Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Effect of ageing on biochar properties and polycyclic aromatic hydrocarbon composition

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Content

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Table S-1: Measured biochar bulk properties.

Sample	C [%]	C stable [%]	H [%]	N [%]	S [%]	ash [%]	O [%]	SSA [m²/g]	µSSA [m²/g]	TPV [cm³/g]	µPV [cm³/g]
Romchar	71.83	92.2	1.53	0.72	0.14	11.78	14.00	89.30	360.29	0.067	0.103
Romchar-H_2O_2	71.14		1.71	0.73	0.14	9.61	16.67	80.74	351.51	0.078	0.102
Romchar-HRP	62.75		1.45	0.51	0.13	22.34	12.82	62.98	330.00	0.066	0.095
Romchar-Field	70.34		1.36	0.75	0.13	11.80	15.62	96.95	390.16	0.084	0.108
MSP700	78.86	97.8	1.42	0.86	0.2	11.55	7.11	38.05	368.82	0.029	0.103
MSP700-H_2O_2	85.05		1.17	0.94	0.18	7.16	5.50	49.75	421.99	0.055	0.118
MSP700-HRP	80.30		2.33	1.54	0.19	8.55	7.09	34.85	409.06	0.040	0.118
MSP550	76.60	95.7	2.10	0.59	0.35	12.15	8.21	15.60	319.57	0.024	0.092
MSP550-H_2O_2	79.85		2.09	0.53	0.23	9.01	8.29	38.06	350.18	0.041	0.102
MSP550-HRP	76.47		3.11	1.07	0.17	9.19	9.99	15.61	328.15	0.022	0.098

The two artificial-ageing methods (H_2O_2 and HRP) affected the physical-chemical properties of the three biochars. Enzymatic-ageing with horseradish peroxidase (HRP) lead to a greater increase in the ash content than with H_2O_2-ageing, indicating a stronger degradation of biochar structures with HRP. Oxidation is a key process for biochar degradation [1–3] and hence an increase in O-groups upon ageing was expected. However, *Miscanthus* based biochars (MSP550, MSP700) did not always show an increase in oxygen content upon ageing, which may partly be explained by (i) the ageing protocols that include the rinsing and filtration of oxidized samples, and (ii) the high stability of the tested biochars.

Table S-2: Measured 16 US EPA PAHs concentrations (mg/kg) for all biochars.

	NAP		ACN		ACE		FLU		PHEN		ANT		FLUO		PYR	
	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev
Romchar	4.20	0.08	0.98	0.09	0.89	0.22	0.71	0.03	8.47	0.77			2.57	0.02	2.25	0.03
Romchar-H_2O_2	4.00	0.17	0.86	0.01	0.27	0.16	0.66	0.02	8.89	0.48	0.93	0.15	2.60	0.07	2.35	0.07
Romchar-HRP	3.09	0.11	0.43	0.02	0.05	0.01	0.36	0.01	4.43	0.20	0.23	0.05	1.15	0.04	1.08	0.05
Romchar-Field	3.23	0.51	< .01		< .01		1.01	0.60	0.63	0.63	0.27	0.27	0.31	0.02	0.29	0.01
MSP700	1.16	0.05	< .01		0.36	0.36	0.32	0.25	2.35	1.27	< .01		0.05	0.00	0.07	0.01
MSP700-H_2O_2	1.19	0.08	0.30	0.00	< .01		0.30	0.01	0.39	0.05	0.31	0.01	0.33	0.01	0.31	0.01
MSP700-HRP	1.41	0.11	0.28	0.00	< .01		0.28	0.00	0.43	0.00	0.32	0.02	0.33	0.01	0.31	0.01
MSP550	2.20	0.06	< .01		0.21	0.21	0.13	0.13	2.57	1.08	< .01		0.18	0.03	0.17	0.02
MSP550-H_2O_2	2.07	0.08	< .01		< .01		< .01		1.66	0.12	< .01		0.36	0.00	0.16	0.16
MSP550-HRP	2.04	0.09	0.28	0.00	0.24	0.00	0.33	0.00	1.08	0.20	0.42	0.03	0.43	0.01	0.40	0.00

	B[a]A		CHRY		B[b]F		B[k]F		B[a]P		I[1,2,3-cd]P		D[a,h]A		B[g,h,i]P	
	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev	av	stdev
Romchar	0.64	0.00	0.78	0.01	0.25	0.01	0.41	0.01	0.64	0.00	0.78	0.01	0.25	0.01	0.41	0.03
Romchar-H_2O_2	0.60	0.03	0.74	0.03	0.29	0.02	0.35	0.00	0.60	0.03	0.74	0.03	0.29	0.02	0.35	0.07
Romchar-HRP	0.26	0.01	0.34	0.02	0.15	0.00	0.18	0.01	0.26	0.01	0.34	0.02	0.15	0.00	0.18	0.05
Romchar-Field	< .01		< .01		0.02	0.02	0.08	0.00	< .01		< .01		0.02	0.02	0.08	0.01
MSP700	0.05	0.05	0.04	0.04	< .01		< .01		0.05	0.05	0.04	0.04	< .01		< .01	0.01
MSP700-H_2O_2	< .01		0.10	0.00	0.59	0.00	0.21	0.00	< .01		0.10	0.00	0.59	0.00	0.21	0.01
MSP700-HRP	< .01		0.05	0.05	0.59	0.00	0.20	0.00	< .01		0.05	0.05	0.59	0.00	0.20	0.01
MSP550	0.11	0.02	0.11	0.02	0.06	0.01	0.10	0.01	0.11	0.02	0.11	0.02	0.06	0.01	0.10	0.02
MSP550-H_2O_2	0.83	0.05	0.21	0.01	0.13	0.02	0.18	0.01	0.83	0.05	0.21	0.01	0.13	0.02	0.18	0.16
MSP550-HRP	0.04	0.02	0.17	0.02	0.61	0.00	0.23	0.01	0.04	0.02	0.17	0.02	0.61	0.00	0.23	0.00

Abbreviations: av = average, stdev = standard deviation.
Compounds: naphthalene (NAP), acenaphthylene (ACN), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHEN), anthracene (ANT), fluoranthene (FLUO), pyrene (PYR), benzo[*a*]anthracene (B[a]A), chrysene (CHRY), benzo[*b*]fluoranthene (B[b]F), benzo[*k*]fluoranthene (B[k]F), benzo[*a*]pyrene (B[a]P), indeno[1,2,3-*cd*]pyrene (I[1,2,3-cd]P), dibenz[*a*,*h*]anthracene (D[a,h]A), and benzo[*ghi*]perylene (B[g,h,i]P)

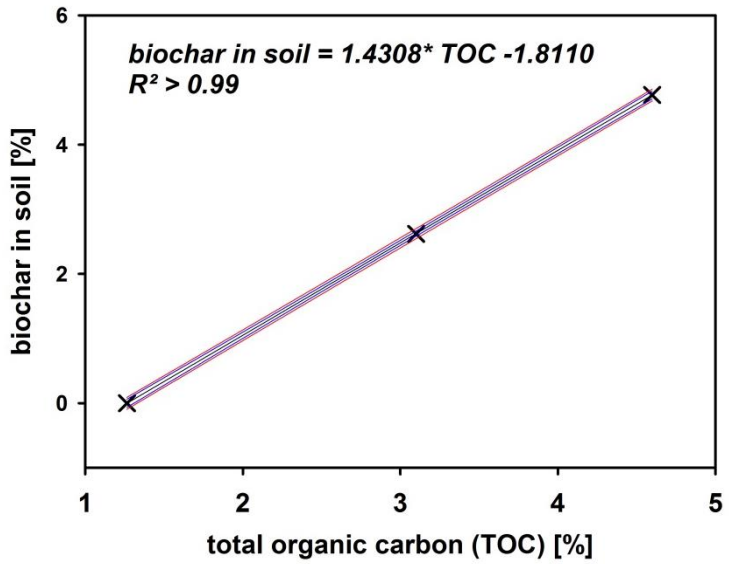

Figure S-1: Total organic carbon based calibration for biochar quantification.

To quantify the biochar in the amended soil, the total organic carbon content (TOC) of the amended soil and the unamended soil from the same site were compared. In addition, the TOC of the unamended soil was measured and the soil was mixed with different amounts of Romchar-Field separated from the amended soil. The TOC of those samples was then used to construct a calibration curve that was used to quantify the biochar content in the biochar amended soil.

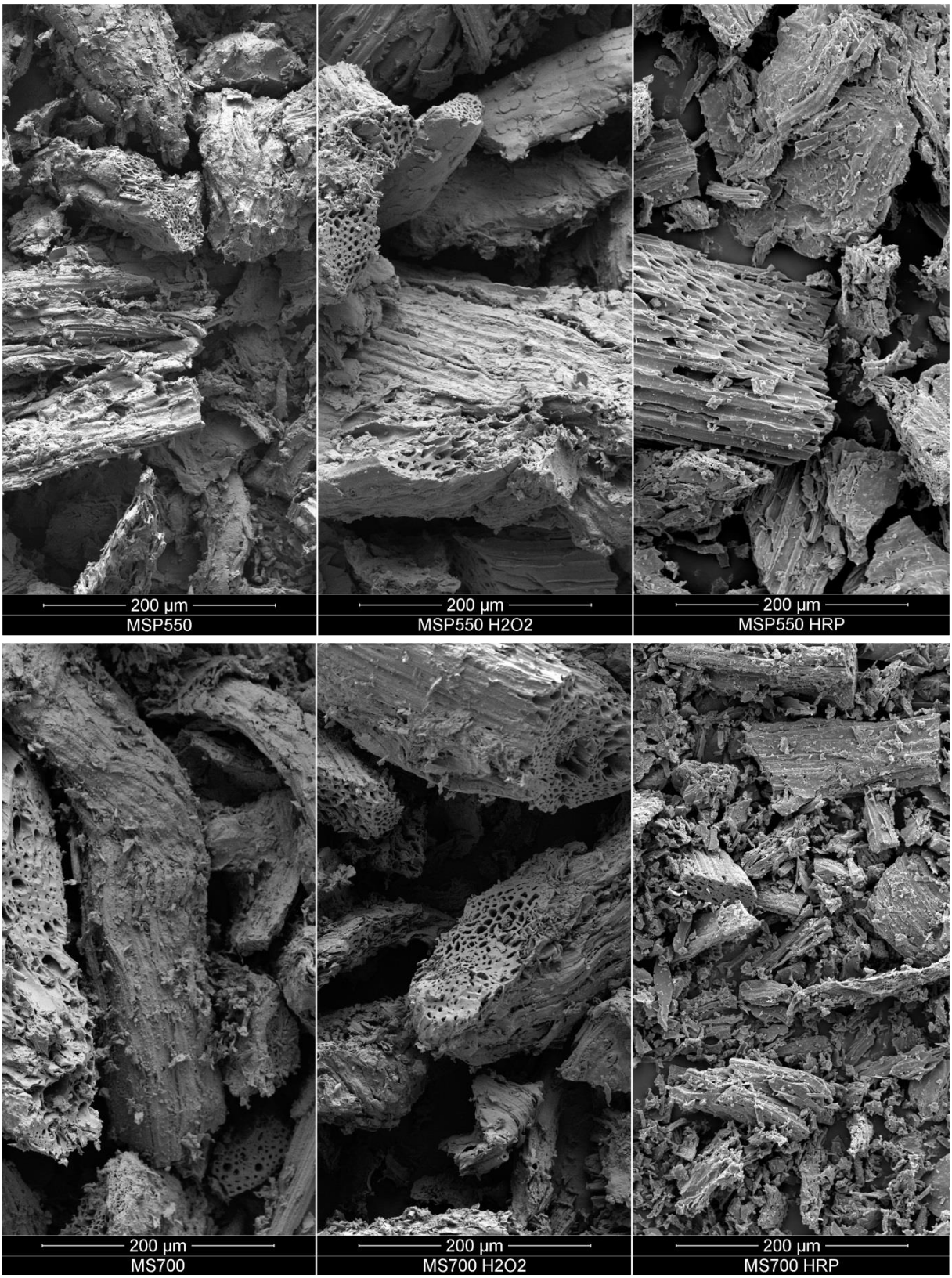

Figure S-2: Scanning electron microscopy images of biochars produced from *Miscantus* at 550 and 700 °C before and after artificial-ageing with chemical oxidation (H_2O_2) and enzymatic oxidation (HRP).

References

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