Sediment Benchmarks Use in Screening and Recent Advances

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Types

Empirical

Mechanistic

Empirical

- Statistical evaluation of sediment chemistry and biological response
- » Units of mg/kg-dw
- » No attempt to factor in properties of sediment
- » Method to develop these can be applied to any stressor

Mechanistic

- » Statistical evaluation of aquatic toxicity endpoints
- » Units of mg/kg-oc
- Include one or more properties of the sediment
- » Specific to a narrow range of chemical classes



Function

Protective

Predictive

Protective

- » Identify contaminant concentrations below which harmful effects on sedimentdwelling organisms are not expected
- » Protect sensitive species (protect 95% of species)
- » Tier 1 assessments
- » Intended to be conservative
- » Can be either empirical or mechanistic

Predictive

- » Identify contaminant concentrations above which harmful effects on sedimentdwelling organisms are expected to occur frequently
- » Can be either empirical or mechanistic
- » Tier 2 and higher assessments
- » Focused toward site-specific receptor protection





Understand types of benchmarks and their application



Pick the most/least influential sediment variable causing an organic chemical to partition to sediment.

- Sediment composition, i.e. percentage fines
- Total organic carbon content
- Black carbon content
- Type of organic carbon or amendment



Pick one or more chemical properties that have the most influence on toxicity to aquatic life.

- Octanol-water partition coefficient
- Solubility in water
- Polarizability
- Mode of toxic action
- Chemical class, i.e., chlorinated or non-chlorinated
- Acidity/basicity
- Molecular size



Pick the most/least environmental variable that influences sediment toxicity and partitioning.

- Temperature
- Weathering
- Resuspension
- Dissolved organic carbon in porewater



How do sediment benchmarks for PAHs stack up?

| Benchmark | Function | Туре | Species Protection | Number of PAHs | Total Organic Carbon | Black Carbon |
|---|------------|-------------|-----------------------|-------------------|----------------------------|-----------------|
| MacDonald et al. TEC | Protective | Empirical | Broad | 13 | No | No |
| Swartz TEC | Protective | Mechanistic | Broad | 13 | Yes | No |
| EPA 2003 ESB | Protective | Mechanistic | 95% species | 34 | Yes | No |
| MacDonald et al. PEC | Predictive | Empirical | Broad | 13 | No | No |
| Persaud et al. SEL | Predictive | Empirical | Broad | 16 | No | No |
| EPA 2017 ESB Hyalella azteca | Predictive | Mechanistic | Hyalella azteca | 34 | Yes | No |
| EPA 2017 EC50 Hyalella azteca porewater | Predictive | Mechanistic | Hyalella azteca | 34 | Yes | No |
| Black Carbon Model | Predictive | Mechanistic | 95% species | 34 | Yes | Yes |



Protective Sediment Benchmark – MacDonald et al. TEC

MacDonald et al. (2000) Threshold Effects Concentration (TEC)

- » Empirical
- » Consensus (averaging of values reported in several studies)
- » Σ 13 PAHs should be < 1.61 milligrams per kilogram dry weight (mg/kg-dw)

MacDonald, D.D., Ingersoll, C.G., and T.A. Berger. 2000. Development of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39: 20-31.



Protective Sediment Benchmark – Swartz (1999) TEC

Swartz (1999) Effects Concentrations

- » Factors in role of organic carbon in determining PAH partitioning and bioavailability.
- » Observed amphipod mortality in 10-day sediment toxicity tests at sites where PAHs were the main contaminant
- » Species richness in benthic community assessments
- » Σ 13 PAHs concentrations normalized to organic carbon content in sediments, micrograms per gram organic carbon, $\mu g/goc$
 - Threshold Effects Concentration 290 µg/goc (TEC)

Swartz, R.C. 1999. Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. Environ. Toxicol. Chem. 18: 780-787.



Protective Sediment Benchmarks – ESB_{5%}

- Equilibrium partitioning sediment benchmarks (ESBs) for 95% species protection (ESB_{5%})
- Target lipid model based on toxicity to aquatic organisms in water-only exposures and partitioning to sediment organic carbon
- Σ toxic unit approach for concentrations of PAHs normalized to organic carbon content in sediments
- 34 PAHs including parent and alkyl-PAHs

USEPA 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks for the Protection of Benthic Organisms: PAH Mixtures. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. EPA-600-R-02-013. November 2003.



Predictive Sediment Benchmark – MacDonald et al. PEC

MacDonald et al. (2000) Probable Effects Concentration (TEC)

- » Empirical
- » Consensus (averaging of values reported in several studies)
- » Σ 13 PAHs should be < 22.8 milligrams per kilogram dry weight (mg/kg-dw)

MacDonald, D.D., Ingersoll, C.G., and T.A. Berger. 2000. Development of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39: 20-31.



Predictive Sediment Benchmark – SEL

Persaud et al. 1993 Severe Effects Level (SEL)

» Σ 16 PAHs concentrations < 100 mg/kg-dw

Persaud D, Jaagumagi R, Hayton A. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Toronto (ON): Water Resources Branch, Ontario Ministry of the Environment. 27 p.



Predictive Sediment Benchmarks – ESB_{H. azteca} & EC50_{H. azteca}

- Equilibrium partitioning sediment benchmarks (ESBs) for Hyalella azteca protection (ESB_{H. azteca})
 - » Gather PAH effect concentrations (ECs) for 28-day test. Use TLM to estimate EC50 (effect to 50% of test organisms) for *H. azteca* in μg/L.
 - » Sum up toxic units for 34 PAH concentrations measured in porewater.
 - » Use organic carbon partition coefficients to calculate sediment benchmarks protective of *H. azteca* in units of μ g/goc.
 - » Compute ΣTU for 34 PAHs by comparing sediment concentrations, normalized to organic carbon content, with sediment benchmarks protective of *H. azteca*.

Burkhard et a. 2017. Developing sediment remediation goals at Superfund sites based on pore water for the protection of benthic organisms from direct toxicity to non-ionic organic contaminants. US-EPA EPA/600/%-15/289. October 2017.



Predictive Sediment Benchmarks–Black Carbon Model

- Use a two-carbon partitioning model to estimate porewater concentrations from black carbon and natural organic carbon concentrations in sediment
- Compare estimated porewater concentrations to PAH-specific final chronic values (FCVs) (EPA 2003)
- Use a sum toxic unit (ΣTU) for 34 PAHs

McGrath et al. 2019. Review of polycyclic aromatic hydrocarbons (PAHs) sediment quality guidelines for the protection of benthic life. IEAM 15(4): 505-518.



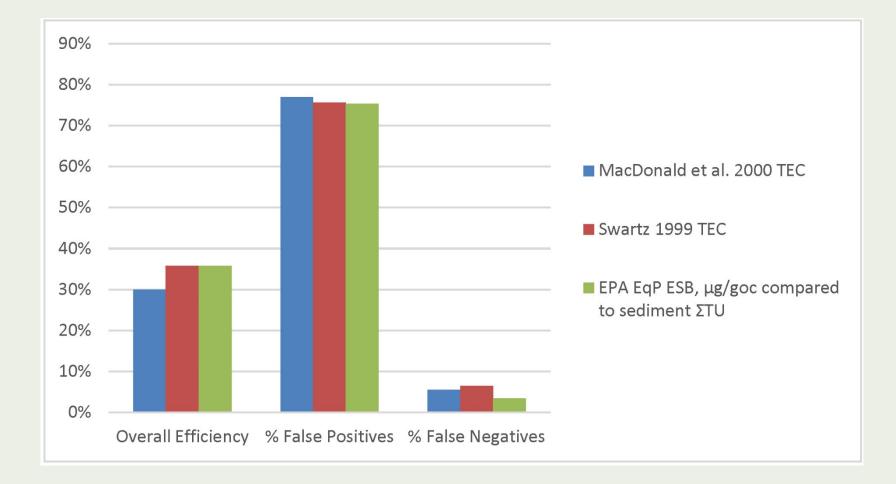
- False positives = Toxicity expected but was not observed
- False negatives = Toxicity not expected but was observed
- % Correct predictions of both toxic and non-toxic samples

Data set for testing benchmarks was from Arp et al. (2011) from 19 former manufactured gas plant sites and smelters.

Arp., H.P. et al. 2011. Predicting pore water EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments Using pyrene content. Environ. Sci. Technol. 45: 5139-5146.

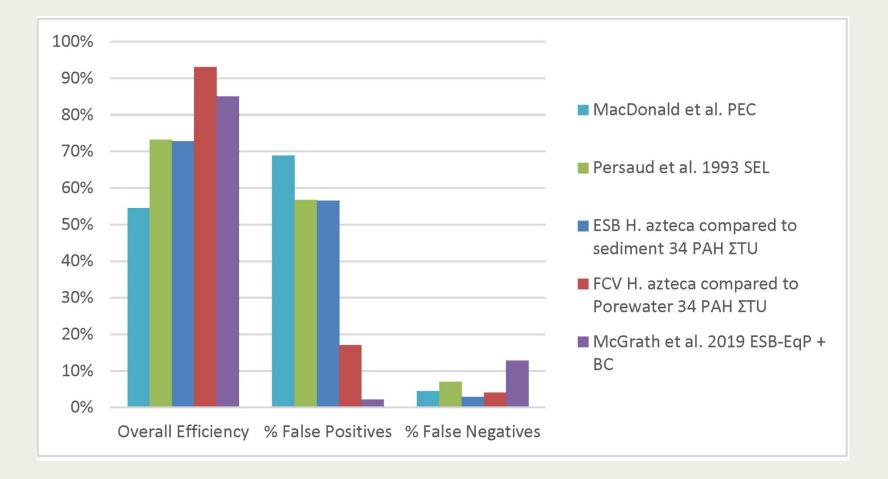


Performance of Protective PAH Benchmarks





Performance of Predictive PAH Benchmarks





Take Home Message

- Screening-level benchmarks are not to be used as cleanup levels.
- It is the freely-dissolved concentration in the porewater that determines toxicity to benthic organisms.
 - » Direct measurements of porewater with membrane devices
 - » Prediction of porewater concentrations from organic carbon and black carbon with 2-carbon model
- Best way is to measure porewater concentration and compare to surface water benchmarks for protection of aquatic life.
- Can measure 16 PAHs and use an alkyl PAH multiplier.



Papers Discussed

- McGrath et al. 2019. Review of polycyclic aromatic hydrocarbons (PAHs) sediment quality guidelines for the protection of benthic life. IEAM 15(4): 505-518.
- Arp., H.P. et al. 2011. Predicting pore water EPA-34 PAH concentrations and toxicity in pyrogenic-impacted sediments Using pyrene content. Environ. Sci. Technol. 45: 5139-5146.
- Burkhard et a. 2017. Developing sediment remediation goals at Superfund sites based on pore water for the protection of benthic organisms from direct toxicity to non-ionic organic contaminants. US-EPA EPA/600/%-15/289. October 2017.
- EPA 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA-600-R-02-013. November 2003.

