Elemental characterization of atrazine treated soil pretreated with sawdust-based biochar types using Energy Dispersive X-ray (EDX) spectroscopy

Yetunde Bunmi Oyeyiola*[1,2], Abiodun Ebenezer Egbinade[2], Asmat Khan Begum[1], Adesanya Olayioye[2] and Beatrice Olutoyin Opeolu[1]
[1]Faculty of Applied Sciences, Cape Peninsula University of Technology, South Africa,
[2]Faculty of Agricultural Science, Ladoke Akintola University of Technology, Nigeria.
*Corresponding Author: yboyeyiola@lautech.edu.ng +2348132555373.

ABSTRACT

The escalating area of degraded farmlands across Africa, attributed to the intensive and indiscriminate use of agrochemicals demands investigation into the speciation of nutrient elements in this herbicide treated soils for devising sustainable management strategies. This study examines the fate of organic carbon, heavy metals, macro and micronutrient compositions in soil treated with atrazine (a widely utilized broad-spectrum herbicide in Africa), both with and without biochar pretreatment using energy-dispersive X-ray (EDX) spectroscopy. Elemental characterization of soil treated solely with atrazine (at 2.5 kg active ingredient/ha) was evaluated under screenhouse condition when factorially combined with four sawdust (SD)-based biochar: SD pyrolyzed with or without poultry manure (PM) at 350°C (tagged SD+PM@350 and SD-PM@350 respectively), and SD pyrolyzed with or without PM at 450°C (tagged SD+PM@450 and SD-PM@450 respectively). Each biochar was applied at 5 and 10 t/ha, equivalent to 2.37 and 4.75 g/950 g soil, respectively. An absolute control soil, that received neither atrazine nor biochar was included. Soil samples collected from appropriately treated soil after two successive maize cropping were analyzed for total metal concentrations using EDX spectroscopy after sputtering each sample with gold on aluminum stubs. Significant ($p < 0.05$) enrichments of Cu, Ni, and Pb by 215%, 165%, and 222%, respectively, were observed in sole atrazine treated soil which were absent (0 ppm) in similar atrazine-treated soils pretreated with SD+PM@350 and SD+PM@450. Similarly, total C decreased by 10% and 17% in sole atrazine and absolute control soils respectively, compared to the baseline value. Biochar pretreatment however, increased total C by a range of 24.5 to 35.9%. Higher percentages of total N, P, Mg, and K were, however, observed in sole atrazine treated soil relative to the baseline and absolute control values, with the total Mg and K contents exceeding those observed in biochar-pretreated soils.

Continued sole atrazine use, therefore, poses potential risks of carbon depletion and heavy metal toxicities in the soil studied. Pretreating soils with sawdust-based biochar, therefore, offers mitigation strategy against these environmental and sustainability risks in soils annually receiving atrazine herbicides.

Keywords: Atrazine, biochar, carbon depletion, EDX spectroscopy, heavy metal toxicity

INTRODUCTION

Herbicides are substances utilized to manage the growth of unwanted plants. Herbicides could be broad spectrum, selective or contact, and their applications occur most frequently in row-crop farming, where they are applied pre- or post-emergently to maximize crop productivity. Atrazine, a chlorinated triazine systemic herbicide and synthetic organic compound, is widely utilized for managing annual grasses and broadleaf weeds before their emergence in field corn, sweet corn, sorghum, and sugarcane cultivations. (Rostami *et al.*, 2021). Although atrazine is effective, its application has sparked debate because of the negative impacts it has on non-target organisms, including amphibians, as well as its long-lasting presence in soil and water (Rostami *et al.*, 2021). Mechanism utilized by atrazine in killing weeds is by disrupting the process of photosynthesis by inhibiting photophosphorylation and impeding electron transfer (Fan *et al.*, 2018).

Herbicides, including atrazine, are recognized for their environmental toxicity, posing risks to soil, surface and groundwater. For instance, the vulnerability of aquatic vegetation to herbicides, resulting in decreased abundance and diversity of aquatic life has been well reported (Klatyik *et al.*, 2024; Mugudamani *et al.*, 2023; Lopes et al., 2022). Atrazine's mobility from soil to water bodies is intensified when it degrades into metabolites such as hydroxyatrazine (HA), deethylatrazine (DAE), and deisopropylatrazine (DIA). This encourages its wider dispersal and persistence in the environment, thereby endangering water quality and aquatic leaching into surface and underground water has been reported to be higher in soils with low clay and organic matter contents (Jing *et al*., 2020).

Maternal exposure to atrazine in drinking water is associated with adverse fetal outcomes, including low birth weight and various congenital disabilities (Carles *et. al*., 2021; Almberg *et al*., 2018;). Studies in mammalian herbicide toxicity have demonstrated delayed fetal development and reduced fetal survival following high-level atrazine exposure during pregnancy (Carles *et al*., 2021). Moreover, atrazine classification as an endocrine-disrupting chemical, has been indicated to disrupt normal hormonal function leading to reproductive tumors, congenital disabilities, and various forms of cancer in animals and humans (Rostami *et al*., 2021; Jing *et al*., 2020).

Concentrations of heavy metals, dominantly Pb, Cd, Ni, Co, Cu, and Zn, are increasing in conventional farmlands annually receiving herbicides and chemical fertilizers. Synergistic interactions have been reported between heavy metal enrichment and indiscriminate herbicide and agrochemical applications (Wan *et al*., 2024; Alengebawy *et al*., 2021; Jing *et al*., 2020; Toth *et al*., 2015; Arao *et al*., 2010). Previous analyses have detected heavy metals in herbicides, either originating from their active ingredients or present as *et al* impurities (Rashid *et al*., 2023; Tudi., 2021; Alnuwaiser, 2019; Defarge *et al*., 2018; Lewis *et al*., 2016). Thus, highlighting the necessity for developing safer strategies for agrochemical use to mitigate their adverse environmental impacts. Various approaches, including the utilization of microorganisms and organic materials such as animal manure, compost, and biochar, have been proposed (Yang *et al*., 2021; Jing *et al*., 2020; Olu-Arotiowa *et al*., 2019).

Energy Dispersive X-ray spectroscopy (EDX) offers a non-destructive, rapid, and cost-effective method for quantitative and qualitative elemental analysis of specimens when subjected to electron beams. Widely utilized for contaminant identification and monitoring. The EDX spectroscopy provides reliable detection and accurate quantification of both major and trace elements, as well as spatial distribution analysis. Given the escalating field application of agrochemicals, including herbicides, their impact on soil carbon and micro/macronutrients remains underexplored despite their widespread use each cropping season. Access to EDX spectroscopy facilities presents an opportunity for rapid elemental characterization of herbicide-treated soil.

This study was therefore intended to assess the effects of atrazine application on total carbon, selected micro/macronutrients and heavy metals in atrazine treated soil using EDX spectroscopy. The trial also evaluated the potential of sawdust-based biochar to mitigate atrazine's adverse effects on total carbon, selected micro/macronutrients and heavy metals in soil.

2.0 Materials and methods

2.1 Soil sampling and routine analysis

The soil sampled for this study was obtained from the top layer (0–15 cm depth) of the arable plot situated at coordinates 8° 10' 25" N and 4° 16' 26" E within the Teaching and Research Farm of Ladoke Akintola University of Technology, Ogbomoso, Nigeria. Air-dried soil samples were crushed and composited for routine laboratory analysis. Soil pH was measured using a 1:2 (soil: water) ratio after a 20-minute equilibration period, using a glass electrode calibrated with buffer solutions of pH 4, 7, and 9. Organic carbon content was determined using the dichromate wet method following the procedure outlined by IITA (1978). Available phosphorus was extracted using Mehlich solution, and its concentration was determined using the Molybdate blue colourimetric method described by Murphy and Riley (1962) on a Spectronic 20 spectrophotometer. Total nitrogen was quantified using the Macro-Kjeldahl method, as outlined by Bremner (1982). Exchangeable cations (Ca, Mg, K, Na) were extracted using 1N NH4OAc (pH=7) at a soil: extracting solution ratio of 1:10 for 15 minutes (IITA, 1978). The concentrations of Ca and Mg were measured using an Atomic Absorption Spectrophotometer, while those of K and Na were determined using a Flame Photometer. The soil was classified as Alfisols (Soil Survey Staff, 2003) and locally as the Gambari soil series (Olatunji, 2011.

2.2 Biochar Preparation

The biochar types utilized in this study were derived from *Gmelina arborea* sawdust (SD), with or without the incorporation of poultry manure (PM). The feedstocks underwent pre-heating at 105°C for 24 hours to eliminate non-flammable components such as moisture and CO_2 (Oyeyiola, et al., 2021). The feedstocks were thereafter pulverized and subjected to pyrolysis in a muffled furnace. Sole SD biochar types (tagged SD-PM) were produced by pyrolyzing 20 g of SD (in triplicate) at either 350°C or 450°C for 20 minutes, while a combination of 10 g of SD with 10 g of PM pyrolyzed at the same temperatures represented SD+PM biochar types. Four biochar types: SD-PM@350, SD-PM@450, SD+PM@350, SD+PM@450 were produced and analyzed for pH and nutrient contents using standard procedures for plant nutrient determination (Oyeyiola *et al*., 2021; IITA, 1978).

2.3 Treatments, design, experimental setup, and spectroscopic analysis

Leaching columns constructed from polyvinyl chloride (PVC) pipes measuring 23 cm in length and 7 cm in diameter were employed for the trial. Each leaching column was lined with three-fold oven-sterilized nylon mesh mounted over a leachate collection cup at one end. Each column was filled with 950 g of soil. The study was a factorial combination of four biochar types: SD+PM@350, SD+PM@450, SD-PM@350, and SD-PM@450 applied at two rates: 5 and 10 t/ha, equivalent to 2.37 and 4.75 g/ 950 g of soil, respectively. Triplicate sets of soil-filled leaching columns were designated for treatments receiving atrazine only (referred to as herbicide alone) and those receiving neither biochar nor atrazine (referred to as Absolute Control).

The appropriate biochar types and rates were incorporated into the soil within the 5 cm depth in each leaching column and moistened to field capacity with 250 ml of distilled water. The setup was covered with aluminum foil and left to equilibrate for two weeks. A similar procedure was carried out for the atrazine alone and absolute control soils. Atrazine stock solution was prepared by dissolving 6.75 g of atrazine powder in a 1000 ml volumetric flask made up to the mark with distilled water to achieve the recommended rate of 2.5 kg a.i/ha for the study area. Subsequently, 20 ml of the atrazine stock solution was applied into all incubated soils (except the absolute control) using a syringe. Basal chemical fertilizer application followed, with 0.1 g of NPK 15:15:15 and 0.03 g of urea to achieve half the recommended rate of chemical fertilizers for maize production in the study area (as the maize plants were not nurtured to maturity). This practice mimics farmers' common approach of applying chemical fertilizer immediately after herbicide application into arable fields. Two maize seeds were sown per column and thinned to one plant per stand a week after sowing.

One leaching event was conducted in each treated soil a week after atrazine application using 100 ml of distilled water to simulate rainfall occurring after herbicide application under field conditions. The maize plants were nurtured for three weeks at room temperature, ranging around 25–27 °C. After maize biomass harvesting at two weeks of sowing, the soil in each column was kept moist under aluminum foil for six months. Subsequently, fresh applications of biochar, atrazine, and basal chemical fertilizers were repeated at previous rates. This was followed by maize seed sowing and nurturing for two weeks, with another leaching event simulated a week after atrazine application using 100 ml of distilled water. Data collected from leachate samples were not included in this paper.

At harvesting, soil samples from each column were air-dried, crushed into powder, and sputtered with gold in preparation for elemental analysis using Energy Dispersive X-ray spectroscopy (EDX) on a Merlin spectrophotometer at the SEM Microscopy Unit, Central Analytical Facilities, Stellenbosch University, South Africa. Three scans were performed per soil sample on the EDX spectrophotometer.

2.4 Data Analysis

Total element concentration data for all treatments underwent a two-way analysis of variance using the Genstat statistical package. Significant means were separated by Least Significant Difference (LSD) test at a 5% probability level.

3.0 Results

3.1 Characteristics of the experimental soil and the pH and nutrient characteristics of the tested biochar

The experimental soil was slight alkaline and severely depleted in organic carbon, available phosphorus, total nitrogen, and marginal concentrations of exchangeable bases (Table 1). Additionally, the soil possesses a higher proportion of sand fraction compared to silt and clay.

Table 2 shows the pH and nutrient composition of the biochar types tested. Biochars derived from *Gmelina arborea* sawdust (SD) co-pyrolyzed with poultry manure (PM) exhibited higher pH levels and nutrient concentrations compared to sole SD biochar, except for organic carbon content, which was higher in the latter. Notably, higher pyrolysis temperatures (450°C) resulted in increased nutrient concentrations and pH levels, regardless of the feedstock combination. Organic carbon content decreased by 39.2% in SD+PM@450 biochar, while macronutrients like nitrogen and phosphorus contents increased by 94.3% and 876%, respectively, compared to SD+PM@350. Consequently, SD+PM@450 biochar exhibited lower carbon-to-nitrogen (C/N) and carbon-to-phosphorus (C/P) ratios of 43 and 23, respectively, in contrast to 117 and 315, observed in SD+PM@350. Similarly, SD-PM@450 biochar demonstrated an 8.2% reduction in organic carbon content, accompanied by a 35.5% increase in nitrogen and a 128.6% increase in phosphorus relative to SD-PM@350. Consequently, SD-PM@450 biochar exhibited lower C/N and C/P ratios of 119 and 312, respectively, compared to 174 and 773, respectively, observed in SD-PM@350.

3.2 Effects of biochar pretreatments on total carbon in atrazine-treated soil

The application rate of biochar significantly influenced the total carbon (C) content in the atrazine-treated soil (Fig. 1). Sole application of atrazine led to a 10.1% reduction in total carbon compared to the baseline value established before the commencement of the study. However, all biochar types and application rates resulted in increased total carbon in the atrazine treated soil. Notably, higher application rates yielded significantly higher total carbon levels compared to lower rates. Specifically, application rates of 10 and 5 t/ha resulted in total carbon contents that were 35.0% and 15.4% higher, respectively, than those observed in the herbicide-alone treatment. Among all the biochar types tested, SD+PM@350 biochar exhibited the lowest total carbon content.

3.3 Effects of biochar pretreatments on total nickel content in atrazine-treated soil

Pretreatment of atrazine-treated soil with biochar led to a significant reduction in total nickel content (Fig. 2). Particularly, soil treated with biochar at lower application rates exhibited a drastic reduction in Ni content compared to higher application rate, herbicide alone, and absolute control treatments. Application rates of 10 and 5 t/ha resulted in reductions of soil Ni content by 37.2% and 92.1%, respectively, compared to the herbicide alone treatment. In contrast, soil treated solely with herbicide experienced a 60.6% increase in Ni concentration at the end of the trial relative to the absolute control.

3.4 Effects of biochar pretreatments on total lead content in atrazine-treated soil

The biochar types, application rates, and their interaction significantly influenced total lead content in the atrazine-treated soil (Fig. 3). Lead content was observed to decrease significantly in the following order: SD+PM@350 < SD-PM@450 < SD-PM@350 < SD+PM@450. Interestingly, no lead was detected in the atrazine-treated soil pretreated with SD+PM@350. Moreover, the application rate of 5 t/ha was significantly more effective than 10 t/ha in reducing lead contents in the atrazine-treated soil. Notably, soil treated solely with atrazine exhibited a Pb content 175.7% higher than the absolute control.

3.5 Effects of biochar pretreatments on total cobalt content in atrazine-treated soil

The biochar types, application rates, and their interaction did not exert a significant effect on total cobalt content of the atrazine-treated soil (Fig. 4). However, it is noteworthy that certain biochar types demonstrated a reduction in cobalt content compared to herbicide alone soil. Specifically, biochar types: SD+PM@350, SD+PM@450, and SD-PM@450 reduced total cobalt contents by 83.5%, 25%, and 25%, respectively, relative to the herbicide alone soil. Conversely, SD-PM@350 was ineffective in reducing cobalt impaction in the soil; instead, it increased cobalt content by 69.5%. Once more, no cobalt was detected in atrazine-treated soil pretreated with SD+PM@350 applied at 10 t/ha, mirroring observations regarding lead content.

3.6 Effects of biochar pretreatments on total copper, iron, and zinc contents in atrazine-treated soil

The concentrations of total copper, iron, and zinc did not exhibit significant variations in all the atrazine-treated soil samples pretreated with biochar (Table 3). However, it is noteworthy that the concentrations of copper and iron were lower in biochar-pretreated soils compared to those treated solely with herbicide, whereas zinc contents were generally higher in biochar pretreated soil. Specifically, soil pretreatment with SD+PM@350 biochar consistently yielded the lowest concentrations of total copper and iron while exhibiting the highest concentration of zinc content in the soil. In the herbicide-alone scenario, copper content increased by 384.6%, while zinc content decreased by 94.1% compared to the absolute control.

3.7 Effects of biochar pretreatments on total nitrogen and phosphorus contents in atrazine-treated soil

Total nitrogen in the atrazine-treated soil was significantly influenced by biochar types, biochar rates, and their interactions (Table 4). Specifically, the SD+PM biochar types exhibited superiority over the SD-PM biochar types in enhancing total N content in the atrazine-treated soil. For instance, SD+PM@350 and SD+PM@450 increased total nitrogen by 37.9% and 20.6%, respectively, compared to soil treated solely with atrazine. Additionally, biochar types pyrolyzed at 350°C were more effective than those pyrolyzed at 450°C in enhancing total nitrogen content in the soil. Pyrolysis at 350°C supported total nitrogen enrichment by 109.1% and 41.7% in SD+PM and SD-PM biochar types, respectively. It is noteworthy that total nitrogen enrichment in soil treated solely with herbicide was higher (0.48%) than in soil treated with the two SD-PM biochar types and the absolute control.

Total phosphorus was only affected by biochar types in the atrazine-treated soil (Table 4). Biochar types produced at 350°C exhibited significantly higher total P compared to similar feedstock biochar types produced at 450°C. However, total P contents were lower in all biochar types (except SD-PM@350) compared to the absolute control, indicating a poor P enrichment potential of these biochar types compared to the generally reported enhancement of P in soil after biochar application. Furthermore, biochar types pyrolyzed at 350°C generally yielded higher total P content compared to soil treated solely with atrazine or biochar pyrolyzed at 450°C. Application of atrazine alone, however, reduced total P by 54.5% compared to the absolute control.

3.8 Effects of biochar pretreatments on total calcium, magnesium, and potassium contents in atrazine-treated soil

The concentrations of total calcium, magnesium, and potassium in the atrazine-treated soil were not significantly influenced by biochar types, biochar rates, or their interaction (Table 5). However, it is notable that all biochar types and rates, except SD-PM@450, resulted in higher mean Ca content compared to soil treated solely with herbicide. Conversely, total Mg and K were enhanced in soil treated solely with herbicide compared to all biochar-amended soil except for SD+PM@450 applied at 10 t/ha. Moreover, higher biochar application rates supported higher Ca, Mg, and K enrichment in the atrazine-treated soil compared to lower application rates.

4.0 Discussion

Indiscriminate field applications of agrochemicals, including herbicides, pose significant challenges to soil health, biodiversity, and water quality worldwide. In this study, effects of repeated atrazine application on soil total carbon, selected macro and micronutrients, and heavy metals, with and without biochar pretreatment were investigated over two incubation trials. All four sawdust-based biochars examined exhibited alkaline pH values ranging from 9.1 to 11.1 and ash contents ranging from 5.6 to 53.1%.

Atrazine application alone resulted in the depletion of total carbon and phosphorus while supporting the enrichment of heavy metals such as lead, nickel, and copper compared to baseline values. However, it also improved total nitrogen, calcium, magnesium, and potassium contents while reducing total iron, zinc, and cobalt contents relative to the absolute control soil. The observed 10.1% reduction in soil total carbon in the sole atrazine-treated soil reinforced our previous findings of depletion of soil organic carbon determined by the Walkley black procedure in the same sole atrazine treated soil (Oyeyiola and Opeolu, 2024). This validates the accuracy of spectroscopic determination of elements in soil by the Energy Dispersive X-ray (EDX) machine. Previous studies (Yang *et al*., (2021); James *et al.,* (2021); Su *et al.,* (2010)) have also documented atrazine's adverse effects on soil organic matter components. The significant increases in total Pb, Ni, and Cu concentrations in atrazine-treated soil underscore the potential of this herbicide, along with basal chemical fertilizers applied, to increase the levels of these heavy metals in the soil with extended usage. Previous research has highlighted the presence of heavy metals in herbicide formulations (Rashid *et al*., 2023; Tudi *et al*. 2021; Lewis *et al*., 2021; 2016; Alnuwaiser, 2019; Defarge *et al*., 2018; PPDP, 2007). This indicates a potential source for increased soil heavy metal concentrations with continued atrazine usage.

Biochar pretreatment demonstrated the capacity to enhance total carbon in atrazine-treated soil, likely due to the high carbon content of the biochar materials, which serve as energy sources for native soil microbes. However, higher application rates had adverse effects on total nitrogen content, suggesting elevated carbon-to-nitrogen ratios in the biochar, potentially leading to nutrient immobilization and foreclosing their use for the supply of N in soils. A decreasing trend in heavy metal concentrations in soil with increasing biochar application rates aligns with previous research (Yang *et al*., 2021). They pinpointed the capacity of biochar to precipitate and form complex compounds with these toxic metals (in decreasing order of Pb> Zn>Cd) via ion exchange and π bond actions as dominant mechanisms for this unique mitigation reaction. Biochar pretreatment at lower application rate was, however, more efficient in reducing total Ni, Pb, Zn, and Fe concentrations compared to higher rate.

5.0 Conclusion

This trial highlights the potential for total carbon and phosphorus depletion, as well as the enrichment of heavy metals such as lead, nickel, and copper, and macronutrients such as nitrogen, calcium, magnesium, and potassium in atrazine-treated soil. Specifically:

Atrazine application alone resulted in a 10.1% reduction in total C compared to the baseline value of 26.7%, indicating carbon depletion in the soil.

Sawdust biochar pretreatment before atrazine application increased total C by a range of 24.5% to 35.9%, demonstrating its potential to mitigate carbon depletion.

Significant enrichments ($p<0.05$) of total Cu, Ni, and Pb were observed in atrazine-treated soil by 215%, 165%, and 222%, respectively, compared to their baseline values, indicating potential heavy metal toxicity.

Higher percentages of total N, P, Mg, and K were observed in sole atrazine-treated soil compared to baseline and control values.

The potential of sawdust-based biochar pretreatment to mitigate carbon depletion and heavy metal toxicity in soils receiving yearly atrazine treatments were identified.

Continued sole use of atrazine, therefore, poses risks of micronutrient and heavy metal toxicity, as well as carbon depletion in the soil. However, biochar pretreatment offers a sustainable mitigation approach to these environmental risks.

6.0 Authors' contributions

YBO: Conceptualization, funding acquisition, investigation, methodology, supervision, writing and editing of the original draft and visualization. AEE: Investigation, data collection and writing of original draft. AKB: Data collection and laboratory analysis. AO: Investigation, data collection and analysis. BOP: Funding acquisition, Supervision and review of original draft.

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8.0 Conflict of interest

The authors declare that the research was conducted in the absence of any financial relationships that could be construed as a potential conflict of interest.

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Table 1. Selected characteristics of the soil studied

Parameters	Values
Soil pH (H_2O)	7.28
Available P (Mehlich, mg/kg)	5.86
Total N (g/kg)	0.85
Organic C (%)	1.47
Ex. Cations (cmol/kg)	
Ca	2.97
Mg	0.68
K	0.15
Na	0.09
Particle sizes (g/kg)	
Sand	780
Silt	100
Clay	120

Table 2. The pH and the nutrient characteristics of the biochar studied

	Biochar Types			
	SD+PM		SD-PM	
Biochar Parameters	350°C	450°C	350°C	450°C
pH	10.2	11.1	9.1	9.7
Ash (%)	8.51	53.1	5.6	8.82
Ca (%)	2.73	6.52	1.36	1.59
Mg (%)	0.35	0.91	0.22	0.45
K (%)	0.97	1.41	0.75	0.98
Na (%)	0.0005	0.0003	0.0003	0.0005
Organic C (%)	41.00	29.45	54.11	50.02
N (%)	0.35	0.68	0.31	0.42
P (%)	0.13	1.27	0.07	0.16

Table 3. Effects of biochar pretreatments on total copper, iron and zinc contents (mg/kg) in atrazine-treated soil

	Cu			Fe			Zn		
	Biochar Rates			Biochar Rates			Biochar Rates		
Biochar Types	10 t/ha	5 t/ha	Mean	10 t/ha	5 t/ha	Mean	10 t/ha	5 t/ha	Mean
SD+PM @ 350	0	433	217	5830	5870	5850	433	333	383
SD+PM @ 450	167	433	300	5970	6370	6170	200	0	100
SD-PM @ 350	267	133	200	6170	7330	6750	333	333	333
SD-PM @ 450	367	200	283	8030	5130	6580	167	100	133
Mean	200	300		6500	6180		283	192	
BT (LSD)	392	ns		1585	ns		390	Ns	
BR (LSD)	277	ns		1121	ns		276	Ns	
BT x BR (LSD)	555	ns		2241	ns		552	Ns	
checks									
Absolute control	130			7170			330		
Herbicide alone	630			6970			170		
Baseline	200			7200			100		

BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. *Significant at $p < 0.05$, ns is not significant.

Effects of biochar pretreatments on total nitrogen and phosphorus contents in atrazine-treated soil

	P (mg/kg)			N (%)		
	Biochar Rates			Biochar Rates		
	10 t/ha	5 t/ha	Mean	10 t/ha	5 t/ha	Mean
	100	200	150	0.33	4.28	2.30
	33	167	100	0.74	1.47	1.10
	600	400	500	0.00	0.35	0.17
	133	133	133	0.00	0.24	0.12
	217	225		0.27	1.58	
	230	**		1.52	*	
	162	ns		1.07	*	
	325	ns		2.15	*	
checks						
Absolute control	367			0.00		
Herbicide alone	167			0.48		
Baseline	100			0.00		

BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. * and ** are Significant at $p < 0.05$ and < 0.01, respectively, ns is not significant.

Table 5. Effects of biochar pretreatments on total calcium, magnesium and potassium contents in atrazine-treated soil

	Ca (%)			Mg (%)			K (%)		
	Biochar Rates			Biochar Rates			Biochar Rates		
Biochar Types	10 t/ha	5 t/ha	Mean	10 t/ha	5 t/ha	Mean	10 t/ha	5 t/ha	Mean
SD+PM @ 350	0.153	0.147	0.150	0.090	0.090	0.090	0.230	0.267	0.248
SD+PM @ 450	0.187	0.167	0.177	0.050	0.093	0.072	0.447	0.313	0.380
SD-PM @ 350	0.160	0.210	0.185	0.053	0.073	0.063	0.217	0.263	0.240
SD-PM @ 450	0.133	0.090	0.112	0.063	0.087	0.075	0.303	0.203	0.253
Mean	0.158	0.153		0.064	0.086		0.299	0.262	
BT (LSD)	0.06 ns			0.050 ns			0.130 ns		
BR (LSD)	0.043 ns			0.035 ns			0.092 ns		
BT x BR (LSD)	0.085 ns			0.071 ns			0.184 ns		
checks									
Absolute control	0.123			0.067			0.233		
Herbicide alone	0.153			0.103			0.443		
Baseline	0.160			0.07			0.45		

BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. * and ** are Significant at $p < 0.05$ and < 0.01, respectively, ns is not significant.

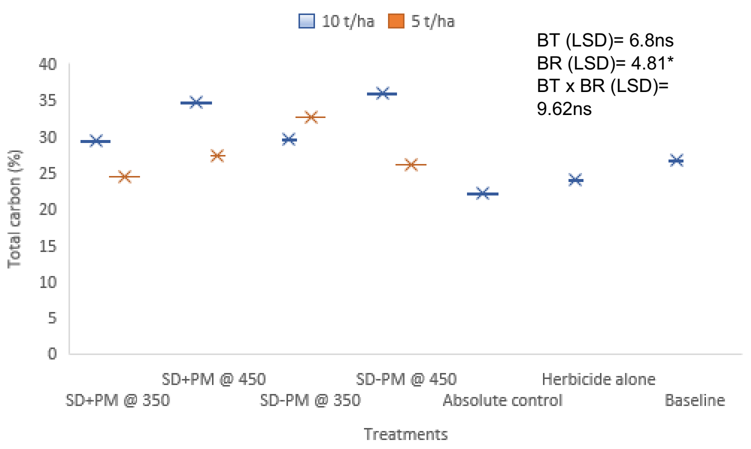
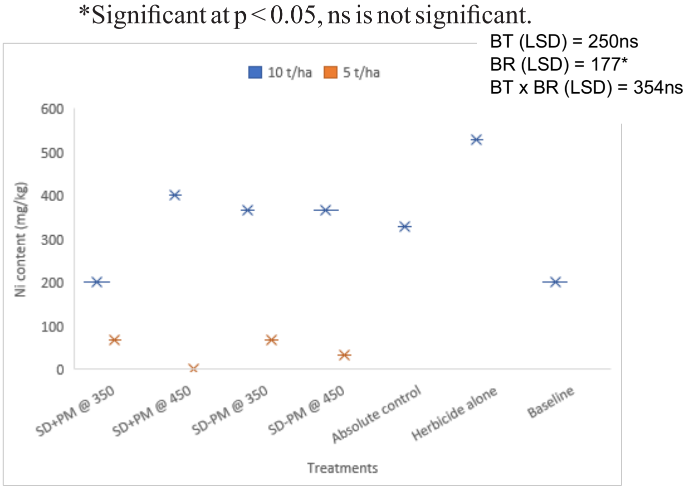


Fig. 1 Effects of biochar pretreatments on total carbon in atrazine-treated soil

BT is biochar type; BR is biochar application rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. *Significant at $p < 0.05$, ns is not significant.



BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. *Significant at $p < 0.05$, ns is not significant.

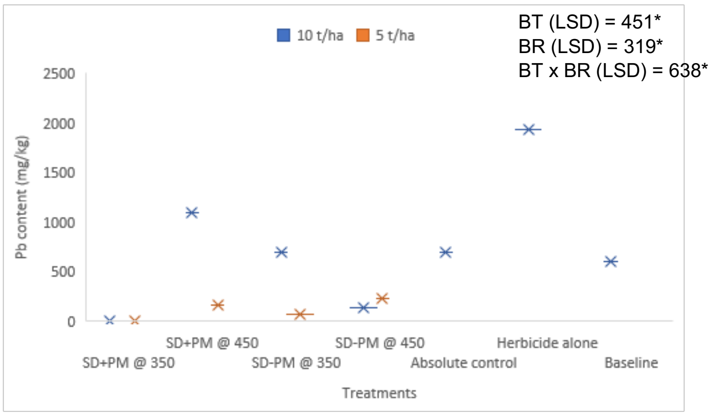


Fig. 3 Effects of biochar pretreatments on total lead content in atrazine- treated soil

BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. *Significant at $p < 0.05$, ns is not significant.

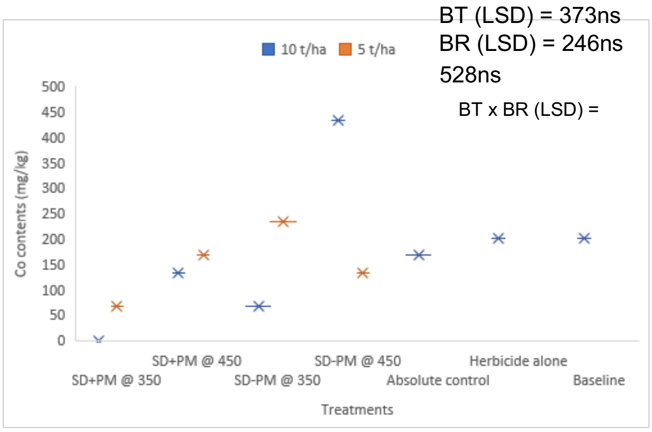


Fig. 4 Effects of biochar pretreatments on total cobalt content in atrazine-treated soil

BT is biochar type; BR is biochar rate; SD + PM@350 and SD + PM@450 are sawdust biochar co-pyrolyzed with poultry manure at 350 and 450 °C, respectively; SD-PM@350 and SD-PM@450 are sole sawdust biochar pyrolyzed at 350 and 450 °C, respectively. *Significant at $p < 0.05$, ns is not significant