



Effectiveness of biochar in soil conditioning under simulated ecological conditions

Samia Qadeer¹, Aniq Batool^{1*}, Audil Rashid¹, Azeem Khalid¹,
Nafeesa Samad¹ and Muhammad Asad Ghufra²

¹Department of Environmental Sciences, PMAS Arid Agriculture University, Rawalpindi

²Faculty of Environmental Sciences, International Islamic University, Islamabad

Abstract

Biochar is getting momentous importance due to its potential use in various fields like agriculture, organic fertilizers and green house gas (GHG) sequestration. The mineralization of biochar in soil is greatly dependent upon the temperature and moisture level of the soil, therefore under simulated ecological conditions, there is varying effect of biochar on soil properties. In the present study, the potential of biochar to improve soil properties was focused under simulated ecological conditions of Pakistan. Experiments were carried out on soils of seven ecological zones of Pakistan applying biochar in 0.6:100 ratio (biochar:soil, w/w) in pot experiments. Temperature and moisture conditions of the experiments were maintained in laboratory according to the respective ecological zones. The effect of biochar was periodically analyzed for two months on various soil parameters such as pH, bulk density, organic matter, total organic carbon and available phosphorus. The results showed that the alkaline nature of biochar contributed to high shift in pH of all the ecological zones. Maximum rise (0.5 units) was observed in Zone 10 (Sulaiman Piedmont, Temperature (T): 46 °C; Field Capacity (FC): 26%). The biochar application showed a decrease in bulk density of the soil of all ecological zones. The high carbon and nutrient content of the biochar contributed to increase in total organic carbon, organic matter and available phosphorus of soils of all the ecological zones. The most profound effect of biochar was observed for Z6 (Wet mountains, T: 36°C, FC: 50%), where the concentration raised from initial 1.15 mg kg⁻¹ to 2.43 mg kg⁻¹. Overall, the study revealed that ecological zones of Pakistan with higher moisture level and temperature conditions cause increase in mineralization of biochar and contributed to nutrients release in the soil which ultimately improved the soil properties.

Keywords: Biochar, soil fertility, soil properties, simulated ecological zones, temperature

Introduction

Depletion in soil nutrients and soil organic matter has attracted attentions worldwide to the use of soil supplements. Changing climate and extensive cropping has further put pressure on nutrient supply of agricultural lands. The chemical fertilizers fail to confirm the agricultural security and subsequently were raised environmental complications. So, the need of organic fertilization and restoration of contaminated sites is momentarily getting importance. Nutrient deficiency in agriculture is of prime concerns particularly in developing countries like Pakistan that are known to be deficit in soil organic matter. Among organic fertilizers biochar application is relatively a novel approach with potential benefits to both agriculture and environment. Application of biochar in soil could help in remediating the polluted soil, increasing soil quality and sequestering C (Barrow, 2012). However, the stability of biochar in changing environmental conditions and among various ecological conditions is questioned.

Biochar is carbon rich product obtained by thermal decomposition of biomass like wood, manure or leaves in

limited or no supply of oxygen (Lehmann and Joseph, 2009). Biomass of all types is usually more environmentally safer and financially feasible to produce biochar through thermal pyrolysis (Roberts *et al.*, 2010). In many terms, biochar is regarded as charcoal because of some common properties. However, the pyrolysis process and the anticipated utilization distinguish biochar from charcoal (Lehmann *et al.*, 2006). The production of biochar from waste and plant biomass is eco-friendly strategy, moreover the recalcitrant nature and high porosity ensure its slow mineralization and provision of nutrients in the soil. Carbon sequestration and soil applications, along with biochar's potential to be used as a low-cost adsorbent, and its response towards various chemical pollutants have raised the need of further studies to harness the potential of biochar (Yao *et al.*, 2011). Biochar contains high carbon content and could be used as soil amendment. Biochar application to soil positively affect the properties of soil, like soil structure, water retention capacity, fertility, and carbon sequestration of degraded soil (Yeboah *et al.*, 2009). Comparative to the other soil amendments like compost, biochar is relatively a slow degrading product (Lehmann *et*

*Email: aniqabatool@uaar.edu.pk

al., 2006). The stability of biochar is of great importance both in terms of the ability for biochar to act as a measure for climate change mitigation and ability of biochar to provide sustained improvement of soil fertility (Bruun *et al.*, 2008).

Pakistan is divided into ten Agro-ecological zones by PARC (Pakistan Agriculture Research Council) depending upon the climatic conditions and variability in temperature and humidity. As the stabilization of biochar is dependent on temperature and humidity conditions, the contrasting environmental conditions of different ecological zones of Pakistan has different extent of biochar stabilization due to variations in temperature (Brunn *et al.*, 2011). The soil of these ecological zones differ considerably in terms of basic soil properties like texture, pH and nutrient potential and affected verily by application of biochar. The present study was designed focusing on effect of plant derived biochar application and its progressive mineralization on different soil properties like pH, OM (organic matter), TOC (total organic carbon) and P_{avail} (available phosphorous) content of different ecological zones of Pakistan.

Materials and Methods

Soil sampling

Soil samples from seven selected ecological zones (Table 1) of Pakistan were taken from 0-15 cm upper soil layer. The zonation of various ecological zones is followed as given by PARC. To keep homogeneity in type of soil all the selected areas were targeted for agricultural soil samples. The humidity and temperature records of the day of sampling were also recorded for the respective area. The selected fields were selected away from any industrial

Biomass pyrolysis

Lantana camara a well-known invasive species was selected for biochar production. Sampling of biomass was carried out from the wild invasion around the Rawal Lake. Initially all the leaves and damaged stems were removed from the biomass and allowed to air dry for a week. The biochar was prepared using the stems of the plant. The dried samples were then chopped in small pieces of 2-3 inches and further dried at 105°C for 1 hour. The drying temperature removed all the moisture and thus aided in pyrolysis with low smoke formation. Further, the oven dried biomass was pyrolysed at 450°C for 20 minutes in muffle furnace and weights were recorded prior and after pyrolysis. Finally, the prepared biochar was crushed into smaller particles for even distribution in soil.

Biochar characteristics

Prior to the application of biochar it was analysed for few basic characteristics viz: pH, EC, turnover rate and bulk density by following standard procedure of ASTM (2007).

Experimental setup

Air dried sieved soils were placed in plastic pots of 4.5 inches height and approximate capacity of 1kg. Biochar was mixed in the soil at 0.6% biochar (w/w). The pots not amended with biochar were used as the control and all experiment was performed in three replications.

Field capacity of the soil was calculated by gravimetric method. All of the soils were maintained at pre-monsoon field capacity (calculated using R statistical model) of respective zone and summer mean temperature given in Table 1. Soil was incubated in simulated ecological conditions in incubators for 60 days in dark and periodic

Table 1: Selected agro-ecological zones of Pakistan and their corresponding incubation condition

Ecological zone	Zone	Area	Incubation temperature (°C)	Field capacity (%)
Zone 1 (Z1)	Indus Delta	Hyderabad	38	40
Zone 3 (Z3)	Sandy Desert; Sandy Desert (b)	Bahawalpur	38	40
Zone 4 (Z4)	Northern Irrigated Plain (a) Northern Irrigated Plain (b)	Faisalabad	40	45
Zone 5 (Z5)	Barani (rain fed) Lands	Rawalpindi	40	20
Zone 6 (Z6)	Wet Mountains	Haripur	36	50
Zone 7 (Z7)	Northern Dry Mountains	Kohat	18	18
Zone 10 (Z10)	Sulaiman Piedmont	D.G Khan	46	26

encroachment or dumping site to avoid any sort of contamination from neighboring areas that may affect the variability in soil parameters. All the samples were air dried and sieved through 2 mm sieve. The sieved soils were subjected to initial analysis for the parameters like pH, moisture and Field Capacity.

sampling after every 15 days was carried out from the pots.

Soil analysis

Soil samples were periodically analyzed after 15 days for the following parameters.



pH

The pH of soil was determined in 1:2 soil to deionized water (DI) ratio (McLean, 1982). The suspension was allowed to stand for 30 minutes after vigorous shaking and pH was measured using calibrated pH multi meter model (MV 400+).

Bulk density

Bulk density was calculated by dividing the weight of biochar occupying 10 cm^3 at 15°C , which covers a vacancy of 10 cm^3 (Özçimen and Karaosmanoglu, 2004).

Organic matter

Soil organic matter (SOM) analyses were carried out by Walkley (1997) titration method. Soil sample (1.0 g) was digested in 250 mL flask by adding 10 mL $\text{K}_2\text{Cr}_2\text{O}_7$ (1 N) and 20 mL H_2SO_4 (99% pure) for 30 min. After digestion, 200 mL water and 10 mL ortho- H_3PO_4 were added to the flask. The samples were allowed to cool and then titrated against 0.5 M ferrous ammonium sulphate (FAS), using diphenylamine (DPA) as indicator. Blank titrations were also carried out for reference (Walkley, 1947).

Total organic carbon

Ferrous Ammonium Sulphate (FAS) titration method was used for calculation of total organic carbon (TOC) in soil. Dichromate digestion method used for organic matter analysis was further processed using formula given below for TOC calculation.

$$\text{TOC in soil} = 1.334 \times \text{Oxidizable organic carbon}$$

Available phosphorous

Available phosphorus (P_{avail}) was determined by modified method of Olsen *et al.* (1982). Soil and extracant mixture (4 g: 50 mL) were shaken on horizontal shaker for one hour, followed by filtration with whatman filter paper No. 40. Filtrate was mixed with mixed reagent and allowed to stand for 10-15 minutes. The intensity of the blue color developed in the sample represented the concentration of P_{avail} in the soil samples, the color was measured spectrophotometrically at 880 nm. Formula used for calculation was:

$$\text{P}_{\text{avail}} (\text{ppm}) = \frac{\text{ppm from Calibration curve} \times (\text{A} \div \text{wt}) \times (25 \div \text{V})}{\text{Available P} (\text{ppm}) = \frac{\text{ppm P (from calibration curve)} \times \text{A} / \text{wt} \times 25 / \text{V}}{\text{Where: A} = \text{Total volume of extract; wt} = \text{weight of air-dry soil; V} = \text{Volume of extract used for measurement}}$$

Statistical analysis

Data obtained were subjected to statistical analysis for computation of mean and standard deviation using

Microsoft Excel 2010. The significance of variation was analyzed by two factor factorial using SPSS version 12.0.

Results

Biochar characteristics

The biomass of the *Lantana camara* was pyrolyzed for the biochar production and the initial analysis showed that the pH of the biochar was very alkaline (9.78). The electrical conductivity of the biochar was 2.22 ds cm^{-1} whereas the bulk density was up to 0.41 g cm^{-3} .

Soil analysis

Comparative difference between the control and amended soil corresponding to the effect of biochar under different simulated ecological conditions on various soil physico-chemical parameters and nutrient content is presented as follows:

pH

It was observed that initially soil pH ranged from 7.2 to 8.5 in all the zones. Whereas after 15 days of incubation only Z6 represented obvious decline in pH from initial 8.5 to 7.78 (Figure 1). The pH of other zones decreased minutely after 15 days of incubation in both control and amended conditions. The effect of biochar was found significant in case of Z10 where pH was increased from 8.5 to 9.2 after 30 days of incubation and further remained consistent till 60 days. Overall biochar amended soil showed more obvious shifts in soil pH as compared to the unamended soil in all ecological zones. All treatments showed a decline in pH after 15 days of incubation, where this decline was followed by a steady increase in pH of biochar amended soil after 30 day till the end of experimental duration (60 days). Soil pH changed by 0.05 units in Z1, Z5 and Z7 in biochar amended soil, where corresponding increase in Z3, Z4, Z6, Z10 was recorded as 0.32, 0.37, 0.51 and 0.73 units after 60 days. In unamended soil, the pH remained stable in Z1, whereas in Z5 a significant ($p\text{-value} < 0.05$) decline was observed. In case of Z10 there was a significant rise in pH after 30 days of incubation in both amended and un-amended soils and remained consistent till end of experiment.

Bulk density

The results regarding bulk density of the biochar showed a non-significant effect on soil. A declining trend was observed in bulk density of soil in all the ecological conditions (Figure 2). Soil bulk density changed from 1.46 - 1.49, 1.62 - 1.59, 0.83 - 0.77, 1.63 - 1.58, 1.5 - 1.44 and 1.65 - 16.1 g cm^{-3} in Z3, Z4, Z5, Z6, Z7 and Z10 correspondingly whereas in control the bulk density remained almost constant. The only increase in soil bulk



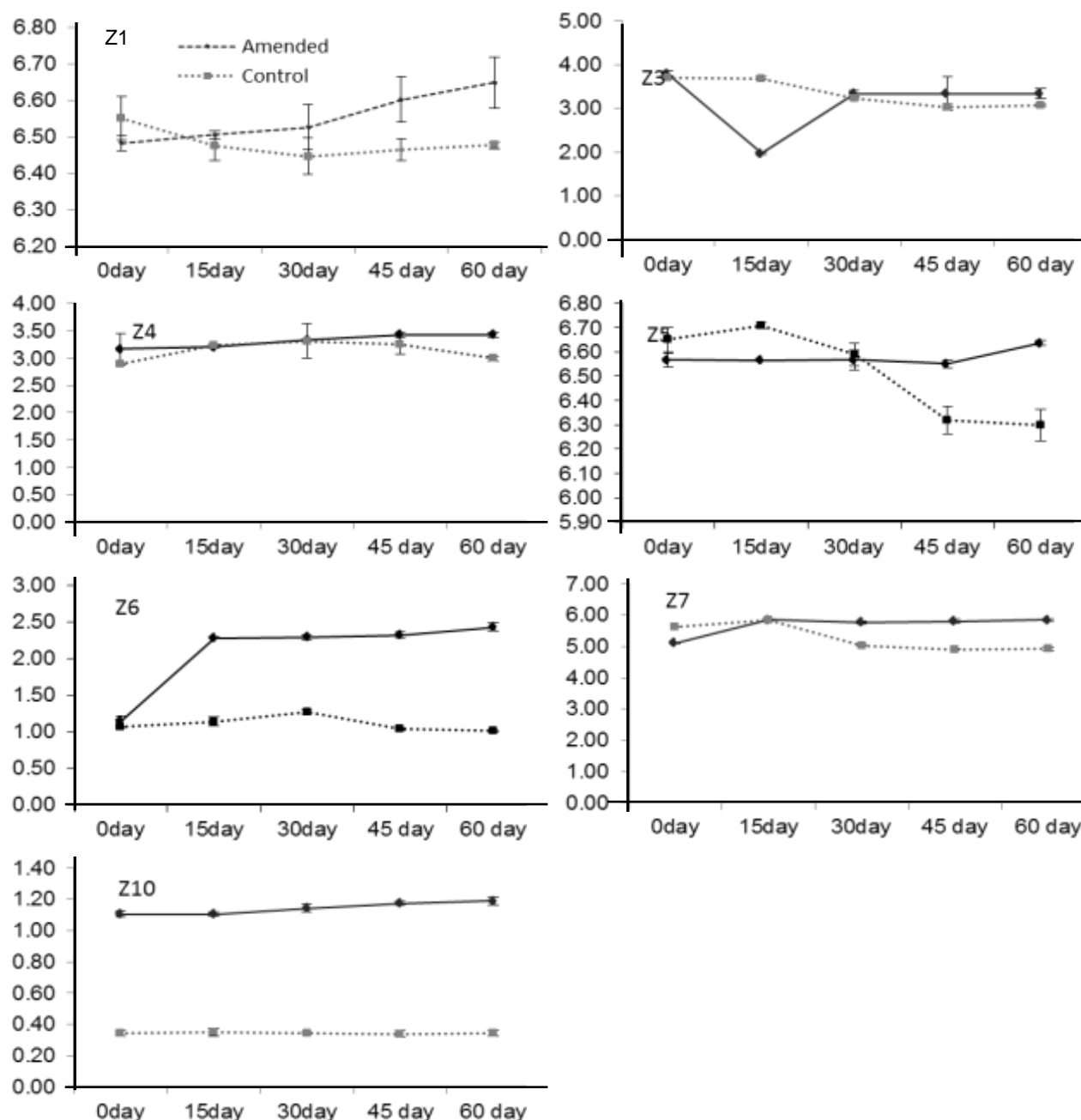


Figure 1: Fluctuation in pH of biochar amended soil under simulated ecological zones (x-axis = incubation period, y-axis = pH values).

density was observed in the case of Z1 where bulk density increased by only 0.02 units from the initial values. The obtained results were found statistically non-significant.

Organic matter (OM)

Biochar amendment to soil represented obvious influence on OM contents of the soil in ecological zones

(Figure 3). The comparative effect of biochar addition is represented in figure 3. Initially at 0 day the % OM in soil were 1.4%, 1.5%, 0.8%, 0.9%, 2.2%, 0.95% and 0.26% under simulated ecological conditions, that is Z1, Z3, Z4, Z5, Z6, Z7, Z10, respectively, of control soil, where addition of biochar changed OM to 1.5%, 2.2%, 0.9%, 1.08%, 2.3%, 1.08% and 1.3% correspondingly. After 30 days, the highest



increase was recorded in Z3 (2.43%) in biochar added soil but the change was found statistically non-significant. Incubation of control soil for 60 days resulted in continuous decrease of %OM except Z5 where a minute rise of 0.03% in OM was observed. Incubation of biochar amended soil showed non-significant rise in OM. Decrease was observed only in Z10 where OM percentage changed from 1.3% to 1.1%. Significant ($p < 0.05$) effect of biochar was observed in case of Z3 where application of biochar resulted in 4.03% increase in OM as factor of maximum stabilized biochar in the soil of different ecological zones under corresponding conditions.

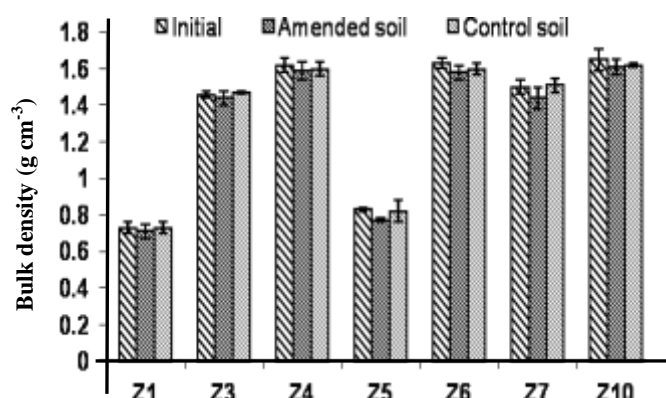


Figure 2: Effect of biochar amendment on bulk density of soil before and after incubation (\pm S.D)

Statistically non-significant change in bulk density was observed in all the zones by two way ANOVA.

Total organic carbon (TOC)

The TOC, estimated as stabilized organic carbon pool by biochar in soil is recorded and presented in Figure 4. Initially the TOC concentration varied from 5.96 mg kg⁻¹ in Z4 to 1324 mg kg⁻¹ in Z6 of control compared to the 5474 mg kg⁻¹ to 13591 mg kg⁻¹ in amended soil. After 15 days, the maximum decline in control soil was recorded for Z4 where 943 mg kg⁻¹ TOC declined as compared to the initial, whereafter 30 days in Z3, TOC declined 3197 mg kg⁻¹ units and 45 days correspond to 3775 mg kg⁻¹ decrement in TOC of Z6 of un-amended soil. TOC concentration of control soil decreased by 2213 mg kg⁻¹, 935 mg kg⁻¹, 1510 mg kg⁻¹, 2076 mg kg⁻¹, 1844 mg kg⁻¹ and 1510 mg kg⁻¹, in Z1, Z3, Z4, Z6, Z7 and Z10 correspondingly. However, Z5 showed 184 mg kg⁻¹ increase in soil TOC. In biochar amended soil after 15 days, maximum rise was observed in Z3 (1122 mg kg⁻¹ units), contrary to this Z4 (-943 mg kg⁻¹), Z5 (-1510 mg kg⁻¹) and Z7 (-180 mg kg⁻¹) showed a decline in TOC concentration. Comparatively, biochar addition raised the TOC content of soil as compared to the control of

respective zone however the rise was not found statistically significant (p -value > 0.05) in most of the cases.

Available phosphorous

Estimated P_{avail} under different ecological conditions is given in figure 5, during the course of incubation. As depicted from the graph, P_{avail} continued to decrease in the control soil, where as in the amended soil the concentration of P_{avail} increased from the initial value. Initially after 15 days of incubation soil P_{avail} content decreased in all the soils in all ecological zones except Z4 and Z7. The observed decline after 15 days ranged from 0.06 to 0.33 units in control soil and 0.00 to 1.14 units decrease in amended soil and were statistically non-significant. However, after 60 days of incubation, soil P_{avail} decreased upto 6.48 mg kg⁻¹, 3.07 mg kg⁻¹, 6.30 mg kg⁻¹, 1.01 mg kg⁻¹ and 4.92 in control soil of Z1, Z3, Z5, Z6 and Z7. P_{avail} concentration declined significantly from the initial concentration in Z5 control soils. Where the proximity of P_{avail} (mg kg⁻¹) in biochar amended soil represented continuous increase after 30 days of incubation upto 60 days of incubation. The observed concentration of P_{avail} varied as 6.65 mg kg⁻¹, 3.42 mg kg⁻¹, 6.64 mg kg⁻¹, 2.43 mg kg⁻¹, 5.85 mg kg⁻¹, and 1.19 mg kg⁻¹ in Z1, Z4, Z5, Z6, Z7 and Z10 correspondingly. Only the concentration of P_{avail} decreased upto 3.33 mg kg⁻¹ of soil in Z3. The most profound effect (p -value < 0.05) of biochar was observed in case of Z6 where the concentration raised from initial 1.15 mg kg⁻¹ to 2.43 mg kg⁻¹. Similarly compared to the control biochar also has obvious effects on P_{avail} content of Z10 as given in Figure 05 that is control vs amended after 60 days were 0.34 mg kg⁻¹ vs 1.19 mg kg⁻¹. Statistically significant differences were only found for Z10 between the unamended and amended soils ($p < 0.05$).

Discussion

Biochar conditioning in different ecological conditions improved the soil health in different aspects. Soil pH increased in all the ecological zone. However, an initial decline in pH of the soil (Figure 1) may be attributed to the biochar cation content. It is also reported that the combination of biochar cation and carbonates of the soil may lead to the formation of slightly soluble carbonates in the soil that limit the hydroxylation of carbonates, so decrease the hydroxyl ions (Liu and Xang, 2012). Further, the oxidation of organic matter in the soil could also produce the acidic matter that is supplemented by the addition of biochar (Costanza *et al.*, 2011). However, as the incubation proceeded the rise in pH was observed in both soil, which was more obvious in biochar amended soil. The interaction of pH of biochar has potential to alter the pH of soil (Liu and Xang, 2012),



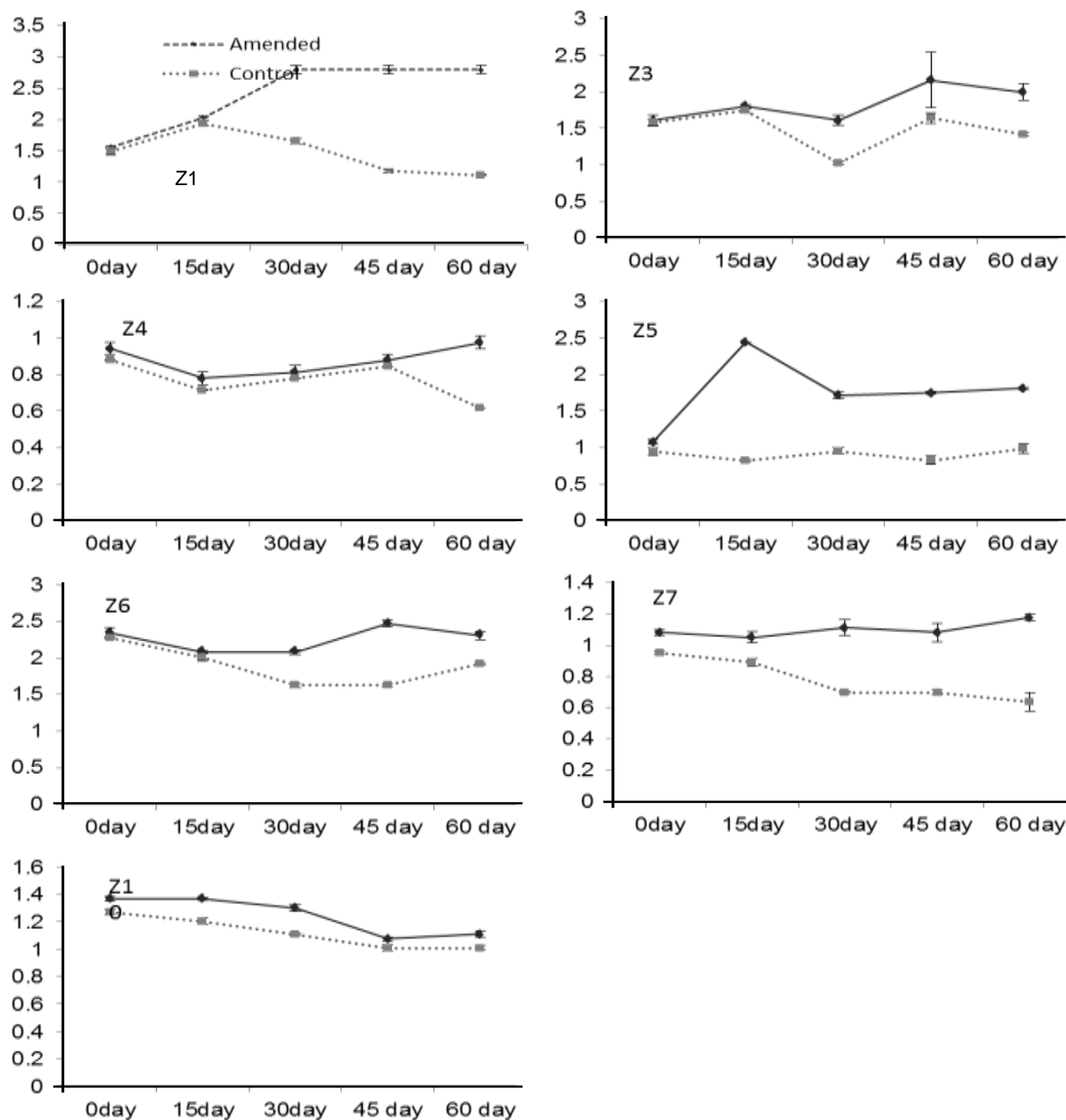


Figure 3: Soil organic matter fluctuations under biochar amendment in different simulated ecological conditions. (values on X-axis: incubation period, values on Y-axis: % OM)

because the biochar is a highly basic product (Barrow, 2012) due to the presence of organic ions and inorganic carbonates (Yuan *et al.*, 2011). Thus it could be the reason for rise in pH during course of incubation after initial decline. During the incubation, evaporation doesn't carry away the elements from the soil. This may lead to the rise

in pH of the soil. Increase in soil pH by the application of biochar could also be explained by another factor that is the high surface area and porous nature of the biochar which contribute to the increased CEC. This property is often endorsed to the change in pH of soil by application of biochar, as 68% variation in pH could be explained by CEC



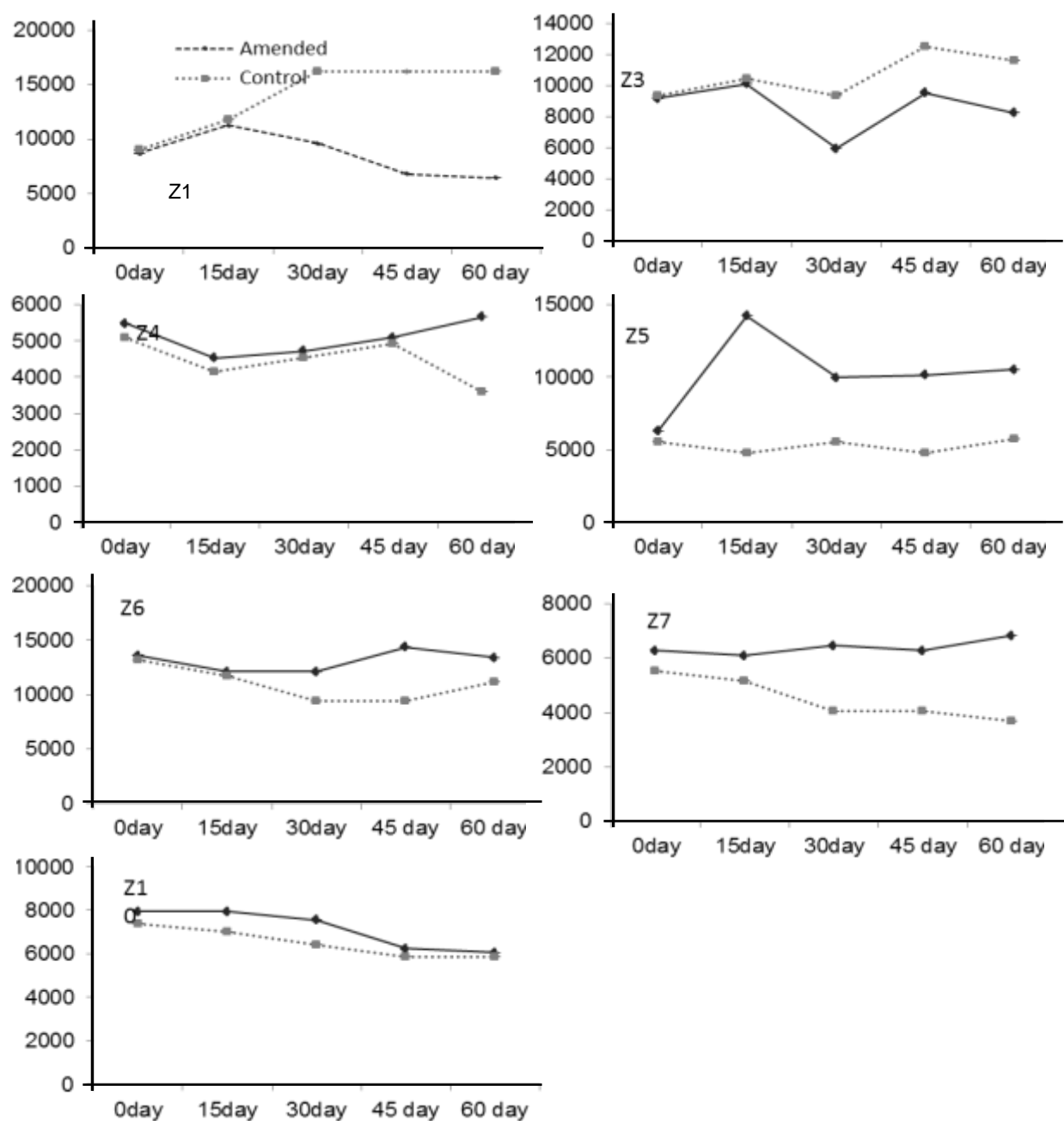


Figure 4: Effect of biochar stabilization on TOC (mg L⁻¹) of soil under simulated ecological conditions (values on X-axis: incubation period, values on Y-axis: TOC (mg L⁻¹))

change in the soil (Nigussie *et al.*, 2012). Application of biochar has previously resulted in more obvious changes in sandy and loamy soil compared to the clayey soil (De Gryze *et al.*, 2005). In the present work, more predominant effect was observed in loamy sand soil (Figure 1).

Biochar is carbon rich product (Lehmann and Joseph, 2009). Mineralization of biochar considerably increases the organic pool of soil. Organic amendments are known to increase the nutrient content in the soil solution by progressive mineralization by micro-organisms (Mehdi *et al.*, 2011). It was observed that initially the application of

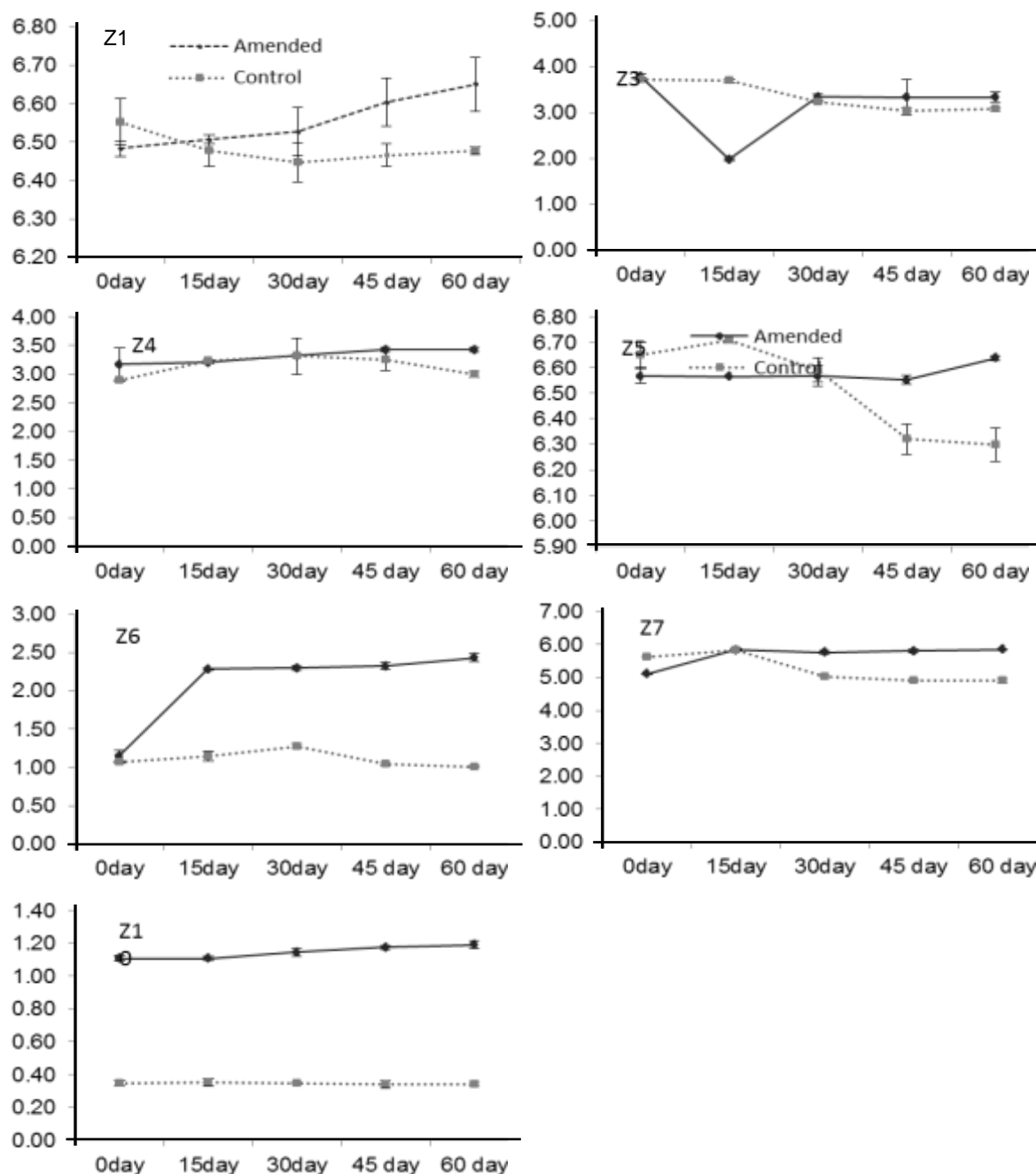


Figure 5: P_{avail} variation during the course of incubation in biochar amended soil under simulated ecological zones (values on X-axis: incubation period, values on Y-axis: P_{avail} (mgL⁻¹))

biochar has resulted in obvious shifts of OM in the soil; this may be attributable to the readily available fraction of organic carbon present in the biochar that decomposed initially in the soil (Bruun *et al.*, 2008). The three zones Z5, Z6, and Z7 are sandy loam in texture, such soil are usually low in nutrient and OM. Application of biochar to these

soils increased the organic carbon content of the soil. However, the highest value of OM was observed in Z6. Although the soil texture was sandy loam, the predominant OM% is attributable to the fact that 50% moisture and 36°C temperature, promoted high mineralization in the soil. It was also regarded that aging of biochar oxidizes the biochar



surface making it suitable for adsorption of various compounds with formation of carboxylate group (Laird *et al.*, 2010). These factors contribute to the mineralization of biochar in the soil, initially upto 2 months biochar is known to loss of 0.26%-0.79% of total carbon (Hamer *et al.*, 2004). Effect of biochar was most predominantly observed in Z3; this may be explained by the texture of soil that is loamy, with high proportion of clay in the soil.

The increase in P_{avail} content of soil was observed in the biochar amended soil (Figure 5). The similar increase in phosphorus was observed in many studies by application of biochar (Lehmann 2007; Cheng *et al.*, 2006; Chan *et al.*, 2007). Application of biochar is known to add direct phosphorous in the soil that resulted in continuous increase in soil P_{avail} (Stevenson and Cole, 1999). However, the application of biochar is also reported to affect the P_{avail} indirectly in the soil where the ash content of biochar has high concentration of phosphorous that contributed to increase in soil P_{avail} content (Steiner *et al.*, 2009). Study by Glaser *et al.* (2002) and Lehmann *et al.* (2003) revealed that addition of biochar to tropical soil increased the concentration of P_{avail} tropical soil as observed in the present study for Pakistani soil that comes under sub-tropical conditions.

Addition of biochar proved to be an effective strategy to be incorporated, that not only supplements soil nutrient content but also ensures environmental security through slow mineralization. Under changing climate conditions, such effective measures will provide better soil conditioning through slow degradation under high temperatures and provision of nutrients for longer duration of time along with the stocking of C in the soil. From the present work it is suggested that biochar is effective intervention in increasing soil nutrient balance of different ecological zones of Pakistan, however the initial considerations of soil pH could be an important determinant to assess the efficacy of biochar.

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