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Permanence of soil applied biochar: Conclusions from the natural pyrogenic carbon cycle validate carbon sink accounting.

Johannes Meyer zu Drewer^{1,2}, Samuel Abiven³, Nikolas Hagemann¹, and Hans-Peter Schmidt⁴

¹Ithaka Institute for Carbon Strategies, Arbaz, Switzerland (schmidt@ithaka-institut.org)

²Ithaka Institut gGmbH, Goldbach, Germany (mzd@ithaka-institut.org)

³Ecole Normale Supérieure de Paris, Paris, France (abiven@biotite.ens.fr)

⁴Agroscope, Campus Reckenholz, Zürich, Switzerland (nikolas.hagemann@agroscope.admin.ch)

Biomass pyrolysis and a non-oxidative use of the produced biochar is widely acknowledged as a negative emission technology and part of Pyrogenic Carbon Capture and Storage (PyCCS). Biochar with a molar H/C ratio < 0.4, which is usually achieved by pyrolysis at 550°C or above, is highly persistent when applied to the soil. Still, the exact residence time remains subject to debate. Practical assessment tools and reliable models for carbon accounting are needed. Persistence of soil applied biochar is often assessed using soil incubation trials of rather short time horizons, lasting several month or years, with consecutive extrapolation of the observed degradation rate. Within such experiments, the decomposition rate of the biochar continues to decrease over time indicating that biochar consists of a broad range of carbonaceous compounds of different recalcitrance. Hydrogen pyrolysis, an analytical method used to determine the degree of aromatisation, suggests that 75% of the carbon in biochar with an overall H/C ratio <0.4 consists of *persistent aromatic carbon (PAC)*, which will persist after soil application for > 1000 years, (Bowring et al., 2022; Howell et al., 2022), independent of the soil type and climate. The remaining 25% of the biochar carbon (heteroaromatic, aliphatic, etc) are considered *semi-persistent carbon (SPC)*, presenting a mean residence time (MRT) in soil of 50 to 100 years, depending on soil type and climate. Based on this, up to 99% of the PyC loss quantified in an incubation trial may be attributed to the spectrum of SPC compounds, while the occurring PAC decay is very small and a neglectable loss in the context of carbon sink accounting. To validate the PAC residence time, data on long-term dynamics of the global, natural PyC cycle provides new insights. Natural PyC is produced from incomplete combustion in e.g. forest fires and is introduced to ecosystems globally at a scale of 0.114-0.383 Gt year⁻¹. Given the global deposits of natural PyC of 550-1,650 Gt a MRT of 1,440 to 14,500 years can be calculated (Bird et al., 2015; Santín et al., 2016; Bowring et al., 2022). Natural PyC is produced in an uncontrolled manner, thus achieving a lower degree of aromatisation, a smaller PAC pool and lower MRT compared to optimized PyC produced by controlled pyrolysis. Therefore, observations from the natural PyC cycle render the assumed PAC residence time conservative. Further research is necessary to enable empirical quantification of the PAC content of biochar across a broad range of feedstock material and pyrolysis conditions. Hydrogen pyrolysis is an elaborate, yet expensive tool not suitable for routine analysis e.g. in biochar and biochar C-sink certification. Thus, further

methods for PAC quantification must be developed and standardized.

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