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A Method for Ranking Contaminated Marine and Aquatic Sites on Canadian Federal Properties

Final Version

1. Background

The National Classification System for Contaminated Sites (CCME 1992) was developed to promote consistency in the assessment of sites under CCME's National Contaminated Sites Remediation Program. This system has been intermittently employed in other federal site assessment programs, most recently the 2000-01 assessment of Department of Fisheries and Oceans sites under the Federal Contaminated Site Assessment Initiative. However, the National Classification System for Contaminated Sites was not developed for and is not readily applicable to assessment of sites with a significant marine or aquatic component.

The ranking method proposed in the following text is intended to complement the NCS classification system. Its purpose is to provide an evaluative framework for ranking marine and aquatic sites within general categories of concern, thereby indicating the need for further action. Like the National Classification System for Contaminated Sites, it is not intended to provide a general or quantitative risk assessment; rather, it is to be used solely as a tool for screening-level identification and prioritization of contaminated marine and aquatic sites.

2. Technical Bases of the Proposed Ranking Method

Environmental conditions at marine and aquatic sites are best measured in the bed sediments, for reasons which have been succinctly described in the Introduction to the CCME (1998) Canadian Sediment Quality Guidelines for the Protection of Aquatic Life:

> As chemicals or substances are released into the environment through natural processes or human activities they may enter aquatic ecosystems and partition into the particulate phase. These particles may be deposited into the bed sediments where the contaminants may accumulate over time. Sediments may therefore act as long-term reservoirs of chemicals to the aquatic environment and to organisms living in or having direct contact with sediments. Because sediments comprise an important component of aquatic ecosystems, providing habitat for a wide range of benthic and epibenthic organisms, exposure to certain substances in sediments represents a potentially significant hazard to the health of the organisms. (CCME, 1998).

As well, when compared to natural or pre-industrial sediment characteristics, the quality of surface and near-surface sediments reflects the nature and magnitude of contaminant inputs related to upland uses and discharges from adjacent properties. Therefore, the assessment of sediment quality at marine and aquatic sites is fundamental to the proposed ranking method.

The proposed classification scheme relies upon the following scientific and technical sources:

- Canadian Sediment Quality Guidelines for the Protection of Aquatic Life adopted by the Canadian Council of Ministers of the Environment (CCME, 1998),
- Recent research into the overall predictive ability of sediment quality guidelines from several jurisdictions and, based upon that research, a site prioritization method which is currently promoted by the British Columbia Ministry of Environment.

2.1 CCME (1998) Sediment Quality Guidelines

Sediment quality guidelines are scientific tools that synthesize information regarding the relationships between the sediment concentrations of chemicals and any adverse biological effects resulting from exposure to these chemicals (CCME, 1998). The CCME (1998) Sediment Quality Guidelines have established limits for individual chemicals in both freshwater and marine (including estuarine) sediments. These guideline limits have been developed from available scientific information on the biological effects of sediment-associated chemicals, and are recommended to support and maintain aquatic life associated with bed sediments. The scientific foundation for these guidelines is provided in CCME (1995) and summarized in the Introduction to CCME's (1998) sediment guidelines.

For each parameter of interest, the CCME (1998) guidelines have identified two numerical limits: the lesser limit is termed the "Interim Sediment Quality Guideline" (ISQG) value and the greater limit is called the Probable Effect Level (PEL). Sediment chemical concentrations below ISQG values are not expected to be associated with any adverse biological effects, while concentrations above PEL values are expected to be frequently associated with adverse biological effects. Chemical concentrations between the ISQGs and PELs represent the range in which effects are occasionally observed.

In some instances, there has been a tendency by some regulators and the public to view the guideline values as absolute predictors of effects and as unchangeable, stand-alone clean-up levels. Regardless of this trend, it should be recognized that the SQGs were designed to be modified on a site-specific basis to derive higher or lower recommended values. Typical modifying factors include those controlling bioavailability (e.g., Total Organic Carbon [TOC], particle size) and/or various site characteristics (e.g., sensitive indigenous species or background concentrations). Further investigations or assessments may be required to provide supplemental information and to confirm the extent of predicted toxicity.

Thus, in the scientific and technical community, sediment quality guidelines generally (and in the Canadian context, the CCME [1998] Sediment Quality Guidelines) are recognized as flexible interpretive tools for a) evaluating the toxicological significance of sediment chemistry data and b) prioritizing management actions.

2.2 Recent Research Concerning the Predictability of Sediment Quality Guidelines

Marine Sediment Guidelines

Several national, provincial, and state jurisdictions have formulated and/or adopted sediment quality guidelines. Typically, these guidelines were derived from empirical analyses of data from numerous field and laboratory studies performed in many bays and estuaries of North America. Technically, the guidelines appeared valid, but until recently, the accuracy of sediment quality guidelines in predicting toxic and non-toxic conditions had not been evaluated.

Long and McDonald (1997) and Long *et al.* (1998) examined that issue, and found that lower threshold limits for contaminants included in the various sediment guidelines (e.g., the ISQG limits in the CCME [1998] sediment quality guidelines) were highly predictive of non-toxicity. Their analysis also showed that

- the percentage of toxic samples generally increased with increasing numbers of upper threshold values (e.g., the PEL limits in the CCME [1998] sediment quality guidelines) which were exceeded, and
- the incidence of toxicity also increased with increases in concentrations of mixtures of chemicals normalized to (divided by) upper threshold values in the sediment quality guidelines.

Put more simply, the probability of observing toxicity was shown to be a function of both the number of substances exceeding the guidelines as well as the degree to which they exceed the guidelines.

The number of substances in a sample exceeding the sediment guidelines is self-evident, but concept of "degree of exceedance" requires further explanation. In the Long and McDonald (1997) and Long *et al.* (1998) studies, the degree to which substances exceed guidelines is quantified by calculation of "mean PEL quotients". That calculation is a three-step process:

1. The concentration of each substance in each sediment sample is divided by its respective PEL. PEL-quotients are calculated only for those substances for which reliable PELs are available.
2. The sum of the PEL-quotients is calculated for each sediment sample by adding the PEL-quotients that were determined for the priority substances.
3. The summed PEL-quotients are then normalized to the number of PEL-quotients that are calculated for each sediment sample (i.e., calculate the mean PEL-quotient for each sample; Canfield *et al.* [1998] and Long *et al.* [1998]). This normalization step is conducted to provide comparable indices of contamination among samples for which different numbers of chemical substances were analyzed.

To illustrate, Appendix A shows the derivation of mean PEL quotients for two hypothetical sediment samples (Note: these examples use only a partial list of the parameters which would normally be analyzed in a sediment sample).

Finally, the Long and MacDonald (1997) and Long *et al.* (1998) studies established empirical relationships between the expected incidence of toxicity and the number and/or degree to which sediment quality guideline values were exceeded. From those empirical relationships, Long and MacDonald (1997) proposed four relative levels of priority (Highest, Medium-High, Medium-Low, and Lowest) based upon the number and/or degree of guideline value exceedances (Table 1 recreates the prioritization matrix presented in Long and MacDonald [1997]).

Table 1. Long and MacDonald (1997) Site Prioritization Scheme

Objective: To Identify and Prioritize Sites of Concern (Saltwater)

Highest Priority Sites Have:

- mean ERM quotients > 1.5 — 74%
- mean PEL quotients > 2.3 — 76%
- > 10 ERMs exceeded — 85%
- > 21 PELs exceeded — 85%

Medium-high Priority Sites Have:

- mean ERM quotients 0.51 - 1.5 — 46%
- mean PEL quotients 1.51- 2.3 — 50%
- 6 - 10 ERMs exceeded — 52%
- 6- 20 PELs exceeded — 53%

Medium-low Priority Sites Have:

- mean ERM quotients 0.11 to 0.5 — 30%
- mean PEL quotients 0.11 to 1.5 — 25%
- 1 – 5 ERMs exceeded — 32%
- 1 – 5 PELs exceeded — 24%

Lowest Priority Sites Have:

- mean ERM quotients < 0.1 — 11.6%
- mean PEL quotients < 0.1 — 10.4%
- no ERMs exceeded — 11%
- no TELs exceeded — 9%

Percentages indicate probability of toxicity in amphipod tests

Note: ERM and ERL are acronyms for Effects Range – Median and Effects Range – Low respectively. These terms are not relevant to the proposed classification scheme for Canadian federal marine and aquatic sites, but have been reproduced here to maintain integrity with the original.

Aquatic (Freshwater) Sediment Guidelines

The predictability of sediment quality guidelines for freshwater sediments has only recently been carried out. Ingersoll *et al.* (2000) evaluated the ability of consensus-based Probable Effect Concentrations (analogous to the PEL values discussed above) using a PEC quotient approach (again, analogous to the PEL-quotient approach of Long and MacDonald [1997] and Long *et al.* [1998]). As for marine sediments, they concluded that there was a similar increase in the incidence of toxicity with an increase in mean PEC quotient. However, the empirical relationship is not as clear-cut for the freshwater sediment and toxicity data: it appears that the relationship may be in part related to the length of toxicity tests carried out on some sediments.

3. Proposed Marine and Aquatic Site Ranking Method

3.1 Ranking Matrix

The essence of the proposed ranking method for Canadian federal Marine and aquatic sites is found in the British Columbia Ministry of Environment's recommended Sediment Evaluation Methodology. British Columbia's method advocates the Long and MacDonald (1997) PEL quotient approach, and uses sites' mean PEL quotients and/or number of PELs exceeded to determine relative site priorities (M. MacFarlane, memorandum, April 1998). Relative site priorities are determined by the matrix shown in Table 2:

Table 2. Ranking Matrix for Potential Marine and Aquatic Sites of Concern

Relative Priority Ranking	Determination of Relative Priority Ranking	NCS-type Hazard Ranking Score
Highest Priority Sites	Mean of (mean sample PEL quotients) > 2.3 **and/or** 21 or more PELs exceeded	**1**
Medium-high Priority Sites	Mean of (mean sample PEL quotients) 1.51 - 2.3 **and/or** 6-20 PELs exceeded	**2**
Medium-low Priority Sites	Mean of (mean sample PEL quotients) 0.11 - 1.5 **and/or** 1-5 PELs exceeded	**3**
Lowest Priority Sites	Mean of (mean sample PEL quotients) < 0.1 **and/or** No ISQGs exceeded	**N**

	Insufficient data to adequately determine site sediment quality	**I**

Note: PELs and ISQG s are acronyms for the CCME (1998) Probable Effect Levels and Interim Sediment Quality Guidelines respectively.

To determine an overall mean PEL quotient for a site, the mean PEL quotients for each sediment sample are added and the mean of that sum is calculated as follows:

$$\frac{\Sigma\ (\text{mean PEL quotient}_{\text{Sample 1}} + \text{mean PEL quotient}_{\text{Sample 2}}\ \ldots\ \text{etc.})}{\text{n of samples}} = \text{Overall mean PEL quotient for site}$$

The overall mean PEL quotient for the site and the total number of PEL exeedances are both compared to the Determination of Relative Priority Ranking criteria in the second column of Table 2. From that exercise, a relative priority for further action can be identified.

To allow relative comparisons between marine/aquatic and onshore sites, the four priority ranking groups in Table 2 can be assigned National Contaminated Site-type hazard ranking scores (from 1 to "N" or "I").

3.2 Hazard Ranking Score Categories

As with the NCS system, marine and aquatic sites will be categorized into one of five classes with an associated indication of the need for further action:

Class 1: Action Required

The available information indicates that action (e.g., mitigation or elimination of contaminant sources, risk management, or remediation) is needed to address existing sediment quality concerns. Typically, Class 1 sites will have widespread and high levels of sediment contamination, and measured or observed impacts on species composition/diversity and tissue burden will have been documented.

Class 2: Action Likely Required

The available information indicates there is a moderate to high potential for adverse biological effects and action (such as those described for Class 1 sites) will likely be necessary to address the sediment quality concerns. Class 2 sites will typically be those with localized areas of moderate to high contamination. Impacts to biological components are indicated, but may not have been assessed.

Class 3: Action May be Required

The available information indicates there is a low to moderate potential for adverse biological effects and action may be necessary to address the sediment quality concerns. Class 3 sites will typically be those with localized areas of low to moderate contamination. Additional sediment and biological assessments may be carried out to affirm the site classification and identify requirements for further action.

Class N: Action Not Likely Required

The available information indicates there is likely no significant environmental concerns related to sediment quality. There is no indicated need for action unless new information indicates a higher level of concern. In that case, a re-assessment of the site is warranted.

Class I: Insufficient Information

There is insufficient information to classify the site, and a comprehensive sediment assessment is required to address data gaps.

3.3 Closure

This marine and aquatic site ranking method is intended only as a framework for classifying sites within broad categories of concern. Like the National Classification System for Contaminated Sites, it is not intended to provide a general or quantitative risk assessment, but rather as a tool for screening-level identification and prioritization of contaminated marine and aquatic sites. It must be recognized by all interested parties that investigation and remediation of sediments is difficult and expensive. Therefore, any assessment, risk management or remediation activity must be pragmatic and consistent with existing regulatory requirements for marine and aquatic contaminated sites. Before any management decisions are made, there needs to be 1) a thorough understanding of the risks posed by sediment contaminants, and 2) a recognition that risk management or remediation requirements will vary between sites depending on the risks and associated urgency of action.

Other Applications of the PEL Quotient Approach

The PEL quotient approach is applicable in ways other than the determination of an overall site priority ranking. For example, a site's mean PEL quotient can be compared to the mean PEL quotient of background samples to assess the relative contribution of a) naturally-occuring and b) anthropogenic inputs to overall site contaminant levels.

As well, the mean PEL quotients for single or multiple groups of contaminants (e.g., PAH coumpounds, metals or mixtures of both) can be partialed out from the overall site mean PEL quotient to assess the realtive contribution of those contaminant groups to overall site contamination conditions.

REFERENCES

Canadian Council of Ministers of the Environment. 1992. National Classification System for Contaminated Sites.

Canadian Council of Ministers of the Environment. 1995. Protocol for the derivation of Canadian sediment quality guidelines for the protection of aquatic life. CCME EPC-98E. Prepared by Environment Canada, Guidelines Division, Technical Secretariat of the CCME Task Group on Water Quality Guidelines, Ottawa.

Canadian Council of Ministers of the Environment. 1998. Canadian Sediment Quality Guidelines for the Protection of Aquatic Life.

Canfield, T.J., E.L. Brunson, F.J. Dwyer, C.G. Ingersoll, N.E. Kemble. 1998. "Assessing sediments from the upper Mississippi river navigational pools using a benthic community invertebrate evaluations and sediment quality triad approach." *Archives of Environmental Contamination and Toxicology*, 35, 202-212.

Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kimble, R.A. Lindskoog, C. Severn, and D.E. Smorong. 2000. "Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines." United States Geological Survey (USGS) final report for the U.S. Environmental Protection Agency (USEPA) Great Lakes National Program Office (GLNPO). EPA 905/R-00/007, June 2000.

Long, E.R. and D.D. MacDonald. 1997. "Effects Range Low and Median, Threshold and Probable Effects Levels". In: *Use of Sediment Quality Guidelines in the Assessment and Management of Contaminated Sediments".* Society of Environmental Toxicology and Chemistry (SETAC), 1997 short course.

Long, E.R., L.J. Field and D.D. MacDonald. 1998. "Predicting Toxicity in Marine Sediments with Numerical Sediment Quality Guidelines". *Environmental Toxicology and Chemistry*, 17, No. 4, pp. 714-727.

Appendix A. Derivation of Mean PEL Quotients for Two Hypothetical Sediment Samples

Sample #1

Sediment Parameter	Measured Concentration	$CCME_{98}$ Guideline Limit (PEL)	**Mean PEL Quotient Derivation Steps** Step 1: Derive PEL quotients	Step 2: Sum the PEL quotients derived in Step 1	Step 3: Derive mean PEL quotient for the sample
Cadmium	1.4 mg/kg	4.2 mg/kg	(Measured contaminant concentration ÷ PEL) 1.4 ÷ 4.2 = 0.33	0.33 + 3.01 + 2.18 + 1.87 + 0.30 + 0.05 + 0.10 + 0.00 + 0.32 = 8.16	(Sum of PEL quotients ÷ the number of PEL quotients calculated in Step 1) 8.16 ÷ 9 = 0.91 Sample #1 mean PEL quotient is 0.91
Copper	325 mg/kg	108 mg/kg	325 ÷ 108 = 3.01		
Lead	244 mg/kg	112 mg/kg	2.18		
Zinc	508 mg/kg	271 mg/kg	1.87		
Benzo(a)pyrene	232 µg/kg	763 µg/kg	0.30		
Dieldrin	0.2 µg/kg	4.3 µg/kg	0.05		
Fluoranthene	145 µg/kg	1494 µg/kg	0.10		
PCBs, total	0.08 µg/kg	189 µg/kg	0.00		
Pyrene	454 µg/kg	1398 µg/kg	0.32		

Sample #2

Sediment Parameter	Measured Concentration	$CCME_{98}$ Guideline Limit (PEL)	**Mean PEL Quotient Derivation Steps** Step 1: Derive PEL quotients	Step 2: Sum the PEL quotients derived in Step 1	Step 3: Derive mean PEL quotient for the sample
Cadmium	0.4 mg/kg	4.2 mg/kg	(Measured contaminant concentration ÷ PEL) 0.4 ÷ 4.2 = 0.10	0.10 + 13.94 + 5.45 + 2.77 + 1.98 + 0.05 + 1.57 + 0.00 + 1.21 = 27.07	(Sum of PEL quotients ÷ the number of PEL quotients calculated in Step 1) 27.07 ÷ 9 = 3.01 Sample #2 mean PEL quotient is 3.01
Copper	1505 mg/kg	108 mg/kg	1505 ÷ 108 =13.94		
Lead	610 mg/kg	112 mg/kg	5.45		
Zinc	750 mg/kg	271 mg/kg	2.77		
Benzo(a)pyrene	1508 µg/kg	763 µg/kg	1.98		
Dieldrin	0.2 µg/kg	4.3 µg/kg	0.05		
Fluoranthene	2350 µg/kg	1494 µg/kg	1.57		
PCBs, total	0.08 µg/kg	189 µg/kg	0.00		
Pyrene	1690 µg/kg	1398 µg/kg	1.21		

Two types of information should be noted in the above examples.

First, the number of substances exceeding the CCME (1998) sediment guideline PELs is readily evident in both examples. In Sample #1, three substances (copper, lead and zinc) exceeded the PELs but in Sample #2, six substances (copper, lead, zinc, benzo(a)pyrene, fluoranthene and pyrene) exceeded PELs. Any parameter-specific PEL quotient value >1.00 reflects an exceedance of the PEL for that parameter.

Second, the degree to which substances exceeded the CCME (1998) sediment guideline PELs, can now be seen. The "mean PEL quotient" values calculated in Step 3 of both examples are relative (although not necessarily linear) measures of the degree of exceedance, and from the examples above, it could be expected that Sample #2 will exhibit greater toxicity (and therefore be of greater environmental concern) than Sample #1.