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OCDE/GD(92)170

ENVIRONMENT MONOGRAPHS

No. 60

REPORT OF THE OECD WORKSHOP ON EFFECTS ASSESSMENT OF CHEMICALS IN SEDIMENT

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

Paris 1993

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REPORT OF THE OECD WORKSHOP ON
EFFECTS ASSESSMENT OF CHEMICALS IN SEDIMENT

Copenhagen

13th-15th May 1991

ENVIRONMENT DIRECTORATE

ORGANISATION FOR ECONOMIC CO-OPERATION AND DEVELOPMENT

1992

FOREWORD

The objective of OECD work on hazard assessment is to promote awareness and improvement of procedures for hazard assessment used by Member countries and, to the extent possible, to harmonize those procedures in order to assist Member countries in protecting human health and the environment from the potentially harmful effects of chemicals.

Activities in the period 1989-1991 focused on aquatic effects assessment, in particular on the application of quantitative structure activity relationships to estimate aquatic toxicity data, the extrapolation of laboratory data to the real environment and the effects of chemicals in sediments. These issues were addressed at workshops held respectively at Utrecht in September 1990, at Arlington in December 1990 and in Copenhagen in May 1991. The stategic aim is to integrate the results of the three aquatic effects activities into an OECD scheme for aquatic effects assessment.

Orientation for work on hazard assessment is provided by the Hazard Assessment Advisory Body (HAAB) which also reviews the results obtained and reports the progress made to the Joint Meeting of the Chemicals Group and the Management Committee of the Special Programme on the Control of Chemicals. The current composition of the HAAB is given at the end of this monograph. Meetings of the HAAB are attended by an observer from the International Programme on Chemical Safety.

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RESUME

Un atelier de l'OCDE sur l'évaluation des effets de produits chimiques dans les sédiments a été tenu à Copenhague du 13 au 15 mai 1991 sous l'égide du Ministère de l'environnement danois en coopération avec la Commission des Communautés Européennes. Neuf pays Membres de l'OCDE y ont délégué trente-six experts.

Objectifs de l'atelier

Contrairement aux méthodes de caractérisation chimique et biologique de substances contaminant le milieu aquatique, largement utilisées dans le cadre réglementaire de nombreux pays, les méthodes visant l'évaluation des effets dans les sédiments ne sont pas très répandues. Ces dernières manquent également d'uniformité.

Des substances toxiques, en s'adsorbant sur des particules, peuvent s'accumuler dans les sédiments qui deviennent ainsi une source d'émission de produits contaminants dans les eaux de surface. Cette contamination, intégrée dans le temps et dans l'espace, constitue un danger pour les organismes aquatiques qui ne peut être cerné sur la seule base des concentrations des substances dans la colonne d'eau. Les sédiments sont également des repères historiques pour les changements dus à la pollution, que celle-ci provienne d'activités humaines ou soit causée par des phénomènes naturels.

Les effets sur la faune benthique sont préoccupants car, dans beaucoup d'écosystèmes, celle-ci joue un role prépondérant dans le recyclage des détritus vers la faune pélagique. Il existe donc un besoin de définir des objectifs de qualité relatifs aux sédiments qui pourraient servir de base scientifique à l'élaboration de normes destinées à protéger les écosystèmes des effets des sédiments contaminés et de gérer à long terme la contamination des sédiments.

Les objectifs de l'atelier consistaient donc

1) à prendre en considération les méthodes disponibles pour définir des critères de qualité de sédiments et établir un consensus sur les plus appropriées, et, en particulier,

2) à faire des recommandations concernant les méthodes permettant d'évaluer:
   (a) la toxicité des sédiments, et
   (b) la toxicité d'une substance ou d'une catégorie de substances pour les organismes vivant dans les sédiments.

L'atelier a été étayé par un document préparé par des experts du laboratoire de Duluth appartenant à l'Agence de protection de l'environnement des Etats-Unis (EPA). Ce document figure en annexe.

Lors de la première journée les présentations suivantes ont été faites;

-- *Equilibrium partitioning for developing sediment quality criteria for nonpolar organics*, par Dominic Di Toro, USA.

-- *Methods for developing sediment quality criteria for metals*, par David Hansen, USA.

-- *Toxicity test methods for sediments -- marine*, par Richard Swartz, USA.

-- *Toxicity test methods for sediments -- freshwater*, par Gerald Ankley, USA.

-- *Toxicity identification and evaluation techniques for assessing sediments*, par Gerald Ankley, USA.

-- *Sediment quality triad for assessing sediments*, par Cees van de Guchte, Pays-Bas.

Le deuxième jour, l'atelier s'est scindé en deux groupes de travail. Les rapports de ces groupes forment les chapitres 3 et 4 du présent document.

Groupe de travail A - Méthodes pouvant servir à élaborer des objectifs de qualité pour des sédiments

Le Groupe a délibéré des deux questions suivantes:

1) Quelle est la meilleure manière pour définir des objectifs et critères de qualité à l'aide des données qui sont actuellement disponibles?
2) Quelles autres données, qui seraient à acquérir, pourraient être les plus utiles afin d'améliorer les critères?

Le Groupe a examiné plusieurs méthodes:

- partage à l'état d'équilibre
- qualité de l'eau interstitielle
- toxicité de sédiment dopé par traces ajoutées
- concentrations de référence
- seuil d'effets observables
- concentrations ne présentant pas de danger
- triade d'essais (analyse chimique, toxicité et diversité biologique)
- résidus dans les tissus

Chaque méthode a été évaluée par rapport à sept caractéristiques: spécificité chimique, rapport de cause à effet, effets chroniques, bioaccumulation, état d'avancement, disponibilité biologique et applicabilité.

Recommandations du Groupe de travail A

Le Groupe a recommandé l'emploi de trois méthodes dans l'élaboration d'objectifs de qualité de sédiments:

1) Le partage à l'état d'équilibre

L'application de cette méthode est limitée aux substances pour lesquelles un modèle est disponible qui donne le partage en fonction, d'une part, des propriétés de la molécule et, d'autre part, des caractéristiques du sédiment. Le Groupe a recommandé qu'une ligne directrice soit développée pour un essai adéquat permettant de mesurer des coefficients de partage n-octanol/eau des substances organiques non ionisables ($\log P_{oe} > 5$).

2) Qualité de l'eau interstitielle

Cette méthode est similaire à la précédente à la différence près qu'au lieu de faire une estimation de la concentration dans l'eau interstitielle, celle-ci est mesurée. La méthode est à utiliser lorsqu'un modèle adéquat de partage à l'état d'équilibre n'est pas disponible.

3) Toxicité de sédiment dopé par traces ajoutées

Il s'agit d'une détermination empirique de données dose-réponse relatives à des substances spécifiques et des mélanges. Par une extrapolation aux conditions existant dans l'environnement réel des niveaux seuils d’effets probables sont estimés. La méthode est applicable à condition qu’il existe des techniques analytiques pour la détermination de la concentration dans l’eau interstitielle.

Groupe de travail B - Essais de toxicité de sédiments

L’objectif de ce groupe a été d’établir un consensus sur les meilleures méthodes, actuellement disponibles, pour l’évaluation de la toxicité de sédiments ainsi que pour la détermination de la toxicité de substances vis à vis des organismes présent dans les sédiments.

Plusieurs questions ont été soulevées au cours des débats:

1) Quelle partie du sédiment doit-on utiliser dans les essais?

2) Quelles sont les méthodes disponibles et quelles sont leurs limitations?

3) Dans quelle mesure les méthodes d’identification-évaluation de toxicité sont-elles utilisables pour l’évaluation de sédiments contaminés?

4) Comment valider sur le terrain les essais de toxicité de laboratoire? Cela est-il nécessaire?

5) Quelles variables doivent être prises en compte dans les essais de laboratoires:

   - les organismes,
   - les cultures d’organismes,
   - les différents effets de toxicité,
   - les méthodes statistiques,
   - le type de sédiment,
   - les effets dus à la taille des particules,
   - d’autres?

6) Faut-il prendre en considération les essais sur le terrain et *in situ?* Dans ce cas, quelles sont les variables significatives?

Les experts ont développé les raisons pour lesquelles il faut élaborer et utiliser les essais de toxicité de sédiments. Ils ont examiné les méthodes actuellement utilisées avec différentes parties de sédiments. Ils ont travaillé sur le choix de la fraction de sédiment à soumettre aux essais ainsi que sur les facteurs à prendre en considération lors de l’isolation de l’eau des pores et la préparation de l’eau de décantation.

Le problème de la caractérisation de sédiments a été traité. Eu égard à la multitude de paramètres qui peuvent avoir une importance, le Groupe n’a pu évaluer complètement tous les paramètres ni approfondir les raisons pour lesquelles il conviendrait de déterminer tel paramètre plutôt que tel autre. Plusieurs paramètres-clefs ont cependant été identifiés. Le Groupe s’est attardé sur les paramètres physico-chimiques qui doivent être controlés au cours de essais, sur l’échantillonage et la conservation des sédiments soumis à essai. Trois techniques pour doper des sédiments propres avec une ou plusieurs substances ont été examinées.

Conclusions du Groupe de travail B

1) Les essais de toxicité sont utiles à l’évaluation des effets de sédiments contaminés dans le milieu aquatique. Ces essais, principalement la méthode de dopage de sédiments propres, permettent également de définir des objectifs de qualité. Il faut définir avec soin les buts des études avant de choisir le genre de sédiment et les organismes qui seront soumis à essai, ainsi que l’effet à étudier. L’organisme choisi doit

être sensible aux substances auxquelles il sera exposé. Dans le choix des techniques d'échantillonage et de traitement des sédiments il faut tenir compte du but fixé pour l'étude. Finalement, pour que les essais de toxicité de sédiments puissent constituer une base solide pour des décisions réglementaires, ils doivent être validés sur le terrain.

2) Une solution idéale consisterait à fonder les décisions réglementaires sur une évaluation complète comme celle qui fait appel à une triade d'essais et dans laquelle sont inclus les données sur la structure de la population benthique et les effets toxiques, ainsi que les résultats d'analyse chimique. Il s'agit cependant plus d'un objectif à long terme que d'une possibilité immédiate.

3) Les procédures d'identification-évaluation de toxicité, basées sur une fragmentation en fonction de la toxicité, sont les seules actuellement diponibles qui permettent d'associer des effets observés de toxicité à des contaminants spécifiques présent dans les echantillons de sédiments prélevés sur le terrain. Ces procédures se situent dans le prolongement des approches méthodiques intégrées, telle que l'approche de la triade d'essais.

Report of the OECD Workshop on Effects Assessment of Chemicals in Sediment

1. Introduction

This is the report of the OECD workshop on effects assessment of chemicals in sediment, which took place in Copenhagen, Denmark, on 13th-15th May 1991. The workshop was hosted by the Danish Ministry of the Environment and sponsored by the European Commission. There were 36 participants, representing nine OECD Member countries.

Workshop objectives

While methods for the chemical and biological characterisation of water-borne contaminants are applied in regulatory and monitoring programmes in many countries, methods for the assessment of sediments are less widely or uniformly established.

Sediments may act as a sink for, and source of, toxic chemicals through sorption of contaminants to particulate matter. The effects of surface water contamination become integrated over time and space, and a hazard to aquatic communities (both pelagic and benthic) is created which is not directly predictable from observations of contaminant concentrations in the water column. Sediments can serve as historical records of change due to both man-made pollution and natural environmental causes. For example, lake sediments reflect surface water quality more consistently than do flowing rivers even though there may be seasonal changes in the lake environment, e.g. metal cycling in hypolimnetic waters.

Effects on benthic organisms are of concern because in many ecosystems the sediment community plays an important role in the recycling of detrital material to the pelagic community. In addition, benthic organisms are a critical component of a variety of aquatic food webs. Thus there is a need for sediment quality objectives that may be used as a scientific basis for the development of standards to protect ecosystems from the effects of sediment contamination, and to manage contaminated sediment in the long term.

The objectives of the workshop were therefore:

(i) to consider the methods available for use in developing environmental quality objectives (or criteria) for sediments, and to reach consensus on the methods most appropriate for this purpose;

(ii) to recommend the most appropriate test methods to assess:

  (a) the toxicity of sediments;
  (b) the toxicity of a particular chemical or group of chemicals to sediment-dwelling organisms.

2. Workshop Summary

A background paper summarising methods for assessing contaminated sediments and deriving sediment quality criteria was prepared by the Duluth Laboratory of the United States Environmental Protection Agency. A revised version of that paper is presented in Annex 1.

The first day of the workshop was devoted to a series of presentations on quality and effects assessment of chemicals in sediment:

-- *Equilibrium partitioning for developing sediment quality criteria for nonpolar organics*, Dominic Di Toro, USA.

-- *Methods for developing sediment quality criteria for metals*, David Hansen, USA.

-- *Toxicity test methods for sediments -- marine*, Richard Swartz, USA.

-- *Toxicity test methods for sediments -- freshwater*, Gerald Ankley, USA.

-- *Toxicity identification and evaluation techniques for assessing sediments*, Gerald Ankley, USA.
-- *Sediment quality triad for assessing sediments*, Cees van de Guchte, the Netherlands.

On the second day, workshop participants divided into two working groups on, respectively, methods which could be used in the development of sediment quality objectives, and test methods for assessing toxicity of sediments. The reports of the two working groups are presented in chapters 3 and 4 of this document.

Working Group A

Participants in Working Group A considered the methods available for developing environmental quality objectives for sediments. They were asked to reach consensus on the most appropriate methods currently available, and to address the following questions:

(i) What is the best way to set sediment quality objectives (criteria) using data currently available?

(ii) What data, not yet available, would be most beneficial for improving the objectives set?

The working group considered a number of potentially useful methods, namely:

-- equilibrium partitioning;
-- interstitial water quality;
-- spiked sediment toxicity;
-- reference concentrations;
-- apparent effects threshold;
-- screening level concentrations;
-- sediment quality triad;
-- tissue residue.

Details of these methods are given in the report of Working Group A and in the background paper (Annex 1). Each method was evaluated with respect to seven characteristics: chemical specificity, causality, chronic effects, bioaccumulation, state of development, bioavailability and applicability.

Recommendations of Working Group A

Three methods were recommended for use in the development of sediment quality objectives.

(i) Equilibrium partitioning:

The equilibrium partitioning method is limited to chemicals for which a partitioning model is available describing the partition as a function of the properties of the chemical and the characteristics of the sediment. It was recommended that an appropriate guideline be developed to measure K_{ow} for non-ionic organic chemicals (log $K_{ow}>5$).

(ii) Interstitial water quality:

This method is similar to the equilibrium partitioning method except that, instead of interstitial water concentrations being predicted, they are measured. The interstitial water quality method could be used for chemicals for which no adequate partitioning model is available.

(iii) Spiked sediment toxicity:

This method is an empirical determination of dose-response data for individual chemicals and chemical mixtures. The test data are used to predict concentrations of concern under field conditions. The method is only applicable to chemicals for which analytical techniques for determining interstitial water concentration are available.

Working Group B

Participants in this group considered test methods for assessing toxicity of sediment, and for determining chemicals' toxicity to sediment-dwelling organisms. They too were asked to reach consensus on the most appropriate available methods.

In the context of these discussions, consideration was given to a number of questions:

(i) Which sediment phase is most appropriate for testing?

(ii) What test methods are available and what are their limitations?

(iii) How might toxicity identification evaluation (TIE) methods be used in assessments of contaminated sediments?

(iv) How might toxicity tests be field validated? How necessary is this?

(v) Which laboratory test variables need addressing?
   -- organisms;
   -- organism culture system;
   -- toxic endpoint;
   -- statistical method;
   -- test sediment type;
   -- effects of particle size;
   -- others.

(vi) Do field or *in situ* methods need addressing? If so, what are the significant test variables?

Participants outlined the reasons for developing and using sediment toxicity tests and considered the methods currently in use for testing different sediment phases. They also addressed the choice of the sediment fraction to be tested. The factors to be considered in preparing pore water and elutriate for testing were reviewed, and a preferred technique for preparation of pore water was proposed. Several considerations were identified as particularly important in selecting and carrying out appropriate sediment toxicity tests.

The issue of sediment characterisation was also addressed. However since a wide range of parameters may be relevant in characterising the sediment depending on the purpose of the investigation, it was considered that a full evaluation of and rationale for measuring each parameter was beyond the scope of the workshop. Nevertheless several key parameters were identified. The group also looked at the physical-chemical parameters to be monitored during aqueous tests, and the sampling and storage of test sediments. Three sediment spiking techniques for adding one or more chemicals to clean sediments were examined.

Conclusions of Working Group B

(i) Toxicity tests can be useful tools for assessing the degree and extent of impacts of contaminated sediments on aquatic ecosystems. They are also useful for deriving sediment quality objectives via spiking of test chemicals into clean sediments. Careful consideration must be given, however, to the study objectives when selecting appropriate sediments, test organisms and response endpoints. The test species selected must be appropriate for the study objective and shown to be sensitive to relevant chemicals or classes of chemicals. Study objectives must also be carefully considered when designing sampling strategies and techniques for handling sediments. Ultimately, in order to provide a solid regulatory basis for the use of sediment toxicity tests the approaches used must be subjected to rigorous field validations and testing as well as laboratory development in order to determine optimal testing procedures.

(ii) Ideally, regulatory decisions should be based upon sediment assessments such as the sediment quality triad where all the following data would be available: benthic community structure, toxicity test results and chemical analyses. This is seen as a strategic aim rather than an immediate possibility.

(iii) Toxicity identification evaluation (TIE) procedures which utilise toxicity-based fraction approaches are the only methods currently available to link toxicity to specific contaminants in a causal manner for field-collected sediments. These procedures present a logical and useful extension of integrated assessment approaches, such as the sediment quality triad.

3. Report of Working Group A: Methods which could be useful in the development of sediment quality objectives

Potentially useful methods

Eight methods were evaluated as being potentially useful for deriving sediment quality objectives. These were:

- equilibrium partitioning;
- interstitial water quality;
- spiked sediment toxicity;
- reference concentrations;
- apparent effects threshold;
- screening level concentrations;
- sediment quality triad;
- tissue residue.

A detailed description of each method is given in the background paper (Annex 1).

Each method was evaluated with respect to the following characteristics:

(i) Chemical specificity: Can the method be used to derive a concentration for a specific chemical?

(ii) Causality: Are the observed effects caused by the specific chemical?

(iii) Chronic effects: Does the method consider chronic toxicity endpoints?

(iv) Bioaccumulation: Does the method consider food chain accumulation and ingestion of contaminated sediment for (i) benthos, (ii) fish?

(v) State of development: Is the method ready for use (tested, validated, used)?

(vi) Bioavailability: How generally applicable is the method across sediment types? Are sediment quality objectives a function of the bioavailable phase?

(vii) Applicability: Is the method applicable to bedded sediments or suspensions?

(viii) Recommendation: On the basis of the foregoing evaluations, can the method be recommended for use in deriving sediment quality objectives?

Scores are shown in Table 1.

The most important characteristics were felt to be chemical specificity, causality, chronic effects, state of development and bioavailability. Causality and bioavailability were considered particularly important. If a method failed to meet one or more of these criteria, it was eliminated. None of the methods was judged acceptable, in the present state of development of sediment quality objectives, for chemical substances that bioaccumulate.

Table 1: Evaluation of the present state of development of eight methods for deriving sediment quality objectives

Elements/characteristics Method	Chemical Specificity	Causality	Chronic Effects	Bioaccumulation benthos/fish	State of development	Bioavaila-bility	Applicability a)	Can be re-commended
Equilibrium Partitioning	++	++	+	+/--	++b)	++b)	B S*	yes
Interstitial Water Quality	++	++	+	-/--	-	+	B	yes
Spiked Sediment Toxicity	++	++	+ c)	+/--	+d)	+e)	B S*	yes
Reference Concentrations	++	--	--	+/	++	--	B S	no
Apparent Effects Threshold	++	--	-/+f)	-/--	++	+e)	B	no
Screening Level Concentrations	++	--	+	-/--	-	+	B	no
Sediment Quality Triad	--	--	+	-/--	+	-	B	no
Tissue Residue	*	*	*	*/--	--	*	B*S*	no

Table key:

++ High - Low
\+ Medium -- Very low
a) To bedded sediments (B), suspended sediments (S).
b) Well developed for organic chemicals and is being developed for metals and other chemicals.
c) For freshwater organisms only.
d) Methods and guidelines need to be developed.
e) If concentrations are properly normalised to reflect biological availability, e.g. by organic carbon or acid volatile sulphides.
f) Chronic effects on benthic organisms in field situations can be considered.
* There is potential for development.

The working group reached consensus on recommending the use of:

- -- equilibrium partitioning;
- -- interstitial water quality;
- -- spiked sediment toxicity.

The reasons for selecting or not selecting methods are outlined below. Proper use of the three methods chosen is also indicated.

Equilibrium partitioning (EqP)

This method derives sediment quality standards from water quality standards by predicting interstitial water concentrations. The approach is based upon the observation that interstitial water concentrations are correlated more closely than bulk sediment concentrations with toxicity to and/or bioaccumulation of environmental contaminants in benthic organisms (Di Toro et al., 1991a; US Environmental Protection Agency, 1989; Van der Kooij et al., 1991). The method assumes that:

(i) the concentrations in sediments and interstitial water are at equilibrium;

(ii) the concentrations in any of these phases can be predicted using appropriate partition coefficients and concentrations in one phase;

(iii) the effect concentrations in sediments, on an organic carbon basis, can be predicted using partitioning predictions and effect concentrations; and

(iv) the water quality objective (WQO) is an appropriate effects concentration for deriving sediment quality objectives.

The formula for deriving the sediment quality objective (SQO) is:

$$SQO = K_p \ WQO$$

where SQO is the sediment concentration (µg/kg dry weight), K_p is the partition coefficient (l/kg), and WQO is the effects-based water quality objective. The advantage of the EqP method is that the theoretical basis is well established.

The EqP approach has been tested for non-ionic hydrophobic chemicals and metals. Biological effects have been demonstrated to be related to interstitial water concentrations and appropriately normalized sediment concentrations. The procedure for normalizing sediment concentrations requires a model for chemical partitioning, K_p, that relates solid phase and liquid phase concentrations. At present models are available for non-ionic organic chemicals, certain metals and a few ionic organic chemicals.

The EqP method can be applied to all chemicals (including toxic metals) for which water quality standards (also known as water quality criteria) have been derived. The method is applicable to marine and freshwater sediments and across sites.

Interstitial water quality

This method is similar to the equilibrium partitioning method except that, instead of interstitial water concentrations being predicted, they are measured. The method can be used for chemicals for which no adequate partitioning model is available.

The same assumptions are made as those listed for equilibrium partitioning, except that the dissolved uncomplexed concentration in the interstitial water does not have to be estimated using sorption constants.

This method can be applied to all chemicals (including toxic metals) for which water quality standards (water quality criteria) are available. The requirement of measured concentrations in the interstitial water may be the most serious limitation. The method is applicable to marine and freshwater sediments and across sites.

Spiked sediment toxicity

This method is a toxicological approach to the generation of sediment quality standards using laboratory dose-response data. The test organisms are exposed to sediments spiked with a range of chemical concentrations. Biological endpoints such as survival, growth, reproduction or behaviour are monitored. With this method it is assumed that spiked sediment in the laboratory behaves similarly and gives effects similar to natural *in situ* sediments.

This method is an empirical determination of dose-response data for individual chemicals and chemical mixtures. The method is chemical-specific and demonstrates a clear causality. The test is suited to investigations of chronic toxicity and bioaccumulation. The results reflect the bioavailability of the tested substance. The test has been used for bed and suspension studies and may be applied across sites. The method is developed and test data are used to predict concentrations of adverse effects under field conditions.

A major limitation of the method is that the techniques for spiking sediments have not been well established and may need standardization. Moreover, no true chronic endpoints have yet been developed.

Reference concentrations

The reference approach is a comparison of concentrations from an unimpacted (reference) site with the concentrations from a selected site.

This method is chemical-specific, well developed, and widely used in regulatory applications. However it is not recommended for the development of numerical sediment quality criteria (SQC) because it does not show causality and does not consider chronic effects or bioavailability.

Apparent effects threshold (AET)

The AET concentration for a specific endpoint is the concentration of a chemical above which all higher concentrations caused the specific effect. This method is chemical-specific, is in an advanced state of development, and can be modified to consider biological availability for chemicals for which normalizing variables exist. It has been used for regulatory applications at limited locations in the United States, but is not recommended for development of numerical SQC because it does not establish a causal link between specific chemical concentrations and the effect endpoint. Furthermore it does not consider chronic effects and many of the published AET concentrations do not consider bioavailability. AETs that are properly normalized, e.g. by non-ionic organic chemicals on a sediment carbon basis, could however provide lower limits to the effects concentration at the specific endpoint considered.

Screening level concentrations (SLCs)

The SLC is a lower bound estimate of a safe concentration developed from field data which enumerate the presence of species of benthic organisms occurring in sediments with specific chemical concentrations. SLCs are chemical-specific. They consider chronic effects in that the presence of organisms in sediments is a reflection of the absence of chronic effects. This approach considers biological availability. However it is not recommended for development of numerical sediment quality standards because it does not establish the causal link between specific chemical concentrations and the effect endpoint.

Although evaluations of the SLC approach are limited in scope, SLC concentrations have been published. Generally these concentrations reflect a lower bound value, as do AETs. The method has never been applied in a regulatory context.

Sediment quality triad

The sediment quality triad compares chemical concentrations in sediments, toxicological responses and benthic community health to evaluate overall acceptability of sediments from specific sites (Chapman, 1986). The sediment quality triad approach has several advantages. First, the approach uses empirical relationships to provide a direct measure of sediment quality. Second, it does not require *a priori* assumptions concerning specific mechanisms of interaction between organisms and toxic contaminants. Finally, it can be used to develop SQC for any measured contaminant. However the criteria could be influenced by the presence of unmeasured toxic contaminants. The triad method has been used widely in sediment evaluations in the United States, but it was not selected for use in the development of sediment quality standards because it is not chemical-specific, does not show causality and lacks consideration of biological availability.

Tissue residue

The tissue residue approach seeks to relate chronically acceptable chemical concentrations in benthic organisms to chemical concentrations in sediments using equilibrium partitioning. This test method is theoretical because of the absence of a database relating tissue concentrations to chronic effects. The tissue residue approach has the same relative strengths and weaknesses as the interstitial water toxicity method and is even less developed. One of its strengths is that it allows a predictive approach using kinetically driven sediment exposure.

Recommendations of Working Group A

The Group recommended for use in the development of sediment quality objectives the equilibrium partitioning, interstitial water quality and spiked sediment toxicity test methods

Equilibrium partitioning

(i) For non-ionic organic chemicals:

The following recommendations were made regarding the derivation of K_p values for non-ionic organic chemicals:

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

where f_{oc} = weight fraction of organic carbon in the sediment and K_{oc} is the chemical partition coefficient to sediment organic carbon. Regression formulas for deriving K_{oc} from the octanol-water partition coefficient K_{ow} are available (US Environmental Protection Agency, 1989). K_{oc} is approximately equal to K_{ow}. This partition model permits the development of SQOs expressed on an organic carbon basis, i.e.:

$SQO_{oc} = K_{oc}$ WQO

where SQO_{oc} has the units µg chemical/g organic carbon. This provides a concentration that applies to all sediments with f_{oc} greater than approximately 0.1%. Since the derived SQOs strongly depend on the octanol/water partition coefficient that is applied, it is extremely important that correct log K_{ow} values are available.

The working group suggested two methods for log K_{ow} determination not yet addressed by OECD Test Guidelines 107 and 117, namely, the generator-column method and the slow-stirring method.

(ii) For other organic chemicals, additional models have been developed:

-- for anionic surfactants (Di Toro et al., 1990a);

-- for ionisable chemicals such as phenolic compounds (Jafvert, 1990 and 1991; Jafvert et al., 1990; Jafvert and Heath, 1991).

It was also recommended that when no partition models are available, the interstitial water method be used. There is a need for further research to develop EqP models for other groups of chemicals.

(iii) For metals:

Two approaches utilising partitioning models have been proposed to relate biological effects to interstitial water and sediment concentrations:

In the Netherlands, K_p values for metals were obtained from field measurements in suspended sediment from surface waters. These K_p values were used together with water quality standards to obtain sediment quality standards (Van der Kooij et al., 1991).

In the United States, a partitioning model has been proposed that relates interstitial water concentrations and biological effects to the molar ratio of sediment metal and acid volatile sulphide (AVS) concentrations (Di Toro et al., 1990b and 1991b). The procedure relies on a measurement of sediment sulphide concentration and metals that are simultaneously extracted using cold acid. The extracted metals are referred to as simultaneously extracted metals (SEM). The model has been shown to apply individually to Cd, Cu, Ni, and Zn, and to mixtures of these metals. It has been found to apply to freshwater and marine sediments, although this has not been empirically demonstrated in freshwater sediments for all of the previously mentioned metals. It is also thought to apply to Pb, Hg, and Ag. The model predicts that no acute toxicity will occur in sediments where:

$$SEMCd + SEMCu + SEMNi + SEMPb + SEMZn < AVS$$

i.e., the molar sum of the simultaneously extracted metals is less than the molar concentration of AVS. In sediments where the molar sum exceeds AVS, and interstitial water concentrations exceed one toxic unit, sediments may be toxic to sensitive organisims.

This method has only been tested using ten-day acute lethality as the endpoint. Therefore its applicability to predicting chronic effects is uncertain at present. As a consequence, its immediate application to the development of SQOs is limited to acute toxicity predictions.

It is recommended that AVS, SEM and interstitial water concentrations for field-collected sediments be made where metals may be of concern. In addition these measurements are also recommended as part of laboratory studies designed to investigate organism responses to metals in sediments.

Need for further testing/validation of equilibrium partitioning: It was recommended that field validation of SQOs be done. Additional recommendations were made for further analysis. These include:

(i) To examine limits of applicability of SQOs based on equilibrium partitioning relative to field sites which contain a gradient of sediment concentrations for specific chemicals above and below SQO concentrations. Emphasis should be on the analysis of benthic community health and individual organism toxicological responses to the gradient;

(ii) To facilitate the development of SQOs based on EqP for substances likely to bioaccumulate, monitoring data should be reviewed or obtained relating concentrations of non-ionic organic chemicals of concern in benthic species on a lipid basis to concentrations in sediment, on an organic carbon basis, to develop biota sediment factors (BSFs) and associated uncertanties. The BSFs may then be used to predict concentration in benthic organisms from concentrations in sediment.

Interstitial water quality

The interstitial water quality method is recommended for use when no partitioning model is available. Pore water measurement is the only available normalization for chemicals that have no existing partitioning theory. The chemical classes for which this method could be used include anionic metals, ionisable organics (phenolic chemicals), and acid and bases (e.g. acidic pesticides).

Pore water sampling and chemical analysis techniques are in the developmental stages. Some of the associated difficulties are small sample size and lack of precision.

Spiked sediment toxicity

The spiked sediment toxicity test method requires toxicological data from a variety of species to provide sufficient information to quantify a sediment quality objective. This ‘minimum data set’ should include acute and chronic effects on species representing different phyla, substrate relations and routes of exposure of sediment contaminants. All of the methods needed are not presently available, especially chronic sediment bioassay techniques. When the methods necessary to provide the minimum data are developed, it may be possible to derive SQOs the same way that water quality criteria (WQC) have been derived from comparative toxicology by the US EPA.

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4. Report of Working Group B: Toxicity test methods for sediments

Objectives of sediment toxicity tests

At all times it is important to be clear about the objectives of contaminated sediment studies, as the objectives are vital to selection and/or development of appropriate test systems.

There are a number of reasons for developing and utilising sediment toxicity tests:

(i) to aid in setting quality standards for individual compounds;

(ii) to assess the impact of discharges of sediments associated with receiving waters, such as sediment disposal associated with dredging activities;

(iii) to assess the persistence of toxicity in sediments following the alteration, amelioration or cessation of toxic discharges;

(iv) to predict the impact on sediment-dwelling organisms exposed to new substances that may be released to the environment;

(v) to estimate the degree to which toxicity is responsible for low benthic species diversity in impacted systems.

Factors to consider when selecting and carrying out the appropriate sediment toxicity tests

Developing and using a biological test method always includes striking a balance between the ideal and the practical. The selection of appropriate toxicity tests for contaminated sediments should be based first on the objectives of the assessment. For example, tests selected for a screening study necessarily would be quite different from those used for a comprehensive assessment of impacts on specific indigenous organisms or benthic community structure. Also, consideration must be given to the test fraction of concern. For example, it is not feasible to test some species of benthic or epibenthic organisms in aqueous sediment phases such as pore water or elutriate. Finally, given differences in species sensitivity, it generally would be desirable to have a suite, or battery, of test organisms for routinely assessing contaminated sediments. A non-exhaustive list of factors to be considered is given hereafter.

Species selection: This is probably the most important variable. In effect, species selection determines the ecological relevance and relative sensitivity of the test method. It can be based on site specificity (i.e. select local species) or chemical specificity [i.e. select taxa known to be sensitive to specific chemicals such as molluscs (sensitive to TBT) and crustaceans (sensitive to DDT)]. There is a growing consensus that several species should be tested in sediment toxicity evaluations.

Response criteria: Responses of interest can range from acute lethality to chronic effects on the intrinsic rate of population growth, ‘r’, or even effects on community structure in recolonisation tests. Various responses can be justified to meet specific study objectives. Emphasis should generally be placed on ecological relevance and interpretation in a regulatory context.

Standard test methods: These are essential in regulatory programmes and for comparison of results between investigations. They should reflect a large consensus within the scientific community (e.g. the OECD Guidelines for Testing of Chemicals) and agreement on standardization (e.g. ASTM standards).

Field validation: Ideally, field evaluation(s) of the relation between toxicological results and ecological conditions is necessary before a sediment bioassay can be accepted as a valid indicator of environmental pollution. However in the United States field validation is not required for testing of Toxic Substance Control Act (TSCA) chemicals.

QA/QC: This measures the acceptability of a particular test result against *a priori* performance standards. For example, in some tests a negative control with 90 per cent survival is needed to show that the test was conducted correctly. Also, a test with a reference toxicant is useful for showing that the sensitivity of the test animals is within an accepted range.

Statistical power: An analysis is needed to show how statistical power varies with the number of replicates and the number of individuals/replicates. This is essential to minimise the possibility of Type II error.

Natural environmental variables e.g. salinity, temperature, organic carbon, dissolved oxygen, particle size and acid volatile sulphide: These natural environmental variables should be within the known tolerance limits of the test species. Certain of these variables may also affect exposure and bioavailability of sediment-associated contaminants, and thus may be critical to the interpretation of test results. (Also, see the section on sediment characterisation below)

Intermethod and interlaboratory calibrations: These comparisons establish the relative sensitivity of the test method and the reproducibility of toxicological results.

Protocol specification: Design factors such as those listed below help define the exposure of test specimens to sediment contaminants. They must be standardized and should be adjusted to promote the ecological relevance of the test.

(i) Exposure chamber: size and shape should meet species requirements and scaling factors.

(ii) Sediment depth and volume: should meet species requirements and scaling factors.

(iii) Water system: static system with aeration may be adequate, especially for acute exposures with infaunal species. Flow-through systems may be necessary for chronic methods or spiking experiments. The water system used is especially important if overlying water is an important route of exposure. Aeration may affect physico-chemical characteristics of chemicals and concentrations in the water column, and is not appropriate when testing industrial chemicals. Flow-through systems are preferred.

(iv) Test duration: must be appropriate to the response criteria under investigation.

(v) Photoperiod: continuous light is sometimes specified to minimise emergence of infaunal species. Photoperiod may be critical for certain response criteria, e.g. reproduction.

(vi) Food: feeding should be avoided unless starvation becomes a problem or food is a critical route of exposure.

Factors to consider in selecting tests for routine use

- Tests should be (relatively) rapid, simple and reproducible both within and among laboratories. However it should be noted that rapid tests may miss chronic effects;
- Tests should be standardized and of moderate cost;
- Test species should represent taxa that are sensitive to common sediment contaminants such as metals, pesticides and polycyclic aromatic hydrocarbons; this could be ascertained through

previously collected data concerning sensitivity of species for both single contaminants and environmental samples;

- The test species chosen should be relevant to the system of concern (i.e. representative of important taxa) and should include evaluation of appropriate routes of exposure (e.g. it may be inappropriate to use pelagic rather than benthic species in solid phase tests);

- Ideally, the test or suite of tests chosen should be field-validated, i.e. endpoints (either acute or chronic) should be relatable to impacts *in situ*;

- It would be desirable to choose test species for which there is an established regulatory precedence.

Methods currently in use for testing different sediment phases

Whole sediments, pore water and elutriates have been studied, with a range of benthic, epibenthic and pelagic organisms. Although a number of species and test endpoints have been utilised, there are several for which relatively standard techniques exist including marine amphipods (ASTM E1367-90; Nipper et al., 1989; Swartz et al., 1985) and freshwater amphipods and chironomids (ASTM E1383-90).

Table 2 summarises some methods currently in use for the testing of whole sediments. In respect of pore water and elutriates, the whole range of aquatic toxicity tests has been used on invertebrates, protozoa, bacteria and algae. Some of these tests have been carried out on non-standard test organisms. Various toxic endpoints have been measured, both lethal and sub-lethal. Certain tests have advantages because they require relatively small amounts of test medium, for example oyster and echinoderm larvae LC50 tests.

Selection of the sediment fraction to be tested

The alternative fractions are whole sediment, interstitial (pore) water, and elutriate (water extract) of the sediment. It has also been suggested that elutriates may be used with the corresponding solid phase present in the testing chamber. The results may vary depending on which phase is tested. This variability may occur because the experimental protocols are different and because there is uncertainty over which fraction best represents the bioavailable fraction of contaminants in sediments.

The selection of the phase to test depends on the objectives of the study. For example, if the toxicity of a sediment to benthic animals has to be determined, then the whole sediment should be used for toxicity tests. On the other hand, if the pore water or elutriate approaches can be used, this

Table 2: Some methods in use for testing whole sediment toxicity

TEST ORGANISM(S)	TYPE	PURPOSE OF TEST	ADVANTAGES	LIMITATIONS	STANDARD METHODS
Lumbriculus variegatus	Benthic oligocheate	Study impacted sediment	Large organism; good for bioaccumulation	Not very sensitive	No
Various chironomids	Benthic organisms	Study impacted and spiked sediments	Methods looking at acute and chronic endpoints		No
Nereis virens	Benthic polycheate	Assessment of oil product amended sediments	Commercially available test organisms; bioaccumulation; sublethal endpoint	Low sensitivity	No
Rhepoxynius/ Echaustrorius/ Corophium/ Bathyporeia/Diporeia/ Leptocheirus/ Grandidierella/Hyaleila	Infaunal and epibenthic amphipods	Study impacted and spiked sediments. Field validation, i.e. reasonable simulation of real benthic systems. Regulatory precedence. Standard method. Extensive literature. Site specificity via species selection.	High sensitivity relative to other major taxa, e.g. molluscs and polychaetes.	Only acute exposure methods are developed. Sediment processing (collection, storage, etc.) may alter bioavailability. Tolerance limits of some tests species may produce false positives associated with grain size, salinity, organic carbon, etc.	
Echinocardium Spp		Oil product amended sediments	Lethal and sublethal endpoints	Relatively insensitive	No
Microtox	Bacterium	Rapid screen	Cost	Not sensitive or relevant	

may help reduce the need to develop new tests with benthic species because it may be possible to use existing protocols with pelagic species. Existing data suggest that pore water is an appropriate fraction for predicting bulk sediment toxicity, while elutriate is not (Ankley et al., 1991). However elutriates may be an appropriate test fraction if sediment suspension is of concern.

Sediment handling procedures

Table 3 shows sediment handling procedures for different toxicity tests.

Preparing pore water and elutriate for testing

There are a number of points to consider when using pore water or elutriate as a sediment test fraction. Foremost among these are the methods for isolating these fractions. Suggested protocols are as follows:

Pore water preparation

Various methods have been used for pore water collection, including:

- centrifugation at speeds of 2,000 to 30,000 xg;
- dialysis through a filter or membrane (e.g. with *in situ* peepers);
- displacement by inert gases (e.g. nitrogen);
- squeezing through a filter;
- microsyringe extraction.

Virtually any technique used to isolate pore water will result in some degree of alteration in the ‘true’ pore water.

For gas displacement and squeezing, it has been observed that pore water samples may be subject to drastic alteration, particularly in conjunction with the filtration process inherent in these approaches. For certrifugation and dialysis, exact alterations in pore water are uncertain.

Centrifugation yields the greatest volume of pore water volume for a given effort. For the other techniques, considerably more effort is required to obtain comparable volumes.

Centrifugation is the most widely used technique for the isolation of pore water samples for use in bioassays. Dialysis and squeezing are more often used for chemical analysis purposes. Gas displacement is infrequently used.

Filtration of pore water samples is not recommended, because loss of bioavailable toxicants has been observed upon filtration. Nevertheless, for some types of bioassays (e.g. algal tests) filtration may be needed.

Preferred technique: Centrifugation at moderate speed = 2,000 to 10,000 xg for 30 minutes. Temperature is optional; preferably at 4°C or at the final bioassay temperature. The test should be conducted as soon as possible after isolation of the pore water, preferably within two to three days. Pore water samples can acceptably be stored at 4°C during this time.

Table 3: Sediment handling procedures for different toxicity tests

HANDLING PROCEDURE	SCREENING TOXICITY ASSESSMENT	DETAILED TOXICITY ASSESSMENT	HAZARD ASSESSMENT OF DREDGE SOIL	TESTING SPIKED SUBSTANCES
SAMPLING				
composited*	+	-	n.a.	n.a.
worst case	-	-	n.a.	n.a.
disturbed*	+	+ -	+	+ -
worst case	+	+	+	+
storage time until treatment:	asap	asap	asap	asap
conditions	4°C	4°C	4°C	4°C
PRE-TREATMENT				
Water addition*	+	+ -	+	+ -
worst case	-	-	-	-
mixing*	+	+ -	+	+
sieving*	+ -	+ -	+ -	+
sterilizing	-	-	-	+ -
storage time until test medium preparation	≤ 14d	≤ 14d	≤ 14d	14d
conditions	4°C	4°C	4°C	4°C

Key:
+ technique currently used
- technique not used
+ - technique can be used
n.a. not applicable

* Handling will influence anaerobic conditions.

Table 3 continued

HANDLING PROCEDURE	SCREENING TOXICITY ASSESSMENT	DETAILED~ TOXICITY ASSESSMENT	HAZARD ASSESSMENT OF DREDGE SOIL	TESTING SPIKED SUBSTANCES
<u>PREPARATION OF TEST MEDIUM</u>				
<u>Whole Sediment</u>				
dilution*	+	+	+	+ -
worst case	-	-	-	-
mixing*	+	+ + -	+	+ +
settling time	depending on grain size			
storage time	≤ 4d max: end test	≤ 4d max: end test	≤ 4d max: end test	≤ 4d max: end test
conditions	4°C	4°C	4°C	4°C

Key:	+	technique currently used
	-	technique not used
	+ -	technique can be used
	n.a.	not applicable

* Handling will influence anaerobic conditions.

Elutriate preparation

Sediment elutriates are prepared by mixing a certain amount of sediment with dilution water. A preferred method cannot be given, the choice depending on the test organisms and the objectives of the study. Some characteristics of importance for elutriate preparation are:

(i) **Sediment-water ratio**: A ratio of 1:4 on volume or wet weight basis has often been used. For some sensitive tests (e.g. oyster larval test) a ratio of 1:50 has been used. It is recommended that researchers make dry weight determinations of their sediments for retrospective use in evaluating the results of elutriate tests on a whole sediment basis.

(ii) **Method of mixing**: A roller mill is preferred, but other techniques such as shaker tables, aeration and hand shaking also have been used.

(iii) **Time of mixing**: Periods of ten seconds up to seven days have been used. It was felt that mixing at least overnight (ca. 12 h) is advisable.

(iv) **'Dilution' water**: Culture water for the test animals or comparable control water is appropriate for use in preparing elutriates.

(v) **Separation of elutriate and solid phase**: Centrifugation and natural settling have been used. The last method, however, can require weeks for total settling. Some tests do not separate the aqueous and the solid phase fractions; the settling suspension is used as a test medium (e.g. oyster larval test).

(vi) As in the case of pore water, filtration of the aqueous phase is not recommended.

(vii) As in the case of pore water, extended storage of elutriates is not recommended.

Sediment characterisation

A wide range of parameters may be relevant in characterising the sediment associated with solid phase tests; they depend on the purpose of the investigation. A full evaluation of, and rationale for, measuring each parameter was considered beyond the scope of this document. However the following key parameters are frequently necessary for interpretation of the toxicity test results:

-- **Particle size distribution**:

Particle size may influence the partitioning of chemicals, particularly ionisable organics, between sediment and water. In solid phase tests, the tolerance range of the chosen organism to particle size must also be considered (Dewitt et al., 1989).

-- **Dissolved oxygen**:

A critical factor to monitor in overlying water, particularly in sediments with high biological or chemical oxygen demand.

-- **Organic carbon content**:

The dominant normalizing factor for bioavailability of nonpolar organic chemicals.

-- **Total ammonium concentration**:

Frequently a source of toxicity in sediments from eutrophic water systems, resulting from the natural degradation of organic matter, and should be measured in overlying water or in some instances pore water.

-- **Acid volatile sulphides (AVS):**

A dominant factor controlling the bioavailability of some cationic heavy metals.

-- **pH**:

A key factor influencing the bioavailability/toxicity of some contaminants (e.g. ammonia), pH is also an important determinant in evaluating the tolerance range of some organisms. It should be measured in overlying water and the solid phase sample, if possible.

The following may also be relevant on a site-specific basis:

-- Biochemical Oxygen Demand;
-- Chemical Oxygen Demand;
-- nitrate/nitrite;
-- chloride;
-- sulphate;
-- redox (Eh) potential;
-- Dissolved Organic Carbon (pore water);
-- conductivity;
-- salinity;
-- hydrogen sulphide;
-- suspected or spiked chemical contaminants.

Physical-chemical parameters monitored during aqueous phase tests

Dissolved oxygen concentration, pH and temperature in aqueous phase tests (elutriate, pore water) should be monitored during the test, together with ammonia concentration, salinity, total hardness, alkalinity and conductivity as appropriate.

Sampling and storage of test sediment

Sediments for toxicity tests should be fresh, and handled in a way that minimises alterations that may affect the toxicity to organisms exposed in the laboratory. When sediments are sampled for toxicity tests, parallel samples are often subjected to chemical, physical and/or biological investigations. Therefore the combined objectives of the particular investigation determine the sampling design, including the equipment used, sampling points, depth of sediment and time for sampling.

Sediments for biological investigations (evaluation of benthic community structure) are usually processed (screened) and preserved on-site, while samples for chemical and physical characterisation are handled and stored according to procedures more or less specific to the particular test. For purposes of sediment toxicity evaluations it is important to obtain sediments with as little disruption as possible, to allow for realistic laboratory evaluation of *in situ* conditions.

In order to make it possible to verify test results from a toxicity test, the following points should be considered carefully:

(i) The point of sampling is described in enough detail (map, coordinates, water depth).

(ii) The time (year, month, day, hour) of sampling and person (organisation) responsible for sampling are reported.

(iii) The equipment (sampling device) and the approximate amount and depth of sediment taken should be recorded. If toxicity test results will be compared with other measurements, then samples must be collected in the same way.

(iv) Sediments for toxicity testing must be kept cool (4°C) during transport and storage. This is to minimise alterations that may occur.

(v) Toxicity tests should be initiated as soon as possible after sampling. The time between sampling and test initiation should be as soon as possible, but preferably in less than two weeks. This is applicable when sediments have been stored at 4°C. Freezing is not recommended for sediments to be used in toxicity tests.

More detailed guidelines on collection, storage, characterisation and manipulation of sediments for toxicological testing are provided in ASTM E1391-90 and in references cited in that document.

Sediment spiking techniques

Sediment spiking consists of adding one or more chemicals to clean sediments. Sediment spiking is based on geochemical processes and, if possible, geochemists should be consulted concerning appropriate spiking methods. Various methods have been used and include:

(i) Glass plating technique: the chemical is dissolved in a solvent and coated on the inside walls of a bottle or jar. The sediment is added and rolled until the chemical is homogeneously distributed through the sediment.

(ii) Water is saturated with the contaminant(s) of concern, and is passed over and through the sediment until equilibrium is reached.

(iii) The compounds of interest are inserted, and the sediments rolled for some period of time and allowed to sit until equilibrium is reached.

Equilibrium between pore water and sediment particles for the spiked compound is reached when pore water concentrations are relatively constant over time. This is very compound-specific. For example, non-polar organic compounds with high K_{ow} tend to bind quickly, although final equilibrium may only be reached after weeks.

Concentrations for cationic metals spiked into sediments may be normalised to an appropriate factor such as AVS concentration; for non-polar organic chemicals, normalisation to organic carbon concentrations is appropriate.

Generally, compounds should be spiked into homogenised sediment samples and pore water and bulk sediment chemistry should be monitored over time, including at the start and end of the toxicity test.

Assessing contaminated sediments

When possible it is recommended that regulatory decisions be based upon sediment assessments for which all of the following data are available:

- toxicity test results;
- benthic community structure;
- chemical analyses.

This type of approach, commonly referred to as the sediment quality triad (Chapman, 1986), ensures that all available data, based upon independent lines of reasoning, can be used in a decision-making framework. It is recognised, however, that in some cases limited resources or specific legislative mandates may mean that toxicity tests, chemical analyses or evaluation of benthic community structure, either alone or in some specific combination, may be required in an initial screening phase to detect potential impacts. For example, an approach currently proposed by environmental toxicologists from the Netherlands uses initial evaluation of benthic community structure, followed by toxicity tests and appropriate chemical analyses at impacted sites.

Along the lines of an integrated approach to assessing contaminated sediments, methods were recently published which enable association of observed toxicity with specific contaminants in sediment samples (US Environmental Protection Agency, 1988; 1989a; 1989b). These toxicity identification evaluation (TIE) procedures utilise toxicity-based fraction approaches and are the only methods currently available to link toxicity to specific contaminants in a causal manner. The ability to define contaminants responsible for toxicity in contaminated sediments provides a unique opportunity for insights concerning remedial and regulatory activities, including:

(i) identification of discharges responsible for sediment contamination resulting toxicity;
(ii) identification of unsuspected contaminants responsible for toxicity in sediments;
(iii) identification of point versus non-point source impacts resulting in toxic sediments;
(iv) evaluation of disposal options for dredged materials.

One of the most attractive features of the TIE for evaluating contaminated sediments is that it enables a toxicologically and chemically focused approach to identifying cause and effect relationships. Overall, it is felt that TIE procedures represent a logical and useful extension to integrated assessment approaches such as the sediment quality triad.

Conclusions of Working Group B

(i) Toxicity tests can be useful tools for assessing the degree and extent of impacts of contaminated sediments on aquatic ecosystems. They are also useful for deriving sediment quality objectives via spiking of test chemicals into clean sediments. Careful consideration must be given, however, to the study objectives when selecting appropriate sediments, test organisms and response endpoints. The test species selected must be appropriate for the study objective and shown to be sensitive to relevant chemicals or classes of chemicals. Study objectives must also be carefully considered when designing sampling strategies and techniques for handling sediments. Ultimately, in order to provide a solid regulatory basis for the use of sediment toxicity tests the approaches used must be subjected to rigorous field validations and testing as well as laboratory development in order to determine optimal testing procedures.

(ii) Ideally, regulatory decisions should be based upon sediment assessments such as the sediment quality triad where all the following data would be available: benthic community structure, toxicity test results and chemical analyses. This is seen as a strategic aim rather than an immediate possibility.

(iii) Toxicity identification evaluation (TIE) procedures which utilise toxicity-based fraction approaches are the only methods currently available to link toxicity to specific contaminants in a causal manner for field-collected sediments. These procedures present a logical and useful extension of integrated assessment approaches, such as the sediment quality triad.

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ANNEX 1: BACKGROUND DOCUMENT

A Summary of Proposed Methods for Assessing Contaminated Sediments and Deriving Sediment Quality Criteria

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Table of Contents

Foreword

This document summarizes a number of proposed methods for assessing contaminated sediments and deriving sediment quality criteria (SQC). The purpose of the document is to provide environmental scientists/managers, who are not intimately familiar with contaminated sediment research, with a broad understanding of different technical approaches that have been proposed for regulatory use. The information contained in this document does not include sufficient detail to evaluate the technical validity of any of the approaches. It should not be inferred, at this juncture, that any approach is preferable to another. It should be noted that there may be other approaches, of which the authors of this document were not aware, for assessing contaminated sediments or deriving criteria.

Much of the information contained in this document was derived from a draft report compiled by the U.S. Environmental Protection Agency entitled Sediment Classification Methods Compendium. The authors of the various chapters included in that report are: Catherine Krueger (Apparent Effects Threshold); Betsy Day, Gary M. Braun, and Gordon R. Bilyard (Benthic Community Structure); Richard C. Swartz, Nelson Thomas, and Dave Hansen (Bulk Sediment Toxicity Testing); Christopher S. Zarba (Equilibrium Partitioning-NonIonic Organics); Gerald Ankley and Nelson Thomas (Interstitial Water Toxicity Identification Evaluation); Peter M. Chapman (Sediment Quality Triad); Richard C. Swartz, Nelson Thomas and Dave Hansen (Spiked-Sediment Toxicity Testing); Anthony R. Carlson, Philip M. Cook and Henry Lee II (Tissue Residue Approach).

Associated with the summary of each approach are several references which would provide further details/insight concerning the method. Key papers are indicated by asterisks; these are included in the mailing package to participants of the OECD Workshop. The additional references can be obtained by contacting:

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Apparent Effects Threshold

The apparent effects threshold (AET) approach is an empirical method used to assess sediment quality. The objective of the approach is to determine the concentration of a particular sediment contaminant above which statistically significant biological effects are always expected. Test (impacted) and reference (nonimpacted) sediments are collected and analyzed for chemical concentrations and biological effects. Biological effects data generally are obtained from laboratory sediment toxicity bioassays or the assessment of benthic community structure. Effects data, however, also may be obtained from measurements of bottom-fish histopathology and bioaccumulation of contaminants.

The generation of AET values requires the development of a large chemical and biological effects database. The AET approach is based on the assumption that appropriate indicators of bioavailability and bioeffects can be determined from field and/or laboratory data.

The AET approach has been used in the Puget Sound (Washington USA) region to provide guidelines for regulatory decisions. With this approach, sediment quality values were developed to evaluate the potential toxicity of contaminated sediments in urban bays. Also, the AET approach was used to determine the necessity for biological testing of dredged sediments proposed for open-water disposal. Finally, AET values have been used to establish draft sediment standards to classify sediments that may cause adverse biological effects. AET values have been generated for over 60 inorganic and organic chemicals commonly associated with contaminated sediments.

The AET approach has several advantages. First, AET values can be generated for any measured contaminant using a specified biological effect indicator. Second, the AET approach does not require an a priori assumption concerning the specific mechanisms of interaction between an organism and toxic contaminant. Finally, the method is well suited to identify areas impacted by sediment contaminants. The major limitation of AET is that SQC derived from the approach cannot account for the effects of abiotic factors and unmeasured or multiple contaminants. Moreover, the approach is inherently site-specific. Finally, the cost associated with developing the database can be quite large.

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Benthic Community Structure

The benthic community structure approach is an in situ method used to evaluate sediment quality. The main objective of this approach is to identify environmentally degraded sediments by examining alterations in the community structure of sediment dwelling organisms. The approach is a descriptive method and cannot be used alone to generate numerical SQC; however, the approach is commonly used in assessments of contaminated sediments. In order to establish SQC, the benthic community structure approach may be used as a component of other methods such as the Apparent Effects Threshold or the Sediment Quality Triad.

In this approach, changes in benthic community structure are used to measure the potential ecological impact of pollutants. Implementation of the approach requires the collection of field data to determine benthic community structure and sediment quality at reference (nonimpacted) and test (impacted) stations. In general, assessment of benthic community structure requires the determination of: the number of species present; the spatial distribution of species and individuals; and the distribution of individuals among species and higher taxa. Typical measurements include: replicate sampling at each station; sorting and identification of organisms to species or lowest possible taxon; analysis of the numbers of taxa and individuals; determination of sample biomass; and identification of the dominant taxa. In addition, corresponding sediment samples are collected to determine physical/chemical parameters such as organic carbon content and grain size. Statistical analyses then are used to establish relationships between benthic community structure and sediment quality.

The analysis of benthic community structure is a relatively old assessment tool. It has been used extensively to examine sediment quality in areas affected by organic carbon enrichment, contamination by toxic metals and organic chemicals, and natural disturbances. The benthic community structure approach is based on several assumptions. First, benthic community structure reflects the chemical and physical environment at the sampling location due to the sedentary nature of benthic infauna. Second, benthic community structure may be altered in a predictable manner over space and time by chemical and physical disturbances. Finally, proper data collection and subsequent statistical analyses can be used to detect and evaluate trends in community structure over space and time.

The benthic community structure approach has several advantages: (a) the approach has been used extensively as an assessment tool to examine the ecological effects of potentially contaminated sediments; (b) it is an in situ method and therefore establishes an empirical relationship between benthic community structure and sediment quality; and (c) the method is well suited for assessing the spatial and temporal effects of toxic chemical contamination and/or organic carbon enrichment in a variety of sediment types. Limitations to this approach include: (a) the large number of factors that influence benthic community structure at a given site makes it difficult to isolate chemical-specific effects; (b) it is a descriptive method and can not be used alone to generate numerical SQC; and (c) the method involves costly and time- consuming field studies and laboratory analyses.

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Bulk Sediment Toxicity Testing

The bulk sediment toxicity test approach is a toxicologically based method used for sediment quality assessment. The main objective of this approach is to derive toxicity data to determine whether the test sediment will adversely affect benthic organisms. The sediment toxicity approach is a descriptive method and cannot be used to generate numerical sediment quality criteria (SQC); however, it is routinely used in assessment of contaminated sediments. To establish SQC, the bulk sediment toxicity approach may be combined with other sediment quality methods such as the Apparent Effects Threshold and the Sediment Quality Triad.

In the bulk sediment toxicity approach, organisms are exposed in the laboratory to field-collected sediments from contaminated and reference or control areas. At the end of the exposure, the response of the test organism is examined in terms of a specified biological endpoint such as survival, growth, reproduction or behavior. Sediment toxicity is determined by comparing results obtained from contaminated sediment exposures to those observed in the reference or control sediments. The bulk sediment toxicity approach is based on the assumption that the behavior of chemicals in the test sediment in laboratory exposures will be similar to their behavior in natural, in situ sediments.

Various sediment toxicity procedures have been developed for testing field sediments. Currently, there are several bulk sediment toxicity tests under review by the American Society for Testing and Materials (ASTM). Test species should include more than one type of organism to ensure a range of sensitivities to various types of sediment contaminants. Commonly used test organisms are freshwater chironomids Chironomus tentans and Chironomus riparius, the freshwater/estuarine amphipod Hyalella azetca, marine amphipods such as Rhepoxynius abronius and Ampelisca abdita and freshwater oligochaetes such as Lumbriculus variegatus and Tubifex tubifex. Test length varies with the biological endpoints of interest for the species used, but theoretically should include both acute and chronic endpoints.

A major advantage of the bulk sediment toxicity test approach is that it considers the interaction among chemicals in contaminated sediments. The method can be used for all classes of sediments and any chemical contaminant. The method does not require costly individual chemical measurement. The approach also can be used to monitor temporal and spatial distribution of contaminated areas. A disadvantage of the approach is that bioassays conducted with field collected sediments cannot provide chemical-specific SQC. Also, due to its non-specific nature (i.e., inability to identify specific contaminants), this method has limited use in source control.

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Equilibrium Partitioning-NonIonic Organics

The equilibrium partitioning (EP) approach has been proposed for developing numerical chemical-specific SQC. In this approach, a theoretical model is used to predict the partitioning of a contaminant between sediment and interstitial water. Concentrations of the contaminant in interstital water are then compared to existing water quality criteria (WQC). The EP approach has been extensively applied to nonionic organic contaminants; however, efforts are also underway to model toxic metal partitioning in sediments.

A key observation in the EP approach for deriving SQC is that for benthic organisms toxicity correlates more closely with the concentration of contaminants in the interstitial water than with the total concentration of contaminants in the bulk sediment. If the predicted interstitial water concentration for a specified contaminant is less than the WQC, the sediment would not be expected to cause adverse effects. For nonionic hydrophobic organic chemicals, organic carbon has been identified as the principal factor influencing sediment contaminant binding. The equilibrium interstitial water concentration of the contaminant is calculated according to the model:

$$C_{IW} = C_S/K_{OC} * foc$$

where,

C_{IW} = contaminant concentration in interstitial water (ug/L)
C_S = contaminant concentration in bulk sediment (ug/kg dry sed) K_{OC} = organic carbon (oc)/water partition coefficient (L/kg oc)
foc = fraction organic carbon in sediment (kg oc/kg dry sed)

The EP approach makes several assumptions including: (a) the chemical sensitivity range of benthic and water column organisms (for which WQC were derived) are similar; (b) an equilibrium state exists between the solid and aqueous phases in an aquatic system and the uncomplexed concentration of the contaminant in the interstitial water can be estimated from sorption constants; (c) for benthic organisms, the interstitial water concentration rather than the bulk sediment concentration of a chemical correlates with the observed biological effect; and (d) the partitioning of nonionic hydrophobic organic chemicals is primarily dependent upon the organic carbon content of the sediment.

The EP approach has several advantages: (a) it uses existing WQC, so that once the approach has been validated, the only field measurements needed are the contaminant concentration in the sediment and the appropriate sediment sorption parameter (i.e., organic carbon content for nonionic organic chemicals); (b) the theory of EP is well established for nonionic hydrophobic organic chemicals and partition coefficients are available; and (c) these criteria can be extended to include a range of sediment types so that there is a standard basis for comparison both within and between sites, which is necessary for development of widely-applicable SQC.

The EP approach has several limitations: (a) SQC developed from the EP approach are chemical specific and do not consider interactions among chemicals in contaminated sediments; (b) the approach is currently applicable only to nonionic organic chemicals (although a technical approach is being developed for toxic metals); (c) criteria based on biological effects cannot be directly developed for chemicals that have no existing WQC; and (d) concentrations of extractable contaminants in sediment are influenced by sample collection and storage techniques.

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Equilibrium Partitioning-Metals

As described in the previous section, one approach to assessing risks associated with contaminants in sediments, as well as the development of SQC, is the quantitive prediction of bioavailability based on partitioning relationships. A good deal of empirical data indicates that the appropriate sediment partitioning phase for predicting the bioavailability of nonionic organic chemicals is organic carbon. As described previously, this serves as the technical basis for deriving SQC for these compounds. However, it was uncertain whether it would be feasible to develop comparable partitioning relationships for cationic metals, which are extremely common sediment contaminants. Various researchers have attempted to predict metal activity in sediments via sequential extraction schemes, however, these approaches were quite operationally-defined, and of limited value with respect to assessing actual metal bioavailability.

Recent studies at the U.S. Environmental Protection Agency research laboratories at Narragansett and Duluth, and Manhattan College, indicate that it is possible to predict the bioavailability of certain cationic metals in aquatic sediments through evaluation of the formation of metal sulfides. Specifically, a number of cationic metals of concern in sediments (cadmium, nickel, copper, lead, zinc) will displace iron from iron monosulfide complexes and form insoluble, biologically-unavailable sulfide complexes via the following reaction:

$$\mathrm{Me^{++} + Fe\,S \rightleftarrows Me\,S + Fe^{++}}$$

A measure of the amount of sulfide available to undergo this reaction in sediments can be obtained by determining the acid volatile sulfide (AVS) content. The concentration of AVS in the sediment sample then can be used to predict the binding capacity of the sediment for metals. Thus, sediments with molar metal/AVS ratios less than one (i.e., "excess" AVS) theoretically should not exhibit metal toxicity, while sediments with ratios greater than one should have the potential for metal toxicity.

To test this hypothesis, a series of laboratory exposures were conducted with several marine and freshwater sediments of varying AVS content, which were spiked with cationic metals (cadmium, copper, nickel, lead, zinc), as well as field-collected sediments contaminated with elevated concentrations of both cadmium and nickel. The sediments were subjected to 10-day toxicity tests with a variety of marine (*Ampelisca abdita, Rhepoxynius hudsoni*) and freshwater (*Hyalella azteca, Lumbriculus variegatus, Helisoma sps.*) benthic invertebrates. Survival of the organisms was compared to metal/AVS ratios in the samples. Figure 1 presents data from the experiments with cadmium and nickel. The top panel plots percent mortality of the test species versus total concentration of metals in the sediments; it is quite apparent that it is impossible to predict toxicity based on total metal concentration. The bottom panel of Figure 1 depicts sediment toxicity plotted versus metal concentration normalized to AVS, i.e., metal/AVS ratios. It is clear that this results in a predictable relationship with regard to metals and toxicity; in samples with metal/AVS ratios less than one,

significant mortality never occurred. However, as the metal/AVS ratio approached and exceeded one, metal toxicity was observed consistently. Although the data are not shown, similar results also have been obtained for copper, lead and zinc.

These data indicate that it may be possible to routinely utilize metal/AVS relationships to predict the bioavailable fraction of metals in sediments. This is significant not only from the standpoint of SQC development, but just as importantly, for assessments focused upon evaluating aquatic risks associated with metal-contaminated sediments. It should be noted, however, that a good deal of research remains to be done in order to completely validate this approach for deriving SQC. For example, studies to date have been performed using only acute toxicity as an endpoint; the approach also needs to be evaluated for chronic toxicity. Also, the approach has yet to be validated in a field situation (e.g., comparison of metal/AVS ratios to benthic community structure). Finally, it is unlikely that AVS is an important partitioning phase for metals in some types of sediments (e.g., highly aerobic environments); futher work is needed to define appropriate partitioning phases for metals in these types of situations.

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Interstitial Water Toxicity Identification Evaluation

Laboratory toxicity tests are an important component of sediment assessments. However, to use toxicity test results logically in a decision-making framework for identifying remediation options, it is essential to identify the specific chemicals responsible for observed toxicity. Attempts to identify contaminants responsible for sediment toxicity have traditionally relied upon correlative techniques that compare measured chemical concentrations with toxicity. The correlative approach, however, has some significant shortcomings in that: (a) there is no way to ensure that chemicals responsible for toxicity actually are measured, (b) it is nearly impossible to account for toxic interactions that may exist between the complex mixtures of chemicals generally present in sediments, and (c) it is difficult to resolve the actual bioavailability of all measured chemicals. To address these problems, the U.S. Environmental Protection Agency has been developing toxicity identification evaluation (TIE) procedures to identify specific contaminants responsible for acute toxicity in complex aqueous samples such as effluents, ambient water, hazardous waste leachates, and sediment elutriates and/or interstitial (pore) water. The key to the TIE process is that it is a bioassay-directed technique, i.e., toxicity to the organism of concern is tracked through various sample manipulations and fractionations that characterize, identify and confirm compounds as sample toxicants. Therefore, the approach ensures that toxic chemicals of concern actually are measured, it enables evaluation of possible interactions among toxicants, and it accounts for bioavailability questions. TIE procedures have been used to successfully identify a number of compounds and/or classes of compounds as responsible for toxicity in different acutely toxic samples. Some of these compounds include ammonia, metals (e.g., copper, zinc, nickel, cadmium), organophosphate insecticides (e.g., malathion, diazinon), organochlorines (e.g., pentachlorophenol) and surfactants.

For contaminated sediments, TIE work generally is conducted with pore water; however, if toxicity of suspended sediments is of concern, elutriate (e.g., some mixture of sediment and water) also can be used as a test fraction. Test organisms utilized for sediment TIE have included both upper-water column and benthic species. Although certain steps for sediment TIE can require relatively sophisticated analytical equipment (e.g., high pressure liquid chromatography, gas chromatography/mass spectroscopy), a great deal of information also can be derived from some relatively straight-forward and inexpensive sample manipulations.

The major advantage of TIE for assessing contaminated sediments is that it currently is the only approach available for directly identifying compounds responsible for sample toxicity. As such, TIE offers a logical basis for utilizing toxicity data in a decision-making framework for remediating contaminated sediments. Current disadvantages of the approach include: (a) it is only suitable for evaluating acute (rather than chronic) toxicity, and (b) some relatively specialized training is necessary to conduct and interpret TIE experiments successfully.

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Sediment Quality Triad

The sediment quality triad approach is a method used for the development of descriptive and numerical SQC. The approach consists of three components: sediment chemistry measurements; sediment toxicity bioassays; and in situ studies such as evaluation of benthic community structure. The chemical and biological response data from these components then is used to identify or predict areas where pollution-induced sediment degradation may be occurring.

The sediment quality triad requires collection of field samples from reference and test stations. The first component of the triad involves identification and quantification of inorganic and organic contaminants in the sediment, as well as, total organic carbon content and grain size. The second component involves identification and quantification of toxicity based on laboratory tests on field collected sediments. Some of the test species and biological endpoints that have been used in these toxicity tests were identified in the Bulk Sediment Toxicity Testing section. The final component of the triad involves evaluation of biological alterations in situ. Assessment of benthic community structure is the most common in situ evaluation (see section on Benthic Community Structure); however, measurements of resident organism histopathology and/or bioaccumulation of contaminants also may be included. Analysis of the sediment chemistry, toxicity and benthic infauna data is then used to assess the degree of sediment quality degradation at each station.

In general, the sediment quality triad approach is used as a descriptive sediment quality assessment technique. However, in Puget Sound the approach has been used to establish SQC for lead, polycyclic aromatic hydrocarbons and polychlorinated biphenyls. These criteria were developed by examining large data sets. The triad of data identified areas and contaminant concentrations that were associated with no or minimal biological effects.

The sediment quality triad approach has several advantages. First, the approach uses empirical relationships to provide a direct measure of sediment quality. Second, the approach does not require a priori assumptions concerning specific mechanisms of interaction between organisms and toxic contaminants. Finally, the method can be used to develop SQC for any measured contaminant. However, the criteria could be influenced by the presence of unmeasured toxic contaminants.

The triad approach has three major limitations. First, rigorous statistical criteria for calculating single indices from each of the triad components have not been developed. Also, the approach requires development of large and costly databases. Finally, the triad approach is extremely site-specific.

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Spiked-Sediment Toxicity Testing

The spiked sediment toxicity test approach is a toxicologically based method that can be used for generating numerical SQC. The objective of the approach is to derive laboratory concentration-response data. The data are used to predict concentrations of specific chemicals that would have an adverse effect on benthic organisms under field conditions.

In the spiked-sediment toxicity test approach, test organisms are exposed in the laboratory to sediments spiked with a range of chemical concentrations. At the end of the exposure, the response of the test organism is examined in relation to a specified biological endpoint such as survival, growth, reproduction or behavior. The toxic effects concentration of the test chemical is determined by comparing the results from the spiked sediment exposure to those observed in the reference or control sediment. The spiked sediment toxicity test approach is based on the assumption that the behavior of chemicals in spiked sediment in laboratory exposures will be similar to their behavior in natural, in situ sediments.

Various spiked sediment toxicity test procedures are under development. The biological test procedures and sediment spiking procedures are currently under review by the American Society for Testing and Materials (ASTM) sediment toxicology subcommittee. Test species should include more than one type of organism to ensure a range of sensitivities to various sediment comtaminants. Commonly used test species are the same as listed in the section entitled Bulk Sediment Toxicity Testing. Additional species that have been used are the polychaetes Neanthes arenaceodentata and

Capitella capitata. The length of the test varies with desired biological endpoints for the species used; however, as for bulk sediment testing, both acute and chronic endpoints should be examined.

The spiked sediment toxicity test approach uses both biological and chemical data. Chemical concentrations in the spiked sediment and interstitial water are determined at the beginning and end of the exposure. The sediment partitioning phase that controls chemical bioavailability (e.g., organic carbon, AVS) should be identified and measured to facilitate comparisons between sediment types.

The spiked sediment toxicity test approach has several advantages. (a) it determines empirically dose-response data for individual chemicals or chemical mixtures; (b) the procedure to derive SQC is similar to the approach to derive WQC, therefore the procedure and rationale are technically acceptable and legally defensible; (c) chemical specific data can be generated for a wide variety of chemical classes and sediment types; and (d) the approach can be used to experimentally validate SQC derived from other approaches. Limitations of the spiked sediment toxicity test approach are: (a) the techniques for dosing sediments and measuring interstitial water chemical concentrations have not been well established; and (b) an extremely large number of chemical mixtures would have to be tested to develop a database useful for regulatory purposes.

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Tissue Residue Approach

The tissue residue approach has been proposed for establishing numerical SQC. The objective of this approach is to determine the sediment chemical concentration that results in unacceptable tissue residue levels in aquatic species such as benthos and fishes. The approach entails the identification and quantitation of chemicals in sediment and corresponding tissue samples associated with undesirable toxic effects. Two requirements are needed for the tissue residue approach to be applied to SQC development. First, unacceptable tissue residues for aquatic organisms must be derived for a variety of sediment-associated contaminants. Second, methods are needed to determine tissue residue concentrations that will result when organisms are exposed to contaminated sediments.

Several methods for deriving unacceptable tissue residues have been proposed: the water quality criteria (WQC)-residue approach; the experimental approach; and the human health approach. The WQC-residue approach establishes a maximum safe tissue residue (MSTR) for a particular chemical observed at the chronic WQC water concentration. MSTRs may be obtained through actual residue measurements associated with laboratory toxicity tests or by multiplying the WQC by an appropriate bioconcentration factor (BCF) or bioaccumulation factor (BAF). In the experimental approach, acceptable tissue residues are derived through the use of laboratory chronic dose-response experiments or field correlations. The data are then used to establish the relationship between residue concentrations and toxic effects. Finally, the human health approach may be used to establish acceptable tissue residues by examining health risks associated with the consumption of contaminated aquatic species.

In the tissue residue approach, the relationship between organism residue and sediment chemical concentration also must be established. This can be accomplished by: measurement of site-specific sediment/organism partition coefficients; use of fugacity or equilibrium partitioning models to predict organism residue levels; or application of pharmacokinetic-bioenergetic models to predict organism residues resulting from exposure to chemicals in foodchain, water and sediment.

The tissue residue approach is still in the developmental stage. However, it has been used to establish the concentration of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in Lake Ontario sediments that will result in acceptable TCDD levels in lake trout. The approach assumes organism residues provide a reasonable measure of the exposure associated with chemical contaminants in sediment. Also, the approach assumes a reduction in sediment TCDD concentrations over time will result in a reduction of organism residues. Therefore, the potential for toxic effects will be lowered. A final assumption is that the route of exposure responsible for residue accumulation does not influence the residue-toxicity relationship.

Advantages of the tissue residue approach are: (a) the method could provide a direct link between human health and SQC development when residue levels are determined for organisms that are a human food source; (b) the approach is suitable for different sediments and aquatic organisms; and (c) it provides site-specific data that can be used to examine the environmental impact of in-place pollutants. Limitations of the tissue residue approach include: (a) the method is in the developmental stage and has not been validated; (b) it is not useful for examining sediment toxicity associated with non-residue forming toxic chemicals such as ammonia, hydrogen sulfide and polyelectrolytes; (c) the method requires development of a database containing residue-effects data for complex chemical mixtures typically found in sediments; and (d) it is often difficult to obtain sufficient benthic biomass for chemical analysis.

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Screening Level Concentration

The screening level concentration (SLC) approach is a field based approach proposed to develop SQC. The SLC method is designed to estimate the highest concentration (normalized to sediment organic carbon concentration) of a particular nonpolar organic contaminant in sediments that can be tolerated by approximately 95% of benthic infauna. An important objective of the SLC approach is to determine if a particular chemical is present in sediments at sufficiently high concentrations to be of environmental concern and warrant further investigation. To derive SLCs, large databases are required that contain synoptic data on sediment chemical concentrations, benthic invertebrate distributions and sediment total organic carbon concentrations.

Calculating a SLC for a particular nonpolar organic contaminant is a two step process. The first step involves calculating a species screening level concentration (SSLC). Data from a minimum of 20 stations is needed to calculate each SSLC. The presence of a selected benthic indicator species is matched with the sediment concentration of a given chemical (normalized to sediment organic carbon concentration). This step is necessary to determine the concentration representing the 90th percentile of the cumulative distribution function for the contaminant at stations where the selected species is present. The concentration is called the SSLC. SSLC values are calculated for all species for which the appropriate minimum dataset is available. The second step in the calculation process involves constructing a cumulative distribution function of SSLCs. This information is used to determine the contaminant concentration above which 95% of the SSLCs occur. This 5th percentile value of all calculated SSLCs is called the SLC. The SLC is designed to provide a SQC which in theory will predict 95% of all species 90% of the time. A complete discussion and examples of the SLC calculation can be found in Neff et al. (1986) and Neff et al. (1988).

A basic assumption of the SLC approach is that the data set includes locations containing the full range of contaminant concentrations to which each species is tolerant. This is important so that a reasonable estimate of the threshold concentration can be obtained. However, this assumption may be difficult to meet since the full tolerance range of most species is not known.

The SLC approach has several advantages: (a) it can be developed using existing databases and existing methodologies; (b) the method uses field data on the co-occurrence of resident infauna and concentrations of chemicals in sediments which make laboratory to field extrapolations unnecessary; (c) it utilizes data on the presence of species in sediment containing a known chemical concentration so no a priori assumptions are made concerning the causal relationship between levels of sediment contamination and resident infaunal distributions; (d) valid a posteriori inferences can be made about the range of contaminant concentrations that benthic infauna can tolerate in sediments since field data are used on the co-occurrence of benthic infaunal species and chemical concentrations in sediments.

The SLC approach has several disadvantages: (a) it is difficult to determine a direct cause-effect relationship between any one contaminant and the distribution of benthic organism since multiple contaminants are usually present in field situations; (b) calculation of the SLCs is greatly affected by the range and distribution of contaminants concentrations and particular species used to generate them; (c) a precise level of infaunal taxonomic identification is required together with a large data set which may make the method costly to use; (d) selection criteria for species has not been established so the level of inclusion of representative sensitive species in the SLC method is variable.

To date, SLCs have been calculated for five contaminants in freshwater sediments (total PCBs, DDT, dieldrin, chlordane and heptachlor epoxide). SLCs have been calculated for nine contaminants in saltwater sediments (total PCBs, DDT, naphthalene, phenanthrene, fluoranthene, benz(a)anthracene, chrysene, pyrene, and benzo(a)pyrene).

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Sediment Background Concentration

In the sediment background concentration approach, concentrations of contaminants in a sediment of interest are compared to concentrations from reference background sites, where contaminant levels are deemed to be of acceptable quality. Implementation of the background approach requires selection of a suitable reference site. A reference site may be derived by determining historical background chemical concentrations in dated sediment cores. The core data provides background levels prior to industrialization. As a result, the pre-industrial data would provide background levels only for metals and not for anthropogenic organic contaminants. Adoption of a contemporary sediment standard would be required for anthropogenic organic contaminants.

The background approach has certain advantages: (a) the approach is relatively simple and the data requirements are minimal; (b) the need for additional data collection can be reduced by using existing databases that contain only measured chemical concentrations in sediments; and (c) toxicological data is not required so the method avoids the need to provide mechanistic chemical explanations for contaminant behavior or biological effects.

The background approach has several disadvantages: (a) the approach has no biological basis since biological effects data is not examined; (b) the exclusive use of chemical data implies that sediment characteristics (e.g., grain size, organic carbon content) have no influence on biological effects; (c) the approach assumes that chemicals are present in their biologically available form and does not consider sediment-chemical interactions; and (d) the selection of a suitable or generic reference site tends to be a difficult task.

The approach can be modified to include biological effects data which would made the method similar to the apparent effects threshold and the sediment quality triad approaches. Inclusion of effects data would provide a more technically and legally defensible method of criteria development.

Water Quality Criteria Approach

The water quality criteria approach compares the concentrations of individual contaminants present in sediment interstitial water with U.S. EPA water quality criteria (WQC). Existing WQC have been developed from a broad range of toxicological studies using a wide range of aquatic organisms. These criteria have been used in the regulatory context to specify contaminant levels that if not exceeded will protect 95% of aquatic life from adverse effects.

A major assumption of the approach is that water column organisms used to develop WQC have the same sensitivities as infaunal benthic organisms. Also, it is assumed that the major route of contaminant exposure is from the interstitial water and exposure from ingestion of contaminants on sediments is not significant.

The principal advantage of this approach is that it relies on existing toxicological databases used to develop WQC. The approach requires only the additional measurement of the contaminant concentration in the interstitial water.

The approach has several disadvantages: (a) WQC are available only for a limited number of contaminants; (b) the toxicological data used to develop WQC were from sediment-free bioassays so there is no consideration of the effect that soluble or particulate organic matter, present in interstitial water, may have on contaminant bioavailability; (c) the potential to increase contaminant body burden through ingestion or direct contact with sediment contaminants is not taken into account; and (d) suitable methods are still being developed for the isolation and measurement of contaminant concentrations in interstitial water.

ANNEX 2: WORKSHOP PARTICIPANTS

OECD Workshop on Effects Assessment of Chemicals in Sediment

13th-15th May 1991, Copenhagen, Denmark

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