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Letter

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Nitrapyrin in Streams: the First Study Documenting Off-Field Transport of a Nitrogen Stabilizer Compound

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Abstract

Nitrapyrin is a bactericide that is co-applied with fertilizer to prevent nitrification and enhance corn yields. While there have been studies on the environmental fate of nitrapyrin, there is no documentation of its off-field transport to streams. In 2016, 59 water samples from 11 streams across Iowa were analyzed for nitrapyrin and its degradate 6-chloropicolinic acid (6-CPA) along with three widely used herbicides acetochlor, atrazine, and metolachlor. Nitrapyrin was detected in seven streams (39% of water samples) with concentrations ranging from 12-240 ng/L; 6-CPA was never detected. The herbicides were ubiquitously detected (100% of samples; 28 to 16,000 ng/L). Greater nitrapyrin concentrations in streams were associated with rainfall events following spring fertilizer applications. Nitrapyrin persisted in streams for up to five weeks. These results highlight the need for more research focused on the environmental fate and transport of nitrapyrin and the potential toxicity this compound could have on non-target organisms.

Introduction

The application of nitrogen fertilizer has been a long-standing agricultural practice to enhance crop productivity. To improve the efficiency of nitrogen fertilizers, nitrogen stabilizers can be co-applied during field treatment.[1,2] Nitrogen stabilizers are registered for use on corn, wheat, sorghum, and strawberry crops.[3,4] One of the most active (mass used) chemicals present in stabilizer formulations is nitrapyrin (Table 1).[5] Nitrapyrin was first registered in 1964[3] and is a bactericide that inhibits the activity of soil nitrifying bacteria *Nitrosomonas*, thereby limiting the first step of nitrification.[6] With limited nitrification, there is more ammonium (NH_4^+) in the soil root zone available for plant uptake and less nitrate (NO_3^-) available to leach through the soil profile.[6,7] Therefore, applying nitrapyrin with fertilizers can potentially enhance crop production and improve environmental quality by reducing nitrogen mobility off of agricultural fields.[8,9]

Nitrapyrin effectiveness depends on a number of soil characteristics (*e.g.*, temperature, moisture content, organic matter content, and texture)[10] and mode of application (*e.g.*, broadcast on the surface versus soil incorporation, the placement of fertilizer below the soil surface using tillage methods).[11] Soil conditions influence fate and transport processes such as volatilization, photolysis, sorption, degradation, and leaching. Nitrapyrin is moderately sorptive, distribution coefficient (K_d) ranges from 0.95 to 20 L/kg, and it exhibits a low to moderate mobility, octanol-water partition coefficient (log K_{ow}) is 3.4.[12] Nitrapyrin can undergo rapid photolysis and volatilization (around 0.5 days) if not incorporated after application.[11,13] Nitrapyrin also undergoes chemical hydrolysis, a process that increases with increasing soil temperature.[14] Previous research documented a maximum hydrolysis half-life of 1.5 days in warm soils (35°C).[13] Thus, the recommended timing for nitrapyrin applications is in the fall or spring when soil temperatures are near 10°C.[15] Nitrapyrin can persist in soil from 5-92 days.[10] When nitrapyrin degrades, it typically forms 6-chloropicolinic acid (6-CPA; Table 1).[9]

The above chemical properties suggest that the off-field transport of nitrapyrin and persistence in the environment should be limited and may explain the lack of studies on the environmental fate and transport of nitrapyrin.[11,16] To our knowledge, there have been no studies to date investigating the occurrence of nitrapyrin in streams. Such off-field transport of nitrapyrin to streams could have potential direct or indirect effects to corresponding non-target organisms. In terms of human risk, nitrapyrin has been classified as "suggestive evidence of carcinogenic potential" by the United States Environmental Protection Agency (USEPA) and as a "carcinogen and developmental toxin" by the state of California.[4,17]

This reconnaissance study is the first to assess potential off-field transport of nitrapyrin to streams. A total of 59 water samples from 11 sites of varying basin size (12-220,000 km^2; Table S1) across Iowa were collected and analyzed for nitrapyrin and its degradate, 6-CPA. For reference purposes, all samples were also analyzed for three widely used and often detected corn herbicides: acetochlor, atrazine, and metolachlor.[18] The objective of this study was to provide first-ever baseline data for nitrapyrin occurrence in streams, data that are critical for directing future toxicity and ecological studies regarding nitrapyrin.

Materials and Methods

Site selection and sampling

Over 12 million hectares of Iowa are in row crop agriculture, with 5.5 million hectares in corn (*Zea mays* L.) production, the most of any U.S. state.[19] The USEPA reported that corn production accounts for 99% of nitrapyrin usage.[3] Thus, Iowa streams were ideal for determining the potential for off-field transport of nitrapyrin and its degradate 6-CPA. Stream sites were selected according to drainage basin size (12-220,000 km^2) and location (Figure 1). Sites chosen represented small streams to large rivers, as well as spatial distribution across the state.

Grab or depth-width integrated composite 1-L water samples were collected in amber glass bottles.[20] Samples were collected from March to June, 2016 to encompass snowmelt conditions prior to spring fieldwork (to capture residual concentrations that may have persisted from the fall 2015 fertilizer application period), the spring fertilizer application period, corn planting, and the early corn growth period (Figure S1). Four streams (West Branch Wapsinonoc Creek, English River, Old Mans Creek, and Clear Creek) were sampled using a hydrologic-based approach. These streams were sampled both during storm events either at or near peak flow and during base flow conditions. The remaining seven sites were sampled bi-weekly to monthly.

Laboratory extraction and analysis

Upon arrival at the laboratory, all 1-L samples were filtered through baked 0.7 μm glass fiber filters (GF/F, Whatman, Florham Park, NJ) and split for two analyses; 500 mL for nitrapyrin and herbicides using a gas chromatogram (GC) coupled to a mass spectrometer (MS) and 500 mL for 6-CPA using a liquid chromatogram (LC) coupled to a tandem mass spectrometer (MS/MS).

Nitrapyrin and Herbicides analysis

The first 500 mL split was spiked with the surrogate compound di-*N*-propyl-d_{14}-trifluralin (Cambridge Isotope, Andover, MA) at a concentration of 200 ng/L. Samples were processed through an Oasis® HLB solid-phase extraction (SPE) cartridge (6 cc, 500 mg; Waters Corporation, Milford, MA) using a previously described method.[21] The ethyl acetate eluent (12 mL) from the SPE was reduced to 200 μL under nitrogen and spiked with 20 μL internal standard (d_{10}-acenaphthene; Cambridge Isotope). Samples were analyzed on an Agilent (Santa

Clara, CA) 7890 A GC coupled to a 5975 C inert XL EI/CI MS. The limit of detection (LOD) for nitrapyrin was 4 ng/L, and the method reporting limit (MRL) was 12 ng/L. The LODs for acetochlor, atrazine, and metolachlor, were 4 ng/L, 20 ng/L, and 4 ng/L, and the MRLs were 12 ng/L, 60 ng/L, and 12 ng/L respectively. More details on extraction recoveries and the GC/MS conditions are provided in the Supporting Information.

6-CPA analysis

The second 500 mL split was acidified with hydrochloric acid to pH 3 and extracted with an Oasis® HLB SPE cartridge (6 cc, 500 mg). The cartridge was eluted with 12 mL of 99:1 acetonitrile: 1M hydrochloric acid. The eluent was reduced to 200 µL under nitrogen and analyzed on an Agilent 1260 bio-inert LC coupled to a 6430 MS/MS. The measured LOD was 40 ng/L, and the MRL was 120 ng/L. More details on extraction recoveries and the LC/MS/MS conditions are provided in Supporting Information.

Results and discussion

Nitrapyrin was detected at least once at 7 of the 11 sites (Figure 2), with an overall detection frequency of 39% (23 of 59 samples), and concentrations ranging from 12 to 240 ng/L (Table S2). 6-CPA was never detected in any of the samples. The nitrapyrin detection rate was 50% or greater in 5 of the 7 small to medium sized watersheds and was 20 and 33% in two of the larger watersheds (Figure 2, Table S1). In the two remaining large watersheds, Cedar River and Mississippi River, nitrapyrin was not detected. At the sites using a hydrologic-based sampling approach, nitrapyrin was detected more frequently and at higher concentrations than the remaining sites. This is likely due to the nature of the sampling approach (*i.e.*, event-driven samples) and that the basin areas for these sites were much smaller than the remaining sites (Table S1). Previous research has documented a general inverse relation between pesticide concentrations and basin size.[22] The distribution of nitrapyrin throughout the state and its presence in both small streams and large rivers suggests that nitrapyrin is both widely used across Iowa and is available for off-field transport.

Nitrapyrin was not detected in any samples collected during March 2016 prior to the spring application period (Table S2), which included snowmelt conditions (Figures 3, S2, S3). Thus, there does not appear to be carryover of nitrapyrin residues from the previous application in the fall of 2015. It should be noted, however, that record rainfall and runoff occurred across Iowa during December 2015[23] potentially flushing any remaining nitrapyrin residues from the soil. Except for a single nitrapyrin detection at English River on May 28, 2016, which was collected during a large runoff event, all of the nitrapyrin detections occurred between April 6 and May 11 (Table S2). This marks a roughly 5-week window of routine nitrapyrin detections in the streams sampled. Spring anhydrous ammonia applications occurred generally between late March and April, and spring corn planting occurred roughly between mid-April and late May.[24] At West Branch Wapsinonoc Creek (Figure 3) and Old Mans Creek (Figure S3), the first nitrapyrin detection occurred during the anhydrous ammonia application period but before any corn was planted, indicating an immediate response to the co-application of anhydrous ammonia and nitrapyrin. At seven of the sampling sites, detections continued beyond the anhydrous ammonia application period, suggesting that nitrapyrin can be transported off site for several weeks after fertilizer application had ceased. This is in contrast to published literature suggesting limited nitrapyrin persistence and transport as a result of sorption characteristics and chemical degradation.[10,11,12]

The results from this study document a clear temporal pattern to stream nitrapyrin concentrations. Pulses of nitrapyrin in streams were associated with fertilizer applications prior to corn planting and subsequent rainfalls. At West Branch Wapsinonoc Creek (r=0.99, p=0.0001) and English River (r=0.93, p=0.02) a statistical correlation (Pearson) existed between nitrapyrin concentrations (April-May) and stream discharge (Figures 3, S2). At Old Mans Creek (r=0.30, p=0.62) and Clear Creek (r=0.28, p=0.72), (April-May), there was not a statistically significant correlation (Figures S3, S4). At the hydrologic-based sampling sites, higher nitrapyrin concentrations were generally seen during storm events at or near peak flow conditions (Figures 3, S2, S3, S4). Thus, the results of this study indicate that stream nitrapyrin detections corresponded with rainfall events.

The herbicides acetochlor, atrazine, and metolachlor were also measured in these 59 water samples. These herbicides were chosen as a reference because they represent another class of organic pollutants that have a history of heavy usage on corn crops, off-field transport, and high detection frequencies and concentrations in streams.[18] All three herbicides were detected in the samples collected, atrazine and metolachlor were detected in 100% of the samples while acetochlor was detected in 89% of the samples; detected concentrations ranged from 29 to 16,000 ng/L (Table S2). This is in contrast to the more limited detection of nitrapyrin; these herbicides are more widespread and persistent and were detected at much higher concentrations than nitrapyrin. The flush of herbicides into nearby surface waters with spring and summer rainfall events is an annual phenomenon that has been well documented.[18,25]

In terms of environmental toxicity, the nitrapyrin stream concentrations measured (ng/L) were orders of magnitude below the USEPA reported LC_{50} toxicity levels for freshwater vertebrates and invertebrates, 1.7 to 9.3 mg/L.[3] They were also lower than the established minimum toxicity level that can affect non-target soil organisms such as bacteria, fungi, and actinomycetes (10 mg/L) [26] and the toxicity level (0.05 mg/L) for target soil nitrifying bacteria.[7]

However, there are no data on how nitrapyrin in aquatic systems could affect downstream microbial communities. Repeated exposure to nitrapyrin has been shown to increase its potency and enhance soil bacteria sensitivity.[27] Similar effects could potentially occur in aquatic systems and affect microbial community composition and function.

This study was the first to document off-field transport of nitrapyrin to streams. In addition, transport to streams appears to be driven by precipitation. At least in the spring, nitrapyrin and herbicides appear to follow similar flushing patterns. More research is needed to understand how the stream transport of nitrapyrin and 6-CPA may differ between the fall and spring application periods. Detected nitrapyrin concentrations were below USEPA toxicity levels for aquatic vertebrates and invertebrates, but the effects on natural downstream microorganisms are still unknown. Results from this study highlight the need for more research focused on nitrapyrin fate and transport pathways and potential ecological effects.

Supporting Information

Experimental methods including quality assurance, site specific drainage area and detection frequencies for each compound (Table S1), stream discharge and concentrations of nitrapyrin and herbicides for each sample (Table S2), mass spec ions (Table S3), temporal photos documenting stream and crop conditions during sampling period for West Branch Wapsinononc Creek (Figure S1), and hydrographs for three hydrologic-based sampling sites: English River (Figure S2), Old Mans Creek (Figure S3) and Clear Creek (Figure S4).

Notes

The authors declare no competing financial interest.

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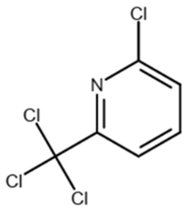
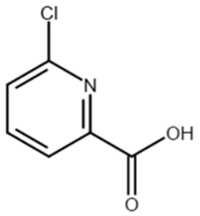
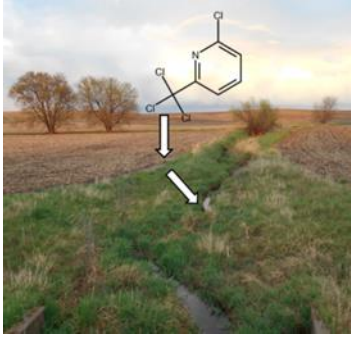
TABLES

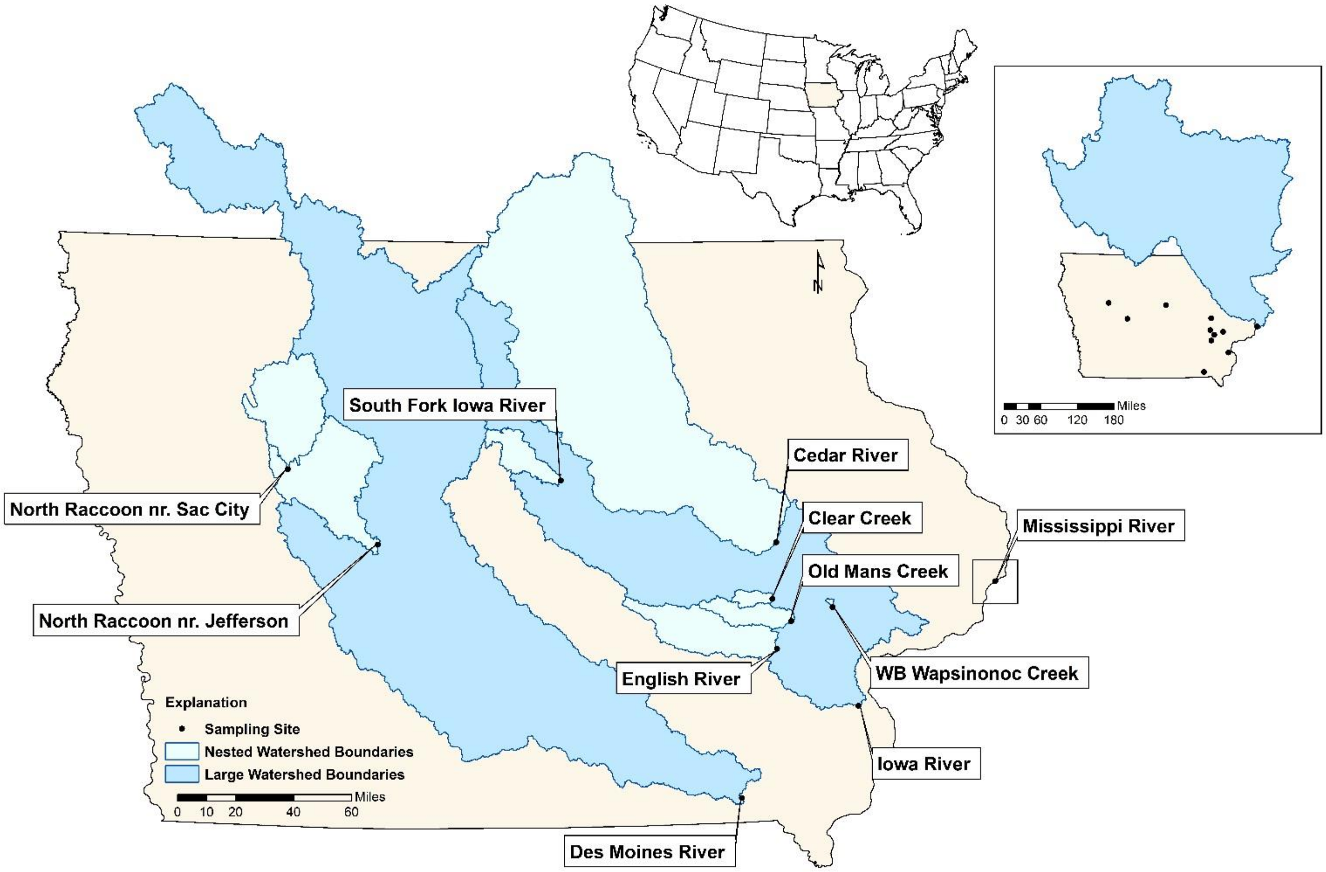
Table 1. Select physical properties for nitrapyrin and its degradate, 6-chloropicolinic acid. Solubility and vapor pressure values are reported at 25°C.

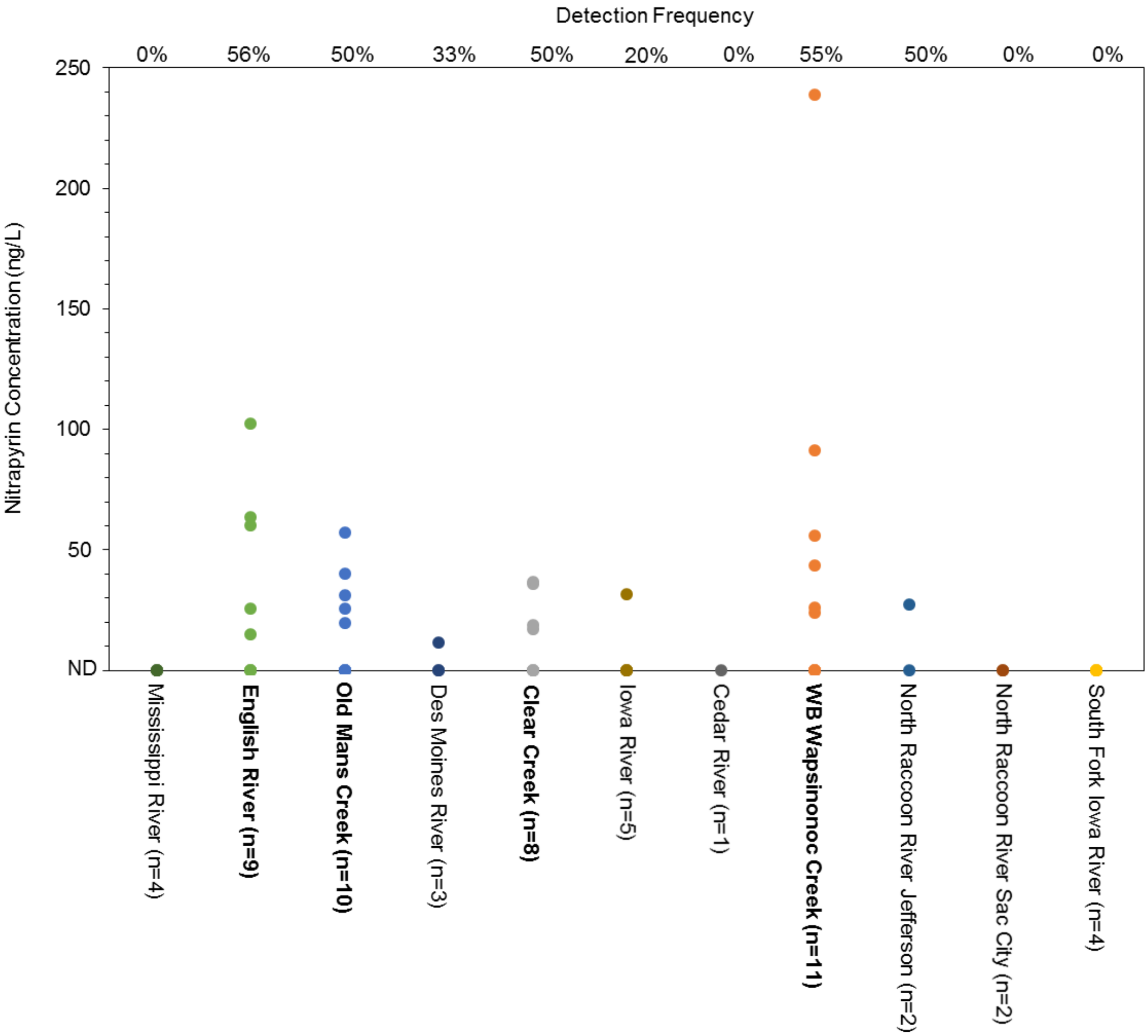
Compound	**Structure** [a]	**Molecular Mass** [b] **(g/mol)**	**Water Solubility** [b] **(mg/L)**	**Vapor Pressure** [b] **(mm Hg)**
2-Chloro-6-(trichloromethyl)pyridine (Nitrapyrin)		230.91	72	0.0048
6-chloropicolinic acid (6-CPA)		157.55	3680	0.0012

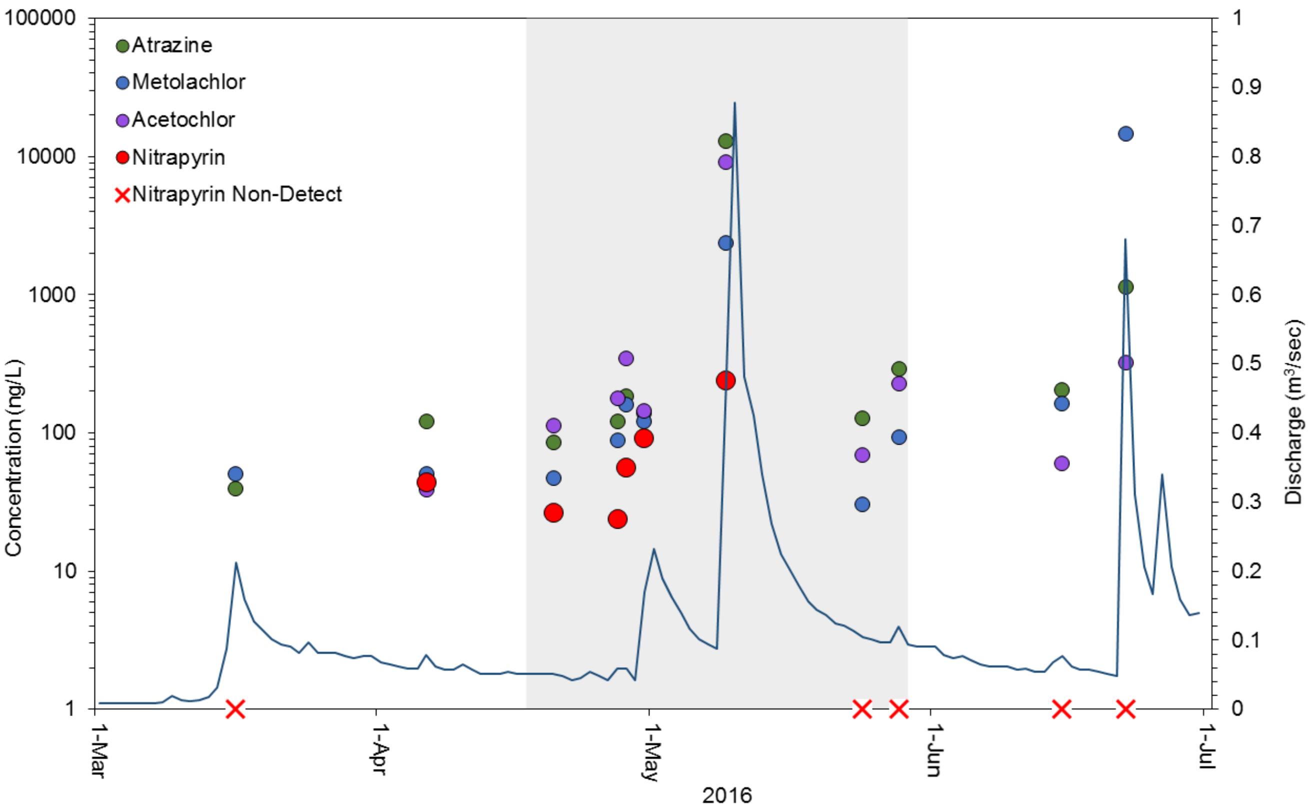
[a] Structures taken from Chemicalize property viewer[28]. [b] Data from ChemIDplus, a U.S. National Library of Medicine toxicology database[12].

TOC Art




South Fork Iowa River
Cedar River
North Raccoon nr. Sac City
Clear Creek
Mississippi River
Old Mans Creek
North Raccoon nr. Jefferson
English River
WB Wapsinonoc Creek
Iowa River
Des Moines River
Explanation
Sampling Site
Nested Watershed Boundaries
Large Watershed Boundaries
Miles
0 10 20 40 60
N
Miles
0 30 60 120 180


Detection Frequency
0%
56%
50%
33%
50%
20%
0%
55%
50%
0%
0%
Nitrapyrin Concentration (ng/L)
250
200
150
100
50
ND
Mississippi River (n=4)
English River (n=9)
Old Mans Creek (n=10)
Des Moines River (n=3)
Clear Creek (n=8)
Iowa River (n=5)
Cedar River (n=1)
WB Wapsinonoc Creek (n=11)
North Raccoon River Jefferson (n=2)
North Raccoon River Sac City (n=2)
South Fork Iowa River (n=4)


● Atrazine
● Metolachlor
● Acetochlor
● Nitrapyrin
✕ Nitrapyrin Non-Detect
Concentration (ng/L)
100000
10000
1000
100
10
1
Discharge (m³/sec)
1
0.9
0.8
0.7
0.6
0.5
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