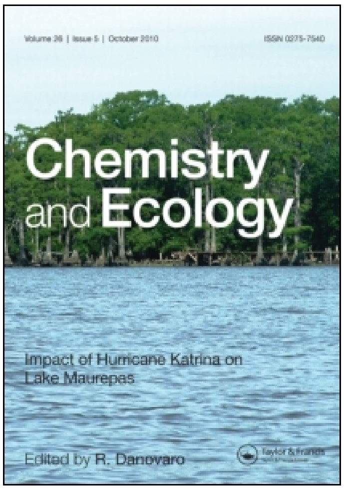

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A GEOCHEMICAL AND BIOLOGICAL BASIS FOR MARINE SEDIMENT QUALITY GUIDELINES

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This document describes a basis for the establishment of marine sediment quality guidelines for regulatory applications. It outlines a geochemical basis for identifying potential anomalies in the presence of inorganic contaminants in marine sediments and a biological or ecotoxicological basis for determining concentrations unlikely to result in adverse biological effects. These approaches are discussed in an exploratory fashion. It is intended that both approaches could be combined in a manner that takes account of sedimentary nature and composition as a conceptual and practical approach to the establishment of guidelines for regulatory applications associated with the protection of the marine environment.

Keywords: Sediment quality; geochemistry; biology; Canada

INTRODUCTION

The Canadian Federal Government needs sediment quality guidelines for various applications, including the characterisation and control of wastes intended for disposal at sea. This discussion focuses on the two main elements of procedure for the derivation of Canadian guidelines for chemical contaminants in marine sediments. It outlines first, a

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geochemical approach for discriminating between anthropogenically augmented sediments and natural sediments from the perspective of contamination and then secondly a biological effects approach to the evaluation of sediment condition. The requirements and considerations for using these approaches in a regulatory context, *i.e.*, for establishing marine sediment guidelines, are then examined.

GEOCHEMICAL BASIS FOR MARINE SEDIMENT GUIDELINES

Scope and Purpose

The purpose of the geochemical approach described below is to provide a mechanism for determining excessive (*i.e.*, above natural variance) levels of chemical contaminants in marine sediments on a generic basis. With various geochemical normalisation techniques, it is possible to identify chemical concentrations that are outliers, probably reflecting anthropogenic influence, in defined areas such as the Gulf of St. Lawrence, the St. Lawrence Estuary, the Bay of Fundy. It is more difficult, and undoubtedly less precise, to do this on a generic basis that enables guidelines to be established for larger geographical areas such as the entire coastal/shelf area of Canada.

Background

All chemicals of natural origin can occur in the marine environment, including in marine sediments. Marine sediments comprise particulate material of diverse provenance, mineralogy and grain-size in a matrix of interstitial water. The distribution of natural chemicals among different minerals reflects both origenic (unchanged from original composition) and authigenic (derived composition *in situ*) factors. Nevertheless, with certain exceptions (discussed below), these are characteristics of the chemical distribution that relate to grain-size. It is necessary to define two components of natural chemical abundance in marine sediments – detrital and non-detrital. The detrital component represents chemical constituents bound within mineral particles. The non-detrital component represents chemical constituents that are associated with sediment particles in a weakly-bound form that makes them more exchangeable with other phases such as water.

Fine-grained sediments, having high surface-to-volume ratio, are higher in the non-detrital phase. The coarser the sediment particles become, the more their composition reflects the weathered, mineral composition. Typically, in the size range of muds (*i.e.*, particle sizes less than 63 μm) the distribution of natural chemical composition with grain-size is roughly linear reflecting the dominance of metal-bearing alumino-silicates. For sand-sized particles between 63 μm and 2 mm, the distributions of natural chemicals are roughly constant reflecting the dominance of metal-poor detrital components such as quartz and feldspars. Normally, in marine sediment analyses, particles of size > 2 mm are ignored and excluded from the sample prior to analysis. In any event, the contribution to overall concentration of naturally-occurring inorganic chemical constituents by the >2 mm fraction is usually negligible. A specific exception to this description of chemical distribution, or partitioning in sediments, arises in the case of the presence of significant amounts of material of glacial origin. Glacial erosion, unlike the more common combinations of chemical and physical weathering processes, produces particles of similar composition over a wide range of particle size that can enter the marine environment in an essentially chemically-unmodified form relative to the source rocks. This phenomenon will clearly have to be considered in any development of sediment guidelines for application within Canadian jurisdiction. Fortunately, there is a way of "normalising" natural chemical concentrations that compensates for grain-size variations and takes account of glacially-weathered materials. This is through the use of lithium (Li) as a granulometric normalizer (Loring 1990, 1991).

Geochemical Approach

Let us first depict the distribution of a natural chemical with grain size. Figure 1 below depicts a somewhat idealised distribution in which it is assumed that the coarser material, such as silicates (sand), has a relatively invariant composition with increasing grain-size.

The slopes of the lines in the > silt-sized and < sand-sized ranges will vary among locations and sediment types. Further, the relation-

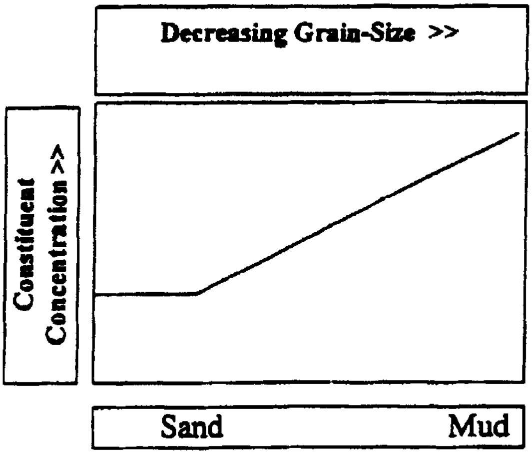


FIGURE 1 Idealized grain-size distribution of a naturally-occurring chemical.

ships in the two grain-size regimes may not be linear when variations in mineralogy occur. The use of a general relationship, such as that depicted in Figure 1, leaving aside these latter complications, would require some representation of the grain-size composition of sediments in an area to determine the range of uninfluenced concentrations of natural constituents. Fortunately, there is an alternative approach that solves these difficulties through the use of a normalising element. The ideal choice of such an element is lithium which acts as a surrogate for grain-size and also takes account of admixtures of glacially-eroded material (Loring, 1990, 1991).

The relationship between individual metallic constituents of sediments and lithium in a homogeneous sediment is a linear function of the form:

$$C_{\mathrm{mnat}} = AC_{\mathrm{Li}} + B \qquad (1)$$

where A and B are constants, C_{mnat} is the naturally-occurring concentration of constituent m, and C_{Li} is the lithium concentration, both determined by total digestion procedures. This is illustrated by the relationships with lithium for a range of metals in marine sediments of various areas of the Canadian East Coast and shelf (Tab. I).

TABLE I Relationship between trace metals and lithium in marine sediments of eastern Canada

Area	*Cu*			*Pb*			*Zn*		
	A	*B*	*B*+2*SD*	*A*	*B*	*B*+2*SD*	*A*	*B*	*B*+2*SD*
St. Lawrence Estuary,	0.66	0.99	7	0.46	13.8	25	2.5	24.4	40
Upper Gulf of St. Lawrence,	0.80	0.58	7	0.32	12.9	23	2.1	26.4	42
Open Gulf of St. Lawrence	0.68	0.74	6	0.27	10.6	18	2.4	1.1	20
Bay of Chaleur	0.65	0.62	5	0.20	14.1	20	2.2	−2.8	5
Baffin Bay	0.49	3.16	10				1	17.0	35
Bay of Fundy	0.23	7.14	11	0.32	11.0	20	1.3	12.4	22
Overall Sites	0.80	12.0		0.50	25.0		2.6	45.0	

Table I designates the values of the constants A and B of the regression equations $C_m = AC_{\mathrm{Li}} + B$ for various areas of Eastern Canada. It also provides an indication of the variance of the intercept by presenting this as 2 standard deviations ($B + 2SD$) for individual regressions and the constants of an equation for an overall metal-lithium relationship to allow for variance of and among the individual regression based on 3 standard deviations. All numerical values are respective to metal and lithium concentrations expressed in units of $\mathrm{mg\,kg^{-1}}$ dry weight.

A plot of the Zn/Li relationship for four of these areas is shown in Figure 2 below.

Assuming that the variance envelopes are not too large, this makes it possible to define a range of ambient chemical concentrations, in relation to the normalising element lithium, for a wide variety of coastal/shelf sediments. The use of contemporary data on the prevailing distributions of natural chemicals in fairly large shelf areas (such as those in Tab. I) to define natural variability infers an assumption that the degree of augmentation of such sediments by man-made activities is negligible. Generally, for the areas for which data is given in Table I, this appears to be a reasonable assumption. A further check can be provided by comparing the concentrations of individual elements in relation to lithium with those in texturally-equivalent sediments compiled from the scientific literature. Accordingly the relationships between sedimentary constituents and lithium provide a

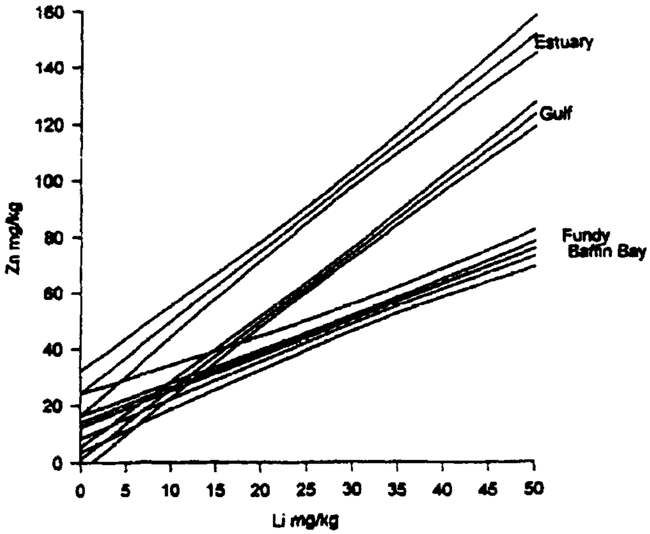


FIGURE 2 Relationships between zinc and lithium in marine sediments of the Estuary and Gulf of St. Lawrence, the Bay of Fundy and Baffin Bay (assuming 3 *SD* values).

basis for identifying outliers in the distribution of natural chemicals that would indicate independent influences, such as additional contributions from man-made activities or unusual natural abundances of constituents. Such augmentation would appear as a further term in Equation (1), above, as follows:

$$C_{\mathrm{mtot}} = C_{\mathrm{mnat}} + C_{\mathrm{maug}} = AC_{\mathrm{Li}} + B + C_{\mathrm{maug}} \qquad (2)$$

where C_{mtot} is the total concentration of constituent m and C_{maug} is the additional concentration constituent m resulting from man-made activity. We have, therefore, created a basis for defining guidelines that can be used to determine when sediment concentrations of natural chemicals are essentially within the range of natural variations and where they exceed that range due to other factors.

It might be necessary, in the cases of elements such as mercury and cadmium that are associated to a significant degree with organic matter in sediments, to include an additional term in Equation (2) of the form DC_{org}. This, however, should only be necessary for sediments in marine salts rich in organic matter.

Application to Guideline Derivation

First, application of such a system in practice will require the following prerequisites:

1. all measurements are made on the basis of total digestion (*i.e.*, for inorganic constituents digesting acid must include hydrofluoric acid) of the < 2 mm fraction of marine sediments;
2. the lithium concentration in sediment samples must be determined simultaneously by a similar total digestion method;
3. measurement of total organic carbon (TOC).

It should be noted that total digestion (including hydrofluoric acid) will also be required for quality control/quality assurance purposes through the analysis of Certified Reference Materials (CRMs) which are only certified for total digestion methods.

Secondly, it will require the selection of criteria for bounding the natural variation in concentrations in marine sediments. As in Figure 2, there are natural variations in constituent *versus* grain-size relationships as reflected by the differing slopes and intercepts of the constituent *versus* lithium relationships for the various areas. Accordingly, it would be simplest and most specific to define guidelines for specific coastal/shelf areas, based on the corresponding variance of the constituent-lithium relationship within that defined area. However, the guidelines for application at national rather than regional levels are required and it is necessary to consider the overall variance in the constituent-lithium relationship among all coastal areas of Canada. Fortunately, for east coast areas, data exist on the concentrations of a wide range of elements and lithium which can be done if similar data can be found for Pacific, and Arctic coastal/shelf sediments. Clearly, the variance envelope for multiple areas in combination will be considerably larger than the variances within individual coastal areas. This will be the price of setting guidelines for a geographically-broad application, such as at a Canadian national level.

It is possible to develop guidelines set at various levels of confidence regarding the inclusion/exclusion of normal distributions of natural sediment constituents. A guideline level set at 3 standard deviations (*i.e.*, as in Fig. 2) would embody 95% of the natural variance within the definition of "normal". This would mean that, on average, only

1 out of 20 samples having natural concentrations of a constituent would be identified as an outlier from the range and suspected of being augmented in concentration by non-natural sources/processes (*i.e.*, correspond to a "false positive"). The actual nature and cause of any augmentation will, of course, require further evaluation. The guidelines are merely established to enable the detection of potential outliers. To a large extent, the particular choice of criterion to define the range of natural variability will be likely to differ among natural inorganic constituents with the proximity of the upper concentration boundary for natural variability to the threshold where deleterious biological effects occur, being of primary consideration. This is why it is so important to select the criterion for each element in the context of biological effects which will constitute the other component of a procedure for establishing guidelines.

The procedure for establishing geochemical guidelines for elements would be as follows:

1. determine the range of relationships between the concentration of each constituent m and lithium for a wide variety of marine sedimentary environments in the Canadian coastal zone and shelves;
2. establish an overall relationship bounded by uncertainty bands (say, 2 *SD*, 3 *SD* and 4 *SD* envelopes of variance);
3. determine which of the ranges of uncertainty provides assurance that levels at the upper bound are below biological effects criteria for particular sediment mixtures, using lithium concentration values as surrogates for sediment grain-size;
4. select an appropriate uncertainty envelope and establish the linear relationship $C_m = AC_{\mathrm{Li}} + B$ (or $C_m = AC_{\mathrm{Li}} + B + DC_{\mathrm{org}}$ for significantly organically-bound constituents in organic carbon-rich sediments) representing the highest range of uncertainty that is acceptable from a biological effects perspective;
5. use this linear relationship to define the guideline for constituent $\boldsymbol{m}$; such guidelines can be established for a range of different lithium concentrations (typically in the range 0 – 50 mg kg^{-1} lithium) in sediments or as a formula or define a guideline value for constituent m pertaining to a given grain-size composition;
6. evaluate the results of sediment analyses of $\boldsymbol{m}$ and lithium against the guideline to identify instances in which the concentration of $\boldsymbol{m}$ is

augmented relative to its natural abundance in marine coastal/shelf sediments.

Geochemical Basis for Organic Constituents of Sediments

It is possible to develop geochemical screening mechanisms to establish the probable ambient concentrations of natural organic constituents of sediments such as hydrocarbons through examination of both the amounts and the composition of organic carbon in sediments. It may even be possible to define acceptable background levels for classes of natural organic constituents, such as low molecular weight and high molecular weight polycyclic aromatic hydrocarbons (PAHs), aromatic and aliphatic hydrocarbons in marine sediments, as not yet attempted.

In contrast, it is much more difficult and fortunately, probably unnecessary, to develop a geochemical basis for the presence of ubiquitously-distributed synthetic organic substances. In the case of such substances, it is probably more appropriate to base the setting of guideline entirely on the basis of biological effects.

BIOLOGICAL EFFECTS-BASED GUIDELINES

Having discussed the geochemical basis for establishing background concentrations of naturally-occurring elements that would serve as a basis for deriving sediment quality guidelines, it is necessary to examine the biological effects based approach for establishing sediment quality guidelines. Environment Canada is incorporating biological responses into its marine Sediment Quality Guidelines. The resulting chemical concentrations will be used as screening levels, below which no unacceptable environmental effects are expected, but above these, "further evaluation" would be recommended. Biological responses, in the form of specific toxicity tests or bioassays, could then be used where "further evaluation" is considered necessary.

Background

The development of the biological basis for sediment quality guidelines is not as clear-cut as the geochemical procedure. The geochemical guidelines look at defining the levels of contaminants in marine sediments in order to distinguish between natural and augmented concentrations of chemical constituents. In contrast, the biological-effects based guidelines define levels that should not cause adverse effects on marine life inhabiting the sedimentary environment. Environment Canada and the Canadian Council of Ministers of the Environment (CCME) decided in 1992 (MacDonald *et al.*, 1992) to develop a protocol for the derivation of sediment quality guidelines. Several reviews of possible "effects-based" approaches have been conducted by Environment Canada and others (Beak Consultants, 1987, 1998; Chapman, 1989; Sediment Criteria Subcommittee, 1989; Adams *et al.*, 1992; Persaud *et al.*, 1992; Lamberson and Swartz, 1992; Long and Morgan, 1990). The U.S. Environmental Protection Agency (USEPA) recognises the value of a variety of different assessment tools but is deriving a process for establishing sediment quality criteria based largely on equilibrium partitioning (Ankley *et al.*, 1996a). This holds that the bioavailable fraction of contaminants in sediments is correlated with their interstitial water concentrations (DiToro *et al.*, 1991) and assumes that toxicity is caused by exposure to water only. This neglects the reality of the uptake of metals by biota being both species and phase dependent.

Two approaches were favoured by Environment Canada and the CCME to develop national effects-based sediment quality guidelines. One was the approach taken by Long and Morgan (1990) as part of the U.S. National Status and Trends Program (NSTP) of the National Oceanic and Atmospheric Administration (NOAA). The other involves spiking of sediments with individual contaminants to gauge toxicity of individual chemicals to marine biota at various concentrations. The spiked-sediment toxicity approach is a complimentary approach for which the methods are not yet fully developed.

The NSTP approach involves the compilation of data for many chemicals that are generated from models (equilibrium partitioning theory), spiked sediment toxicity test data, and field studies (co-occurrence data consisting of matching chemistry and biological effects data) (Long and Morgan, 1990; Long, 1992; MacDonald, 1993; Long *et al.*, 1995). This information is used to establish associations between concentrations of chemicals in sediments and adverse biological effects (CCME, 1995).

In order to adapt the NSTP approach to the Canadian situation, Environment Canada re-evaluated the data-entries, with relevant Canadian data, and compiled a table on a chemical-by-chemical basis, sorted according to ascending chemical concentration, into the Biological Effects Database for Sediments (BEDS). The BEDS database comprises the measured chemical concentration, location, sediment type, total organic carbon concentration analysis type, test duration, end point measured and life stage tested. It should be noted that as data for BEDS is obtained primarily from previously published sources, with a range of purposes, not all data points (*e.g.*, sediment type) are available for each compilation. Data are sorted into effects and no-effects results (CCME, 1995). Guideline values are selected from the database as explained below.

The Canadian Protocol describes how to derive the guidelines. It was developed under the auspices of Canadian Council of Ministers of the Environment (CCME) Task Group on Water Quality Guidelines and is similar in philosophy to the Canadian Water Quality Guidelines (CCREM, 1987). The guidelines are numerical limits or narrative statements recommended to support and maintain aquatic life associated with bed sediments (CCME, 1995).

Guideline Development and Information Criteria

The development of effects-based guidelines involves data pertaining of biological "responses" and absence of responses (*i.e.*, "no-response" or "no-effect" conditions) and calculating a Probable Effects Level (PEL) and a Threshold Effects Level (TEL) (CCME, 1995).

The entire data set (all concentrations associated with effects and those not associated with effects) are used in the calculation in order to ensure that the guidelines are based on data that represent a broad range of sediment types, chemical concentrations and biological responses. Rather than adopting "outliers" or extreme values as the TEL and PEL values, a mathematical formula is used to establish consistently the concentrations (TELs) below which adverse effects will occur only rarely and concentrations (PELs) above which adverse effects will occur frequently. Such an approach ensures that all relevant information is used in the calculation while limiting the influence of outliers on the results (Environment Canada, 1995). Figure 3 illustrates how the data used in the calculation of the TEL and PEL levels for cadmium were distributed (Environment Canada, 1996).

The TEL is normally recommended as an interim sediment quality guideline. The TEL is also the level which the Disposal at Sea Programme is considering applying as a screening level. It should be noted that, as shown in Figure 3 for cadmium, the entries in the diagram are from all sediment types. Because BEDS data represent a variety of sediment types, the guidelines are expected to be applicable across a range of conditions; one would not expect a similar magnitude of biological response to identical concentrations of a contaminant in sands and in sediments comprising predominantly fine silts and clays. It would be desirable, therefore, to normalise to a characteristic sediment type. This could be done in BEDS, if and when enough relevant information became available. Alternatively, site-specific adjustment, or normalisation, could be done.

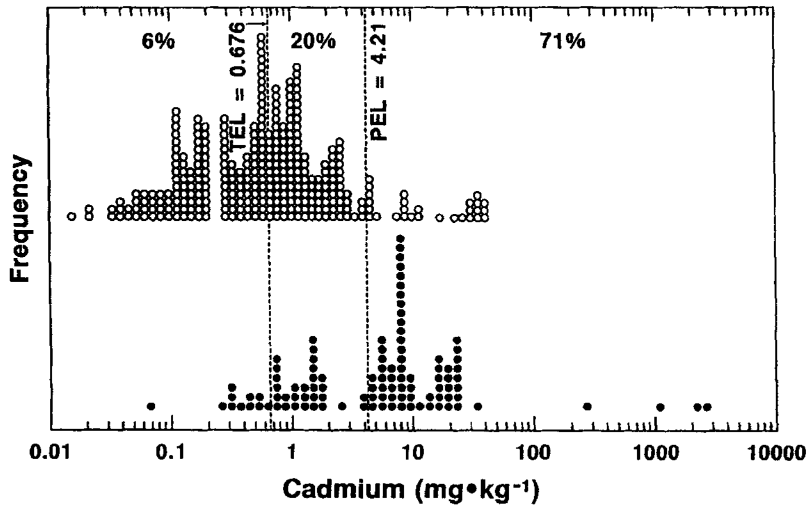


FIGURE 3 Distribution of cadmium concentrations in marine and estuarine sediments that are associated with adverse biological effects (•) and no adverse biological effects (o). Percentages indicate proportions of concentrations associated with effects in ranges below the Threshold Effect Level (TEL), between the TEL and the Probable Effect Level (PEL), and above the PEL.

Minimum Data Requirements

Table II defines the minimum data requirements for setting TEL and PEL values using the BEDS database.

If the minimum data requirements set forth above are met for the modified NSTP approach, a TEL can be selected that corresponds to the geometric mean of the lower 15th percentile of the effects data and the 50th percentile of the no-effects data. As the BEDS database is dominated by no-effects data, it allows establishment of a level below which adverse biological effects are never, or almost never, observed (CCME, 1995).

SEDIMENT QUALITY GUIDELINES DEVELOPED

To date, interim sediment quality guidelines have been recommended by the CCME for cadmium and mercury. A number of other interim guidelines for metals and organics are also nearing completion; the metals include arsenic, chromium, copper, lead and zinc. The organics include dioxins/furans, total PCBs, PAHs and toxaphene. Detailed chemical-specific supporting documents for several of these substances are in preparation (Environment Canada, 1997).

GUIDELINES FOR OCEAN DISPOSAL

The development of no-effects-based guidelines or TELs is still in its early stages and a number of outstanding issues need to be examined

TABLE II Minimum toxicological data set requirements for interim sediment quality guidelines

1. The effects data set for the chemical must contain at least twenty (20) entries in the guideline derivation table prepared from BEDS (NSTP).
2. The no-effects data set for the chemical must contain at least twenty (20) entries in the guideline derivation table (NSTP).
3. At least four studies are required on two or more sediment resident invertebrate species that occur in North American Waters, including a benthic amphipod species (SSTP).
4. At least two of these studies must be partial or full life-cycle tests that consider ecologically relevant end points (*e.g.*, growth, reproduction, developmental effects) (SSTP).

before the Disposal at Sea Programme can adopt them as screening levels. Some of these complicating features are discussed below. They are not in order of priority nor are they explored fully; they are presented to illustrate some of the impediments to further development and applied use of sediment quality guidelines.

Definition of Sediment Grain-size Composition

One potential problem arising from the application of the Canadian Protocol can be the inadequate specification of grain-size composition of the sediments to which apply the data in the BEDS database. BEDS does have provisions for specifying the nature of the sediments, but so far there has been a lack of information from studies that report sediment chemistry and corresponding biological effects. The absence of this information is significant, as a measure of grain-size distribution is the dominant feature that needs to be considered in "normalising" biological responses to sediment type, since grain size often determines the partitioning of a chemical and accordingly, its bioavailability.

It is important to have a method of defining the sediment grain-size composition so that users can select data that apply to sediments of a specific type. This can be any specific mixture of grain-size comprising predominantly mud (*i.e.*, silts and clays) but, this does not resolve the problem of "normalising" for different mixtures of fine-grained material. However, as demonstrated in the geochemical discussion earlier in this paper, there exists a satisfactory proxy for grain-size mixture in the form of lithium.

This would mean that BEDS-type data compilations that are to be used for setting biological effects-based guidelines should seek to encourage the collection and inclusion of more detailed specification of the sediments. TOC concentrations are already included in the database specifications, which allows an independent evaluation of the amount of organic matter in the sediments and provides additional indications of the extent of fine-grained material in the sediments. Additional data, such as grain-size composition and lithium concentration (or other normalising variables), would assist in refining the guidelines. The inclusion of lithium comes at very minimal expense – merely the cost of another analytical determination on the sediment digest. Further, the grain-size representation can be simplified to reduce additional expense by restricting the required information to grain-size proportions that can be determined by sieving only. The basis suggested is as follows: $< 2\,mm > 63\,\mu m$; $< 63\,\mu m > 37\,\mu m$; $< 37\,\mu m > 16\,\mu m$; and $< 16\,\mu m$. These fractions can be determined by simple physical sieving (although separation at the 16 μm level is more efficiently achieved using gravity settling) while providing a sufficient basis for characterising the sediment mixture to which the ecotoxicological results apply. The main difficulty remains that of reliance of BEDS on currently published data from a multitude of sources. Whereas the Protocol could specify these requirements for accepting a given data set, it has no ability to require that this data be generated in the first place.

Background Levels

The effects-based approach of the Canadian Protocol allows for guideline adjustment in consideration of geographical and other factors, such as background concentrations, to create site-specific objectives. General guidance on this topic is available (Gaudet *et al.*, 1995; CCME, 1995; Smith *et al.*, 1996). For the purposes of the Disposal at Sea Programme, the relationship between effects-based guidelines and the geochemical guidelines needs clarification. With the use of data from all over North America, a limited number of commonly-used species and tests making up most of the current database, and a "weight-of-evidence" approach to setting guidelines, there are cases where the effects-based sediment quality guideline may produce a lower value than the geochemical approach for setting background concentrations at specific sites. An evaluation of the Disposal At Sea database, which contains chemical data from Canadian permit applications, confirms that some ambient levels of metals from sites known to be remote from sources of marine contamination are indeed higher than proposed interim effects-based guidelines. Background levels show a fairly wide range. Cadmium, for example, has been assigned a TEL of $0.7\,mg\,kg^{-1}$ and a PEL of $4.2\,mg\,kg^{-1}$ (Environment Canada, 1996). Table III illustrates background concentrations of cadmium in sediments in Canadian jurisdictions.

TABLE III Background concentrations of cadmium (mg kg^{-1} dry weight) in Canadian marine and estuarine sediments. Values represent sediment from greater than 2 cm depth core samples (NA = not available)

Location	*mean* (*mg kg^{-1} ± S.D.*)	*Range* (*mg kg^{-1}*)	*Sample size*	*Reference*
Atlantic				
St. Lawrence Estuary	0.16 ± 0.03	0.09 – 0.22	32	Gobeil, 1991
Gulf of St. Lawrence	0.30 ± 0.06	0.22 – 0.42	24	Gobeil, 1991
Pacific				
North B. C. coastline	0.72 ± 0.25	0.09 – 4.7	210	Brothers, 1990
South B. C. coastline	1.2 ± 0.39	0.10 – 6.14	26	Brothers, 1990
Alice/Hastings Arm	2.55[1] ± 3.12	0.60 – 17.6	83	Goyette and Christie, 1982
Loughborough Inlet	0.43 ± 0.16	0.22 – 0.63	15	Goyette, 1990
Belize/Seymour Inlets	0.67 ± 0.12	0.48 – 0.82	9	Goyette, 1990
Ucluelet Inlet, B. C. (Vancouver Island)	4.24[2] ± 1.53	1.4 – 8.2	37	Pederson *et al.*, 1989
Strait of Georgia, Ballenas Basin	0.22 ± 0.05	NA	50	Macdonald *et al.*, 1991
Arctic				
Beaufort Sea	0.31 ± 0.13	0.08 – 1.09	97	Gobeil *et al.*, 1991
Beaufort Sea	1.04 ± 4.7	0.02 – 6.2	455	Thomas *et al.*, 1982
Beaufort Sea	0.20 ± 0.05	0.12 – 0.28	13	Mudroch, 1987
Crozier Strait (Arctic Archipelago)	0.30 ± 0.10	0.14 – 0.51	48	Thomas and Erickson, 1983

[1] Trace metal enrichment in sediment cores possibly attributable to local mining activities.

[2] Cadmium enrichment due to diffusion of dissolved trace metals (Pederson *et al.*, 1989).

Source: Environment Canada, 1996.

Depending on circumstances it may be desirable to define the criteria for establishing site-specific background levels in addition to national background levels. It is anticipated that the geochemical background levels generally would have the effect of raising the no-effects based guideline levels (TELs) at a particular site, rather than lowering them.

Quality Assurance

The quality assurance of data entries in BEDS-type databases is a critical consideration. From a geochemical perspective, this is most acute in respect to the chemical measurements that are used to determine the levels to which biological responses are correlated. As already stated, any procedures used to measure inorganic constituents in sediments should yield data that can intrinsically be quality assured through the use of Certified Reference Materials (CRMs). This, in turn, means that the methods would have to employ total sediment digestions using hydrofluoric acid because there exist no CRMs applicable to weak digestion methods. Unfortunately, these procedures are used rarely in ecotoxicological studies, which focus on biologically relevant sediment phases. Researchers are more likely to report "near-total" concentrations such as those derived following an aqua regia digestion. Thus, essentially all data entries containing inorganic chemical measurements, with the exception of mercury, made on the basis of weak digestions, would have to be rejected and not used for setting guidelines if the geochemical and biological approaches were to be combined. In a similar fashion, determinations of organic constituents would have to be made using methods that provide a basis for standardisation using appropriately certified CRMs. In cases where quality assurance of organic chemical measurements cannot be adequately demonstrated, entries would also be rejected for setting guidelines. There is a need for the rigorous definition of procedures for the entire range of chemicals of interest. In the case of inorganic constituents of sediments, there already exists an internationally-recognised methods manual that incorporates specification for quality assurance procedures (UNEP, 1995). In this case, where the method specifications would result in the rejection of most of the otherwise useful data, it may be necessary to explore means of generating a new database, where these parameters can be controlled. In a BEDs type database, there is no control over what data is generated, or how, but only regarding the data that BEDs, or other databases, choose to accept.

Site-Specific Biological Effects Testing

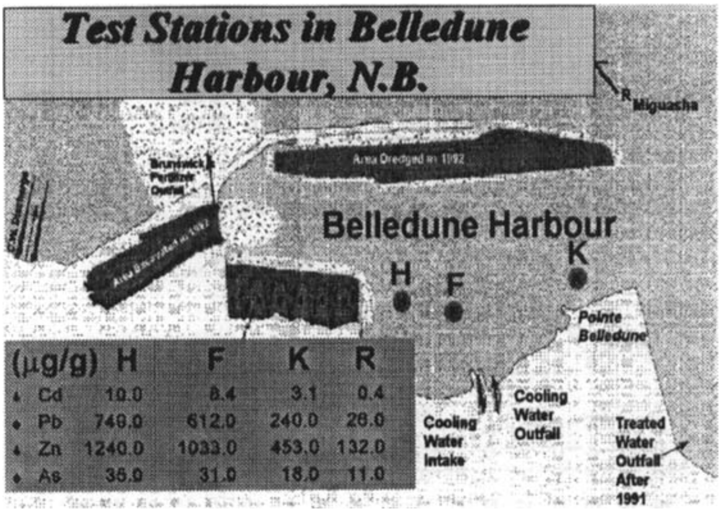
Sediment quality values for disposal at sea were originally set, in 1975 as rejection levels, and were not related to potential effects. Clients who wished to apply for a permit to dispose of material at sea were able to judge in advance if their permit was going to avoid rejection on the grounds of chemical composition by conducting preliminary chemical analyses. The introduction of screening levels (effects-based guidelines) has provided clients with the option, when a specific chemical level is exceeded, of performing bioassays to determine that sediment is unlikely to give rise to adverse biological effects. While this is a positive step, the present cost of carrying out the newly-developed battery of bioassays is high. The issue is further complicated by the concept of bioavailability that, in many cases, cannot be unambiguously linked to dry weight whole sediment concentrations. Recent research has indicated that dry weight metal concentrations that elicit toxicity can vary by one or more orders of magnitude among different sediments, even among similar sediment types (DiToro *et al.*, 1990).

The United States Environmental Protection Agency (USEPA) and many collaborators from academic institutions are in the process of developing sediment quality criteria based on the fraction of the contaminants that are thought to be bioavailable. For non-polar organic compounds, this is done using an equilibrium partitioning (EQ) model (DiToro *et al.*, 1991). For cationic metals, such as cadmium, copper, nickel, lead and zinc, the EQ concept has been expanded to include acid-volatile sulphide (AVS) binding of metals in interstitial water. Many papers have now demonstrated that when molar AVS concentrations exceed the summed molar concentrations of metals (SEM), simultaneously extracted with the AVS, metal concentrations in the interstitial water are low and toxicity is not observed (Ankley *et al.*, 1996a). Complementary approaches are also being considered based on the measurements of the composition of interstitial water, AVS, organic carbon and constituent partitioning (Ankley, 1996).

The Journal of Environmental Toxicological and Chemistry (1996) recently devoted an issue to studies relating to AVS. Although, in general, papers supported the theory, some studies of bioaccumulation found linear bioaccumulation of metals with increasing sediment metal concentrations irrespective of the metal/AVS ratio (Ankley, 1996). Other researchers have also failed, at times, to find a relationship between AVS levels and biological responses (Hare *et al.*, 1994). This may be related to the uncertainty of the application of the AVS concept to positive redox conditions as it is strictly only applicable, in geochemical terms, to negative redox potential sediments.

Recent Environment Canada Research on AVS

In 1995, Environment Canada undertook a major research project to evaluate how its new battery of sediment bioassays functioned in an evaluation of a sediment regime containing a metals gradient (Porebski *et al.*, 1998: Fig. 4). A metals gradient was selected using the



(µg/g)	H	F	K	R
◆ Cd	10.0	8.4	3.1	0.4
◆ Pb	748.0	612.0	240.0	26.0
◆ Zn	1240.0	1033.0	453.0	132.0
◆ As	36.0	31.0	18.0	11.0

FIGURE 4 Sampling stations for pollution gradient study (*H* is most contaminated, *R* is least contaminated and used as a "clean" reference station).

interim effects-based sediment criteria developed at the time. Cadmium levels for example, ranged from 0.4 mg kg^{-1} at station *R* (below the current interim sediment quality guideline (TEL) of 0.7 mg kg^{-1}) to 10 mg kg^{-1} at station *H* (above the suggested PEL of 4.2 mg kg^{-1}; Environment Canada, 1996).

Other metals showed similar ranges across the gradient. Some of the bioassays did not respond as expected above the PEL levels. Calculation of the SEM/AVS ratios (Fig. 5), illustrated that, according to the AVS model, toxicity would not be expected at any station except the most contaminated (*H*). Figure 5 also compares grain size at each station.

Bioaccumulation of lead and certain other metals at the high concentration stations were not explained on the basis of the AVS model. This is in keeping with the findings of Ankley (1996) and Hare *et al.* (1994). Further, there was a stronger relationship ($p = 0.055$) between the bulk sediment chemistry levels and effects on benthic

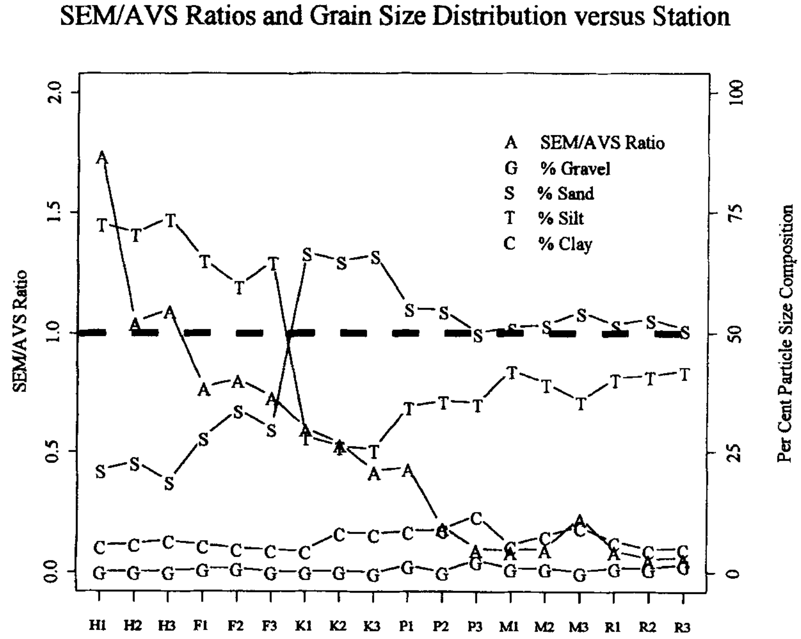


FIGURE 5 SEM/AVS: Simultaneously extracted metals to acid volatile sulphides ratio. Gradient is from most (*H*) to least (*R*) contaminated. Source: Porebski *et al.*, 1998.

community structure than between benthic community structure and the physical factors such as TOC, particle size, ammonia and sulphide (analysis using Mantel's test: Mantel, 1967). Although there was a limited number of samples, this type of result stresses the possibility that, whereas short term bioavailability could be explained by the AVS binding model, longer term and community level effects may not be seen and any adjustment of national guidelines using the AVS, or similar models, should await confirmation of the applicability and conditions of applicability of the AVS approach through further research. In 1997, a similar study was undertaken along a spatial sediment gradient for organic compounds (predominantly PAHs) in Sydney Harbour, Nova Scotia.

CONCLUSIONS

The discussion proposed geochemical and existing ecotoxicological bases for establishing sediment quality guidelines within Canada. While the principles underlying the setting of such guidelines have been expounded, a variety of issues remain to be resolved for their practical use in the Disposal at Sea Programme. To date, interim guidelines have been established using the effects based Protocol for a small number of substances. The development of effects-based, guideline values should continue. The programme will continue to evaluate the implications of adopting each guideline as it becomes available. The likely balance between the effects-based and the geochemical approach for the programme, will be to use the effects based numbers as general screening levels and to use the geochemical approach to supply additional site-specific information in cases where the background concentration of a naturally occurring metal is in question. Towards this end, more emphasis should be placed on recording and analysing sediment grain-size within the BEDS database, with the view to refining new and existing effects based guideline values. In particular, the specification of data entries within databases, intended to provide the basis for correspondence between contaminant concentrations and biological responses in sediments may be refined through the provision of more detailed information on the grain-size composition of the sediment matrix to which the biological tests correspond and quality assurance of chemical measurements. The use of normalising elements, such as lithium, is also desirable and should be investigated in terms of whether this information could be obtained readily, from the available ecotoxicological literature, now or in the future. The Disposal at Sea Programme may consider analysing for lithium during assessment or disposal site monitoring operations.

Finally, further standardisation of Environment Canada's marine sediment bioassays for site specific assessment and field validation purposes would be advisable. The full implementation of the ocean disposal site monitoring program would also make an important contribution to ensuring that sediment quality guidelines can provide long-term marine environmental protection.

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