Agriculture, Ecosystems and Environment 193 (2014) 83–95

Contents lists available at ScienceDirect

Agriculture, Ecosystems and Environment

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

Annual and seasonal differences in pesticide mixtures within channelized agricultural headwater streams in central Ohio

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ARTICLE INFO

Article history:
Received 17 September 2013
Received in revised form 18 April 2014
Accepted 25 April 2014
Available online 17 May 2014

Keywords:
Herbicides
Fungicides
Water quality
Headwater streams
Agriculture

ABSTRACT

Only a limited amount of information on pesticide mixtures within agricultural headwater streams is available. A greater understanding of the characteristics of pesticide mixtures and their spatial and temporal trends within agricultural headwater streams is needed to evaluate the risks of pesticide mixtures. We measured concentrations of 13 pesticides within seven channelized agricultural headwater streams in central Ohio for 5 years to document what types of pesticide mixtures occur, trends in pesticide mixtures with increasing watershed size, and annual and seasonal trends in pesticide mixtures. Pesticide mixtures consisted mostly of combinations of herbicides or herbicides and fungicides. Only one of 14 response variables differed between watershed sizes. Seasonal trends in the percent occurrence, complexity, concentration, and types of pesticide mixtures differed annually. Our results suggest channelized agricultural headwater streams with watershed sizes ranging from 0.7 to 4.5 km^2 will exhibit greater temporal variation than spatial variation in pesticide mixtures.

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1. Introduction

Seasonal trends in concentrations of individual pesticides (i.e., herbicides, fungicides, and insecticides) within agricultural streams in the Midwestern United States are well known. Pre-emergent applied herbicides exhibit increased concentrations following the first rainfall after spring pesticide applications (Thurman et al., 1991; Richards and Baker, 1993; Lerch et al., 2011a,b). Fungicides are typically used as a protective measure and applied multiple times throughout the year (Battaglin et al., 2011; Reilly et al., 2012). Insecticides are applied throughout the year on an as needed basis to control for pest outbreaks (Larson and Gilliom, 2001). Stream concentrations of individual fungicides and insecticides also exhibit increases following rainfall events after application, but these increases are not limited to a specific season like for herbicides (Wauchope, 1978; Larson and Gilliom, 2001). These seasonal trends in pesticide concentrations within agricultural streams result in these streams periodically exceeding the drinking water and aquatic life criteria (Battaglin et al., 2005; Gilliom, 2007; Smiley and Gillespie, 2010; Smiley et al., 2010, 2012; Lerch et al., 2011b). Pesticide concentrations also differ spatially within agricultural streams as those with smaller watershed sizes typically exhibit greater maximum concentrations and greater variability in concentrations of individual pesticides than streams with larger watershed sizes (Richards and Baker, 1998; Baker and Richards, 2000; Crawford, 2001).

A nationwide assessment of pesticides within large streams and rivers in the United States indicated that pesticides occur more often in streams as pesticide mixtures (i.e., combinations of two or more pesticides) than as individual pesticides (Gilliom, 2007). Thus, our understanding of the impacts of pesticides on stream ecosystems is limited because it is based on what is known about individual pesticides, not pesticide mixtures. There are only a few studies that have documented the trends in pesticide mixtures within agricultural streams. Findings from the United States (Belden et al., 2007; Gilliom, 2007) and Europe (Schafer et al., 2013) suggest that within large agricultural streams and rivers pesticide mixtures will frequently contain 10 or fewer pesticides and will frequently contain herbicides. Research findings from small agricultural headwater streams in the United States have also documented the frequent occurrence of pesticide mixtures with 10 or fewer pesticides (Reilly et al., 2012; Smiley et al., 2012). Additionally, mixture concentrations (sum of all pesticide concentrations in a mixture) and the composition of pesticide mixtures have been observed to change seasonally within agricultural streams in the Midwestern United States and Europe (Thurman et al., 1991; Polard et al., 2011).

Our current understanding of pesticide mixtures comes mostly from research conducted in large agricultural streams and rivers (Thurman et al., 1991; Gilliom, 2007; Belden et al., 2007; Battaglin

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http://dx.doi.org/10.1016/j.agee.2014.04.022
0167-8809/Published by Elsevier B.V.

et al., 2011; Polard et al., 2011; Schafer et al., 2013). More information on pesticide mixtures within agricultural headwater streams is needed, particularly from channelized agricultural headwater streams. Channelized agricultural headwater streams (i.e., agricultural drainage ditches) are first, second, and third order streams have either been modified or created for draining excess water from adjacent agricultural fields. Subsequently, these streams exhibit physical and chemical habitat degradation that includes loss of riparian habitat, loss of instream habitat, altered hydrology, increased nutrient loadings, and pesticide contamination as a result of channelization, use of subsurface tile drains, and current nutrient and pesticide application practices. Despite the degraded habitat conditions many channelized agricultural headwater streams serve as habitat for fishes and other aquatic animals (Smiley and Gillespie, 2010; Smiley et al., 2010, 2011, 2012). Channelized agricultural headwater streams are common within agricultural watersheds throughout the United States, Canada, and Europe (Smiley and Gillespie, 2010). In Ohio these small streams receive protection under Ohio's National Pollutant Discharge Elimination System and the Clean Water Act section 401 Water Quality Certification programs.

Pesticide mixtures represent a threat to the biota within agricultural streams because of the potential for the toxicity of pesticide mixtures to be greater than that of individual pesticides, even at concentrations below the aquatic life criteria (Lydy et al., 2004; Schwarzenbach et al., 2006; Belden et al., 2007; Battaglin et al., 2011). A greater understanding of the characteristics of pesticide mixtures and how these characteristics fluctuate temporally and spatially within agricultural streams are needed to fully characterize the exposure to pesticide mixtures that the biota within agricultural streams experience. Understanding the characteristics of pesticide mixtures and their subsequent temporal and spatial trends within agricultural streams is a critical first step in evaluating the risks of pesticide mixtures and can contribute to developing watershed management plans to restore these degraded streams and protect downstream drinking water sources. Thus, we sampled water from nine sites within seven channelized agricultural headwater streams in central Ohio over a 5 year period to document the characteristics of pesticide mixtures within channelized agricultural headwater streams. We address the following research questions: (1) *What type of pesticide mixtures occur in channelized agricultural headwater streams?*; (2) *Does watershed size influence pesticide mixtures within channelized agricultural headwater streams?*; and (3) *Do pesticide mixtures change annually or seasonally within channelized agricultural headwater streams?*

2. Materials and methods

2.1. Study area and sampling sites

Upper Big Walnut Creek (UBWC) is located in central Ohio (Fig. 1) and is part of the Scioto River watershed. Cropland consisting of corn and soybean is the dominant land use in the UBWC watershed. UBWC watershed is located in the humid continental, hot summer climatic region of the United States. Daily temperatures range from an average minimum of −9.6 °C in January to an average maximum of 33.9 °C in July (King et al., 2008). Mean annual total precipitation within the watershed during our study ranged from 903 mm to 1334 mm (Table 1). Seasonal trends in mean total precipitation differed annually and the greatest seasonal means occurred either the early spring (2007, 2011) or late spring (2008, 2009, 2010) (Table 1). Thunderstorms during the spring and summer produce short duration intense rainfalls. Moisture from December to March occurs primarily in the form of frozen precipitation or snow.

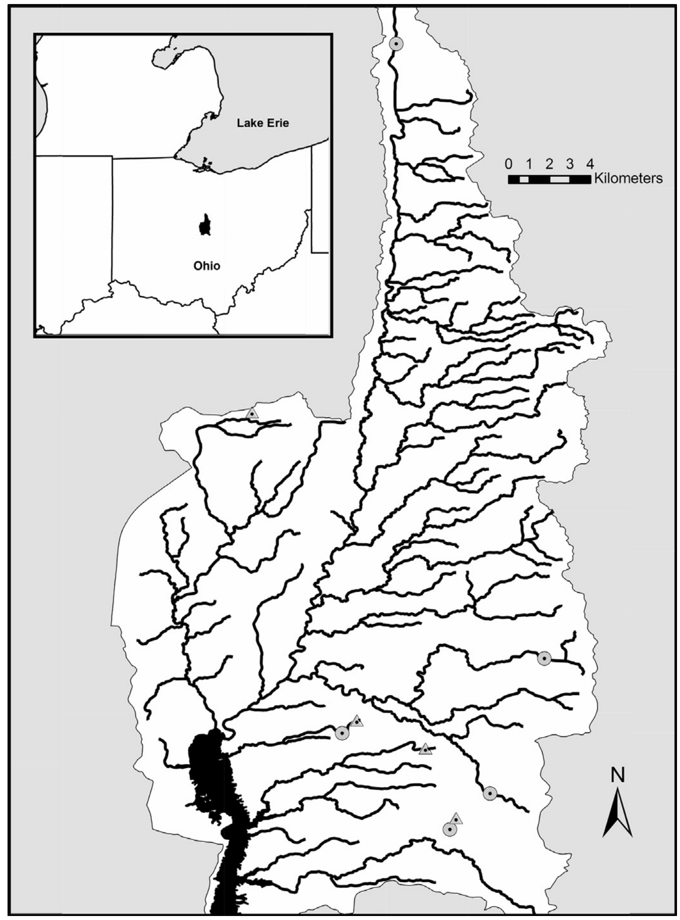

Fig. 1. Location of sampling sites within channelized agricultural headwater streams in the Upper Big Walnut Creek watershed, Ohio. Triangles indicate streams with small watershed sizes (mean 1.3 km^2) and circles indicate streams with large watershed sizes (mean 4.1 km^2). The symbols have been sized to ensure their clarity and do not reflect actual site sizes or distances between sites. The inset map depicts the location of the Upper Big Walnut Creek watershed within Ohio.

The majority of headwater streams in the UBWC watershed are impaired by nutrient enrichment, pathogens, and habitat degradation stemming from current agricultural management practices (Ohio EPA, 2005). Pesticides are also a critical environmental issue within the UBWC watershed. Herbicides are contaminants of concern statewide within Ohio because of the occurrence of elevated herbicide concentrations within surface drinking water supplies (Ohio EPA, 2008, 2010). Herbicide concentrations within UBWC headwater streams and its downstream reservoir have periodically exceeded the drinking water standards (Malcolm Pirnie, 1999; Smiley and Gillespie, 2010; Smiley et al., 2010, 2012).

Table 1
Mean (SD) of total precipitation (mm) occurring within the Upper Big Walnut Creek watershed, Ohio in late winter (January–February), early spring (March–April), late spring (May–June), summer (July–August), fall (September–October), early winter (November–December), and annually (January–December) from 2007 to 2011.

Season	2007	2008	2009	2010	2011
Late winter	129 (12)	128 (28)	74 (8)	51 (16)	102 (17)
Early spring	220 (19)	193 (26)	141 (13)	105 (33)	284 (25)
Late spring	130 (21)	323 (26)	242 (39)	272 (41)	222 (26)
Summer	198 (15)	80 (15)	239 (19)	190 (19)	223 (32)
Fall	203 (11)	95 (25)	208 (22)	132 (17)	252 (27)
Early winter	183 (8)	171 (16)	91 (4)	153 (21)	250 (22)
Annual	1062 (51)	989 (87)	995 (74)	903 (118)	1334 (103)