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Complex mixtures of Pesticides in Midwest U.S. streams indicated by POCIS time-integrating samplers☆

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

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1. 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

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

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

2. Study design and methods

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

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