SUPPORTING INFORMATION

Fate of soil organic carbon and polycyclic aromatic hydrocarbons in a vineyard soil treated with biochar

Alessandro G. Rombolà[a], Will Meredith[b], Colin E. Snape[b], Silvia Baronti[c], Lorenzo Genesio[c], Francesco Primo Vaccari[c], Franco Miglietta[c] and Daniele Fabbri[a*]

[a] *Department of Chemistry "Giacomo Ciamician", C.I.R.I. Energia Ambiente and C.I.R.S.A., Università di Bologna, Ravenna Campus, Via S. Alberto 163, 48132, Ravenna, Italy.*
[b] *Department of Chemical and Environmental Engineering, University of Nottingham, Nottingham NG7 2RD, UK*
[c] *Institute of Biometeorology (IBIMET), National Research Council (CNR), Via G. Caproni 8, 50145, Florence, Italy*

Summary 10 pages, 10 tables.

Table S1. Results from the analysis of PAHs in the certified soil material (ERM-CC013a). No significant differences between the mean measured value (n = 3) and the certified value [1].

PAH	**Measured mg kg^{-1}**	**Certified mg kg^{-1}**	**Relative error %**
Naphthalene	2.3 ± 0.2	2.4 ± 0.5	-3
Fluorene	1.22 ± 0.10	1.14 ± 0.11	7
Phenanthrene	12.2 ± 0.4	12.0 ± 0.6	1
Anthracene	1.57 ± 0.22	1.41 ± 0.22	11
Fluoranthene	12.9 ± 0.2	12.9 ± 0.7	0
Pyrene	9.4 ± 0.4	9.6 ± 0.3	-2
Benzo[*a*]anthracene	5.7 ± 0.1	5.6 ± 0.5	1
Chrysene	5.5 ± 0.2	5.3 ± 0.8	3
Benzo[*b*]fluoranthene	7.0 ± 0.3	7.1 ± 1.0	-2
Benzo[*k*]fluoranthene	3.3 ± 0.2	3.4 ± 0.4	-2
Benzo[*a*]pyrene	4.8 ± 0.2	4.9 ± 0.7	-2
Benzo[*ghi*]perylene	4.8 ± 0.5	4.6 ± 0.5	3
Indeno[1,2,3-*cd*]pyrene	4.9 ± 0.7	5.2 ± 1.0	-5

[1] T. Linsinger, Comparison of a measurement result with the certified value, Application Note 1 EC-JRS IRMM (European Commission-Joint Research Center Institute for Reference Materials and Measurements), 2005 revision January 2010, Geel Belgium, 2 pp, available at: http://irmm.jrc.ec.europa.eu.

Table S2. Examples of results from the PAH calibration procedure. Concentration of PAH calibration solutions from serial dilution of the PAH-Mix Supelco: 2.5, 1.0, 0.50, 0.10, 0.1, 0.005 mg L^{-1} for each of the 16EPA PAHs. Calibration model: y (GC peak area), x (mg L^{-1}); LOD, limit of detection and LOQ limit of quantitation (ngPAH g_{soil}^{-1}) as described in [2].

PAH	**equation**	**R^2**	**LOD**	**LOQ**
Naphthalene	y = 0.5642x + 0.0015	0.9999	0.1	0.4
Acenaphthylene	y = 0.5161x - 0.0102	0.9991	0.1	0.5
Acenaphthene	y = 0.3546x - 0.0011	0.9999	0.3	0.9
Fluorene	y = 0.3941x - 0.0075	0.9986	0.1	0.3
Phenanthrene	y = 0.3661x - 0.0032	0.9999	0.5	1.5
Anthracene	y = 0.334x - 0.011	0.9983	0.3	0.8
Fluoranthene	y = 0.3741x - 0.011	0.9985	0.3	0.9
Pyrene	y = 0.3842x - 0.011	0.9984	0.2	0.7
Chrysene	y = 0.3236x - 0.0058	0.9995	0.1	0.3
Benzo[*a*]anthracene	y = 0.3984x - 0.0041	0.9999	0.1	0.4
Benzo[*b*]fluoranthene	y = 0.3269x - 0.0048	0.9994	0.2	0.6
Benzo[*k*]fluoranthene	y = 0.3761x - 0.0062	0.9995	0.2	0.7
Benzo[*a*]pyrene	y = 0.2181x - 0.004	0.9991	0.2	0.7
Indeno[1,2,3-*cd*]pyrene	y = 0.2139x - 0.0081	0.9972	0.2	0.6
Dibenzo[*a*,*h*]anthracene	y = 0.2202x - 0.008	0.9975	0.2	0.7
Benzo[*ghi*]perylene	y = 0.3015x - 0.0063	0.9991	0.2	0.6

[2] Fabbri, D.; Rombolà, A.G.; Torri, C.; Spokas, K.A. Determination of polycyclic aromatic hydrocarbons in biochar and biochar amended soil. *J. Anal. Appl. Pyrol.* **2013**, *103*, 60-67.

Table S3. Results of the ANOVA analysis for $\%BC_{HyPy}$ (BC/SOC%), BC_{HyPy}(mgC g_{soil}^{-1}), non-BC_{HyPy} PAHs, extractable PAHs and soil organic carbon (SOC) of biochar amended soils comparing the different sampling periods (months from the first sampling). S: significant ($p < 0.05$), NS: non significant differences.

BC_{HyPy}

months	0	4	9	21
0	-			
4	NS	-		
9	S	NS	-	
21	S	S	NS	-

$\%BC_{HyPy}$

months	0	4	9	21
0	-			
4	NS	-		
9	S	NS	-	
21	S	S	NS	-

non-BC_{HyPy} PAHs

months	0	4	9	21
0	-			
4	NS	-		
9	NS	NS	-	
21	NS	NS	NS	-

extractable PAHs

months	0	4	9	21
0	-			
4	S	-		
9	S	NS	-	
21	S	NS	NS	-

SOC

months	0	4	9	21
0	-			
4	NS	-		
9	NS	NS	-	
21	S	NS	NS	-

Table S4. HyPy of control soils. *n*-alkane concentrations (µg g^{-1} soil) in the non-BC_{HyPy} fraction. Mean values ± s.d. (n = 5).

	control soil			
n-alkanes	**Aug 2011**	**Dec 2011**	**May 2012**	**May 2013**
nC_{13}	0.59±0.07	0.91±0.58	0.004±0.003	0.064±0.06
nC_{14}	2.6±0.95	3.1±2.1	0.025±0.014	1.1±0.7
nC_{15}	5.3±1.3	5.7±1.2	1.1±0.3	3.0±0.9
nC_{16}	30±5.6	26±2.0	18.8±0.4	25±5.1
nC_{17}	5.3±3.0	5.6±0.8	6.06±0.5	6.1±1.5
nC_{18}	34±8.9	29±3.6	36±2.4	35±11.4
nC_{19}	2.5±0.4	2.1±0.7	2.99±0.3	2.42±1.1
nC_{20}	4.2±3.6	8.0±1.4	9.78±0.8	7.2±3.3
nC_{21}	2.38±0.6	2.4±0.5	3.04±0.4	1.7±0.9
nC_{22}	10±4.2	11±3.1	14±2.3	7.6±4.4
nC_{23}	2.2±1.0	2.1±0.8	2.2±1.3	1.4±0.9
nC_{24}	4.8±2.7	4.9±2.5	6.3±1.1	2.8±1.8
nC_{25}	0.73±0.41	0.66±0.42	0.92±0.19	0.41±0.29
nC_{26}	1.11±0.72	1.01±0.65	1.27±0.3	0.56±0.38
nC_{27}	0.37±0.23	0.32±0.20	0.47±0.33	0.17±0.10
Total nC_{13}-nC_{27}	107±16.7	103±17.7	102±8.0	93.8±18.6

Table S5. HyPy of biochar amended soils. *n*-alkane concentrations (µg g^{-1} soil) in the non-BC_{HyPy} fraction. Mean values ± s.d. (n = 5).

	Biochar amended soil			
***n*-alkanes**	**Aug 2011**	**Dec 2011**	**May 2012**	**May 2013**
nC_{13}	0.52±0.26	0.003±0.002	0.003±0.001	0.024±0.003
nC_{14}	2.8±1.0	0.037±0.017	0.002±0.001	1.04±10.02
nC_{15}	3.5±0.9	1.62±0.9	0.19±0.11	2.8±1.7
nC_{16}	14±5.5	11.3±6.9	7.6±5.3	16±6.7
nC_{17}	2.8±1.2	2.9±0.9	3.4±1.6	3.2±1.1
nC_{18}	12±6.9	18±6.9	20±10	14±5.8
nC_{19}	0.78±0.38	1.4±0.5	1.9±0.9	1.1±0.4
nC_{20}	1.73±1.18	3.2±1.3	4.1±2.6	2.5±1.1
nC_{21}	0.46±0.29	0.81±0.30	1.08±0.7	0.68±0.31
nC_{22}	1.0±1.0	2.9±1.3	3.98±1.9	2.46±1.24
nC_{23}	0.28±0.21	0.60±0.37	0.71±0.55	0.51±0.28
nC_{24}	0.61±0.50	1.1±0.8	1.34±1.42	1.02±0.48
nC_{25}	0.11±0.07	0.14±0.06	0.24±0.20	0.21±0.05
nC_{26}	0.13±0.10	0.16±0.09	0.30±0.26	0.27±0.10
nC_{27}	0.05±0.03	0.17±0.07	0.16±0.15	0.17±0.13
Total nC_{13}-nC_{27}	40.5±17.8	44.4±11.6	45.1±24.0	46.1±18.6

Table S6. HyPy of control soils. PAH concentrations (µg g^{-1} soil) in the non-BC_{HyPy} fraction. Mean values ± s.d. (n = 5). Naphthalene and acenaphthene not detected (n.d.).

	control soil			
non-BC_{HyPy} PAHs	**Aug 2011**	**Dec 2011**	**May 2012**	**May 2013**
Fluorene	0.13±0.02	0.13±0.05	n.d.	n.d.
Phenanthrene	0.75±0.17	0.44±0.13	0.27±0.07	0.22±0.10
Anthracene	0.09±0.05	0.09±0.08	0.05±0.01	0.06±0.02
Dihydropyrene	1.84±0.53	1.57±0.62	1.55±0.18	1.51±0.32
Pyrene	20.5±6.3	17.5±6.6	15.9±2.2	16.7±4.2
Chrysene	0.27±0.11	0.39±0.21	0.30±0.04	0.13±0.08
Benzo[*ghi*]perylene	0.17±0.15	0.18±0.08	0.11±0.09	n.d.
Total PAHs	23.9±7.2	20.6±7.8	18.2±2.4	18.7±4.4

Table S7. HyPy of biochar amended soils. PAH concentrations (µg g^{-1} soil) in the non-BC_{HyPy} fraction. Mean values ± s.d. (n = 5); n.d. not detected

	biochar amended soil			
non-BC_{HyPy} PAHs	**Aug 2011**	**Dec 2011**	**May 2012**	**May 2013**
Naphthalene	0.15±0.32	n.d.	n.d.	n.d.
Acenaphthene	0.33±0.32	n.d.	n.d.	n.d.
Fluorene	0.13±0.06	0.10±0.13	0.09±0.02	0.08±0.12
Phenanthrene	1.4±1.1	1.7±1.7	0.89±0.68	0.91±0.42
Anthracene	0.05±0.03	0.05±0.02	0.08±0.03	0.14±0.07
Dihydropyrene	3.0±1.5	3.3±1.4	2.9±0.9	2.4±1.1
Pyrene	33.2±17.6	36.3±15.5	38.0±14.3	30.3±12.8
Chrysene	0.43±0.12	0.56±0.34	0.55±0.39	0.43±0.06
Benzo[*ghi*]perylene	0.29±0.25	0.40±0.37	0.30±0.21	0.18±0.23
Total PAHs	38.9±20.5	42.4±19.3	42.9±16.4	34.5±14.3

Table S8. Concentrations of solvent extractable PAHs (ng g^{-1} soil) in control soils. Mean values and s.d. (n = 5); n.d. not detected.

control soil	**Aug 2011**		**Dec 2011**		**May 2012**		**May 2013**	
extractable PAHs	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**
Naphthalene	5.6	2.0	6.2	1.3	5.0	2.0	5.6	1.0
Acenaphthylene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Acenaphthene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Fluorene	1.55	0.3	1.61	0.42	1.74	0.14	1.52	0.27
Phenanthrene	7.8	1.4	7.7	1.2	5.66	0.7	6.7	2.0
Anthracene	0.90	0.08	0.82	0.32	0.90	0.32	0.92	0.48
Fluoranthene	2.70	1.0	2.62	0.47	2.12	0.71	1.67	0.53
Pyrene	1.83	0.89	1.81	0.20	1.82	0.57	1.37	0.31
Chrysene	0.50	0.12	0.53	0.08	0.56	0.16	0.62	0.20
Benzo[*a*]anthracene	0.98	0.25	0.84	0.16	0.80	0.13	0.73	0.16
Benzo[*b*]fluoranthene	0.89	0.14	0.82	0.28	1.24	0.46	1.05	0.40
Benzo[*k*]fluoranthene	0.74	0.16	0.79	0.14	0.59	0.10	0.55	0.10
Benzo[*a*]pyrene	0.75	0.03	0.79	0.16	0.63	0.16	0.80	0.18
Indeno[1,2,3-*cd*]pyrene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Dibenzo[*a*,*h*]anthracene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Benzo[*ghi*]perylene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Σ 16 EPA PAHs	**24.2**	**3.08**	**24.5**	**2.01**	**21.0**	**3.97**	**21.6**	**3.01**

Table S9. Concentrations of solvent extractable PAHs (ng g^{-1} soil) in biochar amended soils. Mean values and s.d. (n = 5); n.d. not detected.

amended soil	**Aug 2011**		**Dec 2011**		**May 2012**		**May 2013**	
extractable PAHs	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**	**ng g^{-1}**	**s.d.**
Naphthalene	74.1	20.9	41.1	15.5	34.5	8.1	35.0	5.0
Acenaphthylene	1.7	0.3	1.1	0.4	1.0	0.4	1.0	0.5
Acenaphthene	2.0	1.0	1.4	0.5	1.5	0.4	1.1	0.2
Fluorene	4.8	1.4	2.7	0.6	2.4	0.6	2.4	0.5
Phenanthrene	29.8	11.5	17.5	5.9	18.7	5.4	14.3	5.5
Anthracene	3.5	0.6	2.2	0.9	2.2	1.0	1.5	0.4
Fluoranthene	10.3	3.3	5.9	2.3	6.8	3.5	4.9	1.7
Pyrene	10.3	3.5	5.8	2.2	6.7	3.4	4.9	1.7
Chrysene	3.0	1.0	2.0	0.6	1.4	0.8	1.2	0.3
Benzo[*a*]anthracene	2.9	0.8	2.2	0.9	2.3	0.9	1.9	0.6
Benzo[*b*]fluoranthene	3.8	1.8	3.3	1.8	2.9	1.1	2.8	1.1
Benzo[*k*]fluoranthene	2.5	1.6	1.8	0.9	1.6	0.9	1.6	0.9
Benzo[*a*]pyrene	2.3	0.6	2.0	0.4	2.2	0.6	1.8	0.3
Indeno[1,2,3-*cd*]pyrene	0.91	0.38	0.82	0.28	0.85	0.21	0.90	0.30
Dibenzo[*a*,*h*]anthracene	n.d.	-	n.d.	-	n.d.	-	n.d.	-
Benzo[*ghi*]perylene	1.0	0.42	0.83	0.37	0.95	0.53	0.85	0.42
Σ 16 EPA PAHs	**153.0**	**37.7**	**97.7**	**35.5**	**88.5**	**29.7**	**78.4**	**20.6**

Table S10. Concentrations of solvent extractable and non-BC_{HyPy} PAHs (µg g^{-1} biochar) in biochar utilised in the field experiment (mean values and s.d.; n.d. not detected).

Biochar	**extracted**		**non-BC_{HyPy}**	
PAHs	**µg g^{-1}**	**s.d.**	**µg g^{-1}**	**s.d.**
Naphthalene	2.15	0.67	n.d.	n.d.
Acenaphthylene	0.042	0.01	n.d.	n.d.
Acenaphthene	0.037	0.002	4.7	0.6
Fluorene	0.060	0.007	17	3.5
Phenanthrene	0.67	0.04	419	79
Anthracene	0.092	0.001	10	1.7
Fluoranthene	0.13	0.02	149	23
Pyrene	0.15	0.003	468	110
Chrysene	0.049	0.011	7.0	1.6
Benzo[*a*]anthracene	0.11	0.002	n.d.	n.d.
Benzo[*b*]fluoranthene	0.098	0.004	n.d.	n.d.
Benzo[*k*]fluoranthene	0.088	0.03	n.d.	n.d.
Benzo[*a*]pyrene	0.093	0.007	n.d.	n.d.
Indeno[1,2,3-*cd*]pyrene	0.019	0.006	n.d.	n.d.
Dibenzo[*a,h*]anthracene	0.021	0.002	n.d.	n.d.
Benzo[*ghi*]perylene	0.018	0.002	n.d.	n.d.
Σ 16 EPA PAHs	**3.8**	**0.08**	**1100**	**200**