# Changes in bulk and surface properties of two biochar types during 12 months of field ageing in two West-African soils

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## Abstract

The study investigated the changes in properties of rice husk and corn cob biochars applied in urban agricultural field soils in Tamale (northern Ghana) and Ouagadougou (Burkina Faso), respectively. The biochars were both pyrolyzed at 500 °C with a batch reactor. Fine polyethylene mesh (litter bags) filled with 10 g of each type of biochar were buried at 20 cm depth in urban fields trials with a 3 x 2 factorial layout replicated 4 times. Factor 1 involved soil management practices at 3 levels: (1) farmers' practice (FP), (2) 20 t biochar $ha^{-1}$ and (3) control (no biochar). The second factor was time (duration) at two levels (6 and 12 months). Aged and fresh biochars were analyzed for volatile matter (VM), ash and fixed carbon (FC) contents, pH, effective cation exchange capacity (ECEC), and total surface acidity (Sa) and basicity (Sb). Dissolved organic carbon contents were determined sequentially by cold (cDOC) and hot water extractions (hDOC), respectively and aromaticities of cold water DOC (cSUVA) and hot water DOC (hSUVA) were determined. There was no significant interaction effect of soil management practices and time on measured ageing biochar properties. Time significantly affected most biochar ageing properties except Sa and Sb in rice husk biochar and ECEC in corn cob biochars at 6 months of exposure. In both biochars, Ash content, Fixed carbon (FC), cDOC, hDOC, cSUVA and hSUVA increased whilst pH and volatile matter contents decreased significantly. The hDOC was 2-3 times higher than cDOC contents for both biochars. Aromaticity of DOC contents of aged rice husk biochar exposed to soil management practices and time in the experimental site in Tamale showed persistence with time compared to corn cob biochar exposed in Ouagadougou experimental site. The results imply that rainfall, soil organic matter contents with interplay of soil minerals are key drivers to ageing and sequestration of these biochars and that these forces act at different scales but driven by time.

## Introduction

Biochar is charcoal made to be used as a soil amendment (Lehmann et al., 2006). Biochar is added to soil primarily to improve its fertility and sequester C. The ability of biochar to improve the fertility of highly weathered and especially, very acidic soil has been widely reported (Chintala et al., 2014; Steiner et al., 2007). The ability of biochars to enhance soil fertility depends on their physical and chemical properties, which are influenced by pyrolysis conditions and feedstock characteristics (Brewer et al., 2011; Kloss et al., 2011; Mukherjee et al., 2011; Peng et al., 2011; Singh et al., 2010). Apart from the effects that pyrolysis temperature and feedstock characteristics have on the physicochemical properties of biochars, their bulk surface properties undergo changes when they are applied to soils through processes such as oxidation, solubilization, microbial interaction, as well as interaction with organic matter and solutes from the soil environment (Mukherjee et al., 2014). The above processes lead to biochar ageing (Mukherjee et al., 2014), which changes biochars' quality over time. Many laboratory-based and a few field-based studies investigating biochar ageing have been reported in the literature. The laboratory-based methods include the modified soxhlet extraction of a mineral ash-rich biochar to simulate geochemical weathering (Yao et al., 2010), leaching of laboratory produced black carbons for a 100 day period (Kasozi et al., 2010) , changes in the properties of pine chip and corn digestate-derived biochars of 400 and 600 °C incubated for 100 days in an ancient kiln soil and its adjacent soil . Others include water availability and watering regimes (Masiello and Druffel, 1998; Bird et al, 1999; Nguyen and Lehmann, 2009), nutrient and microbial effects (Hale et al., 2012) and temperature ageing of biochars at 30 and 70 °C (Cheng and Lehmann, 2009). In addition, results from a number of field-based ageing studies have also been reported in the literature. Spokas (2010) exposed biochars in the field and studied their potential to reduce greenhouse gas emissions. Biochar mediated changes in soil quality and plant growth were reported by Jones et al. (2012), physicochemical changes in pyrogenic organic matter after 15 months of field exposure by Mukherjee et al. (2014), exposure of biochars to ambient conditions for half a year (Yang and Sheng, 2003) and the use of buried litter bags by Meng et al. (2014). Biochar is regarded as a refractory carbon (Schmidt and Noack 2000), although, this claim has been refuted by some researchers (Czimczik et al., 2003; Murage et al., 2007).

The full potential of biochar as a soil amendment to improve soil fertility may only be reached after ageing during which oxidation processes occurring on its surface, improve key characteristics such as cation exchange capacity (Mia et al., 2017). For instance, the oxidation of biochar (BC) surfaces is reported to have increased the effective cation exchange capacities (ECECs) which consequently improved the soils' nutrient retention capacity (Glaser et al., 2001; Hale et al., 2011; LeCroy et al., 2013; Liu et al., 2013; Nguyen et al., 2010). Spectroscopic and titration based analyses of aged chars from both laboratory incubations and also from archeological sources showed increased concentrations of O-containing functional groups particularly, phenolic, carbonyls and carboxylic (Cheng et al., 2008; Lin et al., 2012; Mukherjee et al., 2014). The oxidation of biochars increases with soil temperature but other factors such as the watering regime employed in an incubation process (Nguyen et al., 2009), the degree of thermal alteration of the biochar, which is greatly influenced by the pyrolysis condition and feedstock type (Liu et al., 2013; Zimmerman, 2010), and external nutrient supply (LeCroy et al., 2013), all affect the oxidation processes. Many studies have been done to investigate biochar oxidation under controlled conditions, but there is no available information about how soil management practices such as fertilization with inorganic and organic manures, biochar application and unamended control in themselves or their interactions with time after litter bags have been buried affects the biochar ageing in intensive West African agricultural system such as urban vegetable production. It is hypothesized that ageing of biochars will be greater in biochar exposed to soil for six months than those exposed for 12 month. The ageing process is also hypothesized to be dependent on farmers' practices at each site. The short-term duration of the experiment (12 months) as compared to most other long-term ageing experiments would not be problematic as the intense nature of urban vegetable production system having between 2-11 cropping cycles per year depending on the type of crop and whether it is a high or low input system (Drechsel, 2002), would be enough to accelerate biochar ageing. The aim of this study was to investigate the interactive effect of soil management practices and time as well as soil processes that potentially underpin the changing properties of rice husks and corn cob biochars exposed to soil management practices under varying climatic conditions for 12 months in urban vegetable production system in Tamale (Ghana) and Ouagadougou (Burkina Faso), respectively. Although biochar ageing has several operational definitions, in this study however, explanation by Mia et al. (2017) is adopted whereby biochar ageing is the weathering or changing of biochar properties brought about by multiple processes including oxidation, hydrolysis, hydration, leaching, freeze-thaw, wet-drying, mineralization and adsorption of dissolved organic compounds unto biochar surfaces.

## Materials and Methods

### *Feedstock collection, biochar production and preparation*

Corn cobs for biochar production were obtained from farms within the neighbourhood of the Soil Research Institute in Kumasi, Ghana while rice husks were collected from a commercial rice mill located in the Ashanti regional capital, Kumasi, Ghana. The feedstocks were air-dried to a moisture content of 10 % and thereafter charred at a temperature of approximately 500 °C in a slow pyrolysis reactor kiln at Soil Research Institute (SRI) Kwadaso, Kumasi, Ghana. The biochar production began by pre-heating the kiln to about 500 °C with waste wood from sawn timber pieces, and thereafter feeding the feedstocks into the charring chamber. After pyrolysis, the kiln was opened and the charred materials were scooped out into a wheel barrow, doused from flaming up with copious amount of water. The biochars were thereafter air-dried and then processed for further analysis and preparation for filling into litter-bags.

### Biochar characterization

#### *Chemical properties*

The fresh and the field aged litter bag biochar samples were analyzed for pH, EC, volatile matter, ash, fixed carbon, DOC, aromaticity, surface basicity and acidity, and ECEC. Specific surface area was determined only on fresh biochar samples. The pH was determined in triplicate in deionized water with a biochar to water ratio of 1:5 (w/v) after shaking for 1 h at 200 rpm (Singh et al., 2010). Electrical conductivity of the biochars was determined using a H198129 pH/conductivity/TDS meter (Hanna Instruments Inc., Woonsocket, RI, USA), using a biochar to water ratio of 1 g to 30 mL of deionized water. The proximate analysis of biochar samples including moisture, volatile matter, ash and fixed carbon contents were determined following ASTM standard methods D 1762-84 with modifications as outlined by Mukherjee et al. (2011). Biochar moisture content was determined as weight loss after drying in the muffle furnace at 105 °C for 2 hours. Volatile matter was determined at 850 °C for 6 minutes, instead of the 950 °C for 11 minutes as stated by ASTM standards D 1762-84 on the previous dried 105 °C samples and the percent weight loss recorded as the volatile matter content of the respective biochars. The modification was to allow for simplicity and replication (Mukherjee et al., 2011). Ash content was determined on the volatile matter samples at 750 °C for 6 hours and the ash content recorded as the ash weight over the 105 °C samples by 100. Fixed carbon was determined by difference. This was done by subtracting from hundred, the moisture content, volatile matter and the ash content and recorded in percentages. The elements C, H, and N were directly determined using a CHN analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) in an oxygen enriched helium atmosphere, with O determined by difference. These results were used to further calculate the O/C and H/C ratios of the biochars. Effective Cation exchange capacity of the biochars was determined by the Cobaltihexaminechloride (Cohex) method (Ciesielski et al., 1997) with some modifications. A 0.63 g of biochar was weighed and 25 mL of cohex solution added and shaken on a mechanical shaker for 1 hour and filtered using 0.45 µm filter paper. Extractable Ca, Mg, K and Na were determined by the ICP-OES (Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve, Germany). The treatment was repeated with deionized water to remove soluble salts and after accounting for the soluble salts, ECEC was estimated as sum of the basic cations. Biochar was weighed in triplicates for both extractants. Total macro nutrients (Ca, Mg, K, and P) of biochars and feedstocks were analyzed following modified procedures of Enders et al. (2012). Briefly, 0.4 g of biochars and their biomass samples were ashed at 500 °C for 8 hours in a muffle furnace and digested using microwave digestion method with the addition of 10 mL $HNO_3$ acid which is finally topped up to 20 mL by addition of 10 mL deionized water, filtered and measurements done. The elements were measured by an inductively coupled plasma-optical emission spectroscopy (ICP-OES, Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve, Germany).

Dissolved organic carbon (DOC) was determined sequentially by first extracting with 0.01 M $CaCl^2$ (1:25, w/v) herein after referred to as cold water extractable DOC (cDOC) for 1 h and then filtered through a 0.45 µm membrane filter after which cDOC concentration was read with a Dimatoc 2000 (DIMATEC Analysentechnik GmbH, Essen, Germany) by measuring non-purgeable organic carbon after acidification (pH 2) to remove inorganic carbon from the extracts. The aromaticity of the DOC extracted by this method referred to as Cold SUVA (cSUVA) was determined by using the specific UV absorbance at 254 nm wavelength with a Lambda 2 UV/Vis spectrometer (Perkin Elmer, Waltham, MA, USA). The specific UV absorbance at 254 nm of DOC of filtered extract, normalized for DOC, has been used as a surrogate of DOC aromaticity (Weishaar et al., 2003). Specific UV absorbance (SUVA) (L $mg^{-1}$ $m^{-1}$) values were calculated by dividing UV absorbance at 254 nm ($m^{-1}$) by DOC concentration (mg $L^{-1}$) (Weishaar et al., 2003). The residue remaining after cDOC extraction was then carefully rinsed back into its centrifuge tubes with 25 mL of deionized water and then warmed at 80 °C for 16hrs on a water bath following the procedure of Ghani et al. (2003). The hot water extractable DOC (hDOC) was determined as described for cold water extractable DOC (cDOC) and the hot water extractable DOC aromaticity (hSUVA) was measured as described earlier for cold water extractable DOC aromaticity (cSUVA). The Specific Brunauer Emmet Teller (BET) surface area was measured with a Coulter SA 3100 instrument using nitrogen adsorption at 77 K in liquid nitrogen. The BET equation (Brunauer et al., 1938) was then used to calculate the specific surface area of the sample. Prior to determination, the samples were out-gassed at 300 °C for 5 h, in accordance with ASTM Standard D4820-97 for powdered black carbon samples.

### Total surface acidity and basicity

Surface acidity of biochar (BC) was measured by ‘‘base adsorption”, whereas surface basicity was measured by ‘‘acid adsorption” (Boehm, 1994; Goertzen et al., 2010). A 0.4 g subsample of field aged biochar was weighed and 20 mL of either 0.05 N NaOH for surface acidity or 0.05 N HCl solution for surface basicity was added and shaken with an end-over-end shaker for 24 h at 200 rpm. The BC slurry was then vacuum-filtered with a 0.45μm cellulose paper to separate particles from filtrates. An aliquot of 5 mL of the NaOH filtrate was pipetted and acidified with 10 mL 0.05 N HCl solution to ensure complete neutralization of the base. The solution was back-titrated with 0.05 N NaOH against a phenolphthalein indicator and a glass electrode probe pH meter using a Metrohm 725 Dosimat (Metrohm AG, Herisau, Switzerland). Carbon dioxide interference which could influence the back-titration process was eliminated by a constant stirring with a magnetic stirrer and degassing assured by bubbling with $N_2$ during titration. The titration was carried out to an end point pH of 7 and the titre volume recorded. For surface basicity an aliquot of 5 mL of the HCI filtrate was directly titrated with 0.05 N NaOH. The base or acid uptake of biochar was converted to the content of surface acidity or surface basicity (mmole $g^{-1}$), respectively.

The concentration of surface acidity (Sa) was calculated according to Goertzen et al. (2010) as:

Where

$$Csa = \frac{[B]*VB-([HCl]*VHCl-|NaOH|*VNaOH)*\frac{VB}{Va}}{w}*1000 \qquad (1)$$

Csa is the surface acidity (mmol $g^{-1}$),

VB is the volume of the reacting base added to the biochar (L),

[B] is the concentration of the reacting base added to the biochar (mol)

[HCl] is the concentration of the acid mixed with the aliquot (mol),

VHCI is the volume of the acid mixed with the aliquot (L)

[NaOH] is the concentration of the titrant (mol),

VNaOH is the volume of the titrant required to reach the endpoint (L),

Va is the volume of the aliquot taken from VB (L), and

W is the sample weight (g).

The concentration of the surface basicity (Sb) was calculated in the same way according to Goertzen et al. (2010) as:

### *Soil sampling and analyses*

$$Csb = \frac{[A]*VA-[NaOH]*VNaOH*\frac{VA}{Va}}{w}*1000 \qquad (2)$$

Soil was sampled from plots at both experimental sites at depths of 0-20 cm. The soils were analyzed for pH, total carbon, total nitrogen, available P, total P, ECEC, exchangeable bases (Ca, Mg, K and Na) and Al, and particle size distribution. The pH of the soils were measured in 1:2.5 (soil: water ratio), total carbon and N were determined by dry combustion of ground samples using an Elementar Vario EL elemental analyser (Elementar Analysesysteme GmbH, Hanau, Germany). Determination of ECEC and exchangeable bases occurred by percolating 2.5 g soil with 100 mL 1 M ammonium chloride and basic cations were measured with an ICP-OES (Ciros CCD, SPECTRO Analytical Instruments GmbH, Kleve, Germany). Available P was determined by using Bray P 1 solution extract (Bray and Kurtz, 1945) and total P by microwave assisted digestion with $HNO^3$. Particle size distribution was measured after soil organic carbon (SOC) removal with the addition of $H_2O_2$. Particle sizes were then measured by laser diffraction using an Analysette 22MicroTec plus with a wet dispersion unit (Fritsch GmbH, Idar-Oberstein, Germany). Before the soil samples were added, 5 mL $Na_4P_2O_7 \cdot 10H_2O$ (0.1%) and one drop Dusazin 901 were pipetted into the water in the measuring chamber.

### *Climatic data*

Climatic data were obtained from a weather station at the experimental sites which recorded values at 20 min intervals. The data included temperature and precipitation. Average daily temperature at the Tamale site was 28.4 °C and a total precipitation of 856 mm was recorded for the 6 months experimental period. For the 12 months period, average daily temperature was 28.7 °C with a total precipitation of 904 mm; meaning over 95 % of the rainfall was in the first 6 months period with just 49 mm of precipitation for the last 6 months. During the first 6 dry season months, a total irrigation of 718 mm was applied to treatment plots, while the last 6 months received a total irrigation water of 847 mm. At the Ouagadougou site, average temperature for the first 6 months was 28.6 °C with 27.6 °C recorded for the entire 12 months period. Total precipitation recorded for the first 6 months period was 730 mm and together with the entire 12 months period recording 882 mm indicating that only 152 mm of rains, representing 17.2 %, were recorded in the second half of the exposure period. A summary of average climatic data for both experimental sites are presented in Figure 1. At the Ouagadougou site, treatment plots were irrigated with 527 mm of water during the first 6 months and 926 mm during the second 6 months.

### *Experimental procedure*

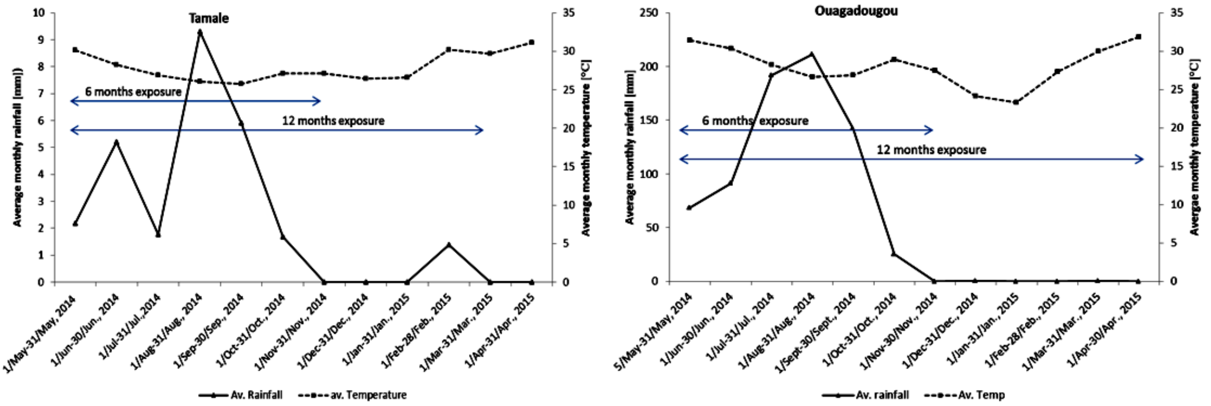

Figure 1: Average monthly rainfall and temperature for Tamale and Ouagadougou experimental sites within the period of exposure of litter bags with rice husk and corn cob biochars buried at 20 cm depth for periods of 6 and 12 months for the respective fields

For the ageing experiment, 10 g of rice husk (RHB) or corn cob (CCB) sieved to particle size range of 200-2000 µm were weighed into nylon mesh bags of mesh size 100 µm and 1.5 cm thick. The corn cob litter bags were buried at the Ouagadougou site (12°24′16N, 1°28′40W) at 20 cm depth on plots from 5 May 2014 to 4 April 2015 for 12 months exposure period with 6 months sampling done on 5 November, 2014. Litter bag technique was adopted for this ageing study because decomposition of the biochars was supposed to be monitored. However, this was not feasible as some replicates were later found damaged and litter contents lost due to manual tilling of the field with hoe. At the Tamale site (9°28′29N, 0°50′53W), rice husk biochar litter bags were buried on 14 May, 2014 to 12 March, 2015 for 12 months at 20 cm depth and 6 months RHB meshes retrieved on 5 November, 2014. The two biochars selected for use in the ageing experiment in each site was based on the availability of these feedstocks predetermined through a survey of these two sites. In Tamale, the predominant feedstock was rice husk whilst corn cobs abound in Ouagadougou in proximity to the experimental site. In addition, the decision not to have both biochars applied in each field was for the avoidance of contamination as a result of the installation of certain sensitive equipment and measurements which were ongoing simultaneously. In Tamale, the greater part of the 6 months period was during the dry season with latter stages experiencing some rains. Litter bags exposed over 12 months received earlier rains with latter stages being the dry season (Figure 1). Rainfall patterns for both sites during the experimental period are presented in Figure 1. The climate in the Ouagadougou site was similar to that of Tamale since both locations belong to the drier parts of sub-Saharan West Africa in which unimodal rains typically last from May to September. During the experimental periods in both cities, the Tamale site had 7 cropping cycles for the 12 months periods comprising maize (*Zea mays*), Lettuce (*Lactuca sativa* L.), Cabbage (*Brassica oleracea* L.), Amaranth (*Amranthus cruentus*), Lettuce (*Lactuca sativa* L.), Amaranth (*Amranthus cruentus*) and Ayoyo (*Corchorus olitoriuos* L.), in that order (Kyei and Manka, 2018). Biochar in litter bags retrieved at the 6 months period had maize (*Zea mays*), Lettuce (*Lactuca sativa* L.) and Cabbage (*Brassica oleracea* L.). In Ouagadougou, similar cropping cycles as for Tamale was adopted within the 12 months period with the exception of maize (*Zea mays*) and Ayoyo (*Corchorus olitoriuos* L.) which were not cultivated (Manka et al., 2020). In this regard, the CCB litter bags buried on 5 May, 2014 and retrieved on 5 November, 2014 coincided with vegetables such as Lettuce (*Lactuca sativa* L.), Cabbage (*Brassica oleracea* L.) and Amaranth (*Amranthus cruentus*). The total number of biochar-filled litter bags buried at each site on treatment plots was 24, comprising 3 treatments, 4 blocks as replicates and 2 sampling periods (6 and 12 months). The treatments consisted of control (no fertilization but watering was done as for all other treatments), farmers' practice (FP, which consisted of inorganic fertilization at the Tamale site and the application of largely organic with supplemental applications of inorganic fertilizers at the Ouagadougou site) and biochar application (20 tons ha$^{-1}$,)(rice husk for Tamae and corn cob for Ouagadougou site) (Häring et al., 2017). The details of fertilizer types and quantities and to which crops they were applied on in fields of the two cities were described in an earlier publication (Häring et al., 2017). Plots were hand irrigated over the 12 months period of the experiment with clean water totaling 958 L m$^{-2}$ and 1053 L m$^{-2}$ for Tamale and Ouagadougou, respectively. After 6 and 12 months of field exposure of biochar litter bags, one set of biochar litter bags were collected, cleaned of fine root hairs, stones and fungal mycelial; air-dried and processed for further analysis.

*Statistical Analysis*

Main effects and interactions of soil management practices and time of exposure effects on biochar properties were assessed using linear mixed model (GenStat 12th Edition, VSN International Ltd., Hemel Hempstead, UK) after normality tests of residuals were conducted using Shapiro-Wilks at $p < 0.05$. Where significant treatment differences existed, mean separation was done using Tukey's HSD test at $p < 0.05$.

## Results

*Biochar and soil characteristics*

The soil from the Ouagadougou experimental sites showed higher pH, bulk density, total organic carbon, C/N ratio, ECEC and available P than the Tamale soil. Tamale site recorded higher total P but less available P was observed. The higher content of soil organic carbon in the Ouagadougou soil also reflects the use of organic fertilization by farmers at the Ouagadougou site (Table 1). The rice husk biochar recorded higher ash contents than corn cob biochar (Table 2). The surface area was slightly higher in rice husk biochar than in corn cob biochar while ECEC was higher in corn cob biochar than in rice husk biochar. Corn cob biochar had higher pH than rice husk biochar with higher FC contents than in the rice husk biochar.

TABLE 1

Soil characteristics of experimental sites in Tamale (Ghana) and Ouagadougou (Burkina Faso)

| Site | pH | BD | Texture* | TOC | TN | CN | Ca | Mg | K | Na | Al | ECEC | TP | Bray I-P |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | g/cm$^3$ | | % | | | mmolc kg$^{-1}$ | | | | | | mg kg$^{-1}$ | |
| Tamale | 5.1 | 1.4 | Silt loam | 0.43 | 0.05 | 9.4 | 13.9 | 4.8 | 0.9 | 0.3 | 0.1 | 38.9 | 122.9 | 2.2 |
| Ouagadougou | 6.0 | 1.6 | Sandy loam | 0.57 | 0.06 | 10.4 | 28.5 | 4.6 | 0.7 | 2.3 | bd | 69.03 | 58 | 54.9 |

*texture based on USDA classification bd means below detection

TABLE 2

Biochar characteristics prior to application to the field. Analyses were done in triplicate except for BET surface area, total carbon and nitrogen which are based on single measurements. Values are means ± one standard error (in parenthesis)

| Biochar | VM | Ash | FC | pH | EC | ECEC | Surface area | Sa | TC | T N | CN | O/C | P | K | Ca | Mg |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | % | | | | µS cm$^{-1}$ | cmolc kg$^{-1}$ | m$^2$ g$^{-1}$ | mmolc g$^{-1}$ | % | | | | mg kg-1 | | | |
| Rice husk | 23.2 | 45.2 | 22 | 9.1 | 900 | 8.1 | 62.9 | 6.6 | 42.4 | 0.6 | 71 | 0.27 | 1406 | 3296 | 1572 | 949 |
| | (2.6) | (0.8) | (4.7) | (0.1) | (75) | (0.1) | | (0.1) | | | | | (19) | (3) | (124) | (24) |
| Corn cob | 19.6 | 18.5 | 56.5 | 10.3 | 2425 | 11.2 | 43.5 | 6.3 | 68.4 | 0.9 | 76 | 0.16 | 861 | 977 | 3513 | 1150 |
| | (1.3) | (0.6) | (2.2) | (0.1) | (79) | (0.4) | | (0.1) | | | | | (25) | (38) | (58) | (16) |

## Treatment effects on biochar bulk and surface properties

*Proximate properties of field aged rice husk and corn cob biochars*

There was no significant effect of soil management practices on proximate properties of aged rice husk biochar exposed at the Tamale site. However, volatile matter, ash and fixed carbon contents of field aged rice husk biochar changed significantly with time of exposure. For instance, volatile matter content decreased from approximately 23 % to approximately 18 % within the first 6 months, with no further changes thereafter (Figure 2, Table 3). Conversely, both ash and fixed carbon content of rice husk biochar increased with time of exposure (Figure 2c and 2e). The ash content of field aged rice husk biochar was significantly ($P < 0.05$) higher at 12 months compared to 6 months field aged ones, however, the 12 months field aged rice husk biochar did not differ from the ash content at time 0 (Figure 2). Soil management practices did not significantly affect proximate properties of field aged corn cob biochar at the Ouagadougou site, similar to what was observed for the field aged rice husk

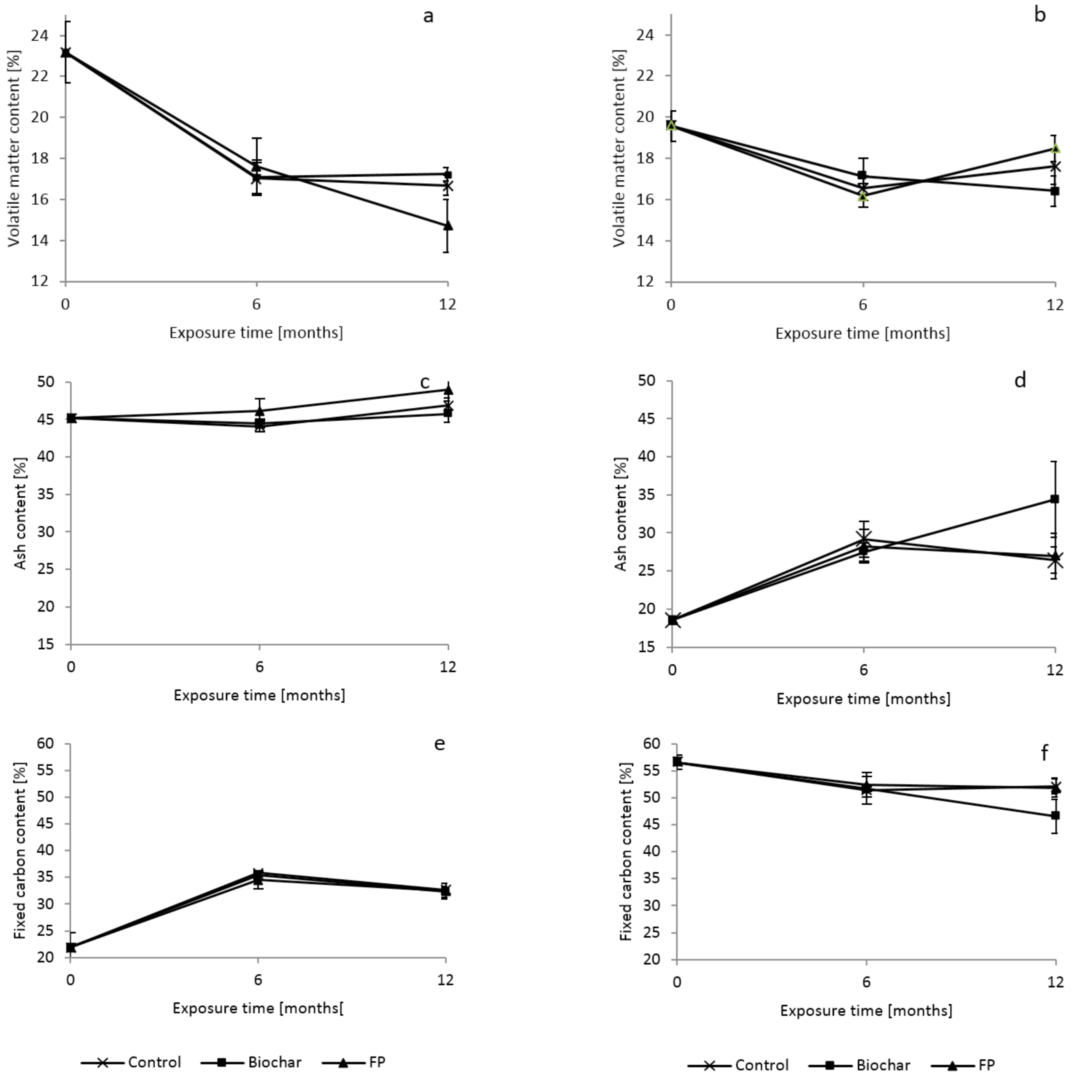

Figure 2: Effects of soil management practices and periods of exposure of buried litter bags on proximate values of rice husk biochar (a, c and e) at the Tamale (Ghana) site and corn cob biochar (b, d and f)- at the Ouagadougou (Burkina Faso) site. Periods 0 refer to the fresh biochar properties prior to burial of biochars at the respective sites. Values show means ± SE (n=4) for aged biochars and (n= 3) for time 0

TABLE 3
Two-way ANOVA for categorical factors of treatments, time and their interactions for pH, effective cation exchange capacity (ECEC), surface acidity (Sa), surface basicity (Sb), volatile matter, ash, fixed carbon contents, dissolved organic carbon (DOC) extracted at room temperature (cDOC), DOC extracted at 80 °C (hDOC), specific UV absorption at 254 nm for cDOC (cSUVA) and for hDOC (hSUVA) for rice husk biochar in Tamale (Ghana) and corn cob biochar in Ouagadougou (Burkina Faso). Significant F values are in bold and followed by *,** and *** corresponding to $p < 0.05$, $p < 0.01$ and $p < 0.001$, respectively

| Site | Parameter | Treatment | Time | Treatment*Time |
|---|---|---|---|---|
| Tamale | pH | 1.28 ns | **361.95*** ** | 1.0 ns |
| | ECEC | 1.21 ns | **8.01** ** | 0.44 ns |
| | Sa | 1.98 ns | **0.32 ns** | 0.64 ns |
| | Sb | 0.36 ns | **0.55 ns** | 0.12 ns |
| | Volatile matter | 0.33 ns | **39.81*** ** | 0.70 ns |
| | Ash | 2.15 ns | **4.38* ** | 0.583 ns |
| | Fixed carbon | 0.08 ns | **66.67*** ** | 0.993 ns |
| | cDOC | 2.01 ns | **125.85*** ** | 0.77 ns |
| | hDOC | 1.74 ns | **12.47*** ** | 0.59 ns |
| | cSUVA | 0.45 ns | **370.46*** ** | 1.74 ns |
| | hSUVA | 2.73 ns | **91.93*** ** | 0.90 ns |
| Ouagadougou | pH | 1.26 ns | **967.64*** ** | 1.03 ns |
| | ECEC | 0.39 ns | **0.23 ns** | 0.34 ns |
| | Sa | 0.08 ns | **458.89*** ** | 0.42 ns |
| | Sb | 0.03 ns | **1546.69*** ** | 0.13 ns |
| | Volatile matter | 0.21 ns | **13.68*** ** | 1.18 ns |
| | Ash | 0.75 ns | **17.21*** ** | 1.29 ns |
| | Fixed carbon | 1.0 ns | **9.05** ** | 0.88 ns |
| | cDOC | 0.57 ns | **26.26*** ** | 0.17 ns |
| | hDOC | 0.90 ns | **12.03*** ** | 0.93 ns |
| | cSUVA | 1.10 ns | **89.49*** ** | 1.02 ns |
| | hSUVA | 0.18 ns | **225.22*** ** | 0.17 ns |

biochar. However, the volatile matter and the fixed carbon contents of field aged corn cob biochars decreased significantly while the ash contents significantly increased (Figure 2), only at 12 months. Volatile matter and fixed carbon contents of aged corn cob biochar were significantly reduced at 6 and 12 months but did not differ from each other (Figure 2).

### *Surface reactivity of field aged rice husk and corn cob biochars*

Soil management practices did not significantly (P > 0.05) affect any of the surface reactive properties of aged rice husk biochars at the Tamale site (Figure 3, Table 3), but time significantly affected pH and ECEC but not surface acidity (Sa) and surface basicity (Sb) of field aged rice husk biochars at the Tamale site (Figure 3, Table 3). The effect of time on ageing saw a sharp and significant decrease in pH of rice husk biochars at 6 months and remained unchanged at 12 months (Figure 3a) whilst, the ECEC of the aged rice husk biochars was significantly higher at 6 and 12 months exposure periods compared to time 0 (Figure 3c), but, the ECEC between 6 and 12 months were not significantly different.

At the Ouagadougou site, soil management practices did not significantly (P > 0.05) affect the measured surface reactive properties of

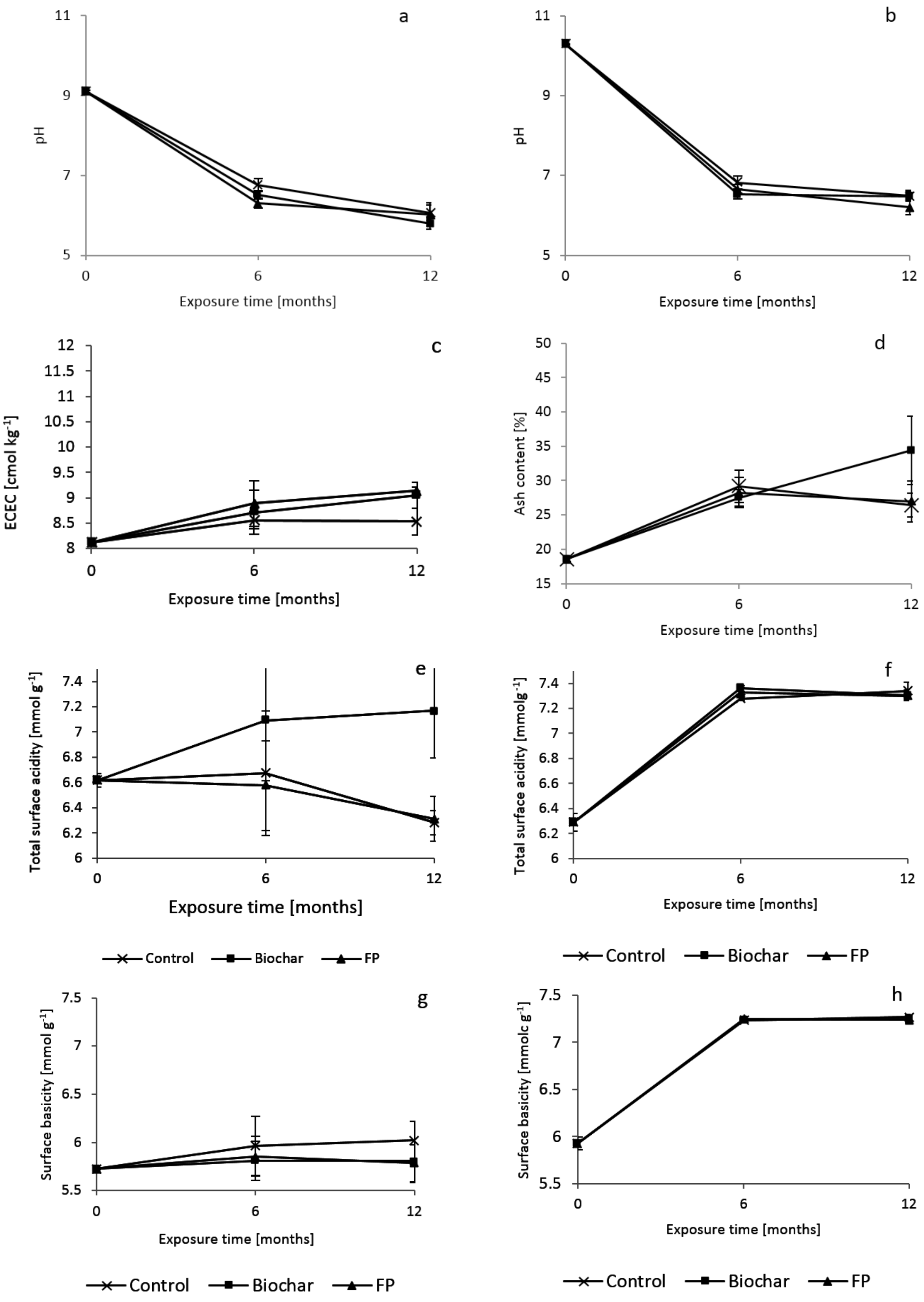

Figure 3 continued: Effects of soil management practices and periods of exposure of buried litter bags on surface reactivity properties of rice husk biochar (a, c, e and g) at the Tamale (Ghana) site and corn cob biochar (b, d and f and h) at the Ouagadougou (Burkina Faso) site. Periods 0 refer to the fresh biochar properties prior to burial of biochars at the respective sites. Values show means ± SE (n=4) for aged biochars and (n= 3) for time 0 field aged corn cob biochars which includes pH, ECEC, Sa and Sb. However, time significantly ($P < 0.05$) reduced pH, increased Sa and Sb but had no significant effect on the ECEC of field aged corn cob biochar (Table 3). The reduction in pH and the increase of surface acidity and surface basicity of corn cob biochar were largely observed during the first 6 months and remained unchanged at 12 months.

*Quantities of DOC and the SUVA aromaticities of aged biochars*

Soil management practices neither influenced cold water DOC (cDOC), hot water extracted DOC (hDOC), cold water extracted DOC aromaticity (cSUVA) nor hot water extracted DOC aromaticity (hSUVA) of field aged rice husk biochars from the Tamale site. However, time of exposure continuously remained the driver of the measured aged properties with significant ($P < 0.05$) effect on cDOC, hDOC, cSUVA and hSUVA of field aged rice husk biochar (Figures 4 and 5; Table 3). During the first 6 months of exposure, the cold and hot water extractable DOC contents of field aged rice husk biochars increased significantly compared to the DOC contents extracted at time 0 (Figure 4a and 4c). The cold water extracted DOCs (cDOC) content in the 6 month aged rice husk biochar was 290.8 mg DOC $kg^{-1}$ and 274.3 mg DOC $kg^{-1}$ in the 12 months field aged rice husk biochar. The cold water extracted DOCs (cDOC) contents in the above respective exposure periods represents an increase of 153% and 139% for 6 and 12 months exposure periods compared to cDOC content of 115.0 mg $kg^{-1}$ at time zero.

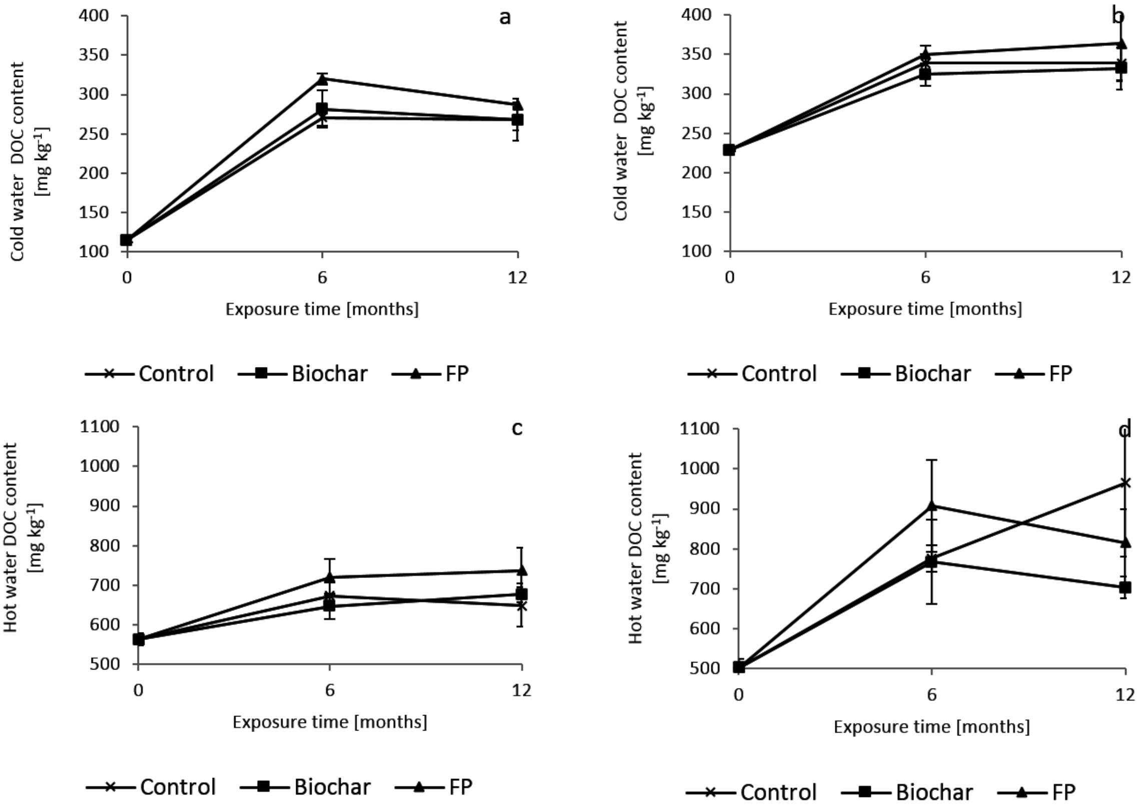

Figure 4: Effects of soil management practices and periods of exposure of buried litter bags on dissolved organic carbon contents on surfaces of buried rice husk biochar (a, c and e) at the Tamale (Ghana) site and corn cob biochar (b, d and f) at the Ouagadougou (Burkina Faso). Periods 0 refer to the fresh biochar properties prior to burial of biochars at the respective sites. Values show means ± SE (n=4) for aged biochars and (n= 3) for time 0

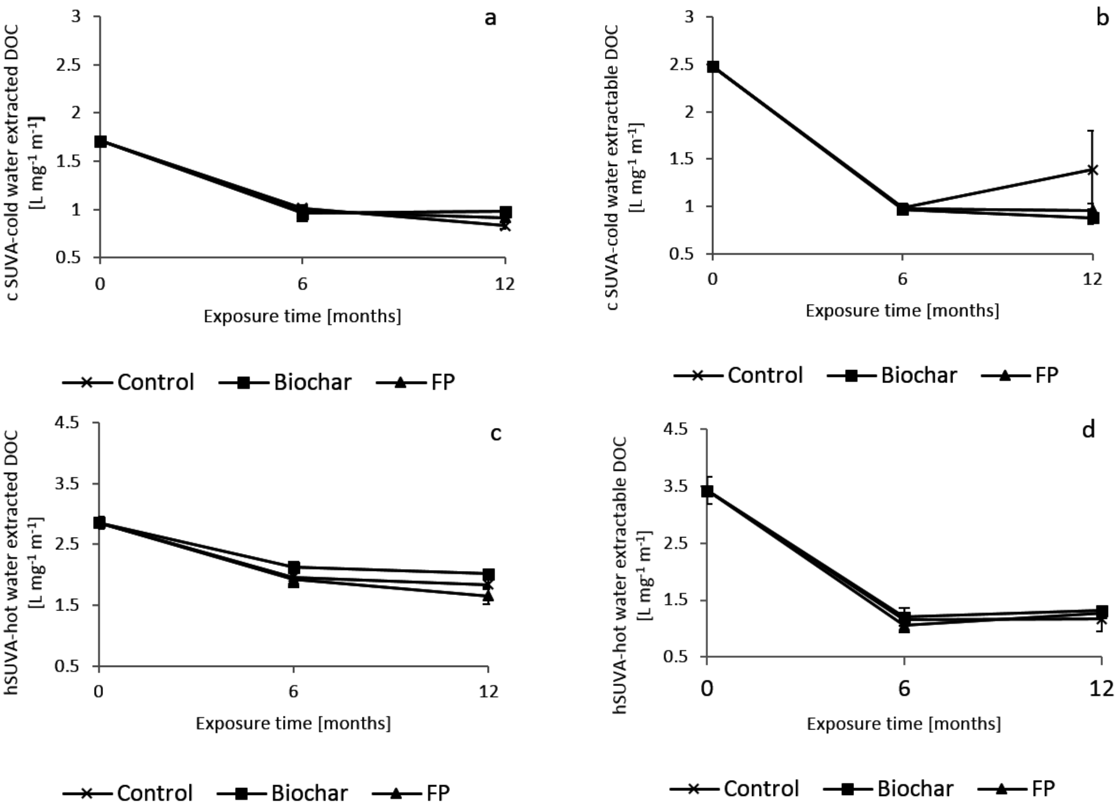

Figure 5: Effects of soil management practices and periods of exposure of buried litter bags on dissolved organic carbon contents and their aromaticities measured at specific ultraviolet absorbance-254 nm wavelength (SUVA254) for sequentially extracted cold and hot water DOC contents on surfaces of aged rice husk biochar (a, c and e) at the Tamale (Ghana) site and corn cob biochar (b, d and f) at the Ouagadougou (Burkina Faso) site. Periods 0 refer to the fresh biochar properties prior to burial of biochars at the respective sites. Values show means ± SE (n=4) for aged biochars and (n= 3) for time 0

Furthermore, there was a decline of 16.5 mg DOC $kg^{-1}$ in cDOC in the 12 months aged rice husk biochar compared to the 6 months aged rice husk biochar representing a minus 14.5 %. The hDOC contents of field aged rice husk biochar increased by 21 % on average across both exposure periods compared to the initial hDOC content of fresh rice husk biochar. Time of exposure significantly ($P < 0.05$) increased the DOC aromaticity (SUVA) of the field aged rice husk biochar (Figure 4). The SUVA values for both cold and hot water extracted DOCs of field aged rice husk biochar saw declines from time 0 to 6 months, but remained same between 6 and 12 months (Figure 4). The SUVA values of hot water extracted DOC (hDOCs) were higher than cold water extracted DOC (cDOC) by 1.149 L $mg^{-1}$ $m^{-1}$ at time 0. Similarly, the hot water extracted DOC (hSUVA) of field aged rice husk biochars at 6 months recorded 0.147 L $mg^{-1}$ $m^{-1}$ hSUVA higher than its cold water extracted DOC (cSUVA) counterpart of the same period, and 0.96 L $mg^{-1}$ $m^{-1}$ hSUVA value higher than its cold water extracted cSUVA counterpart at 12 months.

From the Ouagadougou experimental site, the DOC contents of the field aged corn cob biochars and their aromaticities represented by cDOC, hDOC, cSUVA and hSUVA were not significantly ($P > 0.05$) influenced by the interactive effect of time and soil management practices on one hand as well as the main effect of soil management practices. However, time of exposure significantly ($P < 0.05$)

increased cDOC and hDOC, but decreased cSUVA and hSUVA of field aged corn cob biochars (Table 3). For instance, the cold water extracted DOC (cDOC) contents of aged corn cob biochar significantly increased from 228.8 mg cDOC kg-1 in fresh corn cob biochar to 337.0 mg cDOC kg$^{-1}$ in field aged corn cob biochar at 6 months with further increase of 345.0 mg cDOC kg$^{-1}$ in field aged corn cob biochar for 12 months samples. These represent gross increases of 47% and 57% cDOC contents for the 6 and 12 months periods compared to that of time 0. Time of exposure significantly increased the hot water extracted DOC (hDOC) contents in the field aged corn cob biochars by 63.5 % compared to hDOC contents at time 0. Furthermore, time significantly affected the aromaticities (SUVA) of the extracted DOC contents in the field aged corn cob biochars (Table 3). The results also showed that the aromaticities of the DOC in the field aged corn cob biochars of both cold and hot water extracts significantly ($P < 0.05$) decreased between time 0 and 6 months but did not significantly decrease beyond 6 months of exposure (Figure 4).

## Discussion

### Effects of soil management practices and time of exposure on field aged biochar properties

*Proximate properties*

Soil management practices did not have any effect on the proximate properties of the biochars (Figures 2, 3, 4 and 5). Conversely, time of exposure significantly affected the volatile matter, ash and FC contents of both biochars exposed separately in these fields. Time of exposure significantly impacting on the proximate properties agrees with other studies (Cheng et al., 2008; Cheng and Lehmann, 2009; Hardy et al., 2017; Mukherjee et al., 2014).

Exposure time of 6 months of the rice husk biochar at the Tamale site led to a significant reduction in the volatile matter content and increases in the ash and fixed carbon (FC) contents. The decline in the volatile matter content is as a result of rapid degradation and decomposition of tarry compounds, volatile organic compounds and DOCs which are usually among the first dynamic processes when fresh biochars are introduced into soil (Joseph et al., 2010). The rapid decline in the volatile matter contents by the first 6 months was not systematically examined. However, it is possible that the initially high amount of labile volatile organic compounds stimulated microbial growth. Thus the decline in volatile organic carbon content with time may be due to microbial utilization of soluble C as energy source (Zimmerman, 2010). The addition of fresh labile carbon is known to favour the K-strategist microbes- that release extracellular enzymes in order to continuously breakdown complex biopolymers (Shen and Bartha, 1997). The decreased volatile matter contents of aged biochars at 6 months of exposure is consistent with literature (Mukherjee et al., 2014). The stalled decomposition of the volatile matter content of aged rice husk biochar beyond 6 months is possibly due to a resistance phase. This refractory phase reached by the volatile matter portion of the biochar has been attributed to a build-up of more refractory portions of the rice husk biochar (Bird et al., 1999) or has been attributed to the protection of the biochar surface by soil-mineral interaction (Bird et al., 2002; Hardy et al., 2017). The biochar-soil-mineral protection mechanism is probable since there was an observed increase in the ash content of aged rice husk biochar (Figure 2c) with further biochar surface-soil-mineral enhancement supported by the increased total surface acidity at 6 months (Figure 3e). Increased surface O-containing functional groups facilitating biochar-soil-mineral interaction has been observed with ageing (Hardy et al., 2017), which leads to increases in polarity of biochar surfaces (Criscuoli et al., 2014). The reactivity of organic molecule towards metal cations and soil minerals surfaces increases with polarity (Kleber et al., 2015). The increase in the FC contents of field aged rice husk biochar is closely related to a dilution effect resulting from increased surface adsorption of DOC and surface attraction of soil minerals and fine soil particles. This mechanism is confirmed by the continuous decline in volatile matter contents of field aged rice husk biochars (Figure 2a). The increase in FC contents of field aged rice husk biochars is in sharp contrast to the findings of Mukherjee et al. (2014). The possible explanation to the differences in FC trends is the lack of dilution effect in the work of Mukherjee and co where biochar ageing was done in containers screened to create a physical barrier between macro-fauna and other soil particles and mineral contamination. The volatile matter (VM) content of field aged corn cob biochar exposed at the Ouagadougou site also declined at 6 months similar to field aged rice husk biochars, contrary to findings of Mukherjee et al. (2014). Over all, the decline in VM content was rapid between 0 to 6 months of exposure and stalled at 12 months, similar to what was observed in rice husk biochar in the Tamale field. The reason for the rapid decline at the initial stages could be similar to the mechanisms explained earlier for field aged rice husk biochar which was attributed to decomposition of low molecular weight volatiles.

On the quantum of volatile matter loss, aged corn cob biochar lost 15.3 % volatile matter content at 6 months compared to 10.7 % at 12 months exposure, indicating reduced loss of volatile fractions of corn cob biochar with time. This is in sharp contrast to trends of volatile matter loss of 29.5% in 6 months compared to 30.2% loss in 12 months for field aged rice husk biochar from the Tamale site. Averaged over the 12 months period, the percentage loss in the volatile matter fractions was generally higher in aged rice husk biochar (28.1%) than in aged corn cob biochar (13.0%). This can be attributed to the interplay of several factors such as differences in biochar properties such as volatile matter contents, molar O/C ratios, soil and climate. It has been suggested that the volatile matter (VM) contents of biochars reflect the thermal alteration or carbonization of a biomass (Antal and Grønli, 2003). High VM contents in biochars have been shown to contain high levels of phenolic compounds compared to low volatile matter contents of similar biochars (Deenik et al., 2010). These phenolic compounds lead to higher microbial respiration (Saravanan et al., 2008). In an incubation study, Zimmerman (2010) found a strong correlation between the VM contents of different biochars and the percent mineralized C, which were positively correlated. Therefore, the significant loss of VM contents in the aged rice husk biochars compared to the aged corn cob biochars is a reflection of the initially higher VM contents in fresh rice husk biochar than in the fresh corn cob biochar. Moreover, the high lability of the rice husk biochars compared to the corn cob biochars can be related to differences in the molar O/C ratios which were found to be 0.27 for rice husk and 0.16 for corn cob biochars, respectively (Table 2). Spokas (2010) identified an inverse relationship between the molar O/C ratio and the mean residence time of biochars aged in soils estimated from several incubation experiments.

*Surface reactive properties*

The changes in biochar surface reactive properties including pH, ECEC, Sa and Sb have been used as indicators for ageing (Cheng et al., 2008, 2006; Hardy et al., 2017; Heitkötter and Marschner, 2015; Mukherjee et al., 2014). However, these properties showed varied quantum differences and directions as far as each biochar is concerned. The pH of both biochars declined with increasing exposure time which is consistent with other studies (Cheng and Lehmann, 2009; Cheng et al., 2006; Mukherjee et al., 2014). The decline in pH of aged biochar has been attributed to dissolution and leaching of basic compounds, such as carbonates, oxides or hydroxides (Yao et al., 2010). The pH decline in the aged rice husk biochar at 6 months was -2.6 units and -3.2 units at 12 months compared to the initial biochar pH. On the other hand, the level of pH decline in the field aged corn cob biochars were -3.6 units (6 months) and -3.9 units (12 months) compared to the initial biochar pH (Figure 3a and 3b). The generally high pH decline recorded in aged corn cob biochar compared to the aged rice husk biochars could be attributed to differences in the initial high volumes of average rainfall recorded for the Ougadougou site. From Figure 1, it is seen that litter bags buried at the Ouagadougou site had significantly much higher amount of average rainfall compared to the Tamale site, which potentially facilitated leaching of basic cations. It must be mentioned that the amounts of rainfall values presented in Figure 1 measures the average in view of the fact that there were quite a number of heavy rainfall events recorded intermittently largely at the beginning of biochar exposures than in the latter stages (Figure 1). The 12 months exposed biochars recorded a much less pH decline generally and much less for corn cob biochar than for rice husk biochar by difference between 6 months and 12 months (Figure 3a and 3b). The observation of lower pH decline in corn cob biochars than in rice husk biochars in the 12 months exposed biochars could be attributed to interplay of soil buffering capacity impacted by organic matter differences, fertilizer practices and total Ca amounts in these fields. In a study from these sites, Häring et al. (2017), reported a rapid pH decline in the fertilized soils of Tamale than in Ouagadougou, which the authors attributed to acidity-induced nitrification effect arising from inorganic fertilizer usage which was the prominent practice in the Tamale site compared to the Ouagadougou site where organic manure usage was high and applied along with inorganic fertilizers. High organic matter and Ca contents of the soils in Ouagadougou enhanced the pH buffering capacity of the soil and as well impacted on the corn cob biochars' low pH decline. In a long term study of 22 years investigating the impact of fertilization on pH and on the pH buffering capacity of calcareous soil, high pH buffering capacities of the soil was directly linked to high organic matter and calcium carbonate contents of the soil (Zhang et al., 2016). Furthermore, it was expected that the rapid pH decline in the aged corn cob biochars at 6 months would continue into the 12 months period and translate to increased ECEC but this was not the case and the lack of significant increases in the ECEC of aged corn cob biochars could be due to a halt in further surface oxidation as evidenced in total surface acidity remaining unchanged beyond 6 months of exposure (Figure 3f). On the other hand, the ECEC of aged rice husk biochars significantly increased after 6 months compared to the ECEC of the starting material. However, the ECEC of the aged rice husk biochars between 6 and 12 months were not significantly ($P > 0.05$) different (Figure 3c). The significant increases in ion exchange capacity (ECEC) of the aged rice husk biochars with time of exposure agree with others (Cheng et al., 2008; Cheng and Lehmann, 2009; Heitkötter and Marschner, 2015; Mukherjee et al., 2014). Higher ECEC of freshly produced biochars are known to correlate with the volatile matter content of fresh biochars (Mukherjee et al., 2011). The quantity of volatile matter in the aged rice husk biochar was much larger compared to that observed in aged corn cob biochar. This clearly indicates that the increased ECEC of aged rice husk biochar can be attributed to sorbed DOC on the rice husk biochar surfaces that potentially contributed to the increased ECEC through enhanced surface negative charge development. The role of organic matter and humic acids derived from aged biochars and their influence on surface charge development has been reported (Hiemstra et al., 2013). The high silt and clay contents of the Tamale site potentially contributed to the high ECEC of the aged RH biochars than in aged CC biochars from the Ouagadougou site. The role of soil separates such as clay and silt contents in surface negative charge development of aged rice husk biochar is a possible additional mechanism. Sokołowska (2019) reported increases of amount of Cu sorbed in a Haplic Luvisol with high clay and silt contents compared with the Haplic Podzol which had significantly low clay and silt contents. The enhanced Cu sorption by the presence of high amounts of clay was linked to the direct bonding of the outer d-electrons with the negative charges on these clay mineral surfaces. Furthermore, the potential of precipitated minerals on aged biochar surfaces contributing to the enhanced ECEC cannot be discounted (Joseph et al., 2010). The lack of significant increases in the ECEC of the aged corn cob biochar despite the overall high amounts of total DOC extracted could not be explained by this experimental set up.

### *DOC contents and DOC aromaticities dynamics*

Total amount of adsorbed DOCs extracted from aged biochars increased at 6 months and in some cases, declined slightly with further exposure at 12 months. The increased in quantities of extracted DOC in the first 6 months of biochar exposure compared to its initial DOC contents was rather surprising as the DOC contents of these biochars were expected to decline at the first 6 months of exposure, at least by percolating water from irrigation and rains as greater part of the first exposure periods of both biochars saw a significant amount of rains (Figure 1). It has been suggested that the first reactions that fresh biochar would undergo when added to soil is the dissolution of soluble salts and organic compounds present in the biochar (Joseph et al., 2010), and more so under moist soil condition and rain event (Shinogi et al., 2003). The increased in quantity of extracted DOC contents during the first 6 months of exposure to soil management practices can be related to a multiplicity of factors which includes biochar quality (VM contents and surface area), gradual biodegradation by microbes and synthesis and sorption of microbially-derived organic matter and root exudates from various crops cultivated during this period. The degradation of volatile organic compounds which forms an integral part of the volatile matter fractions after fresh biochar addition to soil is suggested to degrade rapidly along with tarry compounds that initially filled voids within the biochar structures. This mechanism along with rice husk biochar's high specific surface area (Table 2), would help accelerate the adsorption of DOCs. The lack of further increases in the quantity of extracted cold and hot DOC contents from aged rice husk biochar beyond 6 months could be related to decreases in the quantities of VM contents of the age rice husk biochar (Figure 2a) that could serve as a potential sources of leached DOC in itself, on one hand, or a complete blockage of available pores through earlier increased microbial degradation and subsequent sorption of microbially-derived surface organic matter coatings (Mia et al., 2017), on the other hand. It is suggested that volatile matter contents of biochars are directly related to the amount of DOC leached over time (Mukherjee and Zimmermann, 2013). With VM contents decreasing with time (Figure 2a), the source of DOC contents of aged rice husk biochar at 6 months is assumed to have come from both adsorbed organic matter and from tarry condensates that were occluded from microbial decomposition in the pores of these biochars. The lack of increased amounts of extracted DOC beyond 12 months of exposure of rice husk biochar is related to lack of available pores and available surfaces of the biochar that could accelerate further sorption of DOC. The low quantities of extracted DOC contents obtained from 6 months aged corn cob biochar from the Ouagadougou site could be related to high amounts of rains recorded within the first 6 months. The evidence of 10 folds magnitude of rainfall in Ouagadougou compared to Tamale is shown in Figure 1. The DOC contents in the hot water extracts of aged corn cob biochars were 2 -to- 3- times higher than in the cold water extracts of the same biochar material which agrees with earlier findings (Chantigny et al., 2010; Gregorich et al., 2003; Zhao et al., 2013). The increases in DOC contents in hot water extracts compared with cold water extracts may be attributed to hot water-initiated depolymerization of soil organic matter, a decrease in the viscosity of soil humus at high temperatures, physical state changes of soil organic matter, and killed microbes (Chantigny et al., 2010). The DOC contents of cold and hot water extracts obtained from aged corn cob biochars were 2- to 3-times higher than in those obtained from aged rice husk biochars. This could be related to the high organic carbon contents of the soil at the Ouagadougou site (Table 1). The high organic carbon content of this soil is linked to the local practice of incorporation of high amount of organic manure in Ouagadougou compared to the dominant practice of application of inorganic fertilizer with little or no organic manure additions- a practice adopted for the farmers' practice plots in Tamale (Häring et al., 2017). The control plots hot water extracts showed consistently greater amount of DOC than the biochar-applied and farmers' practice plots in the Ouagadougou site where corn cob biochar was exposed (Figure 4d). Aromaticities of the DOC contents assessed by SUVA-254 nm of cold and hot water extracts generally recorded lower values with increasing exposure time with SUVA values between 6 and 12 months remaining same but significantly lower than the SUVA values at time 0. These indicate that the increasing sorption of DOC contents from the extracts of cold and hot water as seen in Figure 4 for 6 and 12 months periods of exposure is mainly as a result of sorption of smaller and less-aromatic molecules or moieties, since SUVA-254 nm absorption has been reported to negatively correlate with biodegradability of organic matter (Kalbitz et al., 2003; Saadi et al., 2006). Furthermore, the similar amounts of cSUVA values measured for aged rice husk and corn cob biochars at 6 and 12 months exposure periods is an indication of similar DOC components extracted by cold water between these two time periods. It has been shown that SUVA-254 nm value has a direct strong correlation with the hydrophobic organic fraction of DOM (Spencer et al., 2012) with Weishaar et al.(2003) positing its usefulness as a proxy for DOM aromatic contents and Chowdhury (2013) buttressing the usefulness of this index as a direct measure of molecular weight of DOM. Generally, the amount of lost aromatic contents in the DOC extracted in the aged rice husk biochar for the two time periods was lower than the amount of lost aromatic contents recorded in the aged corn cob biochar as shown in Figure 5. This indicates a possible protection of degradation of more aromatic compounds in aged rice husk biochar possibly through the soil-mineral-biochar complex as potentially explained by the high ash contents of aged rice husk biochar compared to lower ash contents recorded for aged corn cob biochar (Figure 2c and 2d). In addition, the quantum of hot SUVA values recorded for aged rice husk biochar at 6 and 12 months saw a dip of 0.94 and 1.21 L mg$^{-1}$ m$^{-1}$, respectively, compared to a much greater dip of 2.4 and 2.2 L mg$^{-1}$ m$^{-1}$ over the same period for aged corn cob biochar. This means there was a significant decline in the aromaticity of the DOC contents in the hot water extract from aged corn cob compared to the aromatic contents of aged rich husk biochar. This level of recalcitrance shown by aged rice husk biochar can be attributed to interplay of different soil processes acting at different intensities and scales, however, the possibility of protection of exposed biochar from microbial degradation of more aromatic compounds in aged rice husk biochar through soil-mineral-biochar- organic matter complexes cannot be ruled out as high ash contents of aged rice husk biochar compared to lower ash contents of aged corn cob biochar were observed (Figure 2c and 2d). However, the strict interpretation of SUVA values based on the DOC contents extracted may not be sufficient as other confounding factors such as extractant pH and species of molecules and elements such as NO3- and Ferric iron (Weishaar et al., 2003) potentially influence SUVA-254 nm readings.

## Conclusion

The results of the study indicated that there was not significant interaction effect of time of exposure and soil management practices on measured aged biochar properties. However, time and not soil management practices in these two sites accelerated ageing of the biochars. Time significantly affected all measured ageing properties of rice husk except surface acidity (Sa) and Surface basicity (Sb) and for corn cob all but ECEC was not affected. These ageing effect was largely observed at 6 months of exposure; a confirmation of the recalcitrance of these biochars with short to mediumterm labilities. The reduction in pH of aged biochars is largely attributed to the amount of rainfall with potential to leach basic cations and soluble ash components of the biochars. Increased ECEC of rice husk biochars in the short-term (6 months period) is related to DOC contents and surface precipitation of minerals. With time, adsorption of and maintenance of more-aromatic DOCs on surfaces of rice husk biochars than on corn cob biochars was observed and attributed to organo-mineral complexation of rice husk biochar protecting the biochar against microbial decomposition coupled with possibly low rainfall recorded within the exposure period. The interaction of the high level of sorbed DOC contents and large quantities of ash contents recorded in rice husk biochar would mean longer periods of sequestration of rice husk biochar for the Tamale site than in corn cob biochar for the Ouagadougou site.

## Acknowledgements

We thank the German Federal Ministry of Education and Research (BMBF) and the German Federal Ministry for Economic Cooperation and Development (BMZ) for funding the research of the UrbanFoodPlus project under the GlobE-initiative (FKZ: 031A242-A,B). We also appreciate the competent assistance received from the following individuals : Ben Amoah (SRI-CSIR, Ghana), Heidiun Kerkhoff, Bettina Röhm, Sabine Fröhlich and Katja Gonschorek – Laboratory staff at Ruhr Universität, Bochum, Germany.

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