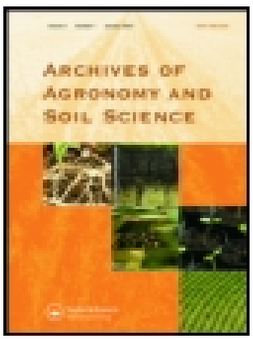

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Biochar concomitantly increases simazine sorption in sandy loam soil and lowers its dissipation

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Abstract

Biochar application has been receiving much attention as pesticide pollution mitigator because it reduces harmful chemicals. However, direct comparisons between the effect of biochar and straw on the simazine fate in soils remain poorly understood. We explored the impact of biochars and straw on the simazine behavior in a soil using a ^{14}C labelling approach. Biochar was

produced by the thermal treatment of wheat straw at four contrasting temperatures (250, 350, 450 and 550 °C) and was incorporated into a sandy loam soil. The sorption of simazine in the biochar soil from 83.9% to 87.5% was significantly higher than 43.0% in the un-amended soil and 35.7% in the soil amended with unprocessed straw, thus resulting the low in samizine leaching from 21.8% to 42.6% in the biochar soil. However, biochar application suppressed the simazine decomposition, which is contrast in the straw soil. Furthermore, the biogeochemical behavior of simazine varied with the pyrolysis temperature. These results indicate biochar application can significantly increase simazine adsorption and reduce leaching, which is benefit to the environmental pollution. In conclusion, the simazine behaviors in the soil are strongly influenced by the biochar properties. In comparison to straw, biochar has potential to mitigate simazine pollution.

Keywords: black char, biodegradation, leaching, pyrolysis, sorption

Introduction

Simazine (1-Chloro-3, 5-bisethylamino-2, 4, 6-triazine) is a popular pesticide that is widely used in agriculture and forestry to control broadleaf and grassy weeds. It is reported that simazine was the 28th most used pesticide in California with applications (306,100 kg) primarily on fruit and vegetable crops (CDPR 2003). Barber and Parkin (2003) estimated that up to one-third of all pesticides are deposited to soil at the time of application. In addition, previous literature reported that the half- life of

simazine was up to 149 days (Wauchope et al. 1992), even more longer (Jones et al. 2011a). Therefore, over time most simazine application should be accumulated in the soil which lead to the area as a source of simazine subject to leaching and runoff (Jiang et al. 2011). For example, simazine is the second most commonly detected pesticide in surface water and groundwater in the United States, Europe, and Australia, at concentrations of up to several hundred micrograms (Cox et al. 2000; Troiano et al. 2001). Therefore, humans may be exposed to simazine both indirectly, through drinking water and food, and directly, through exposure during its application. This is a huge health risk to humans and ecosystems (Rico et al. 2012) because simazine has been shown to induce limited mutagenic or carcinogenic activity (Bogdanffy et al. 2000; Birnbaum and Fenton 2003; Hayes et al. 2006). Thus, effective approaches are needed to mitigate the pollution and side effects caused by this pesticide in the environment, particularly in soil and water.

Biochar, which is a type of charcoal with a large surface area and strong negative charges (Liang et al. 2006), has gained increasing attention because of its ability to mitigate the physical and biological effects of chemicals in soil, among other functions (Kołodyńska et al. 2012; Ahmad et al. 2014). Once added to soil, biochar increases the adsorption of simazine in the soil, thus decreasing its leaching. For example, Jones et al (2011a) reported that biochar suppressed simazine biodegradation and reduced simazine leaching. However, biochar application also decreases the efficacy of pesticide in controlling pests or weeds (Williams et al. 2015). Although, the increase in number and activity of microorganisms due to the presence

of N and other nutrients in biochar should induced the increasing of the simazine decomposition, it is reported that the simazine decomposition was suppressed by biochar application (Jones et al. 2011a). Based on these discrepancy, we assumed that biochar properties, which are controlled by the type of feedstock (Glaser et al. 2002; McClellan et al. 2007; Spokas et al. 2009) and pyrolysis conditions (Yuan et al., 2011; Al-Wabel et al., 2013; Méndez et al., 2013), play an important role in regulation of simazine biogeochemical behaviors. Changes in pyrolysis temperature, for example, may lead to variation in the biochar's surface area, cation exchange capacity (CEC) and porosity (Wang et al. 2013), which further affects the simazine fate in biochar amended soil (Jones et al 2011a). However, the direction and magnitude of biochar effects on simazine biogeochemical behaviors are complex. Further the underlying mechanistic basis of the responses remains poorly understood.

Our objectives were to (i) explore the effect of biochar application on the simazine biogeochemical behaviors (adsorption, leaching and decomposition), (ii) determine which biochar production conditions favor minimum simazine pollution, and (iii) assess the advantages and disadvantages of using straw or biochar as a simazine mitigator.

Materials and methods

Sample materials

Wheat straw was collected from Henfaes Research Centre, Wales, North Wales (53°14' N, 4°10' W). After the wheat straw was dried in an oven at 80 °C for 24 hours, it was cut into 10 cm chips, loaded into a beaker, and covered with a Duran

crystallizing dish. Next, the beaker was placed in a muffle furnace for pyrolysis. The rate of heating was 20 °C·min^{-1}, and the holding time was 1 hour. Four peak pyrolytic temperatures were used (250, 350, 450, and 550 ° C), and the corresponding biochars were named B_{250}, B_{350}, B_{450}, and B_{550}, respectively.

Soil was collected from the Ah horizon (0–15 cm, sandy loam) of a freely draining, grassland soil (Eutric Cambsiol soil type), which receives regular fertilization (120 kg N, 60 kg K, and 10 kg P annually) and was located at the Henfaes Research Centre. The site is used for both grassland and arable production and has a mean annual temperature of 11 °C (range -5 to 25 °C) and mean annual rainfall of 1060 mm (temperate climate regime). The soil was sieved to pass 5 mm to remove plant residues and stones and then dried at 20 °C prior to use. The major properties of the soil are shown in Table 1 with additional properties shown in Jones et al. (2011b, 2012) and Farrar et al. (2012).

Analyses and calculations

The carbonization rate was calculated with the equation:

$$CR = Cw / Sw \times 100\% \qquad \text{(equation 1)}$$

in which CR is the carbonization rate, Cw is the weight of biochar and Sw is the weight of

wheat straw. The bulk density of biochar was determined following this method, first, biochar powder was filled into a 2 ml small tube, compacted, and filled, until cannot filled, then weigh the tube and calculated the bulk density. The ash content of biochar was measured after the samples were heated at 575 °C in a muffle furnace for 3 hours

(Monti et al. 2008). The pH and electrical conductivity (1:20 w/v with distilled water) of biochar, soil and straw were determined with a standard electrode. The water holding capacity (WHC) was measured using the international standard method, ISO16378. Briefly, approximately 2.0 g biochar (soil or straw) was saturated in distilled water for 4 hours, and then placed on moist sand for 2 hours. The sample was heated in an oven at 105 °C for 24 hours, and the residues were weighed to aid in the calculation of the WHC. The SSA of a biochar sample was measured using a surface area analyzer (Autosorbi/monosorb, Quantachrome Instruments, Boynton Beach, FL, USA), with N absorption at 77 K, using the Brunauer-Emmett-Teller method. The biochar samples were observed under a Hitachi S-520 scanning electron microscope with 15 V of acceleration voltage. The CEC of biochar (soil or straw) samples were measured using a modified NH_4-acetate compulsory displacement method (Gaskin et al. 2008). Briefly, 0.2 g biochar / 0.5 g straw / 1.0 g soil were soaked separately in 20 mL deionized water, shaken, and centrifuged, and then the supernatant was decanted. This process was repeated five times to remove the soluble salts that cause interference. Then, 20 mL of Na-acetate (1M, pH 7) was added to the sample prior to centrifugation at 2500 rpm for 10 minutes, followed by decantation of the supernatant. This process was repeated five times to ensure that the exchange site was saturated with Na ions. Then, the sample was washed with 20 mL ethanol, centrifuged, and the supernatant was decanted. By repeating this process five times, the excess Na ions were removed. Finally, the Na ions were displaced by NH_4-acetate (pH 7) and measured by a flame photometer (Model 410; Sherwood Scientific Ltd, Cambridge,

UK). The total amounts of C, N, H, and S in biochar and straw were determined with a vario MACRO cube analyzer, and the O content was calculated assuming a composition of C, N, H, and O, after deducting the ash content (Zimmerman 2010).

Experimental design

Six treatments were used, including the un-amended soil, the soil amended with biochar (B_{250}, B_{350}, B_{450}, and B_{550}; dry soil to dry biochar ratio of 10:1), and the soil amended with unprocessed straw (dry soil to dry straw ratio of 10:1). To create the amended soils, approximately 40.0 g dry soil was added separately to 4.0 g biochar or unprocessed straw (both ground and sieved with a 0.3 mm mesh) and evenly mixed by hand. All the soil treatments were tested in quadruplicate.

Adsorption of simazine

For each of the samples, approximately 5.0 g was placed in a 50 mL centrifuge tube. Then, the tubes were sterilized in an oven at 80 °C for 30 minutes to minimize microbial degradation (Kuzyakov & Jones 2006). Then, 20 mL ^{14}C-labelled simazine (0.04 mg L^{-1}, 0.05 kBq mL^{-1}) was added to each tube, and the samples were shaken at 200 rpm for 24 hours at 20 °C. During the shaking, 0.5 mL of liquid was removed from each tube at 0.5, 3, and 24 hours, which represented instantaneous, intermediate, and quasi-equilibrium conditions (Kookana et al. 1993), respectively, for measuring ^{14}C-specific activity. For this measurement, 4 mL Optiphase HiSafe 3 scintillation fluid (PerkinElmer Inc., Waltham, MA, USA) was mixed with each sample, and a Wallac 1400 liquid scintillation counter (PerkinElmer Inc., Waltham, MA, USA) was

used to determine ^{14}C-specific activity. The distribution coefficient (K_d) of simazine between the soil and the solution was calculated using Eq. (2):

$$K_d = C_{ads}/C_{apl} \quad (2)$$

where C_{ads} is the concentration of simazine adsorbed into the soil (mg kg^{-1}), and C_{apl} is the concentration of simazine in the solution (mg L^{-1}).

Simazine leaching

For each of the samples, approximately 5.0 g was put into a 25 mL syringe (20 mm diameter) which was inverted and a 1 mm polypropylene mesh was placed at the top before the sample was added to avoid any loss. Next, distilled water was added to saturate the sample. After 0.2 mL of ^{14}C-labelled simazine (2.00 mg L^{-1}, 0.50 kBq mL^{-1}) was added, the sample was placed on a table for 1 hour. Before the start of leaching, another 1 mm polypropylene mesh was placed over the samples to mitigate the impulse of liquid. Then, a pump added distilled water at a rate of 0.2 mL min^{-1}, and the leachate was flowed from the syringe hole and collected. The ^{14}C-specific activity was measured when the leachate reached volumes of 1, 3, 6, 10, 15, 20, and 30 mL.

Simazine decomposition

Approximately 10.0 g of the sample was packed into a 50 mL centrifuge tube, and the humidity was adjusted to 70% of the WHC (Jones et al. 2011b). For microbial recovery, samples were stored at 20 °C for 7 days (Jones et al. 2011b). Then, 0.5 mL of ^{14}C-labelled simazine (0.80 mg L^{-1}, 0.78 kBq mL^{-1}) was added to each sample. A 1 mL NaOH trap (1M) was placed above the sample to capture CO_2 released from the sample. The NaOH traps were replaced after 1, 3, 5, 7, 10, 15, 20, 25, 30, and 40 days.

Finally, the tubes were sealed and incubated in the dark at 20 °C for 40 days. The $^{14}CO_2$ content in the NaOH traps was determined by liquid scintillation counting using Optiphase 3 scintillation fluid (PerkinElmer Corp., Waltham, MA) and a Wallac 1404 liquid scintillation counter (PerkinElmer Corp.).

Statistical analysis

Statistical procedures were carried out with the SPSS 19.0 for Windows software package (SPSS Inc., Chicago, IL, USA). All measurements were reported as mean values with standard error of mean. A one-way analysis of variance followed by a Least Significant Difference test was used to determine if significant differences (cut-off value of 95%) occurred between soil treatments.

Results

Biochar characterization

The physicochemical properties of the biochars are listed in Table 1. With the increasing pyrolytic temperature, biochar pH increased from 5.40 to 9.74, biochar SSA increased from 2.70 to 10.47 $m^2\ g^{-1}$, whereas biochar yield decreased from 47.4 to 30.8% and biochar CEC, electrical conductivity decreased from 68.7 to 22.0 cmol kg^{-1} and 3355 to 1247 μs cm^{-1}, respectively (Table 1). Scanning electron microscope images show that the porosity of the biochar increased with an increase in pyrolytic temperature (Figure 1).

The C concentration in the biochar increased from 64.6 to 82.3% with the increase in the pyrolytic temperature (Table 2). The converse was observed for the H

and O concentrations, which decreased from 4.1 to 3.0% and 29.3 to 12.5%, respectively (Table 2). As the pyrolytic temperature increased, the atomic ratios of H/C, O/C, and (N+O)/C significantly decreased from 0.77 to 0.44, 0.33 to 0.11, and 0.34 to 0.12, respectively.

Simazine sorption behavior

At instantaneous condition (0.5 h), the low simazine sorption were observed in the control (22.8%) and the soil amended with unprocessed straw (24.2%) (Figure 2). The high simazine sorption were observed in the soil amended with biochar (48.0~55.5%). At intermediate condition (3 h), compared to the control (32.9%) and the soil amended with unprocessed straw (28.8%), the sorption was significantly high in the soil amended with biochar from 66.6% to 72.4%. At quasi-equilibrium condition (24 h), the significantly high sorption was observed in the soil amended with biochar from 83.9% to 87.5%, and the low sorption was observed in the control (43.0%) and in the soil amended with unprocessed straw (35.7%). Among the soil amended with biochar, significant high sorption was observed in the soil amended with B_{550} and B_{250} ($P < 0.05$, Figure 2) at instantaneous condition and intermediate condition. However, this discrepancy was decreased at the quasi-equilibrium condition (Figure 2).

Simazine leaching

Significantly higher ($P < 0.05$) simazine was observed in the unamended soil leachate (76.4%) than in the soil amended with biochar (Figure. 3). But the highest simazine loss (90.5%) was observed in the soil amended with unprocessed straw

(Figure. 3). Among the soils amended with biochar, the significantly ($P < 0.05$) high simazine leaching was observed in the soil amended with biochar B_{450}, and the significantly low simazine leaching was observed in the soil amended with biochar B_{250} and B_{550} (Figure. 3).

Simazine decomposition

The significantly ($P < 0.05$) high rate of accumulative simazine decomposition (5.1%) was observed in the soil amended with unprocessed straw (Figure. 4). Compared to the control (4.8%), simazine decomposition was significantly ($P < 0.05$) suppressed in the soil amended with biochar from 3.2% to 4.5%. Among the soils amended with biochar, the accumulative simazine decomposition increased with the increase in the pyrolytic temperature (Figure. 4).

Discussion

Effects of straw and biochar on simazine sorption and leaching

The significantly high simazine sorption in the soil amended with biochar, compared to the unamended soil, indicates that biochar application enhanced the simazine sorption capacity of the soil. This finding is consistent with previous reports (Jones et al. 2011a; Zhang et al. 2011; Zheng et al. 2011). However, the results herein also indicate the unprocessed straw addition reduced the simazine sorption capacity of the soil. Among the soil amended with biochar treatment, the simazine sorption was different, which presumably reflects the influence of biochar properties when biochar was added into the soil. Chen et al (2008) considered that sorption mechanisms of

biochars are evolved from partitioning-dominant at low pyrolytic temperatures to adsorption-dominant at higher pyrolytic temperatures. In our study, although the quasi-equilibrium sorption was not significantly different among biochar amended soil, the instantaneous and intermediate sorption revealed the discrepancy in simazine sorption derived from different sorption mechanism. In addition, the solid-to-solution partition coefficient values listed in Table 3 also showed the similar results. Zhou et al. (2010) suggested that carbonized C adsorbed benzene and nitrobenzene as a surface adsorbent, whereas organic C adsorbed these compounds as a partition medium. With the increasing pyrolytic temperature, the SSA and porosity of biochar also increased, indicating an increase in its surface adsorption capacity (Table 1). On the other hand, the C content increased, whereas the O and H contents decreased (Table 2), with an increase in the pyrolytic temperature, implying that the organic matter in biochar decreased. Overall, irrespective of the pyrolytic temperature, the application of biochar to the soil enhanced the adsorption of simazine.

The results for simazine leaching in the different soil treatments (Figure. 3) indicated that the biochar application into the soil significantly decreased the concentration of simazine in the leachate and the addition of unprocessed straw accelerated the simazine loss. These results shows that biochar application has a potential for mitigating groundwater and surface water pollution (Ahmad et al. 2014; Craig et al. 2015). However, the results also suggest that biochar application to soil can lead to an accumulation of the pesticide in the soil.

Effects of biochar and straw on simazine decomposition

In this study, simazine decomposition was suppressed by the addition of biochar, which is consistent with the report by Jones et al. (2011a). Although the soil type and incubation conditions in this study were the similar with those in Jones et al. (2011a), the differences in simazine decomposition due to the different biochars used in these two experiments indicate that the type of biochar used greatly influences simazine decomposition. Different simazine decomposition patterns among the different soil treatments also indicate that biochar properties play an important role (Figure. 4). Based on observations of a 23-day incubation experiment, Morgante et al. (2012) suggested that most of the simazine (> 70%) was subjected to microbial degradation, which was significantly higher than our results, where the highest rate was 5.1% in the soil amended with unprocessed straw (Figure. 4). We presumed that the differences in the nature of the soil and incubation conditions also play an important role. Previous studies reported that the suppression of simazine biodegradation could be attributed to a rapid and strong sorption of simazine to the biochar (Jones et al. 2011a; Yu et al. 2006), thus preventing access of extracellular enzymes to the simazine (Zhou et al. 2010; Virchenko et al. 1986). Based on these viewpoints, we deduced that more simazine was adsorbed in the soil amended with high temperature biochar because the number of micropores and surface area increased with an increase in the pyrolytic temperature. However, the results in this study also suggest that simazine decomposition increased with increasing pyrolytic temperature. Apparently, the adsorption capacity alone is not sufficient to explain

fully the simazine decomposition for the different treatments. As simazine is chemically unstable at high pH (Hosoi et al. 1995), we hypothesized that the degradation of simazine would increase when it was mixed with biochar, due to an increase in its alkalinity caused by the increase in pyrolytic temperature (Table 2). Overall, we concluded that biochar can inhibit simazine decomposition in sandy loam soil, leading to a gradual accumulation of this pesticide on the soil surface.

Mitigating environmental risks or accelerate environmental risks due to biochar application

From an environmental protection standpoint, biochar application seems to lower significantly the risk of simazine contamination to the groundwater and surface water. However, this may have a negative effect on the soil. For example, the binding of simazine limits its availability to the soil microbial community, which leads to a decrease in simazine efficacy in the soil (Graber et al. 2012; Nag et al. 2011). As previous studies have demonstrated, biochar application to the soil could significantly reduce organism exposure to simazine due to the binding of organic pollutants by the biochar (Jones et al. 2011a; Koelmans et al. 2006; Sun et al. 2009). This effect of biochar on the simazine activity (Jones et al. 2011a; Yu et al. 2009) may cause farmers to over-apply pesticides, leading to greater environmental risks. Thus, policymakers and pesticide manufacturers need to guide farmers on the correct pesticide dosages for biochar-amended soils. Limited information is available on the influence of biochar on pesticide efficacy (Graber et al. 2012; Nag et al. 2011; Yang et al. 2010). The differences in simazine decomposition patterns shown in this study and studies

conducted by Morgante et al. (2012) and Jones et al. (2011a) demonstrated that soil type, biochar characteristics, and experimental conditions greatly affect the biogeochemical cycle of a pesticide. In this study, alone based on the decomposition data, the simazine decomposition in the soil amended with biochar delays more days. If simazine leaching loss are not considered, this will be a bad news for the food security due to more simazine accumulated in the surface soil after several years. Therefore, the utilization of biochar to mitigate the simazine pollution in water should consider the potential threat for food security.

Conclusions

The sorption, leaching, and decomposition of simazine in soil amended with biochar indicated that biochar application can significantly reduce the risk of groundwater and surface water organic pollution, and these effects of biochar varied with biochar's properties. Although biochar application reduces simazine dissipation in soil and efficacy as a pesticide, its benefits include water pollution prevention and reduction in the concentration of simazine in food are conductive to agricultural development. Therefore, further research should be conducted on biochar properties and pesticide efficacy prior to the use of pesticides on soil amended with biochar.

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Table1. Physical and chemical properties of biochar, soil and straw.

	B550	B450	B350	B250	Soil	Straw
CR (%)	30.8±0.3d	33.6±0.3c	37.7±0.4b	47.4±0.8a		
pH	9.7±0.2a	9.2±0.1b	8.8±0.1c	5.4±0.1e	6.4 ± 0.0d	6.4 ± 0.2d
EC (μS cm^{-1})	1242±77d	1384±39c	1825±158b	3355±125a	40.88 ± 0.9f	1026 ± 47e
SSA ($m^2 g^{-1}$)	10.5±0.0a	4.6±0.0b	5.2±0.0c	2.7±0.0d		
CEC (cmol kg^{-1})	22.0±1.3d	40.5±1.2c	58.6±1.7b	68.7±0.5a	7.8±0.1f	18.1±0.5e
WHC (%)	339±12b	355±34b	333±23b	275±11c	35.12±1.1d	406±3a
AC (%)	18.5±0.2[a]	14.7±0.2c	18.8±0.8[a]	16.2±0.7b		
BD (g cm^{-3})	0.3±0.0c	0.4±0.1bc	0.4±0.1bc	0.5±0.1b	0.5±0.0b	0.8±0.0a

CR, EC, SSA, CEC, WHC, AC and BD are the abbreviations for carbonization rate, electrical conductivity, specific surface area, cation exchange capacity, water holding capacity, ash content and bulk density, respectively. All values represent means ± SEM (n = 4, except for the carbonization rate which was calculated 10 times). Different letters represent significant differences between treatments at the $P< 0.05$ level.

Table 2. Carbon (C), hydrogen (H), oxygen (O), nitrogen (N), sulfur (S), and the atomic ratios in biochar and straw.

	Straw	B550	B450	B350	B250
C (%)	44.9±0.0d	82.3±0.0a	73.9±0.1b	74.1±0.6b	64.6±0.1c
N (%)	0.5±0.0c	0.9±0.0b	0.9±0.0b	1.1±0.0a	1.0±0.0a
H (%)	5.6±0.0a	3.0±0.0d	3.7±0.0c	4.2±0.0b	4.1±0.0b
S (%)	0.9±0.1b	1.2±0.1a	1.2±0.1a	1.3±0.1a	1.0±0.1b
O (%)	47.7±0.1a	12.5±0.1d	20.4±0.1c	19.4±0.7c	29.3±0.1b
H:C	1.6±0.0a	0.4±0.0e	0.6±0.0d	0.7±0.0c	0.8±0.0b
O:C	0.8±0.0a	0.1±0.0d	0.2±0.0c	0.2±0.0c	0.3±0.0b
(N+O):C	0.8±0.0a	0.1±0.0d	0.2±0.0c	0.2±0.0c	0.3±0.0b

All values represent means ± SEM (n =3). Different letters represent significant differences between treatments at the P< 0.05 level.

Table 3. Partition coefficients (Kd) describing simazine sorption in different treatments when the sample was incubated for 0.5, 3 and 24 h.

Incubation time (h)	Partition coefficients Kd (L kg^{-1})					
	B550	B450	B350	B250	Soil	Straw
0.5	2.5±0.1	1.9±0.0	1.9±0.1	2.5±0.2	0.6±0.1	0.6±0.1
3	5.0±0.3	3.8±0.1	4.2±0.2	5.0±0.3	0.9±0.1	0.8±0.0
24	13.4±0.9	9.9±0.8	11.3±0.1	11.5±0.3	1.4±0.1	1.1±0.1

All values represent means ± SEM (n = 4).

Figure 1. Scanning electron microscopy photo of biochar.

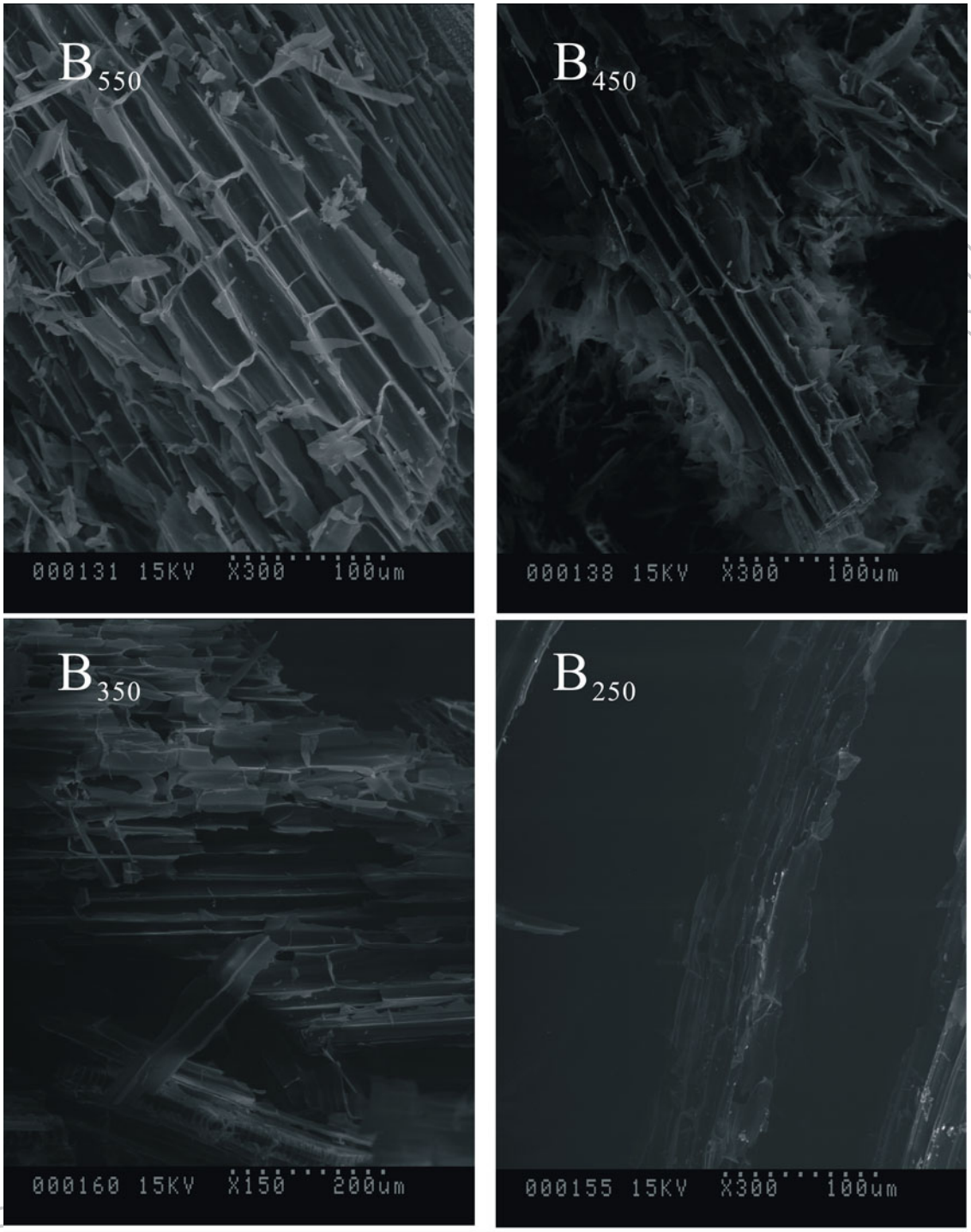

Figure 2. Simazine adsorption in different treated soil samples after 0.5, 3, and 24 hours of exposition. Bars represent the standard error of mean (n=4).

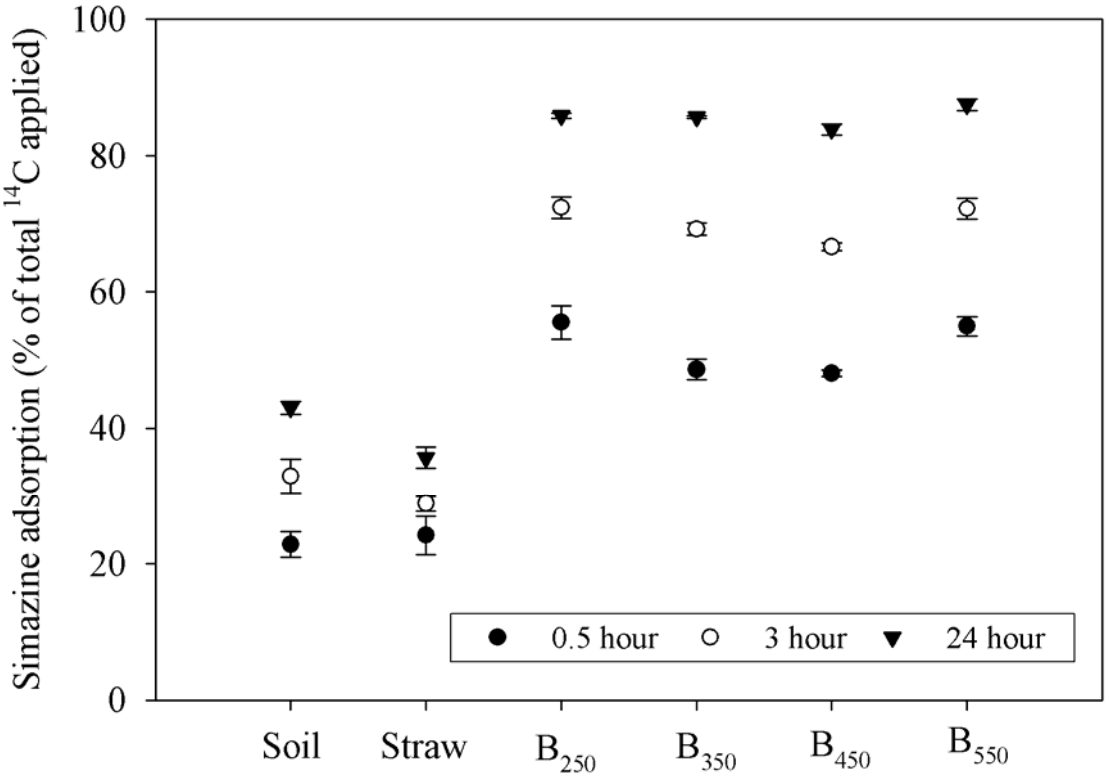

Figure 3. Simazine leaching in different soil treatments. Bars represent the standard error of means (n=4).

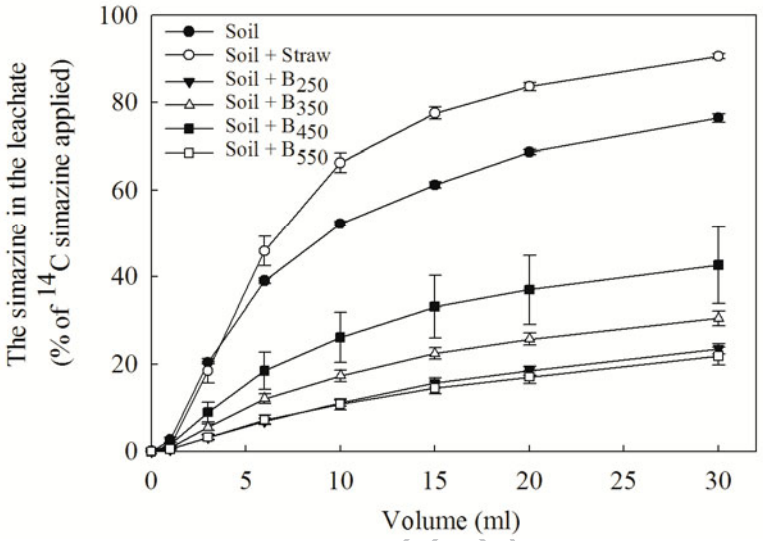

Figure 4. Simazine decomposition in different treated soil samples. Bars represent the standard error of means (n=4).