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Fate of atrazine in switchgrass–soil column system

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HIGHLIGHTS

- Atrazine is taken up and degraded as soon as 1 d after exposure to atrazine.
- Atrazine is degraded into several metabolites by switchgrass.
- Atrazine and metabolite concentrations are below detection limits after 21 d.
- DEA, DIA, DDA and cyanuric acid are the major metabolites present.
- Hydroxyatrazine is not a major metabolite in switchgrass tissues.

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ABSTRACT

Atrazine, a broad-leaf herbicide, has been used widely to control weeds in corn and other crops for several decades and its extensive used has led to widespread contamination of soils and water bodies. Phytoremediation with switchgrass and other native prairie grasses is one strategy that has been suggested to lessen the impact of atrazine in the environment. The goal of this study is to characterize: (1) the uptake of atrazine into above-ground switchgrass biomass; and (2) the degradation and transformation of atrazine over time. A fate study was performed using mature switchgrass columns treated with an artificially-created agricultural runoff containing 16 ppm atrazine. Soil samples and above-ground biomass samples were taken from each column and analyzed for the presence of atrazine and its chlorinated metabolites. Levels of atrazine in both soil and plant material were detectable through the first 2 weeks of the experiment but were below the limit of detection by Day 21. Levels of deethylatrazine (DEA) and didealkylatrazine (DDA) were detected in soil and plant tissue intermittently over the course of the study, deisopropylatrazine (DIA) was not detected at any time point. A radiolabel study using [^{14}C]atrazine was undertaken to observe uptake and degradation of atrazine with more sensitivity. Switchgrass columns were treated with a 4 ppm atrazine solution, and above-ground biomass samples were collected and analyzed using HPLC and liquid scintillation counting. Atrazine, DEA, and DIA were detected as soon as 1 d following treatment. Two other metabolites, DDA and cyanuric acid, were detected at later time points, while hydroxyatrazine was not detected at all. The percentage of atrazine was observed to decrease over the course of the study while the percentages of the metabolites increased. Switchgrass plants appeared to exhibit a threshold in regard to the amount of atrazine taken up by the plants; levels of atrazine in leaf material peaked between Days 3 and 4 in both studies.

1. Introduction

Control of broadleaf weeds in corn, sorghum, and sugarcane crops can be achieved through a reversible inhibition of photosystem II by the triazine herbicide atrazine (Shimabukuro and Swanson, 1969; Kruger et al., 1993; Henderson et al., 2007). With 51 million pounds of atrazine applied across 18 states in 2010 and 6.8 million pounds applied in Iowa alone, it is one of the most widely used herbicides in the agricultural industry (NASS, 2011). Widespread usage has resulted in contamination of both ground water and surface water sources by atrazine and its metabolites. It has been estimated that as many as 2700 community water source wells and 214,000 private wells are contaminated with atrazine (USEPA, 1990). Atrazine was found to be present in all 129 samples from 75 Midwestern rivers and streams in 1998 (Battaglin et al., 2000). In 2003, the United States Environmental Protection Agency implemented an atrazine monitoring program in which approximately 30 community water systems in 10 states were required to monitor for the presence of atrazine in drinking water. The most recent data from 2011 found atrazine to be above

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the limit of detection in 3249 of 3527 raw water samples. Concentrations of the samples ranged from 0.05 ppb to 38.6 ppb (mean: 1.1 ppb; median 0.55 ppb) (USEPA, 2012).

Agricultural fields are a major source of atrazine contamination. As much as 5% of the applied atrazine may be lost from a field through surface water runoff (Mersie et al., 2006). As a result, levels of atrazine in local waterways surrounding agricultural settings may exceed the Maximum Containment Level of 3 ppb for drinking water set by the Environmental Protection Agency (Southwick et al., 1992, 1995; USEPA, 2009). Many strategies have been employed in an attempt to mitigate the concentration of atrazine reaching ground and surface water bodies. Phytoremediation, a well-researched method, uses plants to degrade, sequester, or otherwise neutralize organic or inorganic contaminants in soil and water.

Native prairie grasses are commonly used in phytoremediation strategies. Their extensive fibrous root system can penetrate up to ten feet below the surface and can result in a greater surface area than other vegetation (Aprill and Sims, 1990). Switchgrass (*Panicum virgatum*) is a native prairie grass that is found growing naturally in most of the United States and can survive many extreme weather conditions, pH levels, and various soil types (NRCS, 2009). Phytoremediation studies have shown that switchgrass, alone or in combination with other native prairie grasses, is capable of removing atrazine from the environment. Stands of switchgrass in combination with other native prairie grasses can reduce atrazine in leachate by 43% as well as promote degradation in the rhizosphere (Belden and Coats, 2004). A mass balance study, using a mix of three prairie grasses including switchgrass, showed that atrazine and its metabolites were distributed equally between leaf and root tissue (Henderson et al., 2007). More recent research used a microbe-free environment to show that switchgrass is capable of taking up and degrading atrazine into several metabolites (Murphy and Coats, 2011). That study also showed that significantly more degradation occurred in soil as a result of the presence of switchgrass when compared with natural degradation such as chemical or photolytic degradation (Murphy and Coats, 2011). Finally, another study looked at the bioremediation potential of five different grasses and reported that switchgrass treatments facilitated the most degradation of atrazine in the soil, with more than 80% of the atrazine being degraded into metabolites (Lin et al., 2008).

In preparation for a large-scale phytoremediation study using switchgrass to remediate atrazine in an agricultural setting, it is imperative that preliminary studies be conducted to anticipate forthcoming results from this larger study. The goal of the preliminary fate study is to characterize the uptake, degradation, and fate of atrazine and possible metabolites in a phytoremediation setting similar to one that could be used in an agricultural setting. To accomplish these objectives, atrazine was applied to soil columns with switchgrass that had been established for 3 years and the fate was monitored. At the end of 21 d, soil and above-ground plant biomass were evaluated for quantification and identification of atrazine and its chlorinated metabolites DEA, DIA, and DDA (Fig. 1).

Following the completion of the preliminary fate study, a second study was performed using radiolabeled [^{14}C]atrazine in simulated surface water runoff to track atrazine as it was degraded into a variety of metabolites with more accuracy than was previously possible, in an attempt to observe trends in the fate of atrazine instead of only observing intermittent peaks of metabolites. Additionally, this study tries to determine the presence of hydroxyatrazine, which was not detected in the above study, but has been detected in switchgrass residues in other studies (Henderson et al., 2007; Lin et al., 2008).

2. Methods

2.1. Preliminary fate study

2.1.1. Experimental design

Twenty-seven columns were constructed from PVC pipe (76 cm × 20 cm) and placed in a greenhouse. Each column was filled with soil collected from an agricultural field in Clarke County, Iowa and amended with potting soil. The pH and organic matter of the amended soil were determined to be 7.20 and 9.6%, respectively, and soil composition was determined to be: sand 39.90%, silt 37.19%, clay 22.91%. Switchgrass seeds (Cave-in-rock variety) were planted in each column in the fall of 2006 at a density of 10 plants per cm^2 soil surface. Greenhouse conditions for the experiment were 27 ± 2 °C, 16:8 L:D cycle for March–October and 4.5 ± 2 °C, 16:8 L:D cycle for October–March. Prior to application of atrazine, the switchgrass plants were grown for a period of 30 months. These columns had previously had atrazine applied, however, no atrazine or metabolites persisted in the soil or switchgrass tissues after 21 d and more than 11 months elapsed between the end of that study and the beginning of this preliminary fate study. On Days 0, 3, and 6, 360 mL of water containing 16 μg mL^{-1} (ppm) atrazine (provided in-kind by Syngenta) was applied directly to the soil and allowed to permeate the columns; no leaching of the solution was observed. Although this is a much higher concentration than is typically found in the environment, it was theorized that the higher concentrations of atrazine would result in higher metabolite concentrations to allow better visualization of degradative products. The repeated application 3 d apart was an attempt to simulate multiple runoff evens in a short period of time. Two soil samples and one above-ground biomass sample were taken from each column immediately after application on Day 0. Additional samples were collected on Days 1, 2, 4, 5, 7, 8, 11, 14, and 21.

2.1.2. Extraction of above-ground plant biomass

On each sampling day, three randomly selected columns were used for extraction samples. Above-ground switchgrass biomass was cut off at soil level. Three 10-g samples per column were weighed out and used for extraction. Each 10-g sample was rinsed with water, cut into pieces that were approximately two centimeters in length, and ground with a mortar and pestle in 60 mL of ethyl acetate for 10 min. The solvent was decanted off through a filter containing 15 g of sodium sulfate to absorb any water contained in the sample. The above procedure was repeated for a total of three times. The solvent extract was then placed in a turbovap evaporator and evaporated with nitrogen to a final volume of 1 mL. The extract was quantitatively transferred into a syringe with a 0.45 μm micropore filter attached. The extract was passed through the filter into a volumetric flask to a total volume of 5 mL. Two milliliters of this was then pipetted into a gas chromatograph (GC) vial, and kept at -20 °C until analysis.

2.1.3. Extraction of soil

Two 20-g samples of soil were collected from the top 15 cm of each column per extraction day. Soil was collected in French square bottles, and root and organic debris were removed from each sample. Sixty milliliters of ethyl acetate was added to each bottle and then was mechanically shaken at 300 rpm in a horizontal position for 20 min. The solvent was decanted off through a filter containing 15 g of sodium sulfate and the samples were processed in the same manner as the above-ground biomass samples. This procedure was repeated for a total of three times for each sample.