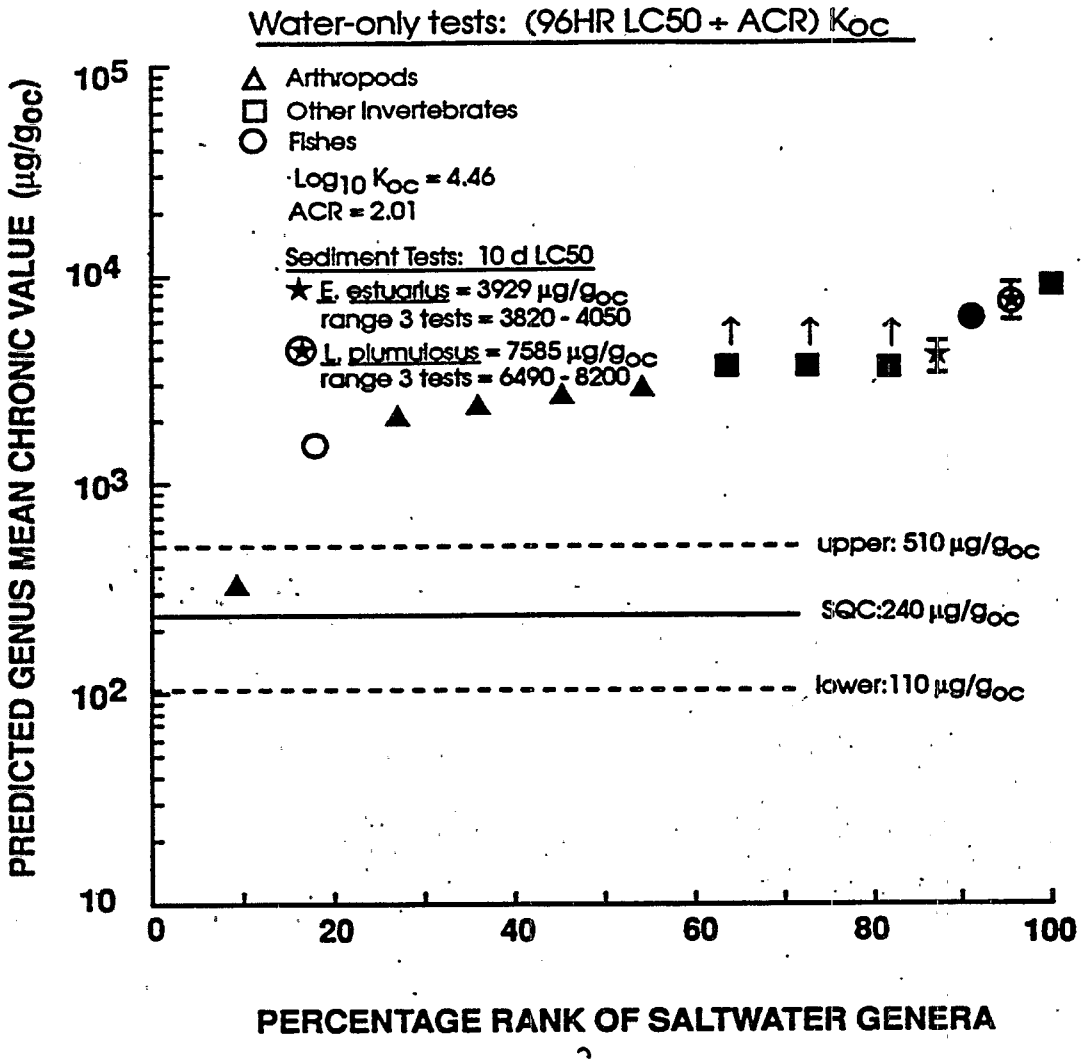


Figure 5-2. Comparison between SQC concentrations and 95% confidence intervals, effect concentrations from benthic organisms exposed to phenanthrene-spiked sediments and sediment concentrations predicted to be chronically safe in salt water sediments. Concentrations predicted to be chronically safe (Predicted Genus Mean Chronic Values, PGMCV) are derived from the Genus Mean Acute Values (GMAV) from water-only 96-hour lethality tests, Acute Chronic Ratios (ACR) and K_{OC} values. PGMCV = (GMAV ÷ ACR)K_{OC}. Symbols for PGMCVs are Δ for arthropods, ○ for fishes and □ for other invertebrates. Solid symbols are benthic genera; open symbols water column genera. Arrows indicate greater than values. Error bars around sediment LC50 values indicate observed range of LC50s.

in water is plotted against the percentage rank of its sensitivity. Results from toxicity tests with benthic organisms exposed to sediments spiked with phenanthrene (Table 4-1) are placed in the PGMCV rank appropriate to the test-specific effect concentration. (For example, the 10-day LC50 for E. estuarius (3,929 $\mu g/g_{oc}$) is placed between the PGMCV of 3,514 $\mu g/g_{oc}$ for the snail, Nassarius, and the PGMCV of 6,155 $\mu g/g_{oc}$ for the minnow, Cyprinodon.) Therefore, LC50 or other effect concentrations are intermingled in this figure with concentrations predicted to be chronically safe. Care should be taken by the reader in interpreting these data with dissimilar endpoints. The following discussion of SQC, organism sensitivities and PGMCVs is not intended to provide accurate predictions of the responses of taxa or communities of benthic organisms relative to specific concentrations of phenanthrene in sediments in the field. It is, however, intended to guide scientists and managers through the complexity of available data relative to potential risks to benthic taxa posed by sediments contaminated with phenanthrene.

The freshwater SQC for phenanthrene (180 $\mu g/g_{oc}$) is less than any of the PGMCVs for freshwater genera. In fact, PGMCVs for all 19 freshwater genera are greater than the upper 95% confidence interval of the SQC (390 $\mu g/g_{oc}$). For phenanthrene, the PGMCVs range over an order of magnitude from the most sensitive to the most tolerant genus. Chronic effect concentrations may, however, occur at concentrations below saturation. A sediment concentration 20 times the SQC would include the PGMCVs of one-half of the 12 benthic genera tested including stoneflies, mayflies, isopods and catfish. Tolerant benthic genera such as the amphipod Gammarus and the crayfish Orconectes might be expected to not be chronically impacted in sediments with phenanthrene concentrations 1000X the SQC. This large margin of safety between all PGMCVs and the SQC results from the need to lower the FCV to protect

intergravel dwelling embryos and sac fry of rainbow trout, Oncorhynchus mykiss. Benthic organisms in habitat where salmonids early life stages are absent may be over protected by this criterion unless species with similar sensitivities are resident at the site.

The saltwater SQC for phenanthrene (240 $\mu g/g_{oc}$) is less than any of the 11 PGMCVs for saltwater genera. Only the PGMCV for the mysid shrimp Mysidopsis bahia (314 $\mu g/g_{oc}$) is lower than the upper 95% confidence interval for the SQC. For phenanthrene, PGMCVs from the most sensitive to the most tolerant saltwater genus range over an order of magnitude. A sediment concentration 11 times the SQC would include the PGMCVs of one-half of the 10 benthic genera tested including four arthropod genera and one polychaete genus. Other genera of benthic polychaetes and fishes are less sensitive and might not be expected to be chronically impacted in sediments with phenanthrene concentrations 20X the SQC. Data from lethality tests with two saltwater amphipods, Eohaustorius estuarius and Leptocheirus plumulosus, substantiate this projection; the 10 day LC50s from three tests with each species range from 16 to 17 times the SQC for E. estuarius and from 27 to 34 times the SQC for L. plumulosus (see Section 4).

5.4 COMPARISON OF PHENANTHRENE SQC TO STORET AND NATIONAL STATUS AND TRENDS DATA FOR SEDIMENT PHENANTHRENE:

A STORET (U.S. EPA, 1989b) data retrieval was performed to obtain a preliminary assessment of the concentrations of phenanthrene in the sediments of the nation's water bodies. Log probability plots of phenanthrene concentrations on a dry weight basis in sediments are shown in Figure 5-3. Phenanthrene is found at varying concentrations in sediments from rivers, lakes and near coastal water bodies in the United States. Median concentrations are generally about 0.1 $\mu g/g$ in each of the three water bodies. There is significant variability with

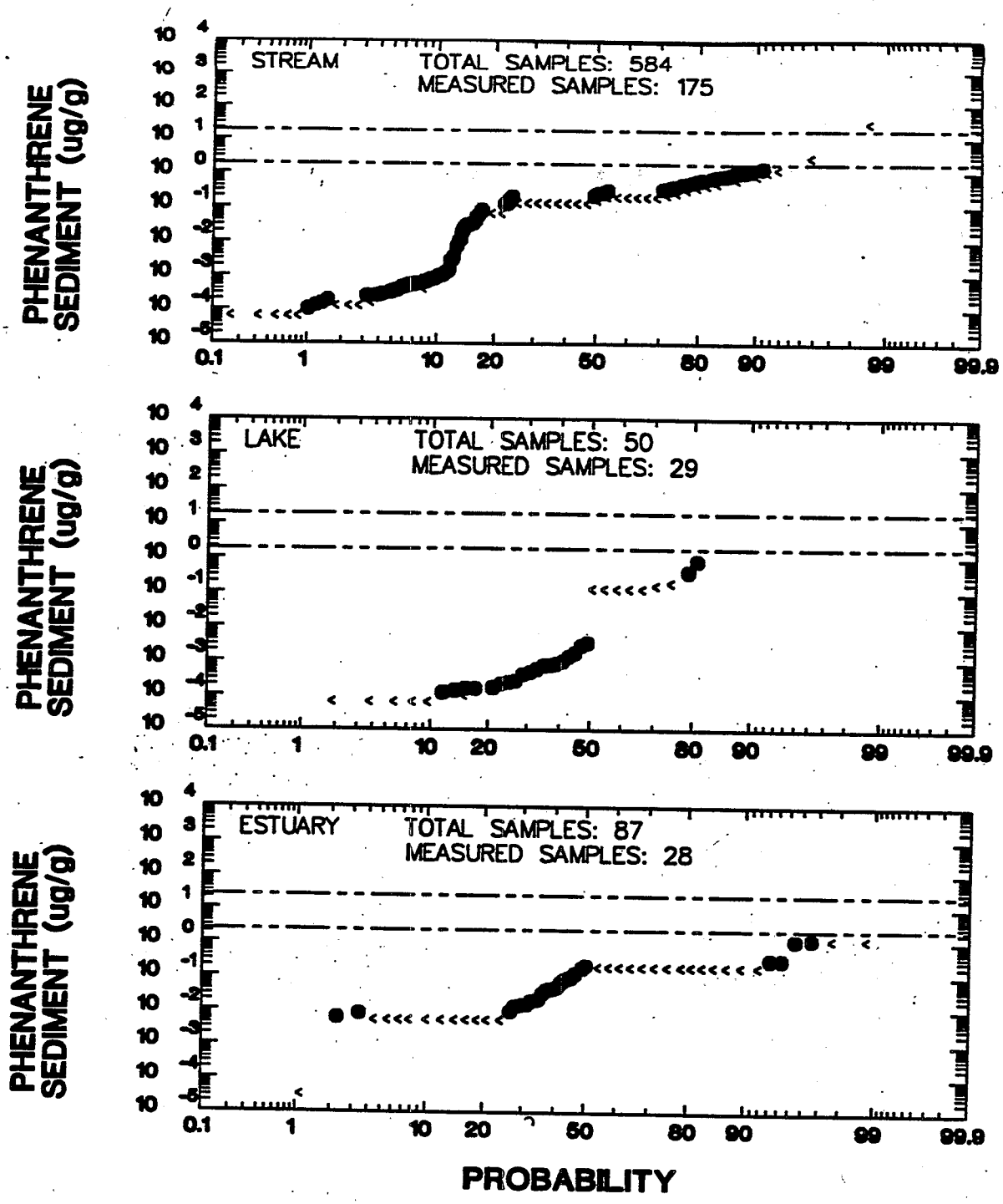


Figure 5-3. Probability distribution of concentrations of phenanthrene in sediments from streams, lakes and estuaries in the United States from 1986 to 1990, from the STORET (U.S. EPA, 1989b) database, compared to the phenanthrene SQC values of 18 ug/g in freshwater sediments having TOC = 10% and 1.8 μg/g in freshwater sediments having TOC = 1% and compared to SQC values for saltwater sediments of 24 μg/g when TOC =10% and 2.4 ug/g when TOC=1%. The upper dashed line on each figure represents the SQC value when TOC = 10%, the lower dashed line represents the SQC when TOC = 1%.

phenanthrene concentrations in sediments ranging over seven orders of magnitude within the country.

The SQC for phenanthrene can be compared to existing concentrations of phenanthrene in sediments of natural water systems in the United States as contained in the STORET database (U.S. EPA, 1989b). These data are generally reported on a dry weight basis, rather than an organic carbon normalized basis. Therefore, SQC values corresponding to sediment organic carbon levels of 1 to 10% are compared to phenanthrene's distribution in sediments as examples only. For fresh water sediments, SQC values are 1.8 μg/g dry weight in sediments having 1% organic carbon and 18 μg/g dry weight in sediments having 10% organic carbon; for marine sediments SQC are 2.4 μg/g dry weight and 24 μg/g dry weight, respectively. Figure 5-3 presents the comparisons of these SQC to probability distributions of observed sediment phenanthrene levels for streams and lakes (fresh water systems, shown on the upper panels) and estuaries (marine systems, lower panel). For streams (n = 584) the SQC of 1.8 μg/g dry weight for 1% organic carbon fresh water sediments is exceeded for 4% of the data and the SQC of 18 μg/g dry weight for fresh water sediments having 10% TOC is exceeded by less than 2% of the data. For lakes (n = 50) neither the SQC for 1% organic carbon fresh water sediments nor the SQC for fresh water sediments with 10% organic carbon are exceeded by the post 1986 samples. Similarly, in estuaries, the data (n = 87) indicate that neither the criteria of 2.4 ug/g dry weight for salt water sediments having 1% organic carbon nor the criteria of 24 μg/g dry weight for salt water sediments having 10% organic carbon are exceeded by the post 1986 samples.

The phenanthrene distribution in Figure 5-3 includes data from some samples in which the phenanthrene concentration was below the detection limit. These data are indicated

on the plot as "less than" symbols (<), and plotted at the reported detection limits. Because these values represent upper bounds and not measured values the percentage of samples in which the SQC values are actually exceeded may be less than the percentage reported.

A second database developed as part of the National Status and Trends Program (NOAA, 1991) is also available for assessing contaminant levels in marine sediments that are representative of areas away from sources of contamination. The probability distribution for these data, which can be directly expressed on an organic carbon basis, is compared to the saltwater SQC for phenanthrene (240 $\mu g/g_{oc}$) on Figure 5-4. Data presented are from sediments with 0.20 to 31.9 percent organic carbon. The median organic carbon normalized phenanthrene concentration (about 5.0 $\mu g/g_{oc}$) is a factor of 32 below the SQC of 240 $\mu g/g_{oc}$. Less than 1% of these samples (n = 900) exceeded the criteria. Hence, these results are consistent with the preceding comparison of the marine SQC to STORET data.

Regional differences in phenanthrene concentrations may affect the above conclusions concerning expected criteria exceedences. This analysis also does not consider other factors such as the type of samples collected (i.e., whether samples were from surficial grab samples or vertical core profiles), or the relative frequencies and intensities of sampling in different study areas. It is presented as an aid in assessing the range of reported phenanthrene sediment concentrations and the extent to which they may exceed the SQC.

5.5 LIMITATIONS TO THE APPLICABILITY OF SEDIMENT QUALITY CRITERIA:

Rarely, if ever, are contaminants found alone in naturally occurring sediments. Obviously, the fact that the concentration of a particular contaminant does not exceed the SQC does not mean that other chemicals, for which there are no SQC available, are not present in

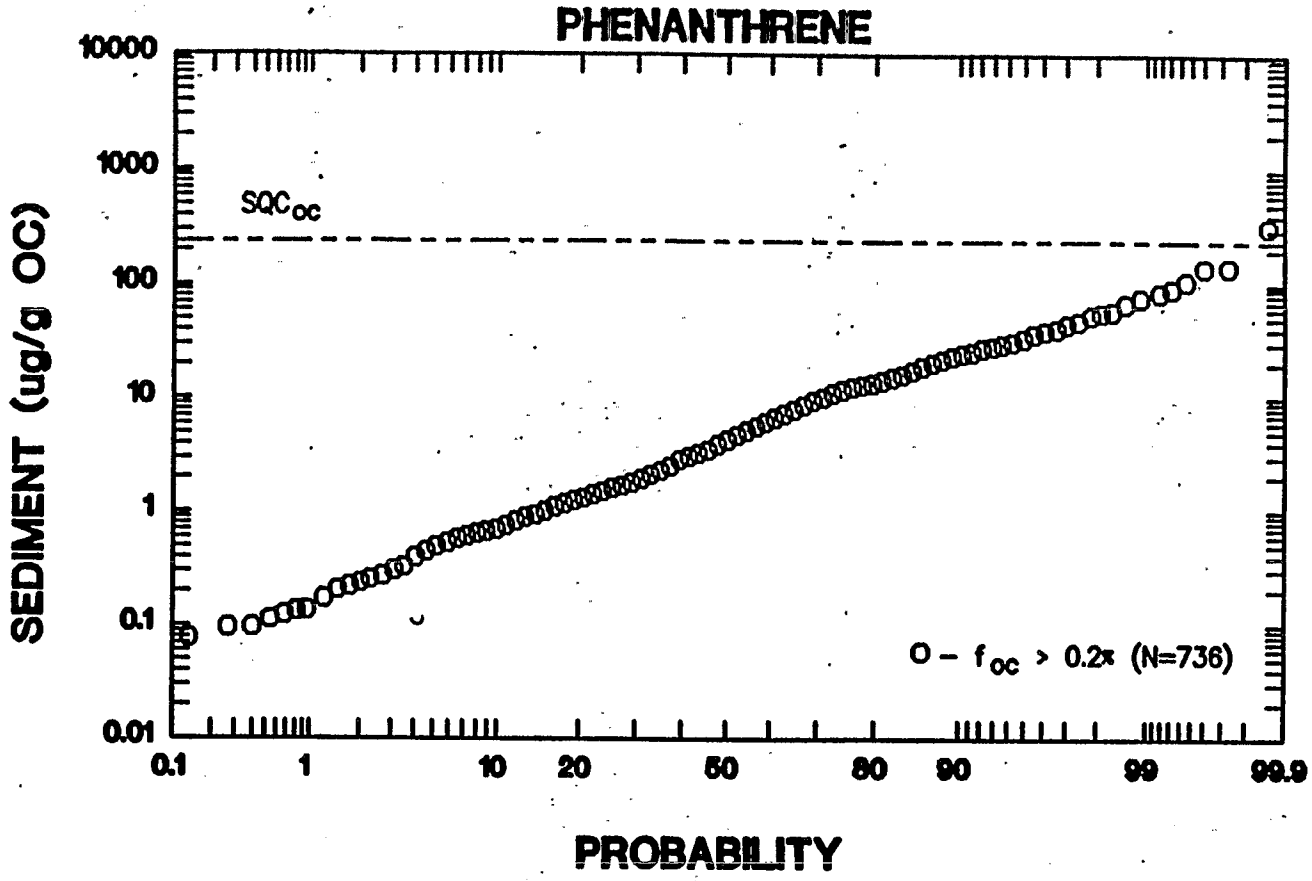


Figure 5-4. Probability distribution of concentrations of phenanthrene in sediments from coastal and estuarine sites from 1984 to 1989 as measured by the National Status and Trends Program (NOAA, 1991). The horizontal line is the saltwater SQC value of 240 $\mu g/g_{oc}$.

concentrations sufficient to cause harmful effects. Furthermore, even if SQC were available for all of the contaminants in a particular sediment, there might be additive or synergistic effects that the criteria do not address. In this sense the SQC represent "best case" criteria.

The concerns about mixtures of contaminants are particularly important with the PAHs, which almost invariably occur as complex mixtures. Some guidance on interpretations of PAH concentrations is possible given the presence of SQC for phenanthrene and other individual PAHs. This is because much is known about the toxicity and structure-activity relationships of the so-called narcosis chemicals, a group of nonionic organic chemicals to which the PAHs belong. The toxicity of the narcosis chemicals is additive (Broderius and Kahl, 1985). The toxicity of these chemicals increases with increasing K_{ow} (Veith et al., 1983) and their bioavailability in sediments decreases as a function of its K_{ow}. Therefore, the toxicities of many PAHs in sediments are likely to be similar. This explains why SQC values for fluoranthene (fresh: 620 $\mu g/g_{oc}$, salt: 300 $\mu g/g_{oc}$), acenaphthene (fresh: 130 $\mu g/g_{oc}$, salt: 230 $\mu g/g_{oc}$) and phenanthrene (fresh: 180 $\mu g/g_{oc}$, salt: 240 $\mu g/g_{oc}$) differ little and why it is theoretically possible to develop an SQC for total PAHs. EPA is currently conducting research aimed at development of SQC for combined PAHs.

It is theoretically possible that antagonistic reactions between chemicals could reduce the toxicity of a given chemical such that it might not cause unacceptable effects on benthic organisms at concentrations above the SQC when it occurs with the antagonistic chemical. However, antagonism has rarely been demonstrated. What should be much more common are instances where toxic effects occur at concentrations below the SQC because of the additivity of toxicity of many common contaminants (Alabaster and Lloyd, 1982), e.g. heavy metals and

PAHs, and instances where other toxic compounds for which no SQC exist occur along with SQC chemicals.

Care must be used in application of EqP-based SQC in disequilibrium conditions. In some instances site-specific SQC may be required to address this condition. EqP-based SQC assume that nonionic organic chemicals are in equilibrium with the sediment and IW and are associated with sediment primarily through adsorption into sediment organic carbon. In order for these assumptions to be valid, the chemical must be dissolved in IW and partitioned into sediment organic carbon. The chemical must, therefore, be associated with the sediment for a sufficient length of time for equilibrium to be reached. In sediments where particles like cinder, soot, or oil droplets contain PAHs, disequilibrium exists and criteria are over protective. In liquid chemical spill situations disequilibrium concentrations in interstitial and overlying water may be proportionately higher relative to sediment concentrations. In this case criteria may be underprotective.

In very dynamic areas, with highly erosional or depositional bedded sediments, equilibrium may not be attained with contaminants. However, even high K_{ow} nonionic organic compounds come to equilibrium in clean sediment in a period of days, weeks or months. Equilibrium times are shorter for mixtures of two sediments each previously at equilibrium. This is particularly relevant in tidal situations where large volumes of sediments are eroded and deposited, yet near equilibrium conditions may predominate over large areas. Except for spills and particulate chemical, near equilibrium is the rule and disequilibrium is uncommon. In instances where it is suspected that EqP does not apply for a particular sediment because of disequilibrium discussed above, site-specific methodologies may be applied (U.S. EPA, 1993b).

SECTION 6

CRITERIA STATEMENT

The procedures described in the "Technical Basis for Deriving Numerical Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic Organisms by Using Equilibrium Partitioning" (U.S. EPA, 1993a) indicate that benthic organisms should be acceptably protected in freshwater sediments containing $\leq$ 180 μg phenanthrene/g organic carbon and saltwater sediments containing $\leq$ 240 μg phenanthrene/g organic carbon, except possibly where a locally important species is very sensitive or sediment organic carbon is < 0.2%.

Confidence limits of 85 to 390 $\mu g/g_{oc}$ for freshwater sediments and 110 to 510 $\mu g/g_{oc}$ for saltwater sediments are provided as an estimate of the uncertainty associated with the degree to which the observed concentration in sediment ($\mu g/g_{oc}$), which may be toxic, can be predicted using the organic carbon partition coefficient (K_{oc}) and the water-only effects concentration. Confidence limits do not incorporate uncertainty associated with water quality criteria. An understanding of the theoretical basis of the equilibrium partitioning methodology, uncertainty, the partitioning and toxicity of phenanthrene, and sound judgement are required in the regulatory use of SQC and their confidence limits.

These concentrations represent the U.S. EPA's best judgement at this time of the levels of

phenanthrene in sediments that would be protective of benthic species. It is the philosophy of the Agency and the EPA Science Advisory Board that the use of sediment quality criteria (SQCs) as stand-alone, pass-fail criteria is not recommended for all applications and should frequently trigger additional studies at sites under investigation. The upper confidence limit should be interpreted as a concentration above which impacts on benthic species should be expected. Conversely, the lower confidence limit should be interpreted as a concentration below which impacts on benthic species should be unlikely.

SECTION 7

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APPENDIX A - SUMMARY OF ACUTE VALUES FOR PHENANTHRENE FOR FRESHWATER AND SALTWATER SPECIES.

COMMON/SCI. NAME	LIFE[a] STAGE	HAB-[b] ITAT	METHOD[c]	CONCEN- TRATION[d]	LC50/[e] EC50	HMAV SPECIES[f]	HMAV GENUS[g]	OVERALL[h] GMAV	REFERENCES[i]
					µg/L	µg/L	µg/L	µg/L	
FRESHWATER SPECIES									
Hydra, *Hydra* sp.	X	W	FT	M	96	96	96	96	Call et al., 1986
Annelid, *Lumbriculus variegatus*	X	I	FT	M	>419	>419	>419	>419	Call et al., 1986
Cladoceran, *Daphnia magna*	X	W	S	U	843	-	-	-	Eastmond et al., 1984
Cladoceran, *Daphnia magna*	1st instar	W	S	M	700	-	-	-	Millemann et al., 1984
Cladoceran, *Daphnia magna*	4-6 days	W	S	U	207	-	-	-	Abernethy et al., 1986
Cladoceran, *Daphnia magna*	X	W	FT	M	117	117	-	-	Call et al., 1986
Cladoceran, *Daphnia pulex*	<24 hr	W	S	U	734	-	-	-	Passino and Smith, 1987
Cladoceran, *Daphnia pulex*	X	W	S	U	> 1150	-	-	-	Geiger and Buikema, 1981, 1982
Cladoceran, *Daphnia pulex*	X	W	S	M	100	100	108.2	108.2	Trucco et al., 1983
Amphipod, *Gammarus pseudolimnaeus*	X	E	FT	M	126	126	126	126	Call et al., 1986
Midge, *Chironomus tentans*	L	I	S	M	490	490	490	490	Millemann et al., 1984
Rainbow trout, *Oncorhynchus mykiss*	J	W	FT	M	375	375	375	375	Call et al., 1986
Fathead minnow, *Pimephales promelas*	J	W	S	M	> 1150	> 1150	> 1150	> 1150	Millemann et al., 1984, U.S. EPA 1978
Bluegill, *Lepomis macrochirus*	J	W	FT	M	234	234	234	234	Call et al., 1986

Appendix A - Phenanthrene: (continued)

COMMON/SCI. NAME	LIFE[a] STAGE	HAB-[b] ITAT	METHOD[c]	CONCEN- TRATION[d]	LC50/[e] EC50	HMAV SPECIES[f]	HMAV GENUS[g]	OVERALL[h] GMAV	REFERENCES[i]
					µg/L	µg/L	µg/L	µg/L	
SALTWATER SPECIES									
Archiannelid, *Dinophilus gyrociliatus*	J	I	R	U	185.4	185.4	185.4	185.4	Battelle Ocean Sciences, 1987
Polychaete worm, *Neanthes arenaceodentata*	A	I	S	U	600	600	600	600	Rossi and Neff, 1978
Mud snail, *Nassarius obsoletus*	A	I,E	R	M	> 245	> 245	> 245	> 245	Battelle Ocean Sciences, 1987
Blue mussel, *Mytilus edulis*	A	E,W	R	M	> 245	> 245	> 245	> 245	Battelle Ocean Sciences, 1987
Soft-shell clam, *Mya arenaria*	A	I	R	M	> 245	> 245	> 245	> 245	Battelle Ocean Sciences, 1987
Mysid, *Mysidopsis bahia*	J	E	FT	M	17.7	-	-	-	Battelle Ocean Sciences, 1987
Mysid, *Mysidopsis bahia*	J	E	FT	M	27.10	21.91	21.91	21.91	Kuhn and Lussier, 1987
Amphipod, *Leptocheirus plumulosus*	A	E	FT	M	198.4	198.4	198.4	198.4	Swartz, 1991
Grass shrimp, *Palaemonetes pugio*	A	E,W	R	U	200.8	-	-	-	Battelle Ocean Sciences, 1987
Grass shrimp, *Palaemonetes pugio*	A	E,W	FT	M	145.4	145.4	145.4	145.4	Battelle Ocean Sciences, 1987
Hermit crab, *Pagurus longicarpus*	A	E	FT	M	163.7	163.7	163.7	163.7	Battelle Ocean Sciences, 1987
Sheepshead minnow, *Cyprinodon variegatus*	J	E,W	R	U	>245	-	-	-	Battelle Ocean Sciences, 1987
Sheepshead minnow, *Cyprinodon variegatus*	J	E,W	FT	M	429.4	429.4	429.4	429.4	Battelle Ocean Sciences, 1987
Atlantic silverside, *Menidia menidia*	A	W	FT	M	108	108	108	108	Battelle Ocean Sciences, 1987

[a]Lifestage: A = adult, J = juvenile, L = larvae, E = embryo, U = lifestage and habitat unknown, X = lifestage un known but habitat known.

[b]Habitat: I = infauna, E = epibenthic, W = water column.

[c]Method: S = static, R = renewal, FT = flow-through.

[d]Concentration: U = unmeasured (nominal), M = chemical measured.

[e]Acute value: 96-hour LC50 or EC50, exceptions from Stephan et al. (1985).

[f]HMAV species: Habitat Mean Acute Value - Species is the geometric mean of acute values by species for benthic and water column lifestages.

[g]HMAV: genus: Geometric mean of HMAV for species within a genus.

[h]Overall GMAV: Geometric mean of acute values across species, habitats and lifestages within the genus.

APPENDIX B. - SUMMARY OF DATA FROM SEDIMENT SPIKING EXPERIMENTS WITH PHENANTHRENE. DATA FROM THESE EXPERIMENTS WERE USED TO CALCULATE K_{oc} VALUES (FIGURE 2-1) AND TO COMPARE MORTALITIES OF AMPHIPODS WITH PORE-WATER TOXIC UNITS (FIGURE 4-1) AND PREDICTED SEDIMENT TOXIC UNITS (FIGURE 4-2).

SEDIMENT SOURCE/ SPECIES TESTED	MORTALITY (%)	SEDIMENT CONCENTRATION, µg/g DRY WT.	SEDIMENT CONCENTRATION, µg/g ORG. CAR.	PORE WATER CONCENTRATION (ug/L)	TOC (%)	Log K_{oc}[a]	REFERENCES
South Beach,	5	0	0	0	0.82		Swartz, 1991
OR.	5	0	0	0	1.02		
Eohaustorius	5	4	400	15	1.02	4.43	
estuarius	5	6.3	620	25	1.02	4.39	
	12.5	10.8	1060	40	1.02	4.42	
	17.5	18	1760	74	1.02	4.38	
	30	26.3	2570	105	1.02	4.39	
	52.5	49.3	4830	174	1.02	4.44	
	97.5	82.5	10070	344	0.82	4.47	
McKinney	15	0	0	0	2.36		Swartz, 1991
Slough, OR.	7.5	0	0	0	2.47		
Eohaustorius	15	11.4	460	18	2.47	4.41	
estuarius	22.5	19	770	30	2.47	4.41	
	12.5	27.2	1100	52	2.47	4.33	
	22.5	48.4	1960	99	2.47	4.29	
	32.5	61.5	2480	118	2.47	4.32	
	72.5	145.5	5870	201	2.47	4.47	
	100	194	8220	291	2.36	4.45	
Eckman Slough	25	0	0	0	2.97		Swartz, 1991
Site 1, OR.	5	0	0	0	3.33		
Eohaustorius	2.5	18.6	560	20	3.33	4.45	
estuarius	5	32.7	980	40	3.33	4.39	
	7.5	50.2	1510	66	3.33	4.36	
	7.5	54.6	1640	79	3.33	4.32	
	10	60.6	1820	88	3.33	4.32	
	35	87	2610	125	3.33	4.32	
	97.5	282	9530	294	2.97	4.51	

APPENDIX B. Phenanthrene (cont'd)

SEDIMENT SOURCE/ SPECIES TESTED	MORTALITY (%)	SEDIMENT CONCENTRATION, µg/g DRY WT.	SEDIMENT CONCENTRATION, µg/g ORG. CAR.	PORE WATER CONCENTRATION (ug/L)	TOC (%)	Log K_{oc}*	REFERENCES
South Beach,	0	0	0	0	0.82		Swartz, 1991
OR.	2.5	0	0	0	1.96		
Leptocheirus	2.5	6.4	320	24	1.96	4.12	
plumulosus	7.5	11	560	42	1.96	4.12	
	5	19.1	970	70	1.96	4.14	
	0	27	1370	117	1.96	4.07	
	5	48.8	2490	168	1.96	4.17	
	35	70.6	3600	268	1.96	4.13	
	60	107.7	13130	478	0.82	4.44	
McKinney	0	0	0	0	2.36		Swartz, 1991
Slough, OR.	2.5	0	0	0	2.5		
Leptocheirus	5	19	760	31	2.5	4.39	
plumulosus	15	30.3	1210	57	2.5	4.33	
	7.5	49.4	1970	98	2.5	4.30	
	5	77.1	3080	159	2.5	4.29	
	10	120	4800	246	2.5	4.29	
	60	173.2	6920	321	2.5	4.33	
	80	270	11440	382	2.36	4.48	
Eckman	7.5	0	0	0	3.6		Swartz, 1991
Site 1, OR.	12.5	27.5	760	39	3.6	4.29	
Leptocheirus	17.5	44.1	1220	62	3.6	4.29	
plumulosus	17.5	61	1690	84	3.6	4.30	
	12.5	76.6	2120	119	3.6	4.25	
	17.5	105	2910	163	3.6	4.25	
	22.5	174.9	4850	232	3.6	4.32	
	52.5	263.4	8870	401	2.97	4.34	
	80	346.4	11660	438	2.97	4.43	

*K_{OC} (L/kg) = sediment concentration ($\mu g/g_{OC}$) ÷ calculated free pore water concentration ($\mu g/L$) $\bullet 10^3$ g/kg.