



## Short Communication

## Charcoal quality does not change over a century in a tropical agro-ecosystem

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## ABSTRACT

Charcoal stocks were determined in a chronosequence of soils which have been converted to agricultural land use by slash-and-burn up to 100 years ago. With time, opposite to our assumptions, the charcoal chemical quality, as measured by molecular markers for pyrogenic carbon, did not change and charcoal stocks did not show a clear decrease. Our results indicate that charcoal may resist chemical degradation even when exposed to intense weathering in a tropical climate.

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## 1. Introduction

Charcoal, also referred to as fire-derived or pyrogenic carbon (PyC), is a residue of incomplete combustion of biomass and is ubiquitous in soils, but loss processes and rates are still poorly understood (Preston and Schmidt, 2006). Up to now there are only a few studies investigating the long-term (i.e. decadal) fate of PyC in soils, and results are ambiguous. Short-term (up to 3.2 years) laboratory incubation experiments revealed that <2% of PyC produced at  $\geq 200$  °C was mineralized (Baldock and Smernik, 2002; Hamer et al., 2004; Bruun et al., 2008; Kuzyakov et al., 2009; Nguyen et al., 2010; Zimmerman, 2010). There are only two published long-term (100 years) field studies which observed loss of PyC in tropical soil by spectroscopy (Nguyen et al., 2008: 70% loss), or in a steppe soil by molecular marker measurements (Hammes et al., 2008: 25% loss), respectively. Nguyen et al. (2008) found increasing oxidation at the surface of manually isolated PyC pieces using X-ray photoelectron spectroscopy (XPS) in the tropical soil. However, qualitative changes of the finely distributed PyC in the bulk soil have not been investigated so far. The unique advantage of the molecular marker method over the previously used spectroscopic methods is to gain greater insight into changes in chemical quality over time of PyC in the bulk

material. For example, one of the molecular markers, B6CA, is particularly useful to estimate the degree of aromatic condensation in the samples (Hammes et al., 2008; Schneider et al., 2010). Indeed, qualitative changes in the bulk material, i.e. preferential accumulation of more condensed aromatic backbone of the PyC structures, were found for the steppe soils using the molecular marker method (Hammes et al., 2008). Here we applied the molecular marker method used in the steppe soil (Hammes et al., 2008) to the tropical soil samples (Nguyen et al., 2008) to follow the PyC in a soil chronosequence (2, 3, 5, 20, 30, 45, 80, 100 years since the last PyC deposition). We hypothesized that we would find a selective enrichment of more condensed (and thus more chemically stable) forms of PyC in the bulk soil.

## 2. Materials and methods

Following a space-for-time approach, the soil samples (Humic Nitosol, FAO-UNESCO, 1998) were collected in an area where forests were converted from forest to agricultural land by slash-and-burn practice up to 100 years ago. Soils were under permanent cultivation with no new fires since the conversion. The area is located in South Nandi (00°04'30" N, 34°58'34" E), western Kenya with altitudes ranging from 1600 to 1800 m above sea level, mean annual temperature of about 19 °C and mean annual precipitation of about 2000 mm (Nguyen et al., 2008). Nine 200 cm<sup>3</sup> core subsamples from the upper 0.1 m of soil were sampled in each field

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and then combined into one composite soil sample (Solomon et al., 2007; Kimetu et al., 2008; Kinyangi, 2008; Nguyen et al., 2008). This chronosequence opened the unique possibility to investigate changes in bulk PyC over 100 years in a space-for-time approach. As a trade-off we had to accept the associated uncertainties, including the varying (and to us unknown) amounts of PyC produced during the different fires, and possible deposition of PyC from near-by burns.

In this study we used benzene polycarboxylic acids (BPCA) molecular markers for pyrogenic carbon (PyC) assessment (Glaser et al., 1998; Brodowski et al., 2005; Schneider et al., 2010). Briefly, samples ( $n = 3$ ) were pretreated with 4M trifluoro acetic acid (4 h, 105 °C), followed by conversion of PyC into BPCA by nitric acid oxidation (8 h, 170 °C). The digest was purified and subsequently derivatized and analyzed on a gas chromatograph equipped with flame ionization detector. The acids with 3, 4, 5, and 6 carboxyl functions (B3CA, B4CA, B5CA, and B6CA, respectively) were identified and summed up to represent the amount of pyrogenic molecular markers derived from the material. Data was normalized to the BPCA-C content measured in a reference soil (Table S1) (Schneider et al., 2010).

### 3. Results and discussion

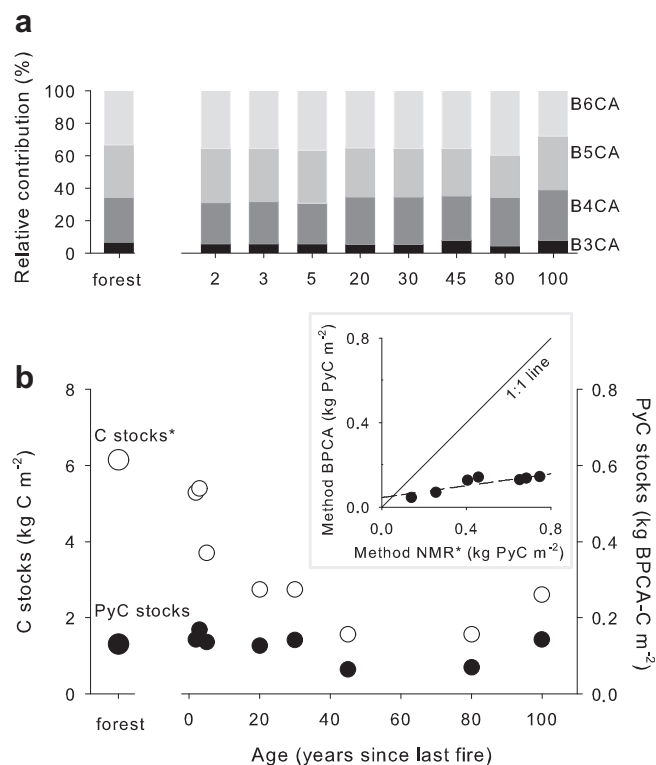
#### 3.1. Quality of PyC

The most striking feature of our data is that the proportions of B6CA remained constant over a century at about 35% (Fig. 1a), which is in contrast to the previous observation of Hammes et al. (2008) for a steppe soil. There, decreasing PyC stocks ( $-25\%$ ) over a century had been accompanied by a preferential accumulation of the highly condensed, aromatic backbone of PyC (Hammes et al., 2008), indicated by increasing proportions of B6CA.

It seems that chemical changes, such as increasing oxidation, are limited to the surface of PyC particles, whereas the more protected PyC particle inside remained largely unaffected by oxidation processes (Nguyen et al., 2008). There are indications that coarser PyC particles after deposition are initially degraded to finer particles (Bird et al., 1999) and then subsequently protected from further degradation by interaction with soil minerals (Nguyen et al., 2008), which could explain the absence of chemical changes in the finely distributed bulk PyC, which was investigated here.

#### 3.2. Quantity of PyC

Both organic carbon (OC) and PyC had been present in the forest before land conversion (labeled as “forest” in Fig. 1), and the last PyC input happened when land was converted to agriculture using slash-and-burn (Nguyen et al., 2008). After conversion and with increasing time of agricultural use, OC stocks decreased rapidly (Fig. 1b), an observation typically made for such land use changes (e.g. Brady and Weil, 2001). For PyC stocks quantified by BPCA, no clear trends could be observed. If there were trends with time, they were obscured by the large spatial heterogeneity of PyC stocks. To test our results for plausibility, we compared them to earlier results by Nguyen et al. (2008), who measured PyC stocks on identical samples but with a different method (nuclear magnetic resonance spectroscopy combined with a molecular mixing model, NMR-MMM). As a result, data of both methods correlate well ( $r^2 = 0.80$ , insert Fig. 1b), and show the typical systematic offset, with BPCA values being approximately 1/5 of those measured by NMR-MMM. The systematic offset reflects the fundamentally different principles of the two methods. The BPCA method measures molecular markers released upon wet chemical oxidation as a representative subfraction of PyC, while NMR-



**Fig. 1.** The PyC quality (a) and quantity of bulk soil organic carbon (SOC) and the fire-derived PyC subfraction (b) in soil chronosequence samples with increasing time of conversion from forest to agricultural land by slash-and-burn. The “forest” sample represented the pre-existing OC and PyC stocks in the forest soil. a) Relative contributions of BPCA marker molecules (B3CA: hemimellitic and trimellitic acid; B4CA: prehnitic, mellophanic and pyromellitic acid, B5CA: pentacarboxylic acid; B6CA: mellitic acid). B6CA, a measure for the degree of condensation in PyC, did not change over the observation period. ( $n = 3$ ; 45 years sample  $n = 1$ ) b) SOC (white circles, left scale) and PyC stocks, measured as benzene polycarboxylic acids carbon (BPCA-C) (black circles, right scale). Insert: comparison of PyC stocks measured by nuclear magnetic resonance spectroscopy with molecular mixing model (NMR-MMM; Nelson and Baldock, 2005) (Method NMR, x-axis) and BPCA molecular markers (Method BPCA, y-axis). Method BPCA yielded consistently lower numbers, but both methods showed a close linear relationship (dashed line,  $r^2 = 0.80$ ,  $y = 0.045 + 0.14 \cdot x$ ,  $p = 0.05$ ). Standard errors for analytical replicates ( $n = 3$ ) are smaller than symbol size. \*Organic carbon stocks and NMR-MMM data taken from Nguyen et al. (2008).

MMM measures the contribution of aryl C to the NMR spectrum and from that calculates the content of PyC (Nelson and Baldock, 2005; Hammes et al., 2007; Kaal et al., 2008).

### 4. Conclusions

Over a century of weathering in a tropical climate,

- The space-for-time approach used in this study showed that OC stocks clearly decreased, but total PyC stocks did not.
- We found no indications for a changing chemical quality of the bulk PyC, although we expected the decomposition of less stable PyC fractions to be accompanied by a relative enrichment of highly condensed aromatic PyC fractions.

Interestingly, we applied the molecular marker method (BPCA) to bulk soil samples and our data on quantity and quality of PyC is consistent with those results obtained by NMR-spectroscopy for quantification of PyC and X-ray photoelectron spectroscopy for chemical properties of hand-picked ground and un-ground char particles.

## Author contributions

The study was proposed jointly by all authors. JL provided sample material, additional data and information about the sampling sites. The experiments and data analysis were carried out by MPWS. Paper writing was completed by MPWS under supervision of MWIS, with contributions from JL.

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## Appendix. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.soilbio.2011.05.020.

## References

- Baldock, J.A., Smernik, R.J., 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red Pine) wood. *Organic Geochemistry* 33, 1093–1109.
- Bird, M.I., Moyo, C., Veenendaal, E.M., Lloyd, J., Frost, P., 1999. Stability of elemental carbon in a savanna soil. *Global Biogeochemical Cycles* 13, 923–932. doi:10.1029/1999GB900067.
- Brady, N., Weil, R., 2001. Soil organic matter (ch. 12). *The Nature and Properties of Soils*. Prentice Hall, Upper Saddle River, NJ. 960.
- Brodowski, S., Rodionov, A., Haumaier, L., Glaser, B., Amelung, W., 2005. Revised black carbon assessment using benzene polycarboxylic acids. *Organic Geochemistry* 36, 1299–1310.
- Bruun, S., Jensen, E.S., Jensen, L.S., 2008. Microbial mineralization and assimilation of black carbon: dependency on degree of thermal alteration. *Organic Geochemistry* 39, 839–845.
- FAO-UNESCO, 1998. ISSS, ISRIC, FAO. World Reference Base for Soil Resources. FAO, Rome. World Soil Resources Reports 84.
- Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as specific markers. *Organic Geochemistry* 29, 811–819.
- Hamer, U., Marschner, B., Brodowski, S., Amelung, W., 2004. Interactive priming of black carbon and glucose mineralisation. *Organic Geochemistry* 35, 823–830.
- Hammes, K., Schmidt, M.W.I., Smernik, R.J., Currie, L.A., Ball, W.P., Nguyen, T.H., Louchouart, P., Houel, S., Gustafsson, O., Elmquist, M., Cornelissen, G., Skjemstad, J.O., Masiello, C.A., Song, J., Peng, P., Mitra, S., Dunn, J.C., Hatcher, P.G., Hockaday, W.C., Smith, D.M., Hartkopf-Froeder, C., Boehmer, A., Luer, B., Huebert, B.J., Amelung, W., Brodowski, S., Huang, L., Zhang, W., Gschwend, P.M., Flores-Cervantes, D.X., Largeau, C., Rouzaud, J.N., Rumpel, C., Guggenberger, G., Kaiser, K., Rodionov, A., Gonzalez-Vila, F.J., Gonzalez-Perez, J.A., de la Rosa, J.M., Manning, D.A.C., Lopez-Capel, E., Ding, L., 2007. Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochemical Cycles* 21. doi:10.1029/2006GB002914.
- Hammes, K., Torn, M.S., Lapenas, A.G., Schmidt, M.W.I., 2008. Centennial black carbon turnover observed in a Russian steppe soil. *Biogeosciences* 5, 1339–1350.
- Kaal, J., Brodowski, S., Baldock, J.A., Nierop, K.G.J., Cortizas, A.M., 2008. Characterisation of aged black carbon using pyrolysis-GC/MS, thermally assisted hydrolysis and methylation (THM), direct and cross-polarisation C-13 nuclear magnetic resonance (DP/CP NMR) and the benzene polycarboxylic acid (BPCA) method. *Organic Geochemistry* 39, 1415–1426.
- Kimetu, J.M., Lehmann, J., Ngoze, S.O., Mugendi, D.N., Kinyangi, J.M., Riha, S., Verchot, L., Recha, J.W., Pell, A.N., 2008. Reversibility of soil productivity decline with organic matter of differing quality along a degradation gradient. *Ecosystems* 11, 726–739.
- Kinyangi, J.M., Soil degradation, thresholds and dynamics of long-term cultivation: from landscape biogeochemistry to nanoscale biogeocomplexity.(2008), Ph.D. Thesis, p. 161. Department of Crop and Soil Sciences, Cornell University.
- Kuz'yakov, Y., Subbotina, I., Chen, H.Q., Bogomolova, I., Xu, X.L., 2009. Black carbon decomposition and incorporation into soil microbial biomass estimated by C-14 labeling. *Soil Biology & Biochemistry* 41, 210–219.
- Nelson, P.N., Baldock, J.A., 2005. Estimating the molecular composition of a diverse range of natural organic materials from solid-state C-13 NMR and elemental analyses. *Biogeochemistry* 72, 1–34.
- Nguyen, B.T., Lehmann, J., Kinyangi, J., Smernik, R., Riha, S.J., Engelhard, M.H., 2008. Long-term black carbon dynamics in cultivated soil. *Biogeochemistry* 89, 295–308.
- Nguyen, B.T., Lehmann, J., Hockaday, W.C., Joseph, S., Masiello, C.A., 2010. Temperature sensitivity of black carbon decomposition and oxidation. *Environmental Science & Technology* 44, 3324–3331.
- Preston, C.M., Schmidt, M.W.I., 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences* 3, 397–420.
- Schneider, M.P.W., Hilf, M., Vogt, U.F., Schmidt, M.W.I., 2010. The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200 °C and 1000 °C. *Organic Geochemistry* 41, 1082–1088.
- Solomon, D., Lehmann, J., Kinyangi, J., Amelung, W., Lobe, I., Pell, A., Riha, S., Ngoze, S., Verchot, L., Mbugua, D., Skjemstad, J., Schafer, T., 2007. Long-term impacts of anthropogenic perturbations on dynamics and speciation of organic carbon in tropical forest and subtropical grassland ecosystems. *Global Change Biology* 13, 511–530.
- Zimmerman, A.R., 2010. Abiotic and microbial oxidation of laboratory-produced black carbon (biochar). *Environmental Science & Technology* 44, 1295–1301.