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Research article

Application of denitrifying bioreactors for the removal of atrazine in agricultural drainage water

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ABSTRACT

Atrazine and nitrate $NO_3 - N$ are two agricultural pollutants that occur widely in surface and groundwater. One of the pathways by which these pollutants reach surface water is through subsurface drainage tile lines. Edge-of-field anaerobic denitrifying bioreactors apply organic substrates such as woodchips to stimulate the removal of $NO_3 - N$ from the subsurface tile waters through denitrification. Here we investigated the co-removal of $NO_3 - N$ and atrazine by these bioreactors. Laboratory experiments were conducted using 12-L woodchips-containing flow-through bioreactors, with and without the addition of biochar, to treat two concentrations of atrazine (20 and 50 $\mu g\,L^{-1}$) and $NO_3 - N$ (1.5 and 11.5 $mg\,L^{-1}$), operated at four hydraulic retention time, HRT, (4 h, 8 h, 24 h, 72 h). Additionally, we examined the effect of aerating the bioreactors on atrazine removal. Furthermore, we tested atrazine removal by a field woodchip denitrifying bioreactor. The removal of both $NO_3 - N$ and atrazine increased with increasing HRT in the laboratory bioreactors. At 4 h, the woodchip bioreactors removed 65% of $NO_3 - N$ and 25% of atrazine but, at 72 h, the bioreactors eliminated all the $NO_3 - N$ and 53% of atrazine. Biochar-amended bioreactors removed up to 90% of atrazine at 72-h retention time. We concluded that atrazine removal was primarily via adsorption because neither aeration nor $NO_3 - N$ levels had an effect. At 4-h retention time, the field bioreactors achieved 2.5 times greater atrazine removal than the laboratory bioreactors. Our findings thus highlighted hydraulic retention time and biochar amendments as two important factors that may control the efficiency of atrazine removal by denitrifying bioreactors. In sum, laboratory and field data demonstrated that denitrifying bioreactors have the potential to decrease pesticide transport from agricultural lands to surface waters.

1. Introduction

Agrochemicals such as nitrogen fertilizers and pesticides, which are applied to agricultural lands to increase crop yields, can be transported to surface and ground waters (Burkart and James, 1999; Guzzella et al., 2006; Mayer et al., 2002). Agricultural activities are recognized as one of the main sources of nitrogen in rivers and lakes (Galloway et al., 2004; Mayer et al., 2002). Excess nitrogen, which contributes to algal blooms in lakes and reservoirs, increases the cost of treatment for public water supplies (EPA, 2015). Decomposition of the blooms depletes oxygen from water and subsequently leads to low-oxygen zones worldwide (Breitburg et al., 2018; Burkart and James, 1999; Smith et al., 1999). Atrazine ($C_8H_{14}ClN_5$: 1-chloro-3-ethylamino-5-isopropylamino-3,4,6-triazines) is the second most commonly used herbicide in the United States (Atwood and Paisley-Jones, 2017). Although atrazine was banned in the European Union (Sass and Colangelo, 2006), it is still used in the United States where detection in shallow groundwater was found above the drinking water standard of 3 $\mu g\,L^{-1}$ (EPA, 1995; Gilliom, 2007; Toccalino et al., 2014). The soil half-life of atrazine varied from 22 to 146 d depending on the moisture and aerobic conditions (Gilliom et al., 2006; Issa and Wood, 2005). Even at low concentrations (1–10 $\mu g\,L^{-1}$), atrazine can limit the growth of phytoplankton, zooplankton, and aquatic plants, as well as the development and swimming patterns of fish (Graymore et al., 2001; Tillitt et al., 2010). The United States Environmental Protection Agency (EPA, 2006) classified atrazine as “not likely to be carcinogenic to humans” but this classification has been debated (Sass and Colangelo, 2006). Denitrifying bioreactors are effective in reducing $NO_3 - N$ discharged from agricultural tile lines (Christianson and Schipper, 2016), but a cost-effective in-situ technique to remove atrazine and other pesticides has not been

Abbreviations: W, woodchip; WB, woodchip with biochar; HRT, Hydraulic retention time

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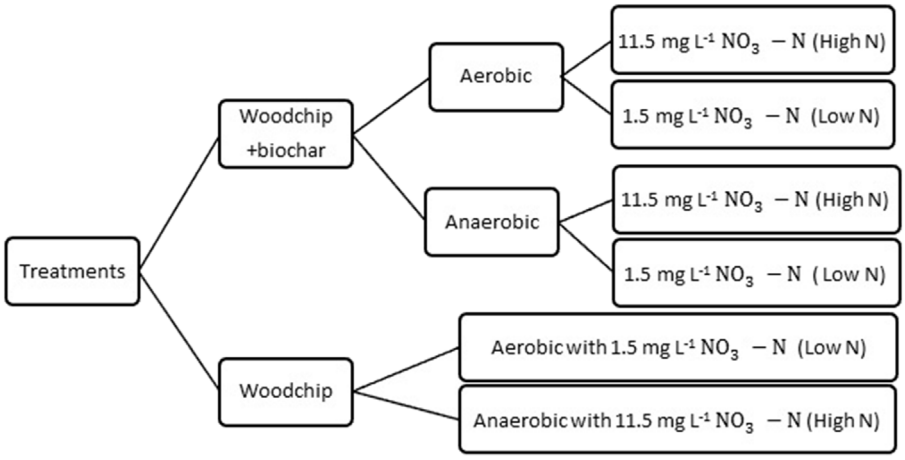

Fig. 1. Experimental treatments, all in duplicates, consisted of treatments that included woodchips, woodchips and biochar, under aerobic and anaerobic conditions at two levels of $NO_3 - N$.

developed. Here we investigate the potential of denitrifying bioreactors to achieve the co-removal of $NO_3 - N$ and atrazine from agricultural tile drain effluents.

The $NO_3 - N$ found in tile drains is leached through the matrix or preferential flow from the root zone to the lower soil profile (e.g., Ernstsen et al., 2015; Marjerison et al., 2016; Mohanty et al., 1998). The $NO_3 - N$ concentration varies depending on land use and the amount of N-fertilizer applied. Reported $NO_3 - N$ concentrations in NY state varied from 0.7 mg L^{-1} at the end of the growing season in a vegetable farm with a perched water table to 62 mg L^{-1} in a cornfield with applied manure (Hassanpour et al., 2017). Atrazine applied to agricultural lands percolates mainly through preferential flow pathways to shallow groundwater, particularly in untilled soils (e.g., Malone et al., 2014; Rothstein et al., 1996; Warnemuende et al., 2007). Various studies reported atrazine concentrations in tile drains ranging from 0.1 μg L^{-1} to 49.2 μg L^{-1} (Buhler et al., 1993; Gaynor et al., 1992; Kladivko et al., 1991; Rocha et al., 2008; Rothstein et al., 1996; Steenhuis et al., 1990). After finding that atrazine concentrations ranged from 0.1 to 49 μg L^{-1} in the streams of a tile-drained agricultural watershed in the spring season when heavy rain followed spraying period, David et al. (2003) concluded that tile drains were the major contributor of atrazine to streams. Therefore, as both $NO_3 - N$ and atrazine are transported via tile drain lines to surface waters, simultaneous removal of both would be valuable to mitigate surface water pollution.

Recently, fast removal of atrazine was achieved in sewage treatment systems with high chemical oxygen demand (Baghapour et al., 2013; Derakhshan et al., 2018b), generally, biodegradation of atrazine takes months in wetland and natural systems and is reduced when nitrogen source is present (Chung et al., 1996, 1995; Ro and Chung, 1995). Therefore, Hunter and Shaner (2010) recommended two sequential bioreactors wherein the anaerobic bioreactor removes $NO_3 - N$ and a subsequent aerobic one to degrade atrazine in aqueous solution. Other researchers have suggested the addition of specific bacterial species to remove both atrazine and $NO_3 - N$, but contamination with undesirable bacteria made this approach challenging (Katz et al., 2001). In-situ woodchip denitrifying bioreactors have been successful in removing $NO_3 - N$ in several countries (e.g., United States, Canada, New Zealand) (Bock et al., 2016; Christianson et al., 2012, 2011b; Pluer et al., 2016; Schipper et al., 2005). The dissolved organic matter from woodchips serves as an electron donor for denitrification (Greenan et al., 2009; Warneke et al., 2011a). These woodchip bioreactors could also achieve removal of atrazine in the bioreactors through adsorption. The adsorption of atrazine to natural soil organic matters and soil organic amendments is well documented (Abate et al., 2004; Lima et al., 2010). A wide range of organic matter including woodchips, charcoal, and biochar has been shown to adsorb atrazine (Cao et al., 2011; Chefetz, 2003; Delwiche et al., 2014; Ilhan et al., 2011; Lupul et al., 2015; Spokas et al., 2009). Biochar was reported to have a high capacity for atrazine adsorption, but this adsorption can be reduced when the biochar surface is modified by sorption of other organics (Delwiche et al., 2014; Wang, 2005).

Since woodchip denitrifying bioreactors have been shown to lower $NO_3 - N$ concentration in tile drains, it is worthwhile to evaluate whether these bioreactors are good candidates for atrazine removal. The present study investigated the co-removal of $NO_3 - N$ and atrazine from tile effluents in laboratory and field settings using anaerobic denitrifying bioreactors filled with woodchips without and with the addition of biochar (respectively, W and WB bioreactors). In addition, we operated these bioreactors under aerobic conditions to investigate the effect of aeration on atrazine removal. We targeted relatively short hydraulic retention times (HRTs; 4 h–72 h) because it is a limiting factor in the design of field denitrifying bioreactors.

2. Material and methods

2.1. Laboratory experiments

2.1.1. Flow-through bioreactors

Twelve up-flow cylindrical reactors, with a 12-L volume each, were constructed with a diameter of 27 cm and a length of 21 cm. A perforated sheet was placed at the bottom of the column (at the entrance) to help distribute the flow evenly. Four of the bioreactors were filled with woodchips (W) and the remaining with woodchips and biochar (WB) at 1:1 v/v. Woodchips from ash trees (*Fraxinus ornus* sp.) were obtained locally from a lumber mill (Wagner Hardwoods, Cayuta, NY). The average woodchip length was 3 cm. The biochar, produced from pine (*Pinus* sp.) and commercially pyrolyzed at 550 to 600 °C, was obtained from Biochar Now® and had a length of 1–2 cm. The porous medium (woodchips with or without biochar) was measured to have similar porosity of 0.61 $cm^3\,cm^{-3}$. Fig. 1 details the different investigated treatments, which includes the two organic media, under anaerobic and aerobic conditions with two different levels of $NO_3 - N$. The aeration of the aerobic bioreactors was achieved by pumping air through two diffusers at the bottom. Although woodchip bioreactors establish anaerobic conditions if not aerated, we reduced influent oxygen content to 3 mg L^{-1} via injection of argon gas (Airgas ®) to assure anaerobic conditions in the entire anaerobic bioreactors. These bioreactors were air-sealed.

2.1.2. Tile drainage water

The tile drain water was made from tap water which was sourced from Fall Creek near Ithaca, NY. The water had a constant $NO_3 - N$

concentration of 1.5 mg L^{-1}. To avoid side-reaction by chlorine in the tap water, the influent was stirred periodically in the influent reservoir for one day prior to each experiment. Then, based on our previous experiments at the Homer C. Thompson Vegetable Research Farm (Hassanpour et al., 2017) where the NO_3-N concentration in the tile line was about 10 mg L^{-1} year around, NO_3-N concentrations were spiked to 11.5 mg L^{-1} for the treatments with elevated NO_3-N content using potassium nitrate (KNO_3). In addition, phosphate-P was supplied at a concentration of 2 mg L^{-1} by addition of monopotassium phosphate (KH_2PO_4) to the water for all treatments. Syngenta atrazine was from AAtrex ® Nine-O ® which comes as water-dispersible granules and is 88.2% atrazine and 11.8% proprietary agent. Two atrazine concentrations, 20 and 50 μg L^{-1}, were used in the synthetic drainage water. These concentrations were within those observed in agricultural tile lines.

2.1.3. Experiments

The fabricated drainage water was pumped to the bioreactors using peristaltic pumps (Masterflex L/S ® from Cole- Parmer) at four different flow rates (30, 15, 5, and 1.7 mL min^{-1}) to achieve four different HRTs (4, 8, 24 and 72 h). For each HRT, at least 5 pore volumes of the influent were pumped through the bioreactors to ensure equilibrium was achieved. During the experiments, the water flow was measured at the effluent of each reactor to calculate the HRT for individual reactors accurately. The flow rates were 4–17% less than intended, thus indicating that the HRTs were only slightly longer than the targeted values.

The water in the influent tanks was kept in the dark and was monitored for NO_3-N, phosphorus and atrazine content throughout the experiment. The experiments were conducted at an ambient room temperature of 21 ± 2 °C. In the first two experiments with HRTs of 72 and 24 h, the bioreactors received synthetic drainage water with 20 μg L^{-1} of atrazine. Subsequent experiments with HRTs of 8, 4, 24 and 72 h used 50 μg L^{-1} of atrazine. There was no flow in the bioreactors for 1–5 days between experimental treatments. Before the experiments started, the tubing connections were tested for possible adsorption of atrazine. No atrazine adsorption was observed.

2.1.4. Chemical analysis

Approximately 500 samples were taken from the influent and effluent of both laboratory and field bioreactors and were filtered through 0.45-μm filters. Laboratory samples were taken after 2 pore volumes had passed and were analyzed for NO_3-N and nitrite (NO_2-N) using ion chromatography (Dionex ICS-2000) within 48 h (Pfaff, 1993). The dissolved oxygen (DO) was measured in-line at the effluent using a YSI 550A probe. The pH of the influent and effluent samples was measured immediately after collection with an Accumet AR50 m. Two series of samples at HRTs of 4 and 24 h were analyzed for total dissolved phosphorus concentrations and cations using inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo iCAP 6500 series). The samples were kept frozen until analyzed for atrazine. Atrazine concentrations were determined using both an enzyme-linked immunosorbent assay (ELISA) and high-resolution liquid chromatography-mass spectrometry (LC-MS) (Smith et al., 2007). The LC-MS analysis was conducted using a Thermo Scientific Accela liquid chromatography system coupled to a Thermo Scientific TSQ Quantum Access triple quadrupole mass spectrometer.

Interference in the ELISA analysis of the effluent samples was a problem due to a high concentration of organic matter. Samples that showed interference were diluted up to 100 times to eliminate it as recommended by Koivunen et al. (2006). Solid phase extraction (SPE) clean-up was used prior to LC-MS analysis. The SPE was performed using HyperSep™ C18 Cartridges (ThermoFisher scientific) as proposed by Mills and Thurman (1992) with some modification. The 200-mg bed cartridges were preconditioned sequentially with 2 mL each of methanol, ethyl acetate, methanol, and milli-Q water. This was followed by the addition of 2 mL of each sample spiked with atrazine internal standard (atrazine-d_5). Finally, 3 mL ethyl acetate flowed through the cartridges and was collected. Along with the ethyl acetate eluent, about 0.5 mL water which was trapped in the cartridges was collected in the test tube. This water and ethyl acetate were mixed thoroughly using a vortex mixer. After settling, the ethyl acetate fraction was collected from the test tube and evaporated until dry under nitrogen gas. The evaporated sample was resuspended in 2 mL of milli-Q water, vortexed and sonicated, then analyzed using LC-MS (full method available in supplemental material S1, and Tables S1–S3). The samples were analyzed for atrazine and its four common degradation products (hydroxyatrazine, atrazine desethyl, atrazine desisopropyl, and atrazine desethyl desisopropyl). The compound standards were acquired from Sigma-Aldrich with more than 98% purity. Fig. S1 shows the calibration for the SPE cleaned standards. Contrary to chemical analysis via ELISA, LC-MS analysis of woodchips leachate with a high concentration of organic matter spiked with atrazine, and its metabolite showed no matrix interference. Based on comparative analysis of the two analytical methods (presented in supplemental material S2, Fig. S2), we only present the data of the ELISA-determined atrazine concentrations for the influents and for the effluent of the WB bioreactors after adjustment.

2.2. Field bioreactor

In June 2017, the influent and effluent of a field bioreactor in Onondaga County in New York State were monitored for atrazine shortly after application to the fields. The W bioreactor at the Onondaga site was constructed in October 2016 at the outlet of a subsurface drainage collector in a field where corn, soybeans, and wheat are grown in contoured strips. This bioreactor is 1 m deep, 3 m wide, and 13.5 m long. Atrazine was applied on the cornfield shortly before corn emergence, in June 2017. In three sampling events, on June 6th, 10th and 12th, 2017, atrazine was detected at the influent and effluent of this bioreactor.

2.3. Statistical analysis

Statistical analysis was performed using JMP (Statistical Discovery™ from SAS). F-Statistics were performed on the data points to characterize the performance of the reactors based on the measured parameters and treatments evaluated in this study.

3. Results

3.1. Nitrate-N removal in the bioreactors

At the high influent NO_3-N concentration of 11.5 mg L^{-1}, there was NO_3-N removal in both anaerobic and aerobic bioreactors (Fig. 2). The NO_3-N removal increased with increasing HRT and followed first order kinetic rates for both aerobic and anaerobic bioreactors (Fig. 2a and b). In both bioreactors, the NO_3-N removal ranged from 50% ($C/C_0 = 0.5$) to 80% ($C/C_0 = 0.2$) at the 4-h HRT and increased to 80–98% ($C/C_0 = 0.2$ to 0.02) at the 8-h retention time (Fig. 2a and b). At 72-h HRT, all NO_3-N was removed from the bioreactor effluent. We note that, at the low influent NO_3-N concentration of 1.5 mg L^{-1}, the NO_3-N removal was erratic due to N-limiting conditions (Fig. 2c and d). Previously, it was determined that in anaerobic woodchip bioreactors, denitrification is responsible for NO_3-N removal (Warneke et al., 2011a, 2011c). In aerobic bioreactors, however, NO_3-N removal coincided with the uptake of phosphorus and potassium (Fig. S3) and likely occurred through cellular assimilation of NO_3-N (Mclatchey and Reddy, 1998; Reddy and Delaune, 2008; Saia et al., 2017).

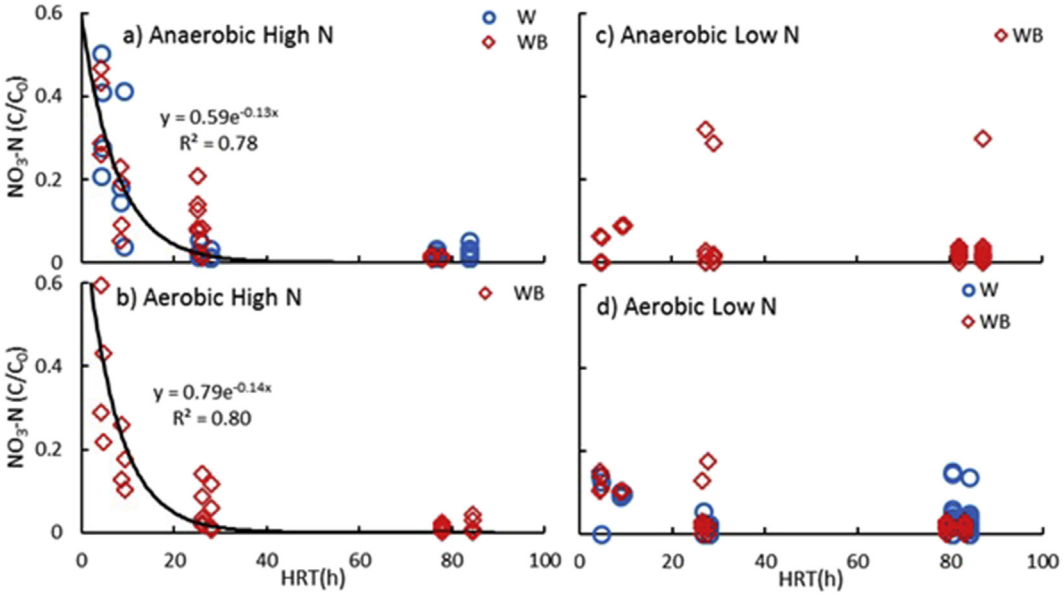

Fig. 2. The C/C_0 (effluent concentration/influent concentration) of $NO_3 - N$ in the different HRTs in both W (woodchips; blue circles) and WB (woodchips and biochar; red diamonds) a) anaerobic bioreactors with the high level of $NO_3 - N$, b) aerobic bioreactors with the high level of $NO_3 - N$, c) anaerobic bioreactors with the low level of $NO_3 - N$, and d) aerobic bioreactors with the low level of $NO_3 - N$. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.2. Atrazine removal as a function of hydraulic retention time and biochar amendment

The bioreactors achieved atrazine removal from the influent for all treatments, but the WB bioreactors were more efficient than the W bioreactors (Table S4). In the experiments with influent atrazine concentration of 20 μg L^{-1}, atrazine concentrations in the effluent were less than 3 μg L^{-1} (2.7 ± 0.2 μg L^{-1}) in WB bioreactors for both 24-h and 72-h HRTs (Fig. 3a). However, at the corresponding HRTs, the atrazine concentration in W bioreactors was, respectively, 13 ± 0.9 μg L^{-1} and 7.3 ± 1.2 μg L^{-1} (Fig. 3a). We also evaluated atrazine removal from higher influent atrazine concentration of 50 μg L^{-1} through both types of bioreactors at four HRTs: 4 h, 8 h, 24 h, and 72 h. We found that, at the higher influent atrazine concentration, the WB bioreactors removed more atrazine than the W bioreactors (Table S4, Fig. 3a). The atrazine concentrations in the effluent of the WB bioreactors were 18 ± 0.8 μg L^{-1} and 3.7 ± 0.6 μg L^{-1} at HRTs of 4 h and 72 h, respectively, whereas the corresponding concentrations in the effluent of the W bioreactors were respectively, 39 ± 1.4 μg L^{-1} and 23 ± 1.5 μg L^{-1} (Fig. 3a).

The atrazine removal as a function of the variation in HRTs is shown in Fig. 3b. Overall, the C/C_0 for the W bioreactors was 0.63 ± 0.03 (atrazine removal = 37%) compared to 0.25 ± 0.04 (atrazine removal = 75%) for the WB bioreactor (Fig. 3b). In 4 h, the W bioreactor removed 24% (C/C_0 = 0.76 ± 0.03) of the inflow atrazine while the WB bioreactors removed 63% (C/C_0 = 0.37 ± 0.02) of atrazine (Fig. 3b). By increasing HRT from 4 h to 8 h, the removal of atrazine increased to 29% (C/C_0 = 0.71 ± 0.02) for the W bioreactor and 72% (C/C_0 = 0.28 ± 0.02) for the WB bioreactors (Fig. 3b). In 24 h, the W bioreactors removed 36% (C/C_0 = 0.64 ± 0.04) of atrazine while the

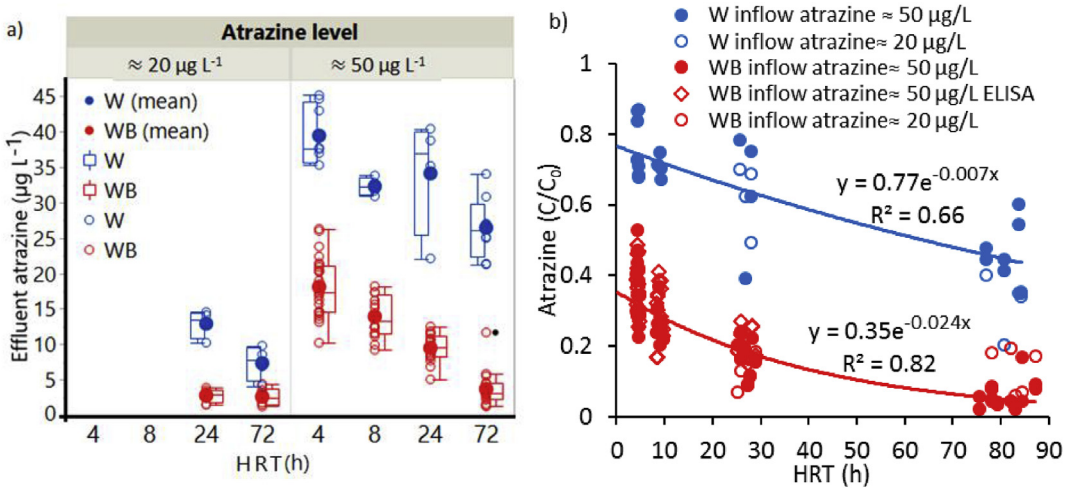

Fig. 3. Atrazine concentration in the laboratory bioreactors. a) Concentrations of atrazine in the effluent of the W (woodchips; blue open dots) and WB (woodchips and biochar; red open dots) bioreactors at different HRTs (Hydraulic Retention times) at the two atrazine levels. Each line on the box plot from top to bottom shows maximum, the first quartile, median, third quartile, and minimum concentrations of atrazine. The closed dots next to each box is the average concentration of atrazine. b) The relationship between atrazine C/C_0 (effluent concentration/influent concentration) versus HRT for both levels of atrazine in the W and WB bioreactors. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

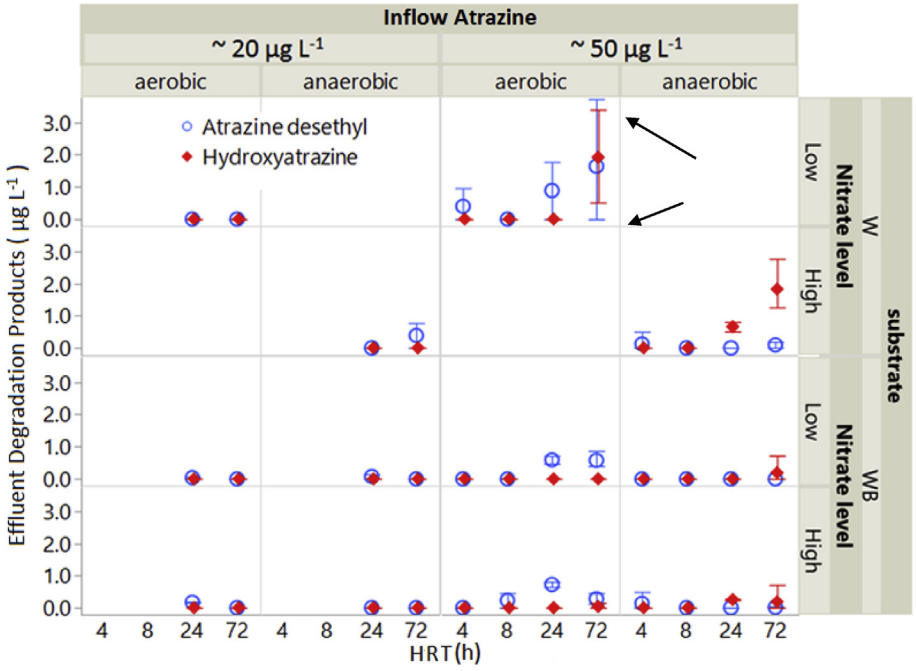

Fig. 4. Degradation products of atrazine, atrazine desethyl (blue dots) and hydroxyatrazine (red diamonds), at the effluent of the W (woodchips) and WB (Woodchips and Biochar) bioreactors at different HRTs (Hydraulic Retention Times). The error bars show the observed range of the concentrations of the degradation product. Note that one of the two air inlets in one W aerobic bioreactor plugged and that bioreactor behaved like an anaerobic bioreactor (shown by the arrows at 72 h HRT). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

WB bioreactors removed 83% ($C/C_0 = 0.17 \pm 0.01$) (Fig. 3b). In 72 h, the W and WB bioreactors removed 55% ($C/C_0 = 0.45 \pm 0.03$) and 93% ($C/C_0 = 0.07 \pm 0.01$), respectively (Fig. 3b). The atrazine removal followed a first-order reaction rate with a constant of 0.024 h^{-1} (or 0.58 d^{-1}) for the WB medium and 0.007 h^{-1} (or 0.17 d^{-1}) for the W medium (Fig. 3b). This finding agreed with previous findings whereby the removal of atrazine by adsorption to organic matter followed first-order reaction kinetics (Liu et al., 2015).

We monitored the presence of common atrazine degradation products in the effluent of the laboratory bioreactors, and only atrazine desethyl and hydroxyatrazine were found at appreciable levels (Fig. 4). It is important to note that there was a small concentration of atrazine desethyl in the influent tanks, but the amount generated inside the bioreactors was greater (Fig. S4). Unlike the atrazine concentration in the effluent, the effluent concentration of the degradation products depended on the aeration of the bioreactors (Fig. 4). Atrazine desethyl, which was present in the effluent of the aerobic bioreactors, had greater concentration in the W bioreactors than the WB bioreactors (Fig. 4). The maximum concentration of atrazine desethyl was 3.7 µg L^{-1} in the aerobic W bioreactors at an HRT of 72 h (Fig. 4). In the aerobic WB bioreactor, atrazine desethyl was found at concentrations of 0.6 ± 0.1 µg L^{-1} for both HRTs of 24 h and 72 h (Fig. 4). Hydroxyatrazine was found in the anaerobic bioreactors and one aerobic bioreactor that became anaerobic due to a failure with an oxygen diffuser (shown with arrows) (Fig. 4). The hydroxyatrazine concentrations varied from 0 to 3.4 µg L^{-1} in the bioreactor effluents (Fig. 4). Hydroxyatrazine first started to appear at an HRT of 24 h in the effluent of the W bioreactors and its concentrations amounted to 5% of the atrazine applied at the influent in 72 h (Fig. 4). Atrazine transformation to hydroxyatrazine is important because hydroxyatrazine is less toxic than the chlorinated metabolites of atrazine and is not phytotoxic (Graymore et al., 2001; WHO, 2010). The increased concentration of atrazine degradation products in the reactors with increasing retention times, agreed with the previous studies that atrazine degradation and the appearance of the degradation products follows the first-order kinetics (Jones et al., 1982; Seybold et al., 2001).

We performed F- test on the measured atrazine concentrations in the effluent to determine the role of each variable: the substrate, HRT, influent atrazine concentration, $NO_3 - N$ concentration and aeration (Table S5). The results showed that atrazine concentrations in the effluent responded to substrate, HRT, and influent atrazine concentrations ($p < 0.0001$ and large F values), whereas influent $NO_3 - N$ concentrations and aeration did not affect effluent atrazine concentrations ($P > > 0.05$). This indicated that the removal of atrazine was primarily abiotic. Additionally, we have conducted separate assay experiments to confirm that biodegradation did not contribute to the removal of atrazine in anaerobic and aerobic conditions with wood as a substrate (Supplemental Material S5 and Figs. S5 and S6).

3.3. Field bioreactor

Results with the field bioreactor supported the findings of the laboratory experiments (Fig. 5). For the three sampling events (on June 6th, June 10th, and June 12th, 2017), the removal of $NO_3 - N$ recorded in the W bioreactor effluent at the Onondaga site was, respectively, 32%, 88%, and 55% (Fig. 5a). Moreover, we found that the removal of $NO_3 - N$ was coupled with atrazine removal (Fig. 5). With respect to atrazine removal, on June 6th, 2017, the Onondaga W bioreactor achieved 62% atrazine removal ($C/C_0 = 0.38$) at 4-h HRT, by reducing influent atrazine from 9.5 µg L^{-1} to 3.8 µg L^{-1} (Fig. 5b). At the subsequent sampling dates, however, the effluent atrazine concentration was slightly greater than that in the influent (Fig. 5b). On June 10th, 2017, at an HRT of 13.4 h, the atrazine concentration increased from 0.4 µg L^{-1} in the influent to 1.37 µg L^{-1} in the effluent (Fig. 5b). In the last sampling event, on June 12th, 2017, when the HRT was 8.7 h, the atrazine concentration increased from 0.3 µg L^{-1} in the influent to 0.9 µg L^{-1} in the effluent (Fig. 5). These results with higher atrazine concentration in the effluent than in the influent thus indicated that desorption of atrazine from the woodchips had occurred. The desorption of atrazine from woodchips and other organic matter was reported in previous studies (Ilhan et al., 2011; Lima et al., 2010). Atrazine desethyl was observed in the influent of the field bioreactor (Fig. 5c). Given that the tile drain collected water from an agricultural field, observing atrazine desethyl in its effluent was expected (Gilliom, 2007; WHO, 2010). Fig. 5c shows that the bioreactors removed atrazine desethyl. It is worthy of note that atrazine degradation products can adsorb to the organic matter (Abate et al., 2004; Krutz et al., 2003). Hydroxyatrazine, however, is greater in the bioreactor effluent than in the influent, indicating the occurrence of atrazine hydrolysis inside the bioreactors (Fig. 5d). Overall, in the field site, about 10% of the

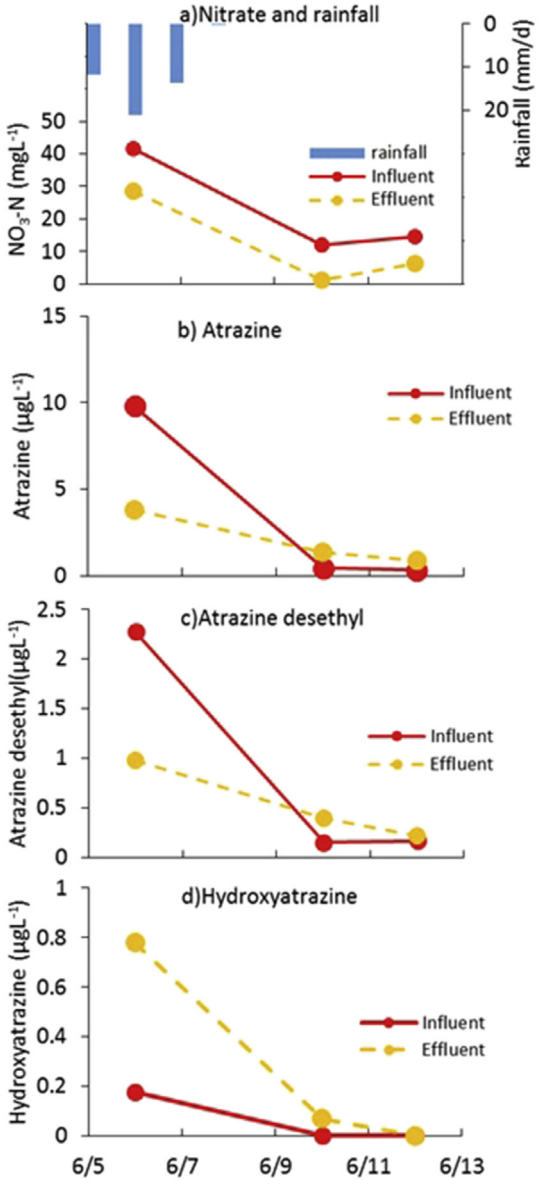

Fig. 5. a) daily rainfall and inflow and outflow of $NO_3 - N$, b) atrazine, c) atrazine desethyl, and d) hydroxyatrazine in Onondaga W (woodchips) denitrifying bioreactor. Note the change in scale of the Y-axis of the graphs.

removed atrazine exited the field bioreactor as hydroxyatrazine (Fig. 5d).

4. Discussion

4.1. Mechanism of atrazine removal

The difference between the adsorption of atrazine onto woodchips versus biochar is related to their surface characteristics. The two most efficient sorption sites for atrazine on the organic matter are the aromatic compounds for π-π interactions (Lima et al., 2010; Zhang et al., 2011, 2013) and carbonyl/carboxylic acid groups for hydrogen bonding interactions (Kulikova and Perminova, 2002; Mackay and Gschwend, 2000). Hardwood is made of cellulose, hemicellulose, and lignin. Lignin with its aromatic components has strong adsorption capacity for atrazine (Dunigan and McIntosh, 1971). Adsorption of monoaromatic carbon to wood was proportional to the lignin content (Mackay and Gschwend, 2000). During pyrolysis for biochar production, at temperatures below 360 °C lignin chars, whereas cellulose and hemicellulose degrade to volatile compounds (Blasi, 1993; Mohan et al., 2006). Therefore, for pyrolysis at 550 to 600 °C, the biochar used here would be comprised mostly of aromatic compounds (Jindo et al., 2014) as confirmed by infrared spectroscopy (spectra presented in Fig. S7). The infrared spectroscopic data highlighted the abundance of aromatic compounds as well as carboxyl and keto groups on the biochar surface. Thus, we attributed the lower adsorption capacity of woodchips for atrazine compared to biochar to the aromatic-enriched surface of the biochar compared to that of the wood.

Atrazine degradation products were detected at the effluent of the bioreactors (Figs. 4 and 5). However, the lack of influence of aeration or $NO_3 - N$ level on atrazine removal led us to conclude that adsorption was the predominant mechanism, especially when removal occurred within hours (Ilhan et al., 2011). In urban wastewater treatment plants with chemical oxygen demand of 1–10 g L^{-1}, rapid co-metabolism was suggested to be responsible for 61–90% atrazine removal in 6–24 h (Baghapour et al., 2013; Derakhshan et al., 2018b, c, a). In our study, however, in anaerobic W bioreactors filled with drainage water with generally relatively low chemical oxygen demand, the assay tests revealed that atrazine removal was primarily abiotic.

Our field observations show a greater atrazine removal in a short HRT compared to the laboratory bioreactors. Taking into consideration that the field bioreactor was older, this difference might be caused by the aging of the wood, resulting in a higher percentage of lignin and a lower percentage of cellulose and hemicellulose (Ghane et al., 2018), which lead to an increase in the capacity of the woodchips to adsorb atrazine.

4.2. Nitrate -N removal rate

To compare our research findings with the research reported in the literature (Schipper et al., 2010; Warneke et al., 2011a, b, c; Addy et al., 2016; Pluer et al., 2019), we converted the reduction in $NO_3 - N$ concentrations in the bioreactors in Fig. 2 to the removal rates defined as $(C_o\text{-}C)/HRT$ where C_o is the inflow concentration (mg L^{-1}), C is the effluent concentration (mg L^{-1}), and HRT is the hydraulic retention time (d). The results are plotted in Fig. 6. The removal rate of the reactors varied between 0.1 mg L^{-1} d^{-1} and 52 mg L^{-1} d^{-1} with the maximum in bioreactors with high N level and short HRTs. The $NO_3 - N$ removal rates in long HRTs and in bioreactors with low N level were less because of the rate-limited conditions ($NO_3 - N$ content < 1 mg L^{-1}; Robertson, 2010).

In the anaerobic bioreactors, the influent dissolved oxygen level was reduced (DO ~ 3 mg L^{-1}) with a temperature of 21 ± 2 °C. Thus, in short HRTs, the $NO_3 - N$ removal rates of the bioreactors with high N level were in the upper ranges of those reported in the literature due to elevated $NO_3 - N$ concentrations and temperature, and readily available anaerobic conditions (Warneke et al., 2011a, b, c; Addy et al., 2016; Hassanpour et al., 2017; Pluer et al., 2019). In aerobic bioreactors $NO_3 - N$ removal rates were similar to those in anaerobic bioreactors (Fig. 6c and d). Due to the presence of dissolved oxygen, cellular assimilation of nitrogen with the uptake of other nutrient and micronutrients was responsible for $NO_3 - N$ removal (Myrold and Posavatz, 2007; Geisseler et al., 2010), especially in the abundance of organic matter (Rice and Tiedje, 1989; Mclatchey and Reddy, 1998; Reddy and Delaune, 2008).

4.3. Atrazine removal in aerobic vs. anaerobic conditions

There was a difference between the produced atrazine degradation products in aerobic and anaerobic conditions. We found that about 5% of the influent atrazine appeared as atrazine desethyl in the effluent of aerobic W bioreactors after 72 h. However, hydroxyatrazine was the degradation product of atrazine in the anaerobic bioreactors, although a trace amount of atrazine desethyl was still observed in these reactors (Figs. 4 and 5). Degradation of atrazine to atrazine desethyl and other

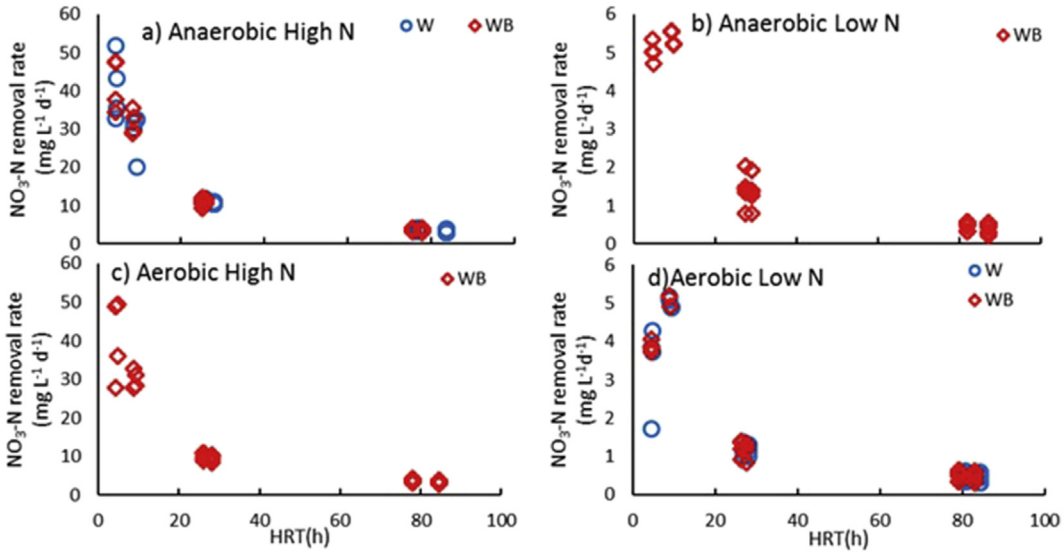

Fig. 6. The NO_3 − N removal rate the different HRTs in both W (woodchips; blue circles) and WB (woodchips and biochar; red diamonds) in a) anaerobic bioreactors with the high level of NO_3 − N, b) aerobic bioreactors with the high level of NO_3 − N, c) anaerobic bioreactors with the low level of NO_3 − N, and d) aerobic bioreactors with the low level of NO_3 − N. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

dealkylated metabolites, which is known to be microbially mediated (Gilliom et al., 2006), has been reported in the soil, riverine systems, and in groundwater (Gilliom, 2007; Gilliom et al., 2006). These dealkylated atrazine metabolites are almost as toxic as atrazine (Graymore et al., 2001). Degradation of atrazine to hydroxyatrazine under anaerobic conditions is consistent with the finding of earlier studies (Chung et al., 1996; Seybold et al., 2001). Hydrolysis of atrazine to hydroxyatrazine has been attributed to chemical degradation through adsorption of atrazine to organic matters, sediments and particles (Armstrong et al., 1967; Lerch et al., 1999; Seybold et al., 2001; Stevenson, 1972). Armstrong et al. (1967) suggested that the enhanced hydrolysis of atrazine in soils can occur due to the presence of catalytic metals on the surface of soil mineral particles, in addition to a low soil pH that can facilitate acid hydrolysis. In equilibrium with atmosphere, the pH of the aerobic bioreactors remained the same as the influent at about 7.5, while in anaerobic conditions the pH dropped to an average of 6.5 (Table S4), which could have contributed in atrazine hydrolysis to hydroxyatrazine (Armstrong et al., 1967; EPA, 2006; Gamble and Khan, 1985; Geller, 1980). Mandelbaum et al. (1993) provided evidence that microbial activity, such as the production of enzymes, enhanced atrazine hydrolysis at neutral pH values in both aerobic and anaerobic conditions. Both the aerobic and anaerobic bioreactors in the current study allowed bacterial growth, therefore, the contribution of microbial activity may not have been substantial in the production of hydroxyatrazine as it was pointed out by Jones et al. (1982).

5. Conclusion

The results of this study showed that both field and laboratory woodchip containing anaerobic bioreactors, also known as denitrifying bioreactors, can achieve co-removed of atrazine and NO_3 − N from tile waters according to first-order kinetics. In anaerobic conditions, atrazine removal was abiotic and primarily through adsorption. Hydroxyatrazine, a non-phytotoxic degradation product of atrazine, was also produced in such conditions. Contrary to the previous proposal by Hunter and Shaner (2010), we showed here that, aeration did not increase atrazine removal and, thus, application of aerobic bioreactors may not be necessary in the field.

One of the challenges in the treatment of agricultural tile waters is handling the peak flow of water and concentrations. With the addition of biochar, which represents a simple adjustment to the substrate of the woodchip denitrifying bioreactors, we found that atrazine removal was improved, particularly at short retention times. In the HRT of 8 h, a previously suggested criterion in bioreactor design (Christianson et al., 2011a), we found that the WB bioreactors could achieve 65% atrazine removal, more than two-fold higher atrazine removal than the W bioreactors.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.03.029.

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