



# Atrazine leaching from biochar-amended soils

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## HIGHLIGHTS

- We studied the effect of biochar on atrazine leaching in varying soil conditions.
- In laboratory columns, biochar reduces atrazine leaching in homogenized soil.
- Macropore flow or facilitated transport negate biochar effect in undisturbed soil.
- In field trials, applying acidified biochar decreases atrazine leaching.
- Irrespective of biochar, atrazine leaching is highly affected by soil structure.

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## ABSTRACT

The herbicide atrazine is used extensively throughout the United States, and is a widespread groundwater and surface water contaminant. Biochar has been shown to strongly sorb organic compounds and could be used to reduce atrazine leaching. We used lab and field experiments to determine biochar impacts on atrazine leaching under increasingly heterogeneous soil conditions. Application of pine chip biochar (commercially pyrolyzed between 300 and 550 °C) reduced cumulative atrazine leaching by 52% in homogenized (packed) soil columns ( $p = 0.0298$ ). Biochar additions in undisturbed soil columns did not significantly ( $p > 0.05$ ) reduce atrazine leaching. Mean peak groundwater atrazine concentrations were 53% lower in a field experiment after additions of 10 t ha<sup>-1</sup> acidified biochar ( $p = 0.0056$ ) relative to no biochar additions. Equivalent peat applications by dry mass had no effect on atrazine leaching. Plots receiving a peat-biochar mixture showed no reduction, suggesting that the peat organic matter may compete with atrazine for biochar sorption sites. Several individual measurement values outside the 99% confidence interval in perched groundwater concentrations indicate that macropore structure could contribute to rare, large leaching events that are not effectively reduced by biochar. We conclude that biochar application has the potential to decrease peak atrazine leaching, but heterogeneous soil conditions, especially preferential flow paths, may reduce this impact. Long-term atrazine leaching reductions are also uncertain.

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## 1. Introduction

While pesticides play an important role in improving crop productivity and resistance to disease, widespread use of these chemicals can lead to environmental contamination. Studies have found pesticide residue in 60% of groundwater samples from urban and agricultural areas of the United States (Gilliom et al., 2006). Atrazine is the most commonly used herbicide in the United States and is also the most frequently detected herbicide in drinking water aquifers and shallow groundwater beneath agricultural areas (Barbash et al., 2001). This is of general health concern, as

atrazine can be an endocrine disruptor in humans (Lasserre et al., 2009). Identifying ways to reduce atrazine leaching to groundwater would be an important gain for protecting environmental and human health.

Increasing atrazine retention within the soil profile through enhanced sorption could help reduce atrazine leaching to groundwater. Recent work on potential pesticide sorbents found that black carbon has a high affinity for sorbing organic contaminants (Accardi-Dey and Gschwend, 2003; Lohmann et al., 2005). In particular, the black carbon form known as biochar readily sorbs atrazine (Cao et al., 2009; Zheng et al., 2010). Biochar is formed from the pyrolysis of organic matter and is used as a soil amendment (Kookana et al., 2011). Recent studies on biochar's enhanced ability to sorb pesticides have concluded that this increased sorption could potentially decrease pesticide leaching to groundwater (Spokas et al., 2009; Zheng et al., 2010). Previous studies have found that

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biochar can reduce leaching of some pesticides in homogenized soil columns (Xu et al., 2011; Jones et al., 2011; Lü et al., 2012; Tatarková et al., 2013). Larsbo et al. (2013) found that in undisturbed columns, biochar's impact on the leaching of multiple different pesticides depended on the soil type. However, to the best of our knowledge, no work has yet been conducted to study biochar effects on atrazine leaching.

Despite evidence demonstrating that biochar can reduce pesticide leaching in homogenized soil columns, the potential impact on pesticide leaching in field conditions is less clear. Factors such as soil macropore structure and colloid-facilitated transport could influence leaching, and a previous study found that in some cases biochar addition to soil can actually increase herbicide leaching (Cabrera et al., 2011). Soil macropore structure has the potential to influence biochar's impact on atrazine leaching. Previous studies have demonstrated that preferential flow through macropores increases contaminant movement through the soil profile (Kookana et al., 1998; Akhtar et al., 2003). Additionally, preferential flow can enhance colloid-facilitated transport (Seta and Karathanasis, 1997; Villholth et al., 2000). Indeed, a field study found that 4.9–30% of total atrazine collected from field lysimeters was associated with colloids (Sprague et al., 2000). Since biochar has been shown to contain colloidal-sized particles that move via soil pore water flows (Zhang et al., 2010; Abiven et al., 2011), colloid-facilitated transport could actually enhance atrazine mobility in the presence of biochar. Here we address three foundational research questions with regards to the impacts of biochar on atrazine leaching: (1) Can increased sorption to biochar reduce atrazine leaching?, (2) Do increasingly complex soil structures impact atrazine leaching in the presence of biochar?, and (3) Does biochar surface treatment or soil organic matter content alter the effect of biochar addition on atrazine leaching?

## 2. Materials and methods

We designed three experiments with increasingly complex soil conditions: homogeneous, packed soil columns; undisturbed soil cores; and field-scale plot treatments. In addition to the biochar and control treatments used in the laboratory experiments, the field study treatments included acidified biochar, peat-biochar mixture, and peat alone. The acidification treatment was designed to return biochar surface pH to neutral conditions (surface pH was 8.5 prior to acidification) and thereby study impacts of biochar surface pH on atrazine leaching. Peat was chosen to study the impact of increased soil organic matter while minimizing additional impacts that more nutrient-rich organic matter additions (like compost) could have caused.

### 2.1. Materials

We used the Syngenta atrazine product AAtrex® Nine-O® which comes as water-dispersible granules and is 88.2% atrazine and 11.8% proprietary agent that aids in granule formation and dispersion. We used two different batches of biochar, purchased in succession from Biochar Solutions Inc. (then Biochar Engineering Corporation, Golden, CO). Both batches were produced for commercial sale from similar feedstock of wood chips (primarily from pine trees) using a proprietary process. Wood chip feedstock is first carbonized in an oxygen-limited environment at 700–750 °C for less than one minute, then held in a sweep gas environment between 400 and 550 °C for approximately 10–14 min. No oxygen is available during the second stage. The biochar had a surface pH of 8.5, a nitrogen content of 0.4 mg g<sup>-1</sup> and a carbon content of 880 mg g<sup>-1</sup>. Brunauer–Emmett–Teller (BET) surface areas were determined by Clark Laboratories LLC (Jefferson Hills, PA) using a

Micromeritics Tristar 3000 with multi-point N<sub>2</sub> adsorption and an outgas temperature of 473 K, and were found to be 195 ± 7.6 m<sup>2</sup> g<sup>-1</sup> for acidified biochar and 161 ± 8.5 m<sup>2</sup> g<sup>-1</sup> for regular biochar.

### 2.2. Homogenized soil column experiments

Soil for homogenized soil columns was collected from the top 0.25–0.5 m of silty loam soil at the Cornell Recreation Center (CRC) field site. Large soil aggregates were air-dried, broken up mechanically, and sieved to 2.8 mm. To improve infiltration capacity, soil was mixed 50/50 by weight with industrial quartz sand. Previous studies have found inert sand to be an effective way to improve soil column drainage (Das et al., 2004; Bi et al., 2010). The soil/sand mixture was loaded into 0.32-m tall and 0.1-m diameter PVC pipes. The soil column was capped on the bottom and perforated to allow leachate to pass through, and a 200-g quartz sand bottom layer prevented soil migration.

Biochar surface application and control treatments were run simultaneously in triplicate. Eight grams of dry biochar was mechanically mixed into the top 4–6 cm of each biochar column at a rate of 1 kg m<sup>-2</sup> (equivalent to 10 t ha<sup>-1</sup>, control column soil was similarly mixed for consistency). We applied 0.85 mg atrazine dissolved in 40 mL deionized water to each column, consistent with a field application rate of 1.1 kg ha<sup>-1</sup> (application rate chosen to allow peak atrazine leaching to be observed during the experimental run). Next we applied tap water at an average rate of 0.75 L h<sup>-1</sup> (9.5 cm h<sup>-1</sup>) per column for 9 h and periodically collected water samples from column leachate. The flow rate was chosen to give saturated flow conditions and to limit leaching experiment timescale, thereby reducing potential atrazine degradation. All samples were filtered to 0.45 µm and frozen until analysis.

### 2.3. Undisturbed soil core experiments

We collected six undisturbed soil cores from the CRC field site. At the time of core collection, the CRC site was covered in grasses, weeds, and scrubby brush, and had been unplowed for decades. Cores were extracted from the soil surface and contained vegetation and plant roots. We hand-excavated soil to expose a 0.3 m column of soil. Commercially available culvert pipe with a 0.18 m diameter was slipped over the exposed soil column, and expanding foam (Great Stuff polyurethane) was injected to fill any gaps between the soil column and culvert pipe walls. Minimal compression occurred within soil cores during this process. The foam was left to cure overnight, and columns were extracted the next day. Cores were stored in a temperature controlled laboratory and periodically watered prior to experimental use, allowing the continued growth of existing vegetation. Since cores were gathered prior to field experiment installation, vegetation in undisturbed cores and subsequent field trial plots was different. Cores were approximately 0.18 m in diameter and 0.3 m long.

In preparation for experimental run, we drip-irrigated all six soil cores until the onset of water leaching. Three cores then received 24.8 g of biochar which was mechanically mixed into the top 4–6 cm of soil at a rate of 1 kg m<sup>-2</sup> (equivalent to 10 t ha<sup>-1</sup>, control cores similarly mixed for consistency). All six cores received 6.29 mg of atrazine in 50 mL of deionized water, equivalent to the 2.2 kg ha<sup>-1</sup>. Atrazine application rate was chosen to match field plot application rate as prescribed by New York state pesticide application guidelines. Each column received artificial rain at a rate of 0.96 L h<sup>-1</sup> (3.8 cm h<sup>-1</sup>) and we periodically collected water samples from the leachate. All samples were filtered to 0.45 µm and frozen until analysis.

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