



# ECO Update

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## Ecotox Thresholds

This Bulletin provides an overview of the development and use of Ecotox Threshold (ET) benchmark values in Superfund ecological risk assessments (ERAs). ETs are defined as media-specific contaminant concentrations above which there is sufficient concern regarding adverse ecological effects to warrant further site investigation. The bulletin describes how ETs are to be used for screening purposes in the Superfund ERA process, and summarizes the methodologies used to calculate ETs for each medium.

Using ETs in the Superfund ERA Process . . .	2
Limitations of ETs . . . . .	3
Media-Specific Methods for Calculating ETs .	4
References . . . . .	8

### INTRODUCTION

The ecological risk assessments (ERAs) performed in the Superfund program often include a procedure to determine which, if any, of the contaminants found at a site are present in concentrations that may be harmful to ecological receptors. In this step, the maximum measured contaminant concentration at a site is compared to an ecotoxicologically-based benchmark; if the concentration exceeds the benchmark, further assessment is warranted to determine the ecological risk posed by the contaminant. This screening step is often useful at Superfund sites, where a large number of contaminants may be

### IN THIS BULLETIN

Introduction . . . . .	1
Format of ETs . . . . .	2

*ECO Update* is a Bulletin series on ecological risk assessment of Superfund sites. These Bulletins serve as supplements to *Risk Assessment Guidance for Superfund, Volume II: Environmental Evaluation Manual* (EPA/540-1-89/001). The information presented is intended to provide technical information to EPA and other government employees. It does not constitute rulemaking by the Agency, and may not be relied on to create a substantive or procedural right enforceable by any other person. The Government may take action that is at variance with these Bulletins.

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detected. While exceeding the benchmark does not indicate the level or type of risk involved, concentrations below the benchmark should not result in significant adverse effects to ecological receptors when appropriately conservative benchmarks are used.

The Superfund program has initiated a project to develop media-specific benchmark values for those chemicals commonly found in surface water, sediment, or soil samples at sites. The values are referred to as Ecotox Thresholds (ETs), and are defined as **media-specific contaminant concentrations above which there is sufficient concern regarding adverse ecological effects to warrant further site investigation**. ETs are designed to provide Superfund site managers with a tool to efficiently identify contaminants that may pose a threat to ecological receptors and focus further site activities on those contaminants and the media in which they are found. ETs are meant to be used *for screening purposes only*; they are not regulatory criteria, site-specific cleanup standards, or remediation goals.

## FORMAT OF ETs

The list of ET values and the equations used to calculate them will also soon be available electronically as computer application software, via the Internet at [HTTP://WWW.EPA.GOV](http://www.epa.gov).

As data on more contaminants become available, and as new methods are included, the number of ETs will grow and some values will change. Having the list available electronically will allow EPA to make regular updates while minimizing the expense of generating and distributing hard copies.

The toxicity of many contaminants is dependent upon some physical property of the medium (e.g., hardness and pH of water, organic carbon content of sediment). The application software permits the user to supply site-specific values for these parameters, and then calculates site-specific ETs.

If site-specific values are not available, the ETs presented in Table 2 of this Bulletin should be used. These values are based on standard default values of 100 mg/L hardness as CaCO<sub>3</sub>, a pH of 7.8, and a sediment organic carbon content of 1 percent.

## USING ETs IN THE SUPERFUND ERA PROCESS

ETs were developed for use as benchmark screening values in the first step of the baseline risk assessment. However, ETs may be useful for decision-making earlier in the Superfund process, such as during the Preliminary Assessment/Site Investigation (PA/SI) or in the Superfund Accelerated Cleanup Model (SACM) integrated site assessment. If early analytical results indicate that a contaminant exceeds its ET value for a medium, future site activities can be focused to gather information sufficient to assess the ecological risk, if any, posed by that contaminant.

To the extent practicable, established, peer-reviewed EPA protocols and verified data have been used to develop ETs, and are listed as the "preferred methods" for calculating ETs later in this Bulletin. However, due to resource constraints and/or insufficient data, EPA has not used these protocols to develop formal "criteria" for many of the contaminants found at Superfund sites. These available protocols are not appropriate for all situations. To fill this void, methods developed by other federal agencies to calculate screening values have been included. For some contaminants, values are available from both a preferred EPA protocol and an alternative source (e.g., EPA's Sediment Quality Criteria [EPA, 1993a; 1993b; 1993c; 1993d; 1993e] and Long et al. [1995] Effects Range -- Low [ERLs] for sediment contaminants). In instances where multiple benchmark values are available for a specific contaminant, the ET derived by EPA protocol is preferred for use,

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regardless of whether it is higher or lower than the alternative value.

Because ETs are to be used for screening purposes, the maximum site concentration of each contaminant in each medium should be compared to its medium-specific ET value. If the maximum site concentration of a contaminant is less than its ET, the contaminant is not an ecological contaminant of concern, and further assessment for the contaminant for the purposes of the ERA is generally not warranted unless additional site information suggests otherwise. If the maximum site concentration exceeds the ET, further investigation is warranted. The nature and scope of this investigatory work is a site-specific decision to be made by the site manager in consultation with the Regional Biological Technical Assistance Group (BTAG). For instance, the spatial distribution of measured concentrations can be examined to determine if contamination is widespread across the site or limited to discrete "hot spots," and further investigation can be planned accordingly.

While ETs will help focus future site activities on the potential contaminants of concern, they should be used in conjunction with any other information about the site to assess the ecological risks posed by contaminants. Risk assessors should consider site-specific physical and chemical conditions that may influence the bioavailability (and thus, the site-specific toxicity) of a contaminant, as the protocols used to develop ETs may not be protective of all plant and animal species at all sites under all circumstances. Site conditions that may affect the bioavailability of contaminants at a site, or the degree of protectiveness of ETs, include the following:

- For surface water: hardness, pH, suspended/dissolved organic matter, salinity, flow rate, and temperature
- For sediment: pH, organic matter content (i.e., total organic carbon), clay content and clay type, grain size, and redox potential

- Surface water/groundwater hydrology patterns
- Presence of:
  - Endangered, threatened, or rare species
  - Species particularly sensitive to the contaminants detected at a site
  - Species of economic or recreational importance
  - Critical or sensitive habitats

The Superfund site manager should also review the site analytical data used in the screening process to ensure that: 1) the number of samples taken is sufficient to characterize site contamination, and 2) analytical detection limits are below the ET value.

At some Superfund sites, the naturally-occurring background concentrations of metals may exceed calculated ETs. However, due to physiological adaptations of resident biota or reduced bioavailability due to physical or chemical conditions, the naturally-occurring concentrations may not result in adverse toxicological effects. In these instances, it is suggested that a statistical comparison between the background concentrations (reported from unimpacted reference locations) and the maximum measured site concentrations be completed. The results of the comparison would provide the site manager with the information needed to make decisions regarding the need for additional site investigation.

## LIMITATIONS OF ETs

The limitations of using ETs as benchmark values are summarized below.

- 1) The ETs represent a measure of direct toxicity to exposed organisms, based upon studies reported in the scientific literature. The endpoints that form the basis for these values typically are limited to reductions in survival, growth, or reproduction of the tested organisms

in either laboratory single-species or small-scale mesocosm studies, or small-scale field studies. Indirect adverse effects to wildlife species via bioaccumulation/biomagnification through food chains are not addressed in this project.

While Superfund recognizes that failure to address adverse effects to wildlife is a serious shortcoming for this project, established, national methods to address this issue are not currently available. These ETs may not be low enough for those chemicals (e.g., methyl mercury, PCBs, DDT, dioxins) where significant bioaccumulation in the food chain may occur at the site.

2) Although there is substantial interest in integrating the human health risk assessment and ERA processes, ETs were developed to address toxicity to ecological receptors only, and are not intended to be protective of human health.

3) For Superfund sites located in states where state-mandated screening guidelines are available, the state guidelines will generally supersede the ETs recommended in this Bulletin.

## MEDIA-SPECIFIC METHODS FOR CALCULATING ETs

### Surface Water

#### Preferred Method - Ambient Water Quality Criteria

The preferred surface water ETs are the chronic Ambient Water Quality Criteria (AWQC), developed by EPA's Office of Water (OW). AWQC are developed under the Clean Water Act Section 304 (EPA, 1986a, 1986b, 1987, 40 CFR 131) for the protection of aquatic life for both freshwater and saltwater environments. Development of a criterion for a chemical in *either* fresh *or* salt water requires results of at least eight acute toxicity tests from eight different families and three chronic tests.

Freshwater AWQC are applicable in waters with salinity less than or equal to 1 part per thousand (ppt), 95 percent or more of the time. Saltwater AWQC are to be used in waters with salinity greater than or equal to 10 ppt, 95 percent or more of the time. For waters with salinity between 1 and 10 ppt, the more stringent of the freshwater or saltwater AWQC is used, unless site-specific information on species inhabiting the water body indicates a different preference.

According to OW policy (October 1, 1993, memorandum on *Office of Water Policy and Technical Guidance on Interpretation and Implementation of Aquatic Life Metals Criteria* [EPA, 1993f]; and *Revised Aquatic Life Metals Criteria in EPA's National Toxics Rule* [EPA, 1995a]), concentrations of dissolved metal, rather than total metal, should be used to set and measure compliance with water quality standards, because dissolved metal concentrations more closely approximate the bioavailable fraction of metal in the water column. For this reason, the surface water ETs for metals are expressed as dissolved concentrations, and many of them are slightly different than the published AWQC.

Freshwater AWQC for many metals are dependent on water hardness. For these criteria, the ETs shown in Tables 1 and 2 correspond to a total hardness of 100 mg/L as CaCO<sub>3</sub>. The following equation is to be used with site-specific hardness data to calculate a site-specific ET criterion for the six metals shown in Table 1:

$$\text{Criterion} = e^{(m_c[\ln(\text{hardness})] + b_c)} * CF$$

where:

m = slope

b = y intercept

**Table 1: Calculation of Freshwater ETs for Metals**

Chemical	Slope (m)	y Intercept (b)	Criterion (ET) <sup>1</sup>	Conversion Factor
Cadmium	0.7852	-3.490	1.0	0.909
Copper	0.8545	-1.465	11	0.960
Chromium III	0.8190	1.561	180	0.860
Lead	1.273	-4.705	2.5	0.791
Nickel	0.8460	1.1645	160	0.997
Zinc	0.8473	0.7614	100	0.986

<sup>1</sup>Assumes hardness of 100 mg/L as CaCO<sub>3</sub>.

CF = conversion factor, ratio of total recoverable concentration to dissolved concentration

Allowable hardness values (expressed as mg/L CaCO<sub>3</sub>) must fall within the range of 25 mg/L - 400 mg/L. If the actual measured hardness value falls outside this range, the respective minimum or maximum allowable value is used in the calculation.

The freshwater AWQC for pentachlorophenol is pH-dependent; the default ET criterion was calculated to correspond with a pH of 7.8. The equation for calculation of a site-specific ET criterion for pentachlorophenol is:

$$\text{Criterion} = e^{[1.005(\text{pH}) - 5.290]}$$

For several of the contaminants reported in Table 2 (i.e., DDT, dieldrin, endrin, heptachlor, methyl mercury, and PCBs), the AWQC were based on levels that would result in an exceedance of a Food and Drug Administration action level for fish consumed by humans. Since ETs are based solely on direct ecotoxicity effects, the use of these values is not appropriate. Consequently, the final chronic values (FCVs) reported by OW are used for these chemicals.

When there are no human fish consumption concerns and there is no final residue value, the FCV is the AWQC. The inorganic mercury FCV is reported in the AWQC document for mercury, while the dieldrin and endrin FCVs are reported in the subsequent *Proposed Sediment Quality Criteria* documents (EPA, 1993b; 1993c).

*Alternative Method - Great Lakes Water Quality Initiative (GLWQI) Tier I and Tier II*

Because non-residue based AWQC have been developed only for a limited number of contaminants, ETs are also calculated using the methodology presented in the *Great Lakes Water Quality Initiative (GLWQI)* (40 CFR 122 et al.). The GLWQI Tier I method is identical to the national AWQC method when final residue values are not used, and is used where enough data are now available (e.g., diazinon), but where AWQC have not been formally produced.

Using the Tier II methodology, ETs can be calculated with less than the complete minimum data (e.g., tests for species from eight families of aquatic organisms) required for a Tier I calculation. The Tier II methodology uses statistically derived "adjustment factors" described by Host et al. (1991) to calculate a

Tier II value. The adjustment factor decreases as the number of representative families increases. The methodology is described in 40 CFR 132, Appendix A. The data set used in the calculation must include a daphnid test and must meet the acceptability criteria outlined in Appendix C of the revised aquatic life guidelines (EPA, 1994).

To date, OW has calculated GLWQI Tier II water quality values and prepared support documents for seven chemicals, four of which are on the ET list: DDT, heptachlor, lead, and toxaphene (EPA, 1992a). Because a chronic AWQC value is available for lead, its GLWQI value is not used. The GLWQI values for DDT, heptachlor, and toxaphene values are used.

OW has also used the GLWQI Tier II method to calculate 18 additional values for ETs, including three chemicals for which AWQC had been published: endosulfan, malathion, and methoxychlor. OW believed that these new Tier II values, based on more recent toxicity data, are more appropriate than the older AWQC values. Technical support documents have not been prepared for these chemicals.

The 34 remaining values used are taken from Suter and Mabrey (1994). These benchmarks were developed using the GLWQI Tier II method, and were reviewed by EPA to verify their accuracy. A copy of the procedure used to conduct the accuracy review is available from EPA OW by request. EPA will not present an ET value based upon data that do not meet existing standards for use in developing criteria.

Tier II values for marine surface waters have not been calculated. While Superfund may elect to develop such values using the Great Lakes Tier II methodology and appropriate marine species in the future, the current procedure is to accept the freshwater ETs as being appropriate for use in a saltwater environment. Using AWQC as a model, the ETs for salt water are higher than the freshwater ETs for nine chemicals, and lower than the freshwater ETs for seven chemicals. For each chemical except selenium, the difference between the saltwater

and freshwater value is less than an order of magnitude.

## Sediment

### Preferred Method - Sediment Quality Criteria

Proposed Sediment Quality Criteria (SQC) have been published by OW (Federal Register, Jan 18, 1994) for acenaphthene, dieldrin, endrin fluoranthene, and phenanthrene (EPA, 1993a; 1993b; 1993c; 1993d; 1993e). These values were derived using the equilibrium partitioning (EqP) method, as described in *Technical Basis for Deriving Sediment Quality Criteria for Nonionic Organic Contaminants for the Protection of Benthic Organisms by Using Equilibrium Partitioning* (EPA, 1993g). The EqP method quantifies the hydrophobicity of the chemical by using the octanol/water partition coefficient,  $K_{ow}$ , and determines the sorption capacity of the sediment by the mass fraction of organic carbon for the sediment,  $f_{oc}$ . The relationship between  $K_{ow}$  and the sediment organic carbon partitioning coefficient,  $K_{oc}$ , is described by the following equation (Di Toro, 1985):

$$\log_{10}K_{oc} = 0.00028 + 0.983 \log_{10}K_{ow}$$

Thus, the equation for the SQC is:

$$SQC = f_{oc} * K_{oc} * FCV$$

where:

- $f_{oc}$  = mass fraction of organic carbon for the sediment
- $K_{oc}$  = organic carbon partition coefficient
- FCV = final chronic value, from chronic AWQC

The sediment values used in the ETs are normalized to 1 percent organic carbon.

Superfund has elected to use the lower limit of the 95 percent confidence interval presented

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in the criteria documents as the ET, rather than the central tendency value. This step was taken to maintain an appropriate level of conservatism for screening purposes.

#### Alternative Method 1 - Sediment Quality Benchmarks

While the SQC for the five chemicals discussed above have been published in draft form, EPA has also derived Sediment Quality Benchmarks (SQBs) using the same EqP approach as a joint effort between OW and the Office of Solid Waste (OSW). SQBs are being used for OW's National Sediment Inventory and OSW's Hazardous Waste Identification Rule as well as this project. The SQB is calculated in the same manner as the SQC except that a Tier II surface water ET is substituted for the AWQC or FCV in the calculation.

The SQB method is appropriate for nonionic organic compounds with log  $K_{ow}$  values between 2.0 and 5.5. The log  $K_{ow}$  values used to calculate SQBs were supplied by Samuel Karickhoff and J. MacArthur Long of the EPA Environmental Research Laboratory - Athens, GA as an unpublished internal report (EPA, 1995b). Karickhoff and Long reviewed available literature  $K_{ow}$  values from a variety of methods, including shake flask, slow stir, reverse-phase high performance liquid chromatography, and generator column, as well as estimated values generated by the SPARC and CLOGP models. Generally, data from a slow-stir test were preferable, followed by estimation by SPARC, and others. For  $K_{ow}$  values less than 4, the shake flask method was preferable. In most cases, an average value was calculated from a variety of acceptable methods.

All sediment ETs presented in Table 2 are normalized to 1 percent organic carbon in sediment.

#### Alternative Method 2 - ERL Values

If neither an SQC nor an SQB has been calculated, the Effects Range Low value (ERL) will be used as the sediment ET. ERLs are included in the "effects range approach" initially developed for the National Oceanic and Atmospheric Administration's (NOAA's) *National Status and Trends Program*, by Long and Morgan (1990). The Long and Morgan method was revised by MacDonald (1992) and the values shown in Table 2 are from Long et al. (1995), using the revised method.

The Long and Morgan (1990) values were based on data from freshwater, estuarine, and marine sediments. Long et al. (1995) derived values on data from estuarine and marine sediments using modeling techniques, as well as laboratory and field studies. Trace metals data were taken only from studies in which a strong acid digestion method was used.

The procedures used to produce the ERLs are described by Long and Morgan (1990; EPA, 1992b). For each chemical, the ranges of chemical concentrations associated with observed adverse biological effects were determined and ordered by weight of evidence. The data were used to develop no-effects, possible-effects, and probable-effects ranges. The ERL value represents the lower 10th-percentile concentration associated with observation of biological effects. According to this method, concentrations below the ERL should rarely be associated with adverse effects.

It should be noted that there is a relatively low correlation, and consequently low accuracy, between the incidence of effects and the concentrations of mercury, nickel, total PCBs, and DDT (Long et al., 1995). The sediment ETs for these four chemicals should be used cautiously.

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## Soil

Methods to address toxicity in soils have not been sufficiently developed to include them in this document. The Superfund program is currently evaluating options in this area and will produce soil ETs when appropriate methods and necessary resources are available.

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**Table 2: Ecotox Thresholds for 67 Chemicals Commonly Found At Superfund Sites**

CAS Number	Chemical	Surface Water (ug/L)			Sediment (mg/kg)			
		Freshwater		Marine	EPA SQC <sup>3</sup>		EPA SQB <sup>4</sup>	ERL <sup>5</sup>
		AWQC or FCV <sup>1</sup>	Tier II <sup>2</sup>	AWQC or FCV <sup>1</sup>	Fresh-water	Marine		
Metals (20)								
22569728	Arsenic III	190		36				8.2 t
17428410	Arsenic V		8.1 *					
7440393	Barium		3.9 *					
7440417	Beryllium		5.1 *					
7440439	Cadmium	1.0 h		9.3				1.2
1308141	Chromium III	180 h						81 t
18540299	Chromium VI	10		50				
7440484	Cobalt		3.0 *					
7440508	Copper	11 h		2.4				34
7439896	Iron	1000						
7439921	Lead	2.5 h		8.1				47
7439965	Manganese		80 *					
7439976	Mercury, inorganic	1.3		1.1				0.15 t
22967926	Mercury, methyl		0.003 *					
7439987	Molybdenum		240 *					
7440020	Nickel	160 h		8.2				21
7782492	Selenium	5.0		71				
7440622	Vanadium		19 *					
7440666	Zinc	100 h		81				150
57125	Cyanide	5.2		1.0				
Organic Compounds (47)								
83329	Acenaphthene	23 S		40 S	0.62	1.1		0.016
71432	Benzene		46 *				0.057	
50328	Benzo(a)pyrene		0.014 *					0.43
92524	Biphenyl		14 #				1.1	
117817	Bis(2-ethylhexyl)phthalate		32 *					

**Table 2 (continued)**

CAS Number	Chemical	Surface Water (ug/L)			Sediment (mg/kg)			
		Freshwater		Marine	EPA SQC <sup>3</sup>		EPA SQB <sup>4</sup>	ERL <sup>5</sup>
		AWQC or FCV <sup>1</sup>	Tier II <sup>2</sup>	AWQC or FCV <sup>1</sup>	Fresh-water	Marine		
101553	Bromophenyl phenyl ether, 4-		1.5 #				1.3	
85687	Butylbenzyl phthalate		19 #				11	
108907	Chlorobenzene		130 *				0.82	
50293	DDT		0.013 +					0.0016
333415	Diazinon	0.043 F					0.0019	
132649	Dibenzofuran		20 *				2.0	
95501	Dichlorobenzene, 1,2-		14 #				0.34	
541731	Dichlorobenzene, 1,3-		71 #				1.7	
106467	Dichlorobenzene, 1,4-		15 #				0.35	
75343	Dichloroethane, 1,1-		47 *					
60571	Dieldrin	0.062 S		0.11 S	0.052	0.095		
84662	Diethyl phthalate		220 *				0.63	
84742	Di-n-butyl phthalate		33 *				11	
115297	Endosulfan, mixed isomers		0.051 #				0.0054	
959988	Endosulfan, alpha		0.051 #				0.0029	
33213659	Endosulfan, beta		0.051 #				0.014	
72208	Endrin	0.061 S		0.01 S	0.02	0.0035		
100414	Ethylbenzene		290 *				3.6	
206440	Fluoranthene	8.1 S		11 S	2.9	1.4		0.6
86737	Fluorene		3.9 #				0.54	
76448	Heptachlor		0.0069 +					
67721	Hexachloroethane		12 #				1.0	
58899	Lindane/Hexachlorocyclohexane	0.08					0.0037	
121755	Malathion		0.097				0.00067	
72435	Methoxychlor		0.019 #				0.019	
91203	Naphthalene		24 *				0.48	0.16
608935	Pentachlorobenzene		0.47 #				0.69	
87865	Pentachlorophenol	13 pH		7.9				

**Table 2 (continued)**

CAS Number	Chemical	Surface Water (ug/L)			Sediment (mg/kg)			
		Freshwater		Marine	EPA SQC <sup>3</sup>		EPA SQB <sup>4</sup>	ERL <sup>5</sup>
		AWQC or FCV <sup>1</sup>	Tier II <sup>2</sup>	AWQC or FCV <sup>1</sup>	Fresh-water	Marine		
1000	Polynuclear aromatic hydrocarbons							4.0
11096825	Polychlorinated biphenyls		0.19 *					0.023
85018	Phenanthrene	6.3 S		8.3 S	0.85	1.1		0.24
129000	Pyrene							0.66
79345	Tetrachloroethane, 1,1,2,2-		420 *				0.94	
127184	Tetrachloroethylene		120 *				0.53	
56235	Tetrachloromethane		240 #				1.2	
108883	Toluene		130 *				0.67	
8001352	Toxaphene		0.011	0.21			0.028	
75252	Tribromomethane		320 #				0.65	
120821	Trichlorobenzene, 1,2,4-		110 #				9.2	
71556	Trichloroethane, 1,1,1-		62 *				0.17	
79016	Trichloroethylene		350 *				1.6	
108383	Xylene, m-		1.8 #				0.025	

<sup>1</sup>USEPA chronic ambient water quality criteria (AWQC) or EPA-derived final chronic values (FCVs) (USEPA, 1986a, 1986b, 1987). Metals concentrations are for total dissolved chemical.

<sup>2</sup>Values calculated using Great Lakes Water Quality Initiative Tier II methodology (40 CFR 9 et al.).

<sup>3</sup>USEPA Sediment Quality Criteria (SQC). Assumes 1 percent organic carbon (USEPA, 1993g). Values are lower limit of 95 percent confidence interval.

<sup>4</sup>Sediment quality benchmarks (SQBs) by equilibrium partitioning. Assumes 1 percent organic carbon. (USEPA, 1995b).

<sup>5</sup>ERL = Effects Range -- Low (Long et al., 1995).

Notes:

ug/L = micrograms per liter.

mg/kg = micrograms per kilogram.

h = hardness-dependent ambient water quality criterion (100 mg/L as CaCO<sub>3</sub> used).

pH = pH-dependent ambient water quality criterion (7.8 pH used).

S = final chronic value derived for EPA Sediment Quality Criteria documents (EPA, 1993a, b, c, d, e).

F = final chronic value calculated using Great Lakes Water Quality Initiative Tier I methodology.

t = value is for total of all chemical forms.

\* = value as calculated in Suter and Mabrey, 1994.

+ = value with EPA support documents.

# = value calculated for this project.