



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

EPA-SAB-EHC-90-005

January 17, 1990

OFFICE OF
THE ADMINISTRATOR

Honorable William K. Reilly
Administrator
U.S. Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Subject: Science Advisory Board's comments on the use of uncertainty and modifying factors in establishing Reference Dose levels.

Dear Mr. Reilly:

At its October 26, 1989 meeting, the Science Advisory Board's Environmental Health Committee reviewed the use of uncertainty and modifying factors in the assessment of the risks of systemic toxicants (non-carcinogens), as summarized in presentations by Office of Research and Development staff. The determination of these factors is important because they are applied to toxicity data to yield the Reference Dose (RfD) --an estimate of a daily exposure to the human population that is likely to be without deleterious effects during a lifetime--which serves as the basis for many subsequent regulatory decisions. Clearly, inadequate compensation for uncertainty in the available data could result in underestimation of risks, leading to underprotection and unsafe exposures, and causing adverse health effects; on the other hand, overcompensation could result in overprotection and unnecessary economic costs.

The Committee has reservations about the current use of the NOAEL (No Observed Adverse Effect Level) or LOAEL (Lowest Observed Adverse Effect Level) to calculate the RfD. Neither of these measures are biological properties, and both are highly dependent upon experimental design in a way that may reward poor experimentation (i.e., higher NOAELS/LOAELS are associated with poor experiments; hence, poor experiments could result in less protective RfDs than better designed experiments). In addition, the NOAEL/LOAEL concept, by focusing on two specific points, ignores much of the available experimental data; if there is

significant trend in response with increasing dose, this trend should be factored into the estimation of the RfD. The NOAEL/LOAEL approach does not consider this trend and can result in an RfD which is not sufficiently protective.

There are alternatives to the NOAEL/LOAEL approach which mitigate the above problems, and, because they utilize all the observed data, tend to reduce the random errors which exist even in well designed experiments. These alternatives include use of the benchmark dose level--the lower confidence limit on the estimate of the dose levels associated with a 10% or 1% response (ED_{10} and ED_{01} , respectively). These may be readily estimable, and the Environmental Health Committee recommends that the Agency consider incorporating the use of these methods in addition to the current NOAEL/LOAEL procedure. Experience with, and comparisons of, both the benchmark and LOAEL/NOAEL methods will aid in the choice of a procedure for the longer run and will help illuminate the impacts of experimental design on the current approaches.

With respect to uncertainty factors, the Committee notes that for certain chemicals, empirical evidence can be used to estimate the magnitude of factors required to extrapolate from animal data to humans. These analyses show that the magnitude of the extrapolation factors required varied greatly among chemicals. A factor of ten is generally protective, except perhaps for extrapolation from animals to humans, where some empirical evidence suggests that greater factors are needed to compensate for inter-species sensitivity. In other cases, e.g. those involving length of experiment or adjustment from acute study to a chronic endpoint, an extrapolation factor of ten may not be necessary. More research is clearly needed to investigate the appropriate magnitude of such factors, but the Agency has no established comprehensive research program to validate the current factors and to improve or replace them where necessary. Given the importance of this area, such research is warranted. It would even be facilitated by an apparently rich data base residing within the Office of Pesticides Programs. Such research should also be undertaken by a multi-disciplinary team including toxicologists, epidemiologists, and biostatisticians. Also, in regards to improving current practices, the Committee strongly recommends that a statistician be added to the RfD Working Group, which reviews the development of these indices from current data.

The Environmental Health Committee would be happy to work with the Agency as it develops and carries out such a research program, and to review this issue as more research results become available.

Raymond C. Loehr
Dr. ~~Raymond~~ Loehr, Chairman
Science Advisory Board

Arthur C. Upton
Dr. Arthur Upton, Chairman
Environmental Health Committee



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

APR 1 1990

THE ADMINISTRATOR

Dr. Raymond C. Loehr
Chairman
Science Advisory Board
Environmental Protection Agency
401 M Street, S.W.
Washington, D.C. 20460

Dear Ray:

The Agency appreciates your thoughtful comments on its Reference Dose (RfD) approach and your recommendations for additional research. Given the importance of the RfD in noncancer health risk assessments, your comments and recommendations are timely. Indeed, the Agency has already taken account of some of your suggestions. The enclosure more fully discusses our response.

I am always pleased to work with you or members of the Board. Your Committee's expertise has proved invaluable to the Agency. Any additional thoughts on this matter are welcome and would contribute significantly to our efforts.

Sincerely yours,

A handwritten signature in cursive script that reads "Bill".

William K. Reilly

Enclosure

**Response to Issues Raised by the Science Advisory Board
During its October 26, 1989 Meeting Regarding
Uncertainty Factors and Reference Dose**

Comment:

"The Committee has reservations about the current use of the NOAEL (No Observed Adverse Effect Level) or LOAEL (Lowest Observed Adverse Effect Level) to calculate the RfD. Neither of these measures are biological properties, and both are highly dependent upon experimental design in a way that may reward poor experimentation (i.e., higher NOAELS/LOAELS are associated with poor experiments; hence, poor experiments could result in less protective RfDs than better designed experiments). In addition, the NOAEL/LOAEL concept, by focusing on two specific points, ignores much of the available experimental data; if there is a significant trend in response with increasing dose, this trend should be factored into the estimation of the RfD. The NOAEL/LOAEL approach does not consider this trend and can result in an RfD which is not sufficiently protective."

Response:

We agree that No-Observed-Adverse-Effect Levels (NOAELs) and Lowest-Observed-Adverse-Effect Levels (LOAELs) are not biological properties. In a given toxicity study, NOAELs and LOAELs are simple tools that the Agency uses to estimate the likely range in experimental threshold of toxic response. Given many studies, the use of these tools allows the Agency to determine more easily the critical effect, a concept useful for many of our goals. The Committee is correct, however, in stating the limitations in use of NOAELs and LOAELs. The Agency has recognized this as well and has been researching various improvements, some of which have recently been published (1,2).

Comment:

"There are alternatives to the NOAEL/LOAEL approach which mitigate the above problems, and, because they utilize all the observed data, tend to reduce the random errors which exist even in well designed experiments. These alternatives include use of the benchmark dose level--the lower confidence limit on the

estimate of the dose levels associated with a 10% or 1% response (ED₁₀ and ED₀₁ respectively). These may be readily estimable, and the Environmental Health Committee recommends that the Agency consider incorporating the use of these methods in addition to the current NOAEL/LOAEL procedure. Experience with, and comparisons of, both the benchmark and LOAEL/NOAEL methods will aid in the choice of a procedure for the longer run and will help illuminate the impacts of experimental design on the current approaches."

Response:

These comments highlight the "benchmark dose level," a concept first published in 1984 (3) and developed through the use of Agency resources. Subsequent publications in this area by Agency scientists and others (4,5) have enhanced the original concept. The Agency will soon publish its quantitative guidelines for noncancer health effects (6) in the Federal Register for public comments. These guidelines describe several quantitative approaches. The "benchmark" model and its data requirements had been discussed in a general fashion. However, based in part on your input at the October 26, 1989 meeting this text has been modified to expand the discussion of this model and the need for review of chemical specific data when choosing an approach. Moreover, EPA's Risk Assessment Forum is sponsoring an internal colloquium on the "benchmark" model in March.

Comment:

"With respect to uncertainty factors, the Committee notes that for certain chemicals, empirical evidence can be used to estimate the magnitude of factors required to extrapolate from animal data to humans. These analyses show that the magnitude of the extrapolation factors required varied greatly among chemicals. A factor of ten is generally protective, except perhaps for extrapolation from animals to humans, where some empirical evidence suggests that greater factors are needed to compensate for inter-species sensitivity. In other cases, e.g. those involving length of experiment or adjustment from acute study to a chronic endpoint, an extrapolation factor of ten may not be necessary."

Response:

The general bases of Uncertainty Factors (UFs) are empirical observations (7) and the Agency's usual use of 10-fold values reflects the known underlying imprecision of these UFs. However, your comment correctly emphasizes the use of scientific judgment rather than rote in the choice of UF. The Agency has based several other-than-10 UFs on chemical-specific information (e.g., see the RfD for Aldicarb or Acephate on IRIS), but we agree that the Agency should more frequently evaluate chemical-specific data as a means of choosing UFs.

Comment:

"More research is clearly needed to investigate the appropriate magnitude of such factors, but the Agency has no established comprehensive research program to validate the current factors and to improve or replace them where necessary. Given the importance of this area, such research is warranted. It would even be facilitated by an apparently rich data base residing within the Office of Pesticides Programs. Such research should also be undertaken by a multi-disciplinary team including toxicologists, epidemiologists, and biostatisticians."

Response:

The Agency and others have investigated the appropriate magnitude of UFs (8,9), but we agree that this research is neither comprehensive nor highly visible. Your comment on the rich data base residing in our Office of Pesticide Programs (OPP) is likewise correct. A recent manuscript by a team of our scientists (composed of toxicologists and a statistician) has tapped the OPP resource (10), but we agree that much more could be done and that additional expertise (e.g. epidemiology) would help.

Comment:

"Also, in regard to improving current practices, the Committee strongly recommends that a statistician be added to the RfD Working Group, which reviews the development of these indices from current data."

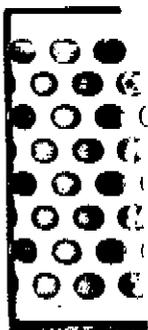
Response:

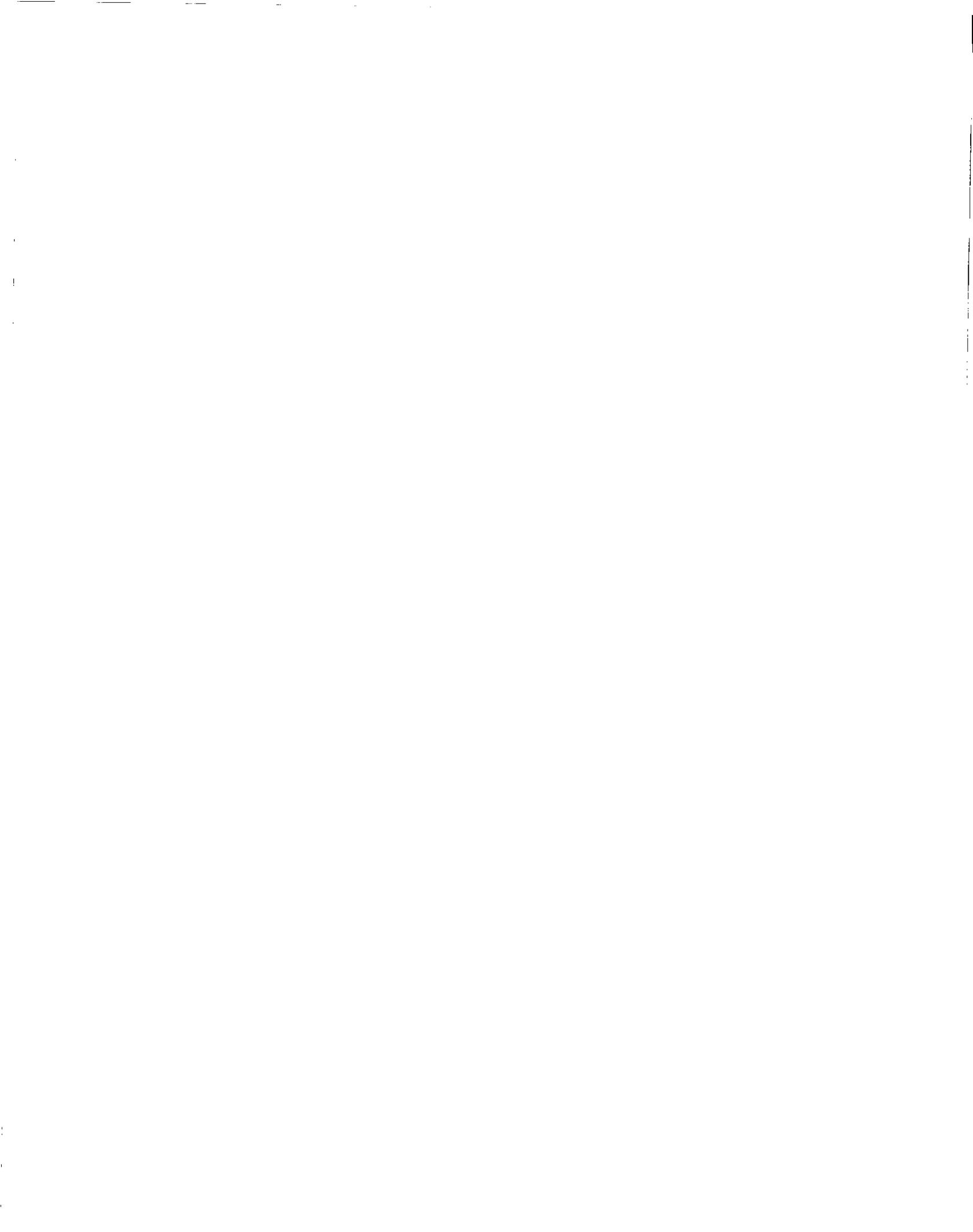
We are now seeking a qualified statistician as a member of the RfD Work Group as per your suggestion.

RESEARCH PUBLICATIONS ON REFERENCE DOSE (RFD)*

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2. Hertzberg, R. 1989. Fitting a model to categorical response data with application to species extrapolation of toxicity. *Twenty-sixth Hanford Life Sciences Symposium, "Modeling for scaling to man, biology, dosimetry, and response."* *Health Physics.* Vol. 57, Supplement 1. Pgs. 405-409.
3. Crump, K.S. 1984. A new method for determining allowable daily intakes. *Fund. and Appl. Toxicol.* 4: 854-871.
4. Dourson, M.L., R.C. Hertzberg, R. Hartung and K. Blackburn. 1985. Novel approaches for the estimation of acceptable daily intake. *Toxicol. Ind. Health.* 1(4): 23-41.
5. Kimmel, C.A. and D.W. Gaylor. 1988. Issues in qualitative and quantitative risk analysis for developmental toxicity. *Risk Anal.* 8(1): 15-20.
6. U.S. EPA, 1990. *General Quantitative Risk Assessment Guidelines for Noncancer Health Effects.* Risk Assesmer Forum, Office of Research and Development, Washington, D.C.
7. Dourson, M.L. and J.F. Stara. 1983. Regulatory history of experimental support of uncertainty (safety) factors. *Toxicol. Pharmacol.* 3: 224-238.
8. Calabrese, E.J. 1985. Uncertainty factors and interindividual variation. *Regulatory Toxicol. Phar.* 5: 190-196.
9. Hattis, D., L. Erdreich, and M. Ballew. 1987. Hur variability in susceptibility to toxic chemicals - preliminary analysis of pharmacokinetic data from volunteers. *Risk Analysis.* 7(4): 415-426.
10. Dourson, M.L., L. Knauf, and J.C. Swartout. 1990. reference dose (RfD) and its underlying toxicity (Submitted).

*This list is not meant to be comprehensive.







EPA

U.S. Environmental
Protection Agency

Washington, DC
EPA-SAB-EPEC-90-006

**Report of The Sediment
Criteria Subcommittee of The
Ecological Processes and
Effects Committee**

**Evaluation of The Equilibrium
Partitioning (EqP) Approach for
Assessing Sediment Quality**



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

February 26, 1990

EPA-SAB-EPEC-90-006

OFFICE OF
THE ADMINISTRATOR

The Honorable William Reilly
Administrator
U.S. Environmental Protection Agency
401 M. Street, S.W.
Washington, D.C. 20460

Dear Mr. Reilly:

The Sediment Criteria Subcommittee of the Science Advisory Board has completed its review of the Equilibrium Partitioning (EqP) approach for judging sediment quality. This approach was developed by or under the auspices of EPA's Office of Water, Criteria and Standards Division, which requested this review.

The SAB was asked to review the sediment assessment approaches in order to:

- 1) Evaluate the scientific and technical foundations for each methodology;
- 2) Evaluate the feasibility of using each method for determining the extent of contamination and risk posed to the environment and man;
- 3) Identify research directions that would provide information to strengthen each methodology; and
- 4) Compare and contrast the strengths and weaknesses of the methodologies available to EPA based on Agency provided documents.

The review was conducted by the Sediment Criteria Subcommittee which was established to review the Agency's technical methodologies for sediment quality assessment. This is their second report. The committee met five times over the past twelve months for this review.

The EqP approach assumes that the critical parameter for gauging sediment quality is the concentration of a chemical in the water that will not cause significant adverse effects to aquatic species of interest. This water concentration can then be used to estimate the corresponding concentration of the chemical in the underlying sediment. The approach, as developed and reviewed to date, pertains only to non-ionic organic compounds.

The EqP approach is considered by the Subcommittee to have major strengths in its foundation in chemical theory, its ease of calculation, and its ability to make use of existing data (e.g., water quality criteria values). In addition, the developers of the approach have begun to explore the uncertainty surrounding the approach, which is to be commended.

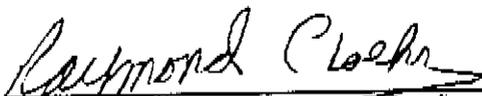
The conceptual basis of the approach is supported by the Subcommittee, however its application at this time is limited. This is because a better understanding of the uncertainty around the assumptions inherent in the approach, including assumptions of equilibrium, bioavailability, and kinetics, all critical to the application of the EqP approach, is needed.

Additional concerns of the Subcommittee relate to the limited number of existing water quality criteria which the EqP approach can use, the compound-specific nature of the approach, and the questionable ability of the method to protect sediment-ingesting organisms. The exposure to organisms by food chain transfer is also not considered and the amount of field data available to validate the approach is limited. Some suggestions for research to explore the sources of uncertainty and the Subcommittee's other concerns are provided in the attached report.

It should be noted that our charge was to evaluate the method relative to its ability to gauge sediment quality. We did not therefore, evaluate its applicability for establishing sediment quality criteria per se. We were unable to compare the strengths and weaknesses of the EqP with other methods as identified in our charge, because appropriate documents were not available at this time.

The Subcommittee appreciates the opportunity to conduct this scientific review. We request that the Agency formally respond to the scientific advice transmitted in the attached report.

Sincerely,



Dr. Raymond Lehr, Chairman
Executive Committee
Science Advisory Board



Dr. Kenneth Dickson, Chairman
Ecological Processes and
Effect Committee



Dr. Robert Huggert, Chairman
Sediment Criteria Subcommittee

cc: LaJuana Wilcher, Martha Prothro, James M. Conlon, Chris Zarba
Catherine Krueger, Donald Barnes

ABSTRACT

This report presents the conclusions and recommendations of the U.S. Environmental Protection Agency's Science Advisory Board summarizing a review of the Equilibrium Partitioning (EqP) approach for estimating sediment quality. The EqP approach relates the level of a chemical that has been found to be acceptable from a biological standpoint to the corresponding concentration of the chemical sorbed to sediments. The value that results, the sediment quality value, is based on the assumption that only the portion of the chemical dissolved in the water surrounding sediment particles is available to exert toxicity on resident biota. The approach, as developed and reviewed to date, pertains only to non-ionic organic compounds. The EP approach is considered by the Subcommittee to have major strengths in its foundation in chemical theory, its ease of calculation, and its ability to make use of existing data. In addition, the researchers responsible for its development have begun to explore the uncertainty surrounding the approach, which is to be commended. The conceptual basis of the approach is supported by the Subcommittee, however its application at this time is limited. This is because a better understanding of the uncertainty around the assumptions inherent in the approach, including assumptions of equilibrium, bioavailability, effect levels, and kinetics, all critical to the application of the EP approach, is needed. Additional concerns expressed by the Subcommittee relate to the limited number of existing water quality criteria which the EP approach can use, the compound-specific nature of the approach, and the questionable ability of the method to protect sediment-ingesting organisms. The exposure to organisms by food chain transfer is also not considered and the amount of field data to validate the EqP approach is limited. Some suggestions for research to explore the sources of uncertainty and the Subcommittee's other concerns are provided in the report.

Key Words: Sediment, EqP; Equilibrium Partitioning approach: Non-ionic organic compounds

U.S. ENVIRONMENTAL PROTECTION AGENCY

NOTICE

This report has been written as a part of the activities of the Science Advisory Board, a public advisory group providing extramural scientific information and advice to the Administrator and other officials of the Environmental Protection Agency. The Board is structured to provide a balanced expert assessment of scientific matters related to problems facing the Agency. This report has not been reviewed for approval by the Agency; and, hence, the contents of this report do not necessarily represent the views and policies of the Environmental Protection Agency or other agencies in Federal government. Mention of trade names or commercial products does not constitute a recommendation for use.

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1.0 EXECUTIVE SUMMARY

The Equilibrium Partitioning (EqP) approach to assessing sediment quality is based on an assumed set of relationships between chemical contaminants sorbed to bottom sediments and living organisms residing in, on or above those sediments. Some of the relationships are supported by thermodynamic principles, others by limited observations.

The approach assumes that only the fraction of contaminant that is dissolved in interstitial water is biologically available, and that this dissolved fraction is inversely proportional to the organic carbon content of the sediment. Additionally, it is postulated that the distribution of the contaminant between pore water and sediment organic carbon is comparable to the distribution of material between water and the organic solvent *n*-octanol (i.e., the octanol/water partition coefficient).

To describe the distribution of a substance between water and bulk sediments, the sediment partitioning coefficient, K_p , is used. The organic carbon normalized sediment partitioning coefficient, K_{oc} , is used to describe the distribution of the chemical between the organic fraction of the sediments and the associated water and it is approximated by K_{ow} , the octanol/water partition coefficient. Therefore, if the assumptions are valid, if the coefficients are known and if the biologically acceptable water concentration of a persistent contaminant is known (e.g., from the establishment of a water quality criterion), the acceptable amount of contaminant in the solid sediment phase can be calculated.

The EqP approach relies on a fundamental chemical parameter, fugacity. The Subcommittee considers this foundation to be a major strength, and supports the conceptual basis of the approach. The relative ease of calculation and the approach's reliance on the use of existing data also contribute to the approach's appeal and potential for application.

The EqP approach shows promise but, in the opinion of the Subcommittee, should not be broadly applied without an understanding of the uncertainty around the assumptions inherent in the approach. Areas of uncertainty that must be explored prior to generic applicability include assumptions of equilibrium, bioavailability, and kinetics.

For instance, the Subcommittee recommends that uncertainty associated with the following facets of the EqP Approach be critically examined:

- o Uncertainty associated with equating K_{oc} and K_{ow} ;
- o Uncertainty associated with the use of water quality criteria, water quality advisories and other estimates of effect levels;

It is recommended that additional research be conducted to evaluate the influence of particle size distribution on sorption and desorption and the role of organic carbon in sediments in regulating the bioavailability of non-ionic organic sediment contaminants.

Finally, the Subcommittee expressed reservations about the limited number of water quality criteria, the higher levels of uncertainty associated with advisories, the inability of the approach to account for mixtures of chemicals, and the questionable ability of the method to protect sediment-ingesting organisms. The Subcommittee was also concerned with the limited amount of data available to validate the EqP approach.

2.0 INTRODUCTION

2.1 Request for Science Advisory Board Review

At the request of the Office of Water, Criteria and Standards Division, the Science Advisory Board (SAB) agreed to conduct a scientific review of the Equilibrium Partitioning (EqP) approach. The SAB's Ecological Processes and Effects Committee (formerly the Environmental Effects, Transport and Fate Committee) authorized the formation of a Subcommittee to perform a series of tasks related to the technical aspects of sediment quality assessment and criteria development, with the approval of the Board's Executive Committee.

2.1.1 Charge to the Subcommittee

This review is the second to be completed in a series of SAB reviews related to sediment quality criteria. Preliminary reviews focused on approaches to examining non-ionic organic contaminants. The first report of the Subcommittee, entitled "Evaluation of the Apparent Effects Threshold (AET) Approach for Assessing Sediment Quality" July, 1989, presented recommendations and conclusions concerned with the AET Approach. The charge accepted by the Subcommittee for the review of the AET and EqP approaches was to:

a) Evaluate individually the scientific and technical foundations for the various methodologies available to the Agency to estimate sediment toxicity and biological impact of contaminated sediments in situ.

b) Evaluate the feasibility of utilizing each methodology to determine extent of contamination and risk posed to the environment and human health.

c) Identify research directions that would provide information to strengthen each methodology.

d) Conduct a technical review of documents provided by the Agency that compare and contrast the scientific and technical strengths and weaknesses of the methodologies available to the Agency to estimate sediment toxicity and biological impact of contaminated sediments in situ.

2.2 Subcommittee Review Procedures

The Sediment Criteria Subcommittee met on August 8 and 9, 1988, in Denver, Colorado, to assess the Agency's activities regarding contaminated sediment and to explore avenues for providing oversight. A second meeting was held on October 27 and 28, 1988, in Seattle, Washington. Informative briefings were provided on the objectives, historical perspective and technical

components of the AET approach. A third meeting was held on February 2 and 3, 1989 in Washington, D.C. to begin the review of the EqP approach. The briefings provided to the Subcommittee were thorough and were supported by documentation which was provided to Subcommittee members prior to the meeting. This preparation and support was provided by Office of Water, Office of Research and Development and associated contractors. Select members of the Subcommittee were convened for writing sessions in Gloucester Point, VA on May 8 and 9, 1989 and in Washington, DC on June 1 and 2 and again on August 17, 1989. The final report has been reviewed and approved by the Subcommittee, the Ecological Processes and Effects Committee, and the Executive Committee of the SAB.

2.3 Expected Future Activities

The Sediment Criteria Subcommittee is reviewing the technical appropriateness of a series of methods that may be applied to assessing sediment quality. These methods are contained in a manual under development by EPA/OW's Contaminated Sediment Technical Committee. The Subcommittee will comment on this manual in the near future.

Other sediment quality assessment methods, including methods for assessing metal contaminants, are expected to be developed and existing approaches refined, and as this occurs, they will be transmitted to the Subcommittee for review.

During the course of these critical evaluation processes, it is likely that areas for additional or future research will be targeted. To facilitate the incorporation of these recommendations into EPA research planning, the Subcommittee may conduct a review of the Office of Research and Development's proposed Sediment Initiative. The time sequence of these proposed events is contingent on their completion by Agency staff.

3.0 EVALUATION OF THE EQUILIBRIUM PARTITIONING APPROACH

The EqP approach focuses on the partitioning of chemicals between particulate or solid (bulk) sediments and interstitial water (i.e., the water between sediment particles), and water quality criteria established for contaminants to indicate their toxicity. Since the contaminants partitioning to the interstitial water appear to be more available to biota than contaminants bound to bulk sediment, the EqP method for generating sediment quality values is based on predicted contaminant concentrations in interstitial water (see Appendix A). Chemically contaminated sediments are expected to cause adverse biological effects if the predicted interstitial water concentration for a given contaminant exceeds the water quality criterion established for that contaminant.

The EqP approach for assessing the quality of bottom sediments relative to chemical contamination relies on a fundamental thermodynamic parameter, fugacity. Fugacity is the tendency of a substance to escape or flow from one phase of a system to another until equilibrium is established. Equilibrium is attained when the energy of that particular system is at its lowest, and under this condition, all concentrations in the system are independent of time.

In the case of chemically contaminated sediments, under conditions which approach ideal, fugacities can be used to predict how a chemical contaminant will be distributed among the various phases making up the system. This system may be in equilibrium, but equilibrium does not imply that the chemical concentrations are equal among the phases. Those phases include: inorganic material, non-living organic material, pore water, dissolved gases, biota, and the overlying water column. Therefore, if one knows the equilibrium concentration of a chemical in any one phase, then the concentrations in the remaining phases can be calculated if the distribution or partition coefficients among the phases are known.

The EqP method assumes relatively ideal conditions and equilibrium. This allows one to estimate the pore water concentration by knowing the concentration of the substance in the solid phases. If the assumption is made that only the pore water fraction is biologically available, and if the aqueous toxicity is known, exposure and hazard can be determined.

Ideal conditions are seldom approached under real-world conditions, and approximations and assumptions must be made. The EqP methodology relies on a number of empirically derived estimates to describe the interactions or relationships among hazardous chemicals, sediments, and indigenous biota.

To describe the distribution of a substance between water and bulk sediments, the sediment partition coefficient, K_p , is used. The organic carbon normalized sediment partitioning coefficient, K_{oc} , is used to describe the distribution of the chemical between the organic fraction of the sediments and the associated water and it is approximated by K_{ow} , the octanol/water partition coefficient. Each of these estimates has an associated uncertainty resulting from experimental errors and, in some cases, assumptions for which accuracy is not known with certainty. There is uncertainty about the impact of non-ideal conditions on partitioning and the estimate of sediment quality derived from partitioning values. The Subcommittee recommends that these assumptions, including assumptions of relatively ideal conditions and equilibrium, be investigated to better characterize the uncertainty that may exist around them.

3.1 Chemical Considerations

The EqP approach for setting sediment quality criteria, like the Agency's water quality criteria approach, focuses on the effects caused by single chemicals. This is recognized as a limitation in both approaches, since the synergistic, additive, and/or antagonistic effects posed by mixtures of contaminants are not taken into account. The following is a discussion of the EqP methodology's strengths and weaknesses from a chemical standpoint, based on the methodology's focus on single chemical compounds. Ongoing studies by the Agency (SAB, 1989) and completed work by others (NRC, 1988 and NRC, 1989) should be examined relative to their usefulness here.

3.1.1 Kinetics

In idealized situations, where thermodynamic equilibrium exists between the solid phase and the aqueous phase of a particular chemical, and when cause/effect relationships are known, the EqP approach is valid and can be used to estimate sediment quality from the partitioning coefficients and the water quality criteria for that chemical. In such situations, the method is very straightforward. However, in field conditions it is necessary to examine whether and how well the assumption of thermodynamic equilibrium is satisfied before applying the methodology. Although the limited data presented in the draft briefing document appeared to support the application of EqP, a few recent studies have indicated that deviation from thermodynamic equilibrium is not uncommon in real world situations.

Witkowski, et al. (1988) reported on the sorption and desorption dynamics of AROCLOR 1242 to natural sediment and found that a two-stage kinetic model, rather than the equilibrium model, was more appropriate for representing sediment uptake and release processes in long-term (up to 16 days) simulations. The data presented show that the partition coefficient can deviate by a factor of 7 from the one corresponding to the equilibrium conditions. Thus, if one uses the sediment quality estimate determined from the EqP approach to set a limit on the solid phase, the limit may be in error. Likewise, calculations of interstitial water concentrations based on measured solid phase concentrations may be in error.

Several studies have strongly indicated that kinetic control rather than equilibrium partitioning, dictates the extent of accumulation of sediment contaminants. Oliver (1984, 1987) suggested that the importance of kinetic control in affecting the accumulation of contaminants by benthos. Klump et. al. (1987) measured the assimilation coefficient of oligochaetes and demonstrated the importance of ingestion in affecting the accumulation of contaminants. In a recent study by Landrum et. al.

(1989), Pontoporeia hoyi were exposed to sediments contaminated with TCB (tetrachlorobiphenol) and BaP (benzoapyrene). Although the partition coefficient of TCB is only twice that of BaP, the uptake rate of TCB was found to be 10 times that of BaP. Landrum et. al. (1989)) and Landrum (1989) concluded that, in their experiment, the accumulation of contaminants is dictated by the rate of desorption of contaminants from sediments and the assimilation of contaminants by benthos instead of partitioning.

In the same study, Landrum et. al. (1989) also found that the time for equilibrium (via adsorption) to be established between contaminants on sediments and contaminants in interstitial water is on the order of one month or longer. The time to approach equilibrium via desorption, which occurs in most depositional areas, is likely to be even longer.

The data of Landrum, et al. (1989) suggest that the time scale depends on rates of desorption, ingestion, and elimination, instead of the simple equilibrium partitioning. Furthermore, physical and biological factors (e.g. temperature, salinity, turbulence level, sediment type, sediment size distribution, degree of flocculation, bioturbation, and decomposition) can also be expected to affect the kinetics. These factors are extremely difficult to reproduce in a laboratory experiment. Moreover, laboratory experiments can only mimic "snap shots" in the field, but cannot simulate the variability in physical and biological factors associated with episodic events. Extrapolation of laboratory results to field conditions thus contains significant uncertainty.

Because of uncertainties produced by the problems mentioned above, and because of uncertainties associated with the determination of partition coefficients due to various other factors (e.g. particle concentration effect, flocculation effect, complex mixtures effect), it is recommended that a more sophisticated uncertainty analysis be carried out for the EqP approach to set limits/bounds on its applicability. Uncertainty analysis may point to needs for additional research in various aspects of the methodology. The uncertainty analysis in the draft briefing document fails to adequately address all these important factors. A more rigorous approach would be to perform uncertainty analyses on both the water quality criteria and the partition coefficient to yield a combined uncertainty on the sediment quality criteria. This point should be addressed in the technical support manual that EPA is to prepare.

3.1.2 Particle Size Distribution (PSD)

Specific to the EqP Approach is the fact that PSD can be an important factor controlling chemical adsorption in certain areas. Bottom sediment may be a mixture of coarse sand-size primary

particles, finer primary particles such as the silts and clays, and organic material, as well as aggregates that may contain both inorganic particles, organic material, and living organisms of assorted sizes. The active benthic zone of bottom sediments may be cohesive or non-cohesive and may well be mixed vertically or stratified by density or particle size. Composition can vary greatly both among sites and within sites. These facts are well known and necessitate a very thorough sampling plan to properly characterize a particular area and document the sample heterogeneity.

It is recognized that the surface area and organic content of sediments often increase as the particle size decreases. In such cases organic carbon and increased surface area produce interdependent effects on sorption. Organic carbon is thought to normalize about 70% of the variability in chemical concentrations on sediments (for sediments with an organic carbon content of 0.5% or more). Based on these observations, it is recommended that additional research be conducted to further evaluate the importance of PSD in controlling or influencing adsorption and desorption in combination with organic carbon. To date much of the published literature reports results in which the two factors are separated and not integrated.

3.1.3 Analysis

The draft briefing document supplied by the Office of Water did not address specific procedures for the analysis of non-ionic organic compounds in sediments or pore water. Detailed analyses of sediment and pore water characteristics such as dissolved organic carbon (DOC), total organic carbon (TOC), and sediment particle sizes were not presented. While not all these factors must be known to carry out a sediment quality criteria calculation by the EqP method, they should be known to be more certain that its application is appropriate.

Procedures for these analyses are reasonably well known and understood, and have been addressed by previous documents. The use and application of the EqP approach will depend on high-quality data with known levels of uncertainty for the K_{ow} , chemical concentration in the sediment, sediment organic carbon, and sediment characteristics. As part of the development of the approach, appropriate methods for all necessary analyses need to be assembled, criteria for use of various procedures defined, quality assurance/quality control evaluations specified, and methods for quantifying uncertainty in the analysis stated. The Subcommittee therefore recommends that the preparation of a procedures and methods manual be undertaken to address both chemical and biological sampling.

3.1.4 Sorption

"Sorption" is the generic and non-committal term which encompasses both adsorption and absorption processes. The distinction between these two processes is sometimes difficult to demonstrate experimentally, but mechanistically they represent two unique processes. Adsorption is an interfacial phenomenon which results in an increase in the concentration of a sorbant in the interfacial layer between the bulk aqueous and solid phases. In contrast, absorption is defined as the transfer of a component from the aqueous phase into the solid phase. The use of partition coefficients does not readily distinguish between these mechanistically different processes, and in practice it is likely that adsorption and absorption occur sequentially, and that their relative importance can have significant consequences for the extent of sorption (Mingelgrin and Gerstl, 1983).

The basic hypotheses related to the sorption and desorption of non-ionic organic chemicals in the EqP methodology state that the sediment/water partition coefficient (K_p) is controlled by the organic carbon fraction (f_{oc}) and the sediment organic carbon/water partition coefficient (K_{oc}), and that the K_{oc} is, in turn, directly related by use of regression equations to the n-octanol/water partition coefficient (K_{ow}). The extent to which these hypotheses operate in real world situations affects the fidelity with which carbon normalization and partition coefficients can reflect sorption phenomena in nature.

K_{ow} values for a given chemical, when run under standardized laboratory conditions are constant and reproducible. K_{oc} values for a given chemical tested under standardized laboratory conditions are fairly reproducible where the organic carbon is 0.5 % or more, although the confidence limits are greater than for K_{ow} calculations. K_{oc} values however, appear unreliable when correlated with K_{ow} below that percentage. While sediment organic matter appears to be the most important sorbent for non-ionic chemicals it is not the only sorbent. Furthermore, different types of organic carbon are likely to have different potentials for partitioning, especially when their surface areas differ (Amidon and Anik, 1980).

The partitioning approach based on the organic carbon content of sediments does not take sorption to sedimentary components other than organic carbon into account. It is well known that major sedimentary constituents, such as SiO_2 and complex silicates are poor substrates for the adsorption of non-ionic organic chemicals, because these common substrates form hydrated ionic double layers about them that pre-empt interactions with hydrophobic chemicals. However, other sedimentary constituents, such as sulfides, ferric oxide (Fe_2O_3), rutile (TiO_2) and elemental sulfur do not form hydrated ionic double layers and can readily sorb non-ionic organic chemicals. In addition, polymers can negate the influence of double layers (Stumm and Morgan, 1981).

3.1.5 Organic Carbon Normalization

Data show the organic portion of sediments to be usually less than 10% on a dry-weight basis, but higher values have been reported. Experimental evidence indicates that the organic carbon fraction of sediment is the principal sorbent for many hazardous organic compounds, especially non-ionic chemicals; therefore normalizing the sediment partition coefficient for the carbon content of a particular sediment adjusts, in principle, the coefficient to better approximate actual environmental conditions.

In many instances sediments may be polluted with high concentrations of natural and/or man-made hydrophobic organic contaminants. At high concentrations, multi-phase systems exist with multiple mass transport interfaces between the interstitial water and sediment, interstitial water and an organic liquid phase, and the organic liquid and the particles. In these instances the non-aqueous material can be both a source of soluble material to the water and another phase for sorbing pollutants. The draft briefing document does not address this situation, which may be common for certain kinds of pollutants and sites (e.g., PCBs, petroleum hydrocarbons, creosote, etc.). Several questions should be addressed. Can the EqP method be used in these circumstances to establish sediment criteria? Are these situations of enough significance to warrant generation of a new or modified methodology? Could a modification to the existing approach incorporate a third phase? Can it be assumed that the biota will not interact with the non-aqueous liquid and therefore that it is not important from a toxicological perspective? Is this an instance of a very complex mixture where we have no adequate method for assessing sediment quality?

3.1.6 Particle Concentration Effect

The use of the EqP approach is based on the empirical observation that in most laboratory experiments K_{oc} is approximately equivalent to K_{ow} . Many of the laboratory measurements used to estimate K_{oc} have been made at relatively low suspended particle concentrations but are applied to bedded sediments. If the sorption properties of high particle concentration aqueous suspension or intact sediments are not the same as the low concentration suspensions used to derive K_{oc} , then there is a basic problem in the application of this method. This observed particle concentration effect suggests that some factor may cause sorption to solids to decrease as the particle concentration increases. A question is therefore raised as to proper ways to estimate bed sediment sorption and desorption.

Additional data exist that indicate the apparent effect of particle concentration on sorption isotherms is an artifact of the way the laboratory experiment is performed. The data of Gschwend and Wu (1985) suggest that apparent particle effects are due to the fact that soluble macromolecules (humic, fulvic acids, proteins, etc.) and colloidal particles are not removed from the liquid phase of isotherm studies using existing centrifugation techniques. The change in the K_p is then a function of the amount of soluble macromolecules and particles left in liquid phase which is directly related to the concentration of solids used in the isotherm study. These conflicting viewpoints indicate that the mechanisms of adsorption and desorption are not fully understood and that there is not yet a universally accepted and applied approach for measuring sorption. Since the relationship between K_{oc} and K_{oc} is such an important aspect of the application of the EqP approach, and since it may impact how future measurements are made, the Subcommittee recommends that additional research into particle concentration effects be conducted.

3.1.7 Spiked versus Natural Sediment Adsorption

The scientific literature clearly indicates that there are major differences in the sorption characteristics of sediment-bound chemicals depending on whether the chemical was spiked onto the sediment or occurred as a result of a release into the natural environment. Major differences in the desorption rates have been reported. These differences are thought to be due to the "aging process" that occurs after sediment and chemical contact has been made. Laboratory experiments support the idea that the longer a chemical has been adsorbed to a sediment, the slower will be the overall desorption/diffusion rate. This implies that chemicals may be more bioavailable in toxicity studies with freshly spiked sediment than with sediments collected from the natural environment with the same chemical.

Much of the data generated to date to test the EqP method has been collected using freshly spiked sediments. While this approach is satisfactory for understanding the basic approach and evaluating whether carbon is a reasonable normalizing factor, there may be considerable error associated with field applications of these data.

The Subcommittee recommend that validation experiments be conducted using natural and/or aged spiked sediments to determine the relationship between duration of contact of sediment and chemical, and sorption/desorption properties of the chemical, sediment and biological effects. It is also recommended that consideration be given to the use of aged sediment-bound chemical desorption partition coefficients in deriving sediment quality

values.

3.2 Biological Considerations

The following is a discussion of the EqP methodology's strengths and weaknesses from a biological standpoint.

3.2.1 Dependency on Water Quality Criteria and Advisories

The EqP method for generating sediment quality criteria appropriate for non-ionic organic chemicals uses water quality criteria (WQC) as the effects concentration in calculating the sediment quality value. Thus the approach is dependent on the availability of a water quality criterion or some surrogate before it can be used. At the present time water quality criteria have not been developed for many non-ionic organic compounds, and the data base for water quality criteria does not contain many chemicals with very high K_{ow} values. In addition, of the chemicals for which water quality criteria do exist, only a relatively small number (approximately 30) have been developed following the National Guidelines for the Development of Water Quality Criteria. Thus, of the available water quality criteria, there are varying degrees of uncertainty regarding their ability to protect aquatic life.

When applying the EqP method to chemicals for which no water quality criteria exist, the user must develop surrogate effects concentration. Such a surrogate will have additional uncertainty associated with it and the degree of uncertainty depends on the approach used to develop the surrogate. For example, Water Quality Advisories might be used to derive an effects concentration, yet all Water Quality Advisories are not equal in terms of amount and quality of data used in their development. Thus, varying degrees of uncertainty exist regarding their ability to protect aquatic life. It is conceivable that an effects concentration for a chemical could be derived from acute toxicity data by applying an application factor. In such a case, the uncertainty of the effects concentration used in the EqP method may be very large.

Because of the critical role the estimate of an effects concentration plays in the EqP approach for the development of sediment quality values and the varying degrees of uncertainty for the various estimates of an effects concentration, the Subcommittee recommends that the developers of the EqP method include a statement of confidence with each sediment quality value developed by the EqP Approach. This quality designation should indicate the certainty or confidence attached to the sediment quality value. Quality designations could take the form of descriptive statements or numerical indicators. Quality designations should also be included as part of any sediment criterion value, regardless of the method that is used to develop the sediment criterion.

3.2.2 Exposure Routes-Water Versus Sediments

The data presented in the EqP support document, on both bioaccumulation factors and sediment toxicity, support the overall contention that carbon normalization does a reasonable job of explaining bioavailability differences among different sediments. However, providing data on selected biota is not equivalent to providing evidence that WQC can be used to establish sediment quality values protective of all benthic organisms regardless of the route of exposure.

A key question surrounding the EqP method has to do with the method's ability to adequately protect species which are detrital feeders, those that may not receive most of their chemical body burden from interstitial water. Data are emerging that indicate some benthic organisms are exposed primarily via detrital feeding (Boese, 1988; with hexachlorobenzene and Macoma sp.). It also has been shown that for certain PAHs (high pK) uptake via the gut can exceed uptake across the gill in freshwater amphipods (Landrum, 1989). It is unknown at this time whether or not there are a large number of benthic species to which this applies, and whether or not these species are more sensitive than other benthic organisms.

Equilibrium partitioning theory, per se, does not assume that the interstitial water is the primary or only uptake route. It is recognized that the thermodynamic potential for transport to the organism (i.e., effective exposure concentration) is the same from the sediment or the water when sediment and interstitial water are at equilibrium. Field data generated to date are not capable of discriminating between the two routes of exposure. However, the bulk of the experimental data have shown that, for many organisms, effect levels attributed to sediment interstitial water concentration match traditional aquatic toxicity values generated without the presence of sediment. This does not prove the route of exposure, it only says that the weight of evidence is that for many organisms the WQC

can be used to estimate sediment effect levels. This approach is vulnerable in that it is not known whether or not organisms which derive their body burden primarily via the gut are affected at the same sediment chemical concentration as those which are affected by the interstitial water. Do water quality criteria adequately protect these organisms?

The Subcommittee recommends that further research be conducted to determine whether or not water quality values and sediment quality criteria developed by the EqP method are protective of benthic organisms whose primary route of exposure is via detrital feeding.

3.2.3 Relevance of Water Quality Criteria to Benthic Organisms

One of the basic assumptions in the development of sediment quality criteria is that water quality criteria (or some surrogate) are adequate estimates of the effects concentration for benthic organisms. The developers of the EqP approach have attempted to validate this assumption by analyzing the relative sensitivity of marine water column species and benthic species by segregating the acute toxicity data base for 30 chemicals for which water quality criteria exist. In addition, data from benthic colonization experiments for six chemicals were examined.

The existing method of data analysis relies on the use of pooled data and comparisons of percentile ranges. This approach does not allow review of data for specific species. The Subcommittee recommends that the species sensitivity data (30 marine and freshwater WQC documents) also be reviewed to determine the two or three most sensitive benthic and water column species in the data set. The data used for the species sensitivity comparisons should be based on studies with animals: a) at a similar life stage, b) tested under similar conditions (e.g. hardness, pH, temperature), and c) exposed for the same period of time. A series of sensitivity ratios could then be developed by dividing the acute values for a benthic species into the acute value for a water column organism for the same chemical. This could help determine if benthic species are as acutely sensitive, on the average, as certain water column organisms.

To date only acute data for benthic and water column marine species has been analyzed. It is important to determine if benthic and water column species have similar chronic sensitivities to chemicals, since chronic toxicity data are essential to the development of WQC. The Subcommittee recommends that the developers of the EqP approach expand the analysis of the Water Quality Criteria data base to include a broader range of species, including macrophytes and deposit feeders, and include considerations and comparisons of both chronic and acute toxicity data.

3.3 Inappropriate Use of Water Quality Criteria (WQC) to Determine Effect Levels in the EqP Approach

The Subcommittee is concerned that the water quality criteria documents could be used inappropriately to determine effect levels for the EqP approach. For instance, some of the WQC are based on residue considerations, i.e., PCBs. It would be inappropriate to use the overall WQC in these cases for deriving sediment quality values. The residue derived WQC are usually estimated based on measured bioconcentration coefficients. Potential user of WQC should not accept these numbers directly without careful reference to the technical support documentation for the WQC to establish the limits of applicability of values that have been selected.

When the expected residue concentrations are to be inferred from the concentrations of contaminants in sediments using the EqP method (or any other method), then the additional extrapolation of sediment-water-biota will introduce an additional uncertainty, making the entire process even less reliable. Use of the data in the WQC document that pertains to chronic effect levels would be more appropriate, such as the final chronic value (FCV). The Subcommittee recommends that very careful use of the WQC documents be made and that guidelines be prepared for using WQC and water quality advisory values in the calculation of a sediment quality values by the EqP approach.

4.0 SUMMARY OF SUBCOMMITTEE CONCLUSIONS AND RECOMMENDATIONS

a. The Subcommittee recommends that the assumptions used in the EqP approach, including assumptions of relatively ideal conditions and equilibrium, be investigated to better characterize the uncertainty that may exist around them.

b. It is suggested that a more sophisticated uncertainty analysis be carried out for the EqP approach to set limits/bounds on its applicability. A more rigorous approach would be to perform uncertainty analyses on both the water quality criteria and the partition coefficients, K_{oc} and K_{ow} to yield a combined uncertainty on the sediment quality values.

c. It is recommended that additional research be conducted to further evaluate the importance of particle size distribution in sediments in controlling or influencing sorption and desorption on mineral soil particles in combination with organic carbon. It is recommended that various inorganic sediment constituents such as SiO_2 and sulfides and various forms of organic carbon be investigated to determine the extent that they influence the sorption and desorption of non-ionic chemicals.

d. As part of the development of the approach, the appropriate methods for all the necessary analyses need to be assembled, criteria for use of various procedures defined, quality assurance/quality control evaluations specified, and methods for quantifying uncertainty in the analysis stated. The Subcommittee therefore recommends that the preparation of a procedures and methods manual be undertaken to address both chemical and biological sampling.

e. Since the relationship between K_{oc} and K_{ow} is such an important aspect of the application of the EqP approach, and since it may impact how future measurements are made, the Subcommittee recommends that additional research into particle concentration effects be conducted.

f. The Subcommittee recommends that validation experiments be conducted using natural and/or aged spiked sediments to determine the relationship between duration of contact of sediment and chemical, and sorption/desorption properties of the chemical, sediment, and biological effects. It is also recommended that consideration be given to the use of aged sediment-bound chemical desorption partition coefficients in deriving sediment quality values.

g. The Subcommittee recommends that the developers of the EqP method include a statement of confidence with each sediment quality value developed by the EqP Approach.

h. The Subcommittee recommends that further research be conducted to determine whether or not water quality criteria and sediment quality value developed by the EqP method are protective of benthic organisms whose primary route of exposure may be via detrital feeding.

i. The Subcommittee recommends that the species sensitivity data (30 marine and freshwater WQC documents) also be reviewed to determine the two or three most sensitive benthic and water column species in the data set.

j. The Subcommittee recommends that the developers of the EqP approach expand the analysis of Water Quality Criteria data base to include a broader range of species, include considerations and comparisons of both chronic and acute toxicity data.

k. The Subcommittee recommends that very careful use of the WQC documents be made and that guidelines be prepared for using WQC values in the calculation of a sediment quality values by the EqP approach.

l. The Subcommittee recommends that field experiments be conducted to validate the EqP approach.

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APPENDIX A:

Briefing Report to the EPA Science Advisory Board on the
The Equilibrium Partitioning Approach

**DRAFT
BRIEFING REPORT**

to the

EPA SCIENCE ADVISORY BOARD

on the

**EQUILIBRIUM PARTITIONING APPROACH
TO GENERATING SEDIMENT QUALITY CRITERIA**

December 1988

**U.S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF WATER
OFFICE OF WATER REGULATIONS AND STANDARDS
CRITERIA AND STANDARDS DIVISION**

SUMMARY

This report has been prepared to assist the EPA Science Advisory Board with its evaluation of the Equilibrium Partitioning method for generating sediment quality criteria. Sediment quality criteria as used in this report refer to numerical values for individual chemicals that are applicable across the range of sediments encountered in practice. They are intended to be predictive of biological effects and protective of the presence and uses of benthic organisms. As a consequence they could be used in much the same way as water quality criteria - as the concentration of a chemical which is protective of the intended use.

The specific regulatory uses of sediment quality criteria have not been established. However, the range of potential applications is quite large since the need for the evaluation of potentially contaminated sediments arises in many contexts. Sediment quality criteria are not meant to replace direct toxicity testing of sediments as a method of evaluation, but rather to provide a chemical by chemical specification of what sediment concentrations would be protective of aquatic life and their uses.

TOXICITY AND BIOAVAILABILITY OF CHEMICALS IN SEDIMENTS

The principal technical difficulty that must be overcome in establishing sediment quality criteria is to determine the extent of bioavailability of sediment associated chemicals. It has frequently been observed that similar concentrations of a chemical in units of mass of chemical per mass of sediment dry weight (e.g. $\mu\text{g chemical/g sediment}$) can produce widely different biological effects in different sediments. If the purpose of sediment quality criteria is to establish chemical concentrations that apply across sediments of differing types it is essential that the reasons for this varying

bioavailability be understood and that they be explicitly included in the criteria. Otherwise the criteria cannot be presumed to be applicable across sediments of differing properties.

The importance of this issue cannot be underestimated. For example, if 1 ppm of Kepone is the LC50 for an organism in one sediment and 40 ppm is the LC50 in another sediment, then unless the cause of this difference can be associated with some explicit sediment properties it is not possible to decide what the LC50 would be of a third sediment without a direct toxicity test.

An additional difficulty is that the results of toxicity tests used to establish the toxicity of chemicals in sediments would not be generalizable to other sediments. Imagine the situation if the results of toxicity tests in water depended strongly on the particular water source - e.g., Lake Superior versus well water. Until the source of the differences were understood, it would be fruitless to attempt to establish water quality criteria. It is for this reason that the issue of bioavailability is a principal focus of this report.

The observation which provided the key insight to the problem of quantifying the bioavailability of chemicals in sediments was that the concentration-response curve for the biological effect of concern could be correlated not to the total sediment chemical concentration (μg chemical/g sediment) but to the interstitial water (i.e., pore water) concentration (μg chemical/liter pore water). Organism mortality, growth rate, and bioaccumulation data were used to demonstrate this correlation, which is a critical part of the logic behind the equilibrium partitioning approach to developing sediment quality criteria. A substantial amount of data is presented in the Report to illustrate the generality of this finding (Sections 3.1 through 3.3).

This correlation can be interpreted in a number of ways. In particular it is premature to conclude that the route of exposure for the organism is only

via the pore water. The reason is that the solid phase is in equilibrium with the liquid phase and the effective exposure concentration is likely to be the same via either route. However from a purely empirical point of view the correlation suggests that if it were possible to either (1) measure the pore water chemical concentration or (2) 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, the partitioning of chemicals between the solid and the liquid phase in a sediment becomes a necessary component of sediment quality criteria. It is for this reason that the methodology is called the equilibrium partitioning (EP) method.

In addition, if it were true that benthic organisms are as sensitive as water column organisms - and as shown in Section 5 the evidence appears to support this supposition - then a sediment quality criteria could be established using the water quality criteria, CWQC, as the effects concentration, and the partition coefficient, K_p , to relate the pore water concentration to the sediment quality criteria concentration, r_{SQC} via the partitioning equation. The calculation procedure is as follows. If CWQC ($\mu\text{g/L}$) is the water quality criteria for the chemical of interest, then the sediment quality criteria, r_{SQC} ($\mu\text{g/kg}$ sediment) is computed using the partition coefficient, K_p (L/kg sediment) between sediment and water:

$$r_{SQC} = K_p c_{WQC}$$

This is the fundamental equation from which sediment quality criteria are generated. Its utility depends upon the existence of a methodology for quantifying partition coefficients.

PARTITIONING OF NON-IONIC ORGANIC CHEMICALS

The partitioning of non-ionic organic chemicals between particles and water is reasonably well understood and a standard model exists for describing the

process. The chemical property of importance is the octanol-water partition coefficient, K_{ow} . The important particle property is the mass fraction of organic carbon, f_{oc} . For particles with $f_{oc} > 0.5\%$ the organic carbon appears to be the predominant sorption phase. The partition coefficient, K_p , the ratio of sediment to pore water concentration is given by:

$$K_p = f_{oc} K_{oc}$$

where K_{oc} is the partition coefficient for particle organic carbon.

The only other environmental variable that has a dramatic effect on partitioning appears to be the particle concentration itself. There is considerable controversy regarding the mechanism responsible for the particle concentration effect and a number of explanations have been offered. However, all the interpretations yield the same result for sediment-pore water partitioning, namely that $K_{oc} = K_{ow}$ for sediments. Hence sediment quality criteria are calculated from:

$$F_{SQC} = f_{oc} K_{ow} C_{WQC}$$

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

$$\frac{F_{SQC}}{f_{oc}} = K_{ow} C_{WQC}$$

If we define:

$$F_{SQC,OC} = \frac{F_{SQC}}{f_{oc}}$$

as the organic carbon normalized sediment concentration (μg chemical/kg organic carbon) then:

$$r_{\text{SQC,OC}} = K_{\text{ow}} c_{\text{WQC}}$$

Hence we arrive at the following important conclusion: for a specific chemical, with a specific K_{ow} , the organic carbon normalized total sediment concentration is proportional to the dissolved free effects concentration, c_{WQC} , for any sediment for $f_{\text{oc}} > 0.5\%$.

Hydrophobic chemicals tend to partition to colloidal sized organic carbon particles (DOC) as well. Although DOC affects the apparent pore water concentrations of highly hydrophobic chemicals the DOC-bound chemical appears not to be bioavailable and the above equation still applies (Sections 4.2 through 4.4). The available field data for sediment partitioning is reviewed and related to the model presented above.

The above discussion suggests that toxicity and bioaccumulation data for sediments should be normalized by the sediment organic carbon concentration. It is found that responses which are quite variable on a dry weight normalized basis are either statistically equivalent or the differences are significantly reduced on an organic carbon basis. The low carbon sediments are seen to depart from the normalized results as is expected (Section 4.6).

FIELD VALIDATION OF SEDIMENT QUALITY CRITERIA

The most convincing demonstration that sediment quality criteria are sound would be a demonstration that they can predict the degree of toxicity of natural sediments. There are three technical difficulties that apply to all field data based approaches: bioavailability, chemical mixtures and control sediments.

Bioavailability

Contaminated sediments contain many chemicals. In order to use the magnitude of the chemical concentration as a measure of its potential to have biological effects, it is necessary that its bioavailability in that particular sediment be assessed. For toxic metals and ionic organic chemicals there is as yet no comprehensive partitioning theory that identifies the normalization quantities and provides the parameters to predict free dissolved concentration. Hence bioavailability cannot be directly assessed.

Chemical Mixtures and Causality

If the bioavailability problem were solved there remains a difficulty with using naturally contaminated sediments. Just as with water quality criteria it is always possible that there is present another chemical or chemicals that are biologically very active but, which have yet to be identified. If this chemical is the cause of significant toxicity then it would cause a biological effect that would not be predicted from the application of sediment quality criteria.

Control Sediments and Non Toxic Variations

Variations in sediment toxicity test results and community structure can be caused by variations in sediment characteristics other than chemical contamination. Grain size distribution and organic carbon content are well known examples. In order to judge the toxicity of a sediment it is necessary that a comparative control response be obtained. The perfect control is the same sediment without any chemical contamination. Since this is not available, sediments from an unimpacted site are assumed to approximate the response of the perfect control. The degree to which this approximation is inappropriate limits the assessment of comparative toxicity.

These three major difficulties appear to render a direct field validation of sediment criteria beyond current capabilities. Nevertheless it would be helpful if some evidence that criteria developed from laboratory toxicological data are at least reasonable. A methodology is presented that can be used to establish lower bounds for sediment quality criteria from field observations of organism presence and sediment chemistry.

EFFECTS CONCENTRATION

The other principal assumption in the development of sediment quality criteria is that the water quality criteria are adequate estimates of the effects concentrations for benthic organisms. Two sets of analyses are presented to examine this question. The acute toxicity data base from the water quality criteria are segregated into benthic and water column species and the relative sensitivity of each group are compared for the 30 water quality criteria chemicals. In addition benthic colonization experiments for six chemicals are examined.

The conclusion from this examination is that the sensitivities of benthic species are sufficiently similar to those of water column species to tentatively permit the use of water quality criteria for the derivation of sediment quality criteria in the equilibrium partitioning approach. The acute toxicity database derived from 30 water quality criteria documents suggests that the most sensitive infaunal species is typically less sensitive than the most sensitive water column (epibenthic and water column) species. When both infauna and epibenthic species are classed as "benthic", the sensitivities of the most sensitive benthic and water column species are on the average similar (Section 5).

UNCERTAINTY

The sediment quality criteria methodology employed above relies on an empirical model to compute the free interstitial water concentration from the solid phase measurements. As a consequence there is an uncertainty associated

with the use of the model. In addition there is uncertainty with respect to the K_{ow} associated with the specific chemical since it is an experimentally determined quantity. Finally the assumption that water column and benthic organisms have similar sensitivities has a level of uncertainty.

The quantification of the level of uncertainty for sediment quality criteria has only been accomplished in a preliminary way (Section 7.1). It is anticipated that a complete uncertainty analysis will accompany a sediment quality criteria and that, for example, 95% confidence limits will be specified as well as the most probable value.

PRELIMINARY SEDIMENT QUALITY CRITERIA

An initial attempt to compute equilibrium partitioning based sediment quality criteria for 13 chemicals is presented in Section 7.2. The 95% confidence limits are computed from a method which is known to exaggerate the uncertainty. For chemicals where either field data derived lower bounds or sediment toxicity experiments are available the results are reasonable.

TOXIC METALS

The rationale for establishing sediment quality criteria for toxic metals is similar to that developed for non-ionic organic chemicals. The bioavailable fraction is identified and a partitioning model will be investigated in order to predict the bioavailable fraction. Water column experiments point to the fact that biological effects can be correlated to the divalent metal activity (Me^{2+}). The implication to be drawn from these experiments is that the partitioning model required for establishing sediment quality criteria should predict (Me^{2+}) in the pore water (Section 6.1 - 6.2).

METAL SORPTION MODELS AND EXTRACTIONS

The state of the art of modeling metal sorption in laboratory systems is well developed. Models for natural soil and sediment particles are less well

developed. However, recent applications suggest that similar models can be applied to soil systems. An approach is presented which envisions three sorption phases in aerobic sediments (Section 6.3).

In addition to the sorption phase concentrations it is necessary to quantify the fraction of total sediment metal that is chemically interacting with the pore water. A substantial effort is needed over several years to determine the bioavailable portion of trace metals in soils and sediments using chemical extractions. Initial results are reviewed and preliminary directions are suggested (Section 6.4).

CONCLUSION

Methodologies are being developed to establish sediment quality criteria using sediment equilibrium partitioning. The importance of bioavailability and the role of partitioning between sediment and pore water is clarified. The effects concentration for benthic organisms can be estimated from the water quality criteria. For non-ionic organic chemicals an adequate partitioning model exists and is presented in this document. As a result sediment quality criteria can be computed. For metals initial studies indicate that the same rationale can be used. The development of sediment criteria for metal contaminants using equilibrium partitioning is the focus of future sediment criteria development activities.

SECTION 1.

INTRODUCTION

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

Toxic contaminants in bottom sediments of the Nation's lakes, rivers, wet lands, and coastal waters create the potential for continued environmental degradation even where water-column contaminant levels comply with established water quality criteria. In addition, contaminated sediments can lead to water quality degradation, even when pollutant sources are stopped. The absence of defensible sediment quality criteria makes it difficult to accurately assess the extent of the contaminated sediment problem and to identify and implement appropriate remediation activities when needed. As a result of the need for a procedure to assist regulatory agencies in making decisions concerning contaminated sediment problems, a EPA Office of Water Regulations and Standards, Criteria and Standards Division (OWRS/CSD) research team was established to review alternative approaches. Each approach had both strengths and weaknesses and no single approach was found to be most applicable in all situations. The equilibrium partitioning method was selected, because it appeared to provide the most practical and effective regulatory tool for addressing contaminated sediments on a national basis. The three principal

observations that underlay the equilibrium partitioning method of establishing sediment quality criteria are:

1. for sediment dwelling organisms, the pore water concentration of a chemical correlates to observed biological effects across a range of sediments,
2. the range of sensitivities of benthic organisms to chemicals are similar to water column organisms so that the currently established water quality criteria can be used to define acceptable pore water levels; and,
3. partitioning models which relate pore water concentrations to bulk sediment concentrations either exist (for non-ionic organic chemicals) or can be developed (for toxic metals and, perhaps, for ionic organic chemicals).

The data that support these observations will be examined in subsequent sections of this report.

Sediment quality criteria generated using the equilibrium partitioning method are suitable for use in providing guidance to regulatory agencies because they are:

1. Numerical values
2. Chemical specific
3. Applicable across sediments
4. Predictive of biological effects
5. Protective of the presence and uses of benthic organisms

As is the case with water quality criteria, the sediment quality criteria reflect the use of available scientific data to: (1) assess the likelihood of significant environmental effects from contaminants in sediments and to (2) derive regulatory requirements which will protect against these effects.

Over the past several years research activities have focused on the evaluation and development of the equilibrium partitioning methodology for generating sediment quality criteria for use in providing guidance to regulatory agencies. It is the purpose of this report to describe results that support the equilibrium partitioning method for establishing sediment quality criteria. This report is structured in the following way:

The historical framework and statutory basis for developing sediment quality criteria are discussed in Section 2. Toxicity and bioavailability of chemicals in sediments are discussed in Section 3 where the importance of pore water concentration is established. This leads to a discussion of partitioning behavior of chemicals and their division into two major classes: non-ionic organic chemicals and metals, for which partitioning models have been proposed.

Non-ionic organic chemicals are discussed in Section 4. Sections 4.1 through 4.5 concentrate on partitioning and the role of particulate and dissolved organic carbon. The models available to evaluate the partitioning of chemicals in sediments are presented in Section 4.1 for particle suspensions and Sections 4.2 through 4.4 for in-place sediments, including a discussion of the effect of DOC complexing. Field data, related to partitioning in sediments, are analyzed in Section 4.5. The results of organic carbon normalization of toxicity and bioaccumulation experiments are presented in Section 4.6. The issue of pore water versus sediment as the route of exposure is addressed in Section 4.7. This section concludes with a review of the field validation of sediment criteria in Section 4.8, where a screening level methodology is presented.

The applicability of using water quality criteria for the effects concentration in sediments is examined in Section 5. A discussion of the overall similarity of the sensitivities of benthic and water column species is included in this section.

Section 6 reviews the current status of sediment quality criteria development efforts related to toxic metals. The difficulties in using pore

water metal concentration directly are discussed in Section 6.1. This leads to a discussion of the data demonstrating the correlation of toxicity to divalent metal activity which is presented in Section 6.2. The state-of-the-art of metal sorption models is discussed in Section 6.3. The suitability of extraction methodologies to quantify the bioavailable fraction is examined in Section 6.4. The remainder of Section 6 describes the initial approaches that are being pursued in order to establish sediment metal criteria.

Finally, Section 7 describes the generation of interim sediment quality criteria for non-ionic organic chemicals. The uncertainty associated with the criteria is discussed (Section 7.1) and preliminary values are presented (Section 7.2).