

# Impact of Glyphosate Contamination on Chemical Properties of Inceptisols Amelioration with Biochar from Rice Husks, Young Coconut Waste, and Bamboo

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**Abstract.** Growing concerns over glyphosate herbicides, if not applied carefully, can have unintended consequences on agroecosystems. The objective of this research was to study glyphosate contamination on the chemical properties of Inceptisols ameliorated with biochar of rice husk (B-RH), young coconut waste (B-YCW), and bamboo (B-B). This study used a completely randomized design (CRD) with five treatments and three replications, namely A = Control (without ameliorants and glyphosate); B = Soil + 100 mg l<sup>-1</sup> glyphosate; and C = Soil + B-RH + 100 mg l<sup>-1</sup> glyphosate; D = Soil + B-YCW + 100 mg l<sup>-1</sup> glyphosate and E = Soil + B-B + 100 mg l<sup>-1</sup> glyphosate. The results showed that contamination from glyphosate had a significant effect on surface changes (pH, EC, CEC, Mineral, and SOM) and nutrients (SOC, total N, and available P) of Inceptisols that had been improved with 40 t ha<sup>-1</sup> biochar. The correlation and equation of linear regression between residues on glyphosate (RG) had a significant interaction with chemical properties of Inceptisols amended with biochar, namely exchangeable Ca [ $r=0.611^*$  and  $RG=0.0232(Ca)-0.0079$ ;  $R^2=0.3728$ ]. CEC [ $r=0.593^*$  and  $RG=0.0018(CEC)-0.0312$ ;  $R^2=0.3514$ ]; available P [ $r=0.590^*$  and  $RG=0.0061(P_2O_5)-0.0232$ ;  $R^2=0.3472$ ] and total N [ $r=0.570^*$  and  $RG=0.257(N)-0.0621$ ;  $R^2=0.4312$ ].

**Keyword.** Bamboo Biochar, Glyphosate, Inceptisols, Rice husk, Young coconut waste

## 1 Introduction

Glyphosate, as the active component in the herbicide chemical Roundup, can have a profound contaminating effect on ecosystems. Glyphosate is an environmental pollutant used at a rate of 600,000 to 750,000 tons per year over an area of about 36 million square kilometers. Its use in agricultural and other contexts has steadily increased from 0.6 Mg in 1974 to 125.5 Mg in 2014, making it the most widely used herbicide in the world [1]. The presence of glyphosate in the soil is complex and related to mineralization, degradation, immobilization, and leaching. Its presence in the soil can affect adsorption, leaching, and mineralization [2]. Glyphosate is an amphoteric small molecule that has three polar functional groups. The groups are phosphonomethyl, amine, and carboxymethyl groups arranged linearly. Glyphosate is a highly polar ionic molecule (log KOW = -3.20) that is soluble in water (10.5 g L<sup>-1</sup> at 20°C). Glyphosate is a polyprotic acid with pKa values ranging from 0.7 to 2.2, 5.9 to 10.6. The pH of the solution affects the speciation of the molecule.

Monovalent and divalent anions are the dominant species at normal soil pH levels [3].

The impact of glyphosate contamination and its residues are determined by soil type, the suitability of the herbicide's biophysical-chemical properties, and the time gap between pesticide application and rainfall [4]. The quantity of glyphosate and its mineralization kinetics in the soil is influenced by temperature, pH, and total organic carbon (TOC) [5]. Glyphosate degrades rapidly in most soils, with half-lives ranging from 7 to 60 days [6]. The increase in pH, EC, CEC, and SOM at a glyphosate concentration of 100 ppm with a glyphosate solution pH of 5.20 indicates that Inceptisols ameliorated with 40 t ha<sup>-1</sup> rice husk biochar as a soil improver can adsorb glyphosate in the soil [7]. This is also evident from the results of Fourier Transform Infra-Red (FT-IR) spectroscopy which shows a decrease in transmittance in O-H, C=C, C-O, C-H, and mineral groups indicating an increase in sorption capacity in the improved Inceptisols soil. Changes in functional groups also favor glyphosate adsorption. Interestingly, the physicochemical characteristics of Inceptisols have a significant role in regulating the adsorption capacity of glyphosate to bind to the soil. Therefore, there is a need

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to test with the comparison of potential biochar types as different ameliorant technologies to address glyphosate residues in Inceptisols.

Biochar is a porous carbonaceous substance made by pyrolyzing some forms of biomass [8][9]. Biochar has promising applications in the reduction of agricultural environmental pollutants such as pesticides, particularly herbicides [10]. Biochar has various benefits, including a large surface area with a porous structure, decreased toxicity, abundance of functional groups, and redox activity. The sorption and desorption behavior of glyphosate in soil has been widely researched and reviewed. pH, phosphate content, and the presence of iron and aluminum oxides are known to affect glyphosate sorption in soil. Glyphosate sorption increased in soils amended with biochar, indicating the role of soil physicochemical parameters in influencing glyphosate sorption capacity. In addition, biochar has been shown to sorb glyphosate from aqueous solution, and attempts to investigate the sorption process using isotherm models and kinetics data revealed some possible interactions, including - electron donor-acceptor interactions, H-bonding, and heterogeneous H-bonding [11]. Biochar has great potential with diverse materials such as rice husk, young coconut waste, and bamboo, and strategic comparisons among these materials may provide much-needed new insights into sorption mechanisms and identify biochar properties that affect glyphosate residues in soil.

## 2 Material and Methods

This study will be conducted in the Laboratory of Chemistry and Soil Fertility, Faculty of Agriculture, Andalas University (UNAND), Padang starting from January to May 2023.

### 2.1 Experimental Design

This research used a completely randomized design (CRD) consisting of five treatments with three replications. The experiment was conducted by observing the effect of 100 ppm glyphosate equivalent to 0.07 ml of glyphosate in 250 ml of water on the chemical properties of inceptisols with 40 t ha<sup>-1</sup> biochar. The experiment design is presented in the following:

- A = Control (without ameliorants and glyphosate);
- B = Soil + 100 mg l<sup>-1</sup> glyphosate;
- C = Soil + rice husk biochar (B-RH) + 100 mg l<sup>-1</sup> glyphosate;
- D = Soil + young coconut waste biochar (B-YCWB) + 100 mg l<sup>-1</sup> glyphosate and
- E = Soil + Bamboo biochar (B-B) + 100 mg l<sup>-1</sup> glyphosate.

### 2.2 Ameliorant, Glyphosate and Soil Sampling

*Biochar Production* [12] [13][14].

#### 1. Rice Husk

Rice husk (RH) is a waste from the rice milling industry. Biochar from RH is produced using the Drum method through a pyrolysis process. Pyrolysis was performed in

iron drums with a diameter of 58 cm, a height of 86 cm, and a capacity of 200 liters and combined with the Kon-Tiki method at temperatures up to 650°C. The maximum pyrolysis temperature was kept constant for 45 min to ensure the completion of the final process.

#### 2. Young Coconut Waste

Young coconut waste (YCW) from green coconut (*Cocos nucifera* L.) is cut to a length of about 10\*5 cm and dried for one week in the Greenhouse of the Faculty of Agriculture, Andalas University until it achieves a moisture content of 18.20%. Furthermore, the manufacturing process is carried out using a method that has been tested three times. Figure 1 shows the process of producing YCW biochar with a weight of up to 10 kg and the following technique specifications, The Kon-Tiki method is made of conical steel which has a top diameter of 100 cm, a height of 90 cm, a wall slope of 63.50°, and a capacity of 827 liters.

#### 3. Bamboo

The preparation process for biochar production uses bamboo (B) biomass from the type of bamboo Betung (*Dendrocalamus asper*) and is cut to a length of approximately 30\*6 cm and dried for one week in the Greenhouse of the Faculty of Agriculture, Andalas University until it reaches moisture of 20.48%. Furthermore, the production process is carried out based on the method that has been carried out with three repetitions. In the production process of bamboo biomass biochar used as much as 10 kg with the specifications of The Kon-Tiki method is made of conical steel which has a top diameter of 100 cm, a height of 90 cm, a wall slope of 63.50°, and a capacity of 827 liters. The results of the production of biochar from each method are watered to stop the combustion process.

All biochar is dried in a 40-70°C oven for 2\*24 hours with the aim of homogeneous biochar water content and the next step is to analyze the characteristics of biochar in the laboratory.

#### *Glyphosate Concentration from Round-Up Herbicide*

Glyphosate used in soil contamination is a type of herbicide with the trademark Roundup Biosorb 486 SL (GRB-486 SL). Glyphosate used in soil contamination is a type of herbicide with the trademark Roundup Biosorb 486 SL (GRB-486 SL). The concentration of glyphosate contaminated in the soil was 100 mg l<sup>-1</sup> glyphosate from Round-up Biosorb 486 SL herbicide or equivalent to 0.07 ml GRB-486 SL in 250 ml H<sub>2</sub>O with 100g SC 5kg<sup>-1</sup> soil based on recommendations [7].

#### *Soil Sampling*

Inceptisols was taken in Nagari Sariak, Sungai Pua District, Agam Regency in West Sumatera, Indonesia with GPS coordinates of -0021'56" LS and 100024'0" BT. Soil samples were taken at a depth of 0-20 cm from 5 collection points which were then composited. Then, the soil was air-dried for 2\*24 hours. After air-drying, the samples were pulverized and sieved with a 2 mm sieve. After that, soil samples were taken for preliminary soil analysis. The soil samples were weighed as much as 5 kg equivalent absolute dry weight into 6 polybags. The soil in 3 polybags was watered with glyphosate solution

until it reached field capacity and the other 3 polybags were added biochar based on recommendations, then mixed well and watered with glyphosate to field capacity. Furthermore, the soil was incubated for 2 weeks. After the incubation, soil samples were analyzed in the laboratory.

### 2.3 Analysis of Soil, Residual of Glyphosate, and Statistical Analysis

Soil analysis conducted such as pH (H<sub>2</sub>O, KCl, and PZC by using formula 1), Mineral, SOM, CEC, SOC, total N, available P, K, exchangeable Ca, and Mg [15][16][17].

$$\text{pH PZC} = (2 \times \text{pH KCl}) - \text{pH H}_2\text{O} \quad (\text{F.1})$$

Analysis of glyphosate residues was conducted using the High-Performance Liquid Chromatography (HPLC) method [18][19][20]. The results of all analyses were statistically analyzed using SPSS 16.0, Statistic 8, and Excel 2016 software. R<sup>2</sup> coefficient and p-values [\*\* = Significant correlation at the 0.01 (2-tailed) level and \* = Significant correlation at the 0.05 (2-tailed) level] were calculated using bivariate correlation and two-sided significance tests.

## 3 Result and Discussion

### 3.1 The impact of glyphosate on surface change of Inceptisols ameliorated with biochar

The effect of glyphosate contamination on Inceptisols was substantial, with a decrease in pH, SOM, and CEC of Inceptisols by 0.16; 6.26; and 0.27 cmol(+) kg<sup>-1</sup> at a concentration level of 100 mg l<sup>-1</sup> glyphosate (Tables 1 and 2). Glyphosate is a pure chemical known as a highly polar molecule, a polyprotic acid with pKa values of 2; 2.3; and 5.6 [21]. The soil solution can lower the pH. Glyphosate contamination in the soil decreases the SOM composition, which is inversely related to the mineral composition of the soil. Increased accumulation of glyphosate residues in the soil will drastically reduce soil carbon [22]. This can also be seen in the CEC value of inceptisol soil which has decreased due to glyphosate contamination. The presence of glyphosate in the soil is influenced by the cation exchange capacity (CEC) of the soil [23]. The pH of Inceptisols PZC increased by 0.06 due to the effect of glyphosate contamination compared to the control (Table 1), indicating a decrease in the sorption capacity and negative charge of Inceptisols soil. The main site of glyphosate sorption is on the negatively charged surface of the soil mineral layer [24].

The considerable impact of glyphosate contamination necessitates the use of appropriate technologies, such as biochar-based amelioration technologies, to address glyphosate residues in Inceptisols. It has been demonstrated that the application of three forms of biochar at the rate of 40 t ha<sup>-1</sup> can improve Inceptisols soil surface changes by increasing pH, CEC, SOM, and CEC. Young coconut waste biochar has the largest increase in pH and CEC values when compared to rice husk and bamboo biochar by 0.83; 0.99; and 0.28 dS m<sup>-1</sup>, respectively, compared to the control and glyphosate-contaminated Inceptisols. This is because young

coconut waste biochar has higher pH and CEC values compared to rice husk and bamboo biochar, which are 10 and > 2 dS m<sup>-1</sup>, respectively compared to the control and glyphosate-contaminated Inceptisols, bamboo biochar increased SOM by 7.07 and 13.33%, respectively. The increase in pH and SOM in Inceptisols influenced the CEC, where the CEC in the application of young coconut waste biochar was greater than bamboo charcoal and rice husk by 20.78 and 21.05 cmol(+)kg<sup>-1</sup> respectively compared to the control and glyphosate-contaminated Inceptisols.

**Table 1.** The impact of glyphosate on surface change of Inceptisols ameliorated with biochar

Treatment	pH H <sub>2</sub> O	pH KCl	<sup>a</sup> pH PZC	EC
	unit			dS m <sup>-1</sup>
Control	4.97 c	4.77 c	4.57 ab	0.08 d
Soil + 100 mg l <sup>-1</sup> Glyphosate	4.81 d	4.72 c	4.63 a	0.08 d
Soil + B-RH + 100 mg l <sup>-1</sup> Glyphosate	5.40 b	4.93 b	4.47 b	0.25 c
Soil + B-YCW + 100 mg l <sup>-1</sup> Glyphosate	5.80 a	5.07 a	4.33 c	0.36 a
Soil + B-B + 100 mg l <sup>-1</sup> Glyphosate	5.67 a	5.07 a	4.47 b	0.33 b
<b>CV</b>	<b>1.40</b>	<b>1.08</b>	<b>1.43</b>	<b>3.11</b>
<b>Duncan's Test</b>	<b>**</b>	<b>**</b>	<b>**</b>	<b>**</b>
<b>SE</b>	<b>0.06</b>	<b>0.04</b>	<b>0.05</b>	<b>0.006</b>

Remarks: EC = electrical conductivity; SE = standard error; n = 15; \*\* = significant at the 0.01 level (2-tailed).

Glyphosate uptake in Inceptisols can be improved by applying 40 t ha<sup>-1</sup> biochar to the soil. Biochar contains OH functional groups, which can increase soil pH when added to it. Glyphosate belongs to anions in the relevant soil pH range and can only be adsorbed on variable charged surfaces, not permanently (negatively) charged surfaces, on the distribution of glyphosate species as a function of pH with acid dissociation constants (pKa1 = 2.22, pKa2 = 5.44, and pKa3 = 10.13) of carboxyl and amino groups [25].

**Table 2.** The impact of glyphosate on mineral, SOM, and CEC of Inceptisols ameliorated with biochar

Treatment	Mineral	SOM	CEC
	%		cmol(+)kg <sup>-1</sup>
Control	74.47 b	25.53 c	30.25 c
Soil + 100 mg l <sup>-1</sup> Glyphosate	80.73 a	19.27 d	29.98 c
Soil + B-RH + 100 mg l <sup>-1</sup> Glyphosate	69.13 c	30.97 a	46.05 b
Soil + B-YCW + 100 mg l <sup>-1</sup> Glyphosate	70.27 c	29.60 b	51.03 a
Soil + B-B + 100 mg l <sup>-1</sup> Glyphosate	67.40 d	32.60 a	46.03 b
<b>CV</b>	<b>1.02</b>	<b>1.80</b>	<b>1.67</b>
<b>Duncan's Test</b>	<b>**</b>	<b>**</b>	<b>**</b>
<b>SE</b>	<b>0.60</b>	<b>0.39</b>	<b>0.55</b>

Remarks: SOM = soil organic matter by gravimetry methods; CEC = cations exchange capacity; SE = Standart error; n = 15; \*\* = significant at the 0.01 level (2-tailed).

The increase in CEC of Inceptisols due to the effect of biochar application is determined by a simple force



balance involving an electric field and solution viscosity resistance. The most important soil surface electrochemical parameters (E0) include exchangeable sodium percentage (ESP), cation exchange capacity (CEC), soil specific surface area (S), soil surface charge density (0), soil surface potential (0), and soil surface electric field strength [22]. while biochar application on Inceptisols increases the concentration of SOM, which helps to decrease the phytotoxicity of glyphosate. On the other hand, soil minerals play an important role in glyphosate uptake, although mineral composition was reduced after biochar application. The addition of SOM to the soil affects the amount of complex organic molecules present in the soil SOM components [26]. Biochar clay-carbon interactions with a strong affinity for hydroxyl groups. The amount of aluminum hydroxy complexes included in the clay, as well as its chemical composition and charge characteristics, all affect changes in its electrochemical properties. The point of zero charges (PZC) is affected by the number of interlayers on the cation exchange capacity of clays [27]. Cyclic organic compounds have high molecular weight, long chains, and active phenolics (-OH), which act as binders to bind cations, and anions (pH-dependent charge) at certain pH levels. Some carboxylates are released below pH 6, leaving negatively charged functional groups. The use of biochar can broaden the spectrum of negative charges on the surface charge of soil colloids. The pH PZC of Inceptisols on young coconut waste biochar decreased by 0.24 and 0.30, respectively compared to the control and glyphosate-contaminated Inceptisols. However, the biochar showed an increase in the negative charge of Inceptisols in preventing glyphosate contamination and sorption after treatment in general. On hydroxyl functional sites, protons and other inorganic and organic contaminants are adsorbed. PZC is defined as the presence of equal amounts of positive and negative charges. This indicator is crucial for determining good soil quality to combat soil contamination and pollution. Several parameters, including mineral composition, SOM, and pH, affect the presence and behavior of glyphosate [26].

### 3.2 The impact of glyphosate on the nutrient of Inceptisols ameliorated with biochar

Glyphosate contamination had a significant effect on the nutrient of Inceptisols, with reductions in SOC, available P, K, Ca, and exchangeable Mg at 100 mg l<sup>-1</sup> glyphosate-containing 0.80% C; 0.12 ppm P<sub>2</sub>O<sub>5</sub> and 0.03; 0.04 and 0.06 cmol(+)/kg<sup>-1</sup> compared to the control (Table 3 and Figure 1). The nutrient reduction of Inceptisol is affected by glyphosate contamination, and phosphate is taken up through ligand exchange at differently charged surface sites under strong bond formation. As a result, there is competition for absorption sites between glyphosate and nutrients, which can impact glyphosate binding and consequent leaching. Since prescriptions prevent glyphosate uptake and ingested glyphosate is mobilized (adsorbed), soil mineral glyphosate and nutrient uptake show competition and uptake preference. Glyphosate and nutrients may compete for soil surface area, thereby

reducing glyphosate uptake. In addition to competitive uptake, glyphosate, and nutrient uptake can be additive, meaning that certain surface areas can absorb both sorbates while others can only absorb glyphosate or nutrients. Glyphosate has a sorption capacity of 2.61 mol m<sup>-2</sup>, phosphate has a sorption capacity of 2.85 mol m<sup>-2</sup>, and glyphosate + phosphate has a sorption capacity of 4.17 mol m<sup>-2</sup>. The presence of two types of sites, general and specialized, explains this difference. It can also be explained by sorption on different planes, which occurs when glyphosate is adsorbed onto phosphate via metal cations [28].

**Table 3.** The Impact of glyphosate on SOC, total N, and available P of Inceptisols ameliorated with biochar

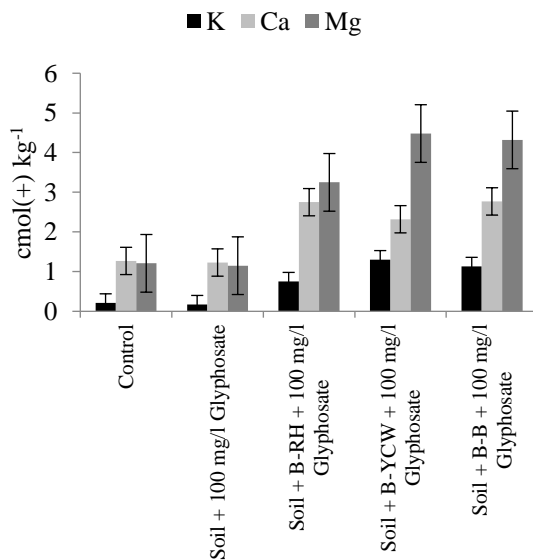
Treatment	SOC	Total N	Available P
	%		ppm P <sub>2</sub> O <sub>5</sub>
Control	2.97 d	0.32 b	7.40 b
Soil + 100 mg l <sup>-1</sup> Glyphosate	2.17 c	0.32 b	7.28 b
Soil + B-RH + 100 mg l <sup>-1</sup> Glyphosate	4.10 a	0.46 a	12.35 a
Soil + B-YCW + 100 mg l <sup>-1</sup> Glyphosate	4.22 a	0.46 a	11.99 a
Soil + B-B + 100 mg l <sup>-1</sup> Glyphosate	3.83 b	0.44 a	12.54 a
<b>CV</b>	<b>2.29</b>	<b>3.96</b>	<b>7.16</b>
<b>Duncan's Test</b>	<b>**</b>	<b>**</b>	<b>**</b>
<b>SE</b>	<b>0.08</b>	<b>0.01</b>	<b>0.60</b>

Remarks: SOC = soil organic carbon by Walkley and Black methods; SE = Standart error; n = 15; \*\* = significant at the 0.01 level (2-tailed).

The interaction between glyphosate and nutrients is more than just a matter of fluctuating or permanently charged soil mineralogy. Soils have general and specialized sorption sites, but the sorption sites are highly regulated by the soil mineral type. After this herbicide was introduced in 1974, competition in the uptake of glyphosate and nutrients by plants proved to be a major problem. The most important element affecting glyphosate uptake or leaching is nutrient content. Environmental problems associated with glyphosate competition for nutrients caused by reduced glyphosate uptake in the soil can increase the danger of glyphosate leaching into the water environment. Soils have a large capacity for glyphosate uptake at equilibrium sorption, but soils are also affected by high hydraulic conductivity, which implies an increased risk of leaching if applied before rainfall. In soil solution, glyphosate can form chelates or complexes with micronutrient metal ions. Compared to Ca and Mg ions, Cu and Zn ions in solution can combine quite strongly with glyphosate at physiologically relevant pH values. Plant uptake of complex metal ions has been linked to glyphosate contamination [29].

Application, 40 t ha<sup>-1</sup> of the three biochar can increase SOC, total N, available P, K, exchangeable Ca, and Mg. However, young coconut waste biochar can increase the proportion of C and N up to 4.22% and 0.46% respectively when compared with other biochar products, such as rice husk (4.10% and 0.46%) and bamboo (3.83% and 0.44%). Compared to rice husk biochar (12.35 ppm P<sub>2</sub>O<sub>5</sub>) and young coconut husk

(11.99), bamboo biochar was able to increase P availability up to 12.54 ppm  $P_2O_5$  (Table 3). Biochar application has the potential to increase soil uptake of glyphosate at variably charged surface sites, while uptake by the permanently charged silicate layer is limited. Organic matter treatment increases specific surface area and sorption, which has an indirect influence on glyphosate sorption but may stabilize oxide minerals [30].



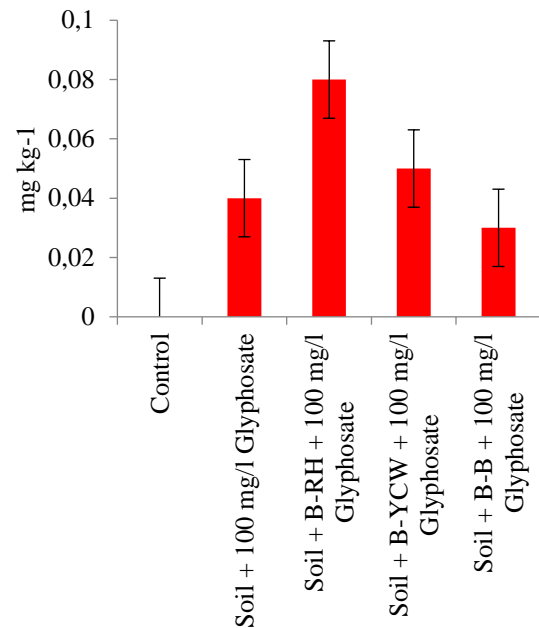
**Fig. 1.** Effect of glyphosate on exchangeable K, Ca, and Mg of Inceptisols ameliorated with biochar

Absorbed glyphosate generates mononuclear, monodentate, or binuclear, bidentate surface complexes with one coordinated surface site. For the available surface space, glyphosate and nutrients compete [31]. Glyphosate uptake in the soil is also time-dependent, doubling in soils with 3.1% organic carbon [32]. Biochar-based amelioration technology can reduce metal oxide phosphate sorption, increase organic C, total N (Table 3), and soil-accessible P, as well as exchangeable K, Ca, and Mg in Inceptisols soils. The largest increase in K and Mg values in young coconut waste biochar was 1.30 and 4.48  $cmol(+)kg^{-1}$ , respectively, while the highest increase in Ca value in bamboo biochar was 2.77  $cmol(+)kg^{-1}$  (Figure 1).

### 3.3 Correlation Between Residual of Glyphosate with Surface Change and Nutrient of Inceptisols ameliorated with biochar

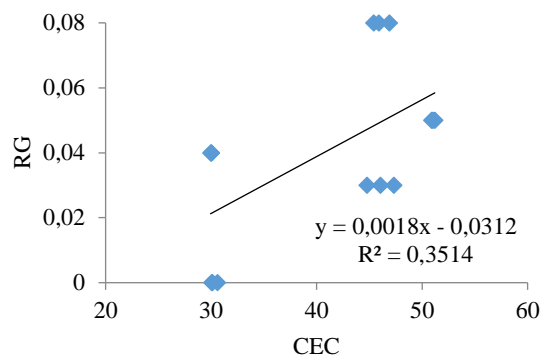
The effect of glyphosate contamination on Inceptisols has an influence on the residual value of glyphosate in the soil. Inceptisols contaminated with glyphosate had a residue value of 0.04 mg kg. This shows that Inceptisols can naturally absorb glyphosate (Figure 2). The uptake of glyphosate in soil usually consists of a rapid initial uptake that constitutes the bulk of the uptake, followed by a delayed reaction that can last several days and absorbs only a small amount of glyphosate. Temperature impacts the kinetics of glyphosate uptake and degradation, but the rate of uptake with temperature is unknown. Every 10-degree Celsius increase in

temperature is estimated to cause interactions between solutes and soil components [33]. Through the use of biochar amelioration technologies can be used to reduce the impact of glyphosate contamination and residues in the soil.



**Fig. 2.** Residual of glyphosate on Inceptisols ameliorated with biochar from young coconut waste, rice husks, and bamboo

Biochar has been shown to improve the chemical properties of Inceptisols and also acts as a glyphosate sink in Inceptisols, where the application of 40 t  $ha^{-1}$  biochar can reduce glyphosate residues in Inceptisols by 0.08 ppm (rice husk) > 0.05% (young coconut husk) > 0.03 ppm (bamboo), and respectively compared to the control and glyphosate-contaminated Inceptisols. Glyphosate absorption can be improved by increasing pH, EC, SOM, and CEC with biochar treatment. Effect of biochar on oxide mineral composition and glyphosate sorption on increasing pH and SOM. Glyphosate sorption by oxides is 1.45-1.85  $mol m^{-2}$ . This is important in terms of the overall number of singly coordinated (possibly adsorbing) hydroxyl groups on the oxide surface, as iron oxide has an average of 3 OH groups  $nm^{-2}$ , which is equivalent to 5.0  $mol m^{-2}$  [34]. Between glyphosate and the oxide surface, mononuclear and monodentate bonds occupy less than half of the singly coordinated OH groups, while binuclear and bidentate surface complexes develop, leaving some OH groups vacant. Mineral composition and SOM appear to have a function in glyphosate sorption in soil. This is due to the clay content interacting with the phenolic groups as well as the pores in the biochar. Thus, biochar has a very high absorption of glyphosate. This absorption is due to the chemical formation of hydrogen bonds with glyphosate, as well as the absorption of glyphosate within the pores of biochar.



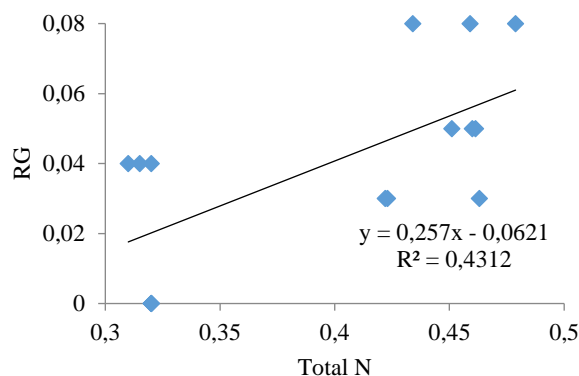
**Fig. 3** Linear regression between residual of glyphosate (RG) with CEC on inceptisols meliorated with biochar

**Table 4.** Matrix correlation Pearson (r) of chemical properties of Inceptisols ameliorated with biochar

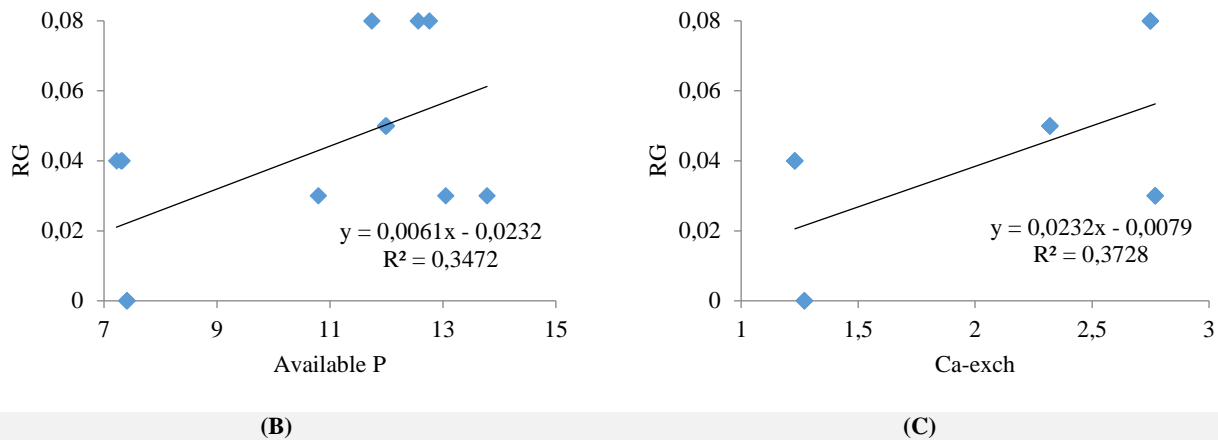
Correlation	pH H <sub>2</sub> O	pH KCl	pH PZC	EC	CEC	Mineral	SOM	SOC	Total N	Available P	exch-K	exch-Ca	exch-Mg	Residual of Glyphosate (RG)
pH H <sub>2</sub> O	1	0.974**	-0.820**	0.971**	-0.845**	0.837**	0.948**	0.894**	.888**	0.878**	0.981**	0.840**	0.977**	0.371
pH KCl		1	-0.672**	0.937**	-0.818**	0.810**	0.905**	0.841**	0.867**	0.866**	0.949**	0.840**	0.953**	0.336
pH PZC			1	-0.819**	0.725**	-0.718**	-0.832**	-0.830**	-0.735**	-0.702**	-0.825**	-0.640*	-0.802**	-0.359
EC (dS m <sup>-1</sup> )				1	-0.814**	0.809**	0.973**	0.887**	0.890**	0.922**	0.982**	0.868**	0.984**	0.481
Mineral (%)					1	-1.000**	-0.833**	-0.929**	-0.808**	-0.876**	-0.812**	-0.902**	-0.849**	-0.294
SOM (%)						1	0.829**	0.927**	0.808**	0.874**	0.804**	0.903**	0.844**	0.298
CEC [cmol(+)kg <sup>-1</sup> ]							1	0.933**	0.940**	0.930**	0.959**	0.901**	0.970**	<b>0.593*</b>
SOC (%)								1	0.882**	0.901**	0.869**	0.877**	0.886**	0.481
Total N (%)									1	0.835**	0.900**	0.879**	0.917**	<b>0.570*</b>
Available P (ppm)										1	.880**	0.957**	0.919**	<b>0.590*</b>
K-exch [cmol(+)kg <sup>-1</sup> ]											1	0.833**	0.993**	0.387
Ca-exch [cmol(+)kg <sup>-1</sup> ]												1	0.891**	<b>0.611*</b>
Mg-exch [cmol(+)kg <sup>-1</sup> ]													1	0.439
Residual of Glyphosate (mg kg <sup>-1</sup> )														1

Remarks: PZC = Point of zero change; EC = electrical conductivity; CEC = cations exchange capacity; SOM = soil organic matter by gravimetry method; SOC = soil organic carbon by Walkley and Black methods; exch = exchange; n = 15; \*\* = Correlation is significant

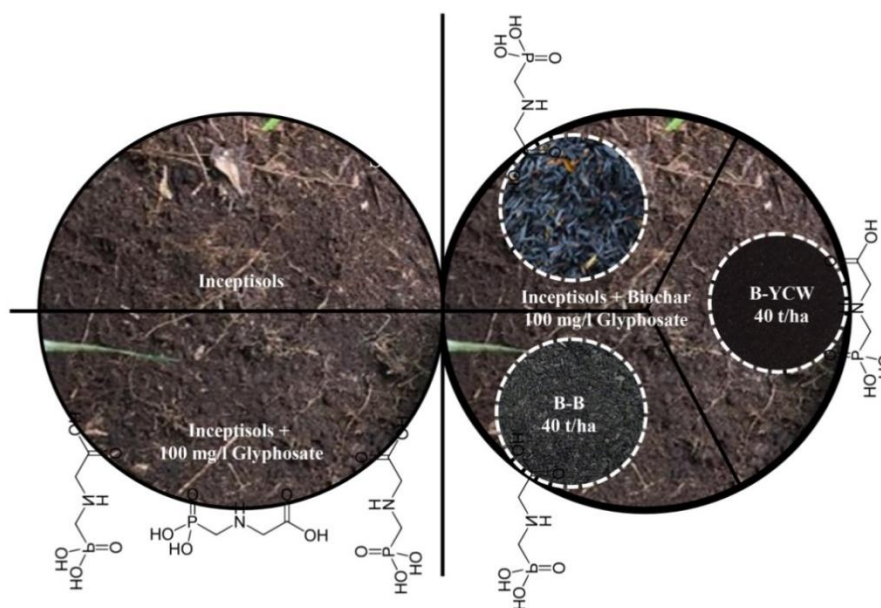
at the 0.01 level (2-tailed); \* = Correlation is significant at the 0.05 level (2-tailed).



(A)



**Fig. 4** Linear regression between residual of glyphosate (RG) with total N (A), available P (B), and exchangeable Ca (C) on Inceptisols ameliorated with biochar



**Fig. 5** Prediction of mechanism process of contamination from glyphosate on Inceptisols ameliorated with biochar

Determining the uptake and leaching of glyphosate in a particular soil is not easy, as it seems to depend on several soil characteristics such as pH, minerals, SOM, and CEC. There is an interaction between residues of glyphosate and CEC [ $r = 0.593^*$  and  $RG = 0.0018$  (CEC) -  $0.0312$ ;  $R^2 = 0.3514$ ]. The increased negative charge caused by the chelation process has a major impact on glyphosate uptake on Inceptisols (Fig. 3). The potential of glyphosate as a chelating agent impacts the competition for binding sites in the soil, demobilizes particle-associated components into the soil solution, and increases their solubility [35]. While in nutrient composition there is also an interaction between residues with Ca [ $r = 0.611^*$  and  $RG = 0.0232$  (Ca) -  $0.0079$ ;  $R^2 = 0.3728$ ] > available P [ $r = 0.590^*$  and  $RG = 0.0061$  ( $P_{2O_5}$ ) -  $0.0232$ ;  $R^2 = 0.3472$ ] > total N [ $r = 0.570^*$  and  $RG = 0.257$  (N) -  $0.0621$ ;  $R^2 = 0.4312$ ]. This also explains that glyphosate can affect nutrient composition in Inceptisols (Fig. 4). The presence of glyphosate affects the binding mechanism between glyphosate and phosphate due to P mobility in the soil through adsorption competition. This competition varies greatly among different soil types [36]. Consequently, the competition for adsorption sites in the soil between

glyphosate and P appears to be quite important and has a considerable influence on the mobility and availability of P as a plant nutrient. The predicted mechanism is depicted in Figure 5, where biochar has hydroxyl groups as the basis of negative charge. Application of biochar on Inceptisols increased OH groups (pH  $H_2O$ ) and the negative charge of the soil (CEC). This indicates that Inceptisols become more active in increasing surface charge supported by SOM content and inter-charge interaction (EC). Thus, soil absorption of glyphosate becomes greater with the decrease of glyphosate residue in Inceptisols after biochar treatment.

## 4 Conclusion

The Contamination from glyphosate had a significant effect on surface change (pH, EC, Mineral, SOM, and CEC) and nutrient (SOC, total N, and available P) of Inceptisols ameliorated with  $40 \text{ t ha}^{-1}$  biochar. The application of bamboo biochar had a significant and better effect than young coconut waste and rice husk biochar on Inceptisols on increasing pH (0.70); SOM (7.07%); 0.12% N; 5.14 ppm  $P_{2O_5}$ , compared to control.



Residual glyphosate concentrations on Inceptisol ameliorated with biochar were 0.08 (rice husk biochar) > 0.05 (young coconut waste biochar) > 0.04 (Inceptisol) > 0.03 mg kg<sup>-1</sup> (bamboo biochar) compared to the initial glyphosate concentration of 100 mg l<sup>-1</sup>, respectively. The correlation between residues on glyphosate (RG) had a significant interaction with chemical properties of Inceptisols amended with biochar (rice husk, young coconut waste, and bamboo) with a linear equation, namely exchangeable Ca (r = 0.611\*); CEC (r = 0.593\*); available P (r = 0.590\*) and total N (r = 0.570\*).

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