Atrazine Transport through a Soil–Epikarst System

R. N. Lerch,* C. G. Groves, J. S. Polk, B. V. Miller, and J. Shelley

Abstract
Row crop and livestock production contaminate soils and groundwater of the karst aquifers within south-central Kentucky’s Pennyroyal Plateau. Transport of atrazine from field application to the epikarstic drainage system beneath a field with active row-crop farming was investigated. The Crumps Cave study site is a shallow autogenic drainage system with a recharge area of ~1 ha that contains two epikarst drains (WF-1 and WF-2) which were monitored for atrazine, deethylatrazine (DEA), and deisopropylatrazine (DIA) concentrations from January 2011 to May 2012. Atrazine concentrations in both drains did not increase above winter background levels for nearly 2 mo after application when levels suddenly spiked and reached peak concentrations for the study during an event in May 2011. Atrazine, DEA, and DIA were detected in 100% of samples, and metabolites accounted for 54 to 94% of the monthly total loads, except in May 2011. Median dealkylated metabolite/atrazine ratios (DMAR) were ~5:1 at both sites, and seasonal DMAR patterns corresponded with changes in soil temperature. These data support the hypothesis that a combination of sorption and degradation in the soil column above the epikarst controlled the transport of atrazine and its metabolites. This resulted in delayed atrazine transport after application and prolonged transport of atrazine and its weakly sorbed metabolites to the epikarst aquifer. Management practices that reduce herbicide inputs, such as diverse crop rotations, cover crops, and use of low-rate and strong-sorbing herbicides, would improve groundwater quality in areas of the Corn Belt with intensive row cropping on karst topography.

Core Ideas
- Atrazine leaching to the epikarst was comparable with surface runoff losses.
- Sorption and degradation in soil controlled atrazine transport.
- After 10 mo, atrazine concentrations showed zero-order kinetic declines.

Because of their vulnerability to contamination, karst aquifers in the United States have been significantly affected by contaminants derived from agricultural production (Pasquarell and Boyer, 1996; Currens, 2002; Panno and Kelly, 2004; Karz et al., 2009; Lerch, 2011). Karst aquifers are major drinking water sources throughout the United States and worldwide (Worldwatch Institute, 2007), and, therefore, contaminant concentrations exceeding maximum contaminant levels (MCLs) are a threat to human health. In addition, cave-adapted organisms (i.e., stygobites and troglobites) may also be harmed by the presence of these contaminants in cave streams and drip waters (Elliott, 2000), leading to degraded karst ecosystems. In contrast with many other types of groundwater systems, karst aquifers are often easily contaminated and of low quality, despite their importance as drinking water sources.

Agricultural production has affected the land use and water quality of the highly developed karst landscape–aquifer systems within Kentucky’s western Pennyroyal region (WPR) (Fig. 1). Gently dipping limestones of the Mississippian-aged Ste. Genevieve and St. Louis Formations have been modified through dissolution by flowing groundwater, and the resulting high-permeability aquifers allow contaminants to enter groundwater with relatively little attenuation. Within the WPR, land use associated with row crop and livestock production has contaminated groundwater with fecal bacteria, pesticides, and nutrients (Currens, 2002). Typical of many karst systems, the WPR is an internally drained region with headwater channels in sinkholes as the main surface drainage features, and higher order stream drainage networks are almost wholly lacking. In these systems, most precipitation flows through the headwater channels and drains to an insurmountable (a point at which water enters subsurface conduits) or directly infiltrates, moving through the soil to the epikarst (soil–bedrock boundary) and then into the highly permeable limestone aquifer.

The epikarst zone (Williams, 2008) represents a portion of the karst recharge pathway in which a shallow, perched saturated region occurs at the soil–bedrock boundary. This perched water table drains under the influence of gravity through the

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vadose zone below and then eventually reaches the main aquifer. Epikarstic zones are common in karst flow systems, as they do not require a lithologically distinct perching layer to create locally saturated conditions. In soil-covered karst settings like in the WPR, water moving from the soil into limestone fractures typically is undersaturated with respect to calcite, resulting in limestone dissolution and widening of existing fractures in the upper bedrock. Ultimately, water in the epikarstic zone may drain to the main part of the aquifer through a few discrete fractures in the bedrock, referred to as epikarst drains. Often, the rate of recharge entering the epikarstic zone exceeds the drainage rate, resulting in a perched saturated zone, with variable storage as the input and output rates vary over time (Perrin et al., 2003; Williams, 2008). Recharge to the perched water table can transport contaminants present in the soil to these epikarst drains.

Atrazine [6-chloro-N-ethyl-N’-(1-methylethyl)-1,3,5-triazine-2,4-diamine] and other herbicides have been shown to affect groundwater quality in karst systems as either dissolved-phase or sediment-bound contaminants (Pasquarell and Boyer, 1996; Currens, 2002; USGS, 2002; Panno and Kelly, 2004; Iker et al., 2010; Lerch, 2011). Lerch (2011) reported that detection frequency of atrazine and two of its metabolites, deethylatrazine (2-chloro-4-amino-6-isopropylamino-s-triazine, DEA) and deisopropylatrazine (2-chloro-4-ethylamino-6-amino-s-triazine, DIA), in losing stream systems ranged from 36 to 95%, and median DEA concentrations were similar to, or greater than, atrazine. Iker et al. (2010) also reported greater DEA concentrations than atrazine over a 1-yr period in a karst spring located in northeastern Iowa. These studies indicated that a portion of the atrazine inputs were degraded in soil prior to transport (Adams and Thurman, 1991). Adams and Thurman (1991) observed greater DEA concentrations entering groundwater than parent atrazine and proposed that the molar ratio of DEA/atrazine (DAR) was an indicator of atrazine residence time in soil. Within the Green River watershed of Kentucky, atrazine was detected in 100% of eight springs sampled, and it had the highest median concentration among the seven herbicides investigated (USGS, 2002). Davidson and Fisher (2007) reported results from a comprehensive study in which samples were collected from ~300 groundwater wells or springs around Kentucky. Results of the study showed that the WPR had the highest frequency of atrazine detections (72%) and the greatest number of sites exceeding the MCL of 3 μg L⁻¹ compared with other regions of the state. These results indicated that some combination of vulnerability to contaminant transport, poor management practices (e.g., spraying over or near sinkholes), and greater row crop intensity on karst topography were important factors to the observed atrazine contamination.

Comparatively little attention has been given to understanding details of the mechanisms by which atrazine and its metabolites enter and are transported through karst systems. In this study, we investigated the hydrologic transport of atrazine from field application to the epikarstic drainage system.
beneath a row-cropped field. Because of the thick residuum soils (~3 m) at the site, the working hypothesis of the study was that soils would exert control on atrazine transport to the epikarst drains. Specific objectives of the research were: (i) to intensively monitor two epikarst drains for the presence of atrazine, DEA, and DIA along with discharge and water chemistry before and after atrazine application in a nearby field; (ii) to use the discharge and water chemistry data in combination with precipitation data to interpret the response time of an epikarst drain to precipitation inputs; and (iii) to use water monitoring data and knowledge of Crumps Cave hydrology and recharge area to interpret transport of atrazine, DEA, and DIA through the soil column and into the epikarst drains. Crumps Cave lies within the WPR and represents a shallow karst aquifer with an epikarstic drainage system fed by autogenic recharge. Although the integrated impact of herbicide application on groundwater has been observed over large areas of mixed land use in karst flow systems draining to springs, this site, for the first time, allows detailed observation of the subsurface behavior of atrazine directly tied to a single application.

Materials and Methods

Site Description

Crumps Cave is a large, horizontal cave located ~1 km northeast of the town of Smiths Grove (37.062° N, 86.198° W) in northern Warren County, Kentucky, at a surface altitude of 194 m. A 1-ha sinkhole contains the entrance to Crump’s Cave, which is formed within the upper part of the St. Louis Limestone (Fig. 1). Bedrock at this site dips ~2° W. Dye tracing established a connection between drainage infiltrating from an adjacent row-crop field and a waterfall in the cave, designated WF-1, establishing a tentative recharge area of ~1 ha. This waterfall is ~25 m below the field’s surface and emerges from the ceiling of Crumps Cave, where water drains from the bottom of the epikarst and into the vadose zone. Water also moves ~200 m laterally, flowing westward along the dip of the bedrock between the field and ceiling of Crump’s Cave (Fig. 1) (Groves et al., 2005). From the standpoint of the drainage network, this upland system is analogous to a headwater stream in a surface drained water system, typically flowing westward along the dip of the bedrock between the karst and into the vadose zone. Water also moves 25 m below the field’s surface and emerges from the ceiling of Crumps Cave, where water drains from the bottom of the epikarst and into the vadose zone. Water also moves ~200 m laterally, flowing westward along the dip of the bedrock between the field and ceiling of Crump’s Cave (Fig. 1) (Groves et al., 2005). From the standpoint of the drainage network, this upland system is analogous to a headwater stream in a surface drained water system, typically flowing westward along the dip of the bedrock between the karst and into the vadose zone.

Water Sample Collection

Two epikarst drains within Crumps Cave were monitored for the presence of atrazine, DEA, and DIA. The main site, WF-1, was equipped with automated samplers and instrumentation to measure discharge and water chemistry. During baseflow periods, grab samples were collected weekly. During high-flow periods, two water samplers were programmed with 8-h resolution but were staggered so that a sample was taken each 4 h. Additional details of the WF-1 sample collection and instrumentation are provided in the supplemental materials and in Miller (2011). The second site, WF-2, did not have instrumentation; grab samples were collected weekly. Samples were collected from January 2011 through May 2012. We analyzed 185 samples from WF-1 and 51 samples from WF-2.

Analysis of Atrazine and Metabolites in Water

Analysis of herbicides in water was performed by C18 solid-phase extraction followed by quantification with gas chromatography–mass spectrometry using external calibration. Although the focus of the study was quantification of atrazine DEA and DIA in water, samples were also analyzed for simazine (6-chloro-N,N,N′-diethyl-1,3,5-triazine-2,4-diamine) and several other herbicides (supplemental materials). Method detection limits were 0.002 μg L⁻¹ for atrazine and DEA, 0.003 μg L⁻¹ for simazine, and 0.013 μg L⁻¹ for DIA. Additional details about the analysis parameters and quality assurance samples are described in the supplemental materials and by Lerch et al. (2015).

Metabolite to Parent Ratios

Using the atrazine and metabolite concentrations, the dealkylated metabolite/parent ratio (DMAR) was computed as

\[ \text{DMAR} = \frac{([\text{DEA}]+[\text{DIA}])}{[\text{atrazine}]} \]  

where [DEA], [DIA], and [atrazine] represent concentration in nanomoles per liter. The DMAR represents an extension of the DAR concept (Adams and Thurman, 1991), as the premise is that chlorinated atrazine metabolites only form because sufficient residence time in soil occurred for microbial activity to dealkylate atrazine. Hydroxylated atrazine metabolites are not useful in this context, since they can form abiotically or biotically in soils, and therefore their presence in groundwater cannot be interpreted unambiguously. The underlying concept was that DAR (or DMAR) values >1 represent sufficient residence time of atrazine within the unsaturated soil zone where soil microbial activity converts it to DEA. Conversely, low DAR (or DMAR) values represent short or no residence time within the unsaturated zone and rapid transport of atrazine to groundwater aquifers. Adams and Thurman (1991) did not include DIA, as it was present only at very low concentrations in their study. However, DIA was always detected in the present study, and it was included in DMAR as a more inclusive means of assessing residence time and microbial degradation of atrazine.

Computations and Statistics

Daily flow-weighted concentrations (FWCs) were computed from the time-based samples collected at WF-1 for the purpose of estimating atrazine, DEA, and DIA loads. For days with more than one sample, each sample concentration was weighted according to its fraction of the total flow for that day. Daily flow-weighted concentrations (FWCs) were computed from the time-based samples collected at WF-1 for the purpose of estimating atrazine, DEA, and DIA loads. For days with more than one sample, each sample concentration was weighted according to its fraction of the total flow for that day.
to the proportion of that day’s flow attributed to the sample, and then the concentrations were summed over all samples collected. For nonsampled days, the FWCs were estimated by linear interpolation between days with observed concentrations. Daily load estimates were then computed by multiplying the daily FWC by the total daily discharge. Five datasets from the study are available (Lerch et al., 2018), including observed herbicide concentrations, daily FWCs and loads, and instantaneous precipitation, discharge, specific conductivity, and temperature data. Since the application rate was not known, atrazine mass balance was based on application rates of 1.12 to 2.24 kg ha⁻¹, and 90% of the recharge area was assumed to be treated. Given its efficacy, atrazine is rarely applied at <1.12 kg ha⁻¹, and the label does not permit a single application to exceed 2.24 kg ha⁻¹. Regression analyses were performed using the FWCs only for days with observed concentrations (i.e., one or more samples were analyzed). Linear and nonlinear regressions were initially performed using SigmaPlot 12.3 (Systat Software, 2012), and final linear regression analyses were done using Microsoft Excel 2013. Water balance calculations used observed rainfall and air temperature data collected near the cave entrance and discharge data at WF-1. Monthly estimates of potential evapotranspiration were computed using the Thornthwaite method (Gupta, 1995). Daily rainfall, total discharge, and potential evapotranspiration were computed and summed for the study period. Water storage was computed by difference [total rainfall – (total discharge + potential evapotranspiration)].

Results and Discussion

Hydrologic Characterization

Discharge, specific conductance, and water temperature at WF-1 all showed rapid responses to precipitation inputs (Fig. 2, Supplemental Fig. S2). Daily discharge at WF-1 ranged from 0.00 to 4.55 L s⁻¹ with a median of 0.05 L s⁻¹ (Fig. 2b). These data were typical of the quick response of discharge and water chemistry at WF-1 and indicated that transport of water from the surface through the soil profile and into the epikarst was extremely fast and very sensitive to precipitation inputs. The computed water balance at WF-1 showed that storage in the epikarst was limited and accounted for only 12% of the precipitation inputs, whereas discharge accounted for 39% of the precipitation. Thus, the WF-1 site represented a setting with fast hydrologic response to precipitation, short travel time from surface to the epikarst, and limited water storage within the epikarstic zone.

Detection Frequency and Concentrations

From January 2011 through May 2012, atrazine, DEA, and DIA were detected in 100% of the samples collected at WF-1 and WF-2 sites (Supplemental Table S1). Simazine was detected in ≥98% of all samples collected at both sites. Other herbicides were detected in 65 to 73% of samples, with similar frequencies between sites (Supplemental Table S1). Median concentrations were very similar between sites, but WF-1 showed a much greater range in concentrations of atrazine, DEA, DIA, and simazine than WF-2 (Fig. 3). Median atrazine concentrations were 0.181 μg L⁻¹ at WF-1 and 0.153 μg L⁻¹ at WF-2, but the maximum concentration at WF-1 was 38.5 μg L⁻¹, whereas it was only 0.834 μg L⁻¹ at WF-2. Atrazine concentrations at WF-1 exceeded the MCL in 12% of samples, but the maximum 60-d running average of 1.97 μg L⁻¹ was below the recently proposed aquatic standard of 3.4 μg L⁻¹ (USEPA, 2016). Similarly for DEA and DIA, WF-1 had peak concentrations (4.45 μg L⁻¹ for DEA and 1.26 μg L⁻¹ for DIA) that were four to six times greater than that observed at WF-2 (Fig. 3). At both sites, median DEA concentrations were greater than that of atrazine, and median DIA concentrations were slightly lower than that of atrazine. Median simazine concentrations were nearly the same at both sites (0.020 μg L⁻¹ at WF-1 and 0.016 μg L⁻¹ at WF-2).
data indicated that herbicide application on nearby cropped fields had a similar impact on the epikarst groundwater quality of both sites, but peak concentrations were attenuated at WF-2. This suggested that compared with WF-1, WF-2 had lower herbicide inputs and/or concentrations were diluted by greater discharge. Although discharge was not measured at WF-2, field observations indicate its peak flow is greater than that of WF-1. Sample collection at WF-2 entailed only grab samples at about weekly intervals, and it is possible that high concentration periods were missed.

**Concentration Dynamics**

Atrazine, DEA, and DIA concentrations varied greatly over time, especially at WF-1, and the data reflected the transport of previously and recently applied atrazine (Fig. 4). From January through April 2011 at both sites, concentrations of all three compounds were consistently low (<0.260 μg L⁻¹) and were in the order DEA > DIA > atrazine. Median concentrations during this time at WF-1 and WF-2, respectively, were: 0.192 and 0.198 μg L⁻¹ for DEA, 0.105 and 0.153 μg L⁻¹ for DIA, and 0.043 μg L⁻¹ for atrazine at both sites. Simazine was also consistently present at both sites during this period (Supplemental Fig. S3). These consistent levels of triazine compounds before application were interpreted as steady-state inputs from soil contaminated by previous atrazine and/or simazine usage within the recharge areas of the two epikarst drains. This residual atrazine and simazine was largely degraded within the soil to DEA and DIA based on the much greater metabolite concentrations present in groundwater during the winter and early spring.

Newly applied atrazine did not appear in the epikarst drains until an event on 2 May 2011, 58 d after application (Fig. 4). From the application date to the early May event, four major discharge events occurred and >2.2 million L of discharge were measured at WF-1, accounting for an estimated 55% of the rainwater inputs during the study (Fig. 4 and 5a). Atrazine concentrations at WF-1 abruptly increased from 0.043 μg L⁻¹ on 29 April to >20.0 μg L⁻¹ on May 2 and peaked at 38.5 μg L⁻¹ on May 3. Atrazine concentrations generally remained at >10 μg L⁻¹ for the next 68 h, then steeply declined to ~1 μg L⁻¹ over the next 18 d. During this early May event, metabolite concentrations reached a maximum of ~1.00 μg L⁻¹, then declined to ~0.500 μg L⁻¹ for DEA and to ~0.300 μg L⁻¹ for DIA. However, peak metabolite concentrations occurred during two small discharge events (peak discharge <1 L s⁻¹) on 24 and 26 May when DEA exceeded 4.00 μg L⁻¹ and DIA exceeded 1.20 μg L⁻¹ (Fig. 5a). From June through October 2011, atrazine concentrations steadily declined to <0.100 μg L⁻¹, whereas metabolite concentrations generally increased throughout the summer and early fall and were present at consistently greater levels than atrazine (Fig. 4). By early September, DIA concentrations declined to <0.100 μg L⁻¹ and, other than minor variations caused by discharge events, this trend continued through May 2012. In contrast, DEA concentrations persisted at ~1.00 μg L⁻¹ until mid-November 2011, when a series of discharge events in late November and early December 2011 initiated an increase in atrazine concentrations and a corresponding decrease in DEA concentrations. The concentration of DEA declined to ~0.060 mg L⁻¹ by the end of November 2011 and then slowly declined to 0.270 μg L⁻¹ by the end of the study in May 2012 (Fig. 5b). From November 2011 until January 2012, atrazine concentrations progressively increased from ~0.100 to ~0.300 μg L⁻¹ and, other than one event in April 2012, it remained steady at ~0.300 μg L⁻¹ through May 2012, 454 d after application. The WF-2 site showed the same general time trends as WF-1, but with greatly constrained peak concentrations of all three compounds (Fig. 4).

There were two major periods in which the transport of atrazine, DEA, and DIA were particularly dynamic; one was from April to May 2011 in association with the recent atrazine application, and the other was from November 2011 through January 2012 (Fig. 5). Before the arrival of the new atrazine at
WF-1, DEA and DIA concentrations showed significant linear increases ($p < 0.01$, $r^2 = 0.19$ for DEA and 0.38 for DIA) during the month of April, whereas atrazine concentrations were generally consistent and did not show a significant linear trend ($p = 0.061$, $r^2 = 0.09$). (Fig. 5a). At WF-2, DEA and DIA concentrations also increased during April 2011, whereas atrazine concentrations remained consistent at $\sim 0.050 \text{ mg L}^{-1}$, but there were too few samples to perform regression analyses (Fig. 4). These trends suggested that some of the recently applied atrazine had degraded to DEA and DIA, which were then transported before the arrival of the new atrazine. Discharge events in November and December 2011 resulted in short- and long-term changes in concentrations (Fig. 5b). The net effect of these events was to increase atrazine concentrations from $<0.100$ to $\sim 0.300 \text{ mg L}^{-1}$ and to substantially decrease metabolite concentrations. By the end of January 2012, atrazine and DEA concentrations were approximately equal ($\sim 0.400 \text{ mg L}^{-1}$), and DIA concentrations decreased to $<0.100 \text{ mg L}^{-1}$. Concentration changes during this period reflected mobilization of atrazine remaining in the system and a decline in metabolite production with the onset of cooler temperatures in fall and winter.

**Loads**

At WF-1, metabolites were the majority of the total load (i.e., atrazine plus metabolites), contributing 54 to 94% of the monthly loads, except in May 2011 (Fig. 6a). Total monthly loads ranged from a low of 11 mg in Oct 2011 to a high of 11,950 mg in May 2011. Atrazine dominated the load only in May 2011, accounting for 91% of the load transported at WF-1 for the month. The load in May 2011 contributed 75% of the total load and 92% of the atrazine transported during the entire study, but only 25 to 30% of the DEA and DIA loads occurred during this month. Monthly loads mirrored the concentration dynamics with the majority of the transport occurring under high discharge conditions from February to May 2011 and from November 2011 to January 2012, with low loads during the summer and early fall.

Cumulative monthly loads showed that the metabolites increased in parallel, but DEA loads were consistently greater than DIA throughout the study (Fig. 6b). In contrast, atrazine cumulative loads were lower than the metabolites from February through April 2011, then dramatically increased in May 2011. Cumulative monthly loads showed two distinct loading rates for all three compounds (Fig. 6b). From February to April 2011, DEA and DIA increased at rates of 200 and 130 mg mo$^{-1}$, respectively, whereas atrazine increased at only 50 mg mo$^{-1}$. However, from May 2011 to May 2012, metabolite rates...
decreased to 150 mg mo$^{-1}$ for DEA and 40 mg mo$^{-1}$ for DIA, whereas atrazine rates increased to 70 mg mo$^{-1}$. These rate differences reflected the greater stability of DEA compared with DIA in the environment (Mills and Thurman, 1994), and the mobilization of stored atrazine observed in late fall 2011. For the study period, the proportions of the total mass transported were 71% as atrazine, 21% as DEA, and 8% as DIA.

Mass balance calculations indicated that the total load of 16.0 g at WF-1 accounted for 0.8 to 1.7% of the atrazine applied within the recharge area. This relative atrazine load was within the range reported for edge-of-field studies (Capel et al., 2001; Ghidey et al., 2005, 2010) and for watershed-scale estimates (Lerch and Blanchard, 2003; Lerch et al., 2011) in which the primary means of transport was by surface runoff. Thus, transport of atrazine and its metabolites to the epikarst drains was of a similar magnitude to that occurring by surface runoff in other agricultural areas of the Corn Belt. One key difference, however, is the timing of atrazine transport through the epikarst compared to surface runoff. The vast majority of atrazine transport by runoff from treated fields occurs within 60 d of application (Ghidey et al., 2005, 2010). In watersheds dominated by runoff, atrazine transport to streams occurred over a 50- to 100-d period with little or no transport in fall and winter months (Lerch et al., 2011). In contrast, atrazine and metabolite transport from a treated field to the epikarst will occur over a period of years. From January to May 2012, the concentration data exhibited slow (zero-order kinetic) declines for all three compounds at WF-1 and significantly increasing atrazine concentrations ($p = 0.044$) at WF-2 (Fig. 4), indicating that additional transport would continue for months to years beyond the duration of this study. Using linear regression to estimate the zero-order rate constants, half-life values at WF-1 were 392 d for atrazine, 263 d for DEA, and 160 d for DIA. At these rates, it would take 130 to 630 d beyond the end of this study before the compounds reached concentrations equal to their limits of detection.

**Metabolite to Atrazine Ratios**

Both sites had similar seasonal DMAR patterns and nearly equal averages (5.4 at WF-1 and 5.3 at WF-2) over the study (Fig. 7). From late January through April 2011, DMAR values ranged from 5 to 12, demonstrating substantial residence time and degradation of atrazine and/or simazine (Supplemental Fig. S2 and S3) in soil from previous application within the recharge area. In May 2011, DMARs dropped to <1 due to the breakthrough of recently applied atrazine; however, DMARs increased to ~2 by early June, indicating rapid formation and transport of metabolites. From late May to early November 2011, DMARs at both sites steadily increased, reaching a maximum of 23 at WF-1 and 11 at WF-2, and were strongly related to soil temperature. Atrazine present in the soil was subject to continual microbial degradation during this time as soil temperatures were generally >15°C. Summer ratios reached nearly twice that of ratios in the winter preapplication period, showing that the metabolites dominated the transport through the course of the summer and early fall. From mid-November 2011 to January 2012, DMARs rapidly declined to ~2 at both sites. This reflected the mobilization of stored atrazine in late fall and early winter in combination with decreased metabolite formation as soil temperatures declined. Despite the seasonal increase in soil temperatures from January through May 2012, DMARs remained in the range of 1.1 to 4.0 and were much lower than the range observed during the preapplication period a year earlier.

The DMARs and the concentration data support the hypothesis that the soils controlled atrazine transport as opposed to fast transport to the epikarst aquifer and subsequent storage before eventual breakthrough to the cave. In this setting, the thick residuum soils controlled atrazine transport by a combination of sorption and degradation as it migrated through the soil profile. Paraiba et al. (2003) developed an herbicide leaching model based on this concept in which each soil horizon is assigned a sorption intensity and degradation rate based on its properties. Evidently, much of the atrazine stayed in the biologically active soil zone during 2011, where it was degraded and subsequently transported as metabolites. By 2012, however, the combination of low DMARs and slowly declining concentration kinetics of atrazine and metabolites suggested that much of the atrazine had migrated to the lower portion of the soil column where biological activity was more limited.

**Implications for Management Practices**

Results of this study directly apply to thousands of hectares of cropland within portions of Kentucky, Illinois, Indiana, and Missouri that occur on karst topography with similar autogenic recharge. According to our findings, atrazine loads to karst aquifers in these areas would be comparable with surface runoff losses that occur in other portions of the Corn Belt. Intensively cropped sinkhole plains present unique challenges in terms of implementing effective management practices that can reduce herbicide transport. A particularly relevant aspect of karst aquifer systems is related to the typically high soil infiltration and percolation rates and absence of surface drainage networks. Thus, practices such as vegetative buffer strips and soil incorporation of herbicides that protect surface waters from contaminated runoff (Staddon et al., 2001; Krutz et al., 2005; Ghidey et al., 2010; Lerch et al., 2013, 2017) may not be effective for protecting karst aquifers that are vulnerable to leaching of herbicides and their metabolites. Further, implementation of vegetative buffer strips in cropped sinkholes will not be effective, as only the area immediately surrounding the sinkhole insulation is protected. As this study has shown, leaching through the soil column and
subsequent lateral flow along the bedrock dip would bypass a vegetative buffer strip established around the insurcense. Other management approaches that improve soil quality such as no-till, diversified crop rotations, and the use of cover crops (Veen et al., 2015) may reduce herbicide transport by promoting sorption and degradation, and but relatively slow and incremental improvements in soil quality will not prevent leaching of herbicides and metabolites to karst aquifers in the short term.

For karst aquifer systems, approaches that reduce herbicide inputs, such as use of low-rate and less toxic herbicides and implementation of production systems with diverse crop rotations and cover crops, could immediately reduce the magnitude of offsite transport. Liebman and Schulte (2015) showed that economically viable 3- and 4-yr crop rotations used less than one-tenth the herbicide application rate of a corn–soybean rotation. Cover crops that produce weed-suppressing benzoaxaindioxide could also lead to decreased herbicide inputs (Rice et al., 2012) and to the formation of less toxic herbicide metabolites (Willet et al., 2016). Numerous herbicides are now available for corn and soybean with application rates that are 10 to 1000 times lower than older herbicides. Lastly, the use of strongly sorbing herbicides, such as glyphosate and glufosinate, that degrade to non-toxic metabolites would reduce offsite impacts to karst aquifers.

Conclusions

Atrazine application in an autogenic drainage significantly affected the water quality of epikarst drains within the recharge area. Over the study, atrazine and its metabolites accounted for ∼1% of the applied atrazine, losses comparable with surface runoff in other areas of the Corn Belt. Data supporting the hypothesis that transport of atrazine to the epikarst was controlled by sorption and degradation in the soil profile included: (i) fast hydrologic response to precipitation and limited water storage within the epikarst zone indicating minimal atrazine storage in bedrock pores; (ii) high average DMAIs indicating atrazine degradation in the soil column rather than storage in the bedrock pores where biological activity is limited; (iii) the importance of metabolites to overall transport (DEA and DIA accounted for ∼30% of the total load); (iv) 58-d lag time for new atrazine to appear in the drains indicating sorption in the soil column; and (v) total loads dominated by high flow periods suggesting mobilization of atrazine and metabolites from the soil. The study showed that transport of atrazine and metabolites to epikarst drains occurs over years, resulting in consistent, long-term inputs to the groundwater aquifer.

Supplemental Material

The supplemental material contains additional site description information, sample collection details, and a description of the analytical method for herbicide analyses. Additional data are also presented, including precipitation and hydrologic data for the WF-1 site, a discussion of simazine transport and degradation, and detection frequency data for all herbicides and metabolites measured.

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References


Data Citation