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Mineralization of atrazine in the river water intake and sediments of a constructed flow-through wetland

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ABSTRACT

The purpose of this study was to assess the role of anaerobic electron acceptors in the biomineralization of atrazine in an established constructed wetland receiving seasonal fluxes of atrazine runoff from an agricultural watershed. The Olentangy River wetland receives river water with a hydraulic residence of about 36 h depending on hydrological conditions. Both sediment samples and suspended solids in the water were of interest in this study. Surface water was collected from the Olentangy River by grab sampling. Samples of sediment top sections were taken from the inlet, middle section, and outlet and combined to a composite for laboratory experiments. Atrazine mineralization in water and sediment samples was based on $^{14}CO_2$ release from [U-ring-^{14}C]-atrazine in biometer enclosures. The half-lives of atrazine mineralization by suspended solids in water ranged from 10 months to 5 years depending on incubation conditions. Sediment samples from the wetland showed considerable variation in the extent of mineralization, shortest half-life of about 7 days and the longest of about 6–7 weeks with or without an anaerobic electron acceptor. The results indicate that trace levels of atrazine entering wetland will likely persist for extended periods, often exceeding the hydrologic residence time of the wetland.

1. Introduction

Atrazine (2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine) is widely used as a pre-emergence broadleaf herbicide in cornfields, especially in the American Midwest (Thelin and Stone, 2010). Its persistence in soils and sediments varies widely. The primary mode of atrazine attenuation in soil is by microbial biodegradation (Krutz et al., 2012; Udiković-Kolić et al., 2012). Numerous soil-borne bacteria have been shown to be capable of partial atrazine biotransformation or complete mineralization (Sadowsky, 2010; Udiković-Kolić et al., 2012). Atrazine at environmentally relevant concentrations of 5–10 μg/l has been demonstrated to have endocrine disruptor effects in experimental animals and human cells and thus could potentially pose adverse ecological impacts to aquatic wildlife (Colborn et al., 1993; Hayes et al., 2003, 2010; Kucka et al., 2012). In contrast to the much higher soil application rates of atrazine, these trace levels may result in much slower biodegradation rates or failure to induce catabolic pathways in atrazine-degrading microorganisms that may be present in aquatic environments. Atrazine can run off from agricultural soils with storm water and erosion (Glenn and Angle, 1987; Seta et al., 1993) and thus its residues are invariably present in rivers in agricultural watersheds. Atrazine biodegradation studies have demonstrated the presence of atrazine-degraders in river water in many different geographical locations (Satsuma et al., 2002; Tappin et al., 2012). Wetlands and riparian strips are important catchment systems in pesticide mitigation in agricultural watersheds (Passeport et al., 2013) and thus knowledge of the overall persistence of atrazine in these ecosystems is relevant to predicting adverse ecological impacts of this widely used herbicide. Atrazine half-lives have been reported to be between one and two weeks in wetland mesocosms (Detenbeck et al., 1996; Weaver et al., 2004). Moore et al. (2000) presented estimates of the size of the wetland in relation to attenuation of atrazine in simulated agricultural runoff but the relative contribution of biological degradation to the overall attenuation was not determined.

Our previous studies of pesticide biodegradation demonstrated that atrazine was mineralized by microorganisms in a constructed wetland system receiving water from a river receiving agricultural runoff (Anderson et al., 2002). This flow-through Olentangy River wetland was constructed in 1993–1994 and is now well established

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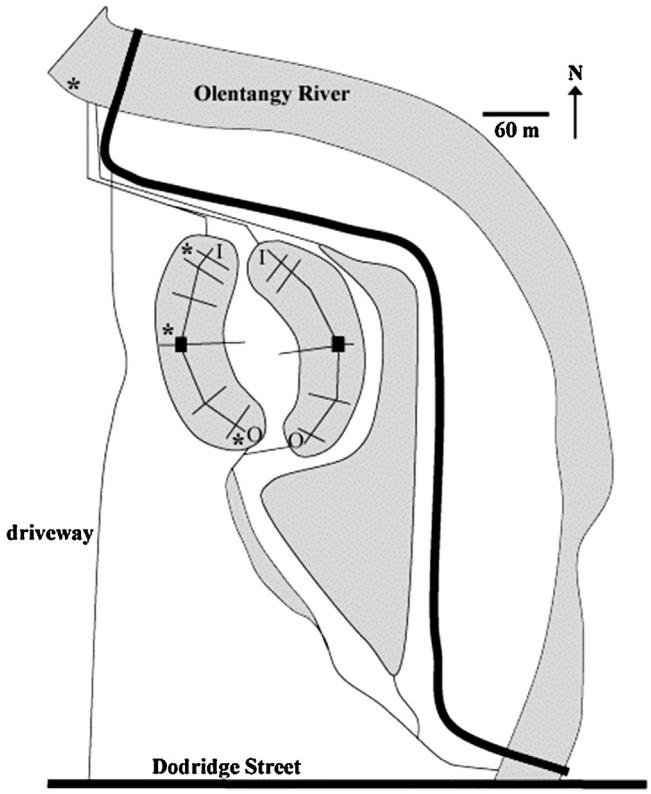

Fig. 1. Sampling sites at the Olentangy River wetland. I, water intake from the river (water inflow); O, outlet to the river; ∗, sampling site. Wetland sediments from the three sampling sites were used as a composite for this study. Lines within wetland indicate boardwalks, and the squares indicate platforms. The heavy line denotes a bike and walking trail.

(Mitsch et al., 2012) with water inlet from and outlet to the Olentangy River. The wetland has an influx of runoff fertilizers and other agrochemicals that vary in concentration throughout the year. As a follow-up to our previous study, we determined atrazine mineralization in intake river water and wetland sediment samples from the Olentangy River wetland under aerobic and anaerobic incubation conditions. Anaerobic incubation studies with several external electron acceptors were performed in an effort to account for the wide variation in atrazine degradation rates previously reported in wetland sediments and overlying waters.

2. Materials and methods

2.1. Sampling

Surface water was collected from the water intake of the Olentangy River by grab sampling. The samples were stored in quart size glass jars (0.95 l) with lids, each representing a composite of three sub-samples. Sediment samples were taken with a core sampler (4.2 cm inner diameter) from the inlet (water inflow), middle section, and outlet from the Olentangy River wetland (Fig. 1). Top 7-cm sediment sections (1 per site) were placed in sterile plastic sample bags at each sampling location and combined to a composite for the laboratory incubation experiments. All samples were collected on September 9, 2004.

2.2. Atrazine mineralization in biometer experiments

Initial biometer experiments demonstrated that the biomineralization of atrazine was negligible in water samples. Subsequently, suspended solids in the river water were pre-concentrated by centrifugation (13,700 × *g*, 10 min), and at a 60-fold pre-concentration of suspended solids the biomineralization of atrazine was readily detected. The pre-concentrated suspended solids were dispensed in 1 ml aliquots and sediment samples in 5 g wet weight aliquots into 50 ml serum bottles used as biometers (Radosevich et al., 1996). Duplicate aerobic biometers for each sample were set up either with or without the addition of glucose (11.1 mM). Each biometer received 0.1 μCi (0.064 μmol) of [U-ring-^{14}C]-atrazine. For trapping $^{14}CO_2$, each biometer had a 2-ml vial suspended from a rubber septum with copper wire. The vials contained 1 ml of 0.5 M KOH as an alkaline trap. Biometers were closed with crimp-sealed rubber septa. For the biometers with 1 ml pre-concentrated suspended solids, the total volume was 2.32 ml.

Duplicate anaerobic biometers were set up with sterile double distilled H_2O instead of an external electron acceptor or one of the following: sulfate as Na_2SO_4 (15 μmol/biometer; 1.44 mg SO_4^{2-}), nitrate as KNO_3 (25 μmol; 1.55 mg NO_3^-), or Fe(III) as ferrihydrite (125 μmol; 14 mg Fe(III)). Each anaerobic biometer contained 0.1 μCi (0.064 μmol) of [U-ring-^{14}C]-atrazine and an alkaline trap. The headspace of these biometers was flushed with oxygen-free N_2 gas prior to sealing the rubber septa with crimp tops. For the biometers with 5 g composite sediment samples, the total liquid volume was 1.32 ml. All biometers contained 13.8 μg atrazine.

At 3–5 day intervals, the alkaline traps were removed and replaced with fresh KOH. The headspace conditions were re-established after each sampling event. The radioactivity in the alkaline trapping solution was measured by liquid scintillation counting using Scintiverse BD (Fisher Scientific, Fair Lawn, NJ) as scintillant. The concentration of atrazine remaining in each biometer was not analyzed. We have previously determined that the ^{14}C mass balance of [U-ring-^{14}C]-atrazine in field samples using the biometer technique is within the range of 97 ± 7% and 95–139% depending on the soil type and incubation conditions (Radosevich et al., 1996; Ostrofsky et al., 1997).

Atrazine mineralization was calculated as the percentage of the total amount of added [U-ring-^{14}C]-atrazine that was mineralized to $^{14}CO_2$. Where the data would allow, half-lives and rate constants of atrazine mineralization were determined by fitting graphs to a first-order rate function, using the equation $P = P_{max}\ (1 - e^{-kt})$, where P = observed percentage of $^{14}CO_2$ evolved, P_{max} = maximum average extent of mineralization for that biometer pair, t = time (d), and k = the rate constant (d^{-1}). Half-lives ($t_{1/2}$) were then calculated using the rate constant in the equation $t_{1/2} = \ln 2/k$ (Guerin and Boyd, 1992). Where data would not fit to a first-order rate function, a linear regression ($y = mx + b$) of the data was performed to determine the slope ($m = k$) and y-intercept (b). Half-lives were then calculated as $t_{1/2} = [(y_{max}/2) - b]/m$. For anaerobic incubations of river water samples, the biometer time courses had large variation among the duplicates. These are separated into single biometer data in graphs but the kinetic parameters were calculated as averages.

3. Results and discussion

3.1. Mineralization of atrazine in suspended solids of river water samples from the intake to the wetland

The concentrations of atrazine in Olentangy River water fluctuate annually between <1 and >5 μg/l reported as monthly averages (King et al., 2012). Peak concentrations may go up to >10 μg/l in early summer, followed by decline to 1–5 μg/l range through the summer and the fall. Atrazine concentrations in the Olentangy