

Guidance on Evaluating Sediment Contaminant Results

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Division of Surface Water

Standards and Technical Support Section

Executive Summary

Division of Surface Water personnel occasionally need to evaluate sediment contaminant data for potential toxicity. The primary purpose of the evaluation is to quickly and efficiently determine proper management or disposal options for contaminated sediment. This analysis can be done in three Tiers; a screening Tier, an evaluation Tier, and a testing Tier. This guidance details how contaminated sediment can be assessed using this tiered process.

Acronyms

AVS Acid Volatile Sulfide

CDF Confined Disposal Facility

DES Division of Environmental Services

DQO Data Quality Objective

EPA Environmental Protection Agency

ESB Equilibrium Partitioning Sediment Benchmark

ESBTU Equilibrium Partitioning Sediment Benchmark Toxic Unit

ESL Ecological Screening Level

FCV Final Chronic Value foc Fraction Organic Carbon goc Grams of Organic Carbon

PAH Polycyclic Aromatic Hydrocarbon
PRG Preliminary Remediation Goal
SEM Simultaneously Extracted Metals
SPME Solid Phase Micro-Extraction
SQG Sediment Quality Guideline
SRV Sediment Reference Value

TOC Total Organic Carbon WQC Water Quality Criteria

μg Microgram μmol Micromole

Table of Contents

Disclaimer	5
Why do we Need Sediment Contaminant Evaluations?	5
Where do we get Sediment Contaminant Data?	5
How do we Collect Sediment Contaminant Data?	6
Why are Data Quality Objectives Important to Sediment Contaminant Data?	6
How do we Evaluate Sediment Contaminant Data?	8
Preliminary	8
Background Contamination	9
Tier I	9
Tier II	11
PAHs	12
Nonionic Organic Chemicals	13
Metals	14
PCBs	16
Tier III	18
Tables	20
References	29

Tables

Table 1	PAH Equilibrium Partitioning Sediment Benchmarks
Table 2	PAH Uncertainty Factors
Table 3	Nonionic Organic Chemical Equilibrium Partitioning Sediment Benchmarks
Table 4	Sediment Quality Guidelines for Metals in Freshwater Ecosystems that
	Reflect TECs
Table 5	Median Lipid Levels by Species, 1998-2006
Table 6	Ohio Fish Consumption Advisory Chemicals
Table 7	Fish Tissue Concentrations for Determining Impairment for the 2008
	Integrated Report (µg/kg)

Figures

Figure 1 Flowchart for Evaluating Sediment Contaminant Data

Disclaimer

This guidance is intended to assist Division of Surface Water staff by providing a context in which to make management decisions regarding sediment contamination levels. The guidance is a compilation and simplification of approaches from several sediment evaluation guidance documents, primarily those used by U.S. EPA and U.S. Army Corps of Engineers. This guidance is not intended to replace or supersede any of the original source documents cited within. Many sediment evaluations are unique and may require referring to the source guidance documents for further information.

This guidance is non-regulatory in nature and should not be construed as standards. This guidance does not impose any regulatory requirements.

Why do we Need Sediment Contaminant Evaluations?

The Division of Surface Water is occasionally required to evaluate sediment contaminant data. The source of the data can be the Division itself, or external sources such as private industry consultants or governmental organizations such as the U.S. Army Corps of Engineers. Evaluating sediment contaminant data is necessary in order to determine whether sediment remediation should be a goal of a larger project. Sediment contaminant evaluations can also be used to help determine appropriate disposal and reuse strategies for dredged sediment. Sediment contaminant evaluations may also be used to determine potential causes and sources of biological impairment.

Examples of sediment contaminant evaluations include, but are not limited to: evaluations to determine disposal options for sediment dredged from harbors and navigation channels; evaluations of the potential for sediments to be toxic to aquatic organisms downstream of a spill or where there is an ongoing surface water contamination problem; evaluations to determine whether sediment is subject to beneficial reuse or requires special disposal management; or evaluating proper management of sediments that have been impounded behind a dam.

Where do we get Sediment Contaminant Data?

The Division of Surface Water may generate its own sediment contaminant data, or may receive external sediment contaminant data from government agencies, consultants, or private industry. The potential impacts of the sediment contaminants on human health or aquatic life are evaluated the same way regardless of the data source.

Ohio's Credible Data law may require data used for certain regulatory decisions, such as use designations, water quality reports, or TMDLs, to be considered level 3 credible data. For questions regarding credible data, refer to sections 6111.50 to 6111.56 of the Ohio Revised Code.

How do we Collect Sediment Contaminant Data?

Sediment sampling guidance for the Division of Surface Water can be found at: http://www.epa.ohio.gov/portals/35/guidance/sedman2001.pdf, Sediment Sample Guide and Methodologies, Second Edition, Division of Surface Water, November 2001.

In addition to the methodologies found in the referenced 2001 guidance, when collecting sediment for contaminant evaluation, additional samples should be collected for organic carbon and acid volatile sulfide (AVS) analyses.

Organic carbon measurements are used in Tier II of the sediment contaminant evaluation process to better estimate the bioavailability of contaminants. Acid volatile sulfide concentrations are a component of Tier II evaluations of the bioavailability of metals in sediments.

Sample Collection, Preservation and Storage for TOC

Samples can be collected in plastic bags (of zipper-lock variety), borosilicate glass jars with screw tops, or Teflon bottles. They should be maintained at 4 $^{\circ}$ C and analyzed within six months from collection.

Sample Collection, Preservation and Storage for AVS

Since the sulfide ion is unstable in the presence of oxygen, sediment samples collected for AVS analysis must be protected from exposure to oxygen during the sample collection and storage process. Sulfide can be formed or lost due to biological activity during storage and sulfide can be lost by volatilization or oxidation. Metal speciation can change as a result of changes in sulfide concentration and other changes in the sample.

Samples should be collected in wide mouth jars with a minimum of air space above the sediment. If possible, the headspace should be filled with oxygen free nitrogen or argon. The jar lids must have Teflon or polyethylene liners.

Samples should be cooled to 4 $^{\circ}$ C as soon as possible after collection. They should be maintained at 4 $^{\circ}$ C and analyzed within 14 days from collection.

Why are Data Quality Objectives Important to Sediment Contaminant Data?

When collecting sediment samples for contaminant evaluation, following the Standard Operating Procedures (SOPs) as referenced above, and sending the samples for analysis to Ohio EPA's Laboratory (DES), will help ensure that the Division's Data Quality Objectives (DQOs) for sample collections and parameter analyses are met.

It is important to ensure that Ohio EPA's DQOs will be met when working with an external organization regarding sample collection for sediment contaminant evaluations. The laboratory reporting limits (RLs) should be below the level of concern for each

chemical being analyzed. In cases where the analytical reporting limit is above the level of concern for a chemical, the analytical method that provides the lowest possible reporting limit should be used.

Meeting DQOs is necessary in order to determine if sediment contamination could adversely impact human health and/or aquatic life. Deficient DQOs may result in the sediment data being inadequate for evaluating the potential effects of the contaminants, and could also result in the need for re-sampling and/or further testing, at a potentially substantial cost.

For a thorough discussion of the DQO process at a project-scoping level, see U.S. EPA's <u>Guidance on Systematic Planning Using the Data Quality Objectives Process</u> at http://www.epa.gov/QUALITY/qs-docs/g4-final.pdf

How do we Evaluate Sediment Contaminant Data?

Note: The tiers presented here differ from those used in other guidance documents, such as the U.S. Army Corps' testing manuals, and are presented for use only in conjunction with this guidance document.

Preliminary

Before entering a Tier I assessment, the reviewer should determine whether humans or aquatic life, or both, could be exposed to the sediment. The following figure illustrates a decision-making flowchart for evaluating sediment contaminant data relative to human health and aquatic life:

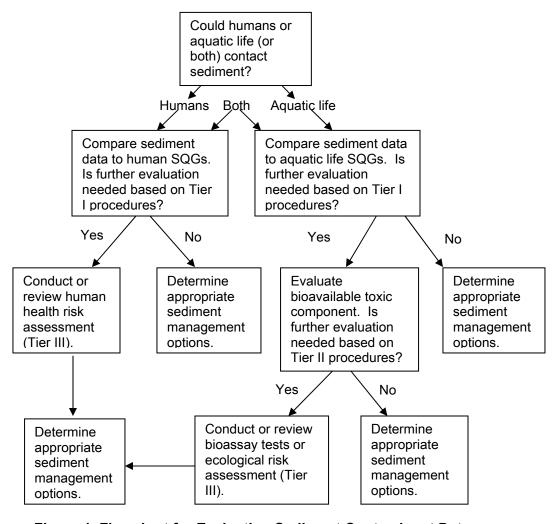


Figure 1 Flowchart for Evaluating Sediment Contaminant Data

The other step the reviewer needs to take is to determine what, if any, statistical analyses to perform on the data prior to evaluation. There is not a single statistical approach that will fit all scenarios, and each assessment tier may require a different calculation depending on the assumptions made.

In some cases, it may be prudent to use the maximum contaminant concentrations as data points in each tier. Other options include but are not limited to a 95% Upper Confidence Limit (UCL), a Surface Area Weighted Concentration (SWAC), an arithmetic mean, or a geometric mean.

Generally, a maximum contaminant concentration provides the most conservative evaluation option for Tier I assessments. Tier II assessments may need to be performed using an average contaminant concentration, or assessments may be made on a sample-by-sample basis to determine potential hot spots of contamination. Tier III assessments typically utilize either a 95% UCL, or a SWAC.

A more thorough discussion of sample design and data assessment for sediment can be found in Ohio EPA, Division of Surface Water's Sediment Sample Guide and Methodologies (2001).

Background Contamination

For the purposes of this guidance, background contamination is defined as contamination that occurs in sediment that is believed to be unimpacted by the processes that may have affected the target sediment samples. In order to determine if contamination exists above background levels, it will be necessary to collect and analyze background samples. The target contaminant levels can then be compared to the background sample data. For example, sample data may exist for locations where dredged materials are proposed to be placed, or data may exist for samples taken upstream of a facility suspected of contaminating sediment. In these cases, and using the decision tree illustrated in Figure 1, the target sample contaminant levels can be compared against the background contaminant levels to help determine whether to proceed to the next evaluation tier, or to the appropriate remediation or disposal option.

Tier I

The first step in evaluating sediment contaminant data is to compare the data to Sediment Quality Guidelines (SQGs). Sediment Quality Guidelines exist to be used as a benchmark below which the risk from a contaminant is expected to be *de minimis*. Sediment Quality Guidelines are of three types: those that consider the risk to human health, those that consider the risk to aquatic life, and those that evaluate anthropogenic contamination through comparison to background levels of a contaminant (generally metals).

If humans will be exposed to the sediment, then human risk should be evaluated. For example, if the sediment is in a stream or lake where people fish, canoe, wade or swim,

human risk should be taken into account. If the sediment will be placed in a dry location as fill that humans may be exposed to through direct contact, human risk should be evaluated. In this latter case, the evaluation should use Soil Screening Levels; for example, U.S. EPA Region IX Preliminary Remediation Goals for Soil (http://www.epa.gov/region09/waste/sfund/prg/files/04prgtable.pdf).

If aquatic life will be exposed to the sediment, such as in a contaminated stream, or dredged material to be redistributed in water, risk to aquatic life should be taken into account. Some circumstances may require both human health and aquatic life risks to be evaluated, such as in a stream with contaminated sediment to remain in place.

Sediment Quality Guidelines are available from a number of sources. Different sets of SQGs can be used, depending on the purpose of the assessment. Some sets of recommended SQGs are:

For human health:

The values for residential soil found in U.S. EPA Region IX Preliminary Remediation Goals, latest edition, http://epa-prgs.ornl.gov/chemicals/

For aquatic life:

Development and Evaluation of Consensus-based Sediment Quality Guidelines for Freshwater Ecosystems, D.D. MacDonald, C.G. Ingersoll, and T.A. Berger, Arch. Environ. Contam. Toxicol. 39, 20-31 (2000). Table 4.

U.S. EPA Region V Ecological Screening Levels, August 22, 2003, http://www.epa.gov/reg5rcra/ca/ESL.pdf

For metal contaminants:

Ohio EPA Sediment Reference Values, http://www.epa.ohio.gov/portals/30/rules/RR-031.pdf#page=70 Attachment H.

Tier I Decision Making

Sediment contaminant concentrations should be compared to the appropriate SQGs, as shown in Figure 1. One of two outcomes will be reached: 1) the sediment passes the screen (i.e., the sediment chemical concentrations are at or below the appropriate SQGs), the sediment is considered to be uncontaminated, or contaminated below levels of concern; or 2) the sediment does not pass the screen (i.e., the sediment chemical concentrations are above the appropriate SQGs), the sediment is considered to be contaminated above levels of concern, and a Tier II or III evaluation is needed.

For human health, if contaminants are found at concentrations above the SQGs, a Tier III evaluation should be performed.

For aquatic life, if contaminants are found at concentrations above the SQGs, a Tier II or Tier III evaluation should be performed.

Alternatively, for either the aquatic life or human health pathway, the sediment can be treated as though it were determined to be contaminated, and appropriate treatment or disposal options can be undertaken.

Ohio EPA does not regulate radiologically contaminated sediment. If the sediment contains detectable quantities of radiologic materials, contact the Ohio Department of Health, Bureau of Radiation Protection.

The SQGs do not address bioaccumulation issues via the fish consumption exposure pathway. The water quality standards, in the human health and wildlife numeric criteria for the water column, do take fish consumption exposures into account¹. Therefore, where bioaccumulative chemicals are present in sediment, it may be necessary to evaluate fish tissue and/or water column data in addition to sediment data in order to determine appropriate sediment management options.

Other sets of SQGs may also be useful as appropriate, but should be reviewed on a case-by-case basis for applicability.

<u>Tier II</u>

The second step in evaluating sediment data that exceeds SQGs is to estimate how the bioavailability of the contaminants affect the toxicity to aquatic life. U.S. EPA has several sets of guidance that can be used to evaluate sediment data, available from: http://www.epa.gov/waterscience/cs/library/guidelines.htm

For sediment, bioavailability of most contaminants is estimated using Equilibrium Partitioning Sediment Benchmarks (ESBs). U.S. EPA has ESB guidance documents for PAHs, nonionic organics, dieldrin, and Endrin, and metals. PCB bioavailability is estimated based on Theoretical Bioaccumulative Potential, also described in this section.

To develop ESBs for sediment for Polycyclic Aromatic Hydrocarbons (PAHs), dieldrin, Endrin, and nonionic organics, the Total Organic Carbon (TOC) content of the sediment is needed. TOC is used to normalize the amount of contaminant per gram of organic carbon, which is then compared against the Final Chronic Value (FCV) for the contaminant.

¹ The human health criteria assume some consumption of local fish. The wildlife criteria assume consumption of local fish by upper trophic level animals (e.g., mink, blue heron).

PAHs

For PAHs, the first step in developing ESBs is to convert TOC concentration of the sediment to a Fraction Organic Carbon (f_{OC}). This is done by dividing TOC by 100. For example, when the sediment TOC = 0.81%:

TOC = 0.81%
$$\frac{0.81\%}{100}$$
 = 0.0081 f_{OC} = 0.0081

Step two is to divide the concentrations of the detected PAHs in $\mu g/g$ by the f_{OC} . For example:

Normalized PAH Concentrations

PAH	Concentration (μg/g)	foc	Normalized Concentration (µg/goc)
Naphthalene	0.0894	0.0081	11.04
Pyrene	0.1710	0.0081	21.11
Fluoranthene	0.0806	0.0081	9.951
Benzo(a)pyrene	0.1640	0.0081	20.25

Example
$$\frac{0.0894\mu g/g \ naphthalene}{0.0081} = 11.04 \ \mu g/g_{OC}$$

Step three is to determine an ESB Toxic Unit (ESBTU) by taking the normalized concentration for each PAH calculated in step 2 and dividing that by its corresponding Final Chronic Value found in Table 1.

However, if the normalized concentration for a specific PAH exceeds its maximum concentration listed in Table 1, use the maximum concentration in the ESB calculation instead of the normalized concentration.

Equilibrium Sediment Benchmark Toxic Unit Calculations

PAH	Normalized	Final Chronic Value	ESB Toxic Unit
	Concentration	from Table 1	
	(µg/g _{oc})	(µg/g _{OC})	
Naphthalene	11.04	385	0.0287
Pyrene	21.11	697	0.0303
Fluoranthene	9.951	707	0.0141
Benzo(a)pyrene	20.25	965	0.0210

Example
$$\frac{11.04 \,\mu g/g_{oc}}{385 \,\mu g/g_{oc}} = 0.0287 \,ESBTU \,Naphthalene$$

Step four is to sum the ESBTUs.

Example $0.0287 + 0.0303 + 0.0141 + 0.0210 = \Sigma ESBTU$

Step five is to apply an uncertainty factor, if needed, to the Σ ESBTU. The uncertainty factor may be needed because the ESB methodology assumes that the "total PAH" analysis includes 34 PAH compounds. However, some analyses include fewer than 34 compounds, commonly 13 or 23. Therefore, Table 2 contains suggested uncertainty factors to apply depending on the number of PAHs analyzed. The uncertainty factor should be chosen based on the number of PAHs analyzed, if less than 34, and the level of certainty required, usually 90 or 95%². If all 34 PAHs are analyzed, no uncertainty factor is required, and therefore no specific level of certainty need be determined. To apply the uncertainty factor, multiply the Σ ESBTU by the selected uncertainty factor, which then becomes an adjusted Σ ESBTU.

If the adjusted Σ ESBTU is less than 1, it is likely that the sediment will not be toxic to aquatic life. If the adjusted Σ ESBTU is 1 or greater, the sediment may be toxic to aquatic life, and further testing or more information is necessary to determine appropriate sediment management options.

Nonionic Organic Chemicals

Nonionic organic chemicals, for example, benzene, pesticides, and chlorinated solvents, each have an individual toxicity factor much like other chemicals. However, each nonionic organic chemical also has a relative narcosis factor, which has an additive effect with other nonionic organic chemicals. Therefore, when evaluating the toxicity of nonionic organic chemicals to aquatic life, both the conventional toxicity and the narcosis potential need to be assessed. (For more information on narcosis or additivity, see U.S. EPA, 2008, Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Compendium of Tier 2 Values for Nonionic Organics.)

Table 3 lists, in $\mu g/g_{OC}$, both conventional and narcosis ESBs for many nonionic organic chemicals. When evaluating nonionic organic chemicals in sediment, the first step is to calculate a normalized concentration for each nonionic organic chemical following the same procedures as shown in steps one and two in the preceding PAH section.

Step three is to use Table 3 to find the conventional and narcosis ESBs for each nonionic organic chemical. Each normalized concentration is then divided by the two corresponding ESBs to obtain the ESB Toxic Units. For example:

² Level of certainty may be determined as a matter of programmatic policy, or by weight of evidence for the specific situation.

Nonionic Organic Chemical Equilibrium Sediment Benchmark Calculations

Nonionic Organic	Normalized	Sediment	Sediment
Chemical	Concentration	Concentration/	Concentration/Narcosis
	(µg/g _{OC})	Conventional ESB	ESB
Benzene	0.9526	0.0595	0.0014
Pentachlorobenzene	2.304	0.0329	0.0014
Tetrachloroethene	0.5316	0.0130	0.0006
Malathion	0.0129	0.1925	N/A

Example
$$\frac{0.9526 \,\mu g/g_{oc}}{16 \,\mu g/g_{oc}} = 0.0595$$
 Conventional ESBTU Benzene

$$\frac{0.9526 \, \mu g/g_{oc}}{660 \, \mu g/g_{oc}} = 0.0014 \, \text{Narcosis ESBTU Benzene}$$

Step four is to sum the Narcosis ESBTUs.

Example
$$0.0014 + 0.0014 + 0.0006 = 0.0034 Narcosis \Sigma ESBTU$$

If the sediment concentration divided by the conventional ESB for any individual nonionic organic chemical is less than 1, it is likely that the sediment will not be toxic to aquatic life. If the sediment concentration divided by the conventional ESB is 1 or greater, the sediment may be toxic to aquatic life, and further testing or more information is necessary to determine appropriate sediment management options.

If the sum of the Narcosis ESBTUs is less than 1, it is likely that the sediment will not be toxic to aquatic life. If the sum of the Narcosis ESBTUs is 1 or greater, the sediment may be toxic to aquatic life, and further testing or more information is necessary to determine appropriate sediment management options.

The conventional ESBTU for each individual chemical and the narcosis ESBTU sum must be less than 1 for the sediment to be considered likely to be not toxic. If either the conventional or the Narcosis ESBTU sums are above 1, the evaluation should continue to Tier III.

Dieldrin and Endrin have their own, separate guidance documents, but for the purpose of this document, the relevant ESBs have been added to Table 3.

Metals

Metal toxicity is evaluated through an indirect estimate of bioavailability based on concentrations of Simultaneously Extracted Metals (SEM).

The first step in evaluating metal toxicity is to determine the concentration of each SEM in µmol. This is done using the following equation and molar masses:

Equation 1
$$\frac{x \mu g}{y \mu g/\mu mol} = z \mu mol$$

Where x is the metal concentration, y is the molar mass, and z is the amount of metal in micromoles.

Metal	Molar Mass
Cadmium (Cd)	112.41
Copper (Cu)	63.546
Lead (Pb)	207.2
Nickel (Ni)	58.693
Zinc (Zn)	65.38
Silver (Ag)	107.86

The second step is to sum the moles of SEM, as follows:

Equation 2
$$\Sigma[SEM] = SEM_{Cd} + SEM_{Cu} + SEM_{Pb} + SEM_{Ni} + SEM_{Zn} + \frac{1}{2}SEM_{Ag}$$

Note that the SEM for silver is halved, because it is a monovalent cation, whereas the others are divalent cations.

If organic carbon data are available, the third step is to calculate (ΣSEM-AVS)/f_{oc}.

Metals Example

Simultaneously Extracted Metals Molar Calculations

Metal	Conc. (µg/kg)	Molar Mass	µmol/kg
Cadmium (Cd)	42000	112.41	373.63
Copper (Cu)	21100	63.546	332.04
Lead (Pb)	17000	207.2	82.046
Nickel (Ni)	17000	58.693	289.64
Zinc (Zn)	114000	65.38	1743.6
Silver (Ag)	18000	107.86	166.88

AVS = 1
$$\mu$$
mol/g f_{oc} = 0.0081

$$\Sigma SEM = 373.63 + 332.04 + 82.046 + 289.64 + 1743.6 + (0.5)(166.88) = 2904.4 \frac{\mu mol}{kg} SEM$$

$$\frac{2904.4 \ \mu mol/kg}{1000 \ g/kg} = 2.9044 \ \mu mol/g$$

$$\frac{2.9044 \ \mu mol/g \ SEM - 1 \ \mu mol/g \ AVS}{0.0081} = 235.11 \ \mu mol/g_{oc}$$

Where $(\Sigma SEM-AVS)/f_{oc}$ is less than 130 μ mols/ g_{oc} , there is little to no risk to aquatic life. Where $(\Sigma SEM-AVS)/f_{oc}$ is between 130 and 3000 μ mols/ g_{oc} , further testing and/or more information is needed to determine the risk to aquatic life. Where $(\Sigma SEM-AVS)/f_{oc}$ is greater than 3000 μ mols/ g_{oc} , there is a likely risk of toxicity to aquatic life.

Since 235.11 μ mols/ g_{oc} falls within the range of possible toxic effects to aquatic life, the evaluations should progress to Tier III.

If organic carbon data are not available, the third step is to compare the ΣSEM from the equation above to the concentration of Acid Volatile Sulfide. Where ΣSEM is less than or equal to AVS, aquatic life toxicity is unlikely to occur. If the ΣSEM is greater than the AVS concentration, then aquatic life toxicity may occur, and sediment management options that limit exposure to aquatic life should be considered, or the evaluation should proceed to Tier III.

PCBs

PCBs can be evaluated using the Theoretical Bioaccumulation Potential (TBP) method described in the <u>Great Lakes Dredged Material Testing and Evaluation Manual</u> (U.S. EPA, 1998).

TBP is intended to take into account the bioavailability of non-polar organic contaminants, including PCBs, to approximate the level of contamination that may accumulate in organisms exposed to sediment.

TBP can be calculated using the following equation:

Equation 3
$$TBP = BSAF \times L \times \frac{C_S}{TOC}$$

Where:

TBP = wet weight of contaminant concentration in fish or organism tissue in mg/kg

BSAF = biota-sediment accumulation factor (default = 4.0)

C_s = concentration of non-polar organic chemical in the dredged material or disposal site sediment, usually expressed as dry weight mg/kg (for PCBs, should reflect total PCBs in sediment, either total congeners or total Aroclors)

TOC = total organic carbon content of the sediment usually expressed as a dry weight decimal fraction (i.e., 2% = 0.02)

L = organism lipid content usually expressed as a decimal (wet weight fraction)

The first step of calculating a TBP for PCBs in sediment is to determine a BSAF. A discussion of how to determine a biota-sediment accumulation factor, as well as a limited number of measured BSAFs, can be found in <u>Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors</u> (U.S. EPA 1995). In the absence of a measured or site-specific BSAF, a default value of 4 should be used (<u>Great Lakes Dredged Materials Testing and Evaluation Manual</u>, U.S. EPA 1998).

When calculating a TBP for PCBs in sediment, the second step is to determine the lipid levels of the target organism. The lipid levels can be measured, for example if fish tissue lipid data are available for the location where the sediment was collected. If measured lipid levels are unavailable, then default lipid levels can be selected. Default lipid levels for select species can be found in several sources, including Section 6 of Appendix C of the Great Lakes Dredged Material Testing and Evaluation Manual (U.S. EPA, 1998), Appendix I of the Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors (U.S. EPA 1995), and Trophic Level and Exposure Analyses for Selected Piscivorous Birds and Mammals, Volume III: Appendices (U.S. EPA, 2002). Default lipid levels can also be found in Table 5 of this document.

The third step is to calculate the TBP using BSAF, the organism lipid content, the sediment PCB concentration, and the sediment TOC. However, if the TOC is less than 0.005 (0.5%), the TBP evaluation is not valid, and analysis should proceed to Tier III.

PCB Example

Parameter	Value	Units
BSAF	4.0	unitless
C_s	2	Mg/kg
TOC	0.03	unitless
L	0.06	unitless

$$TBP = 4 \times 0.06 \times \frac{2 \, mg/kg}{0.03} = 16 \, mg/kg$$

In the above example, sediment with 2 mg/kg dry weight PCBs and 3% TOC has the potential to cause a fish with 6% lipid to have a PCB body burden of 16 mg/kg wet weight.

The fourth step is to compare the TBP to the relevant tissue benchmark for PCBs. The two most commonly used benchmarks are fish tissue levels that trigger fish consumption advisories (see Table 6), or fish tissue levels that are back-calculated from human health water quality criteria (see Table 7). Where the TBP exceeds these PCB levels, appropriate sediment management options should be considered, or the analysis should progress to Tier III.

Tier III

Human Health

If a Tier I evaluation indicates that sediment contaminants may be toxic to human health, and there exists a potential exposure pathway between humans and the sediment, a human health risk assessment should be conducted that quantifies the potential risks of exposure to the sediment.

For help with reviewing or conducting human health risk assessments, contact Central Office, Division of Surface Water, Standards and Technical Support Section.

Aquatic Life

If a Tier II evaluation indicates that sediment contaminants may be toxic to aquatic life, a Tier III evaluation may be conducted.

A Tier III evaluation most often involves conducting bioassays to determine if sediment is toxic to various test organisms that are thought to be representative of in situ aquatic life. U.S. EPA and U.S. Army Corps of Engineers have numerous technical guidance documents detailing bioassay testing, available at: http://www.epa.gov/waterscience/cs/pubs.htm. Further discussion of bioassays is

<u>http://www.epa.gov/waterscience/cs/pubs.htm</u>. Further discussion of bioassays is beyond the scope of this document. If bioassay testing and evaluation is needed, refer to the manuals at the given web link.

As an alternative to conducting a Tier III evaluation, it can be assumed that the sediment in question is toxic to aquatic life. In this case, steps to eliminate or minimize that toxicity can be taken, including but not limited to:

- 1) appropriate sediment removal or disposal;
- 2) sediment remediation; or
- 3) leaving the contaminated sediment in place if current bioavailability is limited or disturbance would increase long-term toxic potential.

A second alternative to conducting a Tier III evaluation is to measure the concentration of contaminants in the interstitial pore water contained within the sediment. A number of the guidance documents referenced in this document (see reference section for a complete list) discuss the techniques involved in interstitial pore water analysis, as well as the merits and shortcomings of measuring interstitial pore water contamination. These guidance documents should be consulted prior to conducting an interstitial pore water analysis or an evaluation of the results of such analyses.

Briefly, measuring the levels of contaminants in interstitial pore water is thought to be a more accurate reflection of exposure of aquatic organisms to sediment contamination than bulk sediment contaminant comparisons. This is because it inherently accounts for the bioavailability of the contaminants to the organisms. Sometimes interstitial pore water is extracted from sediment samples directly, usually through centrifugation. Another technique for measuring interstitial pore water is using Solid Phase Micro-Extraction (SPME), in which a polymer fiber is inserted directly into contaminated sediment until equilibrium is reached, at which point the adhered contaminants are stripped off and analyzed in the laboratory.

Whichever technique is used to measure interstitial pore water contamination, the laboratory will typically report results back in units of $\mu g/L$. Those results can then be compared directly to the Water Quality Criteria to determine if there are any exceedences.

Table 1. PAH Equilibrium Partitioning Sediment Benchmarks

РАН	Final Chronic Value	Maximum
	(µg/g _{oc})	(µg/g _{oc})
Indan	349	127200
Naphthalene	385	61700
C1-naphthalenes	444	
1-methylnaphthalene	446	165700
2-methylnaphthalene	447	154800
Acenaphthylene	452	24000
Acenaphthene	491	33400
1-ethylnaphthalene	507	142500
2-ethylnaphthalene	509	129900
C2-naphthalenes	510	
1,4-dimethylnaphthalene	510	192300
1,3-dimethylnaphthalene	513	157100
2,6-dimethylnaphthalene	513	33800
2,3-dimethylnaphthalene	513	49900
1,5-dimethylnaphthalene	514	62400
Fluorene	538	26000
C3-naphthalenes	581	
2,3,5-trimethylnaphthalene	584	
1,4,5-trimethylnaphthalene	584	129300
Anthracene	594	1300
Phenanthrene	596	34300
C1-fluorenes	611	
1-methylfluorene	612	49700
C4-naphthalenes	657	
2-methylanthracene	667	2420
1-methylanthracene	667	
9-methylanthracene	668	21775
2-methylphenanthrene	669	
1-methylphenanthrene	670	24100
C1-phenanthrene/anthracenes	670	
9-ethylfluorene	673	
C2-fluorenes	686	
Pyrene	697	9090
Fluoranthene	707	23870
2-ethylanthracene	739	
C2-phenanthrene/anthracenes	746	
9,10-dimethylanthracene	748	14071
3,6-dimethylphenanthrene	749	
C3-fluorenes	769	
C1-pyrene/fluoranthenes	770	

PAH	Final Chronic Value	Maximum
	(µg/g _{oc})	(µg/g _{oc})
2,3-benzofluorene	787	558
Benzo(a)fluorene	787	12500
C3-phenanthrene/anthracenes	829	
Napthacene	838	207
Benz(a)anthracene	841	4153
Chrysene	844	826
Triphenylene	846	19400
C4-phenanthrene/anthracenes	913	
C1-benzanthracene/anthracenes	929	
C3-pyrene/fluoranthenes	949	
Benzo(a)pyrene	965	3840
Perylene	967	431
Benzo(e)pyrene	967	4300
Benzo(b)fluoranthene	979	2169
Benzo(j)fluoranthene	981	3820
Benzo(k)fluoranthene	981	1220
C2-benzanthracene/chrysenes	1008	
9,10-dimethylbenz(a)anthracene	1021	124200
7,12-dimethylbenz(a)anthracene	1021	145300
7-methylbenzo(a)pyrene	1058	
Benzo(ghi)perylene	1095	648
C3-benzanthracene/chrysenes	1112	
Indeno(1,2,3-cd)pyrene	1115	
Dibenz(a,h)anthracene	1123	2389
Dibenz(a,j)anthracene	1123	47680
Dibenz(a,c)anthracene	1129	7400
C4-benzanthracene/chrysenes	1214	
C1-dibenz(a,h)anthracenes	1221	
Coronene	1230	821
C2-dibenz(a,h)anthracenes	1325	
C3-dibenz(a,h)anthracenes	1435	
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From: U.S. EPA's <u>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures, Office of Research and Development, November 2003, EPA/600/R-02/013. http://www.epa.gov/nheerl/publications/files/PAHESB.pdf</u>

Table 2. PAH Uncertainty Factors

Percentile	13 PAH Uncertainty factor	23 PAH Uncertainty factor
50	2.75	1.64
80	6.78	2.8
90	8.45	3.37
95	11.5	4.14
99	16.9	6.57

From: U.S. EPA's <u>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures</u>, Office of Research and Development, November 2003, EPA/600/R-02/013. http://www.epa.gov/nheerl/publications/files/PAHESB.pdf

Table 3. Nonionic Organic Chemical Equilibrium Partitioning Sediment Benchmarks

Chemical	Conventional ESB (µg/g _{oc})	Narcosis ESB (μg/g _{oc})
Benzene	16	660
BHC other than Lindane	11	
Gamma-BHC, Lindane	0.37	
Biphenyl	110	1500
4-Bromophenyl phenyl ether	120	1600
Butyl benzyl phthalate	1100	
Chlorobenzene	41	570
Diazanon	0.74	
Dibenzofuran	37	1700
1,2-Dichlorobenzene	33	780
1,3-Dichlorobenzene	170	780
1,4-Dichlorobenzene	34	780
Di-n-butyl phthalate	1200	
Diethyl phthalate	77	
Endosulfan mixed isomers	0.6	
Alpha-Endosulfan	0.33	
Beta-Endosulfan	1.6	
Ethylbenzene	8.9	970
Hexachloroethane	100	1400
Malathion	0.067	
Methoxychlor	1.9	
Pentachlorobenzene	70	1600
1,1,2,2-Tetrachloroethane	140	830
Tetrachloroethene	41	840
Tetrachloromethane	120	770
Toluene	5.0	810
Toxaphene	10	
Tribromomethane (Bromoform)	65	1200
1,2,4-Trichlorobenzene	960	1100
1,1,1-Trichloroethane	3.0	660
Trichloroethene	22	650
m-Xylene	94	980
Dieldrin	12	
Endrin	5.4	C II

From: U.S. EPA's <u>Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks</u> (ESBs) for the Protection of Benthic Organisms: Compendium of Tier 2 <u>Values for Nonionic Organics</u>, Office of Research and Development, March 2008, EPA/600/R-02/016.

http://www.epa.gov/nheerl/publications/files/ESB Compendium v14 final.pdf

Table 4. Sediment Quality Guidelines in Freshwater Ecosystems that Reflect TECs

Substance	Threshold Effect Concentrations
Metals (in mg/kg Dry Weight)	
Arsenic	9.79
Cadmium	0.99
Chromium	43.4
Copper	31.6
Lead	35.8
Mercury	0.18
Nickel	22.7
Zinc	121
Polycyclic Aromatic Hydrocarbons (in μg/kg Dry Weight)	
Anthracene	57.2
Fluorene	77.4
Naphthalene	176
Phenanthrene	204
Benz(a)anthracene	108
Benzo(a)pyrene	150
Chrysene	166
Dibenzo(a,h)anthracene	33.0
Fluoranthene	423
Pyrene	195
Total PAHs	1610
Polychlorinated Biphenyls (in µg/kg Dry Weight)	
Total PCBs	59.8
Organochlorine Pesticides (in μg/kg Dry Weight)	
Chlordane	3.24
Dieldrin	1.90
Sum DDD	4.88
Sum DDE	3.16
Sum DDT	4.16
Total DDTs	5.28
Endrin	2.22
Heptachlor Epoxide	2.47
Lindane (gamma-BHC)	2.37

From: <u>Development and Evaluation of Consensus-based Sediment Quality Guidelines for Freshwater Ecosystems</u>, D.D. MacDonald, C.G. Ingersoll, and T.A. Berger, Arch. Environ. Contam. Toxicol. 39, 20-31 (2000).

Table 5. Median lipid levels by species, 1998-2006

Species	Median Lipid Levels (%)
Black Crappie	0.33
Black Redhorse	3.2
Bluegill Sunfish	0.41
Common Carp	3.86
Freshwater Drum	2.7
Golden Redhorse	1.29
Green Sunfish	0.58
Largemouth Bass	0.37
Longear Sunfish	2.15
Northern Hog Sucker	0.99
Northern Pike	0.44
Pumpkinseed Sunfish	0.33
Quillback Carpsucker	1.78
Rainbow Trout	6.66
Redear Sunfish	0.4
Rock Bass	0.37
Sauger	1.0
Saugeye	0.68
Shorthead Redhorse	10.3
Silver Redhorse	2.1
Smallmouth Bass	0.77
Smallmouth Buffalo	4.3
Spotted Bass	0.43
Spotted Sucker	1.39
Striped Bass Hybrid	1.28
Walleye	1.73
White Crappie	0.31
White Sucker	1.35
Yellow Perch	0.38

From: Ohio EPA. State Of Ohio: Cooperative Fish Tissue Monitoring Program: Sport Fish Tissue Consumption Advisory Program. May 2008. http://www.epa.ohio.gov/portals/35/fishadvisory/FishAdvisoryProcedure08.pdf

Table 6: Ohio Fish Consumption Advisory Chemicals: Fillet Chemical Upper Bound Limit Concentrations (ppm) and Advisory Meal Consumption Rate Using the Great Lakes' Governors Procedure *

Chamical (DfD ug/kg/day)	Unrestricted	1/week	1/month	Ghaor	Do Not Eat
Chemical (RfD μg/kg/day)				6/year	
Aldrin (0.03)	<0.030	0.131	0.568	1.135	>1.135
Total Arsenic (0.3)	<0.150	0.656	2.838	5.676	>5.676
Total Cadmium (1.0)	<0.500	2.188	9.459	18.91	>18.919
Total Chlordane (0.5)	<0.500	2.188	9.459	18.919	>18.919
Total DDT (0.5)	<0.500	2.188	9.459	18.919	>18.919
Dieldrin (0.05)	<0.050	0.220	1.000	1.999	>1.999
Endosulfan (6.0)	<6.000	26.250	131.514	227.027	>227.027
Endrin (0.30)	<0.300	1.313	5.676	11.351	>11.351
Heptachlor (0.5)	<0.500	2.188	9.459	18.919	>18.919
Heptachlor Epoxide (0.013)	<0.013	0.057	0.246	0.492	>0.492
Hexachlorobenzene (0.8) **	<0.800	3.500	15.135	30.270	>30.270
Total Lead (6.0)	<0.086	0.375	1.622	3.243	>3.243
Lindane (6.0)	<0.3	1.313	5.676	11.315	>11.315
Methoxychlor (5.0)	<5.000	21.875	94.545	189.189	>189.189
Mirex (0.2)	<0.200	0.875	3.784	7.568	>7.568
Methylmercury (0.1)	Unrestricted	2/week	1/week	1/month	Do Not Eat
	<0.050	0.110	0.220	0.999	>1.000
Total PCBs (0.05) HPV **	<0.050	0.220	1.000	1.999	>1.999
Total SAS 305 (50.0) **	<50,000	218,750	945,946	1,891,892	>1,891,892
Total SAS 310 (28.6) **	<28,600	125,125	541,081	1,082,162	>1,082,162
Total Selenium (5.0)	<2.500	10.938	47.927	94.545	>94.545
Toxaphene (0.25)	<0.250	1.094	4.730	9.459	>9.45

^{*} Concentrations are reported in mg/kg (ppm) raw fish fillet wet weight. Meal consumption rates are: No restrictions (225 meals/year); One meal/week (52 meals/year); One meal/month (12 meals/year); 6 meals/year; and Do not eat. All metals results are reported as Total metals, including Mercury. Total PCBs are reported as the sum of Aroclors 1016, 1221, 1232, 1242, 1248, 1254 and 1260; Total Chlordane is reported as the sum of Alpha-Chlordane, Gamma-Chlordane, Oxychlordane, cis-Nonachlor and trans-Nonachlor; Total DDT is reported as the sum of DDT and Metabolites (DDE and DDD).

** HPV = Health Protection Value; HCB = hexachlorobenzene; Total SAS 305 is a chemical mixture of the following alkylated biphenyls: o-isopropyl-1,1-diphenylethane, m-isopropyl-1,1-diphenylethane and p-isopropyl-1,2-diphenylethane; Total SAS 310 is a chemical mixture of the following alkylated biphenyls: o-sec Butyl diphenylmethane, m-sec Butyl diphenylmethane, p-sec Butyl diphenylmethane, o-sec Butyl 1,1-diphenyl-ethane, m-sec Butyl 1,1-diphenylethane, p-sec Butyl 1,1-diphenylethane, o-sec Butyl 1,2-diphenylethane, m-sec Butyl 1,2-diphenylethane, and p-sec Butyl 1,2-diphenylethane.

From: Ohio EPA. <u>State Of Ohio: Cooperative Fish Tissue Monitoring Program: Sport Fish Tissue Consumption Advisory Program</u>. May 2008. http://www.epa.ohio.gov/portals/35/fishadvisory/FishAdvisoryProcedure08.pdf

Table 7: Fish Tissue Concentrations for Determining Impairment for the 2008 Integrated Report (μg/kg)

	Lake Erie	Ohio River
	Basin	Basin
Mercury	350	1000
Chlordane	130	310
DDT	140	320
PCBs	23	54
Hexachloro-	29	67
benzene		

From: Ohio EPA. 2008. Ohio 2008 Integrated Water Quality Monitoring and Assessment Report. Section E. Division of Surface Water. May 5, 2008. http://www.epa.ohio.gov/dsw/tmdl/2008IntReport/2008OhioIntegratedReport.aspx

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