2020

Daily Stream Samples Reveal Highly Complex Pesticide Occurrence and Potential Toxicity to Aquatic Life

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Citation Details

Norman, J. E., Mahler, B. J., Nowell, L. H., Van Metre, P. C., Sandstrom, M. W., Corbin, M. A., ... & Asher, W. E. (2020). Daily stream samples reveal highly complex pesticide occurrence and potential toxicity to aquatic life. Science of The Total Environment, 715, 136795.

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Science of the Total Environment 715 (2020) 136795

Contents lists available at ScienceDirect

Science of the Total Environment

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

Daily stream samples reveal highly complex pesticide occurrence and potential toxicity to aquatic life

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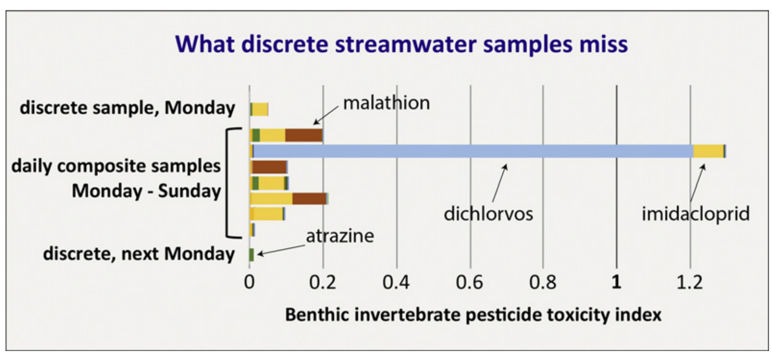
HIGHLIGHTS

- Daily composites contained twice as many pesticide compounds as weekly composites.
- Insecticides were frequently missed by weekly discrete and composite samples.
- 14 Sites: daily samples predicted acute toxicity at 11, weekly discrete samples at 0.
- Pesticide Toxicity Index was related to degraded invertebrate communities in streams.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 30 August 2019
Received in revised form 16 January 2020
Accepted 17 January 2020
Available online 18 January 2020

Editor: Yolanda Picó

Keywords:
Pesticides
Sampling frequency
Sampling method
Acute toxicity
EPT richness

ABSTRACT

Transient, acutely toxic concentrations of pesticides in streams can go undetected by fixed-interval sampling programs. Here we compare temporal patterns in occurrence of current-use pesticides in daily composite samples to those in weekly composite and weekly discrete samples of surface water from 14 small stream sites. Samples were collected over 10–14 weeks at 7 stream sites in each of the Midwestern and Southeastern United States. Samples were analyzed for over 200 pesticides and degradates by direct aqueous injection liquid chromatography with tandem mass spectrometry. Nearly 2 and 3 times as many unique pesticides were detected in daily samples as in weekly composite and weekly discrete samples, respectively. Based on exceedances of acute-invertebrate benchmarks (AIB) and(or) a Pesticide Toxicity Index (PTI) >1, potential acute-invertebrate toxicity was predicted at 11 of 14 sites from the results for daily composite samples, but was predicted for only 3 sites from weekly composites and for no sites from weekly discrete samples. Insecticides were responsible for most of the potential invertebrate toxicity, occurred transiently, and frequently were missed by the weekly discrete and composite samples. The number of days with benthic-invertebrate PTI ≥0.1 in daily composite samples was inversely related to Ephemeroptera, Plecoptera, and Trichoptera (EPT) richness at the sites. The results of

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https://doi.org/10.1016/j.scitotenv.2020.136795
0048-9697/Published by Elsevier B.V.

Pesticide Toxicity Index

the study indicate that short-term, potentially toxic peaks in pesticides frequently are missed by weekly discrete sampling, and that such peaks may contribute to degradation of invertebrate community condition in small streams. Weekly composite samples underestimated maximum concentrations and potential acute-invertebrate toxicity, but to a lesser degree than weekly discrete samples, and provided a reasonable approximation of the 90th percentile total concentrations of herbicides, insecticides, and fungicides, suggesting that weekly composite sampling may be a compromise between assessment needs and cost.

1. Introduction

Current-use pesticides are frequently detected in streams globally, often occur as complex mixtures, and can pose risks to aquatic life (Bereswill et al., 2013; Gilliom et al., 2006; Hageman et al., 2019; Hladik and Kolpin, 2016; Metcalfe et al., 2016; Nowell et al., 2018; Pérez et al., 2017; Stehle and Schulz, 2015; Stone et al., 2014). Short-term peaks in pesticide concentrations in streams can occur as a result of seasonal or event-driven pesticide applications (e.g., infestation or public-health hazard) and streamflow conditions (Liess et al., 1999; Rabiet et al., 2010). Transient high concentrations of pesticides can result in exposure of aquatic organisms to acutely toxic concentrations, but discrete samples are not well suited for assessing short-term peaks in pesticide concentrations (Spycher et al., 2018; Stehle et al., 2019), even with relatively high-frequency fixed-interval sampling such as weekly (Gilliom et al., 1995). States in the U.S. with active ambient pesticide monitoring programs, e.g., Minnesota (Minnesota_Dept_Agriculture, 2019), Washington (Washington_State_Dept_Agriculture, 2019), Illinois (Illinois_EPA, 2014), generally collect samples weekly or less frequently.

Typical fixed-interval sampling programs (e.g., bi-weekly, monthly) can result in a high percentage of non-detections for insecticides (Stehle et al., 2013), which generally are transient and can potentially strongly affect invertebrates in streams (Gilliom et al., 2006; Nowell et al., 2018; Stehle and Schulz, 2015). Stehle et al. (2013) further suggested that increasing the discrete sampling frequency during insecticide application periods would increase monitoring costs but may not improve results. Rather, these authors used exposure modeling to demonstrate that event-based sampling was better able to detect low-frequency/high-risk insecticide occurrence patterns. In a review of global agricultural insecticide occurrence in surface waters, Stehle and Schulz (2015) observed that insecticides were rarely detected, but when detected they often exceeded water-quality thresholds. Further, many of the sites evaluated by Stehle and Schulz had repeated pulses of short-term contamination or had complex mixtures of pesticides. A combination of time- and flow-proportional sampling may be a good compromise to capture occurrence of those pesticides that are introduced continuously, and those, such as insecticides, that occur in brief peak concentrations as a result of runoff or spray drift (Bundschuh et al., 2014). Autosamplers are one option that allows a targeted sampling frequency. Autosamplers commonly are used to collect either discrete or composite samples at regular time intervals or event-triggered samples in response to changes in stream stage or flow, and have been used to obtain samples that are representative of water quality over time (e.g., Madrid and Zayas, 2007; Spycher et al., 2018; Xing et al., 2013).

In 2013, the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Project initiated Regional Stream-Quality Assessments (RSQA) (https://webapps.usgs.gov/rsqa/#!/) to address the question of how chemical and physical stressors affect stream ecology in five regions of the United States. Each regional study characterized water-quality stressors—contaminants, nutrients, and sediment—and ecological conditions and habitat in 75 to 100 wadeable streams during the spring-summer growing season. The Midwest Stream-Quality Assessment (MSQA), in May–August of 2013, and the Southeast Stream-Quality Assessment (SESQA), in April–June of 2014, were the first two RSQA studies (Garrett et al., 2017; Journey et al., 2015). Pesticides were measured in MSQA (Nowell et al., 2018) and SESQA streams in discrete weekly water samples. In addition, the U.S. Environmental Protection Agency (EPA) collaborated with the USGS to assess daily pesticide occurrence in the RSQA studies using small-volume autosamplers deployed at a subset of seven sites in each region. Here we present an analysis of occurrence of 203 current-use pesticide compounds in daily and weekly composite water samples collected by the autosamplers in MSQA and SESQA in relation to occurrence measured by weekly discrete (manual) samples. The objectives of this study were 1) to compare pesticide occurrence as indicated by daily composite sampling to that indicated by weekly composite and weekly discrete sampling, and 2) to compare potential acute invertebrate toxicity, as evaluated by comparison to established toxicity benchmarks and thresholds, determined from daily composite samples to that determined from weekly composite and discrete samples. We hypothesize that pesticides occur more frequently and at higher concentrations—with greater potential acute invertebrate toxicity—in small streams than is revealed by weekly sampling.

2. Methods

2.1. Study design and sampling approach

The 14 sites for the intensive pesticide sampling were chosen from among the MSQA and SESQA study sites (100 and 77 sites, respectively) to represent land use within their respective regions. The 14 sites chosen are in relatively intensively developed watersheds to improve the chances of frequent pesticide detections and facilitate a more robust comparison of sampling methods. Logistical considerations also factored into selection as installation and operation were labor intensive.

The MSQA study area (Supporting information (SI) Appendix F, Fig. F.1) overlies the Midwestern U.S. agricultural region and is dominated by corn and soybean crops. The study area comprises parts of 12 states and 6 ecoregions, and contains several urban centers, including Chicago, Illinois (Garrett et al., 2017). The SESQA study area (SI Appendix F, Fig. F.2) represents the Piedmont Ecoregion in the Southeastern U.S. and comprises parts of five states and the District of Columbia. It contains several urban centers, including Charlotte, North Carolina, and Atlanta, Georgia. Land use is predominantly forest mixed with pasture/hay and urban land, with little row crop agriculture in the study area (Journey et al., 2015).

Autosamplers were deployed at sites on 5 agricultural streams (watershed area 72–580 km^2) and 2 urban streams (watershed areas 28–35 km^2) in the Midwest (Garrett et al., 2017) (SI Appendix F, Table F.1 and Fig. F.1). Because agriculture in the Piedmont ecoregion is largely pasture, autosamplers were deployed on 7 urban streams in the Southeast (watershed areas 15–125 km^2) (Journey et al., 2015) (SI Appendix F, Table F.1 and Fig. F.2). Samples were collected during May 6–August 9, 2013, in the Midwest (12 of 14 weeks) and during April 14–June 13, 2014, in the Southeast (10 weeks).

Details are supplied on the construction and operation of the autosamplers in SI Appendix A and on sample collection in SI Appendix B. In brief, autosamplers were designed to collect eight environmental samples each week—seven daily composite samples and one weekly composite sample—and one field spike sample, for which an ambient water sample was spiked at the start of the week and installed in the sampler to reside there for the duration of the sampling week. The samplers were operated at ambient environmental temperature and were enclosed in a watertight PVC housing and floated inside a vertical PVC pipe installed at a stream site. Daily composite samples consisted of 4 aliquots per day (collected every 6 h by the autosampler) of about 6.5 mL each; weekly composite samples consisted of 2 aliquots per day (collected every 12 h for 7 days) of about 1.8 mL each. Aliquots were delivered through a glass-fiber 0.7-μm, 25-mm syringe filter (Whatman) into a 40-mL vial containing 3 mL methanol solution, to act as a preservative (Aboulfadl et al., 2010). The number of successful daily and weekly composite samples collected at each of the 7 Midwestern sites ranged from 56 to 88 for daily samples, for a total of 513 daily samples, and from 1 to 7 for weekly samples for a total of 35 weekly samples. At the 7 Southeastern sites, 58 to 69 daily composites and 4 to 10 weekly composites were collected at each site, for a total of 463 daily samples and 58 weekly samples (SI Appendix F, Table F.2). Unsuccessful daily or weekly composite sampling sometimes occurred because of filter clogging or autosampler malfunction (e.g., loss of vacuum). Samples were shipped in a chilled container overnight to the USGS National Water Quality Laboratory (NWQL) (Denver, Colorado) where splits of weekly composite and spiked samples were taken (for Southeastern samples only) before shipping to the EPA Office of Pesticide Programs (OPP) Analytical Chemistry Laboratory (ACL) (Fort Meade, Maryland) for pesticide analysis. The splits were subsequently used for an interlaboratory comparison (SI Appendix C).

Weekly discrete water samples for pesticide analysis were collected during the study period using width-integrated methods (U.S. Geological Survey, 2006). Verticals were collected along a cross-section and combined in a methanol-rinsed Teflon churn-splitter from which subsamples of the composited water were withdrawn for analysis. A large-bore syringe (disposable, 25-mm diameter, polypropylene housing with female Luer-lock inlet and male Luer outlet) and disk filter (Whatman GF/F with graded multifiber, 0.7-μm nominal pore diameter) were used to collect 20 mL of filtered sample for analysis of pesticides (Sandstrom and Wilde, 2014). Discrete samples were shipped in a chilled container overnight to the USGS NWQL for pesticide analysis.

At the end of the sampling period, an ecological survey of benthic invertebrates was done at all sites. In the Midwest, invertebrate communities were sampled during July 22–August 7, 2013, along 11 equally spaced transects within the stream reach using EPA protocols, which call for using a D-frame net with 500-μm mesh openings (Waite and Van Metre, 2017). In the Southeast, invertebrate communities were sampled during June 2–14, 2014, using a modified Surber sampler with 500-μm mesh and following USGS protocols, which target the habitat having the greatest diversity of organisms within the stream reach, typically riffles or woody snags (Moulton et al., 2002; Waite et al., 2019). All samples were processed for taxonomic identification of benthic invertebrates at the USGS NWQL following the methods of Moulton et al. (2000). The Invertebrate Data Analysis System (IDAS) software (Cuffney, 2003) was used to resolve taxonomic issues, remove ambiguous taxa (Cuffney et al., 2007), and generate invertebrate metrics. The raw data of species taxonomy and enumeration are available in the USGS BioData Database (U.S. Geological Survey, 2019). Macroinvertebrate data from the two studies were comparable in terms of sampling protocols (similar number of composite samples and total sampled area) and shared laboratory procedures. All macroinvertebrate samples were collected using quantitative collection techniques (either Surber sampler or D-frame nets with 500-μm mesh openings) along a designated stream reach (150 to 300 m in length, depending on stream wetted width). Assessment of ecological condition based on EPT richness for the two methods has been reported as consistent among the two protocols (Gerth and Herlihy, 2006).

2.2. Chemical analysis

Daily and weekly composite samples were analyzed for 221 pesticide compounds at the EPA ACL and weekly discrete water samples were analyzed for 227 pesticide compounds at the USGS NWQL. The 203 pesticide compounds in common between the two methods form the basis of results reported here. EPA and USGS laboratories used a similar direct aqueous-injection liquid chromatography-tandem mass spectrometry (LC-MS/MS) method; the method used by the EPA ACL (Qian, 2015) was a modification of the method used by the USGS NWQL (Sandstrom et al., 2015). Details of the analytical method used at the ACL are described in SI Appendix C, and analytical method performance and quality control for the NWQL pesticide method are described in Sandstrom et al. (2015) and Nowell et al. (2018). Briefly, subsamples (1 mL) of filtered water samples were transferred to instrument autosampler vials and an internal standard solution containing isotopically labeled pesticides was added to each sample. Samples were analyzed by direct aqueous-injection LC-MS/MS on a Waters Xevo TQ MS instrument using two analytical sequences, one in electrospray ionization positive (ESI+) mode (for 185 compounds) and one in electrospray ionization negative (ESI−) mode (for 36 compounds) at the EPA ACL (SI Appendix C, Table C.1).

Because method detection limits (MDL) were higher for the EPA ACL method (ranging from 6 to 21,848 ng/L) used to analyze daily and weekly composite samples than for the USGS NWQL method (1 to 250 ng/L) used to analyze weekly discrete samples, the USGS data for weekly discrete samples were censored at the EPA MDLs prior to comparison of results among sample types. Pesticide data for daily and weekly composite samples and (after censoring to EPA MDLs) discrete weekly samples are provided in Morace et al., 2020. NWQL data for weekly discrete samples from MSQA and SESQA are reported at their original reporting levels in the National Water Information System (NWIS), and for MSQA in Nowell et al. (2017).

Quality control samples consisted of field (equipment) blanks, field matrix water spikes (deployed in autosamplers for a week after spiking), and laboratory matrix water spikes (prepared by spiking field water samples with spiking solution in the laboratory). Details on quality-control methods and matrix spike recovery results are given in SI Appendices D and E. Briefly, no pesticides were detected in field blanks. Median recovery in laboratory matrix spikes was 70–130% for 219 of 225 analytes in spikes analyzed concurrently with autosampler samples and for 222 of 225 analytes in spikes analyzed concurrently with discrete samples during the same time period. In contrast, 50 analytes had median recovery in autosampler field matrix spikes either below 70% (37 analytes, including several organophosphate and pyrethroid insecticides) or above 130% (13 analytes). Eleven degradates appear to have had their concentrations enhanced during the weeklong deployment in the autosampler, because median recoveries were acceptable or high (>70%) in field matrix spikes, but lower in discrete field matrix spikes and laboratory matrix spikes, with a relative percent difference of >20% between autosampler and discrete field matrix spikes. The enhanced recovery may have resulted from degradation of parent compounds to their respective degradate(s) in the autosampler.

Interlaboratory comparison was done by comparing results for splits of weekly composite samples and spiked field samples from the seven Southeastern stream sites analyzed by both laboratories (SI Appendix D). Results were evaluated for those compounds detected in the same sample at both laboratories by computing the logarithmic percent difference (LPD) for each pair of results. Results were similar for the two sample types: median LPDs were 26.5% and 28% for environmental splits and spiked field sample splits, respectively. Results from the EPA were biased slightly high relative to the NWQL results, with the EPA result being higher than the NWQL result in 61 and 62% of the environmental splits and spiked field sample splits, respectively.

2.3. Data analysis

Of the 203 pesticide compounds analyzed by both EPA and NWQL laboratories, concentrations of detected pesticides in each sample were summed to compute the total pesticide concentration (TC) for a sample; because non-detections were assigned a zero value for summation, the TC represents a lower bound. Concentrations of individual pesticides in daily composite samples were compared to EPA OPP acute aquatic-life benchmarks (U.S. Environmental Protection Agency, 2018), which were derived following EPA OPP deterministic procedure for risk assessment of pesticides (U.S. Environmental Protection Agency, 2017). Acute-fish benchmarks (AFB) were rarely exceeded, so analysis here focuses on acute-invertebrate (AIB) and acute nonvascular plant (ANVPB) benchmarks. The AIB for a pesticide is based on the most sensitive acute toxicity value for invertebrates (typically a 48- or 96-hr LC50 or EC50; median lethal and median effective concentration, respectively) in recent EPA risk assessment documents, multiplied by a level of concern of 0.5. The level of concern is a policy tool that EPA uses to analyze potential risk to nontarget organisms and to consider regulatory action (U.S. Environmental Protection Agency, 2017). AIBs are available for 119 of the 203 compounds discussed in this paper. The potential toxicity of pesticide mixtures to benthic invertebrates was assessed using the Pesticide Toxicity Index (PTI), a screening-level tool that assumes additive toxicity for compounds in a sample mixture (Munn et al., 2006; Nowell et al., 2014). To compute the PTI for a sample, the concentration of each pesticide detected in a mixture is divided by its acute toxicity concentration (typically the LC50) towards a specific taxonomic group. The resulting toxicity quotients, or toxic units (TUs), are summed to obtain the PTI value towards that specific taxon. Because pesticide compounds are excluded from the summed TUs (i.e., treated as zero concentrations) if they were not detected in the sample, or if they have no toxicity data available, the PTI represents a lower bound of potential acute toxicity. The PTI was calculated separately for cladocerans (water fleas) and benthic invertebrates. Toxicity concentrations are based on acute standardized tests, typically 48-hr EC50s for cladocerans (most commonly *Daphnia magna*) and 96-hr LC50s for benthic invertebrates (commonly midge or amphipods). Toxicity data are from the EPA ECOTOX database, EPA registration and risk assessment documents cited in support of the OPP aquatic life benchmarks, or, in the absence of data from those sources, the University of Hertfordshire's Pesticide Properties Database (Lewis et al., 2016; Nowell et al., 2014). PTI values computed in this study correspond to Sensitive-PTI values from Nowell et al. (2014), which use sensitive toxicity concentrations (STC)—the 5th percentile (or minimum, depending on the available data) acute toxicity concentrations for each pesticide. The PTI is based on datasets of LC/EC50 values that are very similar to those used by EPA to derive AIBs. Differences between the AIB and PTI toxicity concentrations may arise because: (1) the AIBs apply to all invertebrates, whereas the PTI is calculated separately for cladocerans and benthic invertebrates; (2) the AIBs use the lowest applicable LC/EC50 value, whereas the PTI uses the 5th percentile or lowest value; and (3) the AIBs divide the LC/EC50 by a factor of 2 (level of concern).

We used PTI thresholds of 1, 0.5, and 0.1 to characterize sites or samples in terms of potential for acute invertebrate toxicity. The threshold of 1 is a theoretical threshold for an additive model; because PTI is based on LC50s, the model predicts 50% toxicity (mortality) at a PTI value of 1 (Nowell et al., 2014). A threshold of 0.5 approximates the level of concern applied to LC50 values when determining acute invertebrate benchmarks (U.S. Environmental Protection Agency, 2017). The threshold PTI value of 0.1 applies a safety factor of 10 to estimate a more conservative (protective) threshold of toxicity, and is supported by published field studies in which substantial toxicity to *Ceriodaphnia* occurred in water samples with cladoceran PTI values >0.1 (Nowell et al., 2014).

Pesticide concentrations and PTI in daily composite samples in the 14 Midwestern and Southeastern streams were analyzed in relation to Ephemeroptera (mayflies), Plecoptera (stoneflies), and Trichoptera (caddisflies) (EPT) richness. EPT richness is a common index of invertebrate community condition (Cuffney, 2003; Watershed Science Institute, 2012), and Ephemeroptera, Plecoptera, and Trichoptera are among the four major aquatic insect taxa for which substantial loss of species has been identified (Sánchez-Bayo and Wyckhuys, 2019). EPT richness (which represents the number of EPT species present) for the study was developed from the ecological surveys done at each site the end of the water-sampling period.

3. Results

3.1. Pesticide occurrence and total concentrations

There were nearly 2 times as many unique pesticides detected among the 14 sites in daily samples than in weekly composite samples and almost 3 times as many as in weekly discrete samples during the studies (Table 1). This pattern was similar when sites from a single region were considered. The pesticides detected in a daily sample but not in a weekly sample of either type comprised 30% of the herbicides analyzed, 44% of the insecticides analyzed, and 19% of the fungicides analyzed. Regardless of sample type, herbicide compounds were detected more frequently than either insecticides or fungicides; for each sample type, at least four of the five most frequently detected pesticide compounds were herbicides, with detection frequencies ranging from 24 to 56% (SI Appendix F, Tables F.5–F.7). Atrazine, imidacloprid, and carbendazim were the most frequently occurring herbicide, insecticide, and fungicide, respectively, in all sample types. Differences in detection frequencies among sample types included the more frequent detection of the herbicide prometon, the insecticide synergist piperonyl butoxide, and the fungicide azoxystrobin in daily samples relative to weekly composite and discrete samples.

Complex mixtures of pesticide compounds occurred in all sample types (Table 1). The median number of pesticide compounds detected in a sample was similar among sample types, but the maximum number detected in a daily sample (35) exceeded the maximum number detected in a weekly composite (18) or weekly discrete (27) sample. The number of pesticides reported here as detected in weekly discrete samples from the Midwest are lower than those previously reported in the MSQA study (Nowell et al., 2018) because the concentrations measured by the NWQL (Nowell et al., 2017, 2018) had to be censored at higher MDLs for the present study, for comparability with data from the ACL. Detection frequencies and mixture complexity tend to increase as analytical detection levels decrease.

Total concentrations (TCs) varied greatly by pesticide use group and by sample type (Table 1). The maximum TC for herbicides (TCH) was similarly high for all sample types, but the maximum TCs for insecticides (TCI) and fungicides (TCF) in daily composite samples were several times higher than those in weekly composite samples and more than an order of magnitude higher than those in weekly discrete samples. The more frequent detection of herbicides is reflected for all sample types by a measurable first quartile TC, whereas insecticides and fungicides had both the first quartile and median TCs below detection. A measurable TC for insecticides and fungicides did not occur until the third quartile concentration or (for insecticides in weekly discrete samples) until the 90th percentile concentration.

Daily composite samples provided detailed insight into complexities of temporal pesticide occurrence not captured by weekly composite or discrete sampling. Goodwater Creek, an agricultural stream in Missouri, is used here as an illustration (Fig. 1; SI Appendix F, Figs. F.5 and F.19). Pesticides in samples from Goodwater Creek were dominated by frequent daily detections and relatively stable concentrations of herbicides (atrazine, metolachlor, and several of their degradates). Additional pesticides occurred in single or a few successive daily samples. Although herbicides typically had the highest concentrations in Goodwater Creek, insecticides comprised the largest contribution to benthic invertebrate PTI (Fig. 1b). Similar results were observed for several other streams (SI Appendix F). In Goodwater Creek, the most complex mixtures were observed during weeks 5 and 6 (Fig. 1a); these weeks also corresponded to the period with the highest benthic invertebrate PTI value (Fig. 1b).

Table 1
Summary of occurrence of 203 pesticide compounds by use group, Pesticide Toxicity Index (PTI), and exceedance of the acute invertebrate benchmark (AIB).
[All concentrations in ng/L; TCH, total concentration of herbicides; TCI, total concentration of insecticides; TCF, total concentration of fungicides; Daily, daily composite samples; WeeklyC, weekly composite samples; WeeklyD, weekly discrete samples.]

	All streams			Midwest			Southeast		
	Daily	WeeklyC	WeeklyD	Daily	WeeklyC	WeeklyD	Daily	WeeklyC	WeeklyD
Number of samples	975	93	153	512	35	69	463	58	69
Number of unique pesticides	145	75	51	134	66	42	70	31	22
Median number of pesticides detected in a sample	5	4	5	6	8	7	3	3	3
Maximum number of detections per sample	33	18	27	33	18	27	15	10	8
TCH, 1st quartile	73.5	113	64	120	180	312	41	107	0
TCH, median	442	493	524	725	1976	1521	284	463	160
TCH, 3rd quartile	1530	1225	2199	2462	3273	3705	750	686	854
TCH, 90th percentile	3418	3125	4987	5323	6598	7467	5323	6498	7467
TCH, maximum	34,884	21,749	49,862	34,884	21,749	49,862	4795	2247	5259
TCI, 1st quartile	0	0	0	0	0	0	0	0	0
TCI, median	0	0	0	0	0	0	0	0	0
TCI, 3rd quartile	60.5	61	0	55	52	0	64	62	48
TCI, 90th percentile	180	121	71	290	226	66	290	226	66
TCI, maximum	7715	1634	275	3182	1634	175	1037	278	164
TCF, 1st quartile	0	0	0	0	0	0	0	0	0
TCF, median	0	0	0	0	0	0	0	0	22
TCF, 3rd quartile	39	35	25	32	28	17	48	34	29
TCF, 90th percentile	127	95	49	96	82	45	96	82	45
TCF, maximum	4787	1378	195	3182	268	192	4787	1378	195
Number of cladoceran samples with PTI > 1	23	1	0	15	1	0	8	0	0
Number of cladoceran samples with PTI > 0.5	34	2	0	24	2	0	10	0	0
Number of cladoceran samples with PTI > 0.1	68	5	0	42	3	0	26	2	0
Number of benthic invertebrate samples with PTI > 1	18	1	0	14	1	0	4	0	0
Number of benthic invertebrate samples with PTI > 0.5	28	2	0	23	2	0	5	0	0
Number of benthic invertebrate samples with PTI > 0.1	135	16	15	74	6	10	61	10	5
Number of samples with an exceedance of at least one AIB	47	4	0	33	2	0	14	2	0

3.2. Comparison of pesticide concentrations measured in daily and weekly samples

To determine whether weekly samples, discrete or composite, can be used to estimate the peak concentration that occurs during a week, the relation between the maximum TC in a daily sample for each week was compared to the corresponding weekly composite and weekly discrete samples for each use group (Fig. 2). For herbicides, there was a strong correlation ($r^2 = 0.91$) between the maximum TCH during a week as measured by daily samples and the weekly composite sample; the maximum TCH for the week was about 150% of the weekly composite sample concentration for that week (slope of the regression line = 1.55) (Fig. 2a). The relation between the peak daily TCH and the discrete sample for that week was weaker but significant ($r^2 =$ 0.45, Fig. 2b). Similarly, for fungicides, the weekly composite sample was a weak but significant predictor of peak daily TCF (Fig. 2e), but there was no relation between weekly discrete and peak daily TCF values (Fig. 2f). For insecticides, neither weekly composite nor discrete samples were significantly related to the peak daily TCI (Fig. 2c,d).

Can weekly discrete samples be used to estimate long-term mean concentration? To investigate this, for each site the mean concentration of the most frequently detected herbicide (atrazine), insecticide (imidacloprid), and fungicide compound (carbendazim) in daily samples for the study period (n = 14) was compared to the mean concentration in weekly discrete samples. Agreement in long-term means was greatest for carbendazim and least for imidacloprid (Fig. 3). The long-term mean of discrete samples was similar to that of the daily samples (Fig. 3a,c,e), especially at higher mean daily concentrations (>100 ng/L for atrazine and >10 ng/L for imidacloprid and carbendazim). At lower mean daily concentrations, the divergence tends to be higher in absolute value, more variable (for imidacloprid) or biased low (carbendazim and atrazine) (Fig. 3b,d,f). These low mean concentrations for atrazine, imidacloprid, and carbendazim (<100, <10, and <10 ng/L, respectively) are near or below the MDLs (32, 38, and 16 ng/L, respectively). Because nondetections were treated as zero concentrations in computing means, the means may be biased low at concentrations near the MDL. Moreover, because divergence is expressed as a percentage of the daily mean, percentages are expected to be higher in absolute value at lower concentrations.

3.3. Potential acute invertebrate toxicity

Daily samples better captured the occurrence of pesticide mixtures potentially toxic to aquatic invertebrates than did weekly composite or discrete samples, based on both the PTI and AIBs. Daily samples identified 23 and 18 instances of PTI values >1 for cladocerans and benthic invertebrates, respectively, occurring at 9 sites; weekly composites identified one instance of potential toxicity and weekly discrete samples none (Table 2). Results were similar and more pronounced for comparison to thresholds of 0.5 and 0.1 of the PTI.

Comparison of concentrations of individual pesticides to their respective AIBs was similar to PTI evaluation for mixtures. Daily sampling indicated an exceedance of an AIB in 47 instances (Table 1), with at least one exceedance occurring in at least one sample from 10 of the 14 sites (Table 2). In contrast, weekly composite sampling identified an exceedance at only 3 of the 14 sites, and weekly discrete sampling did not identify any exceedances (Table 2). AIB detection frequencies at individual sites tended to be similar to the frequencies at which PTI values exceeded thresholds of 0.5 or 0.1 (Table 2). More compounds exceeded AIBs in one or more daily composite samples (carbaryl, chlorpyrifos, diazinon, malathion, fipronil, imidacloprid, dichlorvos, diflubenzuron, naled, profenofos, tebupirimfos, and terbufos) than in weekly composite samples (bifenthrin, carbaryl, and malathion).

How likely is it that weekly discrete samples miss acutely toxic pesticide exposure? To estimate this, we computed the probability that the benthic invertebrate PTI in a stream would exceed 1 on a day that a weekly discrete sample was collected, considering scenarios in which the exceedance occurred on only 1 day to as many as 20 days during a 12-week sampling period. We assumed that 12 discrete weekly samples were collected over 12 weeks and that PTI values ≥1 were randomly distributed during these 12 weeks. As the number of PTI exceedances

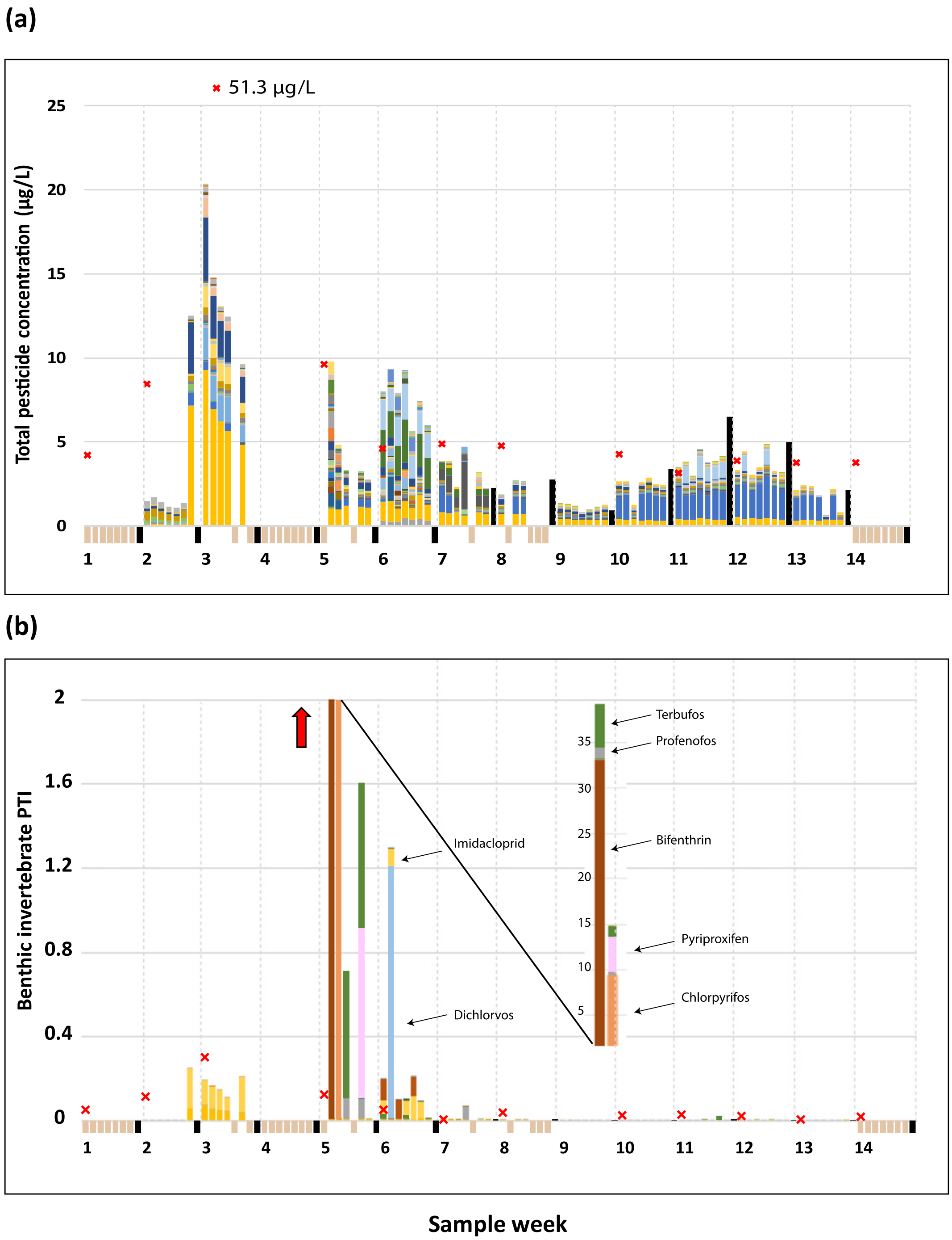

Fig. 1. Total pesticide concentrations (a) and benthic invertebrate Pesticide Toxicity Index (PTI) (b) in Goodwater Creek, Missouri, USA. The stacked bars for daily composite samples show individual pesticides in different colors. Missing daily or weekly composite samples are indicated by tan or black bars, respectively, extending below the x-axis. Weekly composite samples are shown as black bars, and weekly discrete samples as a red x. Two samples with extremely high summed Benthic invertebrate PTI values (>10) are off the Y-axis scale, and are shown at a larger scale in inset. See Supporting information Appendix F, Figs. F.5 and F.19, for legend of all pesticides detected.

during that period increased, the likelihood that all exceedances would occur on days on which a discrete sample was collected decreased, but the likelihood that at least one PTI exceedance would occur on a discrete sample day increased (simulations are shown in SI Appendix F, Fig. F.31). For scenarios of 1 to 5 exceedances over 12 weeks, the highest probability was that none occur on a discrete sample day. If there were at least 6 exceedances, the probability of capturing at least 1 exceedance in a weekly discrete sample was >50%. We conclude that weekly discrete samples are unlikely to detect infrequent occurrences of acutely toxic concentrations in streams, and that measured PTI exceedance rates in weekly discrete samples will tend to underestimate the incidence of potential toxicity threshold exceedances in streams. This is consistent with the results of this study, where individual sites had fewer than 3 exceedances in daily composite samples and no exceedances in weekly discrete samples during the 10 to 12-week study periods.

3.4. Comparison of toxic units measured in daily and weekly samples

To determine whether weekly composite or weekly discrete samples can be used to estimate the maximum sum of TUs (ΣTU) that occurs during a week (i.e., peak daily ΣTU), the relation between the

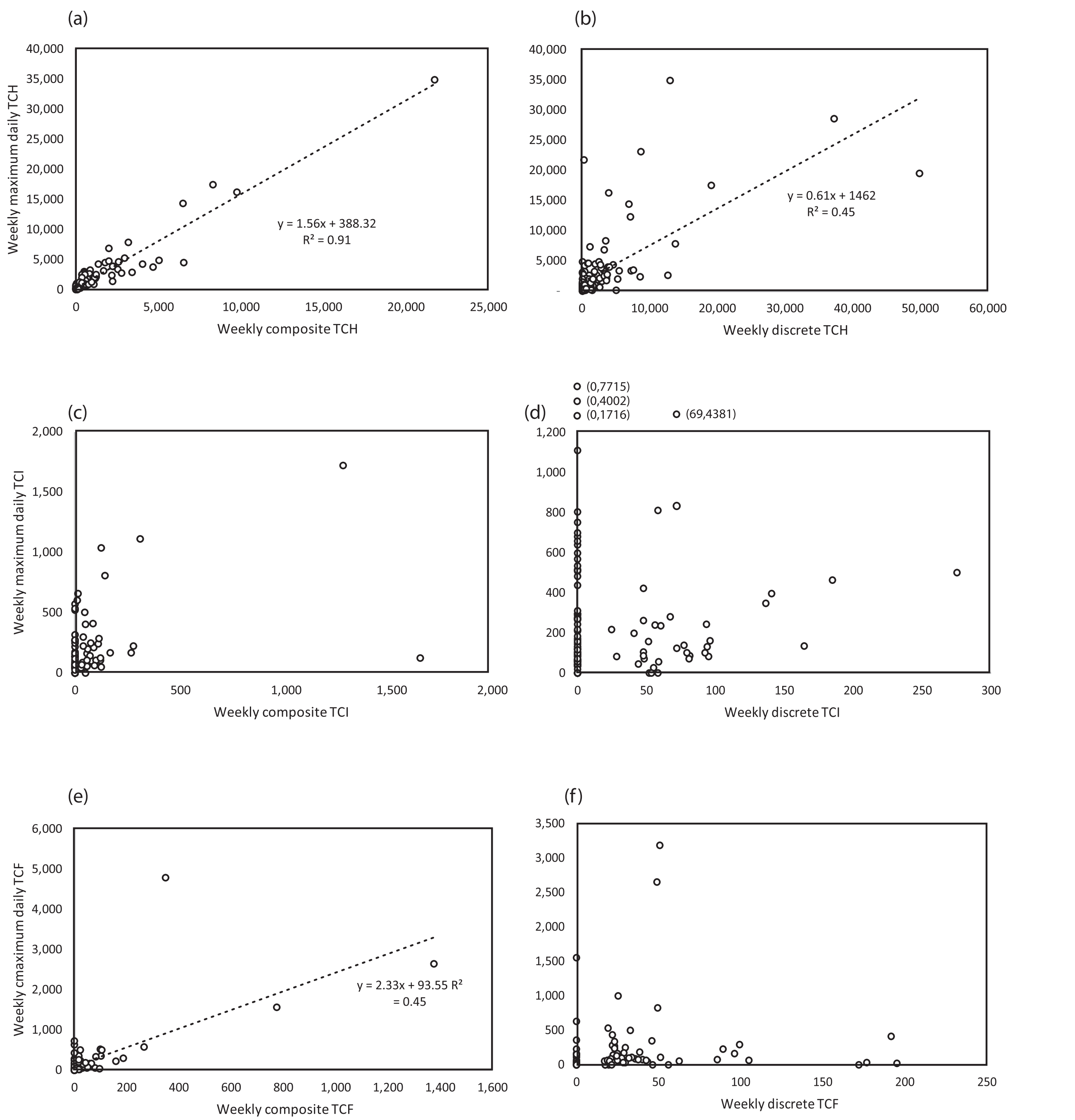

Fig. 2. Comparison of total herbicide concentrations (TCH), total insecticide concentrations (TCI), and total fungicide concentrations (TCF) in weekly composite samples (panels a, c, e) or weekly discrete samples (panels b, d, f) with the maximum total concentration measured in a daily sample for the same week. Where necessary, outliers are shown outside the boundary of the graph. All concentrations in ng/L. Regression line (dashed line) and equation are shown where the relation between the two is significant ($p < 0.05$).

maximum ΣTU in a daily sample for each week and weekly composite and weekly discrete samples was investigated by use group (herbicides, ΣTUH; insecticides, ΣTUI; and fungicides, ΣTUF) (Fig. 4). There was a strong correlation ($r^2 = 0.97$) between the ΣTUH of the weekly composite sample and the peak daily ΣTUH for that week, although the peak daily ΣTUH for the week was about 180% of the weekly composite value (slope of the regression line = 1.81). The relation between the weekly discrete sample ΣTUH and the corresponding peak daily ΣTUH during that week was significant but weaker ($r^2 = 0.52$, Fig. 4b). Similar to comparisons for TCs, both weekly composite and weekly discrete samples were poorer indicators of the peak daily values of ΣTUI and ΣTUF during the week (Fig. 4c–f).

3.5. Temporal potential toxicity occurrence

Temporal changes in potential toxicity of pesticide mixtures to aquatic invertebrates, evaluated using the PTI, have a distinctly different pattern from those of pesticide concentrations. Relatively low concentrations of more toxic pesticides in daily samples, primarily insecticides, appear as peaks in PTI, as illustrated for Goodwater Creek (Fig. 1b). Four daily samples at Goodwater Creek had a benthic invertebrate PTI ≥ 1, indicating a high likelihood of potential acute toxicity, and six insecticides—bifenthrin, chlorpyrifos, terbufos, pyriproxyfen, dichlorvos, and profenofos—had a TU ≥ 1 (indicating likely toxicity) in at least one daily sample. Several other streams had similarly transient high PTI values;

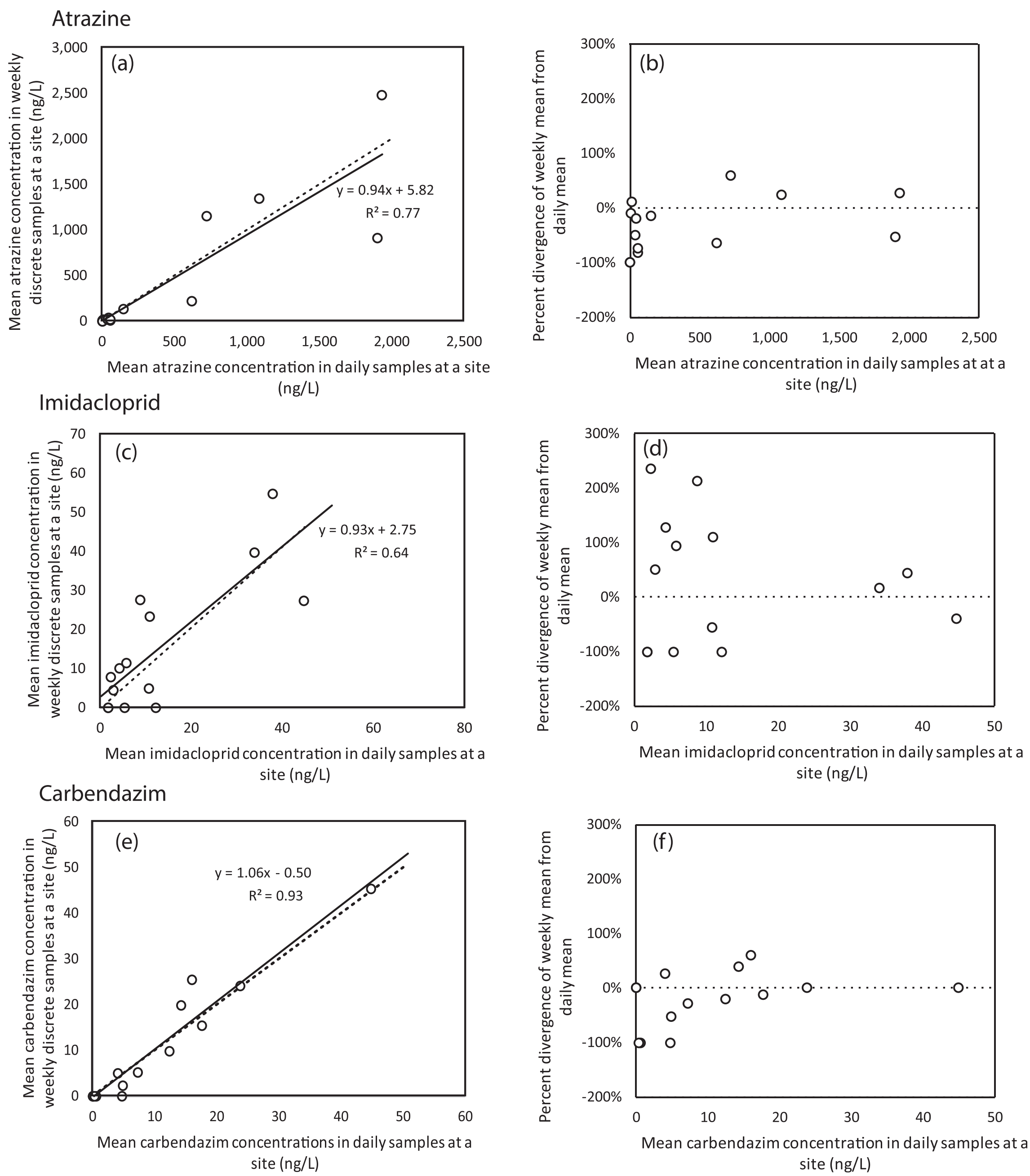

Fig. 3. Comparison of the mean concentration of the most frequently detected herbicide (atrazine), insecticide (imidacloprid), and fungicide compound (carbendazim) measured in daily samples and weekly discrete samples at a site. In panels a, c, and e the solid line is the regression line and the dashed line is a 1:1 relation. Panels b, d, and f compare the divergence of the weekly mean from the daily mean as a percentage (100 ∗ (weekly mean − daily mean) / daily mean), where 0%, indicated by the dashed line, indicates perfect agreement. Sites falling below the dashed line have a weekly mean that is less than the daily mean and vice versa.

detailed time series are provided graphically in SI Appendix F for the 14 streams (SI Figs. F.17–F.30).

The occurrence of insecticides was more transient than that of herbicides and fungicides. This was assessed by counting the number of detections in daily samples for each pesticide compound during each week. Only weeks with at least four daily samples were included. The mean number of detections per week, for all compounds and weeks within each use group, was 0.3 for herbicides and fungicides and 0.05 for insecticides. The number of detections during the week was compared by use group, based on total cases (i.e., weeks in which each compound was detected, for all compound/week combinations). Insecticide compounds were detected only once during the week in 59% of cases and had 4 or more detections during the week in only 19% of cases. In contrast, herbicides were detected only once during the week in 30% of cases and 4 or more times during the week in 45% of cases. Fungicides were intermediate, detected only once during the week in 42% of cases and 4 or more times in 23% of cases (SI Appendix F, Fig. F.32).

3.6. Relations between daily pesticide occurrence and invertebrate communities

The PTI is a screening tool that estimates potential aquatic toxicity of a pesticide mixture. To explore the extent to which the PTI relates to the actual condition of benthic invertebrates in streams, we compared the EPT richness of invertebrate communities surveyed at the study sites to the percentage of sample days with a benthic invertebrate PTI above a threshold of 0.1, which provided a sufficient number of samples for robust analysis. The EPT taxa are generally considered to be

Table 2
Percentage of daily composite samples with a Pesticide Toxicity Index (PTI) > 1, 0.5, and 0.1, exceeding at least one acute invertebrate benchmark (AIB), and exceeding at least one acute nonvascular plant benchmark (ANVP).
Results in bold italics are sites where one or more weekly composite samples exceeded the indicated PTI or exceeded at least one AIB or ANVP. [MW, Midwest; SE, Southeast; Ag, agricultural; Ur, urban].

Site	Region	Land Use	n	Cladoceran PTI			Benthic Invertebrate PTI			AIB	ANVP
				1	0.5	0.1	1	0.5	0.1		
Bell Creek	MW	Ag	81	1.2	2.5	4.9	0.0	0.0	3.7	4.9	14.8
Eagle Creek	MW	Ag	79	1.3	***1.3***	***2.5***	0.0	2.5	***25.3***	***2.5***	***41.8***
Goodwater Creek	MW	Ag	68	5.9	7.4	17.6	5.9	7.4	***22.1***	11.8	***19.1***
South Fork Iowa River	MW	Ag	56	0.0	0.0	0.0	0.0	***0.0***	***1.8***	0.0	***53.6***
Sugar Creek	MW	Ag	88	0.0	0.0	2.3	3.4	3.4	***9.1***	0.0	***28.4***
Honey Creek	MW	Ur	76	1.3	5.3	***7.9***	0.0	2.6	***13.2***	6.6	0.0
Lincoln Creek	MW	Ur	65	***12.3***	***18.5***	***24.6***	***10.8***	***16.9***	***26.2***	***21.5***	0.0
Accotink Creek	SE	Ur	65	7.7	9.2	9.2	0.0	1.5	***38.5***	9.2	0.0
Marsh Creek	SE	Ur	67	4.5	6.0	9.0	3.0	3.0	14.9	6.0	0.0
Swift Creek	SE	Ur	69	0.0	0.0	5.8	0.0	0.0	***23.2***	0.0	0.0
Manchester Creek	SE	Ur	68	0.0	0.0	4.4	2.9	2.9	4.4	1.5	1.5
Reedy River	SE	Ur	69	0.0	0.0	5.8	0.0	0.0	4.3	2.9	0.0
Proctor Creek	SE	Ur	67	0.0	0.0	***3.0***	0.0	0.0	***3.0***	***1.5***	0.0
Sope Creek	SE	Ur	58	0.0	0.0	1.7	0.0	0.0	***3.4***	0.0	0.0

intolerant of degraded water quality and sensitive to pesticides (Liess and von der Ohe, 2005; Rasmussen et al., 2012; Reif, 2002). EPT richness was significantly and inversely related to the percentage of days at each site with PTI ≥ 0.1 ($r^2 = 0.44$, $p = 0.01$) (Fig. 5). Considering the EPT orders individually, the relation to PTI ≥ 0.1 was slightly stronger for Trichoptera ($r^2 = 0.48$, $p = 0.006$) than it was for Ephemeroptera ($r^2 = 0.36$, $p = 0.02$) (no Plecoptera were found at any site).

4. Discussion

The results of the daily composite sampling provide insight into the diversity of pesticides in streams not captured by weekly sampling. Based on daily sampling, almost 3 times as many pesticides were present at least once during the study period than were identified by the weekly discrete samples (Table 1). One-half of the pesticides present—as demonstrated by daily sampling—but not detected in weekly samples were insecticides. Because insecticides tend to be acutely toxic to invertebrates at relatively low concentrations, weekly discrete samples likely underrepresent the potential invertebrate toxicity of small streams with urban and(or) agricultural land use in the basin. In the present study, nine insecticides had EPA MDLs that were higher than AIB values (SI Appendix C, Table C.1), so some potentially toxic concentrations may not have been detected. Additionally, the occurrence of some pesticides reported here may be biased low in daily and weekly composite samples as a result of degradation during their week-long residence in the autosamplers at ambient air temperature (SI Appendix E). Pesticide compounds that may be biased low include several organophosphate insecticides and degradates and pyrethroid insecticides, which are important contributors to PTI. As a result, the PTIs and AIB exceedance rates reported here for all sample types may underpredict potential acute toxicity in the streams sampled to some degree.

Daily sampling demonstrated that a pesticide concentration, or sum of concentrations, frequently peaked and then decreased over several days (e.g., South Fork Iowa River, Appendix F, Fig. F.6, weeks 4–7), but occasionally can be more transient, occurring on only 1 or 2 days (e.g., Bell Creek, SI Appendix F, Fig. F.3, week 6). Such a peak can be missed by a weekly discrete sample that is collected on a different day, or missed by a weekly composite sample if the high concentration is diluted by other daily draws that week with low concentrations. This is particularly true for insecticides and, to a lesser degree, fungicides, for which temporal occurrence tended to be less frequent (Table 1; SI Appendix F, Tables F.6–F.7) and more transient than herbicides (SI Appendix F, Table F.5). Our results expand on those of Crawford (2004), who used Monte Carlo simulation based on intensive datasets at four sites in Ohio (USA) to investigate this issue, and reported that sampling 10 times monthly at small streams provided reasonable estimates (within 50%) of the time-weighted 90th and 95th percentile concentrations of three commonly detected herbicides in the Midwest (atrazine, metolachlor and alachlor). In Crawford's study, however, the one insecticide investigated (chlorpyrifos) was not detected frequently enough to determine at these percentiles (i.e., the 90th and 95th percentiles were censored). In the present study, the 90th percentile concentrations of TCI and TCF in weekly composite samples from the 14 streams combined were within 50% of the daily 90th percentile concentration (although biased low on both counts), but the 90th percentile concentration in weekly discrete samples was not (Table 1). We conclude that concentrations and even occurrence of insecticides and fungicides, many of which are potentially toxic at concentrations near or below the MDL, may be underreported in small streams such as those sampled here.

Daily sampling provided a substantially more comprehensive picture of the potential acute toxicity to aquatic invertebrates than weekly composite or discrete samples. A cladoceran PTI of 1, indicating that acute toxicity was likely, was exceeded in daily samples on 23 instances, but in only one weekly composite sample and in no weekly discrete samples (Table 1). At least one day with potential acute toxicity to invertebrates (i.e., exceeding an AIB and(or) a PTI threshold of 1) occurred at 10 of the 14 streams, whereas weekly composites identified only 3 of those sites and weekly discrete samples (after censoring to EPA MDLs) identified none (Table 2). The degree of potential toxicity of mixtures predicted by the PTI, however, might be overestimated. The PTI assumes additive toxicity for components of a mixture, which technically applies only to compounds sharing a common mode of action. When applied to complex mixtures of pesticides with different modes of action (as in the present study), an additive model may overestimate potential toxicity by a factor of 2–3 (e.g., Belden et al., 2007; Faust et al., 2003; Warne, 2003). In the present study, AIB detection frequencies by individual pesticides in the sampled streams tended to be similar to the frequencies at which PTI values exceeded thresholds of 0.5 or 0.1 (Table 2). This is consistent with how the AIB and PTI thresholds were derived (see Data analysis) and supports the PTI predictions in this study.

Daily sampling demonstrated that the temporal nature of potential acute toxicity was complex, varying among streams and over time within a single stream. In most instances, peaks in PTI values in daily samples were dominated by a single compound (e.g., Sugar Creek, SI Appendix F, Fig. F.21). In a few instances, TUs of two or more pesticides combined to create a PTI > 1 (e.g., pyriproxyfen and terbufos in Lincoln Creek, SI Appendix F, Fig. F.23) or multiple pesticides had TU > 1 at the same time (e.g., Goodwater Creek, Fig. 1b). In some streams the principal contributor to PTI was relatively consistent over time (e.g., imidacloprid in Eagle and

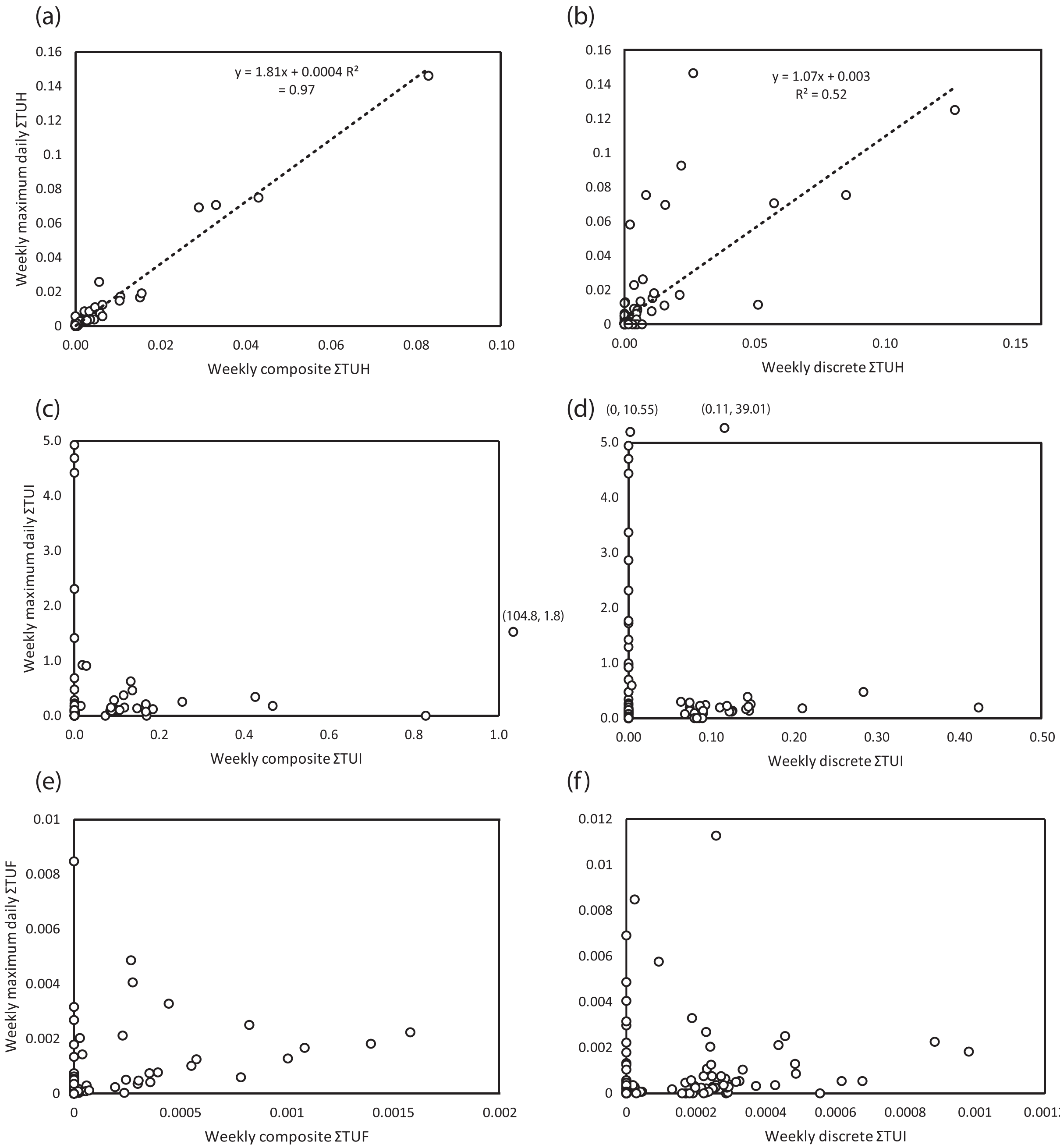

Fig. 4. Comparison of sum of herbicide toxic units (ΣTUH), sum of insecticide toxic units (ΣTUI), and sum of fungicide toxic units (ΣTUF) in weekly composite samples (panels a, c, e) or weekly discrete samples (panels b, d, f) with the maximum sum of toxic units measured in a daily sample for the same week. Where necessary, outliers are shown outside the boundary of the graph. Regression line (dashed line) and equation are shown where the relation between the two is significant ($p < 0.05$).

Swift Creeks, SI Appendix F, Figs. F.18 and F.26), but in other streams the pesticide with the maximum TU varied through the growing season (e.g., Accotink Creek, SI Appendix F, Fig. F.24; Lincoln Creek, Fig. F.23). These results demonstrate that potentially toxic pesticide mixtures are difficult to predict and likely depend on the timing and location of pesticide application, runoff, and land-use management within the basin.

The percentage of samples at a site with a PTI > 0.1, a conservative measure of potential toxicity, was inversely related to EPT richness, a common measure of invertebrate community condition (Fig. 4). This correlation suggests that frequent occurrence of concentrations of pesticide mixtures below the PTI threshold of 1 may be adversely affecting aquatic invertebrates, particularly in light of the fact that PTI exceeded 1 during only about 2% of days (23 of 976 total days). This is consistent with findings of Nowell et al. (2014), who observed from published studies that >50% mortality to the cladoceran *Ceriodaphnia*occurred in 19% of samples with PTI values of 0.1–1. Because the PTI is based on LC50 toxicity concentrations, the PTI model predicts 50% mortality at a threshold of 1 (assuming the components of the mixture show additive toxicity); it therefore is reasonable to infer that substantial mortality could occur at concentrations below the threshold of 1. Sublethal effects (e.g., on growth or reproduction) also can occur at concentrations below acute benchmarks or PTI toxicity concentrations. Furthermore, mesocosm studies have shown that concentrations of imidacloprid in water and bifenthrin in sediment can adversely affect field communities at concentrations far below acute LC50s that were determined in single-species bioassays (Nowell et al., 2018; Rogers et al., 2016). Similarly, field-based changes in invertebrate community structure were three orders of magnitude below acute LC50s measured in single-species

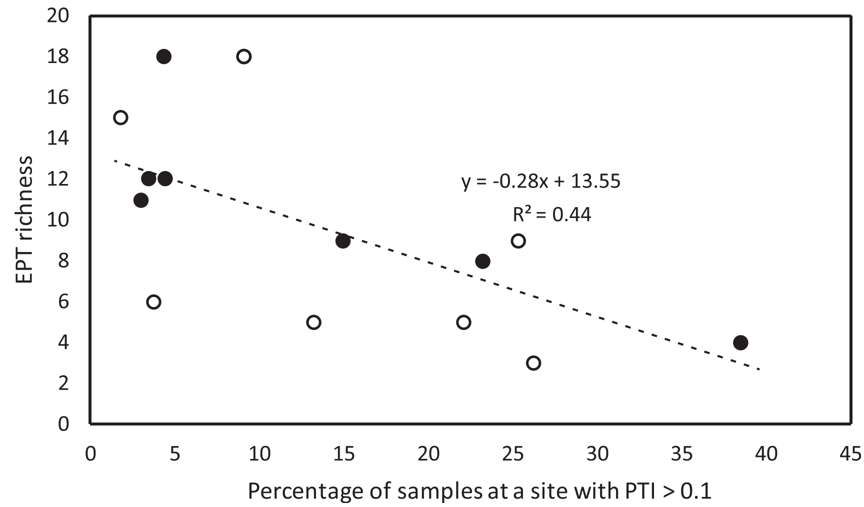

Fig. 5. Ephemeroptera, Plecoptera, and Trichoptera (EPT) richness in the 14 streams (Midwestern, open circles; Southeastern, closed circles) was significantly and inversely related to the percentage of days at each site with a Pesticide Toxicity Index (PTI) ≥ 0.1. The dashed line indicates the linear regression ($p = 0.01$).

bioassays with Cladocera (Liess and von der Ohe, 2005; Schäfer et al., 2012). The relationship shown in Figure 5 is correlative, however, not causative. We note that other in-stream stressors not accounted for in this analysis can contribute to adverse effects on invertebrates; EPT richness has been shown to be related to dissolved oxygen, flow peak intervals, total nitrogen, ammonia, substrate, and sinuosity, in addition to several pesticide metrics (Waite et al., 2019; Waite and Van Metre, 2017).

We hypothesized that the maximum concentration and TU for a week as measured in daily samples could be estimated by the weekly composite sample, although the relationship would not be 1:1. This hypothesis held for weekly maximum and weekly composite TCH and ΣTUH, for which the correlations were strong ($r^2 = 0.91$ and 0.97, respectively) (Figs. 2a and 4a), but did not hold for weekly maximum TCI or TCF. This could be because insecticide and fungicide concentrations were much lower than herbicide concentrations or because they occurred less frequently (Table 1). Spikes in concentrations of individual insecticides and herbicides occurring on just 1 or 2 days during the week might be diluted to below the method detection limit (MDL) in a weekly composite sample. There were occasional outliers for which weekly discrete samples were higher than expected from the peak daily concentration, perhaps reflecting both spatial and temporal differences between these samples; the width-integrated discrete sample may capture pesticides that were missed or diluted in aliquots collected by the autosampler, which had a fixed location within the stream and collected aliquots throughout a 24-hr period. However, the possibility that the pesticides in question may have degraded to below the MDLs in daily samples in the autosampler during the weeklong deployment cannot be ruled out.

Weekly samples, both composite and discrete, better characterized average characteristics, such as the mean, than extremes, such as number of unique pesticides detected, peak concentrations, or exceedances of the PTI. The median number of pesticides detected in a sample was similar for the three sample types (Table 1), and detection frequencies of most pesticides detected in >10% of samples were similar (SI Appendix F, Tables F.5–F.7). The long-term mean concentration of the most frequently detected herbicide (atrazine), insecticide (imidacloprid), and fungicide (carbendazim) at a site as measured in weekly discrete samples was similar to the mean concentration in the daily samples (Fig. 3). Weekly samples reasonably estimated the 90th percentile TCH; weekly composite samples reasonably estimated the 90th percentile TCI and TCF, although the weekly discrete sample 90th percentiles of TCI and TCF were less than one-half of those computed for the daily samples (Table 1).

Overall patterns in detections, concentrations, and incidences of potential toxicity when individual regions were considered were similar to those for both regions combined, despite large differences in land use, topography, and climate. Although only about one-half as many compounds were detected in samples from the Southeastern streams as in samples from the Midwestern streams, general patterns regarding differences in results by sample type were similar between the two regions, with daily samples detecting a much greater number of unique pesticides, much higher maximum concentrations of insecticides and fungicides, and many more exceedances of the PTI and AIB than weekly composite and discrete samples (Table 1). This suggests that the overall conclusions regarding differences among sampling frequencies may be transferable to small streams in regions other than the Midwest and Southeast.

In brief, daily sampling demonstrated that a far more extensive suite of pesticides occurred at the 14 stream sites than was indicated by weekly composite or weekly discrete samples and that temporal patterns of occurrence were complex. The relatively low frequency of occurrence of PTI ≥ 1 and exceedances of AIBs in daily samples translates to a low likelihood of capturing such peaks in discrete weekly samples, and no weekly discrete samples had PTI ≥ 1 or exceeded any AIBs at the method detection levels used in this study. Daily sampling, however, is unfeasible for most sampling programs because of analytical costs. Weekly composite samples were able to capture some of the same dynamics of pesticide occurrence as daily composite samples: the maximum daily TCH during a week and the weekly composite TCH were correlated, and the 90th percentile TCH, TCI, and TCF for weekly composite samples (all sites combined) were within 50% of those for daily samples. Weekly composite sampling therefore might be a compromise as a sampling strategy, being more cost-effective than daily sampling and better reflecting pesticide dynamics than weekly discrete samples, although much information will be missed, particularly for insecticides and fungicides.

There are logistical and technical difficulties associated with the automated samplers used in the present study that complicate collection of even weekly composite samples, including a substantial number of failed samples because of clogging or vacuum loss, and the potential for pesticide degradation in composite samples within the sampler if deployed without cooling (SI Appendix E). Monitoring programs, therefore, would need to balance the greater insights into pesticide occurrence and potential toxicity to benthic invertebrates provided by daily sampling with the lower costs and manpower required for weekly composite and discrete sampling strategies for pesticides in small streams. Alternative strategies, such as event-driven samplers, may be appropriate to consider, if the primary study goal is to assess acute exposure.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Data can be found in ScienceBase at: https://www.sciencebase.gov/catalog/item/5d30ff77e4b01d82ce84ab36 and the National Water Information System at http://waterdata.usgs.gov/nwis. Support for this work was provided by the USGS NAWQA Project of the National Water Quality Program and the U.S. EPA Office of Pesticide Programs (OPP). Additional information on the Regional Stream Quality Assessments can be found at: http://txpub.usgs.gov/RSQA/. The authors are grateful to USGS field personnel for deploying samplers and collecting samples for this study; the USGS National Water Quality Laboratory for analyzing weekly composite and spike samples, the OPP Analytical Chemistry Laboratory for analyzing daily and weekly composite and spike samples; Naomi Nakagaki and Sharon Qi (USGS) for maps; and reviewers Wesley Stone (USGS), and the anonymous reviewers at the journal for their thoughtful reviews of this manuscript. The authors also thank Terence E. Fitzgerald for his assistance in the design and final construction of the autosamplers.

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Appendix A-F:. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.136795.

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