# Chronic Pesticide Toxicity to Macroinvertebrate Benthos in Lake and Stream Sediment

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## Introduction

A paucity of toxicity data to benthic and epibenthic organisms is available in the aquatic toxicology literature regarding pesticides sorbed (combined absorption and adsorption) to lake and stream sediment especially at the chronic level. Conversely, toxicity from dissolved pesticides in the overlying water of lakes, streams, marine and estuarine environments has been extensively tested at acute and chronic levels, which has enabled risk assessment of aquatic ecosystems. Risk assessment of most sediment-sorbed pesticides may only be achieved by relating benthic toxicity to organisms that inhabit overlying water. Pesticides dissolved in water or sorbed to eroded soil sediment that runs off to aquatic systems can be directly measured or estimated by environmental fate computer modeling.

With limited testing of pesticide chronic toxicity to benthos, a methodology is presented to estimate the toxicity thresholds. This may be achieved by correlating the pesticide toxicity to pelagic organisms to that of benthic and epibenthic macroinvertebrates.

## Methods and Materials

Use of pesticide toxicity to aquatic pelagic animal species in lieu of benthic species' toxicity has been previously investigated. Di Toro et al. (1991) determined that acute toxicity (96-hour LC50, the lethal concentration that kills 50% of the population over a 96-hour period) of sensitive fish species (e.g., rainbow trout, bluegill sunfish and fathead minnows) and the zooplankton, *Daphnia pulex* (48-hour EC50, the concentration that effects 50% of the population over a 48-hour period) correlated nearly one to one logarithmically (base 10) with acute toxicity to benthic macroinvertebrates. Subsequent to measuring or computer modeling of pesticide sorbed to sediment, the pesticide soil sorption coefficient (Koc) can we used as an equilibrium constant to estimate pesticide concentration in sediment interstitial water (pore water). Di Toro et al. (1991) related acute benthic macroinvertebrate pesticide toxicity to the pesticide equilibrium concentration in lentic and lotic sediment interstitial water. Using the close toxicity correlation between fish and *Daphnia* to benthic macroinvertebrates, Di Toro et al. (1991) established the concept of the "Pesticide Sediment Toxicity Unit" by determining the ratio of pesticide sorbed to sediment organic carbon and the product of the pesticide Koc and fish acute toxicity (Eq. 1).

**Equation 1.**

$$\text{(Predicted sediment toxicity unit)} = \frac{(\mu\text{g pesticide/Kg sediment})) / (\text{organic carbon fraction})}{(\text{Koc in mL/g}) \times (\text{fish 96-h LC50 in } \mu\text{g/L})}$$

The USDA NRCS/University of Massachusetts Extension Windows Pesticide Screening Tool (2015) or WIN-PST, furthered this concept beginning in 1999, by making the assumption that this toxicity relationship would hold for the chronic condition by substituting a fish chronic toxicity Maximum Acceptable Toxicant Concentration (MATC) for the fish 96-h LC50. MATC can be defined as the geometric mean of the No Observable Effect Level (NOEL) and the Lowest Observable Effect Level (LOEL). The WIN-PST concept was referred to as the Sediment Toxicity Value (STV) (Eq. 2).

**Equation 2.**

$$\text{Sediment Toxicity Value or STV} = \frac{(\mu\text{g pesticide/Kg sediment}) / (\text{organic carbon fraction})}{(\text{Koc in mL/g}) \times (\text{fish MATC in } \mu\text{g/L})}$$

The WIN-PST chronic sediment toxicity method using the temporal modification of the Di Toro et al. (1991) acute toxicity method was later confirmed for chronic sediment toxicity evaluation and deemed the Equilibrium Partitioning Sediment Benchmark method (ESB) as a USEPA sanctioned method (Burgess et al., 2008 and Burgess et al., 2012). These studies showed that risks to the benthic and epibenthic aquatic community can be assessed by determination of either the mass of pesticide sorbed to organic carbon in the sediment or by the soluble pesticide concentration in sediment interstitial water. The researchers verified the accuracy of using chronic toxicity thresholds for dissolved nonionic pesticides (pesticides that do not have a positive or negative charge) relating benthic species' toxicity to sensitive pelagic species. Burgess et al. (2012) recommended using established USEPA chronic toxicity benchmark parameters for pelagic species such as NOELs from EPA's Water Quality Criteria (WQC), Final Chronic Value (FCV), Secondary Chronic Value (SCV) or any other relevant water-exposed toxicity value to sensitive pelagic species to estimate the ESB toxicity units (ESBTU). Equilibrium partitioning using the pesticide Koc can be used in calculating ESBTU for any toxicity endpoint. The unitless ESBTU can be used to evaluate toxicity risk to the benthos from pesticides dissolved in sediment interstitial water (Eq. 3). An ESBTU greater than 1.0 indicates that chronic toxicity is being imposed upon benthic and epibenthic macroinvertebrates.

**Equation 3.**

$$\text{ESBTU} = \frac{(\mu\text{g pesticide/Kg sediment}) / (\text{organic carbon fraction})}{(\text{Koc in mL/g}) \times (\text{WQC, FCV, SCV or other relevant water-only toxicity in } \mu\text{g/L})}$$

FCVs are based on Water Quality Criteria from chronic NOELs from seven aquatic animal groups (Stephan et al. 1985). Two of these aquatic animal groups include sensitive cold water fish species (e.g., rainbow trout and brook trout) and sensitive warm water fish species (e.g., bluegill sunfish, fathead minnows and lake trout). When WQC and FSV are unavailable, an EPA sanctioned SCV was recommended by Burgess et al. (2008) to be used with the ESB method. These values are similar to the FCV but were established specifically for the Great Lakes Water Quality Initiative (1995). Although Burgess et al. (2008) determined that the WQC, FCV and SCV correlated closely with benthic macroinvertebrate chronic toxicity, benchmarks have been established for only about 50 pesticides.

Unfortunately, that leaves no means to evaluate benthic chronic pesticide toxicity for over 1000 pesticides currently registered for agricultural purposes. This paper proposes a method for acquiring a more comprehensive toxicity dataset.

## Results and Discussion

With limited chronic toxicity testing of benthic and epibenthic aquatic macroinvertebrate for most pesticides, it is necessary to estimate these toxicity thresholds in order to evaluate pesticide toxicity risk in lake and stream sediment. Fish acute toxicity testing has been performed on nearly all pesticides currently used in agriculture as required by the USEPA in the registration process, while chronic fish toxicity has also been determined for pesticides registered during the past 15 or more years. Estimating chronic benthic macroinvertebrate toxicity risk from chronic fish pesticide toxicity requires a nearly complete dataset of chronic fish pesticide toxicity. Furthermore, if chronic fish NOELs could be correlated with benthic macroinvertebrate chronic toxicity, most pesticides could be evaluated for chronic sediment toxicity risk using USEPA's ESB method.

Burgess et al. (2008) concluded that the FCV and SCV NOELs generated from sensitive pelagic organisms were not significantly different from benthic macroinvertebrate toxicity as evaluated for sediment interstitial water concentration. The basis for this conclusion was the ESB Technical Basis Document (USEPA, 2003) which found that benthic macroinvertebrate species as a group have similar sensitivities as pelagic species tested taken as a group. Previously, other researchers found that SCV values for narcotic pesticide effects could be estimated by rainbow trout toxicity within a factor of 1.7 (Di Toro et al., 2000). Two of the seven aquatic animal groups used by the USEPA to establish the FCV and SCV are sensitive cold water fish species of which rainbow trout (*Oncorhynchus mykiss*) is most commonly tested, and sensitive warm water fish species with the most often tested species being bluegill sunfish (*Lepomis macrochirus*) and fathead minnows (*Pimephales promelas*). The FCV and SCV close toxicity correlation of 1.7 with rainbow trout and the nearly one to one correlation between acute toxicity to sensitive fish species and benthic macroinvertebrates by Di Toro et al. (1991), may imply that sensitive fish species' chronic NOELs could be used to approximate the ESB in lieu of benthic macroinvertebrate chronic NOELs.

To further test the validity of using chronic pesticide toxicity to sensitive fish species in lieu of benthic macroinvertebrate chronic toxicity, chronic pesticide benthic macroinvertebrate midge NOELs for sediment interstitial water were paired with sensitive fish species' NOELs taken from the USEPA OPP Ecotox database (USEPA OPP, 2012) and shown in Table 1. USEPA uses fish and *Daphnia* chronic NOEL thresholds in their environmental risk assessments. In these assessments, an aquatic pesticide concentration greater than the NOEL may impose some level of toxicity risk to aquatic organisms.

Table 1. Benthic Macroinvertebrate NOELs to Pesticides in Sediment Interstitial Water and Sensitive Fish Species NOELs to Pesticides in Lake or Stream Water

| Pesticide | Benthos Species | Benthos NOEL (ppb) | Fish Species | Fish NOEL (ppb) |
|---|---|---|---|---|
| Aminopyralid | Chironomus riparius | 82,000 | Fathead minnow | 1360 |
| Bifenthrin | Chironomus tentans | 0.006 | Fathead minnow | 0.04 |
| Cypermethrinl | Chironomus tentans | 0.0013 | Fathead minnow | 0.09 |
| Etofenprox | Chironomus riparius | 1.4 | Rainbow trout | 0.67 |
| Flubendiamide* | Chironomus riparius | 19.5 | Fathead minnow | 60.5 |
| Mancozeb | Chironomus dilutes | 82.7 | Fathead minnow | 2.2 |
| Pyrasulfotole | Chironomus riparius | 79,800 | Fathead minnow | 580 |
| Pyridalyl | Chironomus riparius | 3.5 | Rainbow trout | 49 |
| Spinetoram | Chironomus riparius | 0.048 | Fathead minnow | 186 |
| Spirodiclofen enol metabolite | Chironomus riparius | 3,200 | Rainbow trout | 115 |
| Prothioconazole | Chironomus riparius | 640 | Rainbow trout | 308 |
| Thiacloprid | Chironomus riparius | 1.8 | Fathead minnow | 455 |

- Flubendiamide fathead minnow NOEL was paired with Flubendiamide des-iodo (metabolite) *Chironomus riparius* NOEL.

A Log – Log (base 10) plot of these data (Figure 1) was generated and used to calculate a linear regression equation (Equation 4). The equation can be used to estimate a benthic macroinvertebrate chronic NOEL from a sensitive fish species chronic NOEL for any pesticide that has been tested for chronic fish toxicity. The estimated benthic macroinvertebrate NOEL can then be used in Equation 3 to estimate the ESBTU.

**Equation 4**

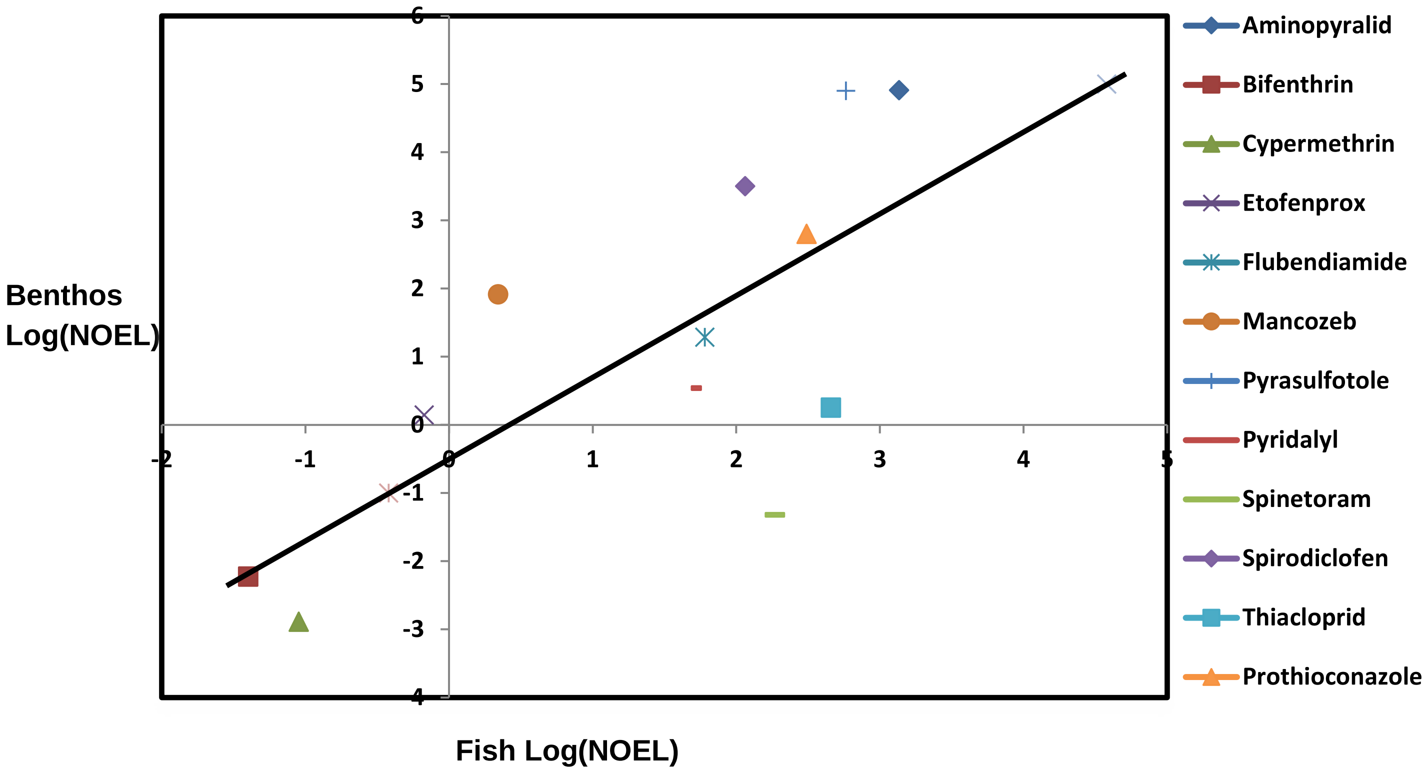
**Log(benthic macroinvertebrate NOEL in µg/L) = 1.2 X (Log(fish NOEL in µg/L)) – 0.5**

**$r^2 = 0.52$**

The 0.52 $r^2$ indicates a moderate correlation between sensitive fish species and benthic macroinvertebrates with a small sample population (N = 12). A higher correlation might have been achieved with a greater sample size. Although this regression equation could be used to estimate benthic macroinvertebrate chronic NOELs based on sensitive fish chronic NOELs, the small sample size decreases the statistical validity of using this approach considering there are over 1000 agricultural pesticides currently in use.

However, a 0.52 $r^2$ does provide additional confirmation to the FSV – rainbow trout toxicity correlation and close FSV – benthic macroinvertebrate toxicity correlation determined by Di Toro et al. (2000) towards using sensitive fish chronic NOELS in lieu of benthic macroinvertebrate NOELS.

**Figure 1. Pesticide Fish Log10(NOEL) in Overlying Water Versus Benthic Organism Log10(NOEL) in Pore Water**




Over 200 chronic fish NOELs are available in the USEPA Office of Pesticide Programs database or Ecotox database (USEPA, 2012). This number of toxicity evaluations falls far short of the over 1000 pesticides in current use. However, there are sensitive fish species' acute 96-hour LC50s in Ecotox for over 90% of the agricultural pesticides currently and formerly in use. These 96-hour LC50s can be used to estimate chronic NOELs using the linear regression (Eq. 5) established by Plotkin (2010, unpublished). The regression equation was determined by correlating same species 96-hour fish LC50s and chronic fish NOELs for the approximately 200 pesticides with both chronic fish NOELs and 96-hour LC50s available in the Ecotox database ($r^2 = 0.81$).

**Equation 5**

**Log10(Fish NOEL) = 0.889 X (Log10(96-hour LC50)) – 0.779   $r^2 = 0.81$**

Use of fish chronic NOELs for environmental assessment is in compliance with the Burgess et al. (2012) recommendation of using established USEPA toxicity benchmark parameters for pelagic species such as NOELs from USEPA's Water Quality Criteria, Final Chronic Value (FCV), Secondary Chronic Value (SCV) or any other relevant water-exposed pelagic fish toxicity threshold to estimate ESB toxicity units

(ESBTU). Likewise, the fish chronic MATC would also be appropriate as currently used in the Windows Pesticide Screening Tool (WIN-PST) to evaluate chronic benthic toxicity risk.

**Example EBSTU Calculations in Environmental Fate Computer Modeling**

In this example, a computer modeler would like to assess benthic toxicity risk from atrazine sorbed to sediment particles running off an agricultural field. Environmental fate computer modeling results show:

Atrazine mean annual sediment-sorbed losses: 200 µg atrazine/Kg sediment

Other required information:

Sediment organic carbon fraction: 0.01 or 1%;
Atrazine Koc: 100 mL/gram;
Brook trout chronic NOEL: 65 µg/L;

Using Equation 3:

$$\textbf{ESBTU} = \frac{\textbf{(sediment pesticide conc.) / (organic carbon fraction)}}{\textbf{(Koc) X (Fish NOEL)}} = \frac{\textbf{(200 / 0.01)}}{\textbf{(100 X 65)}} = \textbf{3.1}$$

Since an ESBTU >= 1.0 indicates potential toxicity risk, this agricultural field's average annual pesticide sediment-sorbed runoff may be moderately toxic to benthic macroinvertebrates.

If more than one pesticide were applied to the field as usually is the case, ESBTUs for all pesticides applied may be aggregated to determine total pesticide sorbed to sediment toxicity risk for this agricultural field.

Additionally, if atrazine was applied to numerous fields in a watershed or river basin, the ESBTUs for the entire watershed or river basin may be aggregated in order to determine the magnitude of potential risk from atrazine to the benthos.

**Non-ionic Versus Ionic Pesticides**

The USEPA ESB method is intended for evaluation of nonionic pesticides (no measurable pKa or pKb). Nonionic pesticides will sorb primarily to organic carbon as opposed to uncharged particles. A pesticide with a high Koc (> 5000 ml/g) will bind tighter and more extensively to organic carbon particles. Approximately two thirds of the more than 1000 synthetic agricultural pesticides are nonionic. The remaining ionic pesticides are chemically charged with a measurable pKa. Ionic pesticides have a proclivity to bind to sediment particles with the opposite charge but tend not to sorb to organic carbon particles. For example, negatively charged clay particles tend to attract positively charged ionic pesticides. Some ionic pesticides are only weakly charged or weakly charged at certain pH levels while strongly being ionic at other pH levels depending upon their pKa.

Burgess et al. (2012) recommended that only nonionic pesticides be used in the ESB method in order to employ the Koc as an equilibrium constant. However, to account for the charged attraction between ionic pesticides and charged sediment particles, Koc "equivalences" have been estimated for ionic pesticides based on the chemical's pKa (Hornsby et al., 1996; USDA NRCS 2015). The accuracy of using estimated Koc values for ionic pesticides can be tested by analyzing the ratio of sediment-bound pesticide to the concentration in sediment interstitial water. These equivalent Koc values for ionic pesticides are used in pesticide fate modeling (e.g., PRZM, Mullins et al., 1993; GLEAMS, Knisel et al., 1993; and APEX, Steglich and Williams, 2008). Though estimating equivalent Koc values for ionic pesticides is technically not chemically correct, it does provide a reasonable pesticide binding estimate that can be used to approximate the sediment-interstitial water pesticide equilibrium. By using estimated Koc values, ionic pesticide exposure to the benthos can be estimated using the ESB method.

## Summary and Conclusions

- Minimal pesticide toxicity testing has been performed using benthic and epibenthic macroinvertebrates. Consequently, it is necessary to employ alternative methods to estimate pesticide toxicity risk to these organisms.

- USEPA and numerous toxicologists have suggested using Equilibrium Partitioning Sediment Benchmarks (ESBs) for the protection of benthic macroinvertebrates employing pesticide Koc values as a chemical equilibrium constant.

- In a USEPA study Burgess et al. (2012) recommended using aquatic ecosystem Final Chronic Values (FCV), Secondary Chronic Values (SCV) and USEPA's Water Quality Criteria (WQC) for toxicity thresholds in estimating the ESB in lieu of direct toxicological testing of benthic organisms for freshwater and marine ecosystems. Unfortunately, FCVs and SCVs have been established for only about 40 to 50 pesticides.

- Burgess et al. (2012) suggested use of chronic toxicity thresholds for sensitive pelagic species (e.g., rainbow trout, bluegill sunfish and *Daphnia pulex*) be used in the ESB method to estimate toxicity to benthos (e.g., MATC and NOEL) when WQC, FCV or SCV are unavailable.

- Over 1000 pesticides are currently in use by agricultural systems.

- Di Toro et al. (2000) found that rainbow trout chronic NOELs were within a factor of 1.7 of SCV values for narcotic toxicity effects including pesticides.

- A Log-Log linear regression was performed using benthic midge chronic NOELs to pesticides dissolved in interstitial water versus sensitive fish species chronic NOELs (rainbow trout and fathead minnow). An $r^2 = 0.52$ indicated a moderate correlation but with a small sample size (N = 12).

- About 200 chronic MATCs (geometric mean of NOEL and LOEL) for sensitive fish species are available in the USDA NRCS/University of Massachusetts Extension Fish Chronic Toxicity Database. Over 700 more MATC thresholds have been extrapolated from 96-hour LC50s using the Log(MATC) versus Log(96-h LC50) linear regression established by Barnthouse et al. (1990).

- About 200 chronic NOELs for sensitive fish species are provided in the USEPA Ecotox database (USEPA OPP, 2014). More than 700 additional NOELs to sensitive fish species can be estimated by the Log(NOEL) versus Log(96-hour LC50) linear regression determined by Plotkin (2010, unpublished). The linear regression was found to be highly correlative with $r^2 = 0.81$.

- Based on the studies cited in this article, the authors are proposing use of sensitive fish species' NOELs or MATCs to be employed in the ESB method to estimate chronic pesticide toxicity risk to benthic and epibenthic macroinvertebrates.

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