1 Complex Mixtures of Pesticides in Midwest U.S. Streams

2 Indicated by POCIS Time-Integrating Samplers

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1. ABSTRACT

The Midwest United States is an intensely agricultural region where pesticides in streams pose risks to aquatic biota, but temporal variability in pesticide concentrations makes characterization of their exposure to organisms challenging. To compensate for the effects of temporal variability, we deployed polar organic chemical integrative samplers (POCIS) in 100 small streams across the Midwest for about 5 weeks during summer 2013 and analyzed the extracts for 227 pesticide compounds. Analysis of water samples collected weekly for pesticides during POCIS deployment allowed for comparison of POCIS results with periodic water-sampling results. The median number of pesticides detected in POCIS extracts was 62, and 141 compounds were detected at least once, indicating a high level of pesticide contamination of streams in the region. Sixty-five of the 141 compounds detected were pesticide degradates. Mean water concentrations estimated using published POCIS sampling rates strongly correlated with means of weekly water samples collected concurrently, however, the POCIS-estimated concentrations generally were lower than the measured water concentrations. Summed herbicide concentrations (units of ng/POCIS) were greater at agricultural sites than at urban sites but summed concentrations of insecticides and fungicides were greater at urban sites. Consistent with these differences, summed concentrations of herbicides correlate to percent cultivated crops in the watersheds and summed concentrations of insecticides and fungicides correlate to percent urban land use. With the exception of malathion concentrations at nine sites, POCIS-estimated water concentrations of pesticides were lower than aquatic-life benchmarks. The POCIS provide an alternative

37 approach to traditional water sampling for characterizing chronic exposure to pesticides
38 in streams across the Midwest region.
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40 KEYWORDS

41 Water quality, insecticides, imidacloprid, pyrethroids

42 CAPSULE

43 Ubiquitous occurrence of pesticides in small Midwest U.S. streams was indicated by high
44 detection frequencies in POCIS time-integrating samplers and water.

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46 GRAPHICAL ABSTRACT:

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2. Introduction

Pesticides in Midwest U.S. streams pose risks to aquatic biota (Hladik and Kolpin, 2016; Stone et al., 2014), but temporal variability in pesticide concentrations makes characterization of their acute and chronic exposure to organisms challenging. The timing and intensity of pesticide applications, the frequency and magnitude of runoff, and the timing and distribution of land-management practices, such as irrigation and artificial drainage, cause short-duration fluctuations in pesticide concentrations, particularly in small streams (Liess et al., 1999; Rabiet et al., 2010). These fluctuations limit the ability of discrete sampling to either capture peak concentrations (acute exposure) or reasonably represent mean concentrations (chronic exposure). One approach to overcome this limitation is to generate time-weighted mean pesticide concentrations by using a sampling strategy that is weighted toward the typical seasonal pattern of pesticide runoff (Battaglin and Hay, 1996; Crawford, 2004). An alternative approach, which characterizes chronic exposure to polar (relatively soluble) organic chemicals, is use of a polar organic chemical integrative sampler (POCIS) (Alvarez, 2010; Morin et al., 2012). POCIS are designed to sample soluble to moderately soluble organic chemicals with log octanol-water partition coefficients (K_{ow}) < 4 (Alvarez et al., 2004). This category includes most pharmaceuticals, polar pesticides, phosphate flame retardants, surfactants, and their metabolites. POCIS typically are deployed for 1–2 months (Alvarez et al., 2004), and uptake rates for most chemicals are linear over this time scale. If a compound-dependent uptake is known, the results can be used to estimate the mean water concentration of the compounds measured over the period of deployment (Alvarez et al., 2007; Harman et al., 2012). If water uptake rates are not known, concentrations of compounds in POCIS

73 deployed at multiple sites nonetheless can be compared in a relative sense (Alvarez,
74 2010).

75 POCIS have been used extensively to characterize chemical occurrence in aquatic
76 settings (Liess et al., 1999; Martinez Bueno et al., 2016; Poulier et al., 2015; Rabiet et al.,
77 2010; Terzopoulou and Voutsas, 2016), sometimes as a direct measure of chemical
78 exposure to organisms (Barranger et al., 2014; Diamond et al., 2016). Several researchers
79 have compared results from POCIS with concurrent water samples (Lissalde et al., 2014;
80 Poulier et al., 2015), although direct comparison of time-weighted average estimates of
81 water concentrations from a passive sampler to the measurement of discrete water
82 samples is challenging. Assuming that chemical uptake is linear (integrative) over the
83 deployment period, the passive sampler results represent the mean chemical
84 concentration in the water, but do not provide information on variations in concentrations
85 (Alvarez et al., 2004). An instantaneous water sample, on the other hand, represents a
86 concentration at a point in time and it is unknown how that concentration compares to the
87 mean over a longer period, such as that during which a passive sampler is deployed.
88 POCIS water concentration estimates are made using sampling rates determined in
89 laboratory calibration experiments (Ahrens et al., 2015). Environmental factors,
90 including flow velocity of the water sampled and biofouling, are thought to affect
91 sampling rates, with flow velocity generally assumed to be the most important factor
92 (Alvarez et al., 2007; Harman et al., 2012; Lissalde et al., 2014). Two recent studies,
93 however, found that moderate variations in flow velocities had no effect on sampling
94 rates (Dalton et al., 2014; Di Carro et al., 2014).

In 2013, the U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA), the USGS Columbia Environmental Research Center (CERC), and the U.S. Environmental Protection Agency (USEPA) National Streams and Rivers Assessment (NRSA) collaborated to assess stream quality across the Midwest United States (Van Metre et al., 2012). The goal of this assessment, called the Midwest Stream Quality Assessment (MSQA), was to characterize water-quality stressors—contaminants, nutrients, sediment, and habitat—and ecological conditions in streams across the Midwest region and to evaluate the relative effects of these stressors on aquatic organisms. The Midwest region was selected because it is one of the most intensively and economically important agricultural regions of the United States and has some of the highest use of pesticides in the nation (Ryberg and Gilliom, 2015).

As part of the MSQA, POCIS samplers were deployed at 100 stream sites in the Midwest region in late June and early July 2013 and retrieved about 5 weeks later, approximately coincident with the end of the MSQA water-sampling period and sediment and ecological sampling. POCIS extracts were analyzed for an extensive suite of pesticides to provide a time-integrated pesticide exposure measure as an alternative to periodic water and sediment sampling for pesticides. Water samples were collected approximately weekly for pesticide analysis coincident with the POCIS deployment and a one-time bottom sediment sample for pesticide analysis was collected.

3. Study design and methods

The MSQA study combined the targeted design of the USGS NAWQA (e.g., Coles et al., 2012; Garrett et al., 2016) and the probabilistic design of the USEPA NRSA (Olsen et al., 1999; USEPA, 2013) to select 100 sites on wadeable streams for sampling

(Figure 1 and Supporting Information (SI) Table S1; POCIS sampling was successful at 97 of the 100 sites). Wadeable streams, meaning streams small enough to be sampled for ecology by wading methods, had depths in most of the ecological survey reach of about 1 m or less during low flow. Fifty sites were randomly selected (“random” sites) by the USEPA following NRSA protocols (Olsen et al., 1999; USEPA, 2013), with the exception that larger, non-wadeable 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 to achieve full coverage of the range in stressor levels in the region, by adding reference, low-intensity agriculture, and urban sites, and to include a subset of sites with long-term monitoring data (Van Metre et al., 2012).

2.1 Environmental setting.

The MSQA study region covered part or all of six USEPA level 3 ecoregions. Land use in the MSQA region is dominated by cultivated crops, primarily corn and soybeans. Land use within the 100 MSQA watersheds reflected land use within the region, with the average watershed having 54% of watershed area in row crop, 11% in pasture and hay, 8% urban (compared to 57, 12, and 10%, respectively, for the whole region), and most of the remainder in woodlands and grasslands.

2.2 Sampling, analytical methods, and quality control.

Twelve water samples were collected at each site over a 14-week period (May 6–August 9, 2013) with a weekly sampling interval except for two 2-week periods (May 27–June 7 and July 1–12) during each of which only one sample was collected. Water samples for analysis of pesticides were collected according to standard USGS protocols, typically by

using a depth-integrating sampler at multiple vertical locations in the stream cross section, composited into a Teflon churn, then filtered from the churn using a disposable syringe filter (0.7 μm) (USGS, 2006). Samples were chilled and maintained at about 4° C until analysis at the USGS National Water Quality Laboratory (NWQL) in Lakewood, CO.

Bed-sediment samples were collected and ecological surveys conducted at 99 of the 100 MSQA sites in July and August, 2013, approximately coinciding with the end of the water-sampling period and retrieval of the POCIS. Sediment samples were composites of up to about 40 surficial (top 2 cm) grab samples from depositional areas along the stream reach, similar to the approach described by Shelton (1994). Samples were chilled and shipped to the CERC where they were homogenized and split for analyses of various chemical and physical characteristics and for laboratory toxicity testing (Garrett et al., 2016). Bed-sediment samples were extracted by using accelerated solvent extraction, then extracts were subjected to clean-up procedures and analyzed for 118 pesticides at the USGS California Water Science Center Pesticide Fate Research Laboratory (Sacramento, CA) by gas chromatography-tandem mass spectrometry (Hladik and McWayne, 2012). Reporting levels were in the 0.5–3.1 $\mu\text{g/kg}$ range.

Three POCIS containing the sorbent Oasis HLB (Waters, Milford, MA) (Alvarez, 2010) were deployed at each of the 100 MSQA sites. Oasis HLB typically is considered a universal sorbent in environmental analyses and has been used to extract a wide assortment of chemical classes from water. POCIS were deployed between June 12 and July 19, 2013, and most were retrieved during the last week of July or the first week of August. The mean deployment was 37 ± 6.7 days. POCIS retrieval occurred for most sites

during the last 2 weeks of water sampling and within 2 weeks of the ecological surveys.

Field deployment followed guidelines provided in USGS Techniques and Methods Book 1, Section D, Chapter 4 (Alvarez, 2010). POCIS extracts were analyzed for the same suite of pesticides and pesticide degradates analyzed in weekly water samples (SI Table S2).

Ten POCIS field blanks were used to assess any accumulation of target compounds from the air during assembly and transport. The blank POCIS canisters were open to the air at the same time and place as the field POCIS samplers during deployment and retrieval.

Between deployment and retrieval of the field POCIS samplers, POCIS field-blank canisters were kept sealed and stored between -20 to 0 °C. All POCIS samplers and blanks were stored on ice during transport to the sampling location.

After the deployment period, the POCIS and field blanks were shipped immediately to CERC or stored at -20 to 0 °C until shipment. At CERC, each POCIS was individually extracted using 25 mL of methanol (Alvarez, 2010). Two of the three sampler extracts from each site (and from each field blank) were combined, concentrated using rotary evaporation and nitrogen blowdown, sealed in 1-mL amber glass ampules, and shipped to the NWQL for analysis. At the NWQL, 90 µL of extract were transferred to an analytical vial and diluted with water (900 µL) and a mixture of internal standards (10 µL). Dilution of POCIS extracts was required because most contained co-extracted matrix material that causes suppression of internal standards. Laboratory blank and laboratory-fortified spike samples were prepared using comparable volumes of water and internal standard and processed with the POCIS extracts (Alvarez, 2010). Water and POCIS extracts were analyzed for 227 pesticide compounds (111 parent compounds and 116 degradates) using direct aqueous injection liquid chromatography tandem mass spectrometry (DAI LC-

MS/MS) (Sandstrom et al., 2016). Samples were analyzed with two injections, one in electrospray ionization (ESI) positive mode and one in ESI negative mode, using two multiple reaction monitoring transitions for each analyte. Method detection levels (MDLs) for water samples ranged from 1 to 106 ng/L for all but six analytes (250–1000 ng/L). The MDLs for POCIS samples ranged from 0.1 to 11 ng/POCIS for 222 of the pesticide compounds, and five compounds had MDLs of 25 ng/POCIS.

In 9 of the 10 POCIS blank samples, detection frequency and the sum of concentration (ng/POCIS) were low, with from 1 to 7 compounds detected and summed concentrations from 0.04 to 3.6 ng/POCIS. In comparison, the median number of detections and summed concentrations in environmental samples were 62 and 5,950 ng/POCIS, respectively. One blank sample had substantial contamination, with 37 compounds detected and summed concentration of 696 ng/POCIS. About 60% of the summed concentration was one compound, metolachlor ethane sulfonic acid (metolachlor SA), a metabolite of the herbicide metolachlor. Metolachlor SA was not detected in the paired environmental sample, however 32 compounds were detected in both the environmental sample and the blank sample, and for those compounds the blank concentration accounted for a median of 30% of the environmental concentration. Concentrations in this environmental sample were blank corrected by subtracting the blank-sample concentration from the environmental-sample concentration.

Because the POCIS samplers were not all deployed for the same time interval, concentrations of pesticides in the POCIS extracts were normalized by the ratio of the deployment period for each sampler to the mean deployment period (37 d). For about two-thirds of the samples, the normalized value was within 20% of the original value.

One POCIS sampler (Green River near Hooppole, IL) was lost in the field and two POCIS samples (Sevenmile Creek near Kasota, MN, and Lincoln Creek in Milwaukee, WI) were damaged with an apparent loss of the Oasis HLB. Any remaining Oasis HLB in these samplers was extracted to qualitatively screen for pesticides; however, Sevenmile Creek had no detections in the POCIS and Lincoln Creek had only 6 detections and a very low summed concentration of 2.4 ng/POCIS. Given that these sites are an intensive agricultural and an urban site, respectively, and that many pesticides were detected in water from both sites, we concluded that these two POCIS samples were compromised and did not include them in interpretations. That left 97 of the 100 sites with POCIS samples suitable for evaluation.

3. Results and discussion

Pesticides and pesticide degradates were detected frequently in POCIS samples, with 28–85 compounds detected per POCIS (median of 62)(SI Table S2). Although the number of compounds detected was relatively similar among sites, varying by a factor of about 3, concentrations varied greatly. Summations of concentrations by use groups—herbicides, insecticides, and fungicides—varied by about 3 orders of magnitude among sites (Figure 1). Of the 227 compounds measured, 141 were detected at least once—76 of these are parent pesticides and 65 are degradates (Table 1).

Among the compound use groups, herbicides and herbicide degradates were most frequently detected and had the highest concentrations (Figures 2,3). Six parent herbicides (acetochlor, atrazine, dimethenamid, metolachlor, prometon, and propazine) and three herbicide degradates were detected at all of the 97 sites sampled. The highest

concentration measured was 32,200 ng/POCIS (time-adjusted concentration 34,000 ng/L) for acetochlor at Spoon River in IL, a site with 92% of the watershed in row crops.

Of the insecticides, imidacloprid, a neonicotinoid insecticide, was most frequently detected (98% of sites) (Figure 3) and had the highest concentrations (SI table S2), accounting for a median of 93% of the sum of parent insecticide concentrations across all 97 sites. The highest imidacloprid concentration was 2,880 ng/POCIS (time-adjusted 2,860 ng/L) at Tomahawk Creek in Overland Park, KS, an urban site. The next two most frequently detected insecticides were methoxyfenozide (93%) and fipronil (89%). Among the insecticide degradates, notable detections are those of fipronil (7 degradates with detection frequencies from 9–91%) and pyrethroids (2 degradates with detection frequencies of 18 and 46%).

Among fungicides, azoxystrobin, metalaxyl, and propiconazole were the most frequently detected (98–100% of samples) (Figure 3) and, including tebuconazole, accounted for a median of 95% of the sum of parent fungicide concentrations (SI Table S2). The highest fungicide concentration was 491 ng/POCIS (time-adjusted 535 ng/L) for tebuconazole at Salt Creek at Western Spring, IL, an urban site. Only 4 fungicide degradates were measured and 3 were detected, with a detection frequency of 30–38%.

The 50 sites selected using the EPA NRSA's probabilistic approach (random sites) can be used to infer conditions in wadeable streams across the region. On the basis of detections at the random sites, 133 of the 227 pesticide compounds measured are at detectable levels in small streams in the Midwest region (Table 1). Detection frequencies and summed concentrations by use groups are similar for the 49 random sites and the 37 targeted agricultural sites, and these frequencies and concentrations differ from those of

the 11 targeted urban sites (Figure 2). We conclude from this finding that a targeted site-selection approach across the dominant land-use gradient in the Midwest can produce results consistent with a probabilistic approach, but that to characterize a high-impact land use with a small footprint, such as urbanization, a targeted selection approach might be needed.

3.1 Comparison to water concentrations.

Detection frequencies for many compounds were higher in the POCIS than in the water samples, in particular for insecticides and fungicides (Figure 3). The median number of compounds detected per POCIS was 62, whereas the median number of compounds detected per site for all water samples collected during the POCIS deployment was 46 (a median of 6 samples per site were collected during the POCIS deployment period). In POCIS samples, 141 compounds were detected at least once, whereas 157 compounds were detected at least once in water samples.

Although pesticide occurrence is generally similar for POCIS and water samples (Figure 3), there are notable exceptions wherein a compound was frequently detected in one sampling medium but not the other. The herbicide degradate deisopropyl prometryn, for example, was detected in POCIS at 98% of sites but in water at only 15% of sites. The insecticide methoxyfenozide had site-detection frequencies of 93 and 1% in POCIS and water samples, respectively. These examples highlight an advantage of using an integrative sampler, in that the mass of a chemical accumulated in the POCIS over time was sufficient to satisfy the method detection limits of the instrument, whereas the concentration in an discrete water sample was less than the instrument's detection capability (Alvarez et al., 2005; Kolpin et al., 2013). Conversely, a few compounds were

frequently detected in water but rarely in POCIS, including the atrazine degradate didealkylatrazine (99 and 14%, respectively) and the fungicide pyraclostrobin (72 and 5%, respectively). The log K_{ow} s for these chemicals (0.32 for didealkylatrazine and 5.5 for pyraclostrobin) are outside the optimal range of log K_{ow} s for the POCIS, resulting in low uptake rates and less chemical accumulated (Alvarez et al., 2007). These differences, however, are more the exception than the rule.

Chemical-specific sampling rates for the POCIS were available from the literature for 52 of the 227 compounds measured (SI Table S3); these allow estimation of the time-integrated water concentration based on the measured POCIS concentration ; and comparison to mean water concentrations measured during POCIS deployment (SI Table S4). Spearman's rank order correlation coefficients (ρ) indicate good (relative) agreement between POCIS-estimated and mean measured water concentrations for the 18 compounds that were frequently detected in both sample types (50 or more paired detections out of 97 sites; Table 2); however ratios of concentrations indicate generally lower values for POCIS than water (Table 2; SI Figure S2). The median POCIS:water ratio ranges from 0.11 for 2,4-D to 1.5 for tebuconazole and the mean of the medians is 0.50. Thus, on average, the POCIS estimate is about one-half the water concentration.

One possible explanation for lower estimated water concentrations based on POCIS than measured in water samples is that water concentrations in small agricultural streams are highly variable, subject to short-term spikes (pulses) in concentration that occasionally are captured by discrete water samples. The effect that the pulse concentration has on the total amount of chemical sampled (meaning the total ng of a chemical measured in the POCIS) will depend on the response of the sampler (largely a

factor of the sampling rate) and the residence time of the pulse at that location before the water concentration decreases (Gale, 1998). Assuming that, for any given chemical, the POCIS is sampling around 0.19 L/d (the median of reported sampling rates under turbulent conditions) (Harman et al., 2012), the water concentration from a pulse would have to remain elevated for a substantial portion of the POCIS deployment period to account for the majority of the concentration of the pulse (Gale, 1998). Thus, it is perhaps not surprising that, in these small streams, the POCIS concentrations tend to be lower than the mean water concentrations. It also is worth noting that POCIS sampling rates reported in the literature often vary between laboratories by a factor of two or more (see, for example, (Ahrens et al., 2015; Alvarez et al., 2007)).

Several studies have compared chemical concentration estimates from POCIS to direct measurements in water samples. Petty et al. (2004) reported a POCIS-estimated water concentration of 930 ng/L for atrazine in the Missouri River compared to 1,160 ng/L in a water sample collected at a nearby site. Diuron was measured in POCIS and discrete water samples collected concurrently at several sites in the River Thames (United Kingdom); POCIS estimates were 1.1- to 1.7- fold higher than measured instantaneous concentrations in water (Alvarez et al., 2004). Bayen et al. (2014) reported good correlations (approximately 1:1) between concentrations in POCIS and mean concentrations in filtered grab samples for chemical contaminants, including pesticides and pharmaceuticals, in tropical waters. Other studies have focused on comparing detections, rather than concentrations, between POCIS results and water samples (Alvarez et al., 2005; Kolpin et al., 2013). In these studies, there often was a high degree of variability in the presence and measured concentration of chemicals in the water

samples relative to the presence of chemicals in the POCIS, which is similar to the variability observed in the MSQA study presented here.

In at least one case, the POCIS recorded a signal of hydrophobic pesticides that was not indicated by water sampling. Pyrethroid insecticides are hydrophobic and only a single pyrethroid (bifenthrin) was included in the DAI LC-MS/MS method used here; moreover, recovery of bifenthrin was mediocre (mean of 62%). Because of its hydrophobicity ($\log K_{ow}=8.15$, www.chemspider.com), bifenthrin is not expected to be present at appreciable concentrations in the dissolved phase, as evidenced by its detection in only one water and one POCIS sample. However, two polar degradates of the pyrethroids bifenthrin, cyhalothrin, tefluthrin, and permethrin were frequently detected in POCIS, although rarely in water: cis-cyhalothric acid ($\log K_{ow}=2.44$, www.chemspider.com) was detected in 46% of POCIS but at only one site in water, and 3-phenoxybenzoic acid ($\log K_{ow}=3.93$, www.chemspider.com) was detected in 18% of POCIS but was not detected in any water samples. The $\log K_{ow}$ values for these compounds are in the optimal range for uptake by POCIS ($\log K_{ow}<4$), and we hypothesize that the higher frequency of detection of the pyrethroid degradates in POCIS, relative to water, is a result of the integrative nature of the POCIS, which might pick up an occurrence signal when concentrations in individual discrete samples are below the method detection limits.

3.2 Comparison to Bed Sediment

Of the 117 pesticides analyzed in bed sediment, 17 were detected at least once and 6 of those were detected in 10% or more of samples: in order of decreasing detection frequency, metachlor, bifenthrin, p,p'-DDE, atrazine, metalaxyl, and dithiopyr (SI Table

S5). Dithiopyr and p,p'-DDE were not analyzed in POCIS. The herbicides metachlor and atrazine, detected in 49 and 19% of sediment samples, respectively, were detected in 100% of POCIS, often at relatively high concentrations. The fungicide metalaxyl was detected in 15% of sediment samples and in 100% of POCIS. The insecticide bifenthrin was detected in 44% of sediment samples and in only one POCIS sample, however, a pyrethroid degradate was detected in 53% of POCIS. Two other pyrethroids, cyhalothrin and tefluthrin, were analyzed in sediment but not detected. Spearman's rank correlations between sediment and POCIS for the 94 sites that were successfully sampled for both were significant ($p > 0.5$) for metachlor, atrazine, and bifenthrin/pyrethroid degradates, but not for metalaxyl.

3.3 Relations to Watershed Variables.

Summations of concentrations of pesticides in POCIS by pesticide use groups are different between urban and agricultural settings (Figure 4). On the basis of the Mann-Whitney U test, summations of concentrations for most use groups (parent and degradate compound groups treated separately) were significantly different between urban and agricultural stream sites (SI Table S6). Herbicide concentrations were greater in streams with agricultural watersheds and fungicide and insecticide concentrations were greater in streams with urban watersheds, which also is apparent in map view (Figure 1). The differences for fungicides and insecticides are especially large, with median concentrations of the sum of all pesticide parents and degradates about 10 and 25 times greater in urban watersheds than in agricultural watersheds, respectively. Imidacloprid, which dominates total insecticide concentrations, has median concentrations of 956 and 32 ng/POCIS at urban and agricultural-gradient sites, respectively (SI Table S6).

Relations to watershed variables were tested using Spearman's rank correlation and two types of relations are indicated: those associated with likely source areas and those associated with factors affecting chemical transport (SI Table S7). Significant relations ($p\text{-value} < 0.05$) to cropland are indicated for total herbicides and herbicide degradates, but not for parent herbicides. Stronger relations to land use are indicated for fungicides and insecticides, especially for fungicide degradates ($\rho = 0.63$) and insecticide degradates ($\rho = 0.62$) in relation to urban land use. We interpret these relations as being source-driven, in that cultivated crops and urban land use are surrogates for chemical use. Three other variables, all of which affect transport of chemicals to streams, have significant relations to some of the pesticide summations in POCIS: extent of subsurface tile drains, base-flow index, and soil permeability (SI Table S7). Relations to tile drains are positive, suggesting that artificial drainage facilitates transport of agricultural chemicals to streams. Relations to base-flow index, an indicator of the contribution of groundwater inflow to the streams, are negative, suggesting that streams with a greater proportion of surface runoff (less base flow) are more likely to be contaminated with pesticides. Soil permeability is related to base-flow index, in that higher soil permeability contributes to more infiltration, in turn contributing to groundwater base flow, and, like the base-flow index, it also correlates negatively to most pesticide variables. The effects of these transport variables might be why some sites in less intensively agricultural parts of the region (e.g., Missouri, southern Illinois, and southern Indiana) had higher pesticide concentrations than some sites in the most intensively agricultural parts of the region (e.g., southern Minnesota and Iowa) (Figure 1). An exception to the relations between insecticides and watershed variables is for pyrethroid degradates, which relate only

weakly to urban land use and are not significantly related to transport variables (SI Table S7). This might reflect application of pyrethroids in both urban and agricultural areas (Weston and Lydy, 2010) and the hydrophobic nature of these chemicals, which likely alters transport properties relative to more soluble compounds.

3.4 Potential Effects on Stream Biota.

For those pesticides with POCIS sampling rates, POCIS results provide estimates of time-weighted mean concentrations in water during the ~5-week POCIS deployment period. Comparison with aquatic-life benchmarks and toxicity thresholds suggests that chronic effects on aquatic organisms caused by exposure to sublethal concentrations of pesticides are of potential concern in some MSQA streams. Atrazine, detected in 100% of POCIS samples, has been shown to impair reproduction in fathead minnow (*Pimephales promelas*) and Japanese medaka (*Oryzias latipes*) by reducing egg production upon exposure to concentrations as low as 0.5 µg/L (Papoulias et al., 2014; Tillitt et al., 2010). In those studies, significant decreases in egg production were observed by day 18 for fathead minnow and by day 24 for medaka. For the MSQA study, POCIS-estimated average atrazine concentrations at 15 of the 97 sites were greater than the 0.5 µg/L threshold, indicating the potential for impaired reproduction of aquatic species in 16% of the streams studied. As noted above, the POCIS-estimated concentrations in water are lower on average than measured mean water concentrations; 37 sites had mean atrazine concentrations in water >0.5 µg/L during POCIS deployment.

Insecticides and fungicides generally are more toxic to invertebrates than herbicides, thus, although herbicides generally occur more frequently and at higher concentrations, insecticides and fungicides have been shown to contribute more to potential toxicity

(Nowell et al., 2014). Among the insecticides of concern, because of the combination of toxicity and their widespread use and occurrence, are organophosphates, neonicotinoids (Gibbons et al., 2015; Hladik and Kolpin, 2016), pyrethroids (Kuivila et al., 2012), and fipronil (Budd et al., 2015; Stone et al., 2014), all of which were detected frequently in the MSQA study (SI Table S2). The analytical methods used for the MSQA study in water and POCIS extracts measure 19 organophosphates and 30 organophosphate degradates, one neonicotinoid (imidacloprid), two pyrethroids (bifenthrin and cis- and trans-permethrin) and two pyrethroid degradates, and fipronil and seven fipronil degradates.

Organophosphates are an important class of pesticides used in agriculture. Of the 49 organophosphate insecticides and degradates measured in this study, the most frequently detected in water and POCIS, respectively, were diazinon (18 and 49%), tebufos (21 and 28%), and malathion (4 and 20%) (SI Table S2). The USEPA has established acute and chronic invertebrate benchmarks for 17 of the 19 parent organophosphate pesticides measured (<https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration>). The only exceedances of any benchmarks based on the POCIS-estimated water concentrations were for malathion. Comparison of POCIS-estimated water concentrations to benchmarks is done as a screening assessment only because of the large uncertainty in these concentrations. The acute benchmark (295 ng/L) was exceeded at 2 sites and the chronic benchmark (35 ng/L) was exceeded at 9 sites; mean concentrations of weekly water samples during POCIS deployment did not exceed these benchmarks (SI Table S4).

The neonicotinoid imidacloprid was reported to be the most widely used insecticide worldwide as of 1999 (Yamamoto, 1999). In agricultural applications, the neonicotinoids are commonly used as a seed treatment. In urban areas, imidacloprid and other neonicotinoids are marketed for control of a wide range of pests (e.g., termites, roaches, Japanese beetles, ants) in turf grass, landscape planting, structural, and indoor applications. Imidacloprid is highly toxic to aquatic invertebrates, but not to fish (USEPA, 2008). Neonicotinoids have been linked to adverse effects on bees (Whitehorn et al., 2012) and aquatic macro-invertebrate communities (Van Dijk et al., 2014). The USEPA has established acute and chronic invertebrate benchmarks of 34.5 and 1.05 µg/L, respectively, for imidacloprid (<https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration>). None of the POCIS-estimated water concentrations exceeded the acute or chronic benchmarks (SI Table S4). Van Dijk et al. (2014) reported that macrofauna abundance drops sharply at 13–67 ng/L imidacloprid and concluded that a norm of 13 ng/L “seems somewhat protective” of aquatic life, although a separate analysis concluded that the effects of imidacloprid could not be isolated from those of other stressors in field studies because of collinearity (Vijver and van den Brink, 2014). Based on POCIS-estimated water concentrations, 28 and 6 sites had average imidacloprid concentrations that exceeded 13 and 67 ng/l, respectively.

Fipronil is a phenylpyrazole insecticide first registered for use in the United States in 1996 to control a wide range of insects, including ants, roaches, termites, and fleas. Home uses include topical pet care products, liquid termiticides, gel baits, and granular turf products (Jackson et al., 2009). Agricultural uses of fipronil in the U.S. primarily are on

maize and turf grass, although very little agricultural use was reported for the MSQA region in 2013 (Baker and Stone, 2014). Fipronil was highly toxic at $\mu\text{g/L}$ concentrations to several aquatic species, including daphnids, mysid shrimp, oysters, fish (USEPA, 1996), copepods (Chandler et al., 2004), and crayfish (Schlenk et al., 2001). Its degradation products fipronil sulfone, fipronil sulfide, and desulfinyl fipronil are more toxic than the parent fipronil to daphnids and fish (Gunasekara and Troung, 2007; Jackson et al., 2009; USEPA, 1996). Fipronil was detected in 89% of POCIS samples but at only 30% of sites in water samples collected during POCIS deployment. We are not aware of a published POCIS sampling rate for fipronil that would allow estimation of water concentration, although mean water concentrations of fipronil indicate that levels in MSQA streams likely were well below toxicity benchmarks for fish and benthic invertebrates (Nowell et al., 2014).

Pyrethroids are used widely in and around households, including on pets, in treated clothing, in mosquito control, and in agriculture (<https://www.epa.gov/ingredients-used-pesticide-products/pyrethrins-and-pyrethroids#reg> review). Pyrethroids are highly toxic to fish and invertebrates (Hill, 1989; Johnson et al., 2010). Because pyrethroids are hydrophobic, they tend to accumulate in sediments. Toxicity of sediments from both agricultural and urban streams to invertebrates, especially the amphipod *Hyaella azteca*, has been attributed to pyrethroids, especially to bifenthrin (Kuivila et al., 2012; Weston et al., 2005; Weston et al., 2004). There is evidence that pyrethroid bioavailability may be reduced by sediment-organic carbon characteristics and aging in some sediments (Johnson et al., 2010). Although bifenthrin was detected only once in a water or POCIS sample in the present study, 67% of MSQA streams had evidence of pyrethroid

occurrence from detection of either bifenthrin in bed sediment (45 streams) or polar pyrethroid degradates in POCIS (51 streams) or both.

4. Conclusions

Results of deployment of POCIS samplers in 97 small streams across the Midwest indicate the occurrence of complex mixtures of pesticides in the streams. The time-integrating nature of the POCIS and the ability of the DAI LC-MS/MS method to detect low levels of compounds resulted in large numbers of detections, with a median of 62 compounds detected per POCIS (site) and a total of 141 compounds detected at one or more of the 97 sites sampled. Almost one-half of the detected compounds were degradates. For the hydrophobic pyrethroid insecticides, the frequent detection of polar degradates in POCIS provided evidence of pyrethroid occurrence in the streams even though the parent pyrethroids were not detected.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGEMENTS

This study was funded by the USGS National Water Quality Program. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government. We wish to thank the many people from U.S.

505 Geological Survey, U.S. Environmental Protection Agency, and the Midwest States who
506 participated in the Midwest Stream Quality Assessment.

507

Figure 1. Maps location of 97 MSQA sites where POCIS samplers were successfully deployed and summations of herbicides (upper) and insecticides plus fungicides (lower). Summations include degradates for the use group. Light brown shade is cropland, pink shade is urban land use. Concentrations were normalized to the mean deployment interval of 37 days.

Figure 2. Frequency distributions by site type for number of detections and summations of concentrations by pesticide use group. Summations are for parent and degradate compounds. Site types refer to selection approach (random or targeted; 49 and 48 sites, respectively) and, within the targeted group of sites, dominant land use in the watershed (37 agricultural gradient sites and 11 urban sites).

Figure 3. Detection frequency of pesticide by use group showing the most frequently detected compounds in POCIS and discrete water samples collected during the POCIS deployment. Water detections reflect a detection in any of the periodic water samples collected at the site during the POCIS deployment period.

Figure 4. Relations between summations of POCIS concentrations by pesticide use group and agricultural and urban land use. Summations are for parent and degradate compounds.

538

Use Group	Analyzed for		Detected (all sites)		Detected (random sites)	
	parent	degradate	parent	degradate	parent	degradate
Fungicides	12	4	10	3	10	3
Herbicides	57	66	46	45	45	41
Insecticides	40	46	19	17	17	16
Other	2		1		1	
Total	111	116	76	65	73	60

539

540 Table 1. Number of compounds analyzed for and detected at least once in POCIS, by use
541 group. “Random sites” are the 49 sites selected following the USEPA’s probabilistic
542 sampling approach (U.S. Environmental Protection Agency, 2013).

543

Pesticide compound	Rho	median
		POCIS:water ratio
2,4-D	0.57	0.11
2-Hydroxyatrazine	0.86	0.61
Acetochlor	0.81	0.38
Ametryn	0.83	0.77
Atrazine	0.83	0.34
Azoxystrobin	0.70	0.12
Bentazon	0.86	0.16
Deethylatrazine	0.79	0.25
Deisopropylatrazine	0.79	0.12
Dimethenamid	0.90	0.40
Diuron	0.68	0.86
Hydroxysimazine	0.89	0.64
Imidacloprid	0.85	0.52
Metolachlor	0.87	0.37
Prometon	0.87	0.53
Propazine	0.85	0.73
Simazine	0.90	0.60
Tebuconazole	0.61	1.5

544

545 Table 2. Spearman’s rank correlation (rho) between POCIS-estimated water
546 concentrations and mean water concentrations and median ratio of those concentrations.
547 All correlations are significant at p-value<0.001.

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