Science of the Total Environment xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Science of the Total Environment

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

Similarities and differences in occurrence and temporal fluctuations in glyphosate and atrazine in small Midwestern streams (USA) during the 2013 growing season

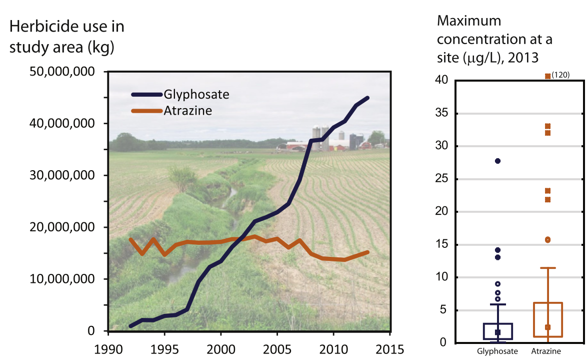
Barbara J. Mahler [a,*], Peter C. Van Metre [a], Thomas E. Burley [a], Keith A. Loftin [b], Michael T. Meyer [b], Lisa H. Nowell [c]

[a] U.S. Geological Survey, 1505 Ferguson Lane, Austin, TX 78754, USA
[b] U.S. Geological Survey, 4821 Quail Crest Blvd., Lawrence, KS 66049, USA
[c] U.S. Geological Survey, 6000 J Street, Placer Hall, Sacramento, CA 95819, USA

HIGHLIGHTS

- Glyphosate > atrazine in 12 urban streams and < atrazine in 88 agricultural streams
- Peak levels of both herbicides in 2-day samples were missed by weekly samples.
- Peak concentrations in 2-day samples were consistent with a spring-flush mechanism.
- Concentrations exceeded aquatic-life benchmarks for atrazine but not glyphosate.
- Use of ELISA resulted in negligible bias relative to LC-MS/MS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 August 2016
Received in revised form 14 October 2016
Accepted 15 October 2016
Available online xxxx

Editor: D. Barcelo

Keywords:
ELISA
Spring flush
Corn Belt

ABSTRACT

Glyphosate and atrazine are the most intensively used herbicides in the United States. Although there is abundant spatial and temporal information on atrazine occurrence at regional scales, there are far fewer data for glyphosate, and studies that compare the two herbicides are rare. We investigated temporal patterns in glyphosate and atrazine concentrations measured weekly during the 2013 growing season in 100 small streams in the Midwestern United States. Glyphosate was detected in 44% of samples (method reporting level 0.2 μg/L); atrazine was detected above a threshold of 0.2 μg/L in 54% of samples. Glyphosate was detected more frequently in 12 urban streams than in 88 agricultural streams, and at concentrations similar to those in streams with high agricultural land use (>40% row crop) in the watershed. In contrast, atrazine was detected more frequently and at higher concentrations in agricultural streams than in urban streams. The maximum concentration of glyphosate measured at most urban sites exceeded the maximum atrazine concentration, whereas at agricultural sites the reverse was true. Measurement at a 2-day interval at 8 sites in northern Missouri revealed that transport of

Abbreviations: MSQA, Midwestern Stream Quality Assessment; POEA, polyethoxylated amines; IARC, International Agency for Research on Cancer; EFSA, European Food Safety Authority; USGS, U.S. Geological Survey; EPA, U.S. Environmental Protection Agency; NRSA, National Rivers and Streams Assessment; ELISA, enzyme-linked immunosorbent assay; TxWSC, Texas Water Science Center; AMPA, aminomethylphosphonic acid; DEA, deethylatrazine; MRL, method reporting level; OGRL, Organic Geochemistry Research Laboratory; LC-MS/MS, liquid chromatography tandem mass spectrometry; NWQL, National Water Quality Laboratory; QC, quality control.

* Corresponding author.
E-mail addresses: bjmahler@usgs.gov (B.J. Mahler), pcvanmet@usgs.gov (P.C. Van Metre), teburley@usgs.gov (T.E. Burley), kloftin@usgs.gov (K.A. Loftin), mmeyer@usgs.gov (M.T. Meyer), lhnowell@usgs.gov (L.H. Nowell).

http://dx.doi.org/10.1016/j.scitotenv.2016.10.236
0048-9697/Published by Elsevier B.V.

Herbicide
Glyphosate
Atrazine

both herbicide compounds appeared to be controlled by spring flush, that peak concentration duration was brief, but that peaks in atrazine concentrations were of longer duration than those of glyphosate. The 2-day sampling also indicated that weekly sampling is unlikely to capture peak concentrations of glyphosate and atrazine.

1. Introduction

Glyphosate and atrazine are the most heavily used herbicides in the United States, where about 135 million and 32 million kg of glyphosate and atrazine, respectively, were applied in 2013 for agricultural use (U.S. Geological Survey, 2015). Use of glyphosate in the United States surpassed that of atrazine in the late 1990s, concurrent with glyphosate coming off patent and the introduction of genetically modified glyphosate-resistant crops. From 2000 to 2013, glyphosate use in the United States increased about 170% (Benbrook, 2016) while atrazine use remained relatively steady (U.S. Geological Survey, 2015).

Although glyphosate and atrazine both are herbicides, differences in chemical properties, modes of action, and use patterns can affect the magnitude and timing of concentrations in streams. Glyphosate (*N*-[phosphonomethyl] glycine) is a weak organic acid with amine, carboxylate, and phosphate groups, and atrazine is a triazine, a class of nitrogen-containing heterocycles. Glyphosate is substantially more soluble in water than is atrazine (solubilities of 10,000–15,700 mg/L at 25 °C and 35 mg/L at 22 °C for glyphosate and atrazine, respectively (Agency for Toxic Substances and Disease Registry, 2003; Mackay et al., 1997)), but binds more strongly to soil (K_d values of 5–900 mL/g (Capri and Vicari, 2010) for glyphosate and 0.7–52.1 mL/g for atrazine (Ahmad and Rahman, 2009)). Half-lives in water are shorter for glyphosate than atrazine (1.7–142 days for glyphosate (Giesy et al., 2000), 6 months for atrazine (Agency for Toxic Substances and Disease Registry, 2003)). In aerobic soil metabolism tests, the half-life for degradation of glyphosate to aminomethylphosphonic acid (AMPA) was about 2 to 5 days (U.S. Environmental Protection Agency, 2008), compared to a half-life of about 140–150 days for atrazine (ranging from 13–1800 days, as reported in the open literature), producing deethylatrazine (DEA) and other degradates (Farrugia et al., 2016). Glyphosate uptake is through leaves (Giesy et al., 2000); application is foliar, and a surfactant, such as polyethoxylated amines (POEA) (Tush et al., 2013), typically is added to enhance penetration of the leaf cuticle. Glyphosate is classified as a post-emergent herbicide, but increasingly is used pre-emergence in no-till settings (Benbrook, 2016). Atrazine uptake is primarily through the roots (Gibson, 2001; Agency for Toxic Substances and Disease Registry, 2003; Curran and Lingenfelter, 2009) and is a pre-emergent herbicide. Both herbicides are used extensively for agriculture—glyphosate on a range of crops (e.g., corn, soybeans, wheat, and cotton) and atrazine primarily on corn (U.S. Geological Survey, 2015). Glyphosate also is the second most heavily used pesticide in U.S. non-agricultural settings (home/garden and industry/commercial/government) after 2,4-D (2007 estimates) (Grube et al., 2011); an estimated 12 million kg were used in non-agricultural settings in 2013 (Benbrook, 2016). Although atrazine is an ingredient in some "weed and feed" products for sale to homeowners, it is not among the top 10 pesticides used in non-agricultural settings (Grube et al., 2011).

In 2015 glyphosate was classified by the International Agency for Research on Cancer (IARC) as a probable human carcinogen (Group 2A) (International Agency for Research on Cancer, 2015), but shortly afterward the European Food Safety Authority (EFSA) concluded that "the evidence does not support classification with regard to its carcinogenic potential" (European Food Safety Authority, 2015). A primary reason for this was that the IARC considered glyphosate formulations, which include adjuvants, whereas the EFSA considered the active ingredient (pure glyphosate) only (European Food Safety Authority, 2015). The IARC has found sufficient evidence in experimental animals for the carcinogenicity of atrazine, but inadequate evidence in humans for classification as a carcinogen (International Agency for Research on Cancer, 1999).

Glyphosate and atrazine both occur frequently in U.S. streams at low concentrations. Glyphosate is not commonly included in broad-scale pesticide monitoring programs (Battaglin et al., 2005). However, in an aggregation of 2001–10 data from 358 U.S. streams (a range of land uses), glyphosate was detected in 52% of 1508 stream-water samples, with a median concentration of 0.03 μg/L (Battaglin et al., 2014). In the same data aggregation (Battaglin et al., 2014), glyphosate was reported to occur much less frequently in groundwater than in surface water; it was detected in only 5.8% of 1171 groundwater samples collected from 807 U.S. groundwater sites. Although detailed temporal patterns in glyphosate concentrations in streams have not been described, Battaglin et al. (2005) reported similar concentrations in samples collected pre-emergence (May or June) and post-emergence (June or July) from Midwestern streams. In contrast, atrazine occurrence in surface water has been extensively studied, especially in the Midwest (e.g., Thurman et al., 1992; Battaglin et al., 2000; Kalkhoff et al., 2003; Scribner et al., 2005). Atrazine was detected in about 85% of samples collected during 1992–2001 from agricultural streams across the United States (Gilliom et al., 2006), and in 98% of post-application samples collected during the 1990s from Midwestern streams (Scribner et al., 2005). Spring flush—a seasonal pulse of herbicide as a result of precipitation that follows pre-planting herbicide application (Stoeckel et al., 2012)—is a dominant mechanism for transporting atrazine from cropland to surface water, resulting in transitory elevated concentrations (Thurman et al., 1991; Gilliom et al., 2006).

Here, spatial and temporal patterns in concentrations of glyphosate in Midwestern U.S. streams during the 2013 growing season (May–July) are compared with those of the more widely studied atrazine. Concentrations were measured in samples collected weekly from 100 small streams and in samples collected every 2 days from a subset of 8 streams. We evaluate the factors that affect glyphosate and atrazine occurrence and transport and examine the effect of sampling interval on identification of peak concentrations.

2. Methods

2.1. Site selection and study design

As part of the U.S. Geological Survey (USGS) Midwest Stream Quality Assessment (MSQA), in collaboration with the U.S. Environmental Protection Agency (EPA) National Rivers and Streams Assessment (NRSA), 100 sites on wadeable streams (less than about 1 m deep in most of the sampling reach at base flow) across the U.S. Midwestern Corn Belt were selected for sample collection (Supplementary Information [SI] Fig. S-1). Fifty sites were selected by the EPA using the NRSA probabilistic design (random sites) (Olsen et al., 1999); the remaining sites (targeted sites) were chosen to represent urban land use (12 sites) or to fill out a gradient in agricultural land use (38 targeted sites plus the 50 random sites). Watershed characteristics and methods for watershed delineation and sources of land use and other spatial variables are described in SI (Section I; Tables S-1 to S-3). The study area covers 600,000 km^2. MSQA watershed areas ranged from 3.5 to 2900 km^2, except for one site with a watershed area of 6350 km^2; median area was 170 km^2. Mean land use for the MSQA watersheds is 54% row crop, 11% pasture and hay,