Screening and Assessment of Contaminated Sediment

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Division of Fish, Wildlife and Marine Resources
Bureau of Habitat

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Terms and Acronyms

Acute - A stimulus severe enough to induce a response rapidly. In aquatic toxicity tests, an effect observed in 96 hours or less is typically considered acute. In sediment toxicity tests, a ten day exposure is generally considered as acute. Mortality is the response usually measured.

ADI – Acceptable Daily Intake: the maximum concentration of a chemical in food that a bird or animal can consume without exceeding a dietary risk value.

AET – Apparent Effects Threshold: The AET is the highest concentration of a contaminant in sediment where no effects were observed, but effects are observed at every higher concentration.

AVS – Acid Volatile Sulfides: The sulfide liberated from wet sediment when treated with cold 1N HCl acid.

AWQS/GV – Ambient Water Quality Standard/Guidance Value: A water quality standard published in 6NYCRR Part 703 or a water quality guidance value published in TOGS 1.1.1.

BAF – Bioaccumulation Factor: The ratio (in liters per kilogram) of a substance's concentration in the tissue of an aquatic organism to its concentration in the ambient water.

BSGV – Bioaccumulation Sediment Guidance Value: A sediment guidance value used to identify contaminant concentrations in sediment that could potentially be toxic to higher trophic level organisms through aquatic food chain bioaccumulation.

Chronic – A stimulus that lingers or continues for a relatively long period of time, often one-tenth of a life span or more. Chronic should be considered a relative term depending on the life span of the test organism. The measurement of a chronic effect can be reduced growth, reduced reproduction, etc., in addition to lethality.

DOC – Dissolved Organic Carbon: The concentration of organic carbon dissolved in water.

ERL – Effects Range Low: The 10^{th} percentile concentration in a range of sediment concentrations for a given contaminant wherein adverse biological effects were observed.

ERM – Effects Range Median: The 50^{th} percentile concentration in a range of sediment concentrations for a given contaminant wherein adverse biological effects were observed.

Fish flesh criterion – The concentration of a contaminant in the tissue of fish that, if exceeded, could potentially be harmful to terrestrial wildlife that consume the fish.

K_{OC} – Organic carbon partitioning coefficient: A measure of the concentration of a contaminant that adsorbs to the organic carbon content of sediment divided by the concentration dissolved in water, after mixing.

K_{OW} – Octanol water partitioning coefficient: The ratio of a chemical's solubility in *n*-octanol and water at equilibrium.

LEL – Lowest Effects Level: The concentration of a contaminant tolerated by 95% of benthic species (see Screening Level Concentration).

LOEL – Lowest Observed Effects Level: The lowest exposure level at which there are statistically or biologically significant increases in frequency or severity of an effect between the exposed population and its appropriate control group.

NOEL – No observed Effects Level: The highest exposure level at which there are no statistically or biologically significant increases in the frequency or severity of any effect between the exposed population and its appropriate control.

PEC – Probable Effects Concentration: A consensus sediment quality guideline derived by taking the geometric mean of similar sediment quality guidelines with the same narrative intent. For the Probable Effects Concentration, the narrative intent is concentrations of contaminants in sediment that above which, adverse impacts would be expected to occur frequently.

PEL – Probable Effects Level: The geometric mean of the 50^{th} percentile of concentrations of contaminants found to have biological effects in different tests and the 85^{th} percentile of the concentrations of contaminants in tests for which no biological effects were reported.

PEL-HA28 – Probable Effects Level-*Hyalella azteca* 28: The Probable Effects Level derived from only one type of biological effect, the result of a 28 day sediment toxicity test with the amphipod *Hyalella azteca*.

POC – Particulate Organic Carbon: The concentration of organic carbon suspended in water in a particulate form.

SEL – Severe Effects Level: The concentration of a contaminant tolerated by only 5% of benthic species (see Screening Level Concentration).

SEM – Simultaneously Extracted Metal: The total concentration of metals (cadmium, copper, lead, nickel, silver, and zinc) extracted simultaneously with acid volatile sulfide when wet sediment is treated with cold 1N HCl acid.

SGV – Sediment Guidance Value: Numeric concentrations of individual contaminants in sediment used in New York State to classify sediment based on the potential for adverse impacts to aquatic life.

SGV_{OC} – A Sediment Guidance Value expressed in units of microgram (μg) of contaminant per gram of organic carbon.

SLC – Screening Level Concentration: A type of sediment quality guideline based on the tolerance of a specific proportion of benthic species to contaminants in sediment.

SPME – Solid Phase Microextraction: A method for extracting contaminants directly from sediment pore water using a glass fiber coated with poly-dimethylsiloxane (PDMS), which is inserted into the sediment sample and allowed to equilibrate.

SQG – Sediment Quality Guideline: A chemically based numerical value or narrative statement designed to protect benthic organisms; support or maintain designated uses of freshwater, estuarine, and marine environments; and to assist sediment assessors and managers charged with the interpretation of sediment quality.

SQT – Sediment Quality Triad: An approach for evaluating sediment contamination based on three factors, bulk sediment chemistry, sediment toxicity testing, and benthic macroinvertebrate community analysis.

TEC – Threshold Effects Concentration: A consensus sediment quality guideline derived by taking the geometric mean of similar sediment quality guidelines with the same narrative intent. For the Threshold Effects Concentration, the narrative intent is concentrations of contaminants in sediment that below which, no adverse impacts would be anticipated.

TEL – Threshold Effects Level: The geometric mean of the 15^{th} percentile of concentrations of contaminants found to have biological effects in different tests and the 50^{th} percentile of the concentrations of contaminants in tests for which no biological effects were reported.

TEL-HA28 – Threshold Effects Level-*Hyalella azteca* 28: The Threshold Effects Level derived from only one type of biological effect, the result of a 28 day sediment toxicity test with the amphipod *Hyalella azteca*.

TOC – Total Organic Carbon: The fraction of organic carbon in sediment, usually given as a percentage.

TOGS - Technical Operational Guidance Series. Technical Guidance documents published by the Division of Water. TOGS 1.1.1 is a listing of established ambient water quality guidance values. TOGS 1.1.4 describes New York State procedures for deriving bioaccumulation factors. TOGS 5.1.9 establishes policies for in-water and riparian management of sediment and dredged material. TOGS are available from the NYSDEC website at: http://www.dec.ny.gov/regulations/2652.html

1. Purpose

Protection of ecological resources, specifically, fish, wildlife, and habitat thereof within New York State is a responsibility of The Division of Fish, Wildlife and Marine Resources (DFWMR). Division staff in the Regions and Central Office may become involved in projects relating to the evaluation of contaminant concentrations in sediment (and other media, such as water, soil, wetlands, etc.), and for assessing the potential risk from such contaminants to aquatic or marine life. This document is intended to provide information and guidance to Division staff for screening, classifying and assessing contaminated sediments in New York State; that is, for determining whether or not a given sediment is toxic and poses a risk to aquatic[1] life.

This document does not discuss background (concentrations that are either naturally occurring or common over the larger geographic area), or identification of the source of contaminants in sediment . The purpose of this document is limited to describing procedures for assessing whether or not contaminants present in sediment at a given site have the potential to pose a risk to aquatic life, regardless of their source or the similarity of contaminant concentrations in the larger area.

In addition to identifying specific numerical sediment guidance values, this document explains the technical basis for the derivation of the guidance values selected, and explains how those values can be modified as more information, such as site-specific data, become available. The document also discusses different lines of evidence for sediment quality assessment that can be used when additional studies are needed, and provides recommendations for sediment toxicity testing.

These values reflect the most current scientific analysis of the DFWMR of the New York State Department of Environmental Conservation (NYSDEC, or Department) regarding the potential for adverse impacts to ecological resources from sediment contamination. It is intended to provide guidelines for sediment quality assessment, but it is not a stand-alone document. The references cited should be consulted when more information is needed, particularly in regards to procedures and methods.

This document supersedes previous editions of "Technical Guidance for Screening Contaminated Sediment," the most recent of which is dated January 1999.

[1] The use of the term "aquatic" throughout this document is also meant to include saltwater (marine) and estuarine organisms, when appropriate.

2. Applicability

The procedures described in this document are applicable to any project that investigates the potential risks to aquatic life from contaminants in sediment. It is most applicable for new projects for which little or no information is available other than the contaminant concentrations in sediment samples, and for smaller scale projects where information on the potential risks to aquatic life are needed in order to make a decision as to whether or not the project may proceed. This guidance is applicable to sediments that comprise the substrate of waterbodies up to the mean high water line. In regards to wetlands, these guidelines can be applied to sediments in permanently inundated wetlands such as marshes and swamps that border waterbodies. They *may* not be applicable to wetlands that are only occasionally submerged, or are more soil-like in composition, however, that applicability should be determined on a case-by-case basis.

This document is not applicable to questions of sediment management, remediation, mitigation, or disposal. Nor should it be used for characterizing the suitability of dredged sediment for upland placement or disposal, or for characterizing ecological risks associated with sediment placed in upland, terrestrial sites. The upland placement of sediments is governed by 6 NYCRR Part 360 (including 6 NYCRR Part 360-1.15 Beneficial Use) and Commissioner Policy CP-51 on Soil Cleanup.

This document is intended for use by DFWMR staff involved in assessing impacts of contaminated sediments. This document is available to other NYSDEC Divisions and the general public interested in understanding the basis for DFWMR's technical opinion regarding assessment of sediment contamination.

3. What is Sediment?

A. Sediment Composition and Classification

Sediment is comprised of all detrital, inorganic, or organic particles eventually settling on the bottom of a body of water (Power and Chapman 1992). However, that description fails to capture the complex and dynamic nature of sediment, particularly when considered on the scale of a watershed. There are several types of sediment, each composed of characteristic materials. clastic (also referred to as mechanical or detrital[2]) sediments are inorganic accumulations of flakes, grains, or pieces of weathered rock such as silt, sand, and gravel. Sediments of chemical origin include natural precipitates such as rock salt and gypsum. Organic sediments are composed of organic remains, such as plant material, coal or shells. Clastic sediments are about three times more abundant than chemical and organic sediments. Finally, water is also an important component of sediment, and is described as interstitial pore water (Shelton 1966, Power and Chapman 1992).

Sediment comes in a large range of sizes. Wentworth (1922) proposed a scale for defining size classes of clastic sediments and provided a descriptive name for each class. The Wentworth scale is still used today to define size classes of sediment particles:

Table 1. Size range of sediment particles as described in the Wentworth scale.

Particle Size Range	Descriptive Name	General category	
> 256 mm	Boulder		Rubble
64 – 256 mm	Cobble gravel	Gravel	
4 – 64 mm	Pebble gravel		
2 – 4 mm	Granule gravel		
1 – 2 mm	Very coarse sand	Sand	
0.5 – 1 mm	Coarse sand		
0.25 – 0.5 mm	Medium sand		
0.125 – 0.25 mm	Fine sand		
0.0625 – 0.125 mm	Very fine sand		
0.004 – 0.0625 mm	Silt	Mud	
< 0.004 mm	Clay		

Mud (silt and clay), is the most abundant sediment. Sand is second, while rubble and gravel are minor contributors (Shelton 1966).

Particle size (also known as grain size) refers to the diameter of a particle, and is the most significant property of sediment as it relates to contamination. Very small clay particles (up to

[2] Detritus is also defined as organic material such as dead or partially decayed plants and animals or excrement, but that definition does not apply in this context.

0.004 mm) exhibit a strong influence from electrical charges on their surface, resulting in cohesive forces. Particle sizes between 0.004 mm and approximately 0.0625 mm are known as silt and are in a transition range. The silt particles are too large to feel much influence from the electromotive forces and too small to mobilize inertia against flowing water. When particle size exceeds 0.0625 mm, electromotive forces are insignificant. These particles are non-cohesive and are classified as sand, gravel, cobble, etc. (Thomas, 1977).

Power and Chapman (1992) proposed that sediments can generally be classified into two groups; coarse, with a grain size > 62 microns (μm), or fine, with a grain size < 62 μm. The coarse fraction is composed primarily of stable, inorganic silicate materials that are non-cohesive and generally not associated with chemical contamination. The fine fraction consists of particles with a relatively large surface area to volume ratio. Typically, surface electric charges cause the fine particles to be more chemically and biologically active, thereby increasing the likelihood of sorption and desorption of contaminants.

B. Stream Sediment

In flowing waters (e.g. streams and rivers), sediment is constantly being moved. Moving sediment in a waterway is referred to as the load. Suspended load refers to those sediment particles which are transported entirely within the body of fluid, making very little contact with the bed. Bed load is that portion of the suspended load that moves essentially in contact with the bed (Thomas 1977).

Rivers can move massive amounts of sediment. For example, in one given year, the suspended load of the Colorado River moving past one monitoring station averaged more than 425,000 tons per day (Shelton 1966). The capacity of a stream to transport sediment increases in more than direct ratio to its discharge. Each time the flow in the Colorado River doubles, the load increases more than four times (Shelton 1966). The coarser the load, the more difficult it is to move via flowing water. As a river enters a lake or reservoir, coarser sediments are deposited first, and the finer sediments are carried much further (Thomas 1977).

C. Lake Sediment

The sediment in lakes is also made up of three main components (besides interstitial pore water): organic matter in various stages of decomposition, particulate mineral matter including clays and non-clay silicates (i.e., clastic materials), and an inorganic component of biological origin, such as diatom frustules and certain forms of calcium carbonate (Wetzel 1983). The profundal sediments of any lake are fine-grained because of the size-sorting that has gone on during transport from littoral (in-shore) regions, and because of the significant portion derived from settled plankton (Cole 1979).

Lakes can be described in terms of their trophic status, where *trophy* refers to the rate at which organic material is supplied by or to the lake per unit time (Wetzel 1983). Organic material can come into a lake from external sources, such as leaves from shoreline trees falling into the lake during autumn, or organic material transported into the lake by rivers and streams. External

sources of organic matter are termed allochthonous. Lakes with a very high component of allochthonous material are known as dystrophic. Autochthonous organic material, conversely, is generated within the lake itself and includes phytoplankton, dead bacteria, and decomposing animal matter. Lakes that are characterized by low nutrient content sustain limited populations of phytoplankton. In turn, primary productivity is low. Such lakes are termed oligotrophic. Eutrophic lakes, on the other hand, are characterized by high nutrient content, sustain a substantial phytoplankton population, and may be highly productive.

Sediments of oligotrophic lakes are dominated by clastic material transported by rivers and streams. Heavier, coarser materials such as gravel and sand will be deposited first, in the littoral or shallow, shoreline areas of a lake. The lighter silt and clay particles will be transported further into the lake and will settle more slowly.

The common sediment found in eutrophic lakes is termed *gyttja* or copropel. These sediments consist of a mixture of humus material, fine plant fragments, algal remains, grains of quartz and mica, diatom frustules, exoskeleton fragments from aquatic arthropods, and spore and pollen relics. This mixture of materials that are largely derived from plankton is mixed and modified by the bottom fauna that both consume and contribute fecal matter to the sediments. Bacterial decay of dead plankton material in eutrophic lakes often causes long periods of anoxia in bottom sediments. Sediments subjected to such conditions are known as sapropel. Sapropel is a glossy, black, watery material that lacks the structure of copropel and emitsH_2S, resulting in characteristic “rotten egg smell” of hydrogen sulfide (Cole 1979).

In dystrophic lakes, another form of sediment, called *dy*, is produced. Dy is a mixture of gyttja and unsaturated humic colloids from partially decomposed allochthonous plant material (Wetzel 1983).

D. Sediment as Habitat

Sediment is important for the habitat that it provides for aquatic organisms. In general, homogenous sand is the poorest habitat, supporting less biota than mud, gravel, and rubble. However, when any of the latter substrates are mixed with sand, biomass often increases. Islands of solid material such as rock, rubble, or tree debris, on sandy areas serve as concentration points for biota. Despite being considered poor habitat, sand still supports a large variety of micro-fauna (Hynes 1970).

Coarse sediment such as gravel and rubble supports more biota than sand, because coarser sediment provides a greater amount of interstitial space to occupy, and it is more likely that organic matter will lodge among stones and provide food. The addition of silt and mud to sand increases its food content. In streams with pool and riffle structure, animal life is considerably denser in riffles where gravel dominates the sediments. In one river study, pools averaged less than 20 animals per square foot as opposed to over 100 animals per square foot at riffles (Hynes 1970).
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4. Chemical Contaminants in Sediment

Sediments are carried by flowing water, and so too are any contaminants associated with the material. Contaminants buried in river sediments (which would generally be contained from the water column), have the potential to be resuspended by events such as storms, high flows, ice scour, or by changes in discharge due to human activities in the river. The resuspended contaminants could then pose a risk to aquatic life. The potential toxicity of contaminants can be altered upon release from the sediment matrix or upon exposure to the chemical environment of the water column. These factors must be taken into consideration when evaluating risks from contaminated sediment.

Prior to evaluating risks of contamination, however, one must decide which substances qualify as contaminants. Contaminants are chemical compounds that have the potential to harm aquatic life, and generally, do not occur naturally in sediment. Some compounds, however, that are thought of as contaminants, can also occur naturally. For example, some metals which are often classified as contaminants are, in fact, natural components of minerals that originated from weathered rock. Similarly, organic compounds such as polycyclic aromatic hydrocarbons (PAHs) are by-products of fuel burning processes, but are also naturally produced during forest fires (Eisler 1987). Other potentially toxic compounds such as ammonia or acetone can be produced within sediment as a result of microbial metabolism.

Concentrations of naturally occurring "contaminants" in sediment can be described as background. More specifically, Rice (1999) defines background as "The concentration that is the result of natural processes, including weathering and subsequent erosion of local soil and bedrock, and atmospheric deposition unaffected by anthropogenic activity." This definition was originally proposed to describe the background concentrations of trace elements in sediment, however it is also useful for describing the concentration of other compounds found in sediment that occur naturally.

The focus of this guidance document is contaminants of anthropogenic origin; that is, synthetic chemical compounds, or *excessive* concentrations of naturally occurring contaminants resulting from human activity. Anthropogenic contaminants can be contained in effluent that is discharged directly into the water, transported to water bodies via runoff from urban, residential, and agricultural areas, transported to surface waters via groundwater, or released into the air and subsequently deposited into surface waters or watersheds. Not surprisingly, the highest concentrations of such contaminants in sediment are generally found close to urban or industrialized areas (although contaminants easily transported through the air have been detected in sediments at great distances from their sources). Unless otherwise stated, the term "contaminants" will hereafter refer to compounds of anthropogenic origin that have the potential to be directly harmful to aquatic organisms, or harmful to terrestrial organisms via bioaccumulation through aquatic food chains.

Because synthetic organic compounds are not produced naturally, no concentration of these compounds in sediment can be described as "background," as defined above. Regarding such

compounds, a different meaning is often associated with background; that is the concentration of the chemical in a defined area of sediment, without regard for the source. That line of reasoning leads to the idea that a compound in sediment at a particular site of interest should not be described as a contaminant if its concentration is generally similar to the concentration of the same compound in sediments throughout the area outside of the site; such contaminant concentrations should be described as "background." The purpose of this document, however, is to describe methods to assess the potential risks to aquatic life from contaminant concentrations in sediment *regardless* of their possible source. Sediment is considered contaminated if it contains a concentration of a compound that is not produced naturally or is present in a concentration other than what would be expected to result from natural processes (i.e., has an anthropogenic source), and that has the potential to be harmful to aquatic life.

The procedures described herein provide standardized methods for assessing whether or not contaminants in sediment pose a risk of toxicity to aquatic life. Identifying the proximal source of contamination and determining whether or not the sediment requires remediation are management decisions beyond the scope of this document.

The toxicity of most contaminants is fairly consistent among different bodies of water; that is, the same concentration of a contaminant that produces a toxic effect in one water body will produce a similar effect in other water bodies. The toxicity of some contaminants, though, is dependent upon the state or form of the contaminant itself, as well as the characteristics of the water in which it is dissolved. The toxicity of copper in water, for example, is proportional to the hardness of the water. Specifically, when water is harder (i.e. has higher than average concentrations of calcium and magnesium cations), copper is less toxic.

Because sediment is a complex material, it can have a much more complicated effect on the toxicity of contaminants than water. Sediment characteristics that can alter the chemical and biological activity of contaminants include but are not limited to the following: pH, cation exchange capacity (CEC), redox potential, oxic state, composition of sediment (e.g., sand, clay, silt), amount and type of clay present (e.g., kaolin, bentonite, montmorillonite, etc.), grain size, pore size, the nature and volume of organic carbon present, and the presence of sulfides, nitrates, carbonates, and other organic and inorganic substances. More specifically, sediment characteristics can alter the degree to which contaminants are *bioavailable*. Sijm, et al. (2000) describes bioavailability is a complex process which includes all kinds of relationships between the concentration of a contaminant in sediment and the portion of that concentration an organism experiences with regards to uptake. Bioavailability is affected by the complex interaction between a given contaminant and sediment.

It is the bioavailable fraction of a contaminant in sediment to which an organism is actually exposed, is available for uptake, and causes toxicity. The bioavailable fraction is not a fixed quantity. It can be altered continuously by physical, chemical, and biological processes as well as through exposure pathways. For example, a metal bound to a clay particle or present as a sulfide precipitate is not available for uptake from pore water through the gills, but that same metal fraction could be bioavailable as it passes through the digestive tract of an organism following ingestion. There can be a high degree of variability in the concentration of a contaminant that is bioavailable and likely to cause toxicity in different sediments, and no single

concentration of a contaminant in sediment can accurately represent a threshold toxicity for benthic organisms in all sediments.

5. The Screening, Classification, and Assessment Process

A. Process Overview

First, some basic nomenclature; from this point forward, a site is defined as the overall area wherein sediment contamination is suspected or is being investigated. A station, or sampling station, is an individual point within a site where sediment was collected for testing or analysis. Sample refers to the sediment that was collected at a particular station. When a sample is subdivided into two or more subsamples, the subsamples are called replicates.

In the context of this document, *assessment* refers to the process of evaluating sediment contamination in order to make a regulatory determination; that is, do contaminants present in the sediment pose a risk to aquatic life? This assessment is, in fact, a risk assessment and the EPA Ecological Risk Assessment Framework should be observed. The EPA process includes the stages of problem formulation, analysis (including characterization of exposure and effects), and risk characterization (U.S. EPA 1998).

Screening refers to the action of comparing the concentration of contaminants in a sample to a set of numeric screening values, known as Sediment Guidance Values (SGVs). The SGVs identify thresholds for various contaminant concentrations in sediments that can be used as a basic screening tool to identify potential risk to aquatic life. Given no information other than the concentration of a contaminant in sediment, these values allow for a reasonable assessment of the potential for the contaminants to be harmful to aquatic life.

There are two different kinds of SGVs; empirical SGVs (used for metals) and equilibrium partitioning SGVs (used for organic compounds). SGVs are used to classify a contaminant in a sediment sample into one of three categories of sediment contamination, relative to its potential risk.

There can be numerous contaminants in a sediment sample from any particular station. The *overall* classification of each station within a site is assigned based on best professional judgment, taking into account both the number of the individual contaminants and the magnitude of their concentration at the same station. Screening and classification are components of the analysis stage of a risk assessment.

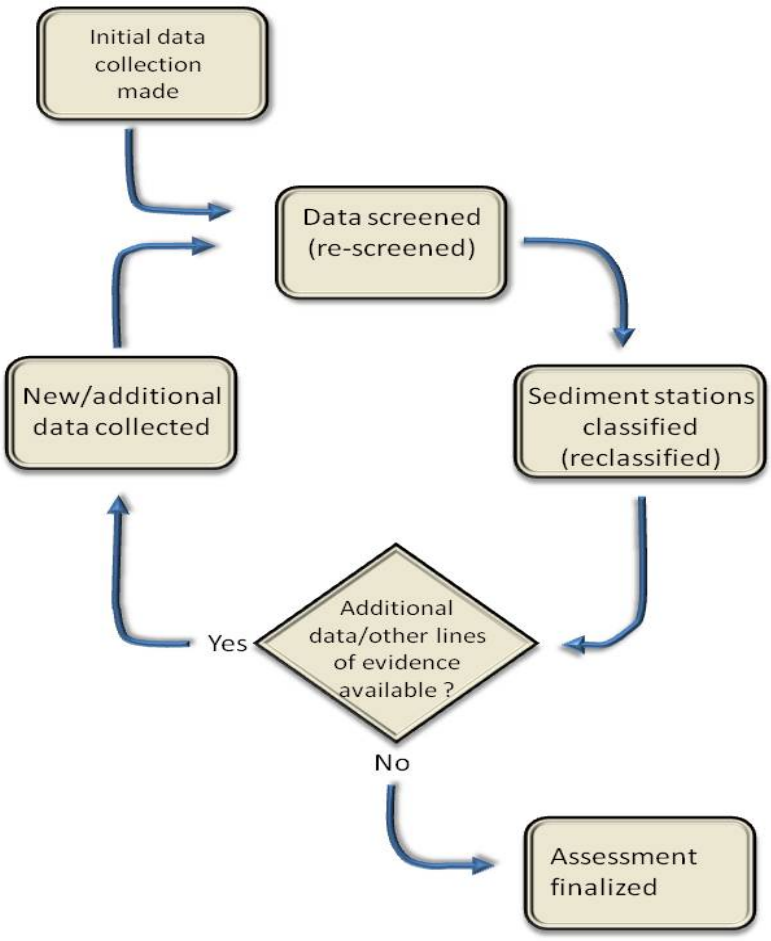
Analysis of contaminants is iterative; it begins with the least amount of information necessary to make an assessment regarding potential risks to aquatic life associated with contaminants in sediment. Then, as more information, such as the physical and chemical characteristics of the sediment, toxicity test results, benthic community analyses, etc. is added, the screening and classification steps are repeated and the initial classifications are revised, as appropriate. This process continues until either no more scientific information can be systematically collected and added to refine the classifications, or the assessor is satisfied with the results (see Figure 1).

The use of both equilibrium-partitioning and empirical SGVs (or sediment quality values, SQVs, as they are more commonly referred to in the literature), is controversial, and both types of SGVs

have been criticized in the literature (Chapman and Mann 1999; Chapman, et al. 1999; O'Connor and Paul 2000; O'Connor 2004). SGVs are useful, however, when only limited information is available. They provide a starting point for the risk assessment process. As additional information and lines of evidence are added, the assessment moves away from SGVs and towards site- and contaminant-specific, effects-based results. SGVs are most useful for initial screening, and for identifying and eliminating individual stations within a larger site that may not be of concern.

Appendix A provides a hypothetical example of how the screening and classification process should be applied. Please note that this is a purely hypothetical example, and is only intended to show how a contaminated sediment site is initially screened and classified. As additional information is added incrementally, the sediment contaminants are re-screened and re-classified, with less reliance on the original SGVs.

Figure 1. Screening and classification of contaminants in sediment. This is an iterative process that is part of the analysis stage of the risk assessment process.



B. Sediment Classification Categories

There is high variability in the concentration of contaminants in sediment that cause toxicity. When reviewing studies that compare sediment bulk chemistry data and toxicity, there is a typical pattern across a contaminant concentration gradient; at low concentrations, there is a range where toxicity does not occur, while at higher concentrations, there is a range where toxicity consistently occurs. In between this range, concentration and toxicity results are mixed. A given contaminant concentration might be toxic in one sediment sample but not in another. Toxicity within this range, therefore, cannot be predicted reliably from the contaminant concentration in sediment. To address this characteristic pattern of sediment toxicity, two SGVs are needed; one defining the concentration of a contaminant below which toxicity is not expected to occur, while the other defines the concentration of a contaminant above which toxicity is expected to occur frequently. By establishing two sets of SGVs, the contaminants in a sediment sample can then be segregated into one of three different categories; Class A, B or C. These categories are defined as:

- Class A – If the concentration of a contaminant in sediment is below the SGV that defines this class, the contaminant can be considered to present little or no potential for risk to aquatic life. For equilibrium partitioning-based SGVs, the Class A threshold concentrations were derived using chronic ambient water quality standard/guidance values (AWQS/GVs). For empirically-based SGVs, the Class A threshold was derived from the threshold effects concentration (TEC) or Effects Range Low (ERL) (see methods, below).

- Class B - If the concentration of a contaminant lies between the SGVs that define Class A and Class C, additional information is needed to determine the potential risk to aquatic life. For equilibrium partitioning-based SGVs, the contaminant concentration is greater than the SGV derived from a chronic AWQS/GV but less than the SGV derived from an acute AWQS/GV. For empirically-derived SGVs, the contaminant concentration is between the TEC or ERL, where toxicity is observed infrequently, and the probable effects concentration (PEC) or Effects Range Medium (ERM) (see methods, below), where toxicity is observed frequently. The potential for risk to aquatic life cannot be ascertained from contaminant concentration data alone.

- Class C - If the concentration of a contaminant is above the SGV that defines this class, there is a high potential for the sediments to be toxic to aquatic life. For equilibrium partitioning-based SGVs, the Class C threshold concentrations were derived using acute AWQS/GVs. For empirically-based SGVs, the Class C threshold was derived from the PEC or ERM (see methods, below).

The SGVs in Tables 5-6 are used initially because there is no information available beyond the contaminant concentration in sediment, and these screening values are, by necessity, conservative. Once a contaminant is classified as Class A, it can be dropped from further iterations of the screening and classification process. As the iterative screening and classification process proceeds and more information is added, the definition of the categories slowly change, from those described above to the more general, “acceptable” for Class A and “toxic” for Class

C, because the classifications are no longer based simply upon exceeding a numerical screening value.

One of the outcomes of the screening and classification process should be the elimination of all contaminant concentrations classified as B. This is accomplished by integrating additional information, evidence, and testing into the process until Class B contaminant concentrations are re-classified to either Class A or Class C. If the assessment procedures do not result in a Class B contaminant being reclassified as acceptable (Class A) or toxic (Class C), then determining the appropriate actions for addressing the contaminants at that station becomes a part of the overall sediment project management for the site.

As additional information, evidence, and test results are added, and the SGVs, as they apply to the specific site under review are revised, the conservative nature of the SGVs and the uncertainty are both reduced.

6. Technical Basis for Sediment Guidance Values (SGVs)

Numerous efforts to develop suitable sediment quality guidelines for classifying sediment as toxic (contaminated) or non-toxic (relatively uncontaminated) have been published in the scientific literature. In order to best protect aquatic resources, the scientific literature was reviewed to identify existing sets of candidate sediment guidelines for use in New York State as numeric Sediment Guidance Values (SGVs), for the purpose of initially classifying sediments with respect to potential adverse impacts. As a result of that review, three methods were chosen for establishing New York State SGVs: (1) equilibrium partitioning (EqP); (2) consensus-based sediment quality guidelines for freshwater sediments (MacDonald, et al. 2000), and (3) ERL/ERMs for marine/estuarine sediments (Long, et al. (1995) .

A. Equilibrium partitioning-based SGVs for nonpolar organic contaminants

The equilibrium partitioning methodology is well-documented in the scientific literature (U.S. EPA, 1991; U.S. EPA SAB, 1992; DiToro, et al. 1991). U.S. EPA (2002) reported that adverse biological effects from the concentration of nonpolar organic contaminants (such as PCBs, PAHs, organochlorine and organophosphate insecticides, etc.) in sediment cannot be correlated with bulk concentration of the contaminants in sediment, but can, however, be correlated with the concentration of the contaminant in interstitial pore water. The effects concentration for a chemical in pore water is essentially equal to that reported for water-only exposures. In other words, the toxicity of a nonpolar organic contaminant to sediment-dwelling organisms is proportional to the concentration of the contaminant that is freely dissolved in the pore water of the sediment.

The equilibrium partitioning theory states that nonpolar organic contaminants in sediment will partition between the organic carbon fraction in sediment and sediment pore water in a constant ratio, and that ratio can be used to predict the fraction of a contaminant that is freely dissolved in pore water from the concentration in sediment. The ratio is referred to as the organic carbon partitioning coefficient, or K_{oc}. Few K_{oc}s have been published for nonpolar organic contaminants, and K_{oc}s for the same compound will vary with different types of total organic carbon (TOC) in the sediment. For example, natural TOC (i.e. humic and fulvic acids), resulting from biodegradation of wood, plant fibers, or peat in sediments, has less sorbtive capacity than soot or black carbon (Word, et al. 2005). The higher the K_{oc} of a nonpolar organic compound, the stronger the contaminant will adsorb to the organic carbon content in the sediment. When more organic carbon is present in sediment, the concentration of a nonpolar organic contaminant freely dissolved in sediment pore water will be smaller, and therefore, proportionally less toxic to aquatic organisms.

The toxicity of contaminants will also be dependent upon the uptake and accumulation of those substances within an organism. The K_{ow}, or *n*-octanol water partitioning coefficient, is a useful surrogate of how nonpolar organic compounds will accumulate in lipids of animal tissue (U.S. EPA 1995). The K_{ow}, is the ratio describing the partitioning of a nonpolar organic compound between water and octanol. K_{ow}s are generally readily available for many common organic compounds, and tend to be similar in value to and vary proportionately with the K_{oc} of a compound (Kenaga, 1980; Voice, 1983). U.S. EPA (1991) refers to DiToro (1985) to define the

relationship between K_{ow} and K_{oc} as:

$$Log_{10}K_{oc} = 0.00028 + 0.983 \bullet log_{10}K_{ow} \quad (1)$$

An equilibrium partitioning-based SGV for a nonpolar organic contaminant is derived by multiplying the ambient water quality standard or guidance value (AWQS/GV) for that compound from 6 NYCRR Part 703.5 or TOGS 1.1.1 by its K_{oc}, as derived from equation 1 (U.S. EPA 1991):

$$SGV_{oc} = AWQS/GV\ \mu g/L * K_{oc} \quad (2)$$

This will result in a SGV in units of microgram of contaminant per gram of organic carbon (µg/gOC) in the sediment (SGV_{oc}). For example, consider the pesticide diazinon, which has a log K_{ow} of 3.81 and a chronic New York State AWQS/GV of 0.08 µg/L (6NYCRR Part 703.5).

The first step would be to estimate the diazinon K_{oc} using equation 1, above:

$$\text{Log } K_{oc} = 0.00028 + 0.983 \bullet 3.81$$
$$\text{Log } K_{oc} = 3.74551$$
$$K_{oc} = 5{,}565.6 \text{ L/kgOC}$$

The Diazinon SGV_{oc} can be calculated using equation 2:

$$\text{Diazinon } SGV_{oc} = 0.08\ \mu g/L * 5{,}565.6\ L/kgOC * 1\ kg/1{,}000\ gOC = 0.445\ \mu g/gOC$$

where 1 kg/1,000 gOC is a conversion factor

The SGV for a nonpolar organic compound is dependent upon the concentration of TOC present in the sediment. In order to publish SGVs that are not dependent on additional, site-specific data (such as the percent TOC in a given sediment sample), the assumption was made that sediments in New York are likely to contain 2% TOC[3]. The SGV_{oc} can be converted to a bulk sediment SGV by simply multiplying by the fraction of organic carbon (f_{oc}) in the sediment, which is assumed to be 2%:

$$SGV = SGV_{oc} \bullet f_{oc} \quad (3)$$

For example:

$$\text{Diazinon SGV} = \text{Diazinon } SGV_{oc} \bullet f_{oc}$$
$$f_{oc} = 2\% \text{ OC/kg sediment} = 20 \text{ gOC/kg}$$
$$\text{Diazinon SGV} = 0.445\ \mu g/gOC * 20\ gOC/kg = 8.9 \approx 9.0\ \mu g/kg \text{ sediment @ 2\% TOC}$$

Because the *chronic* AWQS/GV was used to derive the diazinon SGV, the concentration of 9 µg/kg diazinon is the threshold concentration for Class A sediments. By using the acute

[3] The average TOC for 18 watersheds in New York State ranged from 0.6-3.9% except for the Lake Champlain watershed, which had an average TOC of 10.8%. The statewide average TOC, after discarding Lake Champlain as an outlier, was 2.3%, which was rounded to 2% (Mueller and Estabrooks 2006).

AWQS/GV of 0.17 µg/L from TOGS 1.1.1 for diazinon, the Class C threshold concentration can be determined as well:

Diazinon SGV_{oc} = 0.17 µg/L * 5,565.6 * 1 kg/1,000 gOC = 0.946 µg/gOC

Diazinon SGV = 0.946 µg/gOC * 20 gOC/kg = 18.9 ≈ 19 µg/kg sediment @ 2% TOC

B. Empirically-based SGVs for metals

It is very difficult to predict if a given concentration of a metal in sediment is likely to be toxic or not. Numerous factors alter the toxicity of metals, both in water and in sediment. Divalent metals such as copper and zinc are most toxic when they are present in water as freely dissolved, positively charged ions; however, such ions are very reactive and tend to bind to various inorganic and organic ligands that reduce their bioavailability. Metals can also be adsorbed to and bound by certain negatively charged clay particles such as montmorillonite (Kraepiel, et al. 1999; Schlegel, et al. 1999; Stathi, et al. 2010). In anaerobic sediment (sediment with no oxygen), metal ions can bind with sulfide and be deposited in the sediment as insoluble precipitates (U.S. EPA 2005). Because of the complex chemistry of metals in water and sediment, no single methodology, like equilibrium partitioning for organics, is available to clearly estimate the potential for a given metal concentration in sediment to be toxic or not[4]. Given the lack of a suitable effects-based method for deriving SGVs for metals, an empirical method is used instead.

Empirical methods for deriving SGVs for metals require evaluation of the association between concentration of a contaminant in sediment and the occurrence of biological effects. A database from studies where these parameters have been measured is assembled to derive the SGVs. Concentrations associated with adverse effects are ranked from lowest to highest, and assigned cumulative probabilities (probability (P) = rank(R)/n+1) based on the increasing magnitude of the concentration in order to calculate percentiles associated with observed effects.

There have been several different approaches to deriving empirical SGVs. Persaud (1992) evaluated the number of benthic species present in sediment samples with different contaminant concentrations. He described the lowest effects level (LEL) as the concentration of a contaminant tolerated by 95% of benthic species, and a severe effects level (SEL) as the concentration of a contaminant tolerated by only 5% of benthic species.

Long and Morgan (1991) compiled a database of numerous sediment contaminant concentrations from both fresh waters and marine waters across the United States, along with associated biological effects. The 10^{th} percentile concentration associated with adverse effects was designated as the effects range – low (ERL), and 50^{th} percentile concentration was designated as the effects range – median (ERM). Contaminant concentrations for which no effects were

[4] The AVS-SEM model will be discussed at length in Section 7.B. The biotic ligand model (BLM) is also discussed briefly in Section 11. That model has been applied primarily to copper, and has significant data input requirements.

associated were not used.

Smith, et al. (1996) took a similar approach, but instead of discarding the no-effects concentrations, they also ranked them in order from lowest to highest and assigned cumulative probabilities. They described the threshold effects level (TEL) as the geometric mean of the 15th percentile of the concentration for each contaminant associated with a biological effects and the 50th percentile of the concentration of each contaminant for which no effect was reported. They also described the probable effects level (PEL) as the geometric mean of the 50th percentile of the concentration of each contaminant associated with a biological effect and the 85th percentile of the concentration of each contaminant for which no effect was reported.

As can be seen, all of the methods described above derived two different types of values, each with a different narrative intent. The first type describes a value that below which, toxicity was infrequently observed, and the second type was a value above which, toxicity was observed to occur frequently. MacDonald, et al. (2000) proposed "consensus" values by taking the geometric mean of similar values with the same narrative intent, such as LELs, ERLs and TELs, or SELs, ERMs, and PELs. They proposed a threshold effects concentration (TEC) as the geometric mean of the various published values (i.e. from those references cited above, as well as others) where toxicity was observed infrequently, and the probable effects concentration (PEC) as the geometric mean of published values where toxicity was observed frequently. Next, a database of 347 samples, measuring 28 different contaminants was compiled from 17 datasets representing 12 different geographic locations. About 50% of the samples (174 out of 347) were classified as "toxic" by the original authors. MacDonald, et al. (2000) then compared the toxic and non-toxic concentrations of metal contaminants in the database to the TECs and PECs. A TEC was considered to be "reliable" if it correctly classified as non-toxic a contaminant concentration in sediment from the database that was known to be non-toxic at least 75% of the time. A PEC was considered to be "reliable" if it correctly classified as toxic a contaminant concentration in sediment from the database that was known to be toxic at least 75% of the time. This means that the acceptable error rate for both false positives (samples classified as toxic that were actually non-toxic) for PECs and false negatives (samples classified as non-toxic that were actually toxic) for TECs were both 25%. For the eight metals evaluated, the percentage of samples correctly predicted to be not toxic ranged from 72.0% to 81.6% with the exception of mercury, which was only 34.3%. Similarly, the percentage of samples correctly predicted to be toxic ranged from 76.9% to 100%.

Empirical SGVs cannot predict toxicity. Such values only report the likelihood that, based on a large database of concentration and effects data, concentrations for sediment contaminants where toxicity was unlikely to be observed, and concentrations where toxicity has been observed frequently, without any information on the actual type and magnitude of adverse effect observed or characteristics of the sediment associated with the observed effect. O'Connor (2004) rightly describes these SGVs as points on a continuum of bulk chemical concentrations in sediment that roughly relate to sediment toxicity. Given no other information than the concentration of a contaminant in sediment, they are certainly useful for identifying sediments that are unlikely to be potentially harmful to aquatic life. While Class A contaminant concentrations in sediment can be considered to be acceptable, a determination should not be made that contaminants in sediment are harmful *solely* on the basis of exceeding a Class B or Class C SGV.

1. Freshwater

The TEC and PEC values for metals from MacDonald, et al. (2000) are adopted as the Class A and C SGVs in sediments from freshwater. In general, these values represent a 75% likelihood that toxicity will not be observed if the concentration of a metal is below the Class A SGV, and a 75% likelihood that that toxicity will be observed if the contaminant concentration exceeds the Class C SGV. Exceeding an SGV for a metal cannot provide any information on the type, magnitude, or extent of toxicity that could be observed. The Class A SGV (i.e., TEC) for mercury could be underprotective, as it only correctly identified sediments as toxic 35% of the time, instead of 75%, and should be used with caution.

2. Saltwater

ERL/ERMs described in Long, et al. (1995) were selected as the basis for Class A and Class C SGVs for metals concentrations in saltwater sediments. These SGVs were derived the same way as described above for Long and Morgan (1991), except that Long and Morgan (1991) used a database of both fresh and saltwater sediments, whereas the database for Long (1995) included only marine/estuarine sediments.

Long, et al. (1998) conducted an evaluation of the ability of ERL/ERMs to determine that a given contaminant concentration sediment was likely be toxic or non-toxic. They assembled a database of 1,068 samples from nine different locations/studies from U.S. EPA or NOAA data collected between 1991 – 1993 with both contaminant concentration and amphipod toxicity effects data. They also assembled a smaller database (n=437) with contaminant concentrations and other tests of biological effect besides amphipod toxicity. Results of the tests were expressed as percent of negative laboratory controls. Samples that were not significantly different from controls were designated as non-toxic. Samples with results significantly different from the control, but with concentrations less than the MSD[5] (Minimum Significant Difference) were reported as marginally toxic. Contaminant concentrations significantly different than the control, and greater than the MSD were designated as highly toxic.

Long, et al, (1998) considered an ERL to be adequately predictive of a non-toxic metal concentration in sediment if toxicity was observed in less than 25% of samples in which the metals concentrations were less than the ERL. Similarly, they considered a value to be adequately predictive of toxic metal concentration in sediments if toxicity was observed in more than 75% of the sediment samples in which the concentration of at least one metal contaminant present exceeded an ERM.

Long, et al. (1998) found that at concentrations below the individual ERL for nine trace metals, the occurrence of toxicity in samples classified as non-toxic (i.e., less than the ERL) ranged from 1.9 - 9.4%. For the same metals, the incidence of toxicity ranged from 86 to 100% when the

[5] The MSD is a toxicity test acceptance criterion used to make a judgment about the level of difference between a control and treatment that the test was designed to detect; for example, acceptable results are any that can declare a certain percentage of survival as significantly less than the control, where that certain percentage is the MSD. The MSD is empirically determined from past tests with the same species. See Thursby, et al. (1997).

ERM was exceeded and a variety of different toxicity tests were performed. When only amphipod toxicity was evaluated, the incidence of toxicity ranged from 62 to 81%, suggesting that other toxicity tests could be more sensitive than amphipod toxicity.

It should be noted, however, that the likelihood of toxicity was greater when more than one contaminant exceeded an ERM (or Class C threshold; Long, et al. (1998)). If several metals exceeded the Class C threshold, the likelihood that the sediment would be toxic would be much greater than if only a single Class C threshold was exceeded. This could, and should, affect the classification process for the station. For example, if only one of several metal concentrations in sediment only slightly exceeded a Class C threshold, then the station might be classified Class B, whereas, if several metals all exceeded the Class C threshold by a significant margin, the station would appropriately be classified as Class C at that point in the iterative screening process.

C. Screening Values for PCB, Dioxins, and Furans

Polychlorinated biphenyls (PCBs) are widespread contaminants that are frequently found in sediments in New York. PCB oils have very low solubility, and when discharged into surface water, they adsorb to organic carbon in sediments and accumulate there. These compounds have fairly high K_{oc}s, are very persistent, and are soluble in lipids. The greatest ecological risk associated with PCBs is generally not acute or chronic toxicity to benthic organisms and fish exposed directly, but risk to animals in the upper levels of the food chain exposed through *bioaccumulation*. PCBs *may* cause acute and chronic effects through direct exposure, but are more likely to cause adverse impacts to animals higher in the food chain that consume invertebrates and fish that have accumulated body burdens of PCBs. These higher-order consumers can experience significant adverse impacts of PCBs at concentrations lower than those that produce impacts in organisms directly exposed to the compounds.

The development of risk-based equilibrium partitioning SGVs for PCBs is complicated both by PCB chemistry and lack of data. There are 209 individual PCB congeners, for which toxicity data are scant. Furthermore, PCBs were marketed as Aroclors which are mixtures of PCB congeners. Toxicity data are available for most aroclor mixtures, but generally the data available are insufficient for deriving AWQS/GVs that could, in turn, be used to derive acute and chronic risk-based SGVs.

MacDonald, et al. (2000) proposed a consensus-based TEC and PEC of 60 and 680 µg/kg for total PCBs.

The Department has had a long history of assessing and remediating PCB contaminated sites. While addressing known PCB-contaminated sediment problems, the Department identified a set of values for assessing risks to aquatic life as well as animals higher on the food chain (through bioaccumulation). When the concentration of total PCBs in sediment was less than 100 µg/kg, ecological risk has generally been considered acceptable. Conversely, a concentration of total PCBs in sediment exceeding 1,000 µg/kg is likely to be harmful to aquatic organisms or organisms exposed through the food chain. These same values have been used by the NYSDEC Division of Water in TOGS 5.1.9 for assessing the risk of contaminants regarding the disposal of material generated by navigational dredging. That guidance states that sediments with total PCB

concentrations of less than 100 μg/kg could be disposed of in water, but sediments with total PCB concentrations of greater than 1,000 μg/kg must be removed for upland disposal (DOW, 2004).

These values are generally similar in scale and order of magnitude as the empirical SGVs proposed by MacDonald, et al. (2000). Therefore, the values already in general use in the Department are adopted for use as initial screening SGVs for PCBs. As with all other SGVs used for screening, they are not final, and the finding of whether or not sediments are toxic can be altered by results of other lines of evidence, such as toxicity testing, benthic community analysis.

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-p-furans (PCDFs) are similar compounds, and like PCBs, both PCDDs and PCDFs cause harm to biota more readily via bioaccumulation than via direct exposure to contaminated sediments. Also like PCBs, there are many congeners of PCDDs and PCDFs. The most toxic of the chlorinated dioxins and furans is 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD). Seven of the 75 PCDD and 10 of the 135 PCDF congeners are structurally similar to 2,3,7,8, TCDD and result in similar toxic effects, although on a different scale (U.S. EPA 2008). For the protection of human health, toxic equivalency factors (TEFs) and bioaccumulation equivalency factors (BEFs) have been published in 6 NYCRR Part 703.5 that can be used to equate the toxicity and bioaccumulative potential for mixtures of PCDDs and PCDFs to the equivalent concentration of 2,3,7,8-TCDD. For example, 1,2,3,4,7,8-hexachlorodibenzo-p-dioxin (HxCDD) has a TEF of 0.1 and a BEF of 0.3, meaning that it is approximately a tenth as toxic as 2,3,78-TCDD and has about 1/3rd the bioaccumulative potential. By multiplying the TEF and the BEF together, the toxic equivalency (TEQ) of 1,2,3,4,7,8-HxCDD can be determined: 0.1 x 0.3 = 0.03; that is, a concentration of 100 μg/kg of 1,2,3,4,7,8-HxCDD in sediment has roughly the same bioaccumulative and toxicity potential as a concentration of 3 μg/kg of 2,3,7,8-TCDD. If a mixture of several of the PCDDs and PCDFs for which TEFs and BEFs have been derived are detected in sediment, then the TEQ can be determined for each individual PCDD/PCDF. The individual TEQs are then summed to determine the TEQ of the mixture compared to 2,3,7,8-TCDD.

There are problems with this approach. Primarily, the TEFs and BEFs published in 6 NYCRR Part 703.5 are now somewhat dated, and were derived principally for the protection of human health using mammalian toxicity data. The World Health Organization published updated TEFs for mammals, birds, and fish, allowing risk assessments to be tailored for the protection of individual ecological communities (Van den Berg, et al. 1998; Van den Berg, et al. 2006). The U.S. EPA has proposed a more updated methodology for estimating and applying the toxic equivalence of mixtures of PCDDs, PCDFs, and dioxin-like PCBs (U.S. EPA 2008). These different approaches are better used during the latter stages of an assessment of the toxicity of mixtures of PCDDs and PCDFs in sediment. However, for *initial screening only*, this guidance recommends the use of the TEFs and BEFs from 6 NYCRR Part 703.5 to determine if a concern exists for the overall concentration of a mixture of PCDDs and PCDFs in sediment, by equating the PCDD/PCDF mixture to an equivalent concentration of 2,3,7,8-TCDD.

A Class A SGV for 2,3,7,8-TCDD is included in Tables 5 and 6. This is a bioaccumulation based, equilibrium partitioning SGV derived to protect piscivorous wildlife from 2,3,7,8-TCDD

or its TEQs from other PCDD/PCDFs in sediment. For purposes of initial screening only, if this Class A SGV is not exceeded, then the total 2,3,7,8-TCDD equivalent concentration of PCDD/PCDFs in sediment is unlikely to be harmful to aquatic life or terrestrial organisms that consume aquatic organisms. Exceeding the Class A SGV indicates that further assessment and evaluation of the potential toxicity from PCDD/PCDF contamination is needed.

The 2,3,7,8-TCDD and equivalent SGV is the *only* bioaccumulation-based SGV used as a screening value, and is used in this instance because of the high level of toxicity associated with PCDDs and PCDFs. Other bioaccumulation-based SGVs are not used for screening, and are discussed in Section 8. Table 2 lists the PCDD/PCDF compounds for which TEFs and BEFs have been published in 6NYCRR Part 703.5, and the corresponding TEFs and BEFs.

Table 2. Toxicity equivalency factors (TEFs) and bioaccumulative equivalency factors for polychlorinated dibenzo-p-dioxins and furans, from 6 NYCRR Part 703.5. These TEFs and BEFs are for use only in initial screening to estimate risks from mixtures of PCDDs and PCDFs.

Congener	**TEF**	**BEF**
2,3,7,8-tetrachlorodibenzo-p-dioxin	1	1
1,2,3,7,8-pentachlorodibenzo-p-dioxin	0.5	0.9
1,2,3,4,7,8-hexachlorodibenzo-p-dioxin	0.1	0.3
1,2,3,6,7,8-hexachlorodibenzo-p-dioxin	0.1	0.1
1,2,3,7,8,9-hexachlorodibenzo-p-dioxin	0.1	0.1
1,2,3,4,6,7,8-heptachlorodibenzo-p-dioxin	0.01	0.05
Octachlorodibenzo-p-dioxin	0.001	0.01
2,3,7,8-tetrachlorodibenzofuran	0.1	0.8
1,2,3,7,8-pentachlorodibenzofuran	0.05	0.2
2,3,4,7,8-pentachlorodibenzofuran	0.5	1.6
1,2,3,4,7,8-hexachlorodibenzofuran	0.1	0.08
1,2,3,6,7,8-hexachlorodibenzofuran	0.1	0.2
2,3,4,6,7,8-hexachlorodibenzofuran	0.1	0.7
1,2,3,7,8,9-hexachlorodibenzofuran	0.1	0.6
1,2,3,4,6,7,8-heptachlorodibenzofuran	0.01	0.01
1,2,3,4,7,8,9-heptachlorodibenzofuran	0.01	0.4
Octachlorodibenzofuran	0.001	0.02

D. Screening Values for Polar or Low K_{ow} Organic Compounds

The equilibrium partitioning process for organic contaminants described above only applies to compounds with high K_{ow}s that tend to dissolve in lipids and are likely to adsorb to organic carbon in sediment. Compounds with low K_{ow}s, however, tend to dissolve in water (solubility is inversely related to K_{ow} (Voice, et al. 1983)) and have a lower affinity for organic carbon.

SGVs have not been derived for organic contaminants with a log K_{ow} less than 2.0. These compounds tend not to accumulate in sediment (though they may be found there occasionally). For example, if spilled, volatile organic compounds (VOCs), which have low K_{ow}s, such as 1,2-dichloroethane, 1,1,2-trichloroethane, chloroform, etc. can migrate through soil and become

entrained in groundwater. If the groundwater plume intrudes upon surface water, the transported VOCs can be released into the surface water with very little accumulation in the sediment through which the plume had passed.

To assess the risk from these low K_{ow} compounds to aquatic life, the concentration of the contaminant in porewater should be compared to AWQS/GVs published in 6 NYCRR Part 703.5 or TOGS 1.1.1. If below the chronic water quality value, the sediments would be Class A for that contaminant. If above the acute water quality value, then the sediments would be Class C for that compound. This approach should also be applied to inorganic compounds other than metals. Pore water sampling is discussed in Section 11.

7. Mixtures of Contaminants

While unusual, sometimes sediments contain a single or dominant chemical contaminant that causes unquestionable harm to aquatic life. In such a situation, the effects of other, less abundant, chemicals that may be present are minimal. More commonly, sediments contain mixtures of contaminants. When multiple contaminants are present, it is much more difficult to determine which chemicals are causing adverse impacts.

One method of addressing toxicity of sediments with a mixture of chemicals is by deriving mean SGV quotients[6]. A mean SGV quotient can represent complex chemical mixtures within each unique sediment sample as a single numeric value that incorporates both the magnitude and number of sediment guidance values exceeded (Fairey, et al. 2001). Mean SGV quotients are derived by a three step process. First, the concentration of each contaminant in a sediment sample is divided by a relevant toxicological threshold (e.g., a Class A or Class C SGV) to produce an individual contaminant quotient. Second, the individual quotients are summed. Finally, the sum is normalized to the sediment sample by dividing it by the number of individual contaminants in the sediment (Long, et al. 1998; Hyland, et al. 1999, Fairey, et al, 2001, MacDonald, 2000).

Conceptually, if the mean SGV quotient is below 1.0, then toxicity would not be anticipated; and if the mean SGV quotient is above 1.0, then toxicity would be expected. Specifically, a SGV Quotient ≥ 1.0, indicates that the average of the concentration of contaminants in sediment is equal to or greater than the toxicological threshold used to derive the quotient. Using the mean SGV quotient in practice, Long, et al. (1998) reported that among sediment samples with a mean ERM quotient ≥ 1.0, 60 to 80% were toxic in amphipod toxicity tests; and the percent of false positives decreased to < 25% with mean ERM quotients > 1.2.

The mean SGV quotient approach treats the various contaminants in a sediment sample as acting independently of each other and not additively. If, for example, a sediment contained three contaminants with individual contaminant quotients of 0.3, 0.4, and 0.5, the mean SGV quotient would be 0.4, indicating that even though benthic organisms were exposed to three different contaminants, the overall effect is not predicted to result in toxicity.

It is unlikely that a SGV quotient of 1.0 will clearly and consistently distinguish toxic samples from non-toxic samples. The ability of a mean SGV quotient to reliably predict toxicity largely depends upon how the toxicity thresholds used were derived and the type of harmful effect the thresholds are being tested against. For example, Fairey, et al. (2001) used mean ERM and PEL

[6] In the literature cited, the SGV quotient is referred to as the Sediment Quality Guideline Quotient (SQGQ). The terms SQG and SGV are approximately synonymous. SQG is used more commonly in the scientific literature. The term SGV was selected for use in this document because it is more consistent with the vocabulary used in New York's water quality regulation program. The term Sediment Quality Guideline is more broadly used and may have different connotations that may or may not be applicable to sediment quality assessment and management in New York State.

quotients to predict *acute* toxicity to marine amphipods in laboratory tests. They constructed nine different mean SGV quotients from different groupings of contaminants, and compared them to results from three different datasets. They found that on average, in sediments with mean SGV quotients < 0.5, toxicity occurred in only 8.2% of the samples, and in sediments with mean SGV quotients > 0.5, toxicity occurred in 58% of the samples. In this instance, acute-level SGV quotients were used to predict acute effects.

In another approach, Hyland, et al. (1999) used ERMs and PELs to predict changes in benthic community metrics such as species abundance and diversity, *in-situ*. They found that the probability of observing a sediment sample with degraded benthos was less than 10% when the combined mean ERM/PEL quotient was ≤ 0.024. The probability of the occurrence of degraded benthos in a sediment sample would be relatively high (> 50%) in samples with a combined mean ERM/PEL quotient > 0.077. The fact that the mean SGV quotients were so low reflects that an *acute* SGV quotient was being used to evaluate a *chronic* effect.

A mean SGV quotient is useful for screening, but toxicity testing is ultimately necessary to determine if that contaminant mixture is toxic or not.

For additive chemicals, however, a somewhat different approach is required. As a rule of thumb, mixtures of similar contaminants, for example, metals, organochlorine pesticides, chlorinated benzenes, or BTEX[7] compounds, are more likely to be additive. If determined to be additive, then the individual contaminant quotients are simply summed (i.e. a *total* SGV quotient instead of a *mean* SGV quotient is calculated). Thus, if the three chemicals in the preceding example were known to be additive, then the individual contaminant quotients would be summed and the total SGV quotient would be 1.2, indicating a potentially toxic mixture. Hyland, et al. (1999) states that summed SGV quotients provide additional measures of the cumulative magnitude of individual contaminant concentrations relative to corresponding biological effects and can be a useful basis for ranking conditions among sites at which the same numbers of contaminants have been detected. Ringwood, et al. (1996) applied the summing method for evaluating risks from two groups of contaminants that were likely to be additive, metals and polycyclic aromatic hydrocarbons.

Another way of using the SGV quotient approach for diverse mixtures of contaminants is to determine the total (i.e. summed) SGV quotient for similar contaminants, then determine the mean SGV quotient from the groups of similar contaminants. For example, when investigating contaminated sediments from the Ashtabula River in Ohio, Ingersoll, et al. (2009) first determined the summed PEC quotients for metals, PAHs, and PCBs. A mean PEC Quotient was then calculated from the summed PEC Quotients.

There are, however, limitations to the use of mean SGV quotients. The limitations include the following;

- When evaluating complex contaminated sediments where toxicity data are available,

[7] Benzene, Toluene, Ethylbenzene, Xylene

there must be a statistically significant trend of increasing mean SGV quotient and increasing toxicity (MacDonald, et al. 2000). For screening purposes, if a regression of toxicity with mean SGV quotient yields an R^2 value of less than 0.6, then the relationship is probably too weak to establish that the contaminants measured account for the toxicity observed.

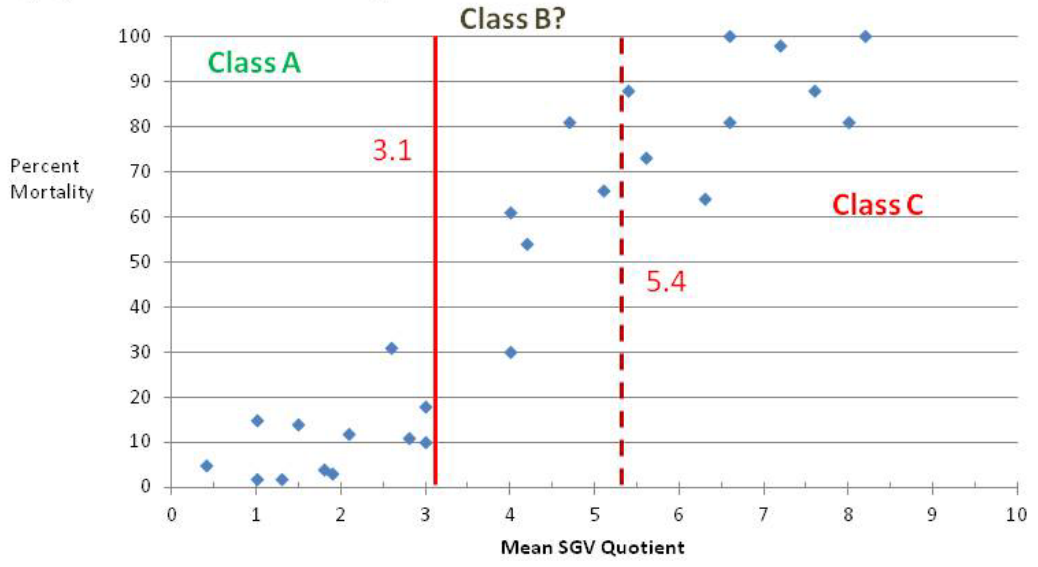
- The individual SGVs used to calculate the individual contaminant quotients must themselves be reliable. For screening purposes, the SGVs in Tables 5 and 6 are considered to be reliable.

- Empirical SGVs and EqP SGVs should not be combined to derive a common SGV quotient for a mixture of metals and organic contaminants (Long, et al. 2006). This is because the narrative intent for each is entirely different. For example, a Class A EqP SGV for an organic contaminant is based on the exceedance of a chronic AWQS/GV by the concentration of a contaminant predicted to be present in sediment pore water. An empirical Class A SGV for a metal is the threshold of the likelihood of the occurrence of a toxic effect based on cumulative probabilities. The meaning of a combining these SGV quotients would be unclear. One recommendation would be to derive separate quotients for compounds with empirical SGVs and EqP SGVs and examine how useful each is independently in explaining toxicity that was observed.

Mean SGV quotients would be most useful in the later stages of the screening, classification, and assessment process. For example, if the results of sediment toxicity tests do not clearly correlate with the distribution of individual contaminant concentrations at different stations, then mean SGV quotients for the mixtures present should be derived, thereby reducing multiple contaminant concentrations to a single numerical parameter for each station. This would be useful if sediment toxicity is not governed by the concentration of a single (or few) dominant compounds.

Mean (or total) SGV quotients can be compared to the distribution of toxic and non-toxic stations. If there is good correlation, that is, increasing toxicity corresponds to an increasing SGV quotient, then that relationship can be used to establish a mean SGV quotient value that can be used to segregate toxic and non-toxic (i.e., Class A and Class C) stations. The absolute value of the mean (or total) SGV quotient is not necessarily important. For example, examine the hypothetical data in Figure 2, with an R^2 value of about 0.82. In this example, a mean SGV quotient value of 3.1 can be visually estimated from the graph as an appropriate value to separate Class A stations from Class C stations. Alternatively, the mean SGV Quotient value of 3.1 could be used to separate Class A stations from Class B stations, and a mean SGV quotient value of 5.4 can be visually estimated from the graph as an appropriate value to separate Class B stations from Class C stations.

Figure 2. Hypothetical example of a regression of mean SGV Quotients calculated for individual stations within a site against percent mortality, following a series of toxicity tests. Each blue diamond represents the mean SGV Quotient for an individual station. The red lines represent mean SGV Quotient values estimated visually that appear to be useful for classifying stations based on toxicity.



A. Mixtures of Polycyclic Aromatic Hydrocarbons

The term Polycyclic Aromatic Hydrocarbons (PAHs) is applied to a large group of compounds that consist of two or more fused benzene or aromatic rings. There are thousands of different individual PAHs, including alkylated forms. The mobile forms, ranging in molecular weight from 128.17 (naphthalene, two ring structure) to 300.36 (coronene, 7 ring structure) are of the greatest environmental concern. PAHs generally originate from three possible sources. *Pyrogenic* PAHs are produced by the incomplete but high temperature, short-duration combustion of organic matter, including fossil fuels and biomass. For example, forest fires can be a major source of naturally-occurring pyrogenic PAHs (Eisler 1987). *Diagenic* PAHs are formed from biogenic precursors such as plant terpenes. The actual synthesis is unclear, but it appears to be an anaerobic process. *Petrogenic* PAHs are created by diagenic processes at relatively low temperatures over large time scales, leading to the formation of petroleum and other fossil fuels containing PAHs. The alkylated structure of petrogenic PAHs reflects the ancient plant material from which the compounds were formed (U.S. EPA 2003).

PAHs always occur in the environment as complex mixtures. While there are thousands of different PAHs, U.S. EPA (2003) identified 34 individual PAHs (18 specific non-alkylated compounds and 16 generic alkylated forms) that constitute "total" PAHs (see table 7). All 34 "total" PAHs listed in Table 7 should be analyzed for in any investigation of sediment contamination where PAHs are suspected as being present.

In the past, different numbers and groups of PAHs have been used by different programs to define "total" PAHs. EPA had originally developed a list of 13 PAHs which they had designated as a list of PAHs of concern, and many monitoring programs used that list to define total PAHs. The National Oceanic and Atmospheric Administration (NOAA) identified a list of 23 PAHs which they used in their monitoring programs to describe total PAHs. Virtually no national monitoring program included alkylated PAHs in the list of total PAHs, which is unfortunate, because alkylated PAHs tend to be more toxic than non-alkylated parent PAHs (U.S. EPA 2003).

PAHs have log K_{ow}s ranging from 3.3 to 7.3, meaning that they are readily bioaccumulated by aquatic organisms. However, most are also rapidly metabolized, so they do not generally biomagnify. Some PAHs are among the most potent carcinogenic compounds known, capable of producing tumors in some organisms through single exposures at microgram quantities (Eisler 1987). Most authorities agree that metabolic activation by the mixed-function oxidase (MFO) system is a necessary prerequisite for PAH-induced carcinogenesis and mutagenesis (Eisler 1987, citing Neff 1979).

One problem in establishing either water quality criteria or SGVs for PAHs is that relatively few toxicity studies have been conducted with most individual PAHs. MacDonald, et al. (2000) and others have derived empirical SGVs for total PAHs and several individual PAHs; however, the empirical SGVs for individual PAHs are questionable because of the low number actually assessed (only 10 of 34), their propensity to always occur in mixtures, and the common mode of action for PAH toxicity.

Because of that common mode of toxicity, however, it is possible to estimate the toxicity of individual PAHs through quantitative structure activity relationships (QSAR). PAHs belong to a group of chemicals classified as narcotics. Narcotics cause toxicity by suppression of the central nervous system. Researchers have advanced a narcosis theory, which posits that narcotics produce no chemical change to an organism. Instead, they produce a physical change owing to the migration of a narcotic compound into the cellular membrane. Therefore, the relative effect depends primarily on the quantity of agent absorbed. Narcosis toxicity is correlated to each compound's affinity for dissolving in lipid, which in turn is defined by a compound's K_{ow} (Shultz 1989). All narcotic chemicals produce the same effect. PAHs are narcotic chemicals, so toxicity resulting from exposure to multiple PAHs is additive, and dependent only on the amount of each individual PAH absorbed and its potency, both of which are related to the log K_{ow} of the individual PAH.

Using a narcosis model to predict the toxicity of individual PAHs based on their K_{ow}, U.S. EPA (2003) described the toxicity of each individual PAH, both in water and sediment (see Table 7). U.S. EPA (2003) then uses a method that is a synthesis of equilibrium partitioning and the SGV quotient method for estimating the toxic potential of mixtures of PAHs in sediment. The method consists of the following steps (see Appendix A):

1. Concentrations of all 34 PAHs and total organic carbon (TOC) are measured in a sediment sample as μg/kg of sediment.
2. The concentration of each PAH detected is normalized to the percent of TOC in the sediment to produce a concentration of each PAH detected in units of μg PAH /g TOC.

3. The concentration of each individual PAH present is divided by its corresponding SGV which was derived from the narcosis model and equilibrium partitioning, based on the individual PAH's log K_{ow} (Table 7, column 5). This quotient is described as a Toxic Unit (TU). In this context, a TU is essentially the same as a SGV quotient, as described previously.
4. The resulting TUs for each individual PAH are summed, to produce a Total TU for the mixture. If the total Toxic Unit is greater than 1.0, the sediment is considered to be potentially toxic. An example of this derivation method is provided in Appendix B.

The correct determination of the total TU for a mixture of PAHs is dependent upon sediment samples being analyzed for all 34 of the PAHs identified by U.S. EPA (2003). Because all PAHs have the same mode of toxic action, PAHs that are present and are not measured will still influence the toxicity of the sediment sample, and the resulting total TU will underestimate the true toxic potential of the PAH mixture.

In order to evaluate the toxic potential of sediment samples collected under older programs that used a total PAH list of either 13 or 23 PAHs, U.S. EPA (2003) calculated correction factors. If only 13 PAHs have been measured in a sediment sample, then the resultant total TU for the mixture must be multiplied by 11.5. If a total of 23 PAHs have been measured in a sediment sample, then the total TU for the mixture must be multiplied by 4.14.

U.S. EPA (2003) only derived correction factors for evaluating data from historical programs where sediments were evaluated for specifically 13 or 23 individual PAHs. However, if other numbers of PAHs were measured, this approach can still be used. The derivation of the correction factors was linear, so correction factors for mixtures consisting of other numbers of individual PAHs can be determined by linear interpolation. For example, another common grouping of PAHs is 18. The correction factor for this group would be 7.87. Correction factors can only be extrapolated mathematically to a maximum mixture of 27 PAHs. If more than 27 but fewer than 34 PAHs were measured in a sediment sample, the resulting extrapolated correction factor is less than one. There is no minimum number of PAHs for which a correction can be estimated, although U.S. EPA (2003) did not propose using correction factors for less than 13 PAHs. Care and professional judgment should be used when applying correction factors.

The toxic potential of individual PAHs can also be evaluated by using the PAH SGVs listed in Table 2. The individual PAH SGVs can be adjusted for site-specific TOC values. Also, by using the SGVs and K_{oc}s listed in Table 2, equilibrium partitioning-based SGVs can also be calculated for individual PAHs.

The SGVs for individual PAHs from U.S. EPA (2003) are derived for protection of aquatic life from chronic toxicity, that is, growth and reproductive impacts. They do not address the potential for carcinogenic or mutagenic effects. The EPA methodology described herein is the preferred method for classifying sediments contaminated with PAHs. If the corrected total PAH TU exceeds 1.0, then the sediments are considered to be Class B. This approach does not allow for the derivation of a Class C threshold.

Tables 6 and 7 contain empirical SGVs for total PAHs. When PAHs are encountered as a

contaminant in sediment during initial screening, the first step should be to compare the total PAH concentrations to the empirical SGV values in Tables 6 and 7. When the total PAH concentrations fall below the Class A SGV for total PAHs, the sediment from that station can be considered as not presenting significant risk to aquatic life from PAHs and classified as Class A, but only if the sediments were sampled for at least the 16 PAHs identified by the U.S. EPA as priority pollutants[8] (U.S. EPA 2009).

If the Class A total PAH SGV is exceeded, then typically, the next step in the screening, classification, and assessment process is to adjust the SGVs for site-specific information such as TOC, and recalculate them. That cannot be done with the total PAH SGVs. If the Class A threshold for total PAHs is exceeded, then the site-specific TOC and individual PAH concentrations are used as described above to determine the number of Toxic Units (TUs) present for the particular mixture of PAHs present. The process requires that the sediment be analyzed for 34 total PAHs, or a correction factor applied. If the total number of TUs present is less than 1.0, the sediment from that station should be classified A. If the total TU exceeds 1.0, then additional studies, such as toxicity testing, are required to determine whether or not the sediments present a risk of toxicity from PAHs.

B. Mixtures of Metals

U.S. EPA published a procedure for evaluating the toxicity of mixtures of six metals in sediment; cadmium (Cd), copper (Cu), lead (Pb), nickel (Ni), silver (Ag), and zinc (Zn). With the exception of silver, these are divalent metals with similar chemical characteristics and behavior. The procedure is based on the partitioning of these metals to acid volatile sulfides (AVS). AVS was operationally defined as the sulfide liberated from wet sediment when treated with cold 1N hydrochloric acid (U.S. EPA 2005).

Sulfate ($SO_4^{=}$) occurs abundantly in both fresh and salt water, and is second only to carbonate as the principal anion in fresh waters (Cole 1979). In anoxic sediments, sulfate is reduced to hydrogen sulfide (H_2S) by the action of sulfate-reducing bacteria. H_2S will react with iron in the sediments to form insoluble iron monosulfide, which is in equilibrium with aqueous-phase sulfide:

$$FeS_{(S)} \leftrightarrow Fe^{2+} + S^{2-}$$

(s) indicates a solid form

If another divalent metal cation is added to the aqueous phase such as cadmium, the cadmium will take up some of the free sulfide anions to form cadmium sulfide ($CdS_{(s)}$). Cadmium sulfide is more insoluble than iron sulfide, so as cadmium takes up the free sulfide, some iron sulfide will dissolve to rebalance the equilibrium. If there is more iron sulfide present than cadmium,

[8] Acenaphthene, Acenaphthylene, Anthracene, Benzo(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, 2-chloronaphthalene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene

then eventually all of the cadmium will be precipitated as insoluble cadmium sulfide. All of the six metals listed above have sulfides that are more insoluble than iron sulfide. So, if the amount of sulfide in a sediment sample, measured in moles, exceeds the amount of divalent metals, also measured in moles, then all of the metal is predicted to be in the form of insoluble metal precipitates (DiToro, et al. 1990). As an insoluble precipitate, the metal sulfide would not be bioavailable; that is, it is not present in a form that can be taken up by an organism where it can have a toxic effect. This method applies to five divalent metals, cadmium, copper, lead, nickel, and zinc; and one monovalent metal, silver, that form insoluble precipitates with sulfide. Silver is monovalent, so one mole of sulfide would bind to two moles of silver.

When wet sediment is treated with 1N HCl to liberate the AVS, any quantities of the five divalent metals and silver present as insoluble precipitates are also dissolved and liberated by the acid. These metals are described as simultaneously extracted metals (SEM). If the molar volume of AVS exceeds the molar volume of SEM (AVS:SEM >1) then the metals present were predicted to be completely bound as insoluble sulfide precipitates and not bioavailable. Alternatively, if the molar volume of SEM exceeds the molar volume of AVS (SEM:AVS > 1), then there is not enough sulfide present in the sediment to bind all of the metals present, and the unbound portion of metals *could* be bioavailable, and toxic. U.S. EPA (2005) goes on to say that free metals, that is, metals in the form M^{++}, will also form metallic complexes with organic carbon and other available ligands present in sediment. Therefore, toxicity from metals in sediment would not be anticipated unless the total combined molar concentration of the six metals Cd, Cu, Pb, Ni, Zn, and Ag exceeds both the concentration of AVS and TOC.

Initially, U.S. EPA (2005) proposed that if the ratio of SEM to AVS (expressed as SEM/AVS) was ≤ 1.0, then toxicity from the sum of the metal concentrations in sediment would not be anticipated. The ratio method was changed to evaluate the difference instead; that is, if SEM-AVS ≤ 0.0, then toxicity from the sum of metals concentrations would not be anticipated. The two approaches are functionally equivalent.

Observed biological impacts of metals in sediment are correlated with metals concentrations in interstitial pore water (U.S. EPA 2005). AVS serves to reduce the potential toxicity from metals by reducing the concentration of metals likely to be dissolved in interstitial pore water. Thus, the potential for toxicity could also be assessed by directly measuring the metals concentrations in porewater as well. U.S. EPA (2005) proposed a second measure for evaluating toxicity from metals, in what was essentially the same method as the total SGV quotient, as described above. The toxicity of the five divalent metals and silver are considered additive. So, an IWTU (Interstitial Water Toxic Unit) can be derived by dividing the concentration of each metal in pore water by its Final Chronic Value (FCV), and summing the individual quotients. If the IWTU was ≤ 1.0, then toxicity from exposure to metals in pore water would not be anticipated. For the five divalent metals, the FCVs are equivalent to the chronic water quality standard (A(C)) for the protection of aquatic life published in 6 NYCRR Part 703.5. For these metals, the toxicity in freshwater is dependent on the hardness of the water, and the FCV is expressed as a formula. Thus, whenever this method is used, the hardness of the interstitial pore water must be measured. The FCVs for the five divalent metals are listed in Table 3, below:

Table 3. Final chronic values of divalent metals, from 6 NYCRR Part 703.5.

Metal	Hardness-based formula for deriving FCV, in µg/L	Freshwater FCV at 100 ppm hardness, µg/L	Saltwater FCV, µg/L
Cadmium	(0.85) exp (0.7852 [ln (ppm hardness)] – 2.715)	2.1	7.7
Copper	(0.96) exp (0.8545 [ln (ppm hardness)] – 1.702)	9.0	3.4
Copper in NY/NJ Harbor			5.6
Lead	{1.46203- [ln (ppm hardness) (0.145712)] }exp (1.273 [ln (ppm hardness)] – 4.279	3.8	8.0
Nickel	(0.997) exp (0.846 [ln (ppm hardness)] + 0.0584)	52	8.2
Zinc	exp (0.85 [ln (ppm hardness)] + 0.50)	82.6	66

A chronic water quality standard has not been published for silver in saltwater, and the standard for silver in freshwater applies only to the ionic form, so an IWTU cannot be derived for silver.

For example, if cadmium, copper, and zinc were present in a sample of interstitial pore water that had a hardness of 100 ppm and concentrations of 3.1 µg/L, 4.4 µg/L, and 52 µg/L respectively, the IWTU value would be equal to:

$$IWTU = \frac{Cd\ \mu g/L}{CD\ FCV\ \mu g/L} + \frac{Cu\ \mu g/L}{Cu\ FCV\ \mu g/L} + \frac{Zn\ \mu g/L}{Zn\ FCV\ \mu g/L} =$$

$$IWTU = \frac{3.1\ \mu g/L}{2.1\ \mu g/L} + \frac{4.4\ \mu g/L}{9.0\ \mu g/L} + \frac{52\ \mu g/L}{82.6\ \mu g/L} =$$

$$IWTU = 1.48 + 0.49 + 0.63 = 2.6$$

With an IWTU value > 1.0, these sediments would be considered likely to be toxic.

U.S. EPA (2005) proposed that both methods of evaluating the risk of metals toxicity in sediment be used in conjunction; that is, if:

$$\text{SEM-AVS} \leq 0.0 \quad \textit{and} \quad \text{IWTU} \leq 1.0;$$

then the sediments are unlikely to be toxic, relative to the concentration of divalent metals present. Supporting studies described in U.S. EPA (2005) have shown that these measures do a reasonably good job at predicting when sediments will not be toxic. Of the two, greater confidence seems to be placed in the IWTU method. In fact, U.S. EPA (2005) provides an example where the AVS-SEM difference predicts that the sediments would be toxic but the IWTU measurement predicts no toxicity, and in that example, greater credibility is lent to the IWTU result.

While these methods, used together, appear to be good predictors of when the concentration of divalent metals in sediment will not be toxic, they do not accurately predict toxic conditions. This is because, as stated above, free metals readily form complexes with organic carbon and other available ligands which can also reduce the bioavailability and toxicity of metals, so that even if the concentration of SEM exceeds that of the AVS present, toxicity does not always result.

After further experimentation and evaluation, U.S. EPA (2005) proposed another modification to the SEM-AVS model that integrates the complexing influence of organic carbon in the sediments on metals toxicity. This approach is designed to predict toxic as well as non-toxic conditions. Organic carbon is taken into account by dividing the SEM-AVS difference by the percentage of total organic carbon present (f_{oc}). This approach was tested using a database of laboratory spiked and field collected sediments compiled from the literature. The results of the analysis showed that when the SEM-AVS difference was normalized for the fraction of organic carbon, toxicity was not observed below an SEM-AVS difference of 130 μmol excess SEM/g_{oc}. At an SEM-AVS difference normalized for the fraction of organic carbon of >3,000 μmol excess SEM/g_{oc}, toxicity was frequently observed. Based on this analysis, U.S. EPA proposed the following:

$$\frac{SEM - AVS}{f_{oc}} < 130 \text{ μmol excess SEM/g}_{oc}\text{, then toxicity is unlikely;}$$

$$\frac{SEM - AVS}{f_{oc}} > 3{,}000 \text{ μmol excess SEM /g}_{oc}\text{, then toxicity is likely.}$$

The studies described in U.S. EPA (2005) suggest that the AVS-SEM difference model generally performs reasonably well (U.S. EPA 2005). However, there are complications. The production of AVS requires anoxic sediment. In oxic sediments, any sulfide present is oxidized back to sulfate, and under certain conditions of low redox and pH, partial oxidation of sulfide occurs and free elemental sulfur may be formed (Wetzel 1983). Surficial sediments are generally oxygenated and metals in the surface sediment layers would not be exposed to AVS, although oxygen is rapidly depleted with depth. DiToro, et al. (1992) suggests that as dissolved metals diffuse through interstitial pore water, concentrations of AVS in the deeper, anoxic sediments may still limit the activity of metal concentrations present in oxygenated sediment layers.

Besser, et al. (1996) reports that there are significant spatial and temporal variations in AVS distribution in sediments. The concentration of AVS in sediments can change diurnally as well as seasonally (e.g., sulfate-reducing bacteria are less active in the winter). Over the long term, the binding effect of AVS might vary as the AVS concentration varies.

When anoxic sediments are disturbed and exposed to oxygen, AVS can be oxidized and free metals released back into the water. While some studies found that the rate of AVS oxidation to be slow, Besser, et al. (1996) documented rapid oxidation of AVS in sediments that contained high concentrations of both copper and zinc.

Long, et al. (1998a) reported that in a comparison study AVS:SEM ratio did not predict the probability of toxicity or the lack of toxicity in a group of sediment samples any more reliably than SGVs such as ERMs or mean ERM quotients.

High AVS concentrations do not ensure that metals biologically unavailable. Studies have reported on the bioaccumulation of metals by sediment-dwelling organisms such as *Chironomus sp*. and *Tubifex sp* (De Jonge, et al. 2009; Lee, et al. 2000). One possible alternative route of uptake is dietary. Organisms that consume sediment can extract metals through the digestive process. Also, burrowing species can create oxygenated microzones in the sediment immediately around their burrows, where AVS can be oxidized and metals released for uptake.

The uncertainty bounds for the SEM-AVS normalized for organic carbon described above (i.e., < 130 μg excess SEM/g_{oc} for the lack of toxicity and >3,000 μg excess SEM/g_{oc} for toxicity) as suggested by U.S. EPA (2005) were generated from a relatively small database of primarily laboratory-spiked sediments. These bounds may not be applicable to larger, or more site-specific situations. More data are needed to validate their usefulness across a broader range of conditions.

The SEM-AVS difference method only applies to sediments contaminated with mixtures of six specific metals; cadmium, copper, lead, nickel, silver, and zinc. If other contaminants are present, such as solvents, BTEX, PAHs, PCBs, pesticides, or industrial chemicals such as chlorinated benzenes, the SEM-AVS difference method, whether normalized for organic carbon or not, cannot be used to predict the presence or absence of sediment toxicity. It could be useful, however, in determining if the metals concentrations present could, by themselves, be sufficient to cause toxicity. If the SEM-AVS difference suggested that the metals were not toxic, then any toxicity observed could probably be attributed to some other contaminant.

Despite these complications, the SEM-AVS method can be useful for screening. For example, two waterbodies were evaluated for sediment contamination. In one rural lake with no industrial runoff, the concentration of copper exceeded the Class C SGV. Copper was high because the lake routinely used copper sulfate for algae control and copper had accumulated in the sediments. The other water body was a pond in an urban park, where the concentration of lead exceeded the Class C threshold, probably as a legacy contaminant from the days when gasoline was leaded. Lead from gasoline accumulated on the ground from atmospheric deposition from auto exhaust, and was washed into the pond by rainfall. In both cases, the AVS present significantly exceeded SEM, SEM consisted of only the single metal (i.e., copper or lead), and both water bodies appeared to have normal, unimpaired biological communities both in the benthos and water column. In both instances, the sediments were considered as unlikely to be toxic, largely on the basis of the AVS and SEM ratios without further toxicity tests.

Another caution in the use of SEM-AVS is that it can be useful in predicting whether or not a sediment is likely to be toxic or not at that instant in time, but it is limited in its ability to predict toxicity if the sediments are likely to be disturbed. Resuspension of sediments can alter sediment chemistry. If sediments are exposed to oxygen, then sulfides can be oxidized and metals released. Similarly, AVS concentrations are not constant, but can vary seasonally. U.S. EPA

(2005) recommends that the SEM-AVS difference be measured in winter when AVS production by sulfur-reducing bacteria is likely to be low.

The SEM-AVS difference is a fairly complicated measurement. U.S. EPA (2005) is clear in that both the SEM-AVS difference and IWTU values are meant to be used together, so both values must be determined. This requires measuring AVS, SEM, total organic carbon (TOC), collecting and sampling interstitial pore water, and determining the hardness of interstitial pore water. In screening, this effort is most likely to occur after it has been determined that one or more of the divalent metals are present, and the concentration exceeds Class B or C SGVs. In some circumstances, such as in the examples provided above, it is possible to make a determination that a sediment is not toxic based solely on an SEM-AVS difference of ≤ 0, or an SEM-AVS difference of < 0 accompanied by an IWTU value of ≤ 1. However, more often than not, it is likely that toxicity testing would be needed to confirm the SEM-AVS predictions, particularly if other contaminants are present.

If the criteria proposed by U.S. EPA (2005) (that is, excess SEM/g_{oc} < 130 µmole is predicted to be non-toxic and excess SEM/g_{oc} $> 3{,}000$ µmole is predicted to be toxic) then the results must be verified with toxicity testing. However, once those values have been found to be valid and applicable for a particular site, they should be able to be used for evaluating the potential for toxicity from other stations within the site without additional toxicity testing, as long as the sediment characteristics remain largely similar. Additionally, organic carbon normalization does not work properly with sediments contaminated with silver, so results obtained when significant concentrations of silver are present are unreliable and alternative methods must be considered

If the SEM-AVS and IWTU methods are to be used, U.S. EPA (2005) states that sediments can be sampled using dredges, grabs, or coring, but mixing of aerobic and anaerobic sediments must be avoided because the trace metal speciation will be altered. Coring is less disruptive and limits potential metal contamination and oxidation if sealed PVC core liners are used. The use of dialysis samplers is the preferred method for obtaining samples of interstitial pore water for metals analysis, particularly for surficial sediments and samples from shallow water. The use of centrifugation under nitrogen followed 0.45 µm filtration with polycarbonate fibers is an acceptable method as well, especially for obtaining interstitial water samples from deeper sediment horizons, or from sediments in deeper aquatic systems.

8. Bioaccumulation Based Sediment Guidance Values

An equilibrium partitioning-based SGV will afford the same level of protection to aquatic organisms as the AWQS/GV used in its derivation. The chronic AWQS/GV for diazinon of 0.08 µg/L was derived to be protective of 95% of aquatic species from chronic toxicity. Therefore, the Class A SGV for diazinon similarly protects most (i.e. 95%) benthic aquatic life from chronic toxicity.

Many nonpolar organic contaminants are bioaccumulative, and pose a hazard to higher trophic level organisms that feed upon fish and benthic organisms that are in direct contact with contaminants in sediment. An equilibrium partitioning-based SGV that protects higher trophic level organisms from bioaccumulative effects can be derived by using a bioaccumulation-based AWQS/GV in equation 2, above. For example, 6NYCRR part 703.5 contains a bioaccumulation-based water quality standard for DDT for the protection of wildlife consumers of fish (W standard) of 1.1×10^{-5} µg/L. The K_{oc} of DDT is 2,190,938 (derived from a log K_{ow} of 6.450 using equation 1), so the bioaccumulation-based SGV (BSGV) that would protect wildlife consumers of fish from the toxicity of DDT in sediment is:

DDT BSGV = $(1.1 \times 10^{-5}$ µg/L * 2,190,938) / 1000 gOC/kg * 20 gOC/kg = 0.48µg/kg
≈ 4.8×10^{-4} mg/kg @ 2% TOC

Bioaccumulation-based water quality standards for the protection of wildlife have been published in 6NYCRR Part 703.5 for four substances; total PCBs, 2,3,7,8-TCDD, mercury, and total DDT. Those bioaccumulation-based AWQS/GVs can be used to derive BSGVs for the protection of wildlife in the same manner illustrated above (see Table 8).

Humans are also consumers of fish. In 6NYCRR Part 703.5, New York State has promulgated numerous bioaccumulation-based water quality standards for the protection of human health from exposure to contaminants through the consumption of fish (H(FC) standard). The equilibrium partitioning methodology can also be used to derive BSGVs for the protection of human health in the same manner as wildlife; that is, a H(FC) bioaccumulation-based water quality standard is multiplied by the K_{oc}, and the resulting value adjusted for an assumed TOC value of 2% (see Table 8).

It is important to state that BSGVs are *not* used to classify sediments. Exceedances of BSGVs are intended to serve only as flags; that is, to identify that a risk from food chain bioaccumulation *might* be present. If a compound is present at a concentration less than its BSGV, then the risk associated with food chain bioaccumulation is considered to be acceptable. However, the opposite is not necessarily the case; that is, exceeding a BSGV does not by itself signify risk.

Numerous factors affect the uptake and accumulation of contaminants by fish and invertebrates as well as birds and mammals higher up the food chain. Factors such as the lipid content of the organisms, complexity of the food chain, the percentage of the diet that comes from contaminated sources, and the degree to which the contaminant is excreted or metabolized can all alter the degree of bioaccumulation, so that exceeding a BSGV does not necessarily mean that the consumers at the end of the food chain are at risk.

If the concentration of a contaminant in sediment exceeds a BSGV, then a separate evaluation is needed to assess the actual bioaccumulation risk. Such an evaluation would involve collecting tissue samples of organisms in the food chain and measuring the contaminant body burden so that accurate bioaccumulation or biomagnification factors can be measured for each step within the food chain. Alternatively, tissue samples from the top predator at the end of the food chain can be sampled to determine if it is being put at risk from food chain bioaccumulation.

Another method for deriving BSGVs for protecting wildlife is contained in the New York State Environmental Regulations. 6NYCRR Part 702.13(b) states that: [water quality] standards and guidance values to protect wildlife shall be derived using levels of chemicals known to be toxic to wildlife in conjunction with a bioaccumulation factor and wildlife consumption rates of aquatic life and water. Newell, et al. (1987) used information on the levels of chemicals known to be toxic to wildlife, wildlife body weights, and food intake rates to derive fish flesh criteria. Fish flesh criteria are the concentrations of chemicals in the flesh of fish that, if consumed by wildlife, have the potential to be harmful. The fish flesh criteria derived by Newell, et al. (1987) were based on No Observed Effects Levels (NOELs), which are the highest concentration of a chemical tested at which no harmful effect was observed. So a corresponding fish flesh criterion would be the highest concentration of a chemical in fish that could be consumed by wildlife and not be harmful.

A fish flesh criterion integrates information regarding body weights and food consumption rates. So in order to be consistent with 6NYCRR Part 702.13(b), a bioaccumulation-based AWQS/GV can be derived by dividing a fish flesh criterion by a bioaccumulation factor (BAF). NYSDEC (1999) derived BSGVs for the protection of wildlife using published BAFs found in the scientific literature. Since that time, however, there have been significant improvements in procedures for deriving BAFs. In February 1998, NYSDEC Division of Water (DOW) published TOGS 1.1.4 which describes procedures for deriving bioaccumulation factors. These procedures were adapted from similar procedures developed by the U.S. EPA as part of the Great Lakes Water Quality Initiative (GLWQI) (FR 1995).

To derive a BSGV for the protection of wildlife, contaminant concentrations in sediment that would not result in an exceedance of fish flesh criteria through bioaccumulation must be identified. An appropriate bioaccumulation factor is therefore essential to deriving a BSGV. The procedure for deriving a BAF is briefly described below. For a detailed explanation, see DOW TOGs 1.1.4 (http://www.dec.ny.gov/regulations/2652.html).

A BAF is the concentration of a chemical in an organism divided by the concentration in the water. However, not all of a chemical in water is available for uptake by an organism. Some will be sorbed to particulate organic carbon (POC) suspended in the water, and some will be sorbed to dissolved organic carbon (DOC) in the water. A *baseline* BAF is a BAF derived from the *freely dissolved* concentration of the chemical in water, instead of the total concentration of chemical in water. The first step in determining the BAF is to determine the baseline BAF.

TOGS 1.1.4 describes four methods for deriving a baseline BAF:

- A measured baseline BAF derived from an acceptable field study;
- A predicted baseline BAF derived from an acceptable measured biota-sediment accumulation factor (BSAF) from an acceptable field study;
- A predicted baseline BAF derived from a Bioconcentration Factor (BCF)[9] in a laboratory study and a food chain multiplier (FCM);
- A predicted baseline BAF derived from the chemical's K_{ow} and a FCM.

The BSGVs described here are derived from the K_{ow} (method four). Alternatively other methods can also be used, if the appropriate data are available, such as a field-measured BAF.

The formula for determining the freely dissolved fraction of a contaminant, from TOGS 1.1.4, is:

$$f_{fd} = \frac{1}{1 + \frac{(DOC)(K_{OW})}{10} + (POC)(K_{OW})} \quad (4)$$

Where: f_{fd} = freely dissolved faction of a chemical in water
DOC = concentration of dissolved organic carbon as kg DOC/L of water
POC = concentration of particulate organic carbon as kg POC/L of water

TOGS 1.1.4 provides standard values for POC and DOC for New York waters. Because actual values for POC and DOC in sediment pore water are unknown, the standard value for DOC from TOGS 1.1.4 was used. Because pore water is, by definition, the water in the pore space between particles, a decision was made that there would be no suspended POC in pore water, or if it was present, it would be adsorbed to and indistinguishable from the larger sediment particles, so the POC term of equation 4 was dropped.

Once the baseline BAF has been determined, it must be modified into a baseline BAF for different trophic levels. In general, there are four trophic levels in a (greatly oversimplified) aquatic food chain:

- Trophic level 1: primary producers – algae, macrophytes;
- Trophic level 2: herbivores – zooplankton, small fish, and invertebrates that graze on primary producers;
- Trophic level 3: omnivores - fish and larger invertebrates that graze on herbivores;
- Trophic level 4: carnivores – larger fish that eat other fish and omnivorous invertebrates.

For trophic level 1 and 2 organisms, the baseline BAF describes uptake of chemical contaminants reasonably well. Chemicals with larger K_{ow}s have a propensity to biomagnify; that

[9] A BCF is a ratio of the concentration of a chemical in an organism divided by the concentration in water, but under controlled conditions so that the only exposure to the chemical is through the water, and not food. A BAF is calculated the same way, but it allows for uptake from both water and food.

is, higher trophic levels bioaccumulate more than organisms at lower trophic levels. In order to account for the higher level of bioaccumulation at higher trophic levels, TOGS 1.1.4 published food chain multipliers (FCMs) for trophic level 3 and 4 organisms, at increasing K_{ow}s in increments of 0.1. For example, Table 1 of TOGS 1.1.4 shows that the FCM for a trophic level 3 organism and a chemical with a K_{ow} of 5.7 is 7.962. For K_{ow}s with values between the 0.1 increments, the FCM can be found by linear interpolation.

To calculate a baseline BAF for trophic level 3 (TL3) and trophic level 4 (TL4) fish from a chemical's K_{ow}, the baseline BAF is multiplied by the TL3 FCM and TL4 FCM, that correspond to the chemical's K_{ow}.

$$\text{Baseline BAF}_{TL3} = \text{Baseline BAF} * \text{FCM}_{TL3} \quad (5)$$

$$\text{Baseline BAF}_{TL4} = \text{Baseline BAF} * \text{FCM}_{TL4} \quad (6)$$

Once taken up by an organism, nonpolar organic chemicals will accumulate in the lipid fraction. Animals with more lipid can absorb more of the contaminant. TOGS 1.1.4 provides standard lipid factions for TL3 fish (6.46%) and TL4 fish (10.31%). A wildlife BAF is determined using the following equations:

$$BAF_{TL3}^{Wildlife} = [(\text{Baseline BAF}_{TL3}) * (0.0646) + 1](f_{fd}) \quad (7)$$

$$BAF_{TL4}^{Wildlife} = [(\text{Baseline BAF}_{TL4}) * (0.1031) + 1](f_{fd}) \quad (8)$$

For the purposes of estimating BSAVs for wildlife, the assumption was made that a piscivorous bird or animal's diet will consist of 75% TL 3 fish and 25% TL 4 fish. Thus, the highest freely dissolved concentration of a nonpolar organic chemical in sediment pore water that will not result in an exceedance of a fish flesh criterion would be:

$$C_{pw} = \frac{C_{ff}}{(BAF_{TL3}^{Wildlife}) \cdot (0.75) + (BAF_{TL4}^{Wildlife}) \cdot (0.25)} \quad (9)$$

Where: C_{ff} = fish flesh criterion
C_{pw} = pore water concentration

Once the pore water concentration that will not result in an exceedance of the fish flesh criterion has been determined, it can be used in the same manner as an AWQS/GV to derive an equilibrium partitioning-based BSGV; by multiplying by the K_{oc} (see section 2.A, above). BSGVs for the protection of piscivorous wildlife have been derived in this manner for the 16 of the 19 chemicals for which Newell, et al. (1987) derived fish flesh criteria. These values were adjusted for an assumed TOC value of 2% (see Table 8). An example of the derivation of a BSGV for the protection of wildlife using this method is provided in Appendix B.

The Newell, et al. (1987) method was only used for chemicals for which a bioaccumulation-based AWQS/GV for the protection of wildlife was not available; that is, the fish flesh criteria

values derived in Newell, et al. (1987) for DDT, PCB, and 2,3,7,8-TCDD were not used. BSGVs for these compounds were derived using AWQS/GVs instead.

Some metals, such as mercury, cadmium, and lead can bioaccumulate, but there is no method currently available for modeling and predicting metals bioaccumulation.

9. Modifications to SGVs for Site-specific Conditions

Initial screening is accomplished at a site with SGVs published in Tables 5 and 6, but those values are not specific to the particular site being evaluated. The purposes of initial screening are to provide a very general overview of the potential for adverse effects from the contaminants present throughout the site, and to eliminate the need for further assessment of stations within the site that are considered to present little risk (Class A). For sites where there is a potential for adverse effects (Classes B and C), site-specific information is gathered that can be used to modify SGVs, reduce uncertainty, and reclassify stations from Class B to either Class A or C. The purpose of this section is to describe procedures for modifying equilibrium-partitioning-based SGVs to integrate site-specific information, and to consider how site-specific characteristics can be reflected in empirical SGVs for metals.

A. Modifying equilibrium partitioning-based SGVs for site-specific conditions

Equilibrium-partitioning-based SGVs can be modified in three ways: make use of site-specific values for TOC, K_{OC}, or a different AWQS/GV.

To simplify the screening process, the equilibrium partitioning-based SGVs were normalized to 2% TOC, which allows for a direct comparison of the SGV with the bulk sediment concentration of nonpolar organic contaminants. However, the sediment at a given site may have more than 2% TOC. Thus, the SGVs derived for 2% TOC would be overprotective, as more TOC present would result in more contaminant being bound to the sediment and less available for uptake by an organism. Similarly, if there is less than 2% TOC present, then the SGVs are likely to be underprotective.

If the percent TOC for a given sediment sample is known, the SGVs can be recalculated. Appendix C contains the information used to derive the equilibrium partitioning-based SGVs. For example, assume a freshwater sediment sample was found to contain the insecticide toxaphene, and it has 4.7% TOC. The Class A and Class C SGVs for toxaphene from Table 5 are 6 µg/kg and 250 µg/kg respectively. At 4.7% TOC, a kilogram of sediment would contain 47 grams of organic carbon. From Appendix C, the freshwater chronic and acute SGV_{oc}s for toxaphene are 0.289 µg/gOC and 12.46 µg/gOC respectively. Using equation 3, the Class A and Class C SGVs for 4.7% TOC can be recalculated:

Toxaphene Class A or C SGV = toxaphene Class A or C SGV_{oc} * f_{oc}

Toxaphene Class A SGV = 0.289 µg/gOC * 47 gOC/kg = 13.583 ≈ 14 µg/kg

Toxaphene Class C SGV = 12.46 µg/gOC * 47 gOC/kg = 585.62 ≈ 590 µg/kg

By using the Class A or Class C SGV_{oc} from Appendix C, any of the equilibrium-partitioning SGVs in Table 5 and 6 can easily be recalculated for a specific value of TOC. Equilibrium partitioning-based SGVs should only be derived for sediments with organic carbon fractions between 0.2 – 12% TOC (EPA SAB 1992). If the TOC content exceeds 12%, then derive the modified SGVs based on a maximum of 12% TOC and determine if they are exceeded or not. If

they are, then the sediments need further evaluation and characterization to determine if it is appropriate to apply the equilibrium partitioning methodology.

In addition to different TOC values, another possible modification to an equilibrium partitioning-based SGV is the K_{oc}. The SGVs in Tables 5 and 6 were derived using the chemical's K_{ow} and equation 1. However, K_{oc}s can be quite variable in different sediments. Different types of carbon might be present with different sorbtive capacities. If a measured K_{oc} is determined for a sediment sample, then that K_{oc} can be used to derive site-specific SGVs. The site-specific SGV is determined by substituting the measured K_{oc} in equation 2. A site-specific K_{oc} can be determined by measuring the concentration of a contaminant both in the sediment and pore water, as well as the TOC in the sediment. The measured K_{oc} can then be calculated as:

$$K_{OC} = \frac{C_{sed}}{C_{pw} \times f_{oc}}$$

where: C_{sed} = contaminant concentration in sediment
C_{pw} = contaminant concentration in pore water
f_{oc} = fraction of TOC in sediment

A measured K_{oc} is only valid if an equilibrium has been established between the contaminant, the TOC in the sediment, and the pore water. Therefore, these measurements would have to be repeated over time until it can be clearly demonstrated that an equilibrium has been established.

An equilibrium partitioning-based SGV is derived by multiplying a chemical's AWQS/GV by its K_{oc}. Appendix C lists the AWQS/GVs used to derive the SGVs listed in Tables 5 and 6. These values are all either water quality standards published in 6 NYCRR Part 703.5, guidance values published in DOW TOGS 1.1.1[10], or an EPA National Water Quality Criterion[11]. Just as a site-specific SGV can be calculated by using a different K_{oc}, a site-specific SGV can also be calculated by using a site-specific AWQS/GV. The different value is substituted into equation 1.

Similarly, a SGV can be derived for a compound that does not appear in Tables 5 and 6, if the K_{ow} is known, and there is sufficient toxicity data to derive an AWQS/GV in accordance with the procedures in 6 NYCRR Part 706.1.

B. Modifications to Empirical SGVs

The empirical SGVs for metals described in this document are derived from large, multi-regional databases. There is no way to modify an empirical SGV for site-specific conditions in a manner similar to the way equilibrium-partitioning SGVs can be modified. If a sediment is classified B or C on the basis of exceeding an empirical SGV, the alternatives are to evaluate the sediments

[10] As of the publication date of this document, about 40 of the AWQS/GVs are still draft, awaiting final revision of TOGS 1.1.1.

[11] An EPA value is used *only* if a New York value has not been derived.

with a different method, such as mean SGV Quotients, the SEM-AVS difference and IWTU method, or SEM-AVS normalized for total organic carbon method. Sediments that are determined as not likely to be toxic based on these methods can *tentatively* be classified as Class A, but that classification would eventually have to be confirmed with toxicity testing.

C. Deriving Site-specific Empirical SGVs

Another approach for evaluating sediment toxicity at a specific site is to conduct simultaneous bulk sediment sampling and toxicity testing. The result is a matrix of sediment stations with known concentrations of contaminants and known toxicity. From that matrix, the concentration of each individual contaminant can be organized in ascending order and associated with the occurrence of toxic effects so that cumulative probabilities can be determined, and site-specific empirical SGVs derived. Ideally, for each contaminant there will be a lower range of concentrations associated with no toxicity, an upper range of concentrations that are consistently toxic, and an area of uncertainty in between. Once empirical, site-specific SGVs are determined for each contaminant, they can be collectively analyzed. This process is illustrated in Appendix E. This guidance recommends that site-specific SGVs should match the minimum levels of reliability defined in MacDonald, et al. (2000); that is, a minimum of 75% of the concentrations below the Class A SGV should be correctly identified as non-toxic, with not more than 25% of the concentrations being toxic. For Class C SGVs, 75% of the concentrations higher than the Class C SGV should be correctly identified as toxic, with less than 25% of the concentrations above the Class C SGV being non-toxic.

This type of analysis can be confounded, however, by conflicting results. A sediment with a very low concentration of one contaminant might be toxic because of the presence of a different contaminant. This might be resolved by evaluating the contaminants present as a mixture, as described in Section 7, above. The concentrations of multiple contaminants could be reduced to a single value (mean SGV quotient) for each station, and compared to the corresponding toxicity measured at each station.

Alternatively, sediment stations can be classified on the basis of a mean SGV quotient value assuming an adequately strong correlation exists between the SGV quotients and toxicity. As discussed in Section 7, SGV quotients can be determined for all contaminants at a site, or for different assemblages of related contaminants that are likely to have similar modes of action, such as metals, PAHs, PCBs, or chlorinated organic hydrocarbons (Long, et al. 2006). SGV Quotients can be summed or averaged, although the summed approach should not be used if there are different numbers of contaminants detected at different stations. The SGVs can be plotted against toxicity and inflection points selected as the thresholds for classifying sediments, as illustrated in Figure 2.

D. Deriving site-specific Bioaccumulation SGVs (BSGVs)

Site-specific BSGVs can also be derived. The simplest site-specific modification is adjusting the BSGV for site-specific TOC. However, most of the variables used can also be modified, including the fraction of dissolved and particulate organic carbon (DOC and POC) in sediment

pore water, the inclusion of trophic level 1 and 2 fish in the diet, the fraction of trophic level 3 and 4 fish in the diet, and even the fraction of fish in the diet. Newell, et al. (1987) developed fish flesh criteria for generic mammalian and avian receptors. However, the fish flesh criteria can be modified for specific mammalian and avian receptors by modifying the food ingestion rate and body weights used. Similarly, newer data on the toxicity of contaminants to birds or mammals can be used to revise both the fish flesh criteria and BSGVs. The example provided in Appendix B can be used as a model, in which different values can be substituted and the BSGV recalculated.

10. Guidance for conducting sediment toxicity testing

Knowledge of only the concentration of contaminants in sediment does not usually provide enough relevant information to assess the potential for harm to aquatic life that could result from those contaminants. Many physical and chemical characteristics of the sediment could serve to enhance or reduce the inherent toxicity of the individual contaminants. To determine if a mixture of chemical contaminants is actually causing harm, it is usually necessary to conduct additional assessments, such as sediment toxicity tests or benthic macroinvertebrate community analysis.

Standard methods for conducting sediment toxicity tests have been developed and published by the U.S. EPA and the American Society for Testing and Materials (ASTM). All toxicity tests must be conducted in a manner consistent with published methodologies. The purpose of this section is not to review or discuss such standard methods for conducting sediment toxicity tests. Rather, this section will discuss several considerations for ensuring that sediment toxicity testing conducted using standardized methods will provide adequate information to assess the true potential for harm to aquatic life. The results of properly conducted sediment tests can be used to derive site-specific SGVs (See section 9.D above, and Appendix E).

A. Station locations should span the gradient of contamination: Sampling must be adequate to cover the gradient of sediment contaminant concentrations. During the initial bulk chemistry sediment sampling, a range of contaminant concentrations is identified. When selecting stations for collecting sediment samples for toxicity testing, the concentrations of contaminants at locations selected should completely cover the range of contaminant concentrations at the site, from lowest to highest. The contaminant concentrations in the individual samples selected for toxicity testing should be as evenly distributed as possible throughout that range.

B. Sediment toxicity tests should test for chronic responses: Standard toxicity testing methods (such as, but not limited to U.S. EPA 1996, U.S. EPA 1996a, and U.S. EPA 2000) have been developed and approved for conducting chronic, whole-sediment toxicity tests with the amphipod *Hyalella azteca* and the midge *Chironomus tentans*[12] in freshwater. Endpoints measured in these chronic tests include effects on survival, growth, emergence (midge), and reproduction in 28-60 day exposures (U.S. EPA 2002). In salt water, standard methods recommend evaluating the growth and survival of any of the amphipods *Ampelisca abdita*, *Eohaustorius estuarius*, *Rhepoxynius abronius*, and *Leptocheirus plumulosus*.

   Although some comparisons of short term and long term sediment toxicity tests find little difference in the results, U.S. EPA (2002) reported longer-term tests in which growth and survival are measured that tended to be more sensitive than shorter-term tests, with an

[12] The scientific name for *Chironomus tentans* was changed to *Chironomus dilutus*. When citing literature that used the original name, *C. tentans*, the name will not be changed.

acute to chronic ratio on the order of six indicated for *Hyalella azteca*. U.S. EPA (2002) also states that relative species sensitivity varies among chemicals and recommends that a battery of tests be conducted to assess sediment quality, including organisms representing different trophic levels. They go on to recommend, however, that if only one test was performed, it would be desirable to conduct chronic (i.e., 28-42 day tests with *Hyalella azteca* measuring survival and growth (as length) instead of 10-14 day tests with *Hyalella azteca, Chironomus tentans,* or *Chironomus riparius*.

Long, et al. (2006) reported on experiments comparing the response of *H. azteca* in laboratory toxicity tests to the response of benthic invertebrates colonizing contaminated sediments in the field. They found that measures of survival, growth, or reproduction in 42 day laboratory tests were required to predict toxic effects observed on benthic communities exposed to similar sediments in the field.

In New York, if ten day, acute sediment toxicity tests are proposed as an alternative to a 28 day (or longer) chronic study, then any resulting site-specific thresholds derived from the use of such acute toxicity tests must be divided by an acute to chronic ratio of *at least* six (Ingersoll 2000) in order to estimate a chronically protective (Class A) threshold from acute data. Alternative acute to chronic ratios for a specific contaminant can be estimated from acute and chronic toxicity data from water only exposures.

C. Sediment toxicity tests should be conducted with both controls and reference site/station[13]: The control is used to verify that the test was correctly done, and it is usually based on a lack of adverse effect to a large fraction of the test species, such as 80 or 90%, as specified in standard methodologies. The reference site/station is used as a point of comparison for the samples. It demonstrates that any toxicity in the samples was due to something different about the sediment, ostensibly, the presence of contaminants, and not related to the sediment itself. The reference site/station must be as physically and chemically similar as possible to the sediment samples being tested, with the exception of contaminants. When the results of a sediment toxicity test from a sample station and a reference site/station are significantly different, then the results are attributed to the presence of contaminants. A reference envelope is the use of several reference sites/stations to define non-toxic conditions as opposed to a single station (Ingersoll, et al. 2009). One approach for selecting reference site/station is to collect bulk sediment chemistry data samples throughout the site, determine the mean SGV quotient for each sample based on the contaminants present, and select reference site/stations from those with a mean SGV quotient of <0.1 (Ingersoll, et al. 2009). Ingersoll, et al. actually selected reference sites from those with a mean SGV quotient < 0.2 (using the PEC as the appropriate SGV), but only because it increased the number of reference sites from two to eight. They go on to state that reference sites with a mean PEC Quotient of < 0.1 would have been preferred. A reference site/station or envelope is not intended to compare sediment toxicity test results to "background" concentrations of chemicals that

[13] A reference site would be a location completely separate from the site being investigated, such as a different lake (with similar characteristics) or upstream location. A reference station would be a location within the overall site under investigation that was found to be relatively uncontaminated.

might themselves constitute contamination. However, at times, this might be unavoidable. Hunt, et al. (2001) discusses the problem of identifying reference sites in San Francisco Bay for monitoring and comparison purposes, where it was unlikely that there were any pristine sites that would be indicative of pre-industrial conditions. In any case, reference site/stations should be as clean as possible, without making presumptions about what concentrations of contaminants might be construed as background. If reference site/stations are unavailable, then toxicity in sediment samples being tested can be ascertained from comparisons with controls, even though that is not their primary intended purpose. Whatever method is used for selecting reference sites, it must be demonstrable that the sediment from the reference site/station is not toxic and is fundamentally similar to sediments from the contaminated site being assessed.

D. Consider breaking sites into sub-sections based on physical characteristics: It is more important that the contaminant concentration gradient be covered than the physical area of the entire site, assuming that the physical characteristics of the sediment are consistent. If sections of the site do differ significantly in terms of physical parameters (i.e. a stream with both fast, riffly sections and slower moving pools), then the overall site should be broken down into sub-sections, and each subsection treated as a separate site. One physical characteristic that can be used to divide larger sites into smaller sections is average sediment grain size. If one section of a site consists of coarse-grained sediment, that is, sediment with an average grain size > 62 μm, and another section of the site consists of fine-grained sediment, or sediment with an average grain size of < 62 μm, then the site should be broken down into fine and coarse sections and each section evaluated separately.

11. Decision-making process regarding contaminated sediment

Screening, classification, and assessment of sediments is an iterative process. It begins with little information, usually only bulk sediment chemistry data, and as additional information is added, sediments are rescreened and reclassified. The goal of the process is to eliminate all Class B contaminants, and reclassify them either as acceptable (Class A), or toxic (Class C).

At any given station within a site contaminated by multiple contaminants, the *overall* classification of each station is assigned based on best professional judgment, taking into account both the number of individual contaminants and the magnitude of their concentration at the same station. For example, see Appendix 1. Seven contaminants were detected in sediment from Station WB004. Three were classified A, three were classified B, and one was classified C. In this case, station WB004 was tentatively classified as Class C, because the concentration of the one particular contaminant alone was believed to be sufficient to raise a concern for toxicity, at least at the initial screening stage.

The screening, classification, and assessment process calls for additional information to be collected and integrated into the screening. In the example shown in Appendix A, additional information included measurement of TOC. At station WB004, the TOC was greater than the 2% value used for the initial screening SGVs. The site-specific TOC value was used to revise the SGVs, and when re-screened, the classification of the contaminant that was originally Class C was revised to Class B. With three Class A contaminants and four Class B contaminants, the classification of station WB004 was revised to Class B.

When contaminant concentrations in sediment are reported, the quantitation limits that were applied to the sample should also be reported, so it can be determined if the appropriate detection limits were used[14]. If a quantitation limit is larger than the SGV, then the presence or absence of that particular chemical, and the potential risk it might present, cannot be ascertained by screening. The historical context and the nature of the specific contaminants present can be considered to make a judgment as to whether a compound with an extremely low SGV could be a concern or not. For example, if the contaminated site was the outfall of a metal electroplating facility, and the sediments were contaminated with copper and zinc, then it is not likely that the sediments would be contaminated with hexachlorobenzene whether it was detected or not.

At some point, no further information can be added to alter or revise the screening results, and direct measurements of sediment impairment are required; specifically, toxicity testing, and benthic community analyses. It is possible that toxicity testing and benthic community analyses will not clearly resolve all issues of toxicity. For example, toxicity could occur at stations where it is not anticipated, and stations with high concentrations of contaminants might not show toxicity at all. To interpret conflicting results, a weight of evidence approach is required.

[14] The method detection limit (MDL) is the lowest concentration of a chemical that can be detected by a given method, but the quantitation limit is the lowest concentration that can be accurately measured. As a general rule of thumb, the quantitation limit is typically 3-4 times the MDL. Detection limits are dependent, however, on the amount of sample being analyzed. If the sample is too small, the MDL will be much higher.

A weight of evidence approach can be very beneficial when evaluating risks from sediment contamination and is likely to result in more defensible sediment assessments. Any meaningful assessment of sediment quality needs to involve consideration of multiple lines of evidence, typically from sediment chemistry, ecotoxicology, and benthic ecology (Bately, et al. 2002). Additional lines of evidence are particularly useful when predictions of toxicity from bulk sediment dry weight concentrations and toxicity test results do not agree.

The use of the bulk chemistry data used for screening, along with toxicity testing and benthic community analysis constitutes a weight of evidence approach known as the sediment quality triad (SQT) (Long and Chapman 1985; Chapman 1990). The following is a sediment quality triad (SQT) decision matrix that demonstrates how the three different SQT components can be used to guide sediment management decisions (Chapman 2007):

Table 4. Sediment Quality Triad decision matrix

Chemical contamination	**Laboratory toxicity**	**Benthos alteration**	**Possible conclusions**
+	+	+	Strong evidence for pollution-induced degradation; management actions required.
-	-	-	Strong evidence against pollution-induced degradation; no management actions required.
+	-	-	Contaminants are not bioavailable; no management actions required.
-	+	-	Unmeasured contaminant(s) or condition(s) have the potential to cause degradation; no immediate management actions required.
-	-	+	Benthos alteration is not due to toxic contamination; no toxic management actions required.
+	+	-	Toxic contaminants are bioavailable but *in situ* effects are not demonstrable – need to determine reason(s) for sediment toxicity.
-	+	+	Unmeasured toxic contaminants are causing degradation – need to determine reasons for sediment toxicity and benthos alteration.
+	-	+	Contaminants are not bioavailable; alteration not due to toxic chemicals – need to determine reason(s) for benthos alteration.

Other conclusions besides the ones described in the table are possible, and can be used to guide sediment management decisions as long as they are defensible and reasonable. For example, when benthos alteration is the only adverse impact observed (line 5, above), consideration must be given as well to the possibility of an unmeasured toxic contaminant that is the cause of the benthos alteration.

Chapman (1996) provides a more detailed explanation of this SQT decision table and how it can be interpreted to make sediment management decisions. There is no reason why the lines of

evidence used to drive a sediment management decision should be limited to three. Chapman and Hollert (2006) indicate that biomagnification has already been integrated into the SQT making it a Sediment Quality Tetrad, and an expanded decision matrix similar to the one above but including biomagnification has been proposed (Grapentine, et al. 2002). Grapentine, et al. (2002) go on to suggest as many as 14 additional lines of evidence that could be used to guide sediment management decisions, such as benthos colonization, fish histopathology, bacterial community structure, and genetic diversity. The more lines of evidence that are added, however, the greater the possibility of conflicting results, which can confound regulatory decisions. A sediment quality assessment should only include that information necessary to make regulatory decisions. Additional lines of evidence should only be added when there are clearly unexplained conflicts between the primary sediment assessment tools (i.e. bulk sediment dry weight concentration, sediment toxicity testing), and benthic community analyses.

Additional lines of evidence can be used to supplement and explain toxicity test results, but they should not replace sediment toxicity testing. For example, SEM-AVS (see Section 7.B) is a line of evidence. A high SEM-AVS difference can serve to explain why sediment toxicity tests indicate no toxicity, despite bulk sediment dry weight concentrations that exceed Class C thresholds. That same high SEM-AVS difference should not be accepted alone *in lieu of* sediment toxicity testing. The high SEM-AVS difference, however, can be used to limit the extent of toxicity testing; that is, if a site with high bulk sediment dry weight concentrations of metals also has a high SEM-AVS difference, then sediment toxicity testing might be limited to a few tests used to validate the prediction of a lack of toxicity from the metals. There are certainly a number of uncertainties that are associated with toxicity testing (Batley, et al. 2002), however, toxicity testing is essential for understanding the risks associated with sediment contamination.

Examples of lines of evidence in addition to sediment toxicity testing that can be employed to assess the toxicity of sediments include (but are not limited to):

- Benthic community analyses
- Alternative sediment toxicity procedures (bioluminescent and enzymatic methods)
- SEM-AVS Difference
- Pore water evaluation and testing (IWTU analysis)
- Sediment contaminant aging
- Biotic Ligand Model
- Biota tissue samples and bioaccumulation/biomagnification

Benthic Community Analyses

A benthic community analysis, or macrobenthic community analysis, is a study that examines the characteristics of the benthic community that inhabits a potentially contaminated site. Such analysis requires the use of a reference site or sites wherein the physical and chemical characteristics of the sediment are comparable to those at the site being evaluated except that the contaminants of concern are absent. Several different biometrics have been proposed for evaluating the health of the resident benthic community. Typical metrics include species abundance and richness.

A benthic community analysis can reflect impacts to aquatic life from contaminants at much lower concentrations then are demonstrated by 10 day or even 28 day sediment toxicity tests with amphipods. For example, Hyland, et. al. (1999) classified benthic communities as degraded based on four metrics; number of species, total faunal abundance, dominance, and abundance of pollution-sensitive taxa. When the concentration of contaminants at degraded sites was divided by ERMs and PELs, mean ERM and PEL quotients fell in the range of 0.02 – 0.096, indicating that community-level adverse impacts were observed well below the expected mean ERM or PEL quotient of 1.0.

A good example of the use of benthic community analysis to guide assessments of contaminated sediment can be found in McPherson, et al. (2008). This study is useful because the reference site was compromised, and bulk sediment chemistry and toxicity testing did not clearly differentiate toxic and non-toxic stations, elevating the importance of benthic community data. It also demonstrates how different statistical procedures such as non-metric multidimensional scaling (NMDS) was used to evaluate benthic communities.

Care is required in the selection of community analysis metrics. Day, et al. (1995) reported in their study that attempts to rank sites using diversity indices (e.g., Shannon-Wiener and Simpson's) failed, because indices were found to be very similar among sites or slightly higher at sites where communities were known to be degraded by metals contamination. They cite Metcalfe-Smith (1994) who reported that the use of diversity indices when toxicity is present causes a decrease in both number of species present and abundance; which in turn results in an increase in "evenness" and a higher diversity index. Thus, multiple metrics are required to accurately assess the status of a benthic macroinvertebrate community.

It is also possible to overly-complicate benthic community analyses with multiple metrics. To avoid this, one must return to the core objective of the community analysis; determining whether the benthic community present at a contaminated sediment site differs significantly from the benthic community present at a representative reference site. A statistical comparison of the numbers of species and individuals present at the two sites might be sufficient for a qualitative assessment.

A detailed description of benthic community analysis is beyond the scope of this document. The Department has published procedures, methods, and metrics for assessing benthic communities in streams (Smith, et al. 2009). The metrics described therein should be the basis for selecting metrics for benthic community analyses, with appropriate modifications for different habitat types. Benthic community analyses should be conducted with methods and metrics that are consistent with those published in the scientific literature.

Alternative sediment toxicity test methods

Sediment toxicity tests are costly, difficult, and time-consuming. alternative methods, however, are available for toxicity testing and can provide useful information more rapidly and at less expense than traditional 28 day sediment testing with benthic invertebrates. These methods typically involve the use of bacteria. An assessment of toxicity is based on enzymatic responses of bacteria to contaminants. It is indicated by a change in luminescence or color of an indicator

dye. Similar enzymatic responses by planktonic species (e.g., *Daphnia*) might also be measured in assessing toxicity of contaminants. A problem with these alternative tests, though, is interpretation; that is, how does an enzymatic response by bacteria to contaminants relate to chronic toxic responses of macrobenthic organisms?

Day, et al. (1995) conducted three alternative bioassays and traditional chronic sediment toxicity tests with four species; *Hyalella azteca, Tubifex tubifex, Chironomus riparius, Hexagenia limbata and H. rigida*. A macrobenthic community analysis on 46 sediment samples from contaminated sites in Lake Ontario, and 6-7 reference sites, was also conducted. A strong concordance between results of some of the alternative test results and traditional sediment toxicity results as well as impaired benthic community structures was demonstrated. In addition to the standard amphipod bioassay, Mueller, et al. (2003) used the Microtox 100% elutriate test, the Microtox Solid Phase Test, and four other microbial assays to test sediments in a remediation study. Mowat and Bundy (2001) used a modified basic solid phase test (mBSPT) and DeltaTox to investigate the toxicity of sediments containing metals and petroleum by-products. Delistraty and Yokel (2007) tested sediment pore water with Microtox and the Daphnia IQ test to evaluate the toxicity of contaminated sediments in the Columbia River. These different alternative tests all had varying degrees of usefulness in predicting the results of traditional toxicity tests, depending on the type of contaminant being evaluated.

These tests are not alternatives to traditional toxicity testing. Instead, microbial, enzymatic, or luminescent tests can be conducted simultaneously with traditional toxicity testing, so that the results of the alternative test can be related to the results of traditional testing. Once a relationship has been established at a site between alternative and traditional toxicity test results, the alternative test methods might be used to predict the presence or absence of toxicity in other stations within the same site where sediment had the same general physical and chemical characteristics. This would allow for a significant expansion of toxicity testing without invoking the costs and delays associated with traditional methods. This approach can only be considered when a suitable battery of both alternative and traditional toxicity testing has been accomplished simultaneously. The use of alternative test methods as surrogates for traditional toxicity testing can only be done on a site-specific basis. The relationship between the two different methods cannot be applied to different sites with different physical and chemical conditions, and different contaminants.

SEM and AVS

The SEM:AVS ratio and SEM-AVS difference methods have been discussed in detail in Section 7.B. The evidence generated by these methods supports the determination that samples are nontoxic (as exhibited by benthic macroinvertebrate community analysis and toxicity testing) and in some instances, may be useful for tentatively classifying a sediment sample as Class A. The SEM-AVS difference method appears to work well for predicting results of acute (10-day) toxicity testing, but much greater uncertainty was noted when using the method for predicting the results of longer term chronic tests (U.S. EPA (2005).

The same can be said about the SEM:AVS ratio method. Kuhn, et al. (2002) found that in ten day toxicity tests with the estuarine amphipod *Ampelisca abdita*, toxicity did not appear until the

SEM:AVS ratio exceeded 1.0. However, in 70 day chronic toxicity tests, significant toxicity (decreased survival) was observed at SEM:AVS ratio as low as 0.82. Reproductive effects were even more sensitive, with a decrease in the number of young produced at an SEM:AVS ratio of 0.51, but this reduction was not significant due to the inherent variance associated with reproduction. Though not significant, a further analysis of the population growth rates at different SEM:AVS ratios shows that the change in population growth rate observed at the SEM:AVS ratio of 0.82 would eventually lead to extinction over a rapid period of time for this species, which has a relatively short life span. Delistraty and Yokel (2007) commented that the complex composition of AVS and its spatial and temporal variability in sediments confound interpretation of the results [of sediment pore water toxicity tests].

Analysts are cautioned to interpret the results of SEM and AVS analysis carefully. Such results should not be accepted as a sole line of evidence that concentrations of metals in sediment are not toxic. Furthermore, disturbance of sediments must be considered. If sediment is likely to be disturbed, then precipitated metal sulfides could potentially be oxidized and free metal released. While this does not, in itself, preclude the use of SEM and AVS methods, it is a factor that must be taken into consideration.

Sediment Contaminant Aging

Another process that can serve to mitigate toxicity of a sediment-bound contaminant is aging; that is, the bioavailability of a contaminant in sediment may change with time. Nonpolar organic compounds will adsorb to organic carbon in sediment. Alexander (1995) reported on decreases in the toxicity of DDT in soil, and hypothesized that toxicity is reduced because increasing quantities of the organic compound adsorb to soil particles with the passage of time. Sorption involves not only the external surface of soil particles but also a slow and continuing diffusion of the contaminant molecules to sites *within* the soil particles. The internal and more remote sites continue to bind more and more of the contaminant with increasing time. Landrum, et al. (1992) studied the effect of aging of PAHs in sediment and found increased partitioning between interstitial pore water and sediment particles over time. Such increased partitioning has been described as movement from a reversible to a resistant pool of bound compound. Aging could explain why low levels of toxicity are observed despite high bulk sediment contaminant concentrations in sediment. Pore water analysis and testing could be a useful tool to confirm that contaminants are more strongly bound to sediments than would be predicted from the K_{ow}.

Biotic Ligand Model

The biotic ligand model is a water quality model used to predict the toxicity of metals in water (Paquin, et al. 2002). The most toxic form of a metal in water is the divalent metal ion (M^{++}) or ionic hydroxide species (MOH^{+}). Various organic and inorganic ligands in water can bind ionic species of metal, and limit their availability for uptake by organisms. The model uses a number of water quality characteristics (temperature, pH, alkalinity, and concentration of dissolved organic carbon (DOC), major cations (Ca, Mg, Na, K), major anions (SO_4, Cl, S)) to predict the availability and toxicity of the metal. The biotic ligand model is the basis for the U.S. EPA water quality criteria for copper (U.S. EPA 2007). The biotic ligand model should only be used with interstitial pore water, and it could be used as a line of evidence to understand why high

concentrations of metals may not exhibit toxicity, even in the absence of AVS.

Pore Water Testing

The function of an equilibrium partitioning-based SGV is to predict the fraction of a contaminant in sediment dissolved in the interstitial pore water, because the fraction dissolved in porewater best correlates with toxicity (U.S. EPA 2002a). One alternative is to measure pore water directly, and compare the results to AWQS/GVs. This approach is particularly useful for estimating risks from contaminants in sediment that have a low K_{ow}, that is, that tend to be more soluble and don't partition strongly to organic carbon in sediment. Examining porewater chemistry is the most direct method currently available to determine the nature of the toxic chemical (Word, et al. 2002). Despite the apparent value of estimating the risk to aquatic life from contaminants in sediment by measuring dissolved contaminants in pore water, there are many problems that need to be considered with this approach. Both sediment and pore water chemistry can vary considerably over a very short vertical distance. For example, sediment and pore water might be oxic at the surface water interface (SWI), but anoxic just two or three centimeters deep. Sampling will, by definition, perturb the chemical form of the pore waters. Alteration of sediment chemistry during sampling will affect the processes of toxicant mobilization, and subsequent bioavailability via toxicant exposure/uptake, particularly for metal contaminants (Bately, et al. 2002a).

There are several methods of collecting pore water, including suction, squeezing, centrifugation, and pore water dialysis (Bately, et al. 2002). Dialysis methods (i.e. "peepers") are best for *in situ* collection of interstitial pore water. Centrifugation of the sample followed by 0.45 μm filtration is the preferred laboratory method for collecting sediment pore water (U.S. EPA 2001, U.S. EPA 2005).

The dissolved concentration of a contaminant extracted from pore water can be evaluated by comparing it directly to the AWQS/GVs published in 6 NYCRR Part 703.5 or TOGS 1.1.1. If the dissolved concentration of a contaminant is less than the corresponding chronic AWQS/GV, then the sediment should be classified as Class A. Alternatively, the quotients of the porewater concentrations divided by the corresponding AWQS/GV can be summed or averaged, depending on the additivity of the particular contaminants. If the average or sum is ≤ 1.0, then the sediment can be classified as Class A. This is similar to the IWTU method described in Section 7.B, except that the IWTU applies only to six specific metals.

Passive Samplers

A newer method for extracting contaminants directly from sediment pore water is through the use of passive samplers. Passive samplers are solid materials that can be put in direct contact with sediment, either *in situ* or in the laboratory, and accumulate contaminants that are dissolved in interstitial pore water. Passive samplers collect information about the dissolved concentration of contaminants, which is a useful measure of the concentration of contaminant bioavailable to aquatic organisms. They do not provide information about the concentrations of contaminants associated with bedded, suspended, or colloidal particles in aquatic systems (U.S. EPA 2012).

U.S. EPA (2012) describes three types of passive sampler materials; polyethylene (PE), polyoxymethylene (POM), and solid phase microextraction (SPME). Studies have shown that these types of samplers can effectively extract nonpolar organic contaminants such as PCBs, PAHs, PCDD/Fs, and chlorinated pesticides such as DDT.

This Department has had extensive experience reviewing studies in which SPME was employed to assess toxicity from PAHs at manufactured gas plant (MGP) sites. With SPME, a disposable glass fiber coated with poly-dimethylsiloxane (PDMS) is inserted into the sediment sample and allowed to equilibrate. Contaminants dissolved in the sediment pore water will diffuse into the PDMS. The SPME fiber can then be placed directly into the injection port of a gas chromatograph, and the contaminants are released for analysis and quantitation by thermal desorption (Mayer, et al. 2000). SPME has proven to be an inexpensive and reliable method for measuring PCBs (Trimble, et al. 2008) and PAHs (Hawthorne, et al. 2005) in pore water. Using the SPME method described by Hawthorne, et al. (2005), McDonough, et al. (2010) measured the bioavailable fraction of mixtures of PAHs in sediment, and reliably predicted toxicity to *Hyalella azteca* in sediment toxicity tests. This method was significantly more accurate in predicting the results of sediment toxicity tests than either bulk sediment dry weight concentrations compared to empirical SGVs, or equilibrium partitioning methods.

Pore water evaluation with SPME has been shown to be a very appropriate line of evidence for evaluating the risks of PAHs detected in sediment, particularly at manufactured gas plant (MGP) sites. MGP sites produced coal tar, a complex liquid of which PAHs are a major constituent. Spills or leaks of coal tar can migrate through the ground in the form of a non-aqueous phase liquid (NAPL) and into the sediments of adjacent waterbodies. Once in the sediments, droplets of highly insoluble coal tar become suspended in the sediment matrix. Some of the PAHs will slowly leach from the coal tar droplets and become bound to the sediment, depending on their individual solubility, volatility, and K_{ow}; where benthic organisms will be exposed to them. However, much of the PAH load will remain concentrated in the coal tar droplets, to which benthic organisms have limited exposure. When sediment samples are analyzed for PAHs, the digestion methods would not differentiate between sediment-bound PAHs or the PAHs in coal tar droplets, and the analytical results would suggest that benthic organisms are exposed to a much greater concentration of PAHs than they really are. This can be reflected by very high PAH concentrations that show very little toxicity in sediment toxicity tests. Sampling the pore water with SPME fibers provides a better measure of the dissolved concentration of PAHs that benthic organisms are actually exposed to, which in turn provides a more reliable measure of toxicity. In addition to SGVs for concentrations of PAHs bound to sediment, Table 7 also provides chronic water quality values for individual PAHs. When using PAH pore water concentrations collected with SPME fibers, the procedure for evaluating the toxicity of mixtures of PAHs described in Section 7.A, above, can still be employed. However, instead of dividing the concentration of each individual PAH present by the PAH SGV (µg/gOC), the SPME pore water concentration of each individual PAH is divided by the WQ Final Chronic Value, µg/L from Table 7 (column 4), for the corresponding individual PAH. The individual quotients thus derived are summed to determine the TU for the site. If the TU is ≥ 1.0, then the Class A threshold would be exceeded.

The SPME method has been extensively reviewed and determined to be effective and appropriate for identifying toxic sediments contaminated with PAHs. At MGP sites, PAHs are the predominant contaminant present. However, even at MGP sites, other contaminants might be present that could cause toxicity that might not be extracted by SPME or measured during analysis. The use of alternative passive samplers for various contaminants has not been evaluated in New York. Therefore, passive samplers should not be the sole determinant in predicting toxicity of contaminated sediment. Passive samplers should be used in conjunction with bulk sediment chemistry and toxicity testing. Once a predictive relationship with a high correlation coefficient has been established between the occurrence of toxicity and pore water contaminant concentrations derived from passive samplers, the passive sampler data can be used to classify sediments and further define areas of sediment contamination.

Tissue samples of biota and bioaccumulation/biomagnification

Organisms that inhabit sediment can function as indicators of the presence of bioaccumulable contaminants that might have detection/quantitation limits that are higher than their corresponding SGV. The detection of a bioaccumulable contaminant in an organism collected at a station, particularly a benthic organism with limited mobility, can be a line of evidence that the same contaminant is likely to be present in the sediment from that station, even if it wasn't detected in the bulk chemistry analysis. Fish are more likely to have tissue residues of contaminants that bioaccumulate and biomagnify, but because of their mobility, it is harder to relate the location of the where the fish was captured to the location of the contaminant within the site.

Contaminants in sediment that only bioaccumulate and do not biomagnify, such as PAHs, present the greatest risk to trophic level 2 and perhaps, to a lesser extent, trophic level 3 organisms. Contaminants that biomagnify present the greatest risk to organisms highest in the food chain (i.e. trophic level 4).

Further discussion of bioaccumulation studies is beyond the scope of this document. Bioaccumulation studies are called for if the BSGVs listed in Table 8 are exceeded. Sediments are not classified on the basis of an exceedance of a BSGV. It is simply a flag that a potential bioaccumulation problem might exist and additional studies are necessary.

12. Summary and Conclusions

- When beginning an initial study of a site for possible sediment contamination, one of the difficult questions that arises is, how many samples need to be collected? The required number of samples can be influenced by the size of the site, the physical characteristics, and the history of contaminant discharges/releases that might have occurred. Absent site-specific information, this guidance recommends that the Balduck Method be used to determine the number of samples that should be collected for an initial evaluation of sediment contamination. Other methods for selecting the number of samples to be collected to characterize the sediment contamination from a site can be used if adequately justified. The Balduck Method is described in Appendix F.

- This document addresses contamination of sediments that biota are most likely to be exposed to. The depth to which these values apply will vary depending on the nature of the biological community present and the potential for re-suspension or exposure due to erosion. Consideration must also be given for animals that will burrow into the sediments to hibernate during winter, and the depth to which the roots of aquatic macrophytes will extend.

- Sediment Guidance Values in Tables 5 and 6 are used to make the initial assessment (i.e., screening) of risk to aquatic life from contaminants in sediment.

- If the concentration of a contaminant is below the Class A threshold value, the sediment is considered to present a low risk to aquatic life relative to that contaminant.

- If the concentration of a contaminant exceeds the Class C threshold value, then the sediment could potentially present a high risk to aquatic life relative to that contaminant.

- If the concentration a contaminant lies between the Class A and Class C threshold values then there is insufficient information available to estimate the potential for toxicity, and additional testing and/or evaluation is needed. The sediments are considered to be Class B.

- The second iteration of sediment screening, classification, and assessment process is to adjust the SGVs for local conditions, such as TOC. This is applicable only to equilibrium partitioning-based SGVs. Once the site-specific TOC has been measured, the equilibrium-based SGVs can be recalculated and the sediments re-screened and re-classified. For metals, SEM-AVS analyses can be conducted.

- Subsequent iterations of the sediment screening, classification, and assessment process is to conduct toxicity testing and benthic community analysis to measure and evaluate the actual occurrence of toxicity from contaminants in the sediment (Sediment Quality Triad). Depending on the results, additional studies can be conducted, constituting a weight of evidence approach; that is, multiple lines of evidence are used to evaluate risk.

- Toxicity testing should include multiple species and endpoints, and must be of sufficient

duration to evaluate the potential for chronic (growth, survival, reproduction) impacts.

- If sufficient concordance between alternative bioassays and traditional toxicity testing is evident, such that macrobenthic effects can be reliably predicted from alternative test results, then the alternative toxicity tests can be used if any additional toxicity testing is required at the same site.

- The use of porewater analysis is a powerful tool for measuring the concentration of contaminants dissolved in interstitial pore water, which are most closely associated with toxicity. Pore water sampling can also be accomplished with passive samplers, such as PE, POM, and SPME, but documentation must be provided that the sampler selected can detect and measure the contaminant in question. Passive samplers might only be effective for specific contaminants and might not broadly evaluate all contaminants present.

- SEM-AVS difference can be used as an additional line of evidence in a weight of evidence approach to validate a lack of apparent toxicity at a sediment sample site, but SEM-AVS is not generally used as the sole line of evidence for determining that a sediment sample is non-toxic. The IWTU should be determined in conjunction with SEM-AVS difference approach.

- Benthic community analyses can provide a good indicator whether or not contaminants in sediment are causing adverse effects. Multiple metrics and/or multivariate analysis to evaluate the level of impairment of benthic macroinvertebrate communities might be needed, if a qualitative comparison of benthic communities from contaminated and reference sites is not clear indication of the presence or lack of impact.

- For bioaccumulative contaminants, the presence of actual risk to either human or wildlife consumers of fish cannot be based solely on the exceedance of a BSGV. Exceedance of a BSGV should signal the need for further bioaccumulation testing. If the concentration of a bioaccumulative contaminant is below the BSGV, then bioaccumulation is not a significant concern.

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Table 5. Freshwater Sediment Guidance Values. Class A sediments are considered to be of low risk to aquatic life. Class B sediments are slightly to moderately contaminated and additional testing is required to evaluate the potential risks to aquatic life. Class C sediments are considered to be highly contaminated and likely to pose a risk to aquatic life. All values are dry weight values rounded to two significant digits.

Compound	Class A	Class B	Class C	Derivation
Metals, mg/kg or PPM				
Arsenic	< 10	10 – 33	> 33	1
Cadmium	< 1	1 – 5	> 5	1
Chromium	< 43	43 – 110	> 110	1
Copper	< 32	32 – 150	> 150	1
Lead	< 36	36 – 130	> 130	1
Mercury	< 0.2	0.2 – 1	> 1	1
Nickel	< 23	23 – 49	> 49	1
Silver	< 1	1 – 2.2	> 2.2	3
Zinc	< 120	120 – 460	> 460	1
Organic compounds, µg/kg or PPB				
Azinphosmethyl	< 0.06	≥ 0.06		2
Benzene	< 530	530 – 1,900	>1,900	2
Benefin (benfluralin)	<1,900	1,900 – 17,000	>17,000	2
Bifenthrin	< 1.6	1.6 – 14	> 14	2
Bis(2-ethylhexyl) phthalate	< 360,000	> 360,000		2
Carbaryl	< 6	6 – 10	>10	2
Carbofuran	< 4	4 – 38	> 38	2
Carbon tetrachloride	<1,070	1070-9,600	>9,600	2
Chlordane	< 68	68 – 38,000	> 38,000	2
Chlorobenzene	< 200	200 – 1,700	> 1,700	2
Chlorpyrifos	< 12	12 – 63	> 63	2
Chlorothalonil	< 7	7 – 62	> 62	2
ΣDDT	< 44	44 – 48,000	> 48,000	2
Diazinon	< 9	9 – 19	> 19	2
Dicamba	< 180	180 – 13,000	> 13,000	2
1,2-Dichlorobenzene	< 280	280 – 2,500	2,500	2
1,3-Dichlorobenzene	< 1,800	1,800 – 7,100	> 7,100	2
1,4-Dichlorobenzene	< 720	720 – 3,300	> 3,300	2
1,1-Dichloroethene	< 520	520 – 4,700	> 4,700	2
trans-1,2-Dichloroethene	< 1,200	1,200 – 11,000	> 11,000	2
Dieldrin	< 180	180 – 780	> 780	2
Endosulfan	< 1	1 – 20	> 20	2
Endrin	< 90	90 – 220	> 220	2
Ethylbenzene	< 430	430 – 3,700	> 3,700	2
Halofenozide	< 850	850 – 6,700	> 6,700	2
Heptachlor	< 75	75-10,000	> 10,000	2
Heptachlor epoxide	< 15	15 – 2100	> 2100	2
Hexachlorobutadiene	<1,200	1,200 – 12,000	> 12,000	2

Compound	Class A	Class B	Class C	Derivation
γ-Hexachlorocyclohexane (Lindane)	< 47	47 - 78	> 78	2
Hexachlorocyclopentadiene	< 810	810 – 8,100	> 8,100	2
Isopropylbenzene (cumene)	< 210	210 – 1,800	> 1,800	2
Malathion	< 0.42	> 0.42		2
Methoxychlor	< 59	> 59		2
Metolachlor	< 240	240 – 3,300	> 3,300	2
Mirex	< 120	> 120		2
Nonylphenol	< 54,000	54,000 – 230,000	> 230,000	2
Pendimethalin	< 3,400	3,400 – 28,000	> 28,000	2
Pentachlorobenzene	< 150	150 – 2,000	> 2,000	2
Pentachlorophenol	< 14,000	14,000 – 19,000	> 19,000	2
Prometon	< 1,700	1,700 – 21,000	> 21,000	2
2,3,7,8-TCDD and equivalent	<0.0005	>0.0005		4
1,2,3,4-Tetrachlorobenzene	< 1,000	1,000 – 5,300	> 5,300	2
1,2,3,5-Tetrachlorobenzene	< 2,500	2,500 – 22,000	> 22,000	2
1,2,4,5-Tetrachlorobenzene	< 3,000	3,000 – 14,000	> 14,000	2
1,1,1,2-Tetrachloroethane	< 9,000	9,000 – 18,000	> 18,000	2
1,1,2,2-Tetrachloroethane	< 2,800	2,800 – 5,400	> 5,400	2
Tetrachloroethene	< 16,000	16,000 – 57,000	> 57,000	2
Toluene	< 930	930 – 4,500	> 4,500	2
Total PAH	< 4,000	4,000 – 35,000	> 35,000	3
Total PCB	< 100	100-1000	> 1,000	5
Toxaphene	< 6	6 – 250	> 250	2
Triadimefon	< 220	220 – 2,500	> 2,500	2
1,2,3-Trichlorobenzene	< 230	230 - 2,800	> 2,800	2
1,2,4-Trichlorobenzene	< 35,000	35,000 – 55,000	> 55,000	2
Trichloroethane (sum of isomers)	< 1,900	1,900 – 3,500	> 3,500	2
Trichloroethene	< 1,800	1,800 – 8,600	> 8,600	2
1,2,4-trimethylbenzene	< 3,400	3,400 – 30,000	> 30,000	2
1,2-Xylene	< 820	820 – 7,200	> 7,240	2
1,3-Xylene	< 480	480 – 4,200	> 4,200	2
1,4-Xylene	< 530	530 – 4,700	> 4,700	2
Xylene, isomer unspecified	< 590	590 – 5,200	> 5,200	2

1. TEC/PEC derived from MacDonald, et al. (2000) (values rounded to two significant digits)
2. Equilibrium partitioning-based on 2% TOC (values rounded to two significant digits)
3. Value from Long and Morgan (1991) (values rounded to two significant digits)
4. Equilibrium partitioning using the ambient water quality standard for the protection of wildlife (bioaccumulation), based on 2% TOC
5. DOW TOGS 5.1.9

Table 6. Saltwater Sediment Guidance Values. Class A sediments are considered to be of low risk to aquatic life. Class B sediments are slightly to moderately contaminated and additional testing is required to evaluate the potential risks to aquatic life. Class C sediments are considered to be highly contaminated and likely to pose a risk to aquatic life. All values are dry weight values rounded to two significant digits.

Compound	Class A	Class B	Class C	Derivation
Metals, mg/kg or PPM				
Arsenic	< 8.2	8.2 – 70	> 70	4
Cadmium	< 1.2	1.2 – 9.6	> 9.6	4
Chromium	< 81	81 – 370	> 370	4
Copper	< 34	34 – 270	> 270	4
Lead	< 47	47 – 220	> 220	4
Mercury	< 0.15	0.15 – 0.71	> 0.71	4
Nickel	< 21	21 – 52	> 52	4
Silver	< 1.0	1.0 – 3.7	> 3.7	4
Zinc	< 150	150 – 410	> 410	4
Organic compounds, µg/kg or PPB				
Azinphosmethyl	< 0.1	> 0.1		2
Benzene	< 460	460 – 1,400	> 1,400	2
Benefin (benfluralin)	< 980	980 – 7,300	> 7,300	2
Bifenthrin	< 0.48	0.18 – 3.5	> 3.5	2
Carbaryl	< 1	1 – 5	> 5	2
Chlordane	<63	63-1,400	>1,400	2
Chlorobenzene	< 660	660 – 4,600	> 4,600	2
Chlorpyrifos	< 8	8 – 17	> 17	2
Chlorothalonil	< 1	1 – 4	> 4	2
Σ DDT	< 44	44 – 5,700	> 5,700	4
Diazinon	< 91	> 91		2
Dicamba	< 630	630 – 4,200	> 4,200	2
1,2-Dichlorobenzene	< 850	850 – 6,100	> 6,100	2
1,3-Dichlorobenzene	< 2,100	2,100 – 7,100	> 7,100	2
1,4-Dichlorobenzene	< 1,200	1,200 – 5,100	> 5,100	2
1,1-Dichloroethene	< 4,000	4,000 – 27,000	> 27,000	2
Dieldrin	< 6	6-2,300	> 2,300	2
Endosulfan	< 0.1	0.1 – 3	> 3	2
Endrin	<6.0	6.0-96	>96	2
Ethylbenzene	< 110	110 – 750	> 750	2
Halofenozide	< 230	230 – 1,800	> 1,800	2
Heptachlor	<71	71-1,100	>1,100	2
Heptachlor Epoxide	< 15	15-220	> 220	2
Hexachlorobutadiene	< 350	350 – 3,500	> 3,500	2
γ-Hexachlorocyclohexane (Lindane)	< 1	1 – 7	> 7	2
Hexachlorocyclopentadiene	< 130	130 – 1,300	> 1,300	2
Malathion	< 0.42	> 0.42		2
Methoxychlor	< 59	> 59		2

Compound	Class A	Class B	Class C	Derivation
Metolachlor	< 290	290 – 2,000	> 2,000	2
Mirex	< 120	> 120		2
Nonylphenol	< 14,000	14,000 – 57,000	> 57,000	2
Pendimethalin	< 3,600	3,600 – 28,000	> 28,000	2
Pentachlorobenzene	< 1,100	1,100 – 14,000	> 14,000	2
Pentachlorophenol	< 21,000	21,000 – 32,000	> 32,000	2
Prometon	< 2,300	2,300 – 16,000	> 16,000	2
2,3,7,8-TCDD and equivalent	<0.0005	>0.0005		
1,2,3,5-Tetrachlorobenzene	< 750	750 – 5,400	> 5,400	2
1,2,4,5-Tetrachlorobenzene	< 2,100	2,100 – 8,500	> 8,500	2
1,1,1,2-Tetrachloroethane	< 1,800	1,800 – 5,800	> 5,800	2
1,1,2,2-Tetrachloroethane	< 540	540 – 1,700	> 1,700	2
Tetrachloroethene	< 2,600	2,600 – 8,800	> 8,800	2
Toluene	< 800	800 – 3,300	> 3,300	2
Total PAH	< 4,000	4,000 – 45,000	> 45,000	4
Total PCB	< 100	100 – 1000	> 1,000	5
Toxaphene	< 54	54 – 76	> 76	2
1,2,4-Trichlorobenzene	< 2,000	2,000 – 7,400	> 7,400	2
Trichloroethane (sum of isomers)	< 1,200	1,200 – 4,600	> 4,600	2
Trichloroethene	< 920	920 – 3,600	> 3,600	2
1,2,4-trimethylbenzene	< 2,000	2,000 – 18,000	> 18,000	2
1,2-Xylene	< 63	63 – 440	> 440	2
1,3-Xylene	< 210	210 – 1,500	> 1,500	2
1,4-Xylene	< 57	57 – 400	> 400	2
Xylene, isomer unspecified	< 91	91 – 640	> 640	2

1. TEC/PEC derived from MacDonald, et al. (2000) (values rounded to two significant digits)
2. Equilibrium partitioning-based on 2% TOC (values rounded to two significant digits)
3. Value from Long and Morgan (1991) (values rounded to two significant digits)
4. ERL/ERM from Long, et al. (1995) (values rounded to two significant digits)
5. DOW TOGS 5.1.9

Table 7. Sediment Guidance Values for PAHs (from U.S. EPA 2003).

PAH Compound	Kow	Calculated Koc	WQ final chronic value, µg/L	PAH SGV, µg/gOC	PAH SGV µg/kg sediment @ 2%TOC
Naphthalene	3.356	3.299	193.5	385	7,700
C1-Naphthalenes	3.8	3.736	81.69	445	8,900
Acenphthylene	3.223	3.168	306.9	452	9,040
Acenaphthene	4.012	3.944	55.85	491	9,820
C2-Naphthalenes	4.3	4.227	30.24	510	10,200
Fluorene	4.208	4.137	39.3	539	10,780
C3-Naphthalenes	4.8	4.719	11.1	581	11,620
Anthracene	4.534	4.457	20.73	594	11,880
Phenanthrene	4.571	4.494	19.13	597	11,940
C1-Fluorenes	4.72	4.64	13.99	611	12,220
C4-Naphthalenes	5.3	5.21	4.048	657	13,140
C1-Phenanthrene/anthracenes	5.04	4.955	7.436	670	13,400
C2-Fluorenes	5.2	5.112	5.305	687	13,740
Pyrene	4.922	4.839	10.11	698	13,960
Fluoranthene	5.084	4.998	7.109	708	14,160
C2-Phenanthrene/anthracenes	5.46	5.367	3.199	745	14,900
C3-Fluorenes	5.7	5.603	1.916	768	15,360
C1-Pyrene/fluoranthenes	5.287	5.197	4.887	769	15,380
C3-Phenanthrene/anthracenes	5.92	5.82	1.256	830	16,600
Benz(a)anthracene	5.673	5.577	2.227	841	16,820
Chrysene	5.713	5.616	2.042	843	16,860
C4-Phenanthracene/anthracenes	6.32	6.213	0.5594	914	18,280
C1-Benzanthracene/chrysenes	6.14	6.036	0.8557	930	18,600
Benzo(a)pyrene	6.107	6.003	0.9573	964	19,280
Perylene	6.135	6.031	0.9008	967	19,340
Benzo(e)pyrene	6.135	6.031	0.9008	967	19,340
Benzo(b)fluoranthene	6.266	6.16	0.6774	979	19,580
Benzo(k)fluoranthene	6.291	6.184	0.6415	980	19,600
C2-Benzanthracene/chrysenes	6.429	6.32	0.4827	1009	20,180
Benzo(g,h,i)perylene	6.507	6.397	0.4391	1095	21,900
C3-Benzanthracene/chrysenes	6.94	6.822	0.1675	1112	22,240
Indeno(1,2,3-cd)pyrene	6.722	6.608	0.275	1115	22,300
Dibenz(a,h)anthracene	6.713	6.599	0.2825	1122	22,440
C4-Benzanthracene/chrysenes	7.36	7.235	0.07062	1213	24,260

Table 8. Bioaccumulation-based Sediment Guidance Values (BSGV) for the protection of human health (fish consumption) and wildlife, rounded to two significant digits.

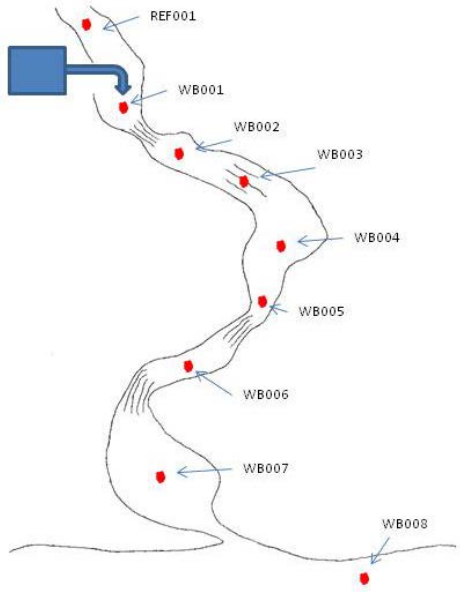
Compound	Human Health µg/kg sediment dry wt. @ 2% TOC	Wildlife µg/kg sediment dry wt. @ 2% TOC	Method code for Wildlife BSGVs
Benzene	25		
Benzo(a)pyrene (Class A – D)	18		
Benzo(a)pyrene (Class SA)	4.4		
Benzo(a)pyrene (Class SB – SD)	12		
Chlordane	0.32	7.6	1
Chlorobenzene	5200		
DDD	1.4		
DDE	0.62		
DDT	0.44		
Σ DDT		0.48	2
Dibenz(a,h)anthracene (Class SA – SD)	9.8		
Dieldrin	0.002		
Aldrin/dieldrin (sum of compounds)		1.1	1
2,4-Dimethylphenol	3600		
2,4-Dinitrophenol	280		
Endrin	5.2	1.4	
Heptachlor	4.0	5.2 (sum of compounds)	1
Heptachlor epoxide	1.2		
Hexachlorobenzene	0.19	6.1	1
Hexachlorobutadiene	12	137	1
α-Hexachlorocyclohexane	0.21	21 (sum of isomers)	1
β-Hexachlorocyclohexane	0.84		
δ-Hexachlorocyclohexane	0.81		
γ-Hexachlorocyclohexane (Lindane)	0.65		
ε-Hexachlorocyclohexane	0.81		
Hexachloroethane	110	2,700	1
Methylene chloride	68		
Mirex	0.12	9.3	1
Octachlorostyrene	0.18	0.37	1
PBDE-47	3.0		
PBDE-99	1.8		
PBDE-153	11		
Σ PCB	0.20	4.1	2
Pentachlorophenol		130	1
Tetrachloroethene	44.0		
2,3,4,6-Tetrachlorophenol		99	1
2,3,7,8-TCDD	0.0001	0.0005	2
Toluene	56,000		
Toxaphene	0.002		

Compound	Human Health µg/kg sediment dry wt. @ 2% TOC	Wildlife µg/kg sediment dry wt. @ 2% TOC	Method code for Wildlife BSGVs
Trichlorobenzene (sum of isomers)		250	1
Trichloroethene	250		

Method codes:
1 - Newell, et al. (1987) using bioaccumulation factors derived by method specified in TOGS 1.1.4
2 – Derived by equilibrium partitioning method using a bioaccumulation-based water quality standard or guidance value.

Appendix A: Hypothetical example of the sediment screening, classification, and assessment methodology.

WB is an industrial facility with a discharge into Small River. The facility is located about a half mile upstream of the confluence of Small River with Large River. The facility is slated to be sold. The new owners are proposing significant modifications to the industrial processes conducted at the facility, and in order to proceed, it was determined that an evaluation of sediment contamination, if any, in Small River below the discharge was needed. Sediment samples were collected at designated stations above the discharge (reference station), at the discharge, and approximately every 300-500 feet downstream. The last sample was collected in a station in the Large River, approximately 600 feet downstream of last station in Small River, and about 300 feet below the confluence. The sediment samples were analyzed for selected metal and organic contaminants, based on the industrial processes and maintenance activities at the WB facility.



Small River Sediment Bulk Chemistry Analysis Results									
Stations:	**WB001**	**WB002**	**WB003**	**WB004**	**WB005**	**WB006**	**WB007**	**WB008**	**REF001**
Contaminant	Metals concentrations in mg/kg (ppm)								
Arsenic	62	12	8	10	10	4	12	2	0.02
Copper	88	51	14	31	28	26	48	4	0.5
Lead	154	32	12	60	52	40	56	5	1.3
Zinc	181	64	16	76	72	20	44	12	0.1
	Organic concentrations in µg/kg (ppb)								
Chlorpyrifos	72	6	ND	12	12	4	2	ND	ND
1,2-Dichlorobenzene	4800	280	40	2600	2540	760	1200	18	ND
Toluene	2400	600	120	360	320	140	4600	24	ND

An initial screening was conducted by comparing the bulk chemistry analysis results with the sediment guidance values (SGVs) from Table 5 of "Screening and Assessment of Contaminated Sediment:

	Class A	Class B	Class C
Metals screening values in mg/kg (ppm)			
Arsenic	<10	10-35	>35
Copper	<32	32-150	>150
Lead	<36	36-130	>130
Zinc	<120	120-460	>460
Organic Screening values in µg/kg (ppb) @ 2% TOC			
Chlorpyrifos	<12	12-63	>63
1,2-Dichlorobenzene	<280	280-2,500	>2,500
Toluene	<930	930-4,500	>4,500

Based on the results of only the initial bulk chemistry sampling, the Small River Stations were classified as follows:

Contaminant	REF001	WB001	WB002	WB003	WB004	WB005	WB006	WB007	WB008
As	A	C	B	A	B	B	A	B	A
Cu	A	B	B	A	A	A	A	B	A
Pb	A	C	A	A	B	B	B	B	A
Zn	A	B	A	A	A	A	A	A	A
Chlorpyrifos	A	C	A	A	B	A	A	A	A
1,2-DBC	A	C	B	A	C	C	B	B	A
Toluene	A	B	A	A	A	A	A	C	A
Overall	**A**	**C**	**B**	**A**	**C**	**C**	**B**	**C**	**A**

The initial screening show that the reference station is suitable for use as a reference, in regards to the presence of contaminants. The initial screening also shows that the contaminant concentrations from stations WB003 and WB008 are both below levels of concern and can be dropped from future analyses.

Sample replicates that were collected during the original sampling were analyzed for percent Total Organic Carbon (TOC) and AVS:SEM. The sampling data were also reviewed to provide a physical characterization of Small River and the individual sample stations:

Station	Physical character	% TOC	Substrate	% Fines	AVS:SEM
REF001	deep riffle	2.1	Sand, silt, and mud	34	1.4
WB001	Deep pool	3.6	Silt and mud	85	1.4
WB002	Deep riffle	1.6	Sand, some silt and cobble	20	0.8
WB003	Fast, shallow riffle	0.7	Gravel, cobble	6	0.6
WB004	Pool	2.4	Sand, silt, mud	54	1.2
WB005	Faster, shallower pool	2.1	Sand, silt, some cobble	42	1.2
WB006	Deep riffle	1.6	Sand, gravel, some silt	20	1.8
WB007	Deep pool	4.4	Silt, mud	60	2.3
WB008	riverine	2.2	Sand and mud	38	2.6

As a result of the TOC analysis, the SGVs for organic compounds were recalculated:

Organic contaminant SGVs adjusted for Site-specific Percent TOC

TOC (Station)	Chlorpyrifos		1,2-Dichlorobenzene		Toluene	
	Class A	Class C	Class A	Class C	Class A	Class C
0.7 (WB003)	4	22	100	890	330	1600
1.6 (WB002)	10	51	230	2,000	740	3,600
1.6 (WB006)	10	51	230	2,000	740	3,600
2.1 (REF001)	12	66	300	2,700	980	4,700
2.1 (WB005)	12	66	300	2,700	980	4,700
2.3 (WB008)	14	73	330	2,900	1,100	5,100
2.4 (WB004)	14	76	340	3,100	1,100	5,300
3.6 (WB001)	20	110	500	4,600	1,700	8,000
4.4 (WB007)	26	140	620	5,600	2,000	9,800
2.0 (Unadjusted)	**12**	**63**	**280**	**2,500**	**930**	**4,500**

The station classifications were re-screened and reclassified, using the TOC-adjusted SGVs for organic compounds. Classifications that did not change because of the re-screening are shaded; classifications that did change are clear. As a result of the re-classification, two stations were reclassified from C to B (WB004 and WB005).

Contaminant	REF001	WB001	WB002	WB003	WB004	WB005	WB006	WB007	WB008
As	A	C	B	A	B	B	A	B	A
Cu	A	B	B	A	A	A	A	B	A
Pb	A	C	A	A	B	B	B	B	A
Zn	A	B	A	A	A	A	A	A	A
Chlorpyrifos	A	B	A	A	A	B	A	A	A
1,2-DBC	A	C	B	A	B	B	B	B	A
Toluene	A	B	A	A	A	A	A	A	A
Overall	**A**	**C**	**B**	**A**	**B**	**B**	**B**	**B**	**A**

A decision was made to conduct toxicity testing to determine if the sediments toxic or not. Testing included 28 day tests with the amphipod *Hyalella azteca*, and 21 day tests with the chironomid *Chironomus dilutus*. Stations WB003 and WB008 were not tested because they were Class A. A sample was considered to be toxic if survival or growth for either species was statistically significantly different from survival and growth observed from the survival and growth observed for both species in sediment from the reference station REF001. Benthic macroinvertebrates were also collected at the stations where sediment was collected for toxicity testing, for a benthic community analysis. The results of toxicity testing and benthic community analysis at stations where impacts were observed are as follows:

Station	WB001	WB002	WB003	WB004	WB005	WB006	WB007	WB008
Toxicity test	Toxic		Not tested	Toxic	Toxic			Not tested
Benthic Community Analysis	Impaired		Not evaluated	Impaired				Not evaluated

The results of the toxicity testing and benthic community analyses were used to re-screen, re-classify, and reassess the stations. The AVS:SEM results were generally inconclusive, although they helped explain the lack of toxicity and benthic impairment at station WB007. After those tests, the DFWMR staff believed that no additional studies or data were needed, and a final set of classifications were assigned to each station.

	WB001	WB002	WB003	WB004	WB005	WB006	WB007	WB008
Screening results following toxicity testing	C	A	Not tested	C	C	A	B	Not tested
Screening results following benthic community analysis	C	A	Not evaluated	C	A	A	A	Not evaluated
Final screening and assessment Classifications	C	A	A	C	A	A	A	A

Analysis:

The final analysis were that sediments from stations WB001 and WB004 showed adverse impacts as a result of the contaminants that probably originated from the WB facility.

Station WB001: This station was toxic because it received the highest contaminant loading. It was a deep pool with a high percentage of fine grained sediment, and a high percent TOC. Thus, a major portion of the contaminants originally discharged had a high likelihood of staying there. When tested, sediments from this station were toxic and showed an impaired benthic community.

Station WB002: This station had low percent TOC and a low percentage of fine grained sediment in the substrate. It was a deep riffle with faster moving water, reducing deposition. Fewer contaminants were able to accumulate.

Station WB003: This station was a shallow, fast riffle with very little TOC or fine grained sediment. Contaminants did not accumulate.

Station WB004: This station was a large, relatively shallow pool. It contained an intermediate percentage of both TOC and fine grained sediment. It was the first station below the discharge with slower water that allowed greater deposition. Suspended particulates that had accumulated contaminants had a greater opportunity to settle to the bottom. The sediments demonstrated both toxicity and an impaired benthic community.

Station WB005: This station was a smaller pool immediately downstream of the pool at station WB004. It was slightly shallower, slightly faster, and had slightly lower percent TOC and percent of fine grained sediment in the substrate. Like WB004, this station was originally Class C for 1,2-dichlorobenzene, but that classification was reduced to Class B when TOC was taken into account. The station demonstrated toxicity, but the benthic community was not impaired. A closer examination of the toxicity test results showed that survival of only one of the two species was reduced, and then, only slightly, even though the difference was significant. Given the lack of an impaired benthic community and the relatively low contaminant loads, a decision was

made that the toxicity observed in the lab tests was attributable to some other, unidentified factor, or that the native biota had adapted to the higher metals loading.

Station WB006: This station was practically identical to Station WB002 in terms of physical characteristics, and it was further downstream from the contaminant discharge.

Station WB007: This station was a large deep pool. It had the highest percent TOC of any station in Small River downstream of the discharge from the WB facility. It had a surprisingly high concentration of toluene. Toluene has a much smaller octanol-water partition coefficient (K_{ow}) than either chlorpyrifos or 1,2-dichlorobenzene, so it might have stayed in solution longer, and taken longer to partition out to the sediments. Regardless, the sediments were Class B for toluene after TOC was taken into account. Sediments were not toxic and the benthic community was not impaired, although the diversity and abundance estimates were on the lower side. The sediments at the station were probably stressed from the contaminants from the WB facility, but the sediments were not toxic and the benthic community was acceptable.

Station WB008: This station is located in Large River, downstream from the confluence with Small River. It did not show any impact from contaminants transported downstream by Small River.

The final assessment of the sediments in Small River from the WB facility was that the sediments at stations WB001 and WB004 demonstrated adverse impacts from the discharge of contaminants into the Small River from the WB facility, and those sediments should be considered contaminated and toxic.

Appendix B. Example of the hypothetical calculation of total TU for a mixture of PAHs.

In this sediment sample, 34 PAHs were measured (Column 1), and nine were detected (Column 2). The SGV in µg/gOC (Column 3) was taken from U.S. EPA (2003). The bulk sediment PAH concentrations are normalized to 2.7% TOC (Column 4), and the sediment concentration in µg/gOC is divided by the corresponding SGV µg/gOC (Column 3) for each individual PAH. The resulting Toxic Units (Column 5) are summed to produce a Total TU for this mixture. Since the total TU exceeds 1.0, this mixture would be considered to be potentially toxic (Class B).

Total TOC = 2.7% **PAHs**	**Sediment concentration in µg/kg (ppb)**	**SGV µg/gOC**	**Sediment concentration in µg/gOC**	**Toxic Units**
Naphthalene	100	385	37	0.096103896
C1-naphthalene		444	0	0
Acenaphthylene	300	452	111.1	0.24579646
Acenaphthene	1200	491	444.4	0.90509165
C2-naphthalene		510	0	0
Fluorene	90	538	33.3	0.061895911
C3-naphthalene		581	0	0
Anthracene	56	594	20.7	0.034848485
Phenanthrene		596	0	0
C1-fluorene		611	0	0
C4-naphthalene		657	0	0
C1-phenanthrene/anthracene		670	0	0
C2-fluorene		686	0	0
Pyrene	33	697	12.2	0.017503587
Fluoranthene		707	0	0
C2-phenanthrene/anthracene		746	0	0
C3-fluorene		769	0	0
C1-pyrene/fluoranthene		770	0	0
C3-phenanthrene/anthracene		829	0	0
Benz(a)anthracene		841	0	0
Chrysene	88	844	32.6	0.038625592
C4-phenanthrene/anthracene		913	0	0
C1-benzanthracene/chrysene		929	0	0
Benzo(a)pyrene	145	965	53.7	0.055647668
Perylene		967	0	0
Benzo(e)pyrene		967	0	0
Benzo(b)fluoranthene		979	0	0
Benzo(k)fluoranthene		981	0	0
C2-benzanthracene/chrysene		1008	0	0
Benzo(g,h,i)perylene		1095	0	0
C3-benzanthracene/chrysene		1112	0	0
Indeno(1,2,3-cd)pyrene		1115	0	0
Dibenz(a,h)anthracene	31	1123	11.5	0.010240427
C4-benzahthracene/chrysene		1214	0	0
Total PAH Toxic Units rounded to two significant digits, uncorrected*				1.47

* If only 13 PAHs had been measured, then the *corrected* total PAH TU would be 1.47 * 11.6 = 17.1.
If only 23 PAHs had been measured, then the *corrected* total PAH TU would be 1.47 * 4.14 = 6.1

Appendix C. Determination of a bioaccumulation-based sediment guidance value (BSGV) for the protection of wildlife from a fish flesh criterion – example calculations

This appendix illustrates an alternative procedure for deriving BSGVs for the protection of piscivorous wildlife from contaminants in sediment. Newell, et al. (1987) originally proposed a procedure for deriving fish flesh criteria for various nonpolar organic sediment contaminants. Fish flesh criteria were then used as the basis for BSGVs following procedures originally described in NYSDEC (1999). In this document, the procedures from NYSDEC (1999) have been altered only in that bioaccumulation factors are derived in accordance with procedures described in TOGS 1.1.4. A detailed understanding of Section 8, above is necessary to follow the example provided below:

1**. Determination of the acceptable daily intake (ADI)**

Newell, et al. (1987) conducted an extensive literature search for dietary concentrations of various nonpolar organic chemicals that are harmful to birds and animals. They identified both lowest observed effects concentrations (LOELs) and no observed effects concentrations (NOELs). For example, for mirex, they documented the following dietary risk values:

Species	Duration	Effect at LOEL	NOEL/LOEL, mg/kg diet	Recommended AF or UF
Rat	1 year	Enlarged liver, decreased litter size	0.25 (LOEL)	0.2 ($AF_{2)}$
Prairie vole	13 weeks	100% dead	0.8 (NOEL)	0.1 (AF_1)
Oldfield mouse	60 weeks	20% mortality	0.28 (LOEL)	0.2 (AF_2)
Mallard duck	25 weeks	Adult mortality, reduced survival of ducklings	100 (LOEL)	0.1 (UF) 0.2 (AF_2)

The dietary risk values (i.e., NOELs or LOELs) were modified by the use of up to three application factors (AF) or uncertainty factors (UF):

1. UF: Interspecies adjustment factor when only one or two species were tested:
   0.1 * chronic lab animal NOEL = wildlife NOEL
2. AF_1: Acute data or Subchronic (single dose to 30 day exposure) data to chronic NOEL:
   0.1 * acute LOEL = estimate of chronic NOEL
3. AF_2: Chronic LOEL to Chronic NOEL:
   0.2 * LOEL = NOEL

Newell, et al. (1987) reviewed the biology and ecology of two piscivorous mammals and 16 piscivorous birds that are likely to be exposed to chemical contaminants in aquatic sediments through their food chain. Based on that analysis they instead described two hypothetical

receptors, rather than identifying specific bird and animal species as receptors. The based the derivation of fish flesh criteria upon: a typical sensitive bird that weighed 1 kg and consumed 0.2 kg of food/day, and a typical sensitive mammal that also weighed 1 kg and consumed 0.15 kg of food/day. It was assumed that fish made up 100% of the hypothetical bird and mammal's diets. The Acceptable Daily Intake (ADI) is the maximum concentration of a chemical in food that a bird or animal can consume without exceeding a dietary risk value. A dietary risk value can be a NOEL or LOEL or other toxicological endpoint. To derive an ADI for wildlife, the dietary risk values were modified using the body weight and food consumption rates for the hypothetical bird and mammal:

$$ADI_{wildlife} = \frac{(Dietary\ risk\ value, mg/kg/day)\ x\ (AF\ or\ UF)\ x\ \ body\ weight, kg}{Food\ consumption\ rate, kg/day}$$

For mirex, the rat LOEL was used as the dietary risk level along with an application factor of 0.2 (AF_2) and the hypothetical mammalian body weight and food intake values to derive the lowest $ADI_{wildlife}$ value of the species for which data were available:

$$ADI_{wildlife} = \frac{0.25\ mg/kg/day\ x\ 0.2\ x\ 1.0\ kg}{0.15\ kg/day} = 0.33\ mg/kg$$

2. Determination of the bioaccumulation factor.

A. Baseline BAF derived from the K_{ow}.

From the log K_{ow} for mirex of 6.89, a K_{ow} of 7,762,471 was calculated. In accordance with TOGS 1.1.4, a baseline BAF is derived from a K_{ow} by multiplying the K_{ow} by a food chain multiplier:

Baseline BAF = K_{ow} * food chain multiplier (FCM)

Baseline BAFs must be determined for each trophic level fish that birds and animals are likely to feed upon. It was assumed that the diet of piscivorous birds and animals was likely to consist of 75% trophic level 3 (TL3) fish and 25% trophic level 4 (TL4) fish. Thus, baseline BAFs are needed for TL3 and TL4.

From table 1 of TOGS 1.1.4, the following FCMs can be obtained.

Log K_{ow}	Trophic Level 2	Trophic Level 3	Trophic Level 4
6.8	1.000	14.355	26.669
6.9	1.000	14.388	26.669

By linear interpolation, the TL3 and TL4 FCMs for mirex with a log K_{ow} of 6.89 were found to be 14.3847 and 26.669, respectively. Baseline BAFs for each trophic level can now be determined as:

Baseline BAF_{TL3} = 7,762,471 * 14.355 = 111,660,819

Baseline BAF_{TL4} = 7,762,471 * 26.669 = 207,017,343

B. Determine the wildlife BAF from the baseline BAF

A wildlife BAF is derived from the concentration of a contaminant freely dissolved in water, or more specifically, interstitial pore water. To determine the BAF, the freely dissolved concentration must first be determined, using the following equation from TOGS 1.1.4:

$$f_{fd} = \frac{1}{1 + \frac{(DOC)(K_{OW})}{10} + (POC)(K_{OW})}$$

Where: f_{fd} = freely dissolved faction of a chemical in water
DOC = concentration of dissolved organic carbon as kg DOC/L of water
POC = concentration of particulate organic carbon as kg POC/L of water

The recommended value of 0.000002 kg/L was used for DOC, and the POC was set at 0:

$$f_{fd} = \frac{1}{1 + \frac{(0.000002)(7{,}762{,}471)}{10} + (0)(7{,}762{,}471)} = 0.3917 \approx 0.39$$

The wildlife BAFs for TL3 and TL4 must be adjusted for the lipid content of fish. TOGS 1.1.4 provides standardized lipid values of 6.46% for TL3 fish and 10.31% for TL 4 fish. The lipid values are used with the concentration of total PCBs freely dissolved in pore water to derive the wildlife BAFs:

$BAF_{TL3}^{Wildlife}$ = [(Baseline BAF_{TL3}) * (% lipid for TL3 fish) + 1](f_{fd})

$BAF_{TL4}^{Wildlife}$ = [(Baseline BAF_{TL4}) * (% lipid for TL4 fish) + 1](f_{fd})

$BAF_{TL3}^{Wildlife}$ = [(111,660,819) * (0.0646) + 1] * (0.39) = 2,813,183

$BAF_{TL4}^{Wildlife}$ = [(207,017,343) * (0.1031) + 1] * (0.39) = 8,323,961

C. Determination of the bioaccumulation-based water quality value.

A fish flesh criterion for the protection of wildlife is the maximum concentration of a chemical that can be present in fish flesh and not be harmful to birds and animals that consume the fish. Similarly, the $ADI_{wildlife}$ is the acceptable daily intake of a chemical through its diet that will not result in an exceedance of the toxic effect used to derive it (i.e., LOEL, NOEL, LE_{50}, etc.). The fish flesh criterion and the $ADI_{wildlife}$ are synonymous for piscivorous wildlife. Since fish acquire chemicals into their bodies by bioaccumulation, a bioaccumulation-based water quality value is the concentration of a chemical in water that will not result in exceedance of the fish flesh criterion for that chemical. To apply this process to sediment, the bioaccumulation-based water quality value is applied to pore water. The pore water concentration (C_{pw}) of mirex that will not result in an exceedance of the fish flesh criterion (C_{ff}) is the fish flesh criterion divided by the bioaccumulation factor. The diet of piscivorous wildlife is estimated to consist of 75% TL3 and 25% TL4 fish, so the C_{pw} for mirex can be found as:

$$C_{pw} = \frac{C_{ff}}{\left(BAF_{TL3}^{wildlife}\right)\cdot(0.75)+\left(BAF_{TL4}^{wildlife}\right)\cdot(0.25)} =$$

$$C_{pw} = \frac{0.33 mg/kg}{(2{,}813{,}183)\cdot(0.75)+(8{,}323{,}961)\cdot(0.25)} = 0.0000000787 mg/L \approx 0.000079 \mu g/L$$

(NOTE: The units for BAFs are L/kg)

D. Determination of the BSGV for the protection of wildlife

Once the C_{pw} value has been determined, the sediment BSGV can be derived by the standard equilibrium partitioning method:

SGV_{oc} = AWQS/GV µg/L * K_{oc} or,

$BSGV_{oc}$ = C_{pw} µg/L * K_{oc}

For mirex:

mirex $BSGV_{oc}$ = 0.0000787 µg/L * 5,931,301 * 1kg/1000gOC = 0.467 µg/gOC

Adjusting this value for an assumed TOC in sediment of 2%:

mirex BSGV = 0.467 µg/gOC * 20 gOC/kg = 9.34 ≈ 9.3 µg/kg

Table B-1. Input values used to derive fish flesh criteria and BSGVs

Compound	log K_{ow}	Source and notes[1]	K_{oc}[2]	Fish flesh criterion, mg/kg[3]	TL3 FCM[4]	TL4 FCM[4]	Fraction freely dissolved	BSGV µg/gOC
Aldrin/Dieldrin	5.299	GLI, value for dieldrin	1,708,048	0.022	12.93	22.32	0.96	0.053
Chlordane	6.00	GLI	2,033,251	0.37	13.30	23.51	0.83	0.382
Endrin	5.2	HSDB	161,881	0.025	4.80	4.73	0.97	0.069
Heptachlor/Heptachlor epoxide	5.739	HSDB, GM of both	791,189	0.2	10.56	16.00	0.9	0.260
Mirex	6.89	GLI	7,960,494	0.33	14.27	26.09	0.39	0.467
Hexachlorobenzene	5.6	GLI	129,384	0.2	4.19	3.87	0.93	0.306
Hexachlorocyclohexane (Σ isomers)	3.765	GLI, GM of isomers	438,245	0.1	8.30	10.93	1	1.045
Hexachlorobutadiene	4.842	GLI	5,931,301	1.3	14.38	26.67	0.99	6.850
Hexachloroethane	4.04	GLI	319,948	14	7.10	8.55	1	133.067
Octachlorostyrene	6.29	GLI	5,027	0.02	1.15	1.04	0.72	0.019
Trichlorobenzene (Σ isomers)	4.085	GLI, GM of isomers	57,539	1.33	2.21	2.01	1	12.396
Pentachlorophenol	5.12	HSDB	9,367	2	1.28	1.08	0.97	6.325
2,3,4,6-Tetrachlorophenol	4.45	HSDB	1,525,281	0.67	12.64	21.50	0.99	4.942

[1] GLI: U.S. EPA (1995); HSDB: Hazardous Substance Data Bank; GM: geometric mean
[2] derived with equation 1
[3] from Newell, et al. (1987)
[4] by linear interpolation from incremental log Kow values provided in TOGS 1.1.4

Appendix D. Derivation information for equilibrium partitioning-based SGVs for nonpolar organic contaminants listed in Tables 5 and 6. The information in this table can be used to derive site-specific SGVs when a site-specific TOC value is known.

Compound	CAS	$\log K_{ow}$*	K_{oc}	FW Chronic WQ value, µg/L	FW Acute WQ value µg/L	SW Chronic WQ value, µg/L	SW Acute WQ value µg/L	FW Class A SGV_{oc} µg/gOC	FW Class C SGV_{oc} µg/gOC	SW Class A SGV_{oc} µg/gOC	SW Class C SGV_{oc} µg/gOC
Azinphosmethyl	86-50-0	2.75	505	0.005		0.01		0.003		0.005	
Benzene	71-43-2	2.138	126	210	760	180	560	26.555	96.105	22.762	70.814
Benefin	1861-40-1	5.29	158,617	0.61	5.3	0.31	2.3	96.756	840.671	49.171	364.819
Bifenthrin	82657-04-3	6	791,189	0.0001	0.0009	0.00003	0.0002	0.079	0.712	0.0024	0.158
Bis(2-ethylhexyl) phthalate	117-81-7	7.6	29,585,574	0.6				17751.344			
Carbaryl	63-25-2	2.36	209	1.4	2.4	0.34	1.3	0.293	0.502	0.071	0.272
Carbofuran	1563-66-2	2.32	191	1	10			0.191	1.909		
Carbon tetrachloride	56-23-5	2.83	606	88	790			53.291	478.407		
Chlordane[1]	57-47-9	6.0	791,189	0.0043	2.40	0.004	0.09	0.594	3.157	0.421	0.827
Chlorobenzene	108-90-7	2.865	656	15	130	50	350	9.833	85.215	32.775	229.426
Chlorpyrifos	2921-88-2	4.96	75,155	0.0079	0.042	0.0056	0.011	0.594	3.157	0.421	0.827
Chlorothalonil	1897-45-6	3.05	996	0.34	3.1	0.029	0.2	0.339	3.089	0.029	0.199
DDT[1]	50-29-3	6.45	2,190,938	0.001	1.1	0.001	0.13	2.191	2410.03	2.191	284.822
Diazinon	333-41-5	3.81	5,566	0.08	0.17	0.82	0.82	0.445	0.946	4.564	4.564
Dicamba	1918-00-9	2.21	149	61	4400	210	1400	9.079	654.881	31.256	208.371
1,2-Dichlorobenzene	95-50-1	3.43	2,355	6	54	18	130	14.129	127.164	42.388	306.135
1,3-Dichlorobenzene	541-73-1	3.53	2,953	31	120	36	120	91.544	354.365	106.31	354.365
1,4-Dichlorobenzene	106-46-7	3.44	2,409	15	69	24	105	36.132	166.207	57.811	252.924
1,1-Dichloroethene	75-35-4	2.13	124	210	1900	1600	11000	26.079	235.952	198.696	1366.038
trans 1,2-Dichloroethene	156-60-5	2.06	106	560	5000			59.354	529.944		
Dielderin[2]	60-57-1	5.299	161,881	0.056	0.24	0.0019	0.71	9.065	38.852	0.308	114.936

Compound	CAS	$\log K_{ow}$*	K_{oc}	FW Chronic WQ value, µg/L	FW Acute WQ value µg/L	SW Chronic WQ value, µg/L	SW Acute WQ value µg/L	FW Class A SGV_{oc} µg/gOC	FW Class C SGV_{oc} µg/gOC	SW Class A SGV_{oc} µg/gOC	SW Class C SGV_{oc} µg/gOC
Endosulfan	115-29-7	3.724	4,581	0.009	0.22	0.001	0.034	0.041	1.008	0.005	0.156
Endrin[2]	72-20-8	5.2	129,384	0.036	0.086	0.0023	0.037	4.658	11.127	0.298	4.787
Ethylbenzene	100-41-4	3.15	1,249	17	150	4.3	30	21.241	187.422	5.373	37.484
Halofenozide	112226-61-6	3.22	1,464	29	230	8	63	42.456	336.719	11.712	92.232
Heptachlor[1]	76-44-8	6.1	992,156	0.0038	0.52	0.0036	0.053	3.77	515.921	3.572	52.584
Heptachlor epoxide[1]	1024-57-3	5.4	203,460	0.0038	0.52	0.0036	0.053	0.773	105.799	0.732	10.782
Hexachlorobutadiene	87-68-3	4.842	57,539	1	10	0.3	3	57.539	575.395	17.262	172.618
γ-Hexachlorocyclohexane (Lindane)[3]	58-89-9	3.673	4,082	0.95				3.878			
Hexachlorocyclopentadiene	77-47-4	5.04	90,074	0.45	4.5	0.07	0.7	40.533	405.334	6.305	63.052
Isopropylbenzene (cumene)	98-82-8	3.66	3,963	2.6	23			10.305	91.157		
Malathion	121-75-5	2.36	209	0.1		0.1		0.021		0.021	
Methoxychlor	72-43-5	5.08	98,610	0.03		0.03		2.958		2.958	
Metolachlor	51218-45-2	3.13	1,194	10	140	12	84	11.942	167.185	14.33	100.311
Mirex	2385-85-5	6.89	5,931,301	0.001	0.001	0.001	0.001	5.931	5.931	5.931	5.931
Nonylphenol	25154-52-3	5.71	410,403	6.6	28	1.7	7	2708.657	11491.27	697.684	2872.818
Pendimethalin	40487-42-1	5.2	129,384	1.3	11	1.4	11	168.199	1423.222	181.137	1423.222
Pentachlorobenzene	608-93-5	5.106	104,587	0.073	0.96	0.51	6.8	7.635	100.404	53.339	711.192
Pentachlorophenol	87-86-5	5.12	107,954	6.7	8.7	9.7	15	723.294	939.203	1047.157	1619.315
Prometon	1610-18-0	2.99	870	98	1200	130	930	85.246	1043.834	113.082	808.971
2,3,7,8-TCDD	1746-01-6	7.02	7,960,494	0.0000000031				0.000025			
1,2,3,4-Tetrachlorobenzene	634-66-2	4.592	32,675	1.6	8.1			52.28	264.668		
1,2,3,5-Tetrachlorobenzene	634-90-2	4.654	37,598	3.3	29	1	7.2	124.073	1090.335	37.598	270.704
1,2,4,5-Tetrachlorobenzene	95-94-3	4.557	30,186	4.9	23	3.5	14	147.913	694.287	105.652	422.609
1,1,1,2-Tetrachloroethane	630-20-6	2.93	759	620	1200	120	380	470.827	911.279	91.128	288.572

Compound	CAS	log K_{ow}*	K_{oc}	FW Chronic WQ value, µg/L	FW Acute WQ value µg/L	SW Chronic WQ value, µg/L	SW Acute WQ value µg/L	FW Class A SGV_{oc} µg/gOC	FW Class C SGV_{oc} µg/gOC	SW Class A SGV_{oc} µg/gOC	SW Class C SGV_{oc} µg/gOC
1,1,2,2-Tetrachloroethane	79-34-5	2.39	224	620	1200	120	380	138.689	268.43	26.843	85.003
Tetrachloroethene	127-18-4	3.4	2,200	370	1300	58	200	814.107	2860.377	127.617	440.058
Toluene	108-88-3	2.713	465	100	480	86	350	46.469	223.049	39.963	162.64
Toxaphene	8001-35-2	4.33	18,058	0.016	0.69	0.15	0.21	0.289	12.46	2.709	3.792
Triadimefon	43121-43-3	2.77	529	21	240			11.102	126.882		
1,2,3-Trichlorobenzene	87-61-6	4.096	10,633	1.1	13			11.696	138.227		
1,2,4-Trichlorobenzene	120-82-1	3.99	8,365	210	330	12	44	1756.586	2760.349	100.376	368.046
Trichloroethane (sum of isomers)	71-55-6 79-00-5	2.169	136	690	1300	430	1700	93.596	176.34	58.328	230.598
Trichloroethene	79-01-6	2.53	307	290	1400	150	590	89.057	429.93	46.064	181.185
1,2,4-Trimethylbenzene	95-63-6	3.78	5,200	33	290	19	170	171.607	1508.058	98.804	884.034
1,2-Xylene	95-47-6	3.12	1,167	35	310	2.7	19	40.861	361.911	3.152	22.182
1,3-Xylene	108-38-3	3.2	1,399	17	150	7.6	53	23.786	209.88	10.634	74.158
1,4-Xylene	106-42-3	3.15	1,249	21	190	2.3	16	26.239	237.402	2.874	19.992

* Log K_{ow}s were first used from U.S. EPA (1995). For compounds that did not have a K_{ow} published in U.S. EPA (1995), K_{ow} was taken from the Hazardous Substance Data Bank (HSDB), a component of the U.S. National Library of Medicine, Toxicology Data Network (TOXNET), available at: http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB

[1] Value freshwater and saltwater values from U. S. EPA (2009)
[2] Saltwater values from U.S. EPA (2009)
[3] Acute values from U.S. EPA (2009). Chronic values derived by applying Tier II procedures for secondary Acute to Chronic Ratios (SACRs) from 6 NYCRR Part 706.1.

Appendix E: Example of the determination of Site-Specific Empirical SGVs

In an actual sediment toxicity study of a large lake in New York State, as many as 120 sediment toxicity tests were conducted with two different species and two different endpoints for each species, growth and survival. Using the data for cadmium, sample sites were classified as toxic on the basis of statistically significantly differences between growth and/or survival for either species between the sample results and the control and/or reference site. The other sample sites were classified as non-toxic. Duplicates of concentrations with the same result (either all were toxic or all non-toxic) were dropped. The resulting dataset was 40 no-effects concentrations and 30 toxic concentrations. In each group, the concentrations were ranked from lowest to highest, and the cumulative probability assigned (P = R/n+1).

Cadmium No-effects concentrations, mg/kg	Rank R	Cumulative probability P	Cadmium Effects concentrations, mg/kg	Rank R	Cumulative probability P
0.24	1	0.024	0.57	1	0.032
0.35	2	0.049	0.64	2	0.065
0.47	3	0.073	0.94	3	0.097
0.54	4	0.098	0.95	4	0.129
0.69	5	0.122	0.99	5	0.161
0.73	6	0.146	1.1	6	0.194
0.77	7	0.171	1.2	7	0.226
0.79	8	0.195	1.3	8	0.258
0.8	9	0.22	1.4	9	0.29
0.85	10	0.244	1.5	10	0.323
0.87	11	0.268	1.6	11	0.355
0.9	12	0.293	1.7	12	0.387
0.97	13	0.317	2.1	13	0.419
1	14	0.341	2.4	14	0.452
1.1	15	0.366	2.5	15	0.484
1.2	16	0.39	2.6	16	0.516
1.4	17	0.415	2.8	17	0.548
1.5	18	0.439	3	18	0.581
1.6	19	0.463	3.1	19	0.613
1.8	20	0.488	3.4	20	0.645
2	21	0.512	3.5	21	0.677
2.1	22	0.537	3.9	22	0.71
2.2	23	0.561	4	23	0.742
2.3	24	0.585	4.1	24	0.774
2.4	25	0.61	4.3	25	0.806
2.5	26	0.634	5.6	26	0.839
2.6	27	0.659	7	27	0.871
2.7	28	0.683	7.8	28	0.903
2.8	29	0.707	8.6	29	0.935
3	30	0.732	14.2	30	0.968
3.3	31	0.756			

Cadmium No-effects concentrations, mg/kg	Rank R	Cumulative probability P	Cadmium Effects concentrations, mg/kg	Rank R	Cumulative probability P
3.4	32	0.78			
3.8	33	0.805			
4	34	0.829			
4.1	35	0.854			
4.6	36	0.878			
4.7	37	0.902			
5	38	0.927			
5.2	39	0.951			
5.8	40	0.976			

SGVs can then be selected that identify and separate toxic sites and non-toxic sites. For use in New York, proposed SGVs should match the minimum levels of reliability defined in MacDonald, et al. (2000); that is, a minimum of 75% of the concentrations below the Class A SGV should be correctly identified as non-toxic, with not more than 25% of the concentrations being toxic. For Class C SGVs, 75% of the concentrations higher than the Class C SGV should be correctly identified as toxic, with less than 25% of the concentrations above the Class C SGV being non-toxic.

To identify the Class C threshold, each individual concentration where an effect was observed was evaluated along with the effects associated with higher concentrations to determine if any concentration reliably predicts toxicity:

Cadmium effects conc., mg/kg	Total number of larger cadmium conc	Number of larger cadmium conc's that are toxic	Number of larger cadmium conc's that are not toxic	Percent of cadmium conc's correctly predicted to be toxic	Percent of cadmium conc's incorrectly predicted (non-toxic)
4	13	7	6	54%	46%
4.1	11	6	5	55%	45%
4.3	10	5	5	50%	50%
5.6	5	4	1	80%	20%
7	3	3	0	100%	0%

This analysis suggests that 5.6 mg/kg cadmium would be an appropriate Class C threshold. Based in site-specific data, there is a > 75% probability that a cadmium concentration > 5.6 mg/kg will be toxic, and a < 25% probability that a cadmium concentration > 5.6 mg/kg would be non-toxic.

The same type of analysis can be conducted to determine the Class A threshold:

Cadmium no-effects conc, mg/kg	Total number of smaller cadmium conc's	Number of smaller cadmium conc's that are not toxic	Number of smaller cadmium conc's that are toxic	Percent of cadmium conc's correctly predicted to be non-toxic	Percent of cadmium conc's incorrectly predicted (toxic)
1.5	26	17	9	65%	35%
1.4	24	16	8	67%	33%
1.2	21	15	6	71%	29%
1.1	19	14	5	74%	26%
1.0	18	13	5	72%	28%
0.97	16	12	4	75%	25%

By this analysis, the Class A threshold could be 0.97 mg/kg. In conclusion, the site-specific SGVs for cadmium for this site are:

Class A	Class B	Class C
<0.97 mg/kg	0.95 – 5.6 mg/kg	> 5.6 mg/kg

Sediments at this site with < 0.97 mg/kg cadmium are considered to be of low risk to aquatic life (Class A). Sediments at this site with >5.6 mg/kg are likely to pose a risk of acute toxicity to aquatic life (Class C). The potential risk to aquatic life from sediments with cadmium concentrations between 0.95 – 5.6 mg/kg cadmium cannot be reliably predicted and more testing/evaluation is needed to determine the degree and extent of the potential risk (Class B).

For purposes of illustration, the data above can be used to calculate other types of SGVs that commonly appear in the literature, such as Effects Range Low and Median (ERLs and ERMs), Threshold Effect Levels and Probable Effect Levels (TELs and PELs), Threshold Effect Concentrations and Probable Effects Concentrations (TECs and PECs), and the Apparent Effects Threshold (AET).

The ERL was calculated as the 10^{th} percentile value of the effects concentrations, and the ERM was calculated as the 50^{th} percentile of the effects concentrations (Long and Morgan 1991).

The TEL was calculated as the geometric mean of the 15^{th} percentile of the effects concentrations and the and the 50^{th} percentile of the no-effects concentrations. The PEL was calculated as the 50^{th} percentile of the effects concentrations and the 85^{th} percentile of the no-effects concentrations (MacDonald, et al. 1996).

The TEC was calculated as the geometric mean of the ERL and the TEL. The PEC was calculated as the geometric mean of the ERM and the PEL.

The AET is the highest concentration of a contaminant in sediment where no effects were observed, but effects are observed at every higher concentration (Barrick, et al. 1988).

The No Observed Effect Level (NOEL) is the highest concentration evaluated at which no adverse impact was observed. The Lowest Observed Effects Level (LOEL) is the lowest concentration where an adverse effect was observed.

Cadmium No-Effects Data
50th percentile = 1.90 mg/kg
85th percentile = 4.02 mg/kg

Cadmium Effects data
10th percentile = 0.95 mg/kg
15th percentile = 1.03 mg/kg
50th percentile = 2.55 mg/kg

The various SGVs were then analyzed to determine their reliability in predicting either toxicity or the lack of toxicity:

Possible Class A thresholds

SGV	Value, mg/kg	Total number of sites below SGV	Number below and not toxic	Number below and toxic	Percentage correctly predicted	Percentage incorrectly predicted
ERL	0.95	14	12	3	80%	20%
TEL	1.40	24	16	8	67%	33%
TEC	1.15	21	15	6	71%	29%
NOEL	0.54	3	0	0	100%	0%
LOEL	0.57	4	4	0	100%	0%

Possible Class C thresholds

SGV	Value, mg/kg	Total number of sites above SGV	Number above and toxic	Number above and not toxic	Percentage correctly predicted	Percentage incorrectly predicted
ERM	2.55	29	15	14	52%	48%
PEL	3.20	21	11	10	52%	48%
PEC	2.86	24	13	11	54%	46%
AET	5.8	4	4	0	100%	0%

From this example, the ERL, NOEL, and LOEL meet the criteria described in for the Class A threshold, in that >75% of the samples were correctly predicted to be non-toxic, and < 25% of the sites were incorrectly predicted to be toxic. However, for the upper threshold, only the AET meets the same level of reliability as described in MacDonald, et al. (2000).

The reason for determining the literature-based SGVs is so they can be compared with corresponding SGVs for the same contaminant in the literature, which would give an indication of the results of the analysis were generally consistent with results of other, similar studies.

Appendix F: Balduck's method for calculating the minimum number of samples that should be collected to characterize a contaminated sediment site

Balduck's Method

The method of gridded sampling proposed by Balduck (in Keillor 1993) may be used for characterizing contaminated sediment sites with certain modifications based on site size, dredge history, environmental flags (e.g., fish consumption advisory), and the presence or absence of potential pollutants in the drainage basin or local environment. Balduck's equation considers the area (not volume) to be evaluated and is used only to determine the number of sediment samples to be collected to provide spatially representative sampling of the site.

Balduck's equation, modified for English units, is:

$$N = (Df)\cdot(30)\cdot\left((W)\cdot(L)\cdot\left(\frac{1}{1.2x10^{6}}\right)\right)^{0.33}$$

Where:

N = the total number of coring (sampling) stations;

Df = a dredge factor consisting of a multiplier (unitless) from 0.5 to 3 based on the site's dredging, environmental or pollutant history and other case specific factors (see below).

W = the width (in yards) of a single contaminated sediment area or the widest contaminated sediment area where there are multiple areas to be evaluated;

L = the length (in yards) of a single contaminated sediment area or the sum of the lengths of the parts of a combined area being evaluated;

$\frac{1}{1.2x10^{6}}$ = factor to convert square yards into square kilometers;

Df equals 1 for sites:

- with no previous sediment data; and
- no suspected likelihood of appreciable contamination.

Df equals 2 for sites:

- with no previous sediment data; but where there is a likelihood of contamination based on history of surrounding land uses (e.g., heavy industry), spills, observed environmental tresses; and dredging has occurred within the last five years; or

- near particularly sensitive features, e.g., water supply intakes, unique habitats.

Df equals 3 for sites:

- with documented contamination from past sediment data; or
- in areas of established fish consumption advisories or spills or site-specific contamination of concern (e.g., copper, mirex, dioxin, PCB's) in the drainage basin; or
- where there is a likelihood of contamination and dredging has not occurred in the last five years.

NOTE: Df equals 0.5 where:

- previous data show no contamination.
- there is no likelihood of contamination.