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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^{-1} 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.

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^{-1} and a carbon content of 880 mg g^{-1}. Brunauer–Emmett–Teller (BET) surface areas were determined by Clark Laboratories LLC (Jefferson Hills, PA) using a Micromeritics Tristar 3000 with multi-point N_2 adsorption and an outgas temperature of 473 K, and were found to be 195 ± 7.6 m^2 g^{-1} for acidified biochar and 161 ± 8.5 m^2 g^{-1} 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^{-2} (equivalent to 10 t ha^{-1}, 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^{-1} (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^{-1} (9.5 cm h^{-1}) 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 Stuf 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^{-2} (equivalent to 10 t ha^{-1}, 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^{-1}. 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^{-1} (3.8 cm h^{-1}) and we periodically collected water samples from the leachate. All samples were filtered to 0.45 μm and frozen until analysis.

2.4. Field leaching experiments

2.4.1. Experimental design

Field plots were incorporated into a broader five-year study on perennial grass biofuels production being conducted at the CRC site. The CRC site contains an upper silty mantle typically 0.45–1.0 m deep and a fragipan layer that extends downwards to approximately 1.5 m, past which is a firm glacial till. Plot treatments included the control and biochar conditions studied in the homogenized and undisturbed column experiments, plus acidified biochar, peat, and peat plus biochar mixture (peat-biochar). The 5 treatments were each repeated in 5 blocks, using a randomized Latin square design. All plots were 2×2 m and separated by 1 m. Chloride tracer experiments conducted in August, 2013 demonstrated that 24 h after adding 100 ml of 2000 ppm chloride to two injection wells, chloride concentrations were 35–164 times higher in the injection well than in adjacent wells (1–2 m away at all 4 points of the compass). One week later, chloride concentrations were still 18–86 times higher in injection wells compared to adjacent wells, indicating minimal lateral groundwater flow between wells.

2.4.2. Experimental installation

We prepared the acidified biochar by soaking biochar in a pH 1.4 solution of HCl. After 24 h, the acidic solution was drained and the biochar rinsed once with tap water. The pH measurements on the rinse water indicated that the biochar pH had dropped from 8.5 to 6.8 ± 0.06. For consistency, the non-acidified biochar was soaked in tap water and drained after 24 h (previous tests showed biochar surface pH after tap-water soaking to be 8.5).

Prior to the experimental installation, the field was mechanically mowed, plowed, and disced. Biochar plots received 4 kg (dry) of biochar at 1 kg m^{-2} (consistent with a loading rate of 10 t ha^{-1}), peat plots received 3.75 kg m^{-2} peat, peat-biochar plots received 1 kg m^{-2} of biochar and 3.75 kg m^{-2} of peat, and all treatments were raked into the top 75 mm (±25 mm) of soil. Immediately after biochar and peat installation, switchgrass seeds were mechanically broadcasted across plots. We then installed 4 shallow groundwater wells per plot, each to a depth of 1.2 m (1.2 m being approximately sufficient to intersect the fragipan layer). Gaps between the well and soil were packed with pea gravel and surface-capped with bentonite clay to reduce water flow into the gravel pack. On August 4, 2011 we applied atrazine at a rate of 2.2 kg ha^{-1} using a backpack sprayer.

2.4.3. Sampling methods

We collected perched groundwater samples at the first occasion when there was sufficient water in the majority of wells (August 30th, 2011), and 7 d later (September 6th, 2011). The August 30th sampling occurred 48 h after 38 mm of rain, and 55 mm of rain fell between August 30th and September 6th (rainfall amounts from Northeast Regional Climate Center, NRCC). Chloride tracer tests described earlier had demonstrated minimal lateral groundwater flow over a 7 d period. During sampling biochar was still distributed across plot surfaces, with no signs of significant transport by surface water runoff. Samples were collected by lowering a 50-mL Teflon centrifuge tube into each well. Samples were filtered to 0.45 μm and frozen until analysis.

2.4.4. Soil sampling

We collected 4 soil samples per plot in December 2011 from the top 0.15 m using a 20-mm long hand-coring device. Samples were air-dried, ground and sieved to 2 mm. Five grams of each sample were combined with 15 mL of 75:25 MeOH:H_2O, shaken for 24 h, and filtered to 0.2 μm. A small subset of soil samples was extracted in duplicate and spiked with 5 μg of atrazine to assess extraction efficiency and precision. Duplicate tests for extractions were within 8% of each other, and spiked samples were within 4% of the expected value. Samples were refrigerated prior to analysis.

2.4.5. ELISA and HPLC measurements

Samples from the column experiments and the groundwater sampling were analyzed using the RaPID Assay® Atrazine Test Kit available from Strategic Diagnostics (acquired by Modern Water). The test kit uses the enzyme linked immunosorbent assay (ELISA) method. Samples were analyzed at 450 nm using a spectrophotometer (either an Ohmicron RPA-1 or a Milton Roy Company Spectronic 501). All samples above 5.0 μg L^{-1} were diluted with deionized water prior to analysis. All samples measurements were performed in duplicate, and duplicate samples with a coefficient of variation above 10% were considered errant and re-analyzed.

Samples from the soil extraction procedure were analyzed using an HPLC (Shimadzu SIL-10advp injector connected to a Shimadzu SPD-10avp UV–VIS detector from Shimadzu, Kyoto, Japan). We used a Chromolith Performance RP-18e 100–4.6 mm column, an isocratic mobile phase of 50:50 MeOH:H_2O, and a detection wavelength of 222 nm. We also conducted a comparison between the ELISA results and HPLC results, and found that HPLC results were within $8 \pm 6\%$ of ELISA results. Statistical analysis was conducted using the statistical software JMP® (produced by SAS Institute Inc., Cary, NC).

3. Results

3.1. Laboratory leaching experiments

Results from the laboratory column data show that in homogenized soil columns, biochar reduced atrazine leachate concentrations ($p = 0.0009$, Fig. 1A). However, in undisturbed soil columns there was no significant reduction in leachate concentrations (Fig. 1B). Biochar amendments to homogenized soil columns also resulted in significantly lower total atrazine leaching ($p = 0.0298$, Fig. 1C). The homogenized biochar columns had lower peak atrazine concentrations (140.7 ± 20.3 μg L^{-1} for control versus 78.3 ± 8.4 μg L^{-1} for biochar, $p = 0.0193$). Differences due to biochar additions in undisturbed cores were not significant at $p < 0.05$ (Fig. 1B). We do not draw statistical conclusions between homogenized columns and undisturbed cores because the homogenized columns were amended with quartz sand to improve drainage, thus complicating direct comparisons between the two.

3.2. Field experiments

Results from the August 30th sampling event indicate that the control, peat, and peat-biochar treatments produced similar atrazine concentrations in perched groundwater (Fig. 2A). The perched groundwater associated with acidified biochar and biochar both appeared to have lower atrazine concentrations than the control, with acidified biochar being significantly lower ($p = 0.0056$). The September 9th samples had lower overall atrazine concentrations than August 30th samples, and no difference between treatments (Fig. 2B). We also note the observation of two atrazine concentration outliers in the August 30th biochar treatment samples (Fig. 2A). These data points are far above the third highest data point found in a control sample and while they could be considered statistical outliers, they may have physical relevance. We would expect such "spikes" in concentration to be transient as the later arriving matrix-flowing water would dilute the earlier arriving, atrazine-rich macropore water. Independent measurements or observations are needed to confirm this.

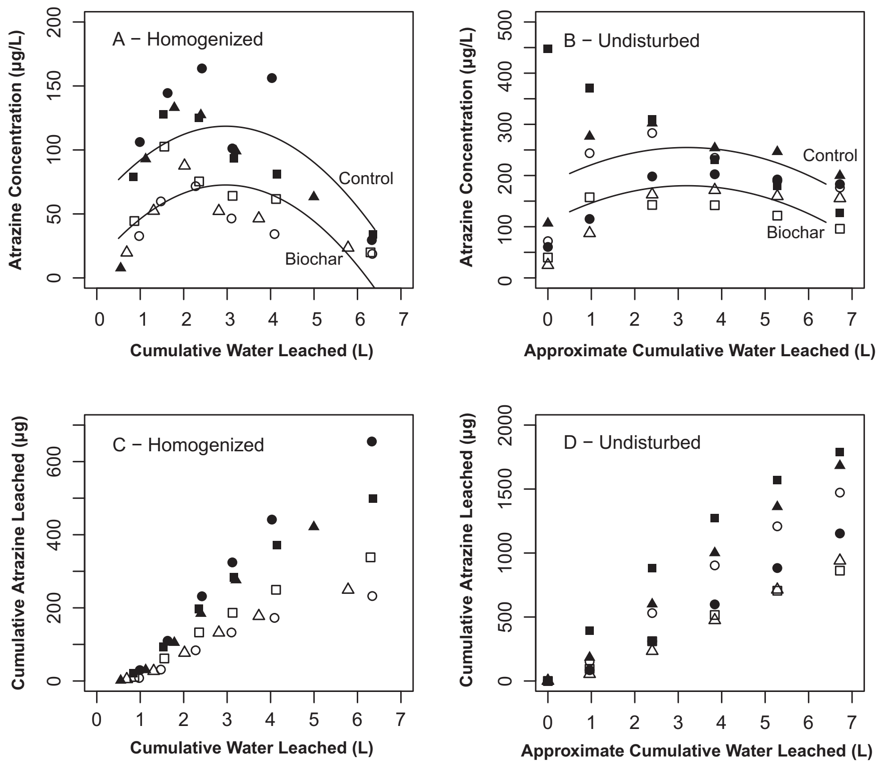

Fig. 1. Atrazine leaching as a function of cumulative water volume leached. Atrazine concentration in μg L^{-1} for homogenized (A) and undisturbed (B) soil columns and cumulative atrazine leached (μg) for homogenized (C) and undisturbed (D) soil columns. Lines represent JMP regression models. Solid points represent control data, hollow points represent biochar data. Individual point shapes represent the 6 repeated measurements taken on each column (6 columns total). Undisturbed columns received 2.2 kg ha^{-1} atrazine while homogenized columns received 1.1 kg ha^{-1} atrazine.

To check the influence of the August 30th sample outliers, we used the nonparametric Kruskal–Wallis method (data did not meet the normality requirements necessary to conduct an ANOVA) and found that there was a significant difference between the 5 treatments with or without the outliers included ($p = 0.0011$ and $p = 0.0002$, respectively). Multiple comparisons using the nonparametric Steel–Dwass method showed that adding acidified biochar resulted in significantly lower atrazine concentrations in perched groundwater than all other additions except biochar (Fig. 2A). Atrazine concentrations from biochar plots were not statistically different from other plots, and when outliers are excluded biochar plot concentrations were only statistically lower than the peat-biochar concentrations. Peat-biochar, control, and peat all resulted in statistically similar atrazine perched groundwater concentrations.

Atrazine concentrations in soil extracts were found to be inversely related to the atrazine concentrations measured in perched groundwater on August 30, 2011 (Fig. 2C). Soil atrazine concentrations are highest when biochar and acidified biochar were added to soil. Conversely, perched groundwater atrazine concentrations were lowest when biochar and acidified biochar were added. (Fig. 2A and C). The Steel–Dwass multiple comparisons demonstrated that both biochar and acidified biochar additions resulted in significantly more atrazine in the surface soil than the control, peat, and peat-biochar additions ($p = 0.0108$ and below for pairwise comparisons, Fig. 2C).

4. Discussion

4.1. Atrazine transport mechanisms

Homogenized soil column results indicate that under simple, packed soil conditions, biochar can reduce atrazine leaching. However, the undisturbed soil column results show no difference between biochar and control treatments, indicating that soil macropore structure may play a significant role in controlling atrazine leaching. For example, one of the control cores experienced the peak atrazine concentration in leachate in the first sample (447.6 μg L^{-1}), which was much higher than the average first value for the other two control columns (83 μg L^{-1}). This rapid leaching event could have been caused by local macropore structure. Field results from August 30, 2011 also demonstrated very high atrazine concentrations in two of the biochar samples. Previous studies have found that preferential flow through macropores is an important factor controlling pesticide leaching (Flury, 1996; Jarvis, 2007).

We observed that cumulative atrazine leaching between control and biochar-amended cores is more similar for undisturbed cores than for homogenized cores. One potential explanation for this is that biochar increased colloid-facilitated transport of atrazine via macropores, since macropores would be more prevalent in undisturbed cores than in homogenized cores. While more work is needed to determine whether colloid-facilitated transport was occurring in our studies, previous work by Seta and Karathanasis (1997), and de Jonge et al. (2000) found links between colloid-facilitated transport and facilitated flow. We also note that atrazine leaching concentrations were on average 55% lower in the homogenized biochar columns than the control columns. For the undisturbed columns, there was statistically no difference in peak leaching concentrations. This would indicate that the combination of biochar addition, macropore leaching, and potential facilitated transport can raise peak atrazine leaching by 55%.

Due to the plowing and discing before experiment implementation, soil conditions in the field plots were likely somewhere between completely homogeneous and undisturbed. Results do indicate a 58% reduction in peak atrazine leaching between

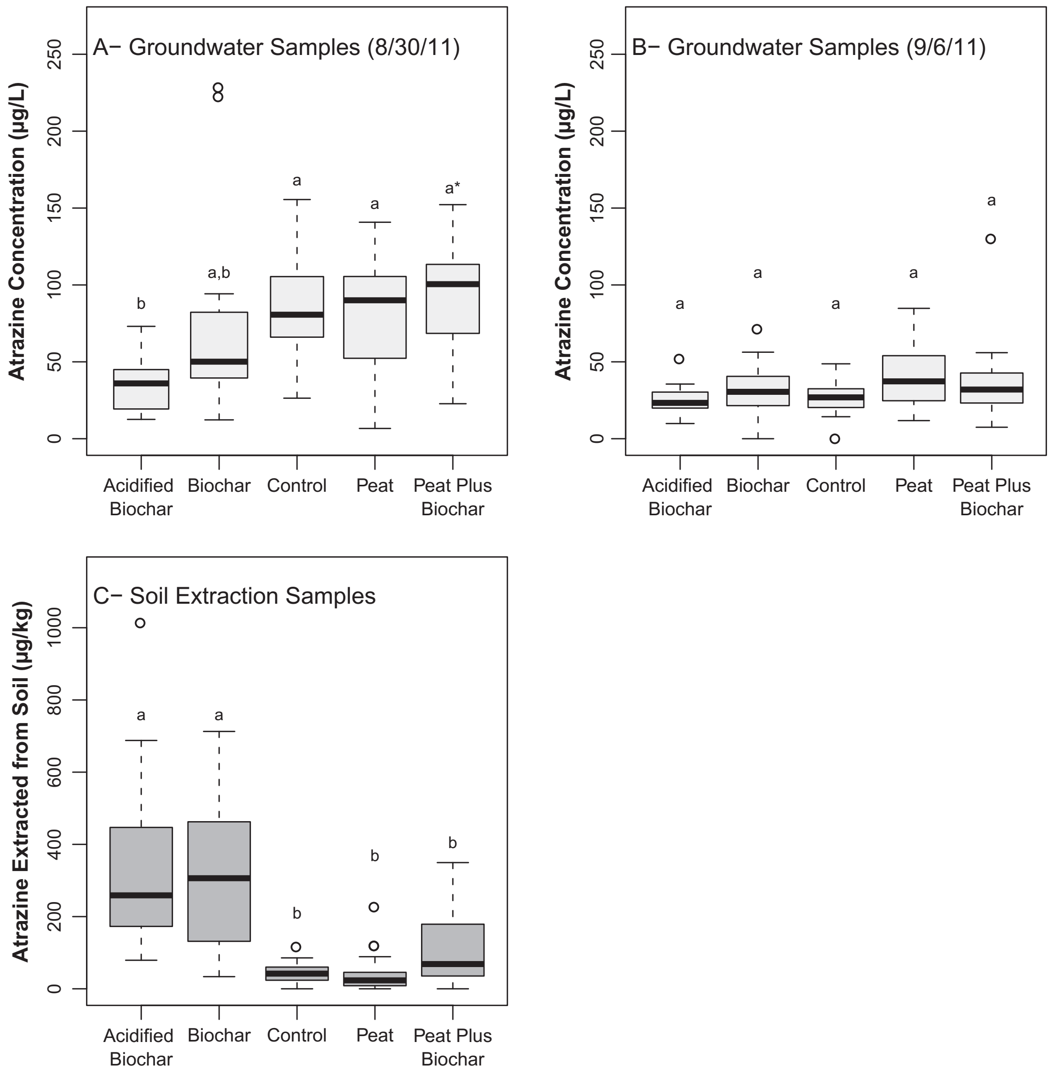

Fig. 2. Atrazine concentrations measured in perched groundwater samples gathered 8-30-11 (A) and 9-6-11 (B), and in soil (C). Boxes represent the interquartile range (IQR) and whiskers extend to 1.5 times the IQR. Data marked with hollow circles fall outside 1.5 times the IQR. Different letters indicate statistically distinct groups at $p < 0.05$ as determined from Steel–Dwass multiple comparisons (including outliers). When excluding outliers (shown with * at the letter), peat plus biochar is significantly different from acidified biochar and biochar, and similar to control and peat. Number of samples represented in figures A(B) are: 14(16) acidified biochar, 15(19) biochar, 18(17) peat, 13(20) peat plus biochar, and 13(16) control. Figure C represents 20 samples in each category.

acidified biochar and control plots (similar to the 55% reduction seen in homogeneous soil columns), and some of this reduction could be attributed to disturbed soil conditions. However, biochar plots exhibited no reduction in atrazine leaching at $p < 0.05$ even though they had similar soil conditions. We also note the potential importance of biological breakdown of atrazine which could have occurred in the field experiments between atrazine application and groundwater sampling, though studying these degradation products was outside the scope of this work.

Since the September 6th samples exhibit no biochar treatment effect, we assume that the impact of biochar on atrazine leaching is likely limited to peak leaching events occurring just after soil saturation. Specifically, biochar appears to have immobilized atrazine that otherwise was rapidly transported to the shallow groundwater, likely via preferential flow paths. Subsequent rain events appear to dilute groundwater atrazine concentrations and minimize the differences seen initially between surface treatments. Soil column experiments also demonstrated this pattern where the greatest differences in atrazine leaching are observed during peak leaching, with differences diminishing as leaching continues. This indicates that while acidified biochar may be able to reduce peak atrazine leaching, long-term reductions in groundwater atrazine leaching are uncertain. This finding is also consistent with Shalit and Steenhuis (1996), and Diess et al. (2004) in which preferential flow initially resulted in high concentrations of percolating solutes that were subsequently diluted by presumably less concentrated matrix flow.

4.2. Retention mechanisms

Atrazine concentrations in the soil extracts indicate that the reduction in peak perched groundwater atrazine concentration (August 30, 2011 sample) observed for the acidified biochar occurred because of higher atrazine retention within the soil profile. We assume that these higher amounts of atrazine were sorbed to biochar particles distributed within the soil of biochar-amended plots. Recent work with C^{14} labeled simazine also found that biochar-induced reduction in simazine leaching corresponded with simazine accumulation around biochar particles (Jones et al., 2011), and other studies found similar links between biochar and soil pesticide accumulation (Yu et al., 2009). Based on our results and previous studies, we attribute the observed reductions in perched groundwater atrazine concentrations to an increased accumulation of atrazine within the soil profile.

The lower peak atrazine concentration in perched groundwater after additions of acidified biochar implies that acidified biochar behaves differently than regular biochar. We conducted follow-up isotherm analyses with biochar and acidified biochar, each with and without peat, to determine if there was any detectable difference in sorption capabilities (details available in Supplementary Information). Both the isotherm analysis and the atrazine concentration in field samples indicate that the acidified biochar treatment may sorb atrazine more effectively than untreated biochar. This could be explained by the BET analysis which showed that acidified biochar had on average 21% more surface area than regular biochar ($195 \pm 7.6\ m^2\ g^{-1}$ versus $161 \pm 8.5\ m^2\ g^{-1}$). Previous studies have found that some untreated biochar surfaces contain tar-like deposits (Jia and Lua, 2008), and that washing pyrolyzed anthracite in HCl increases micropore volume (Lozano-Castelló et al., 2001). It is possible that the biochar acidification step removed surface impurities and therefore exposed more micropores to atrazine sorption. We also note that due to the higher pH of tap water used to make the acidified biochar sent for BET testing, these surface areas likely represent a conservative estimate of the impact of acidification on biochar surface area.

4.3. Organic matter effect on atrazine retention

Adding organic matter in the form of peat does not significantly reduce atrazine concentrations in perched groundwater compared to control plots. When added to biochar-amended plots, peat even has the effect of both increasing concentrations of atrazine in perched groundwater and reducing atrazine retention within the soil, compared to biochar-amended plots (when ignoring outliers). These results are consistent with the isotherm results and the hypothesis that peat reduces biochar's ability to sorb atrazine. This hypothesis is supported by previous studies showing that the presence of organic matter in soils can decrease biochar sorption of organic compounds by blocking char micropores or competing for char surface adsorption sites (Pignatello et al., 2006; Qiu et al., 2009). However, we found that soaking biochar and peat together for 24 h yielded a substantial increase in biochar BET surface area ($320\ m^2\ g^{-1}$ compared with $161\ m^2\ g^{-1}$ for regular char). While more work is needed to understand this increase in surface area, the acidic nature of peat could have removed biochar surface impurities (as discussed for the acidified biochar). This indicates that sorption competition between organic matter and atrazine may be more important than biochar pore-blocking, but more work is needed to understand this interaction between biochar and peat.

5. Conclusions

We conclude that while biochar use as a soil amendment may reduce peak atrazine leaching, this effect will likely be greatest in poorly structured soils or soils with low organic matter. The complexities of soil pore structure (e.g. macroporosity) appear to negate the biochar-induced reduction in atrazine leaching observed in homogeneous soil conditions. Anomalously large leaching events appear to occur irrespective of soil amendment, indicating that localized soil structure heterogeneities play a dominant role in facilitating large leaching events. Even with soil heterogeneities, it appears that if biochar is acidified prior to soil application, it can significantly reduce peak atrazine concentrations in perched groundwater. This may be because the acidification process increased biochar's surface area, thus exposing more atrazine adsorption sites. This also indicates that selecting biochar with a higher surface area than that used in this study could lead to further reductions in peak atrazine leaching. However, since reductions in atrazine leaching appear to be a short-term effect, reduction in atrazine amounts leached over time is likely to be limited. Our research shows that if biochar is applied to soil in conjunction with organic matter such as peat, no reduction in perched groundwater contamination of atrazine is seen. More work is needed to understand the interaction between biochar and organic matter and to ascertain the long-term effects of biochar addition on atrazine leaching.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.09.043.

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