Influence of sediment chemistry and sediment toxicity on macroinvertebrate communities across 99 w....

Article *in* Science of The Total Environment · December 2017

DOI: 10.1016/j.scitotenv.2017.05.035

6 authors, including:

Patrick W Moran
United States Geological Survey

Lisa H Nowell
United States Geological Survey

Nile Kemble
United States Geological Survey

Barbara J Mahler
United States Geological Survey

Science of the Total Environment 599–600 (2017) 1469–1478

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Influence of sediment chemistry and sediment toxicity on macroinvertebrate communities across 99 wadable streams of the Midwestern USA

Patrick W. Moran [a,*], Lisa H. Nowell [b], Nile E. Kemble [c], Barbara J. Mahler [d], Ian R. Waite [e], Peter C. Van Metre [d]

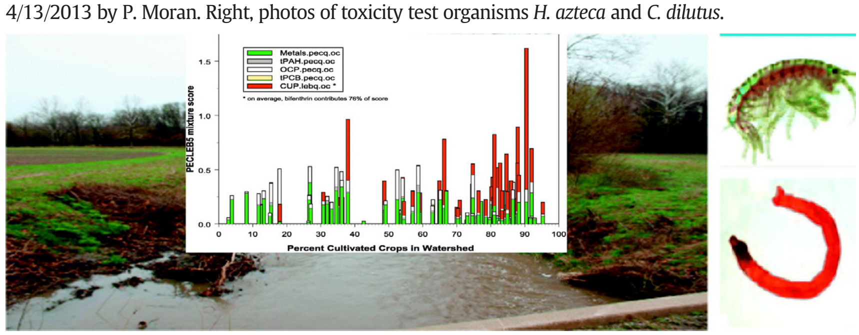
[a] USGS, Tacoma, WA, United States
[b] USGS, Sacramento, CA, United States
[c] USGS, Columbia, MO, United States
[d] USGS Austin, TX, United States
[e] USGS, OR, United States

HIGHLIGHTS

- PCBs, PBDEs and OC insecticides uncommon in sediments from agricultural watersheds
- Of 274 contaminants in sediment, bifenthrin poses greatest potential risk to biota.
- Macroinvertebrate measures declined with sediment bifenthrin concentrations
- Sediment contaminants a significant predictor of macroinvertebrate community

GRAPHICAL ABSTRACT

Bear Creek near Gilliam, MO. Photography of one the agricultural sites shown in Figure 1, overlaid. Photo taken 4/13/2013 by P. Moran. Right, photos of toxicity test organisms *H. azteca* and *C. dilutus*.



ARTICLE INFO

Article history:
Received 7 March 2017
Received in revised form 3 May 2017
Accepted 3 May 2017
Available online xxxx

Editor: Jay Gan

Keywords:
Sediments
Streams
Mixture
Toxicity
Pesticides
Bifenthrin
Hyalella azteca
Chironomus dilutus

ABSTRACT

Simultaneous assessment of sediment chemistry, sediment toxicity, and macroinvertebrate communities can provide multiple lines of evidence when investigating relations between sediment contaminants and ecological degradation. These three measures were evaluated at 99 wadable stream sites across 11 states in the Midwestern United States during the summer of 2013 to assess sediment pollution across a large agricultural landscape. This evaluation considers an extensive suite of sediment chemistry totaling 274 analytes (polycyclic aromatic hydrocarbons, organochlorine compounds, polychlorinated biphenyls, polybrominated diphenyl ethers, trace elements, and current-use pesticides) and a mixture assessment based on the ratios of detected compounds to available effects-based benchmarks. The sediments were tested for toxicity with the amphipod *Hyalella azteca* (28-d exposure), the midge *Chironomus dilutus* (10-d), and, at a few sites, with the freshwater mussel *Lampsilis siliquoidea* (28-d). Sediment concentrations, normalized to organic carbon content, infrequently exceeded benchmarks for aquatic health, which was generally consistent with low rates of observed toxicity. However, the benchmark-based mixture score and the pyrethroid insecticide bifenthrin were significantly related to observed sediment toxicity. The sediment mixture score and bifenthrin were also significant predictors of the upper limits of several univariate measures of the macroinvertebrate community (EPT percent, MMI (Macroinvertebrate Multimetric Index) Score, Ephemeroptera and Trichoptera richness) using quantile regression. Multivariate pattern matching (Mantel-like tests) of macroinvertebrate species per site to identified contaminant metrics and sediment toxicity also indicate that the sediment mixture score and bifenthrin have weak, albeit

* Corresponding author at: US Geological Survey, Washington Water Science Center, 934 Broadway, Suite 300, Tacoma, WA 98402, United States.
E-mail address: pwmoran@usgs.gov (P.W. Moran).

http://dx.doi.org/10.1016/j.scitotenv.2017.05.035
0048-9697/Published by Elsevier B.V.

significant, influence on the observed invertebrate community composition. Together, these three lines of evidence (toxicity tests, univariate metrics, and multivariate community analysis) suggest that elevated contaminant concentrations in sediments, in particular bifenthrin, is limiting macroinvertebrate communities in several of these Midwest streams.

1. Introduction

Contaminants in streambed sediments are potential stressors to benthic organisms; however, large-scale monitoring studies of stream sediment quality, such as Lopes and Furlong (2001) or Kuivila et al. (2012), are limited. Investigations addressing contaminants in sediments are often specific to a given location or a single contaminant or contaminant class; such as pyrethroids (Amweg et al., 2006; Weston et al., 2005), polyaromatic hydrocarbons (PAH) (Scoggins et al., 2007; Cox and Clements, 2013), trace elements (Canfield et al., 1994; Besser et al., 2015a) or polychlorinated dibenzo-p-dioxins and dibenzofurans and polychlorinated biphenyls (PCB) (Khim and Hong, 2014). The broad scale monitoring of current use pesticides in sediments, with the exception of recent studies on pyrethroids, is less common than with other contaminants (Nowell et al., 2016). A more complete sediment assessment should consider multiple measures of condition, ideally chemistry, toxicity testing, and co-located infaunal species. Such approaches are often referred to as the sediment quality triad (Chapman, 1990; Canfield et al., 1994).

Several review studies have recognized that sediment contaminants can have an additive affect and have taken steps to address and incorporate multiple contaminant classes through a common “benchmark” or guideline “quotient” approach. Such reviews (MacDonald and Ingersoll, 2000; USEPA, 2003; Long et al., 2006; Nowell et al., 2016) have established sediment benchmarks, at various likelihoods of observed toxicity, to aid interpretation of sediment chemistry data regarding their potential effects on biota. Guidance for deriving sediment benchmarks for various contaminant classes using an equilibrium partitioning approach has been released by the United States Environmental Protection Agency (USEPA), (USEPA, 2003, 2005), but does not address current-use pesticides (CUP). Some of these reviews note the heterogeneity of sediments, the variable carbon and grain-size fractions, and other factors (e.g. temperature) that can influence toxicity in sediments. Naturally occurring chemical stressors, such as sulfide, ammonia, and various metals (Ankley et al., 1990; Wang and Champman, 1999; Wang et al., 2007; Kinsman-Costello et al., 2015), to freshwaters organisms are also common and warrant consideration. Paired sediment chemistry and sediment toxicity testing, coupled with application of available sediment benchmarks and statistical testing of their utility in interpreting benthic macroinvertebrate communities is needed (Schafer et al., 2007; Cao and Hawkins, 2011), and presented here. Benthic macroinvertebrates are commonly used as a measure of stream ecosystem condition. Although effects of contaminants on stream ecosystems are often suggested, discussed, or evaluated downstream of a known point source, rarely are these ‘toxic’ influences monitored or assessed on a broad geographic scale. Few studies (i.e. Canfield et al., 1994; Winger et al., 2005; Schafer et al., 2011), have tested relations between standard macroinvertebrates and sediment toxicity tests, as well as macroinvertebrates and benchmark quotients, from a common set of streams (Schafer et al., 2007).

The three endpoints of the sediment quality triad—sediment chemistry, sediment toxicity, and macroinvertebrate communities—were evaluated in 2013 at 99 wadable stream sites across 11 states in the Midwestern ‘Corn Belt’ of the United States the US Geological Survey's National Water Quality Assessment project (NAWQA) in partnership with the US Environmental Protection Agency's (USEPA) National Rivers and Stream Assessment (NRSA) program and presented here. The objectives of this evaluation were threefold; 1) to assess the toxic potential (relative to available benchmarks) of several classes of contaminants, including current use pesticides, measured in stream sediments in the region; 2) to evaluate the toxicity of those sediments in standard toxicity tests; and 3) to compare impairment scores from chemistry benchmarks and sediment toxicity tests to macroinvertebrate communities. The data discussed here are part of a larger study conducted by the USGS NAWQA and the USEPA NRSA programs in the spring and summer of 2013 aimed at evaluating multiple stressors and ecology in Midwest freshwater streams.

2. Methods

2.1. Study design and site selection

The study design combined the probabilistic site-selection approach of the NRSA program (Olsen et al., 1999; USEPA, 2013a, 2013b) and a land-use gradient approach (e.g., Gosz, 1992) commonly used by the USGS NAWQA project (such as Coles et al., 2012). Fifty sites (hereafter random sites) were selected from the NRSA probabilistic candidate list of sites, which is based on a random selection from the population of stream reaches in the region. Inclusion or exclusion of these random sites followed USEPA protocols (USEPA, 2013a) with the exception that larger, non-wadable streams and some very small, potentially ephemeral streams were excluded. The remaining 50 sites (targeted sites) were selected by the USGS on the basis of watershed characteristics (Supplemental information (SI), Fig. S1) in order to fully resolve a broad gradient of watershed agricultural intensity. Watershed scale characteristics were generated from geographic information system (GIS) digital coverages of landuse (Homer et al., 2015) upstream of the sampling site; ‘site’ is used hereafter to refer to both the stream reach (defined below) sampled or the upstream watershed. The targeted sites were added to achieve full coverage of the agricultural stressor gradient in the region, to include a subset of sites with long-term monitoring data, and to include representation of urban land use by adding 12 urban indicator sites. Watershed land-use characteristics were calculated from National Land Cover Datasets (NLCD) (Homer et al., 2015). Cultivated crops in the 88 agricultural-gradient watersheds (all 50 random sites and 38 targeted sites) ranged from 0 to 95% (median = 63%). Urban land use (the sum of low, medium, and high development categories (Homer et al., 2015)) for these 88 sites was <8%. Urban land use for the 12 urban indicator sites ranged from 18 to 88%.

2.2. Sample collection

The stream habitat surveys and macroinvertebrate collection followed USEPA NRSA methods (USEPA, 2013a), where a stream reach was a section of stream approximately 40 times the average wetted width in length. Sediment and ecological sampling occurred during late July and early August of 2013. The sediment collection followed Shelton and Capel (1994), where multiple grab samples of the surficial (top 2 cm) sediment were collected in depositional areas, typically dominated by fine-grained sediment, along the length of the reach and composited. Samples were not sieved, but material larger than about 2 mm, such as gravel, sticks, or debris, were removed by hand. Bed-sediment samples were shipped on ice to the USGS Columbia Environmental Research Center (CERC) and refrigerated in the dark at 4 °C for

2–4 weeks pending homogenization and splitting of the samples into sub-samples for chemical analyses and toxicity testing. One site could not be sampled for sediment and ecology because of high water levels and one sediment sample from a second site was not analyzed for metals, leaving 98 or 99 sites depending on the analysis.

2.3. Sediment chemistry

Four analytical methods were used to characterize contaminants from five chemical classes in streambed sediments; two methods were applied to all sediment samples and two were applied to a subset of 27 samples. At all 99 sites, 118 current-use pesticides were analyzed at the USGS Pesticide Fate Research Laboratory (Sacramento, CA) by gas chromatography-tandem mass spectrometry (GC–MS/MS) (Hladik and McWayne, 2012)). This method includes legacy oraganochlorine pesticides, such as p,p′-DDT (and its transformation products p,p′-DDD, and p,p′-DDE), chlordanes, and dieldrin. For 98 sites, 37 major and trace elements were analyzed by the US Geological Survey's Crustal Geophysics and Geochemistry Science Center (Denver, CO) on dried and ground samples from 98 sites, digested on a hotplate using a mixture of hydrochloric–nitric–perchloric–acids, with analysis by inductively coupled plasma–mass spectrometry (Briggs and Meier, 2002).

Samples from 27 of the sites were selected from analysis of polycyclic aromatic hydrocarbons (PAHs) and halogenated organic compounds. The halogenated compound method includes organochlorine insecticides, polychlorinated biphenyls (PCBs), and polybrominated diphenyl ethers (BDEs). A subset of samples was selected as most of these compounds were assumed not to occur frequently in non-urban settings (e.g., Lopes and Furlong, 2001). These 27 sites included 12 urban sites, 13 sites with substantial agricultural row crops (>59%), and two reference sites with low levels of urban and agricultural development. PAHs were analyzed at the U.S. Geological Survey National Water Quality Laboratory (NWQL) in Denver, CO, using accelerated solvent extraction (ASE) and analysis by gas chromatograph/mass spectrometer (GC/MS) (Zaugg et al., 2006). The method included 18 parent PAHs, 10 specific alkyl-PAHs, and 10 other semivolatile organic compounds.

Halogenated organic compounds were analyzed using a custom method at the NWQL with extraction by ASE followed by cleanup by solid-phase extraction and analysis by GC/MS. This halogenated hydrocarbon method, which includes several brominated diphenyl ethers (BDEs), was reported in Mahler et al. (2009) and discussed in detail by Wagner et al. (2014). This method includes analysis of p,p′-DDT, p,p′-DDD, and p,p′-DDE; however, as these compounds are also reported in the current use pesticide method (Hladik and McWayne, 2012), mentioned above, for all sites and at lower detection level, the p,p′-DDE values from the Hladik and McWayne (2012) method were used to calculate the PECQ. The 18 IUPAC congeners quantified by the halogenated compound method were summed as total PCBs, thus, this total is a low estimate of total PCBs. Total chlordane was computed as the sum of *trans*-chlordane, *cis*-chlordane, *cis*-nonachlor, and oxychlordane.

For the purposes of Probable Effect Concentration (PEC) (MacDonald and Ingersoll, 2000) quotient calculation (PECQ) only, concentrations of total PAHs, total chlordane, dieldrin, and total PCBs at the 62 sites where these compounds were not measured were estimated from concentrations at the 27 measured sites. Extrapolated values were never used in detection frequency statistics. For PAHs, concentrations at the remaining 62 sites were estimated using regression equations generated for individual PAHs in relation to urban land use. (Least-squares regression was used for the purposes of calculating PEC quotients across all sites and all PAHs, average $r^2 = 0.79$, see Supplemental material for discussion of total PAH regression). Total PAHs were computed by summing extrapolated concentrations of 12 parent PAHs. These were 12 of the 13 PAHs specified by Ingersoll et al. (2001), because one homologue was not quantified by this method (See Supplemental material, Extrapolation to Unsampled Sites, for more detail.). For total chlordane, dieldrin, and total PCBs, the median of the measured values at the 27 sites, all relatively tiny values, was used to estimate concentrations at the remaining sites, for purposes of PECQ calculation.

2.4. Mixture assessment with PEC and LEB quotients

Organic compound concentrations were converted from dry weight to an organic carbon (OC) normalized basis, and then compared with their respective sediment benchmarks. The benchmarks are the consensus PECs (MacDonald and Ingersoll, 2000) for metals, PCBs, PAHs, and organochlorine pesticides, and the integrated Likely Effect Benchmark (LEB) for current use pesticides from Nowell et al. (2016). Correlations between sediment chemistry and toxicity are often, but not exclusively, stronger when based on a carbon-normalized basis (Long et al., 2006; Nowell et al., 2013) and sediment-organic-carbon normalization is commonly used to predict bioavailable pesticide concentrations (Nowell et al., 2016) and for nonionic organics across a range of sediment conditions (US EPA, 2003). Thus, carbon normalization was preferentially used in this analysis, but raw (unnormalized) concentrations also were evaluated for completeness. Metals were compared to benchmarks with and without OC normalization.

A benchmark quotient (the ratio of an OC normalized concentration to its benchmark) was computed for five contaminant classes, consistent with methods of MacDonald and Ingersoll (2000). For metals, a quotient (the ratio of the dry weight OC-normalized concentration to its benchmark) was computed for each of 7 metals (As, Cd, Cr, Cu, Pb, Ni, Zn) and an average quotient score was taken to represent metals as a class. Similarly, PEC quotients were computed using OC normalized concentrations of p,p′-DDE, dieldrin, and total chlordanes, and the average taken to represent the organochlorine pesticide class. p,p′-DDE was used to represent the DDT family because this congener is the single DDT compound detected most frequently and at the highest concentrations, and because the PEC for sum-DDE met reliability criteria (for predictive ability) in MacDonald and Ingersoll (2000). PEC quotient scores for the PAH and PCB classes were computed using concentrations and available PECs for total PAHs and total PCBs. For current use pesticides, individual benchmark quotients were computed for individual pesticides using LEBs; however, due to the large number of analytes (118) in the pesticide analytical method and the high frequency of non-detections (98% on average) at a given site, the sum rather than the average of the current-use pesticide quotients was used to represent this class. For comparison to OC-normalized contaminant concentrations, the PEC values from MacDonald and Ingersoll (2000) were assumed to apply to 1%TOC in sediment (reflecting sediment levels typical of the data set used to derive PECs (Ingersoll et al., 2009). All non-detected contaminants were treated as zero in PECQ and LEBQ calculations, as other assumptions generated nonsensical patterns. Finally, a combined score reflecting the five classes of compounds (organochlorines, PAHs, PCBs, metals, and current use pesticides), hereafter referred to as the PECLEB5 score, was computed as the sum of the five classes of benchmark quotients (reflecting the five classes of compounds) divided by 5. This is analogous to the mean PECQ of MacDonald and Ingersoll (2000) and Long et al. (2006), and it summarizes the overall potential mixture toxicity at a site.

2.5. Sediment toxicity testing

Sediment-toxicity tests were conducted with amphipod (*Hyalella azteca*) and the fatmucket mussel (*Lampsilis siliquoidea*) (both 28-day exposures) and the midge (*Chironomous dilutus*) (10-day exposures) according to methods outlined in USEPA (2000) and American Society for Testing and Materials (ASTM) International (2012) (additional details are given in SI-Toxicity test conditions). Amphipods and midges were from in-house cultures maintained at CERC and mussels were obtained from juveniles transformed by Chris Barnhart at Missouri State University and reared at CERC. Newly transformed mussels will be cultured in 100 mg/L hardness for about 6 weeks (about 1.5-mm shell length) for testing. Testing with amphipods and midges was performed using sediments collected from all 98 sites, whereas mussel testing was performed with samples from only 24 sites. Sediments were homogenized in a stainless steel bowl and placed in beakers about seven days before test organisms were added. Ten amphipods or midge were exposed to 100 ml of sediment with 175 ml overlying water in 300-ml beakers, with four replicates per treatment per species, and two volume additions of overlying water (Ingersoll et al., 2002). Because there were fewer juvenile mussels available at the start of testing, eight mussels were used in four replicate beakers. Endpoints included survival, growth and biomass for each test species. Response of each endpoint for each species was compared to a standard control sediment, Spring River, MO, (Besser et al., 2015b) using Barlett's 1-way ANOVA (p-value <0.05), and reported as significantly different relative to control, for further evaluation. Steps taken upon conclusion of the toxicity testing to evaluate each endpoint are presented in Concluding Sediment Toxicity Testing, in the SI.

2.6. Benthic macroinvertebrates

Benthic macroinvertebrate sampling and habitat characterization were performed following standard USEPA NRSA (USEPA, 2013a) methods, utilizing a 500 μm mesh, D-frame kick net, on the same day that the bed sediments were collected. Invertebrate samples were preserved and shipped to the USGS NWQL, Biological Unit, for identification and enumeration (Moulton et al., 2000). During taxonomic data processing, the following decision rules were followed: terrestrial adults were deleted, different lifestages for a common taxonomic endpoint were combined, and ambiguous taxonomic 'parents' were distributed proportionately among the 'children' so that no distinct taxa endpoints were deleted. The raw data of species taxonomy and enumeration by site are available in the USGS BioData Database (USGS, 2015, http://dx.doi.org/doi:10.5066/F77W698B). Several measures of the invertebrate community, particularly those most commonly evaluated by management agencies, were evaluated here. Invertebrate species relative abundance is often summarized as univariate metrics (e.g., Ephemeroptera, Plecoptera, Tricoptera (EPT) Richness; Total Richness), and these metrics were generated following methods by Cuffney (2003) and used here. An additional Macroinvertebrate Multimetric Index (MMI) generated and utilized by US EPA, following methods of Stoddard et al. (2008) and USEPA (2013b), was also evaluated. As Plecoptera were very rare in these Midwest stream, the orders of Ephereroptera and Tricoptera were also evaluated separately.

2.7. Statistical analysis

Statistical analyses of toxicity test results were performed using SAS software (SAS/STAT version 9.2; SAS Cary, NC). Differences in a toxicity endpoint among sites were determined by analysis of variance (ANOVA). Toxicity end point data were transformed before ANOVA to improve normality as indicated by the Shapiro–Wilk test (USEPA, 2000; ASTM, 2012). Comparisons of toxicity endpoints and selected chemical stressors (five individual chemicals and the PECLEB5 score) were done using Spearman's rank correlations with statistical significance (p-value) set at 0.05. Processing of the macroinvertebrate count data was completed using the software package IDAS, USGS Invertebrate Data Analysis System, Raleigh, NC. Correlation analysis was performed with Systat, v. 13, San Jose, CA. Ordinary least squares regression and *t*-tests were done in Tibco S-Plus, v 8.1, Boston, MA. Multivariate analysis of the macroinvertebrate community data was performed using Primer-E, v6.1.5, Plymouth, UK, using both a weak and heavy transformation, square root and presence-absence, respectively, of abundance data followed by Bray-Curtis distance matrix and ordination using nonmetric multidimensional scaling (MDS) (McCune and Grace, 2002). Comparison between the species matrix and the toxicity, sediment chemistry, and Geographic Information System (GIS) variable matrices were each done separately using a Mantel-like test via the BEST BVSTEP (stepwise inclusion and deletion) of Primer v6, followed by permutation testing for significance determination.

Contaminants in sediment are most likely to be a limiting factor on stream communities at higher concentrations, and are not necessarily predictive of the mean or median ecological response at all concentrations. In such cases, common in ecological data, scatterplots often result in a classic 'wedge-shaped' response pattern, where statistically significant relations may only be apparent at higher or lower limits of a given ecological response (Cade and Noon, 2003). To address this, quantile-regression was performed with R-Studio (ver 0.98.507) and the R program, (ver 3.3.1), with the package 'quantreg' (ver.5.29) (Koenker, 2015). Statistical significance testing followed the default, quantile-regression sandwich formula, using the Hall-Sheather bandwidth rule (Koenker, 2015).

3. Results

3.1. Contaminants in stream sediments

Organic carbon in the sediments, which influences the bioavailability of many contaminants, had a median concentration of 1.3% (interquartile range of 2.0%). While 94 sites had an OC concentration in sediments <5.0%, five sites had OC ranging from 5.3 and 17.6% (see Table S1 of Kemble et al. (2016) (doi:10.5066/F7Z899HX) for OC and all sediment chemistry data discussed below). Of the 118 pesticides measured in bed sediment using the GC–MS/MS method, 16 were detected (detection levels of 0.6–3.1 μg/kg; SI Table S1). Of these 16 compounds, six were detected in 10% or more samples and three were detected in 25% or more samples; namely, the chloroacetanilide herbicide metalochlor (50%), the pyrethroid insecticide bifenthrin (45%), and the organochlorine pesticide degradate p,p′-DDE (29%) (Table S1 of Kemble et al. (2016). Metolachlor concentrations were significantly higher at the agricultural sites than at the urban sites, whereas bifenthrin and p,p′-DDE concentrations were significantly higher at the urban sites (Mann-Whitney *U* Test; $p < 0.05$). Within the class of current use pesticides, the single compound bifenthrin explained the majority (76% on average where CUPs were found) and nearly all (96%) at sites where it was detected, of the overall LEB quotient.

Of the 37 trace elements measured in sediments at all sites, seven have reliable PEC benchmarks available to evaluate for their potential effects on aquatic biota. Concentrations of these seven elements were generally low relative to PEC benchmarks. In only 12 of 686 cases (7 elements across 98 sites) the concentration exceeded one-half of the PEC value. When normalized to OC content, there were 27 cases of exceeding one-half the trace element PECs. Concentrations of four of the seven elements (Cd, Cu, Pb, and Zn) were significantly greater at the 12 urban sites than at the 87 agricultural gradient sites (Mann-Whitney *U* Test; $p < 0.05$).

PAHs were detected more frequently and at much higher concentrations at the 12 urban sites than at the 15 agricultural gradient sites. Mean detection frequency for the 16 USEPA Priority Pollutant PAHs, for example, was 95% for the urban sites and was 30% for the agricultural gradient sites (see Table S1 of Kemble et al. (2016)). At the urban sites, total PAHs ranged from 0.02–1.1 μg/kg sediment, and from 0.007—0.27 (median = 0.08) for OC-normalized total PAH concentrations. In contrast, OC-normalized PECQ for the 15 agricultural gradient sites ranged from zero to 0.003 (median = 0.0013), about 65 times lower than the median at the urban sites. Total PAH concentrations and OC-normalized PEC-Quotients were significantly higher at the urban sites than at the agricultural sites (Mann-Whitney U; $p < 0.05$).

One or more PCB congeners (18 congeners measured) and one or more BDE congeners (9 congeners measured) were detected at 70 and 93% of the 27 sites measured, respectively. Mean concentrations of the sum of PCBs and sum of BDEs (non-detections treated as zeros) were about 90 and 5 times greater at the urban sites than at the agricultural sites, respectively. One or more chlordane compounds (*cis*-chlordane, *trans*-chlordane, *cis*-nonachlor and oxychlorodane) was detected at 85% of sites, and the mean total-chlordane concentration was almost 30-times greater at the urban sites than at the agricultural sites. Concentrations of total PCBs, BDEs, chlordanes, and DDTs were significantly greater at the 12 urban sites than at the 15 agricultural sites (Mann-Whitney *U* test; $p < 0.05$). As the maximum measured concentrations for total chlordanes, dieldrin, and total PCBs at the 27 sites equaled 58, 4 and 8% of their respective PEC benchmarks, for the purposes of calculating PEC quotients across all remaining 72 sites, which were all undeveloped or agricultural sites, the median value of each of these compounds (0.55, 0.41, and 1.1 μg/kg dw, respectively) was imputed at non-measured sites when generating the mixture score.

3.2. Mixture assessment

The potential toxicity contributed by each of five contaminant classes to the estimated combined sediment mixture toxicity, as represented by the PECLEB5 value, is shown in Fig. 1. In general, the PECLEB5 were low (median 0.26) and increased with increasing agricultural land use, primarily driven by increasing occurrence of current use pesticides. Urban sites have PECLEB5 magnitude among the highest of all sites and show a greater PAH contribution and a more variable trend with landuse. Fig. 1 indicates the relative importance of the detected compounds to each other in their likelihood to contribute to sediment toxicity.

3.3. Sediment toxicity tests

Three test endpoints for each species tested were evaluated: survival, growth- as indicated by the mean ash-free dry weight (AFDW) (or dry weight for *H. azteca)* of the surviving organisms, and biomass- as the weight of surviving organisms divided by the initial number of organisms. The latter two endpoints can be divergent if survival varies substantially, however, in this dataset survival rates were high and the measures of growth and biomass were strongly correlated. Thus, for interpretation, we focus on survival and biomass, which was the more sensitive of the two growth endpoints (see Table 1). Sediment toxicity test responses by site and species for all endpoints are available at SI Table S2, doi:10.5066/F7Z899HX.

The overall incidence of toxicity (as significantly reduced survival or biomass) was low, ranging from 4 to 7% of sites for the *H. azteca* and *C. dilutus* tests and from 8 to 33% of sites for the *L. siliquoides* test (Table 1). As the mussel testing was successfully completed at only 24 of the 99 sites, those data were not included in further evaluations. Because of the low incidence of toxicity for individual endpoints, a cumulative 'Percent toxic endpoints' value (Pct_Tox_Endpoints) was computed from the four arthropod test endpoints following the *H. azteca* and *C. dilutus* sediment toxicity testing. Spearman's rank correlations and scatterplots were used to evaluate the relations between selected contaminants and the toxicity test results.

A review of the contaminant classes and the contaminant benchmark quotients (see Fig. 1 and Table S1), suggested that four trace elements (As, Cd, Cr, Ni), bifenthrin, and the mixture score PECLEB5 warranted further evaluation for their potential to affect biota. The correlations of three toxicity endpoints (*C. dilutus* biomass, *H. azteca* biomass, Pct_Tox_Endpoints) are compared to concentrations of four metals, OC normalized bifenthrin concentration, and the PECLEB5 mixture score in Table 2. The strength of these correlations varies by contaminant and toxicity endpoint. *C. dilutus* biomass, for example, is significantly correlated (p-value < 0.05) to concentrations (not normalized to OC) of all four metals but not to bifenthrin or PECLEB5. *H. azteca* biomass, on the other hand, is significantly correlated to bifenthrin and PECLEB5 but not to any of the metals. None of the contaminants are significantly correlated with the aggregate Pct_Tox_Endpoints. Metolachlor was the most commonly detected organic contaminant, found at 51% of sites, but as the concentrations never exceed one-hundredth of its freshwater LEB of 200 μg/g OC (Nowell et al., 2016) and showed poor relations to toxicity endpoints, it was not considered further.

We performed additional analyses with the four metals, bifenthrin and the PECLEB5 mixture score. These stressor metrics were related to toxicity test results using ordinary least squares (OLS) and quantile regression. OLS was selected for its general familiarity and quantile regression for its appropriateness given the wedge-shaped response pattern and presence of outliers in the MSQA data; see Fig. 2 for examples. Comparison of *C. dilutus* biomass to the PECLEB5 score was not significant using either OLS or quantile regression at the 90th quantile, consistent with the low rank correlations between these (see Table 2). However, *C. dilutus* biomass had a significant inverse trend with the 90th quantile of the bifenthrin quotient. For the amphipod, *H. azteca*, the relations between biomass and both bifenthrin and the PECLEB5 score using OLS were strongly significant, $p < 0.01$, and the 90th quantile regression was significant for bifenthrin but only suggestive for PECLEB5 (Fig. 2). Reanalysis with removal of outliers in concentration or sites where bifenthrin was not detected, not shown, both tended to increase the overall significance of the regression estimates. The four metals that correlated significantly to *C. dilutus* toxicity endpoints

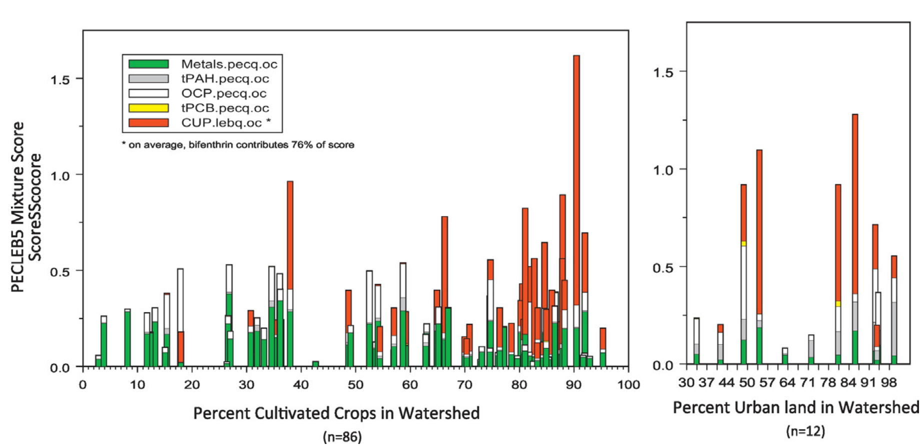


Fig. 1. Potential mixture toxicity score, PECLEB5, measured in stream sediments plotted by percent dominant landuse in the watershed for 98 study sites; agricultural and urban sites shown separately. (Abbrviations include; metals, as As, Cd, Cr, Cu, Ni, Pb, Zn; tPAH, total polyaromatric hydrocarbons; OCP, organochlorine pesticides; tPCB, total polychlorinated biphenyls; CUP, current use pesticides; PECQ, probable effect concentration quotient (MacDonald and Ingersoll, 2000); LEBQ, likely effects benchmark quotient (Nowell et al., 2016), PECLEB5, combined PEC and CUP LEB quotient.

Table 1
Summary of sediment toxicity test responses by species endpoint.

	Number of sites tested	Percent of sites with endpoint significantly reduced from control	Percent of sites with any endpoint significantly reduced
H. azteca enpoints			
Survival (%)	98	5%	
Dry weight (g)	98	4	8%
Biomass (g)	98	5	
C. dilutus endpoints			
Survival (%)	98	6	
AFDW dry weight (g)	98	4	13
Biomass (g)	98	7	
L. siliquoides endpoints			
Survival (%)	24	8	
AFDW dry weight (g)	24	33	42
Biomass (g)	24	8	
		All endpoints/all sites significantly reduced	24

(Table 2) were compared in a similar way to *H. azteca* biomass responses also using OLS and the 90th quantile; few showed an inverse relationship to biomass and none were significant ($p = 0.05$).

3.4. Relationships to macroinvertebrates

3.4.1. Univariate

The instream macroinvertebrate sampling resulted identified between 9 and 69 unique taxon per site, as described by Waite and Van Metre (in review). Quantile regression was used to evaluate several common univariate metrics of the invertebrate community in relation to the contaminants implicated from the correlation analysis (As, Cr, Cd, Ni, Bifenthrin) and the PECLEB5 mixture score. There were consistent and significant decreasing trends of the 75th percentile (and often of the 90th percentile) of benthic macroinvertebrate metric scores (EPT percentage, MMI scores, Ephemeroptera richness, Trichoptera richness) in response to increasing PECLEB5 and the bifenthrin LEBQ, (see Fig. 3, not all relations shown). Similarly, increasing toxicity, as indicated by the Perc_Tox_Endpoints, was significantly related to a decrease in the upper quartile of several invertebrate metrics, and illustrated with the relation of MMI score to Pct_Tox_Endpoints in Fig. 3f. There were no significant relations between the metals and any of the benthic macroinvertebrate metrics (as $p < 0.05$).

3.4.2. Multivariate analysis

Although univarite metrics can be useful and are commonly presented, they force ecological communities into one-dimensional scores that cannot fully represent the diversity of species, and therefore, the breadth of responses occurring in a given community (McCune and Grace, 2002). An alternate approach is to use multivariate ordination techniques to summarize the highly dimensional species matrix, in this case 274 unique taxa identified across 99 sites, in a reduced 2-dimensional space convenient for visualization purposes. The method uses a rank-order approach in summarizing multivariate relationships into two-dimensional plots. The relative location of the points reflects the similarity or dissimilarity of the species collected at the various sites.

Three questions were tested with the multivariate ordination of the macroinvertebrate species matrix using the Mantel-like test from the BEST procedure followed by permutation testing for significance (see 2.4 Statistical Methods above). First, we asked if there is a statistically significant relation between the reduced contaminant matrix (As, Cd, Cr, Ni, bifenthrin, and PECLEB5) and the macroinvertebrate species matrix across all sites? The answer was yes, but contaminants explain little of the overall variability (Global correlation coefficient (Rho) = 0.104; significance equivalence = 1% (as likely to occur from random permutations (analogous to a p-value of 0.01)). This indicates that the pattern between sediment contaminants and the species found at a site are unlikely to have occurred by chance, but that contaminants are only poorly related to species abundance. Further the test indicates that the first and second most important variables in this relation were bifenthrin and PECLEB5. An MDS ordination plot of macroinvertebrate communities, later overlain with two factors (the PECLEB5 score and Pct_Tox_Endpoints) is shown in Fig. 4.

Second, we asked if there is a relation between the toxicity testing results and the species collected at a site. Or more specifically, is a statistically significant relation between the measured toxicity pattern (using the three endpoints of *C. dilutus* biomass, *H. azteca* biomass, and Pct_Tox_Endpoints) and the species matrix across all sites? Similar to the first question, the answer was yes, the relationship is unlikely to be observed by chance (significance equivalence = 1%), but the toxicity pattern explains little of the overall variability (Rho = 0.181) in the species matrix. The test indicated that the only significant explanatory toxicity metric was the aggregate measure, Pct_Tox_Endpoints. This also indicates that evaluating the results of multiple toxicity endpoints provided better relations than either single-species endpoint considered in relation to the community data.

Third, we asked how do the strength of the relations identified in the first two questions compare with relations to other factors commonly reported to influence community structure, such as habitat and watershed land use? GIS variables explained a similar amount of the variability in macroinvertebrate species composition as did the contaminant and toxicity measures (Rho = 0.144), although with lower statistical significance; significance equivalence = 13% as likely to be observed by chance. Here, the first and second most important variables were percent Developed Land-High category (Homer et al., 2015) and percent Mixed Forest (Homer et al., 2015). Similar results were found when these three questions were repeated considering the species matrix on a presence/absence basis instead of an abundance basis.

These tests indicate that sites with higher contaminant and toxicity measures tend to have relatively similar species composition, and sites with little indication of contamination are most different, and- from review of the species matrix- more diverse, than the more contaminated sites. Sites with higher PECLEB5 scores and Pct_Tox_Endpoints tend to group in the center and lower left, whereas sites with low PECLEB5 scores and no measured toxicity are distributed widely across the fringes of the plotting space, see Fig. 4.

Table 2
Spearman's rank correlation coefficients between measured contaminants in stream sediments three sediment toxicity test endpoints. (Significant relations ($p < 0.05$) are indicted in bold font).

	Contaminants in sediments from 98 Midwest streams					
Toxicity test endpoints	As	Cr	Cd	Ni	Bifenthrin_LEB	PECLEB5
H. azteca biomass	−0.05	−0.06	<0.01	−0.03	**−0.35**	**−0.35**
C. dilutus biomass	**−0.21**	**−0.24**	**−0.20**	**−0.25**	−0.16	−0.19
Percent of four test endpoints reduced	<0.01	0.15	0.12	0.07	0.12	0.11

4. Discussion

The occurrence of contaminants in sediment was correlated with land use in the watershed. Urban streams had significantly higher levels of four of seven metals evaluated (Cd, Cu, Pb, and Zn), PAHs, PCBs, BDEs, chlordanes, DDTs, and bifenthrin, than did agricultural streams. A positive relation between urbanization and pyrethorids, and bifenthrin in particular, is consistent with conclusions reached in previous studies of freshwater stream sediments (Amweg et al., 2005, 2006; Schafer et al., 2011; Jorgenson et al., 2013; Nowell et al., 2013; Carpenter et al., 2016; Li et al., 2016). However, there was no significant difference in the incidence of toxicity between urban and agricultural sites in this study.

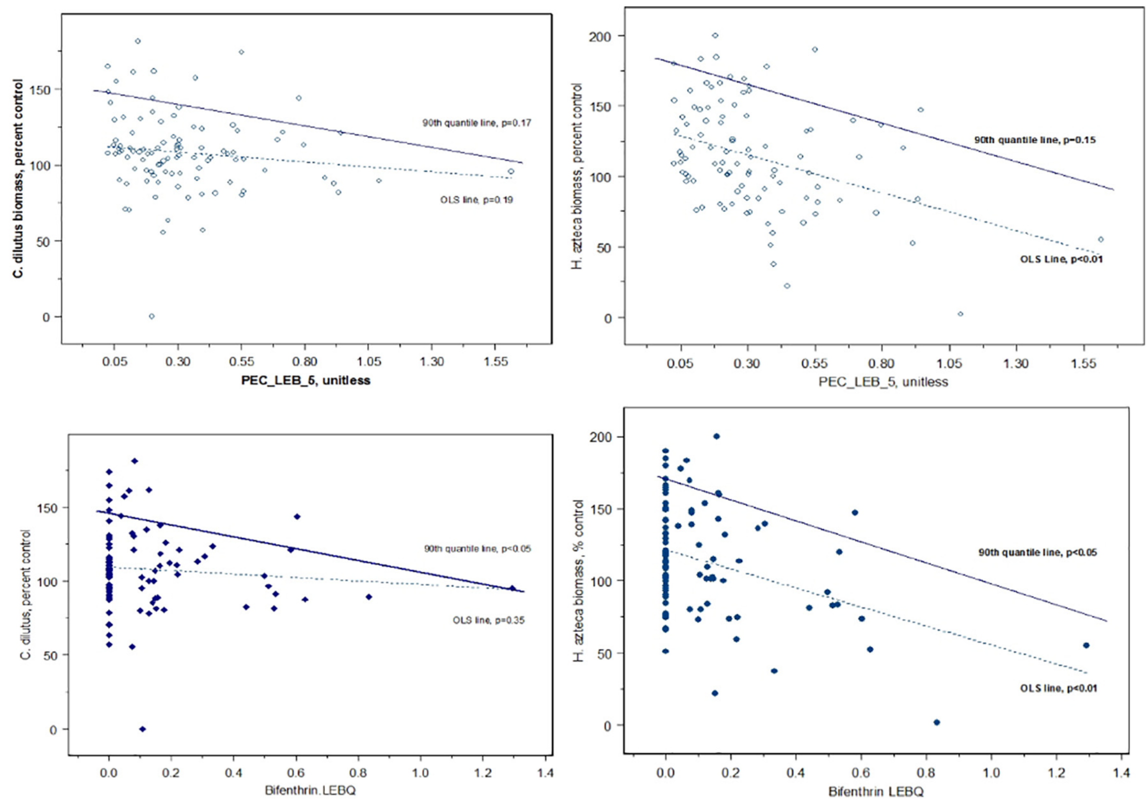


Fig. 2. Scatterplots of *C. diluts* and *H. azteca* biomass and the PECLEB5 score and bifenthrin LEBQ quotient. (Open symbols indicate PECLEB5 score; filled circles indicate bifenthrin LEBQ quotient; least squares line, dotted; quantile regression line of the 90th quantile, solid. Significance indicated by p-value. Software R, ver. 3.1.1 with methods of Koenker (2015 and therein); standard error estimate use of Hall-Sheather bandwidth rule).

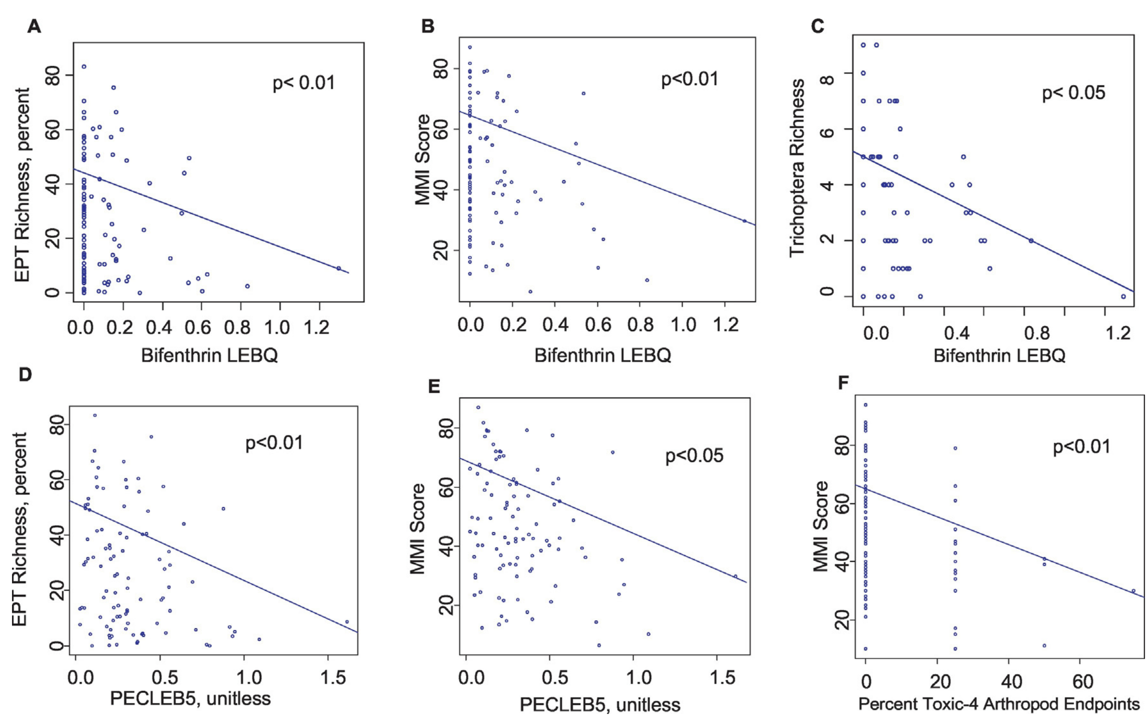


Fig. 3. Quantile Regression of the 75th percentile of stream invertebrate metrics relative to sediment measures of mixture chemistry, bifenthrin, and toxicity measures at all sites. (Software R, ver. 3.1.1 with methods of Koenker (2015); standard error estimate uses Huber local sandwich estimate. EPT-Ephemeroptera, Plecoptera, Trichoptera, MMI-Multi-metric index of macroinvertebrates, Trichr Rich-Tricoptera Richness, EPEM Rich-Emphemeroptera richness, LEBQ, likely effects benchmark quotient (Nowell et al., 2016), PEC, probable effect concentration (MacDonald and Ingersoll, 2000).

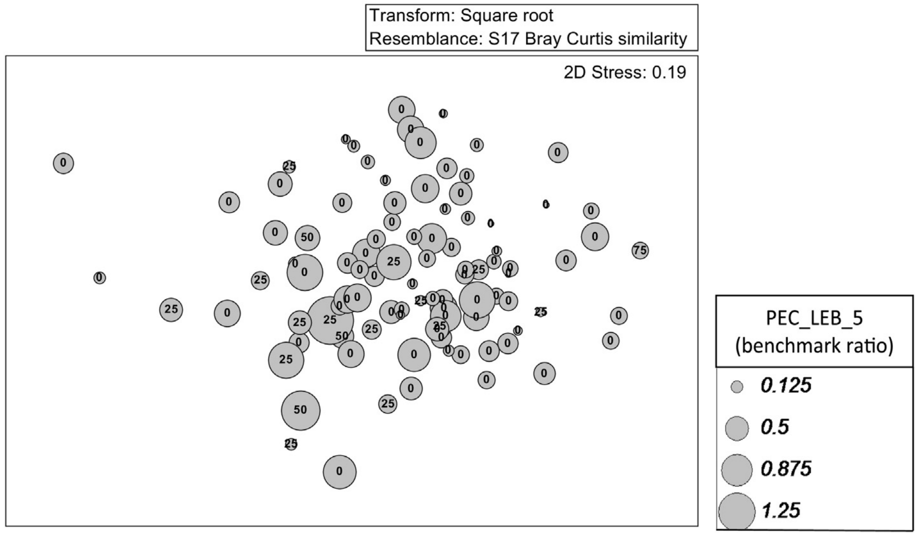


Fig. 4. Multidimensional scaling ordination plot of macroinvertbrate communities across 96 Midwestern sites with two overlays. (Circles indicate scale of PECLEB5 value; numbers indicate Per_Tox_Endpoints (percent of four sediment toxicity test endpoints reduced) from lab testing of stream sediments co-collected with macroinvertebrates; species matrix transformed with square root transformation and Bray-Curtis distance measure.)

Although pesticides are extensively used in this region (Baker and Stone, 2014), just 9 and 11 sites (about 10% of sites overall) had reduced survival or biomass for a test organisms. This is consistent with the relatively low concentrations of most contaminants in relation to their effects-based benchmarks for benthic invertebrates. The median PECLEB5 value across all sites was 26% of the mixture benchmark of 1, and the 90th percentile of the PECLEB5 scores was 65% of the benchmark. Most sites in the MSQA study were dominated by agricultural landuse where herbicides are reported to occur more frequently and at higher concentrations, whereas insecticides tend to occur more frequently and at higher concentrations in urban watersheds (e.g., Gilliom et al., 2006).

We originally hypothesized that the sum of the small fractions of each current use pesticide benchmark quotient (as a summed LEB_{int} quotient) as presented by Nowell et al. (2016) for the pesticides evaluated here, might be a useful descriptor of observed toxicity. However, analysis of the sum CUP $LEBQ_{15}$ score relative to the toxicity endpoints was infrequently significant ($p < 0.05$), and of limited utility in this dataset. The lower predictive capability of the sum $LEBQ_{15}$ in this dataset appears a result of the abundance of herbicides present that contributed small and variable contributions to the overall LEBQ. As invertebrate benchmarks for herbicides are orders of magnitude higher and usually more variable than those of insecticides (as assessment of non-target modes of action are inherently less predictable (Borgert et al., 2004), and for herbicides in particular (Cedergreen and Streibig, 2005)), this may result in less observed toxicity to aquatic invertebrates in agricultural areas than expected from the pesticide quotient. Also, while less transient than water, it is expected that fine grain sediments are subject to constant erosion and deposition and therefore the exposure profile organisms experience from stream sediments will be a balance between delivery, erosion, availability, and the sum of transformation processes. Indeed, the presence and severity of fine sediment itself has long been recognized as an ecological stressor, and for these sites is evaluated specifically under separate studies by Gellis et al. (2016) and Waite (in review).

For the toxicity measures, the Per_Tox_Endpoints from sediment toxicity tests were significantly related to declines in the invertebrate community composition. That these relations are not very strong is perhaps to be expected, as there are many other drivers and stressors affecting ecological communities. Quantile regression is one analysis approach that addresses the limiting effect of one variable in the presence of many other influential factors. As shown on Figs. 2 and 3, there are significant but weak relations between toxicity and contaminants (Fig. 2) and between toxicity, contaminants, and invertebrate community metrics (Fig. 3). This supports that notion that sediment toxicity observed in the lab from field collected sediments, as assessed through the contaminant mixture (as PECLEB5) score, maybe be limiting community structure of macroinvertebrates at those locations through similar stressors, see Fig. 4.

Bifenthrin (either as concentration or normalized to carbon via the LEB quotient) and the PECLEB5 score (of which bifenthrin is key contributor), were significantly related to declines in invertebrate community composition. Bifenthrin was the second most commonly detected pesticide in sediment, found at 45% of sites, and was the contaminant most likely to be found at or above its respective benchmark. On a regional (i.e. multi-state) scale, estimated bifenthrin use in the Midwest is some of the highest on agricultural lands in the conterminous United States (Baker, 2017). On average, bifenthrin accounted for 76% of the potential risk to aquatic invertebrates from the current use pesticide class evaluated in this study. Regression and quantile regression indicated that the bifenthrin concentration in sediment, on either a dry weight basis or carbon-normalized LEBQ basis, was the best predictor of the observed toxicity response of any of the contaminants evaluated in this study. The importance of considering bifenthrin as a stressor of stream communities was also recently reported on the basis of a mesocosm study. Rogers et al. (2016), tested the effects of bifenthrin-spiked sediment on invertebrate communities in flowing mesocosm "streams" and observed a clear dose response at levels of bifenthrin measured in some MSQA stream sediments. They compared the response in the mesocosms to data from MSQA streams and found them to be consistent in terms of bifenthrin concentrations and reduction in selected invertebrate metrics and taxa (e.g., abundance of scrapers and sensitive mayflies).

5. Conclusion

A feature of the MSQA is the overlap of chemistry, laboratory toxicity, and ecological community data at almost 100 sites across a broad region. Significantly higher concentrations of most sediment contaminants were found in streams with higher urban landuse than in agricultural dominated watersheds. Significant, albeit weak, relations were found between the instream community composition and contaminant and toxicity metrics. Correlation and quantile regression analysis indicated that bifenthrin was the best predictor of *H. Azteca* biomass response.

However, while a key contributor to the PEC mixture score and a significant predictor of biomass, bifenthrin was a less important factor at explaining the invertebrate community pattern in a multivariate approach than the PECLEB5 score was, which was significantly related to the overall invertebrate community. A consistent, significant decline in the 75th quantile of several common invertebrate community metrics with an increase in bifenthrin was also observed. As has been previously documented in stream sediments of California (Weston et al., 2004; Amweg et al., 2005, 2006), China (Mehler et al., 2011) and Oregon (Carpenter et al., 2016), multiple lines of evidence presented herein indicate that bifenthrin is likely limiting macroinvertebrate community structure in Midwestern streams. Given the often variable and typically low detection frequencies of pesticides, it is useful they be evaluated on both an individual chemical and mixture basis.

Disclosure statement

None of the authors have any actual or potential conflict of interest including any financial, personal or other relationships with other people or organizations within three years of beginning the submitted work that could inappropriately influence, or be perceived to influence, their work.

Acknowledgements

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. Funding for this work came from the U.S. Geological Survey's National Water Quality Assessment Program and Contaminant Biology Program. The dutiful and demanding field contributions from the USGS Water Sciences, led by Jeff Frey in the Indiana-Kentucky USGS Water Science center, is greatly appreciated. We thank Michelle Hladik and the USGS California Pesticide lab for analytical support, excellent data quality, and continued advisement on many topics related to pesticides in sediments. We thank Dan Button for excellent data management and quality assurance oversight. We thank Chris Ingersoll, John Besser and several members of the USGS Columbia Environmental Research Center, Fish and Invertebrate Toxicology branch for conducting the toxicity testing and their advisement. We thank the colleague and peer reviewers who provided valuable suggestions towards the improvement of this manuscript.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.scitotenv.2017.05.035. These data include the Google map of the 99 study sites described in this article.

References

American Society for Testing and Materials International, 2012. Standard test method for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates (E1706-05 (2010)). Annual Book of ASTM Standards Volume 11.06 (West Conshohocken, PA).

Amweg, E.L., Weston, D.P., Ureda, N.M., 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, California, USA. Environ. Toxicol. Chem. 24 (4), 966–972.

Amweg, E.L., Weston, D.P., You, J., Lydy, M.J., 2006. Pyrethroid insecticides and sediment toxicity in urban creeks from California and Tennessee. Environ. Sci. Technol. 40, 1700–1706.

Ankley, G.T., Katko, A., Arthur, J.W., 1990. Identification of ammonia as an important sediment-associated toxicant in the lower Fox River and Green Bay, Wisconsin. Environ. Toxicol. Chem. 9, 313–322.

Baker, N.T., Stone, W.W., 2014. Annual Agricultural Pesticide Use for Midwest Stream-quality Assessment, 2012–2013. U.S. Geological Survey Data Series 863 (Doi: 10.3133/ds863).

Baker, N.T., 2017. Estimated Annual Agricultural Pesticide Use by Crop Group for States of the Conterminous United States, 1992–2014 (USGS Data Release. Doi: 10.5066/F7NP22KM).

Besser, J.M., Brumbaugh, W.G., Ingersoll, C.G., 2015a. Characterizing toxicity of metal-contaminated sediments from mining areas. Appl. Geochem. 57 (01), 73–84.

Besser, J.M., Ingersoll, C.G., Brumbaugh, W.G., Kemble, N.E., May, T.W., Wang, N., et al., 2015b. Toxicity of sediments from lead-zinc mining areas to juvenile freshwater mussels (*Lampsilis siliquoidea*) compared to standard test organisms. Environ. Toxicol. Chem. 34, 626–639.

Briggs, P., Meier, A.L., 2002. The determination of forty-two elements in geological materials by inductively-coupled plasma-mass spectrometry for NAWQA. In: JEJ, Taggart (Ed.), Analytical Methods for Chemical Analysis of Geologic and Other Materials, pp. 2002–2223 U.S. Geological Survey Open-File Report. (Denver, CO; 16p).

Borgert, C.J., Quill, T.F., McCarty, L.S., Mason, A.M., 2004. Can mode of action predict mixture toxicity for risk assessment? Toxicol. Appl. Pharmacol. 201, 85–96.

Cade, B.S., Noon, B.R., 2003. A gentle introduction to quantile regression for ecologists. Front. Ecol. Environ. 1 (8) (412–320).

Canfield, T.J., Kemble, N.E., Brumbaugh, W.G., Dwyer, F.J., Ingersoll, C.G., Fairchild, J.F., 1994. Use of benthic invertebrate community structure and the sediment quality triad to evaluate metal-contaminated sediment in the upper Clark Fork River, Montana. Environ. Toxicol. Chem. 13 (12), 1999–2012.

Cao, Y., Hawkins, C.P., 2011. The comparability of bioassessments: a review of conceptual and methodological issues. J. North Amer. Benthol. Soc. 30 (3), 680–701.

Carpenter, K.D., Kuivila, K.M., Hladik, M.L., Haluska, T., Cole, M.B., 2016. Storm-event-transport of urban-use pesticides to streams likely impairs invertebrate assemblages. Environ. Monit. Assess. 188, 345.

Chapman, P.M., 1990. The sediment quality triad approach to determining pollution-induced degradation. Sci. Total Environ. 97, 815–835.

Cedergreen, N., Streibig, J.C., 2005. The toxicity of herbicides to non-target aquatic plants and algae: assessment of predictive factors and hazard. Pest Manag. Sci. 61 (12), 1152–1160.

Coles, J.F., McMahon, G., Bell, A.H., Brown, L.R., Fitzpatrick, F.A., Scudder-Eikenberry, B.A., et al., 2012. Effects of Urban Development on Stream Ecosystems in Nine Metropolitan Study Areas Across the United States: U.S. Geological Survey Circular 1373. 138 p. http://pubs.usgs.gov/circ/1373/.

Cox, O.N., Clements, W.H., 2013. An integrated assessment of polycyclic aromatic hydrocarbons (PAHs) and benthic macroinvertebrate communities in Isle Royale National Park. J. Great Lakes Res. 39 (1), 74–82.

Cuffney, T.F., 2003. User's Manual for the National Water-Quality Assessment Program Invertebrate Data Analysis System (IDAS) software: Version 3. U.S. Geological Survey Open-File Report 03–172, Raleigh, North Carolina. At URL:. ftp://ftpext.usgs.gov/pub/er/nc/raleigh/tfc/IDAS/ (Accessed February 14, 2014).

Gellis, A.C., Fuller, C.C., Van Metre, P.C., 2016. Sources and ages of fine-grained sediment to streams using fallout radionuclides in the Midwestern United States. J. Environ. Manag. 194 (1), 73–85.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, et al., 2006. The Quality of Our Nation's Waters - Pesticides in the Nation's Streams and Ground Water, 1992–2001: U.S. Geological Survey Circular 1291 (172p).

Gosz, J.R., 1992. Gradient analysis of ecological change in time and space: implications for forest management. Ecol. Appl. 2 (3), 248–261.

Hladik, M.L., McWayne, M.M., 2012. Methods of Analysis—Determination of Pesticides in Sediment Using Gas Chromatography/Mass Spectrometry, U.S. Geological Survey Techniques and Methods (Book 5, Chapter 3, 18p).

Homer, C.G., Dewitz, J.A., Yang, L., Jin, S., Danielson, P., Xian, G., et al., 2015. Completion of the 2011 National Land Cover Database for the conterminous United States-representing a decade of land cover change information. Photogramm. Eng. Remote. Sens. 81 (5), 345–354.

Ingersoll, C.G., Kemble, N.E., Kunz, J.L., Brumbaugh, W.G., MacDonald, D.D., Smorong, D., 2009. Toxicitye of sediment cores collected from the Ashtabula River in northeastern Ohio USA to the amphipod *Hyalella azteca*. Arch. Environ. Contam. Toxicol. 57 (315–329), 826–827 ([erratum]).

Ingersoll, C.G., MacDonald, D.D., Brumbaugh, W.G., Johnson, B.T., Kemble, N.E., Kunz, J.L., et al., 2002. Toxicity assessment of sediments from the Gand Calumet river and Indiana Harbor canal in northwestern Indiana, USA. Arch. Environ. Contam. Toxicol. 2002 (43), 156.

Ingersoll, C.G., MacDonald, D., Wang, N., Crane, J.L., Field, L.J., Haverland, P.S., et al., 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Arch. Environ. Contam. Toxicol. 2001 (41), 8.

Jorgenson, B., Fleishman, E., Macneale, K.H., Schlenk, D., Scholz, N.L., Spromberg, J.A., et al., 2013. Predicted transport of pyrehtorid insecticides from and urban landscape to surface water. Environ. Toxicol. Chem. 32 (11) (pp 2569–2477).

Kemble, N.E., Hladik, M.L., Moran, P.W., Ingersoll, C.G., Nowell, L.H., Mahler, B.J., 2013. Sediment Chemistry and Sediment Toxicity in Wadable Streams Across the Midwestern United States. U.S. Geological Survey data release http://dx.doi.org/10.5066/F7Z899HX.

Khim, J.S., Hong, S., 2014. Assessment of trace pollutants in Korean coastal sediments using the triad approach: a review. Sci. Total Environ. 470, 1450–1462.

Kinsman-Costello, L.E., O'Brien, J.M., Hamilton, S.K., 2015. Natural stressors in uncontaminated sediments of shallow freshwaters: the prevalence of sulfide, ammonia, and reduced iron. Environ. Toxicol. Chem. 34 (3), 467–479.

Koenker, R., 2015. Quantile Regression in R: Vignette. http://cran.us.r-project.org/.

Kuivila, K.M., Hladik, M.L., Ingersoll, C.G., Kemble, N.E., Moran, P.W., Calhoun, D.L., et al., 2012. Occurrence and potential sources of pyrethroid insecticides in stream sediments from seven U.S. metropolitan areas. Environ. Sci. Technol. 46 (8), 4297–4303.

Li, H., Cheng, F., Wei, Y., Lydy, M.J., You, J., 2016. Global occurrence of pyrethroid insecticides in sediment and the associated toxicological effects on benthic invertebrates: an overview. J. Hazard. Mater. 324b, 258–271.

Long, E.R., Ingersoll, C.G., MacDonald, D.D., 2006. Calculation and uses of mean sediment quality guideline quotients: a critical review. Environ. Sci. Technol. 40 (6), 1726–1736.

Lopes, T.J., Furlong, E.T., 2001. Occurrence and potential adverse effects of seimivolatile organic compounds in streambed sediments, United States, 1992–1995. Environ. Toxicol. Chem. 20 (4), 727–737.

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

Mahler, B.J., Van Metre, P.C., WIlson, J.T., Musgrove, M., Zaugg, S.D., Burkhardt, M.R., 2009. Fipronil and its degradates in indoor and outdoor dust. Environ. Sci. Technol. 43 (15), 5665–5670.
McCune, B., Grace, J.B., 2002. Analysis of Ecological Communities. MJM Software Design, Gleneaden Beach, OR (300p).
Mehler, W.T., Li, H., Lydy, M.J., You, J., 2011. Identifying the causes of sediment-associated toxicity in urban waterways of the Pearl River Delta, China. Environ. Sci. Technol. 45, 1812–1819.
Moulton II, S.R., Carter, J.L., Grotheer, S.A., Cuffney, T.F., Short, T.M., 2000. Methods of Analysis by the U.S. Geological Survey National Water Quality Laboratory – Processing, Taxonomy, and Quality Control of Benthic Macroinvertebrate Samples (U.S. Geological Survey Open-File Report 00-212, 49 p).
Nowell, L.H., Moran, P.W., Gilliom, R.J., Calhoun, D.L., Ingersoll, C.G., Kemble, et al., 2013. Contaminants in stream sediments from seven U.S. metropolitan areas—I. Distribution in relation to urbanization. Arch. Environ. Contam. Toxicol. 64, 32–51.
Nowell, L.H., Norman, J.E., Ingersoll, C.G., Moran, P.W., 2016. Development and application of freshwater sediment-toxicity benchmarks for currenly used pesticides. Sci. Total Environ. 550, 835–850.
Olsen, A.R., Sedransk, J., Edwards, D., Gotway, C.A., Liggett, W., Rathbun, S., 1999. Statistical issues for monitoring ecological and natural resources in the United States. Environ. Monit. Assess. 54, 1–45.
Rogers, H.A., Schmidt, T.S., Dabney, B., Hladik, M.L., Mahler, B.J., Van Metre, P.C., 2016. Bifenthrin causes trophic cascade and altered insect emergence in mesocosms: implications for small stream. Environ. Sci. Technol. 50 (21), 11974–11983.
Schafer, R.B., Caquet, T., Siimes, K., Mueller, R., Lagadic, L., Liess, M., 2007. Effects of pesticides on community structure and ecosystem functions in agricultural streams of three biogeographical regions in Europe. Sci. Total Environ. 382, 272–285.
Schafer, R.B., Pettigrove, V., Rose, G., Allison, G., Wightwick, A., von der Ohe, P.C., 2011. Effects of pesticides monitored with three sampling methods in 24 sites on macroinvertebrates and microorganisms. Environ. Sci. Technol. 45, 1665–1672.
Scoggins, M., McClintock, N.L., Gosselink, L., 2007. Occurrence of polycyclic aromatic hydrocarbons below coal-tar-sealed parking lots and effects of stream benthic macroinvertebrate communities. J. N. Amer. Benthol. Soc. 26 (4), 694–707.
Shelton, L.R., Capel, P.D., 1994. Guidelines for Collecting and Processing Samples of Stream Bed Sediment for Analysis of Trace Elements and Organic Contaminants for the National Water-quality Assessment Program (U.S. Geological Survey Open-File Report 94-458, 20 p).
Stoddard, J.L., Herlihy, A.T., Peck, D.V., Hughes, R.M., Whittier, T.R., Tarquinio, E., 2008. A process for creating multimetric indices for large-scale aquatic surveys. J. North Amer. Benth. Soc. 27, 878–891.
U.S. Environmental Protection Agency, 2000. Methods for Measuring the Toxicity and Bioaccumulation of Sediment-associated Contaminants With Freshwater Invertebrates. second ed. (EPA/600/R-99/064, Washington, DC.
U.S. Environmental Protection Agency, 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. Office of Research and Development (EPA/600/R-02/013).
U.S. Environmental Protection Agency, 2005. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc.). Office of Research and Development (EPA/600/R-02/011).
U.S. Environmental Protection Agency, 2013a. National Rivers and Stream Assessment 2013–2014, Field Operations Manual Wadeable, Version 1.0. United States Environmental Protection Agency, Office of Water, Office of Environmental Information, Washington, DC (EPA-841-B-12-009b).
U.S. Environmental Protection Agency, 2013b. National Rivers and Stream Assessment 2008–2009: Technical Report. Draft. U.S. Environmental Protection Agency, Office of Wetlands, Oceans and Watersheds and Office of Research and Development, Washington, DC.
U.S. Geological Survey, 2015. BioData - Aquatic Bioassessment Data for the Nation available on the World Wide Web. (accessed 3/03/2015, at URL http://dx.doi.org/doi:10.5066/F77W698B).
Waite, I.R., Van Metre, P.C., 2016. Multi-stressor predictive models of invertebrate condition in the Corn Belt. Submitted to Freshwater Science (in review).
Wagner, R.J., Moran, P.W., Zaugg, S.D., Sevigny, J.M., Pope, J.M., 2014. Contaminants of emerging concern in the lower Stillaguamish River Basin, Washington, 2008–11 (Ver. 2.0, June 2016). U.S. Geol. Surv. Open File Rep. 2014–1028 (14 p).
Wang, N., Augspurger, T., Barnhart, M.C., Bidwell, J.R., Cope, W.G., Dwyer, F.J., et al., 2007. Intra- and interlaboratory variability in acute toxicity tests with glochidia and juveniles of freshwater mussels (Unionidae). Environ. Toxicol. Chem. 26 (10), 2029–2035.
Weston, D.P., Holmes, R.W., You, J., Lydy, M.J., 2005. Aquatic toxicity due to residential use of pyrethroid insecticides. Environ. Sci. Technol. 39 (24), 9778–9784.
Weston, D.P., You, J., Lydy, M.J., 2004. Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodes of California's Central Valley. Environ. Sci. Technol. 38, 2752–2759.
Winger, P.V., Lasier, P.J., Bogenrieder, K.J., 2005. Combined use of rapid bioassessment protocols and sediment quality triad to assess steram quality. Environ. Monit. Assess. 100, 267–295.
Zaugg, S.D., Burkhardt, M.R., Burbank, T.L., Olsen, M.C., Iverson, J.L., Schroeder, M.P., 2006. Determination of semivolatile organic compounds and polycyclic aromatic hydrocarbons in solids by gas chromatography/mass spectrometry. U.S. Geological Survey Techniques and Methods (book 5, chap. B3, 44p).