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Sediment Quality Guidelines: Validity of a Single  
Numerical Value

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Sediment Quality Guidelines:  
validity of a single numerical value

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**Abstract** - Guidelines and criteria for sediments developed in many countries are often expressed as a single number for concentrations of different chemicals in the sediments. An investigation was carried out to evaluate how accurately an analytical laboratory can determine the concentrations of the chemicals in the sediments. Results of quantitative determination of concentrations of inorganic and organic contaminants in reference materials were reviewed together with results of analysis obtained by interlaboratory round-robin studies. Great variability existed in results obtained by quantitative determination of contaminants in sediments by different laboratories. The variability was mainly due to different procedures used in the preparation and extraction of sediments prior to the quantitative determination of metals and trace elements and organic contaminants. The results of the investigation suggested that the single number for concentrations of contaminants should be replaced by a concentration range of the contaminant in sediment guidelines. In addition, the sediment guidelines should include standard methods for sediment sampling, sample preparation and analyses.

**Key words** - sediments, sediment guidelines, analytical methods, quality control, sediment geochemistry

## MANAGEMENT PERSPECTIVE

In many countries, criteria were developed by various jurisdictions and agencies to provide guidance for evaluating the quality of surface and ground water, soils, aquatic sediments, different waste material, etc. These criteria have often been used to establish the extent of cleanup necessary to protect the environment and public health and welfare. In many cases, developed criteria and guidelines for soils, sediments, water, etc., are expressed as a single number which represents the concentration of a chemical in the material. Generally, the single number corresponds to a threshold of observed negative effects of the chemical of interest on the ecosystem or is derived from the background concentration of the chemical in the specific environmental material. A single number criteria and guidelines are preferred by many regulatory agencies for their simplicity. However, little attention has been paid to the performance of laboratories which carry out the quantitative determination of concentrations of chemicals listed in the guidelines and criteria, such as metals and organic contaminants. An investigation was carried out to evaluate how accurately an analytical laboratory can determine the concentrations of the chemicals in the sediments. Results of quantitative determination of concentrations of inorganic and organic contaminants in reference materials were reviewed together with results of analysis obtained by interlaboratory round-robin studies. Great variability existed in results obtained by quantitative determination of contaminants in sediments by different laboratories. The results of the investigation suggested that the single number for concentrations of contaminants should be replaced by a concentration range of the contaminant in sediment guidelines. In addition, the sediment guidelines should include standard methods for sediment sampling, sample preparation and analyses.

## INTRODUCTION

In many countries, criteria were developed by various jurisdictions and agencies to provide guidance for evaluating the quality of surface and ground water, soils, aquatic sediments, different waste material, etc. (Tetra Tech Inc., 1986; Canadian Council, 1987; U.S. Environmental Protection Agency, 1988; Fitchko, 1989; McDonald et al., 1990). These criteria have often been used to establish the extent of cleanup necessary to protect the environment and public health and welfare. Approaching the development of different quality criteria and guidelines involves consideration of many factors including objectives for their purpose and use. In many cases, developed criteria and guidelines for environmental material, such as soils, sediments, water, etc., are expressed as a single number which represents the concentration of a chemical in the material. Generally, the single number corresponds to a threshold of observed negative effects of the chemical of interest on the ecosystem or is derived from the background concentration of the chemical in the specific environmental material. A single number criteria and guidelines are preferred by many regulatory agencies for their simplicity. However, little consideration has been given to the effects of the chemicals listed in the guidelines on biota, particularly synergistic effects of different elements and compounds. In addition to this neglect, little attention has been paid to the performance of laboratories which carry out the quantitative determination of concentrations of chemicals listed in the guidelines and criteria, such as metals and organic

contaminants. In 1989, the Ontario Ministry of the Environment and Energy (OMEE), Canada, developed guidelines for the evaluation of sediment quality within the province of Ontario (Beak, 1987, 1988; Jaagumagi, 1991a, 1991b; Persaud et al., 1991). The guidelines, intended to provide guidance during decision making on sediment issues, ranging from prevention of toxic effects to remediation of contaminated sediments, are biologically-oriented to provide for assessment of the impact of sediment-associated contaminants on the Great Lakes ecosystem. They are expressed as a single number for concentrations of different elements and compounds and divided into different levels of effects on aquatic biota by recognizing two concentrations: the "lowest" and "severe" effect levels. The "lowest" effect level is the concentration of a metal/trace element at which actual ecotoxic effects become apparent. The concentration of individual trace element/metal for this effect level was derived using field-based data on the co-occurrence of sediment concentrations and benthic species. The "severe" effect level represents the concentration of a metal/trace element in sediments that could potentially eliminate most of the benthic organisms living in the sediments. For non-polar organic contaminants, the guidelines recognize the following levels of sediment contamination: the "no-effect" level, at which contaminants in sediments do not present a threat to water quality and users, benthic biota, wildlife and human health; the "lowest" effect level, at which actual ecotoxic effects become apparent; and the "severe" effect level, at which most benthic organisms are

eliminated from sediments. Further, the concentrations of non-polar organic contaminants are normalized to total organic carbon (TOC) content in sediments to obtain the guideline value (Persaud et al., 1991).

This study was carried out to evaluate the influence of analytical techniques for quantitative determination of elements and compounds on the formulation of environmental quality guidelines, particularly those which are expressed as a single number in sediment quality guidelines.

#### MATERIALS AND METHODS

The OMEE sediment quality guidelines (Table 1) were used as an example in this study. Readily available results from interlaboratory quality control studies and values for various Certified Reference Materials were compiled for elements and compounds included in the guidelines. Compiled data, particularly ranges of concentrations of each element and compound obtained by different interlaboratory studies, were compared to the single number listed in the guidelines.

Many of the reviewed interlaboratory studies pointed out that considerably large variations in reported concentrations of metals in sediments were due to different methods used in the analysis, particularly the extraction procedures. Therefore we examined the effects of the extraction procedures on the quantitative

determination of metals in sediments in two geochemically different lake sediments. The sediments were collected in depositional areas in Lake Ontario and Hamilton Bay of Lake Ontario by a Ponar grab sampler. A 5-cm surface section of the collected sediment was freeze-dried and homogenized in a mechanical grinder. The extraction of the sediments was carried out in four replicates by five different acid mixtures: 1) 2 ml of HF (conc.) and 8 ml of aqua regia; 2) 5 ml  $\text{H}_2\text{O}_2$  (30%) and 5 ml aqua regia; 3) 10 ml aqua regia; 4) 10 ml  $\text{HCl}:\text{HNO}_3$  (1:1); and 5) 10 ml  $\text{HCl}$  (0.5 N). The extraction mixtures were added to 0.5 g of dry samples in Teflon containers with subsequent mixing. The mixture was allowed to degas overnight at room temperature to prevent vigorous reaction during heating. The containers were covered with Teflon lids to protect the samples from contamination. The samples in the  $\text{H}_2\text{O}_2$  mixture were digested on a hot plate at a maximum temperature of  $200^\circ\text{C}$ . All samples digested with mixtures containing HF were further evaporated in Teflon beakers on a hot plate to ensure all HF was removed before the other steps in the analysis. The samples were extracted in a microwave oven (Floyd, Inc., Model RMS 150) using the following conditions: 3 min. at 30 psi, 5 min. at 50 psi, 5 min. at 100 psi, and 5 min. at 130 psi. The samples were cooled and filtered through 0.4  $\mu\text{m}$  Nuclepore Polycarbonate filters into volumetric flasks. The quantitative determination of eight metals (Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the extracts was carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Jobin Yvon Model 74. The standards consisted of mixed



solutions of high purity solutions of the eight metals (Delta Scientific Laboratory Products, Canada). The detection limits, defined as that concentration equivalent to 3x standard deviation obtained from all sample blanks are summarized in Table 2 together with the analytical conditions of the instrument. The geochemical character of the two sediments was determined by the concentrations of major elements (Si, Al, Fe, Ca, Mg, K, Na, Ti, Mn and P) and inorganic and organic carbon. The determination of the concentrations of major elements was carried out by lithium borate fusion and digestion of the samples by aqua regia followed by ICP-AES analysis. The concentrations of organic and inorganic carbon were carried out using a Leco CR-12 carbon analyzer. Certified reference materials of the National Bureau of Standards, U.S. Department of Commerce, estuarine sediment, NBS-1646, and Buffalo River sediment, NBS-2704, were used for quality control in the analysis. In addition, samples of the reference materials were extracted with the same acid mixtures used for Lake Ontario and Hamilton Bay sediments.

#### RESULTS AND DISCUSSION

Examples of concentration ranges of selected organic contaminants and metals and trace elements obtained in round-robin studies carried out under a Dredging Quality Control Program by the National Water Research Institute, Burlington, Ontario, Canada, are shown in Tables 3 to 5. The choice of the examples was based on the concentrations of the parameters listed in the OMEE sediment

guidelines (Table 1) to show the performance of different laboratories in analyses of sediments containing elements and compounds in the concentration range of the "lowest" or "severe" effects levels. The details of the design of the round-robin studies and preparation of the test materials were described by Stokker and Kokotich (1991) and Lee et al. (1986). Eighteen and fourteen laboratories participated on the 1991 and 1986 studies, respectively. The samples sent to the laboratories for the quantitative determination of metals, trace elements and organic contaminants included freeze-dried, fully homogenized sediments, naturally contaminated reference materials or certified reference materials specially developed for either organic contaminant or metal and trace element analysis. Each sediment was to be extracted and analyzed using the laboratory's own routine methods of analysis. The mean, standard deviation and median values shown in Tables 3 to 5 are those given in the reviewed reports. The means and standard deviations were calculated without any data rejection, and the medians were calculated after rejection of extreme values (Stokker and Kokotich, 1991; Lee et al., 1986). The reference values correspond either to the concentrations for the certified reference materials or were obtained by in-house and external analyses conducted during the preparation of the reference material (Cheam and Chau, 1984; Lee et al., 1986; Lee and Chau, 1987; Cheam et al., 1989).

From a round-robin study including eighteen laboratories, Stokker and Kokotich (1991) concluded that there are some laboratories

capable of accurate quantitative determination of PCB, metals and trace elements in sediments. However, the study also revealed some extreme outlying and/or erratic results from some of the participating laboratories, particularly for total PCB, As, Cd, Cr and Hg.

Examples of the ranges of concentrations of PCB in sediments determined by different laboratories in a round-robin study are shown in Table 3. According to example #1, the results from one laboratory would indicate that the concentrations of PCB in the tested sediment are below the "lowest" effect level, i.e.,  $<0.07$  ug/g, given in the OMEE sediment guidelines. On the other hand, the results from another laboratory would indicate that the concentrations of PCB in the identical sediment exceed many times the "lowest" effect level. Example #2 in Table 3 shows even greater differences in the results of the round-robin study. The concentrations determined by one laboratory would exceed or approach the "severe" effect level of PCB in sediments with 2% or 3% of organic C, respectively. However, according to one laboratory, the concentrations of PCB in the sediment would be below the "lowest" effect level. In example #3, the concentrations of PCB determined by one laboratory would exceed the "severe" effects level in sediments with up to 5% of organic C. The reference values in Table 3 show that the concentrations of PCB in all tested sediments would be well below the "severe" effect levels even with concentrations of organic C at 0.5%. In addition to the

problems with the accuracy in quantitative determination of PCB, no standard method is available for the quantitative determination of organic C in sediments. Therefore the calculations leading to the "severe" effect levels of PCB in the sediment may increase the probability of erroneous evaluation of sediment quality. Stokker and Kokotich (1991) noted that the detection limits for PCB reported by the eighteen laboratories participating in the round-robin study ranged from 0.003 to 0.100 ug/g. Further, six of the eighteen laboratories reported detection limits for total PCB in sediment at or above 0.07 ug/g listed as "low" effect level in the OMEE sediment guidelines.

The results shown in Table 4 indicate that many laboratories experienced problems with the accurate determination of individual PCB congeners in sediments. Two sediment samples used in the round-robin interlaboratory study were certified for ten PCB congeners (Table 4). Total PCB concentrations in the sediments calculated as a sum of the concentrations of the ten congeners determined by eleven laboratories are shown in Table 4. The calculated total concentrations ranged from 0.0012 to 0.0493 and from 0.0135 to 0.7873 ug/g. The laboratories reported approximately 50% correct or acceptable values in the determination of ten selected PCB congeners in the two sediment samples (Mudroch, 1990). It appeared that the wide range of PCB concentrations was mainly due to the differences in analytical procedures used by the laboratories.

The complexity of the quantitative determination of PCB in sediments needs to be considered in the development of the guidelines. Depending on the source, sediments may contain different amounts of the possible 209 PCB congeners. It was shown that the toxicity of PCB to biota depends on the presence of specific congeners (for example, Duinker et al., 1988; Clarke et al., 1989). Therefore using the information on the toxicity of individual congeners in the sediments at specific sites rather than using total PCB concentrations should be considered in the formulation of the guidelines.

Methods for the quantitative determination of total PCB and individual congeners in the laboratory involves many steps outlined below. Extraction of sediment samples can be carried out by different solvents or their mixtures, such as acetone, methylene chloride, hexane, methanol, etc., in a Soxhlet apparatus, a separatory funnel or by an ultrasonic mixer. The extraction is followed by a clean-up procedure to remove substances that could interfere in the quantitative determination of PCB. This typically involves liquid-solid adsorption chromatography, gel permeation chromatography and different chemical methods. The most frequent method for the determination of PCB in the cleaned extract is gas chromatography (GC) with an electron capture detector (ECD). Capillary columns with different stationary phases are used in the GC to determine the presence and quantity of individual congeners. Each stationary phase has specific capability to separate

individual congeners. The information on the concentration of total PCB would require the determination of all congeners present in the sediment sample. The quantification of PCB is carried out using secondary standards, such as commercial PCB mixtures of known composition, or pure standards which contain several congeners. Therefore the results of the determination of total PCB depend on the number of congeners in the standard(s) used by each laboratory and the capability of the stationary phase in the capillary column to separate the congeners in the sample. The determination of only a few selected congeners, such as those indicated as most toxic to biota, enables the use of pure individual congeners as standards with more accurate identification and quantification. Generally, the performance of each laboratory in the determination of contaminants in sediments depends on the analytical procedures, instrumentation, and the experience and skill of the person who carries out the analysis. These factors appear to be particularly important in the quantitative determination of PCB in sediments.

Results of interlaboratory studies with over 150 participating laboratories to evaluate analytical methods for quantitative determination of PCB indicated that for 1 ug/g PCB in sediment one can expect a relative standard deviation about 16%. However, for 1 ng/g PCB in the sediment, the relative standard deviation will increase to about 45%. The results indicated that at the lower concentrations the accuracy of the quantitative determination of PCB will be more affected by the laboratory procedures used in the

determination (Lang, 1992).

Recommended concentrations of PAH in sediments are listed in the OMEE sediment guidelines (Table 1) in addition to PCB and other organic contaminants. The quantitative determination of PAH in sediments is usually based on the determination of the quantities of 18 selected PAH, such as naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benzo(a)anthracene, chrysene, benzo(b)fluoranthracene, benzo(k)fluoranthracene, benzo(a)pyrene, benzo(e)pyrene, perylene, indeno(1,2,3-cd)pyrene, dibenzo(a,h)anthracene and benzo(ghi)perylene. Generally, the extraction and clean-up procedures are similar to those used in the determination of PCB. Selective ion gas chromatography/mass spectrometry (GC/MS) is used in the determination of the 18 selected PAH. Recently, the effect of sample preparation on the quantitative determination of PAH in sediments was reported. The concentrations of PAH in an identical wet and freeze-dried sediment sample were determined to evaluate the sample preparation prior to analysis (Fox et al., 1991). Freeze-drying the sediment generated losses of some individual PAH in the sample. For example, mean losses of naphthalene, pyrene and benzo(ghi)perylene in freeze-dried sediments in three samples were 96%, 42% and 16%, respectively. In many areas, naphthalene is a major component of PAH in sediments. Reporting lower values of PAH may lead to serious underestimation of the acute toxicity of sediments to biota (Fox et al., 1991). The above example shows the importance of testing and selection of

proper procedures for preparation of sediment samples prior to analysis. Tested and approved methods for sample preparation should also be included in the sediment guidelines.

The examples in Table 5 show that some laboratories obtained concentrations of As as low as 1.6 and 3.1 ug/g in sediments with a reference value for As 32.5 ug/g. In the evaluation of sediment quality using the OMEE sediment guidelines, the concentrations of As determined as 1.6 and 3.1 ug/g will identify a "low" effect of As on biota. On the other hand, the reference value for the sediment, 32.5 ug/g As, indicates that "severe" effects on biota can be expected due to As in the sediment (Table 1). Similar problems would occur in the evaluation of sediment quality using concentrations of Cd, Cr, Hg and Ni determined by some laboratories (Table 5). Using the results obtained by some laboratories, Cd, Cr, Hg and Ni in the sediments would have a "low" effect on biota according to the OMEE sediment guidelines. Therefore the sediments would not require any remediation or confined disposal after dredging. On the other hand, the concentrations of Cu and Pb in sediments determined by some laboratories would indicate that Cu and Pb will have "severe" effects on biota (Table 6). The concentrations of Zn in sediments determined by different laboratories in the round-robin study ranged from "low" to "severe" effect levels (Table 6). Therefore the decision for the management of these sediments will depend mainly on which laboratory carried out the analysis of the sediments.



A wide variety of methods was used for the extraction of As, Cu, Cd, Cr, Hg, Ni, Pb and Zn in reference sediment materials in round-robin studies. In addition, the detection limits for each element ranged widely among laboratories (Stokker and Kokotich, 1991). The detection limits were sometimes considerably greater than the "lowest" effect levels given for the element in the OMEE sediment guidelines, particularly for Hg, Cd, Cu and Ni (Table 7).

The effects of different extraction procedures on the quantitative determination of Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn in fine-grained sediments collected in Lake Ontario are shown in Table 8. Five different acid mixtures were used in the extraction of the sediment. Total concentrations of the elements obtained by the analysis are expressed as the median value with the standard deviation obtained by four replicate analysis for each acid mixture. The mixture containing HF extracted considerably greater concentrations of Co, Cr, Fe, Mn, Ni and Zn than the others. The lowest concentrations of the elements were extracted by 0.5 N HCl (Table 8).

In this study, the sediments collected from Hamilton Bay of Lake Ontario was used to compare the effects of sediment geochemistry on the efficiency of the extraction procedures. The sediments in Hamilton Bay are contaminated to a large degree by different metals, trace elements and organic compounds originating from industrial and municipal discharges into the Bay. Mean recovery of

the elements in the certified reference material NBS-2704, Buffalo River sediment, extracted by the five acid mixtures is shown in Table 9. The greatest recovery of Co, Cr, Fe, Mn and Zn was obtained by the acid mixture containing HF. By this mixture, the portion of the elements incorporated in the crystal lattice of different minerals is extracted. Therefore the quantities of elements extracted by the mixture containing HF can be considered total concentrations of the elements in the sediment. The results in Table 8 indicate that most of the acid mixtures extracted similar quantities of Co, Cr, Cu, Mn, Ni and Zn in Hamilton Bay sediments. The quantities of Co, Cr, Fe, Mn, Ni and Zn extracted by different acid mixtures from Lake Ontario and Hamilton Bay sediments are expressed as a percentage of those extracted by HF:HNO<sub>3</sub>:HCl in Table 10.

The differences in quantities of the elements from Lake Ontario and Hamilton Bay sediments extracted by the acid mixtures reflect the effects of sediment geochemistry, chemical forms of each element and chemical/physical association of the elements with sediment particles on the extraction. The geochemical composition of Lake Ontario and Hamilton Bay sediments is shown in Table 11. Hamilton Bay sediments contain more than two-times greater concentrations of Fe than those in Lake Ontario. Iron in Hamilton Bay sediments occurs mainly as amorphous oxyhydroxides on the surface and in the space between fine-grained sediment particles (Mudroch and Zeman, 1975; Mayer and Manning, 1990). Iron oxyhydroxides have the

potential to adsorb many metals and trace elements (for example, Tessier et al., 1985). The adsorbed metals and trace elements are extracted by some acids, such as HCl and HNO<sub>3</sub>, and their various mixtures, in larger quantities than those associated with the crystal lattice of the minerals in the sediments. The results indicate that the sediment geochemistry and different chemical forms of metals can affect their quantities extracted from sediments in different areas.

#### CONCLUSIONS

An investigation was carried out to evaluate the influence of the quantitative determination of selected inorganic and organic contaminants on the formulation of sediment quality guidelines, particularly the contaminants for which a single number is given for their concentrations in the guidelines. Biologically-based guidelines for evaluation of the quality of aquatic sediments in Ontario, Canada, were used as an example in the investigation.

The results of the investigation indicated problems in utilizing a single number given in the guidelines for the assessment of sediment quality. Great variability in the results obtained by quantitative determination of contaminants in sediments by different laboratories involved in sediment analysis, was responsible for the problems. The investigation showed that for some elements and compounds, the concentrations obtained by different laboratories could not distinguish between the different

effect levels on biota, such as "lowest" effect and "severe" effect levels expressed as a single number in the sediment guidelines for Ontario.

Many analytical procedures and instrumentation involved in the quantitative determination of PCB, and the selection of a standard may considerably affect the quantification of PCB in sediments. It was shown that sample preparation prior to the quantitative determination of PAH in sediments can considerably affect the evaluation of toxicity of sediments to biota. Five different acid mixtures were used in the extraction prior to the quantitative determination of Co, Cr, Cu, Fe, Pb, Mn, Ni and Zn in sediments collected in Lake Ontario and Hamilton Bay. Each of the five acid mixtures extracted different quantities of the elements. The results suggested that sediment geochemistry affected the quantities of extracted elements from each of the two sediments.

Replacing a single number by concentration ranges for chemicals listed in sediment guidelines should be considered. In selecting the concentration ranges, the analytical capabilities of different laboratories for quantitative determination of trace elements, organic contaminants and nutrients in sediments from different areas need to be revised. In order to minimize the variability associated with the quantitative determination of concentrations of chemicals in sediments by different laboratories, it is recommended to standardize the analytical methods used in the analysis. In

addition, analytical methods used in the formulation of the sediment guidelines should be considered. The standardization should include sample preparation, such as drying collected solid samples, homogenization and subsampling for different analysis, digestion, extraction and clean-up of the extracts. Further, a protocol is necessary to standardize methods for collecting duplicate samples in the field, and the use of standard reference material in quality control.

The results of the investigation suggested an ultimate need and use of round-robin interlaboratory studies in the analysis of sediments and other environmental materials. It is recommended to continue and expand such studies to include the quantitative determination of all parameters that are of interest to municipal, provincial and federal government agencies. The studies should be carried out on a regular basis and all test material should be properly characterized by concentrations of selected parameters in the sample. The use of standard reference material as additional test material should be considered in round-robin interlaboratory studies.

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## REFERENCES

Beak Consultants Ltd. (1987) Development of sediment quality objectives: Phase I - Options. Report prepared for the Ontario Ministry of the Environment, Mississauga, Ontario.

Beak Consultants Ltd. (1988) Development of sediment quality objectives: Phase II - Guidelines Development. Report prepared for the Ontario Ministry of the Environment, Mississauga, Ontario.

Canadian Council of Resource and Environment Ministers. (1987) Canadian Water Quality Guidelines. Task Force on Water Quality Guidelines, Toronto, Ontario.

Cheam, V. and Chau, A.S.Y. (1984) Analytical Reference Materials. Part IV. Development and certification of the first Great Lakes Sediment Reference Material for arsenic, selenium and mercury. Analyst 109, 775-780.

Cheam, V., Aspila, K.I. and Chau, A.S.Y. (1989) Analytical Reference Materials. VIII. Development and certification of a new Great Lakes Sediment Reference Material for eight trace metals. Sci. Total Environ. 87/88, 517-524.

Clarke, J.U., McFarland, V.A. and Pierce, B.D. (1989) Preliminary recommendations for a congener-specific PCB analysis in regulatory

evaluation of dredged material. Miscellaneous Paper D-89-2, Department of the Army, Waterways Experiment Station, Corps of Engineers, Vicksburg, Mississippi.

Duinker, J.C., Schultz, D.E. and Petrick, G. (1988) Selection of chlorinated biphenyl congeners for analysis in environmental samples. Mar. Poll. Bull. 19, 19-25.

Fitchko, J. (1989) Criteria for contaminated soil/sediment cleanup. Pudvan Publishing Company, Northbrook, Illinois.

Fox, M.E., Murphy, T.P., Thiessen, L.A. and Khan, R.M. (1991) Potentially significant underestimation of PAHs in contaminated sediments. Proc. 7th Eastern Region Conference, Canadian Association on Water Pollution Research and Control, 1991, Universite du Quebec a Rimouski, 80-86.

Jaagumagi, R. (1991a) Development of the Ontario provincial sediment quality guidelines for arsenic, cadmium, chromium, copper, iron, lead, manganese, mercury, nickel and zinc. A draft document prepared for Water Resources Branch, Watershed Management Section, Ontario Ministry of the Environment, Toronto, Ontario.

Jaagumagi, R. (1991b) Development of the Ontario provincial sediment quality guidelines for PCBs and the organochlorine pesticides. A draft document prepared for Water Resources Branch,

Watershed Management Section, Ontario Ministry of the Environment,  
Toronto, Ontario.

Lang, V. (1992) Review polychlorinated biphenyls in the  
environment. J. Chromatogr. 595, 1-43.

Lee, H.B., Abbott, J.A. and Chau, A.S.Y. (1986) Dredging Quality  
Control Study No. 4 (DQC-4). Analysis of PCB and toxic trace metals  
in dry sediment reference materials. National Water Research  
Institute Contribution No. 86-94, National Water Research  
Institute, Burlington, Ontario, Canada.

Lee, H.B. and Chau, A.S.Y. (1987) Analytical Reference Materials.  
Part VII. Development and certification of a Sediment Reference  
Material for total polychlorinated biphenyls. Analyst 112, 37-40.

Mayer, T. and Manning, P.G. (1990) Inorganic contaminants in  
suspended solids from Hamilton Harbour. J. Great Lakes Res. 16,  
299-318.

McDonald, D.D., Smith, S.L., Wong, M.P. and Mudroch, P. (1990) The  
development of Canadian Marine Environmental Quality Guidelines. A  
report prepared for the Interdepartmental Working Group on Marine  
Environmental Quality Guidelines, Environment Canada, Ottawa,  
Ontario.



Mudroch, P. (1990) Compilation report on the determination of polycyclic aromatic hydrocarbons and polychlorinated biphenyls in marine sediments. Report, Inland Waters Directorate, Ontario Region, Burlington, Ontario, Canada.

Mudroch, A. and Zeman, A.J. (1975) Physicochemical properties of dredge spoil. J. Waterways, Harbours and Coastal Eng. Division 101, No. WW2, Proc. Paper 11317, 201-216.

Persaud, D., Jaagumagi, R. and Hayton, A. (1992) The provincial sediment quality guidelines. A draft document prepared for Water Resources Branch, Watershed Management Section, Ontario Ministry of the Environment, Toronto, Ontario.

Stokker, Y.D. and Kokotich, E.A. (1991) Dredging Quality Control Study No. 5 (DQC-5). The analysis of polynuclear aromatic hydrocarbons, PCBs, and toxic metals in sediment reference materials in direct injection solutions. National Water Research Institute Contribution No. 91-107, National Water Research Institute, Burlington, Ontario, Canada.

Tessier, A., Rapin, F. and Carignan, R. (1985) Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. *Geochem. Cosmochem. Acta* 49, 183-194.

Tetra Tech Inc. (1986) Development of sediment quality values for

Puget Sound. Volume 1. Puget Sound Dredged Disposal Analysis Report. Bellevue, Washington, 129 p.

U.S. Environmental Protection Agency. (1988) Interim sediment criteria values for non-polar hydrophobic organic contaminants. Report SCD Number 17. Criteria and Standards Division, Office of Water. Washington, District of Columbia, 22 p.

Table 1. Selected parameters listed in Ontario Ministry of the Environment and Energy sediment guidelines<sup>1</sup>  
(in ug/g dry weight)

Metals and Trace Elements

	Level	
	"lowest" effect	"severe" effect
As	6	33
Cd	0.6	10
Cr	26	110
Cu	16	110
Pb	31	250
Hg	0.2	2
Ni	16	75
Zn	120	820

Organic Compounds<sup>2</sup>

PCB (total)	0.07	530
PAH (total)	2	11,000

<sup>1</sup> Persaud et al., 1992

<sup>2</sup> Number for severe effects are to be converted to bulk sediment values by multiplying by the actual concentration of organic C in the sediments (to a maximum value of 10%). For example, analysis of a sediment gave a total PCB concentration of 30 ug/g and organic C 5%. The value of PCB for the "severe" effect level is first converted to a bulk sediment value by multiplying 530 by 0.05, which results in 26.5 ug/g as the "severe" effect level for that sediment. Therefore the determined 30 ug/g exceeds the guideline.

Table 2. Analytical conditions and detection limits of the eight trace elements determined in Lake Ontario and Hamilton Bay sediments using Jobin Yvon ICP-AES

Element	Wavelength	Detection Limit(ug/L)
Zn	213.759	10.1
Pb	220.353	15.5
Co	228.616	6.1
Ni	231.604	12.4
Mn	257.610	1.8
Fe	259.940	4.9
Cr	267.716	5.1
Cu	324.754	3.6

Table 3. Concentration ranges of PCB in certified sediments determined in round-robin interlaboratory study (in ug/g dry weight)

Example #	Conc. Range	Median	Reference value
1	0.0321 to 0.737	0.5005	0.552
2	0.0258 to 15.415	0.7255	0.822
3	0.300 to 11.699	0.805	0.822
4	0.360 to 29.000	0.930	1.120

Table 4. Concentrations of ten PCB congeners determined in two sediment samples in a round-robin interlaboratory study (in ng/g dry weight)

Sediment #1

Congener No.										
101	138	151	153	170	180	194	196	201	209	TOTAL
0.76	2.2	0.48	2.1	0.43	1.26	0.27	0.43	0.48	0.2	8.61
9	16	2.5	n.a.	4.4	8.7	1.9	2.7	2.8	1.3	49.3
2.1	2.8	0.55	3.2	0.37	1.2	0.14	0.29	0.4	0.08	11.13
6.4	4.3	1.1	3.1	0.79	1.7	n.a.	0.5	0.82	n.a.	18.71
1	1.2	0.6	1.2	0.3	0.7	0.4	0.2	0.2	0.1	5.9
2.4	2.2	0.71	2.2	0.86	1.4	0.3	1.1	0.9	0.32	12.39
2.7	n.a.	n.a.	4.4	0.8	1.1	0.3	0.5	1	0.4	11.2
0.4	0.3	<0.2	0.3	<0.2	0.2	<0.2	<0.2	<0.2	<0.3	1.2
4	n.a.	1	3	n.a.	n.a.	n.a.	n.a.	1	n.a.	9
1	1.3	0.31	1.3	0.3	1	0.41	0.41	0.23	0.09	6.35
2	2.1	0.2	2.5	0.32	1.2	0.5	0.6	0.65	0.42	10.49

Sediment #2

Congener No.										
101	138	151	153	170	180	194	196	201	209	TOTAL
15.4	14.5	6.8	12.5	3.7	8	1.6	2.8	5.7	0.9	71.9
130	213	43	n.a.	67	123	99	40	58	14.3	787.3
3	3.4	0.9	4	0.15	1.9	0.24	0.5	0.7	0.14	14.93
33	14.5	7.5	15.5	11	14	3.6	12	9.6	4.1	124.8
11.6	14.5	4.5	15.5	3.9	9.2	1.8	2.2	2.4	1	66.6
13.5	11.5	4.4	10.5	5.2	9.4	2	6.9	3.8	1.2	68.4
10.2	0.5	3.9	13.8	3.1	5.6	1	1.9	3.1	0.7	43.8
3.1	2.7	1	2.6	0.6	1.3	0.3	0.5	0.5	0.9	13.5
18	7	8	25	n.a.	n.a.	n.a.	n.a.	8	n.a.	66
10.7	15.6	3.7	14.4	4.4	12.1	2.5	4.5	3.7	1.1	72.7
11	12	3	14	1.8	14	2	3.7	7.3	0.65	69.45

n.a. = not analysed

Table 5. Concentration ranges of As, Cd, Cr, Hg and Ni obtained in round-robin studies in reference sediment materials (in ug/g dry weight)

Arsenic				
Example #	Conc. Range	Mean	S.D.	Ref. value
1	1.6 to 40.0	30.4	8.2	32.5
2	3.1 to 35.0	27.9	9.7	32.5
Cadmium				
Example #	Conc. Range	Mean	S.D.	Ref. value
1	0.50 to 14.00	5.81	2.76	5.30
2	<0.30 to 6.00	4.06	1.12	3.80
3	<0.10 to 6.00	1.17	1.85	0.25±0.4
Chromium				
Example #	Conc. Range	Mean	S.D.	Ref. value
1	30 to 131	76	38	123±14
2	31 to 120	74	33	N.A.
Mercury				
Example #	Conc. Range	Mean	S.D.	Ref. value
1	0.079 to 4.12	1.26	0.83	1.09±0.15
2	0.131 to 2.00	0.379	0.553	0.129±0.012
Nickel				
Example #	Conc. Range	Mean	S.D.	Ref. value
1	57 to 1,330	867	267	941
2	36 to 79	57.7	10.5	59.3

N.A. = not available

Table 6. Concentration ranges of Cu, Pb and Zn in sediments obtained in round-robin studies (in ug/g dry weight)

	Concentration Range	Median
Cu	67.9 to 237	80.25
Pb	84 to 212	140
Zn	127 to 1780	192

Source: Lee et al. (1986)



Table 7. Range of detection limits and "low" effect levels for elements in sediments given in the OMEE sediment guidelines (in ug/g dry weight)

Element	Detection Limit <sup>1</sup>	"Low" Effect Value <sup>2</sup>
As	0.002 to 1.0	6.0
Cd	0.005 to 5.0	0.60
Cr	0.001 to 20.0	26.0
Cu	0.001 to 20.0	16.0
Hg	0.002 to 2.0	0.20
Ni	0.001 to 20.0	16.0
Pb	0.001 to 20.0	31.0
Zn	0.001 to 10.0	120.0

Source: <sup>1</sup>Stokker and Kokotich (1991)  
<sup>2</sup>Persaud et al. (1992)

Table 8. Concentrations of trace elements (median and standard deviation) in Lake Ontario and Hamilton Bay sediments extracted with five different acid mixtures. All results are in ug/g dry weight, except Fe and Mn which are in % dry weight

	Co	Cr	Cu	Fe	Pb	Mn	Ni	Zn
<u>Lake Ontario</u>								
HF:HNO <sub>3</sub> :HCl	20 ±3	75 ±8	77 ±10	2.52 ±.11	155 ±31	0.6 ±.03	75 ±10	339 ±12
Aqua Regia	12 ±1	43 ±8	79 ±3	1.99 ±.11	156 ±7	0.4 ±.02	50 ±3	234 ±12
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	12 ±1	47 ±2	78 ±5	1.81 ±.11	139 ±8	0.4 ±.04	52 ±4	246 ±12
HNO <sub>3</sub> :HCl	14 ±1	50 ±2	77 ±4	1.79 ±.08	124 ±5	0.5 ±.02	58 ±2	264 ±12
HCl	1 ±.5	2 ±.2	3.2 ±1	0.37 ±.02	16 ±4	0.2 ±.01	5 ±1	14 ±1
<u>Hamilton Bay</u>								
HF:HNO <sub>3</sub> :HCl	28 ±1	204 ±1	142 ±8	7.58 ±.3	428 ±5	0.2 ±.02	77 ±1	2409 ±43
Aqua Regia	24 ±1	190 ±6	146 ±12	4.77 ±.2	368 ±16	0.2 ±.07	77 ±3	2311 ±99
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	25 ±1	194 ±8	147 ±4	5.57 ±.06	409 ±15	0.2 ±.07	78 ±4	2361 ±64
HNO <sub>3</sub> :HCl	23 ±3	175 ±57	133 ±2	4.33 ±.3	343 ±33	0.2 ±.02	66 ±4	2158 ±15
HCl	20 ±1	119 ±1	57 ±4	0.68 ±.03	295 ±5	0.2 ±.01	36 ±1	754 ±107

Table 9. Mean recovery (in %) of trace elements in certified reference materials after extraction by five different acid mixtures (average of six replicates of analysis)

	Co	Cr	Cu	Fe	Pb	Mn	Ni	Zn
<b>Estuarine sediment</b>								
HF:HNO <sub>3</sub> :HCl	116	92	113	93	106	94	103	94
Aqua Regia	100	53	104	59	74	60	80	68
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	107	58	95	61	76	62	79	69
HNO <sub>3</sub> :HCl	103	51	96	59	72	59	82	69
HCl	51	12	69	17	51	32	41	63
<b>Buffalo River sediment</b>								
HF:HNO <sub>3</sub> :HCl	112	92	94	102	103	96	103	102
Aqua Regia	88	71	96	74	90	89	111	97
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	97	79	100	75	102	87	109	93
HNO <sub>3</sub> :HCl	91	78	94	74	92	85	108	93
HCl	43	4	78	57	72	62	43	70

Table 10. Quantity of elements extracted by different acid mixtures relative to the quantities extracted by HF:HNO<sub>3</sub>:HCl (in % dry weight)

	Co	Cr	Cu	Fe	Pb	Mn	Ni	Zn
<u>Lake Ontario</u>								
Aqua Regia	60	57	103	79	100	76	67	69
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	60	63	101	72	90	77	69	73
HNO <sub>3</sub> :HCl	70	67	100	71	80	82	77	78
0.5 N HCl	5	3	4	15	10	36	7	4
<u>Hamilton Bay</u>								
Aqua Regia	86	93	103	63	86	98	100	96
H <sub>2</sub> O <sub>2</sub> :HNO <sub>3</sub> :HCl	89	95	104	73	96	99	101	98
HNO <sub>3</sub> :HCl	82	86	94	57	80	93	86	90
0.5 N HCl	71	58	40	9	69	79	47	31

Table 11. Geochemical composition of sediments from Lake Ontario and Hamilton Bay (in % dry weight)

	Lake Ontario	Hamilton Bay
SiO <sub>2</sub>	40.2	38.6
TiO <sub>2</sub>	0.6	0.6
Al <sub>2</sub> O <sub>3</sub>	11.7	11.2
Fe <sub>2</sub> O <sub>3</sub>	5.5	12.1
MnO	1.1	0.4
MgO	1.9	2.2
CaO	11.9	8.1
K <sub>2</sub> O	2.4	2.1
Na <sub>2</sub> O	0.6	0.5
P <sub>2</sub> O <sub>5</sub>	0.4	0.9
Organic C	2.9	3.7
Inorganic C	2.3	2.7

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