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Development and application of freshwater sediment-toxicity benchmarks for currently used pesticides

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HIGHLIGHTS

- Sediment-toxicity benchmarks are developed for 129 pesticides in whole sediment.
- Benchmarks can be used to predict or interpret pesticide toxicity in whole sediment.
- Benchmarks are based on spiked-sediment bioassays or equilibrium partitioning.
- Benchmarks correctly predicted amphipod toxicity in 74% of samples in a case study.
- Whole-sediment benchmarks may not always represent bioavailable concentrations.

GRAPHICAL ABSTRACT

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ABSTRACT

Sediment-toxicity benchmarks are needed to interpret the biological significance of currently used pesticides detected in whole sediments. Two types of freshwater sediment benchmarks for pesticides were developed using spiked-sediment bioassay (SSB) data from the literature. These benchmarks can be used to interpret sediment-toxicity data or to assess the potential toxicity of pesticides in whole sediment. The Likely Effect Benchmark (LEB) defines a pesticide concentration in whole sediment above which there is a high probability of adverse

Abbreviations: CA, concentration addition; DER, Data Evaluation Record; EC10, 10% effect concentration; EC20, 20% effect concentration; EC25, 25% effect concentration; EC50, median effect concentration; EqP, equilibrium partitioning; ERL, effects range–low; ERM, effects range–median; ESB, equilibrium-partitioning sediment benchmark; Koc, soil organic carbon/water partitioning coefficient; Kow, *n*-octanol/water partitioning coefficient; LC50, median lethal concentration; LEB, Likely Effect Benchmark; LEB_{cd}, Likely Effect Benchmark based on spiked-sediment bioassays for *Chironomus* species; LEB_{ha}, Likely Effect Benchmark based on spiked-sediment bioassays for *Hyalella azteca*; LEB_{eqp}, Likely Effect Benchmark estimated based on equilibrium partitioning; LEB_{int}, Integrated Likely Effect Benchmark based on spiked-sediment bioassay data; LEB_{ssb}, Likely Effect Benchmark based on spiked-sediment bioassay data; LEBQ, Likely Effect Benchmark quotient; LOEC, lowest-observed-effect concentration; MATC, maximum allowable toxicant concentration; MOA, mode of action; msPAF, Multi-Substance Potentially Affected Fraction (model); NAWQA, National Water-Quality Assessment Project; NOEC, no-observed-effect concentration; OC, organochlorine; OPP, Office of Pesticide Programs; PAH, polycyclic aromatic hydrocarbon; PCB, polychlorinated biphenyl; PEC, probable effect concentration; PECQ, probable effect concentration quotient; PTI, Pesticide Toxicity Index; PWG, Pyrethroid Working Group; Sediment-PTI, Pesticide Toxicity Index for sediment; SETAC, Society for Environmental Toxicology and Chemistry; SPME, solid-phase microextraction; SSB, spiked-sediment bioassay; TEB, Threshold Effect Benchmark; TEB_{cd}, Threshold Effect Benchmark based on spiked-sediment bioassays for *Chironomus* species; TEB_{ha}, Threshold Effect Benchmark based on spiked-sediment bioassays for *Hyalella azteca*; TEB_{eqp}, Threshold Effect Benchmark estimated based on equilibrium partitioning; TEB_{int}, Integrated Threshold Effect Benchmark based on spiked-sediment bioassay data; TEB_{ssb}, Threshold Effect Benchmark based on spiked-sediment bioassay data; TEBQ, Threshold Effect Benchmark quotient; TEC, threshold effect concentration; TU, toxic unit; USEPA, U.S. Environmental Protection Agency; USGS, U.S. Geological Survey.

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effects on benthic invertebrates, and the Threshold Effect Benchmark (TEB) defines a concentration below which adverse effects are unlikely. For compounds without available SSBs, benchmarks were estimated using equilibrium partitioning (EqP). When a sediment sample contains a pesticide mixture, benchmark quotients can be summed for all detected pesticides to produce an indicator of potential toxicity for that mixture. Benchmarks were developed for 48 pesticide compounds using SSB data and 81 compounds using the EqP approach. In an example application, data for pesticides measured in sediment from 197 streams across the United States were evaluated using these benchmarks, and compared to measured toxicity from whole-sediment toxicity tests conducted with the amphipod *Hyalella azteca* (28-d exposures) and the midge *Chironomus dilutus* (10-d exposures). Amphipod survival, weight, and biomass were significantly and inversely related to summed benchmark quotients, whereas midge survival, weight, and biomass showed no relationship to benchmarks. Samples with LEB exceedances were rare (n = 3), but all were toxic to amphipods (i.e., significantly different from control). Significant toxicity to amphipods was observed for 72% of samples exceeding one or more TEBs, compared to 18% of samples below all TEBs. Factors affecting toxicity below TEBs may include the presence of contaminants other than pesticides, physical/chemical characteristics of sediment, and uncertainty in TEB values. Additional evaluations of benchmarks in relation to sediment chemistry and toxicity are ongoing.

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1. Introduction

Historically, sediments have been sampled to assess the occurrence within a hydrologic system of particulate-associated contaminants such as legacy organochlorine (OC) insecticides, polychlorinated biphenyls (PCB), polycyclic aromatic hydrocarbons (PAH), and metals. To assess the biological significance of such residues, both empirical and theoretically based benchmarks for these traditional sediment contaminants have been used for decades (e.g., MacDonald et al., 2000; U.S. Environmental Protection Agency, 2004; Wenning et al., 2005). However, a number of currently used pesticides also are hydrophobic (e.g., fipronil and pyrethroid insecticides), and have been analyzed in sediment in recent monitoring and research studies (e.g., Ding et al., 2010; Gan et al., 2012; Hintzen et al., 2009; Hladik and Kuivila, 2012; Nowell et al., 2013; Phillips et al., 2012; Phillips et al., 2014). This is especially true for pyrethroid insecticides, which because of their toxicity to invertebrates and their extensive use in nonagricultural applications, have been targeted (and detected) in metropolitan areas across the United States (e.g., Amweg et al., 2006; Holmes et al., 2008; Kuivila et al., 2012; Nowell et al., 2013; Weston et al., 2011; Weston et al., 2005). Such studies of currently used pesticides in sediment address a variety of objectives, such as to assess the occurrence, spatial distribution, trends, and relation to potential sources; support development of models to predict concentrations in unmonitored streams; and predict or explain adverse biological effects. The U.S. Geological Survey (USGS) has begun to analyze up to 118 currently used pesticides in stream sediment as part of 2 national-scale programs, the National Water-Quality Assessment (NAWQA) Project of the National Water Quality Program and the Toxic Substances Hydrology Program. Analytical reporting levels for pesticides in sediment are in the 0.5–3 μg/kg range (Hladik and McWayne, 2012). As a result, there is a need for tools, such as effects-based sediment benchmarks, with which to interpret or predict the biological significance of low levels of currently used pesticide residues in stream sediments.

The objectives of this study were to (1) develop effects-based sediment benchmarks for currently used pesticides for protection of freshwater benthic invertebrates using available toxicity data, including available spiked-sediment bioassays (SSB); and (2) evaluate the utility of the benchmarks when applied to monitoring data in relation to ambient sediment-toxicity data, considering pesticides both individually and as mixtures. This study addresses the current need to put the growing body of literature on currently used pesticide concentrations reported in whole sediments into some context for biological significance.

2. Background

2.1. Approaches for sediment benchmark development

Sediment-quality benchmarks have been developed in the past for legacy OC pesticides using both empirical and mechanistic methods (Wenning et al., 2005), but existing benchmarks for currently used pesticides are rare (Section 2.1.2). Common methods for deriving benchmarks for hydrophobic organic contaminants—biological effects correlation, equilibrium partitioning, and spiked-sediment toxicity approaches—differ in their advantages and limitations regarding applicability towards currently used pesticides.

2.1.1. Biological effects correlation

Empirical benchmarks take a biological effects correlation approach, in which a database of matching sediment chemistry measurements and biological effects measurements is used to identify a concentration of concern (a benchmark) for a particular contaminant on the basis of the probability of observing adverse effects on benthic invertebrates. Examples of empirical benchmarks for OC pesticides include the apparent effects threshold (Barrick et al., 1988), effects range–low (ERL) and effects range–median (ERM) (Long et al., 1998; Long and Morgan, 1991), threshold effect concentration (TEC) and probable effect concentration (PEC) (MacDonald et al., 2000), and a logistical model (Field et al., 2002). Many empirical benchmarks come in pairs, with one benchmark denoting a concentration above which adverse effects are expected to occur more often than not (e.g., ERM and PEC), and a second benchmark denoting a concentration below which adverse effects are not expected (e.g., ERL and TEC). MacDonald et al. (2000) proposed a mean PEC-quotient (PECQ) to address contaminant mixtures, in which concentrations of individual contaminants were divided by their respective PECs, the PECQs were summed for each constituent class in the mixture, and the overall mean-PECQ for these constituent classes was determined (Ingersoll et al., 2001). Adverse effects on benthic invertebrates have been observed in association with mean-PECQ values > 0.5 (MacDonald et al., 2000) or mean quotients >0.2 or >0.1 (Ingersoll et al., 2005).

Empirical benchmarks are based on empirical associations between chemical contamination and biological effects, and do not indicate a direct cause-and-effect relationship. This approach may overestimate toxicity due to one particular chemical with benchmark exceedances because the empirical benchmarks are based on associations with toxicity in field sediment samples that often contain mixtures of chemical contaminants (Wenning et al., 2005). These benchmarks also assume that the influence of the chemical contaminant(s) is greater than the influence of environmental conditions (Long and Morgan, 1991). The biological effects correlation approach is not a viable option for currently used pesticides, because the needed datasets of matching chemistry and biological effects measurements for field-collected sediments are not widely available.

2.1.2. Equilibrium-partitioning sediment benchmarks

Equilibrium-partitioning sediment benchmarks (ESB) for nonionic organic chemicals were developed by the U.S. Environmental Protection Agency (USEPA) on the basis of equilibrium-partitioning (EqP) theory,