

Redox Properties of Plant Biomass-Derived Black Carbon (Biochar)

The Faculty of Oregon State University has made this article openly available.
Please share how this access benefits you. Your story matters.

Citation	Klүpfel, L., Keiluweit, M., Kleber, M., & Sander, M. (2014). Redox properties of plant biomass-derived black carbon (biochar). <i>Environmental Science & Technology</i> . 48(10), 5601-5611. doi:10.1021/es500906d
DOI	10.1021/es500906d
Publisher	American Chemical Society
Version	Accepted Manuscript
Terms of Use	http://cdss.library.oregonstate.edu/sa-termsfuse

1 **Manuscript**

2
3 **Redox properties of plant biomass-derived black carbon (biochar)**

4
5 Laura Klüpfel[†], Marco Keiluweit^{§,‡}, Markus Kleber^{§,¶}, and Michael Sander^{†,*}

6
7 [†] Department of Environmental Systems Sciences
8 Institute of Biogeochemistry and Pollutant Dynamics
9 Swiss Federal Institute of Technology (ETH) Zurich, 8092 Zurich, Switzerland

10
11 [§] Department of Crop and Soil Science
12 Soil and Environmental Geochemistry
13 Oregon State University, Corvallis, OR 97331, United States

14 [¶] Institute of Soil Landscape Research, Leibniz-Center for Agricultural Landscape
15 Research (ZALF), 15374 Müncheberg, Germany

16
17 [‡] Department of Environmental Earth System Science
18 Soil and Environmental Biogeochemistry
19 Stanford University, Stanford, CA 94305, USA

20
21
22 Submitted to
23 Environmental Science & Technology

24
25
26 *To whom correspondence should be addressed.

27 E-mail: michael.sander@env.ethz.ch

28 Phone: +41-(0)44 6328314

29 Fax: +41 (0)44 633 1122

30
31 Number of pages: 30

32 Number of figures: 4

33 Number of tables: 1

34 Number of words: 7261

35 (=5161+ 300 Table 1 + 600 Figure 1 + 600 Figure 2 + 300
36 Figure 3 + 300 Figure 4)

37

38 **Abstract**

39 Soils and sediments worldwide contain appreciable amounts of thermally altered
40 organic matter (chars) of both natural and industrial origin. Additions of chars into
41 soils are discussed as a strategy to mitigate climate change. Chars contain
42 electroactive quinoid functional groups and polycondensed aromatic sheets that were
43 recently shown to be of biogeochemical and enviro-technical relevance. However, so
44 far no systematic investigation of the redox properties of chars formed under different
45 pyrolysis conditions has been performed. Here, using mediated electrochemical
46 analysis, we show that chars made from different feedstock and over a range of
47 pyrolysis conditions are redox-active and reversibly accept and donate up to 2 mmol
48 electrons per gram of char. The analysis of two thermosequences revealed that chars
49 produced at intermediate to high heat treatment temperatures (HTTs) (400-700°C)
50 show the highest capacities to accept and donate electrons. The electron accepting
51 capacities (EACs) increase with the nominal carbon oxidation state of the chars.
52 Comparable trends of EACs and of quinoid C=O contents with HTT suggest quinoid
53 moieties as major electron acceptors in the chars. We propose to consider chars in
54 environmental engineering applications that require controlled electron transfer
55 reactions. Electroactive char components may also contribute to the redox properties
56 of traditionally defined "humic substances".

57

58 **Introduction**

59 Char black carbon is formed by incomplete combustion of biomass and is
60 ubiquitous in the environment.¹⁻⁶ Chars make up significant fractions of the organic
61 matter in many soils and sediments.^{7,8} By contributing to the slow cycling carbon
62 pool in these systems, chars link into the global carbon cycle.^{3,9-11} In addition to their

63 biogeochemical relevance, chars also play a role in environmental engineering as
64 high affinity sorbents for organic and inorganic pollutants.¹²⁻²⁰ Sorption to chars
65 strongly affects the transport and bioavailability of xenobiotics in natural systems, and
66 char amendments are considered as effective means to immobilize contaminants.²¹⁻²³
67 An increasingly discussed aspect of char functionality is their apparent role as
68 electron transfer catalysts in redox reactions of both biogeochemical and enviro-
69 technical relevance.^{24,25} Chars catalyze the reductive transformation of organic
70 contaminants by facilitating electron transfer from bulk chemical electron donors to
71 the receiving organic compounds.²⁶⁻³² Electron shuttling towards denitrifying
72 microorganisms in soils was invoked to rationalize lower N₂O emissions from char
73 amended soils compared to non-amended control treatments.³³⁻³⁵

74 Electron transfer catalysis by intermediate and high temperature chars may involve
75 two types of redox-active structures: quinone-hydroquinone moieties and/or
76 conjugated π -electron systems associated with condensed aromatic (sub-) structures
77 of the char.^{26,27,32} The presence of quinone moieties is directly supported by evidence
78 from carbon Near-Edge X-ray Absorption Fine Structure Spectroscopy
79 (NEXAFS)^{36,37} and from electron paramagnetic resonance spectroscopy,³⁸ which
80 suggests that certain chars contain radicals of semiquinone-type character. These
81 spectroscopic analyses find highest quinone concentrations in intermediate to high
82 temperature chars. The alleged importance of quinone/hydroquinone pairs as electron
83 accepting and donating moieties in chars is supported by the fact that these moieties
84 are major contributors to the redox properties and reactivities of other types of
85 organic matter and carbonaceous solids, including dissolved organic matter,³⁹⁻⁴²
86 particulate organic matter,^{43,44} activated carbons and carbon black.⁴⁵⁻⁴⁹ In addition to
87 quinone/hydroquinone moieties, the condensed aromatic (sub-) structures of chars

88 may be electroactive by allowing electrons to be transferred across the conjugated
89 π -electron systems. Electron conductance in and electron transfer to and from such
90 systems is well established for graphite, carbon nanotubes,^{50,51} fullerenes,^{52,53} and
91 graphene oxide.^{54,55} The extent of aromatic ring condensation and hence the ratio of
92 sp^2 to sp^3 hybridized carbons in chars increases with increasing charring
93 temperature.^{36,56-59} At heat treatment temperatures (HTTs) above 600°C, conjugated
94 aromatic sheets grow sufficiently large for chars to achieve conductivity.^{25,32,60}
95 However, while an increase in HTT increases aromaticity and the extent of ring
96 condensation, it concomitantly decreases the char oxygen content and yield.^{36,58}
97 Based on these opposing trends, it is reasonable to expect that the contribution of
98 quinone/hydroquinone moieties to the electron transfer properties of chars would
99 decrease with increasing HTT while the contribution of conjugated π -electron
100 systems should increase with HTT.

101 The presence of redox-active moieties in chars and the growing evidence that
102 chars are important electron transfer catalysts in biogeochemical and pollutant redox
103 reactions calls for a systematic assessment of the redox properties of chars. Up to
104 now, such a systematic investigation has been hampered by the lack of an appropriate
105 experimental technique. Traditional approaches to characterize the redox properties
106 of dissolved and particulate natural organic matter rely on measuring the reduction of
107 a chemical oxidant, typically complexed Fe^{3+} species or iodine.⁶¹⁻⁶⁴ Among these
108 approaches is the ferric reducing antioxidant power assay, which was recently used to
109 quantify the electron donating capacities of char water extracts.⁶⁵ Quantification of
110 electron transfer by these traditional approaches is, however, only indirect (i.e.,
111 conversion of the added oxidant Fe^{3+} or I_2), unidirectional (i.e., in the oxidative
112 direction but not in the reductive direction), and not conducted at a constant reduction

113 potential, E_h (i.e., the E_h decreases as the chemical oxidant is being reduced). These
114 shortcomings were recently overcome by mediated electrochemical analysis, a novel
115 analytical approach which allows for a direct and bidirectional quantification of
116 electron transfer to and from humic substances^{40,41,66} and Fe-bearing mineral
117 phases⁶⁷⁻⁶⁹ under constant and well-controlled redox conditions.

118 The goal of this study was to systematically assess how redox properties may vary
119 among a variety of char types. More specifically, we aimed at (i) validating the use of
120 mediated electrochemical analysis to characterize the redox properties of chars, (ii)
121 systematically quantifying the changes in the electron accepting and donating
122 capacities of chars formed under different pyrolysis conditions, including variations
123 in HTT and feedstock, and (iii) assessing the reversibility of electron transfer to
124 chars. To address these points, we quantified the electron accepting and donating
125 capacities of a total of 19 chars and investigated the reversibility of the electron
126 transfer to these chars. The chars examined included two thermosequences of six
127 temperature steps (200-700°C) each from a grass and a wood feedstock as well as
128 seven reference chars.

129

130 **Experimental Section**

131 **Chemicals.** Acetic acid (puriss. p.a.), hypochloric acid (37%), potassium chloride
132 (puriss. p.a.), sodium borohydride (puriss. p.a.), and sodium hydroxide (32%) were
133 purchased from Fluka. Sodium phosphate dibasic (p.a.) and ubiquinone (Q₁₀) (>98%)
134 were from Sigma-Aldrich. The electron transfer mediator 2,2'-azino-bis(3-
135 ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS) (>99%) was from
136 Fluka and the zwitterionic viologen 4,4'-bipyridinium-1,1'-bis(2-ethylsulfonate)
137 (ZiV) was synthesized and purified as detailed elsewhere.⁶⁹

138 **Solutions.** Nanopure water (resistivity, $\sigma > 18 \text{ M}\Omega\cdot\text{cm}$) was used for all
139 experiments. All solutions prepared under oxic conditions were made anoxic by
140 purging with N_2 (1 h at 80 °C and 1 h at room temperature) prior to transfer into the
141 glovebox ($\text{O}_2 < 0.1 \text{ ppm}$).

142 **Chars.** A total of 19 chars were analyzed. Two sets of six chars each were from a
143 grass (tall fescue, *Festuca arundinacea*) and a wood (ponderosa pine, *Pinus*
144 *ponderosa*) char thermosequence that was previously characterized³⁶ (abbreviated as
145 GX and WX, respectively, where X corresponds to HTT's ranging from 200 to
146 700°C). Five additional chars were produced in a semi-industrial retort following a
147 procedure described elsewhere⁷⁰ and included chars from hazelnut (HZ, *Corylus*
148 *avellana L. varietas 'Barcelona'*) shell/wood formed at 400, 550, and 700°C and
149 Douglas-fir (DF, *Pseudotsuga menziesii* at 400 and 700°C. Two reference chars⁷¹⁻⁷³
150 from rice straw (*Oryza sativa* Arborio) and chestnut (*Castanea sativa*) wood
151 (abbreviated as RS and CW, respectively) were charred in a N_2 -atmosphere at a HTT
152 of 450°C. Key physicochemical properties of the wood and grass thermosequence
153 chars are given in **Table 1** and of the other chars in **Table S1**.

154 **Preparation of char suspensions.** All chars were finely ground in Eppendorf tubes
155 using ball mills, as detailed in the Supporting Information (SI). The particle size
156 distributions of the pulverized chars are shown in **Figure S1**. The chars were placed
157 under vacuum in the antechamber of an anoxic glovebox over night to remove
158 adsorbed O_2 , then transferred into the glovebox, and suspended in anoxic buffer
159 solution (pH 7, 0.1 M phosphate, 0.1 M KCl) in glass vials to final concentrations of
160 1 or 4 g char L^{-1} . The glass vials were crimp-capped with butyl rubber stoppers,
161 transferred out of the glovebox, and positioned in a water bath underneath an
162 ultrasonic tip (Sonics Vibra-cell VCX 500 with microtip, amplitude 150 W, 10 min)

163 to finely disperse the chars. The chars were transferred back into the glovebox for
 164 electrochemical analysis.

165

166 **Table 1.** Elemental composition, nominal average carbon oxidation state (C_{ox}),
 167 double bond equivalents (DBE), aromaticity index (AI), and C=O contents of the
 168 grass (GX) and wood (WX) thermosequence chars, where X corresponds to the
 169 charring temperature in °C.

170

Char specimen	Elemental composition [mmol element (g char) ⁻¹] ^a				Nominal C oxidation state C_{ox} ^b	DBE ^c [mol DBE (mol C) ⁻¹]	AI ^c [mol DBE _{AI} (mol C) ⁻¹]	C=O ^d content [mmol C=O (g char) ⁻¹]
	C	N	H	O				
G700	78.4	0.50	15.3	2.3	-0.14	0.92	0.92	0.80
G600	74.1	0.71	24.7	4.8	-0.20	0.85	0.85	1.66
G500	68.4	0.78	33.2	8.4	-0.24	0.78	0.75	2.60
G400	64.4	0.89	47.0	10.4	-0.40	0.66	0.60	2.79
G300	49.7	0.73	66.4	20.4	-0.50	0.36	0.00	2.33
G200	39.3	0.44	71.1	28.2	-0.36	0.13	0.00	0.25
W700	76.8	0.06	16.1	3.8	-0.11	0.91	0.90	1.2
W600	74.1	0.04	29.7	5.0	-0.27	0.81	0.80	1.7
W500	68.2	0.06	35.1	9.1	-0.25	0.76	0.72	2.8
W400	61.7	0.04	49.1	13.1	-0.37	0.62	0.52	3.1
W300	45.6	0.04	64.5	24.2	-0.35	0.32	0.00	1.7
W200	42.4	0.03	68.9	26.4	-0.38	0.21	0.00	-

171 ^a Elemental composition data from reference³⁶. ^b Calculated according to reference⁷⁴
 172 ^c Calculated from elemental composition data according to reference⁷⁵. ^d quinoid C=O content
 173 based on NEXAFS spectra from reference³⁶.

174

175 ***Q₁₀ recovery experiment.*** Increasing amounts of apolar ubiquinone, Q₁₀, were
 176 added from an ethanolic stock solution (0.94 ± 0.01 mM) to suspensions of G500 and
 177 G400 chars (both at 1 g L⁻¹) to final concentrations between 0.19 and 0.53 mmol Q₁₀
 178 (g G500)⁻¹ and between 0.19 and 0.76 mmol Q₁₀ (g G400)⁻¹. The char suspensions
 179 were stirred for 30 min to allow for Q₁₀ sorption, followed by electrochemical
 180 analysis. Extensive sorption of Q₁₀ to the chars was verified by electrochemical
 181 quantification of the dissolved Q₁₀ in the supernatant of the char following
 182 centrifugation of the samples, as detailed in the SI.

183 ***Redox cycling of charcoals.*** All chars were reduced with borohydride (NaBH₄)
 184 and subsequently re-oxidized by O₂ in air. Changes in the char redox states were

185 determined by electrochemical analysis (see below) of untreated, NaBH₄-reduced,
186 and re-oxidized chars. Detailed descriptions of the borohydride reduction step and the
187 oxygen re-oxidation steps are provided in the SI.

188 ***Electrochemical analysis.*** The redox states of the chars were quantified by
189 mediated electrochemical reduction (MER) and oxidation (MEO), adapted from a
190 previously published method.⁴⁰ A nine mL glassy carbon cylinder (Sigradur G, HTW,
191 Germany) served both as the working electrode (WE) and electrochemical reaction
192 vessel. This WE setup significantly increased measurement sensitivity compared to
193 the original setup in which we used a vitreous carbon WE.⁴⁰ The applied redox
194 potentials E_h were measured against Ag/AgCl reference electrodes (Bioanalytical
195 Systems Inc., USA) but are reported with reference to the standard hydrogen
196 electrode. The counter electrode was a coiled platinum wire separated from the WE
197 compartment by a porous glass frit. The WE cylinder was filled with 6 mL buffer (0.1
198 M KCl, 0.1 M phosphate, pH 7) and equilibrated to the desired redox potential ($E_h = -$
199 0.49 V in MER and +0.61 V in MEO). Subsequently, 130 μ L of stock solutions (10
200 mM) of the electron transfer mediators ZiV (in MER) or ABTS (in MEO) were added
201 to the cells, resulting in reductive and oxidative current peaks, respectively. After re-
202 attainment of constant background currents, small volumes (i.e., 20-100 μ L) of the
203 char suspensions were spiked to the cells. The resulting reductive (MER) and
204 oxidative (MEO) current peaks were integrated to yield the electron accepting
205 capacities (EAC) and donating capacities (EDC) (both [mmol e⁻ (g char)⁻¹]) of the
206 chars added:

$$207 \quad \text{EAC} = \frac{\int \frac{I_{\text{red}}}{F} dt}{m_{\text{char}}} \quad \text{Eq. 1a}$$

$$208 \quad \text{EDC} = \frac{\int \frac{I_{\text{ox}}}{F} dt}{m_{\text{char}}} \quad \text{Eq. 1b}$$

209 where I_{red} and I_{ox} (both [A]) are the baseline-corrected reductive and oxidative
 210 currents in MER and MEO, respectively, F (=96485 [sec A/mol_e-]) is the Faraday
 211 constant, and m_{char} [g char] is the mass of added char. All char samples were analyzed
 212 in at least duplicates (and most in triplicates) with $t= 30$ min between the analyses to
 213 ensure baseline-separation of individual current peaks. The electron exchange
 214 capacity (EEC= EAC + EDC) [mmol e⁻ (g char)⁻¹] of a char describes its total
 215 capacity to accept and donate electrons.

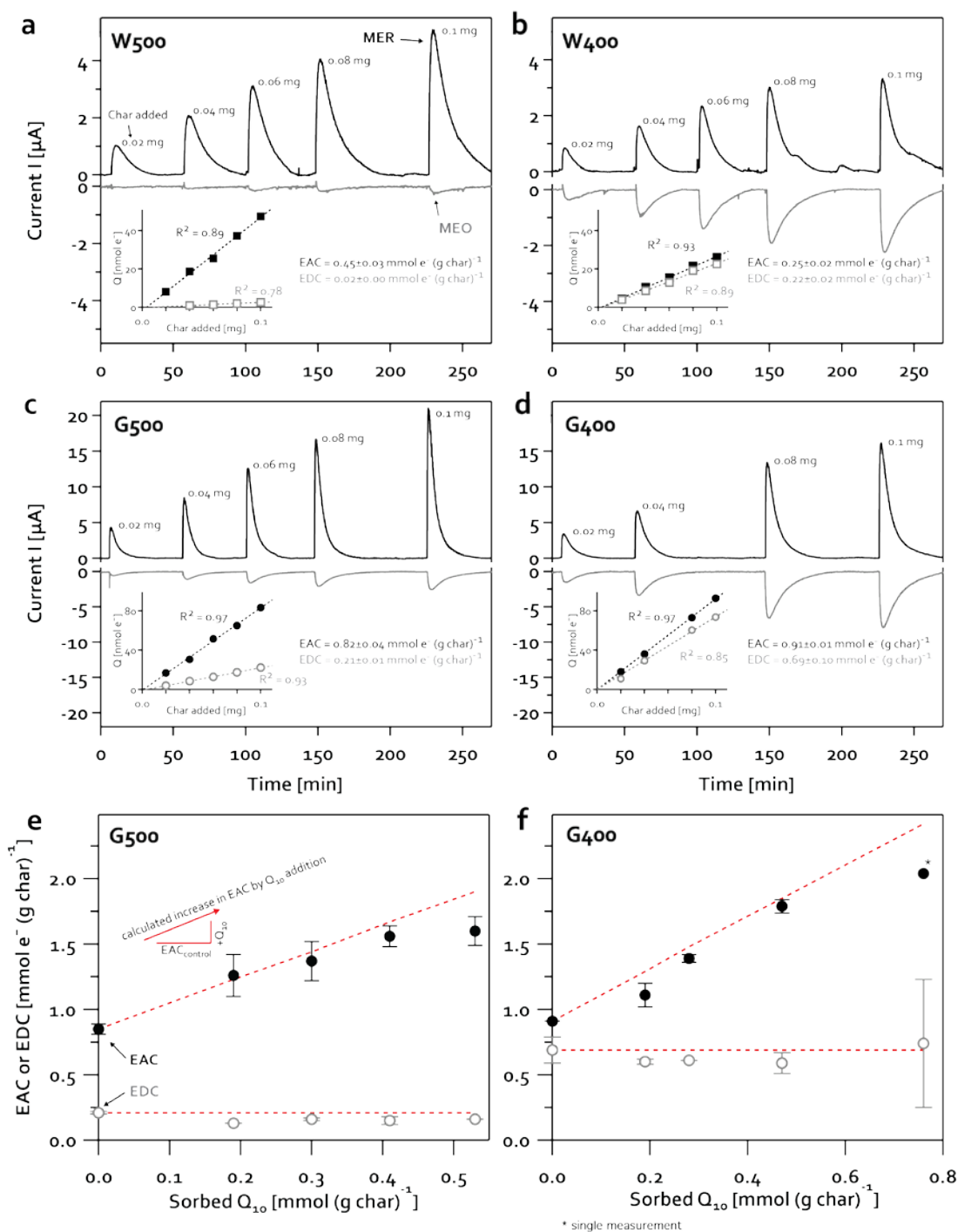
216

217 **Results and Discussion**

218 *Mediated electrochemical analysis of chars.* The applicability of mediated
 219 electrochemical analysis to characterize the redox properties of chars was assessed by
 220 analyzing four char specimen (G400, G500, W400, and W500) by MER and MEO.
 221 **Figure 1a-d** shows the reductive and oxidative current peaks in MER and MEO,
 222 respectively, that resulted from adding increasing amounts of the chars to the
 223 electrochemical cells. Char masses smaller than 100 μg yielded strong current
 224 responses, demonstrating the high sensitivity of MER and MEO. The high initial
 225 reductive and oxidative currents following each char addition reflect high initial
 226 electron transfer rates to and from the chars, respectively. The currents subsequently
 227 decreased as the electron accepting and donating moieties in the chars approached
 228 apparent E_{h} equilibrium (and hence no net electron transfer) with the E_{h} of the
 229 mediators (= the E_{h} applied to the WEs). All chars showed well defined and base-line
 230 separated current peaks, except for W500 with only small current responses in MEO
 231 (panel a). Base-line separation implies that each char had come to apparent E_{h} -

232 equilibrium in the cells prior to addition of the next char sample. Electron transfer
233 kinetics to and from G400 and G500 were faster than to and from W400 and W500,
234 as evidenced by sharper current peaks of the former than the latter. Integration of the
235 current peaks yielded the numbers of electrons transferred to and from the chars, Q
236 [nmol e⁻]. For all chars tested, Q was linearly proportional to the char mass analyzed
237 in both MER and MEO (**Figure 1a-d**, insets).

238 In addition to establishing linear responses of MER and MEO, we assessed the
239 extent to which MER and MEO quantified redox-active species on the char surfaces.
240 To this end, we sorbed increasing amounts of ubiquinone (Q₁₀) to the surfaces of
241 G500 and G400, followed by MER and MEO analysis. Sorption of the added Q₁₀ to
242 G500 and G400 was extensive (adsorption of at least 92 % and 94 % of the added
243 Q₁₀, respectively), as detailed in the SI. **Figure 1e,f** shows that increasing amounts of
244 sorbed Q₁₀ resulted in increasing EAC values of G400 and G500 that was in good
245 agreement with the expected increase based on a two-electron reduction of each Q₁₀
246 molecule. The EDC of G400 and G500 were not affected by Q₁₀ sorption, consistent
247 with expectation since Q₁₀ does not donate electrons. The lower than expected EAC
248 values measured at the highest sorbed Q₁₀ concentrations likely resulted from an
249 ethanol co-solvent effect on the electrochemical measurement (i.e., the volumetric
250 contribution of ethanol to the char suspension was 44 % at the highest added Q₁₀
251 mass).



252

253 **Figure 1 a-d.** Reductive and oxidative current responses to increasing amounts of
 254 char specimen W400, W500, G400, and G500 analyzed by mediated electrochemical
 255 reduction (MER; $E_h = -0.49$ V, pH 7; black traces) and mediated electrochemical
 256 oxidation (MEO $E_h = +0.61$ V, pH 7; grey traces). The numbers above the current
 257 peaks denote the analyzed char masses. The numbers of electrons transferred to and
 258 from the chars, Q , increased linearly with increasing masses of char analyzed
 259 (inserts). The slopes of the linear regression lines of Q versus char mass correspond
 260 to the electron accepting and donating capacities (EAC and EDC; reported as
 261 averages \pm standard deviation). **e,f.** EAC (black symbols) and EDC (grey symbols)
 262 values of G500 and G400 samples containing increasing adsorbed amounts of added

263 ubiquinone, Q₁₀. Error bars represent maximum and minimum values of duplicate
264 measurements. The asterisk in panel f indicates a single measurement. The red
265 dashed lines correspond to the EAC increase expected for the transfer of two
266 electrons per added Q₁₀ molecule.

267
268 The high sensitivities and linear responses in Q to the analyzed char masses in
269 MER and MEO (**Figure 1a-d**), and the quantitative detection of exogenous Q₁₀
270 adsorbed to selected chars in MER (**Figure 1e,f**) demonstrated the applicability of
271 mediated electrochemical analysis to characterize the electron accepting and donating
272 properties of chars.

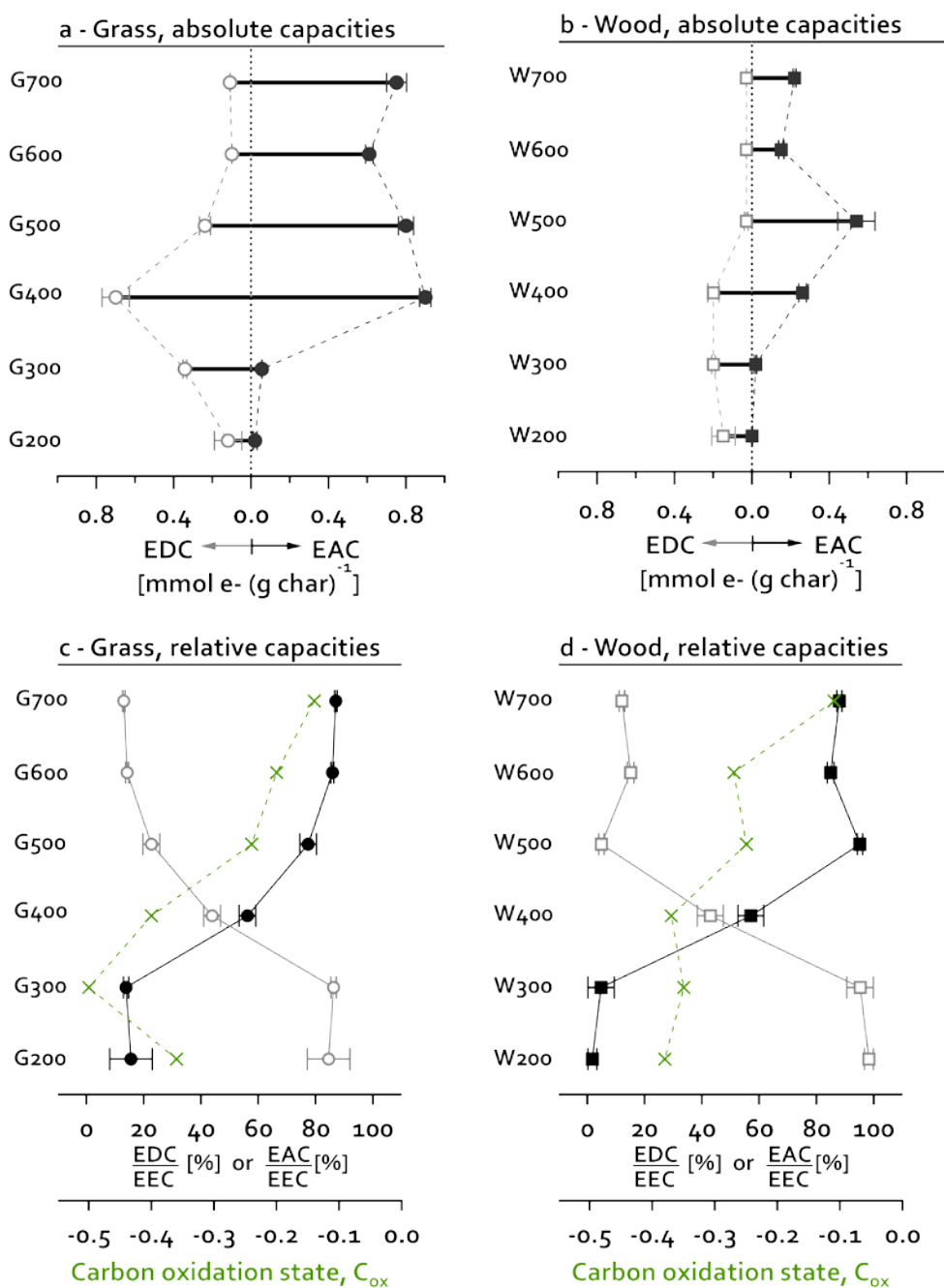
273 *Effect of heat treatment temperature (HTT) on char redox properties.* HTT is a
274 major factor that determines the physicochemical properties of chars.⁷⁶ We
275 systematically assessed the effect of HTT on char redox properties by quantifying the
276 EAC and EDC values for two thermosequences formed from grass and wood
277 feedstock. Only HTTs were varied in the formation of these chars, while all other
278 conditions were kept constant.³⁶

279 **Figure 2a,b** shows that all tested grass and wood chars accepted and donated
280 electrons at the E_h applied in MER and MEO, respectively. At any given HTT above
281 200°C, the grass chars had higher absolute EAC (black symbols), EDC (grey
282 symbols), and EEC (horizontal black bars) values than the corresponding wood chars.
283 While there were differences in absolute capacities of grass and wood chars, the HTT
284 had comparable effects on the relative changes in the EAC, EDC, and EEC values for
285 both thermosequences. The EAC values were lowest for low-HTT chars (i.e., 200 and
286 300°C), highest for intermediate-HTT chars (i.e., 400 and 500°C; with maxima of
287 EAC= 0.90 mmol e⁻/g for G400 and 0.54 mmol e⁻/g for W500), and intermediate in
288 high-HTT chars (i.e., 600 and 700°C). The EDCs of the grass chars increased with
289 HTT from 200°C to a maximum at 400°C (0.70 mmol e⁻/g) and decreased with HTT
290 above 400°C. The EDC values of the wood chars were little affected by HTTs

291 between 200 and 400°C and decreased to small values for $\text{HTTs} \geq 500^\circ\text{C}$. These
292 trends in EAC and EDC resulted in EEC values that were relatively small for chars
293 formed at low HTTs. EEC values increased with increasing HTT to maximum EEC
294 values at intermediate HTTs of 400 to 500°C to decrease again with increasing $\text{HTT} >$
295 500°C.

296 The absolute EAC and EDC values in **Figure 2a,b** show that both grass and wood
297 chars had a predominance of electron donating (i.e., oxidizable) over electron
298 accepting (i.e., reducible) moieties in low-HTT specimens, while the electron
299 accepting moieties were more abundant than electron donating moieties in high-HTT
300 chars. This effect of HTT becomes more apparent in **Figure 2c,d**, in which the EAC
301 and EDC values are re-plotted as their relative contributions to the total EEC. The
302 EECs were dominated by electron donating moieties in both low-HTT grass and
303 wood chars. Charring at about 400°C led to equal contributions of electron accepting
304 and donating moieties to the EECs. Both char thermosequences showed a similar
305 transition from EDC- to EAC-dominated EECs at HTTs between 300 and 500°C. At
306 $\text{HTTs} \geq 500^\circ\text{C}$, the EECs of both grass and wood chars were dominated by the
307 electron accepting moieties. These shifts are consistent with a previous study that
308 reported a decrease in the capacity of sucrose-derived chars to reduce Ag^+ with
309 increasing HTT.⁴⁶

310



311

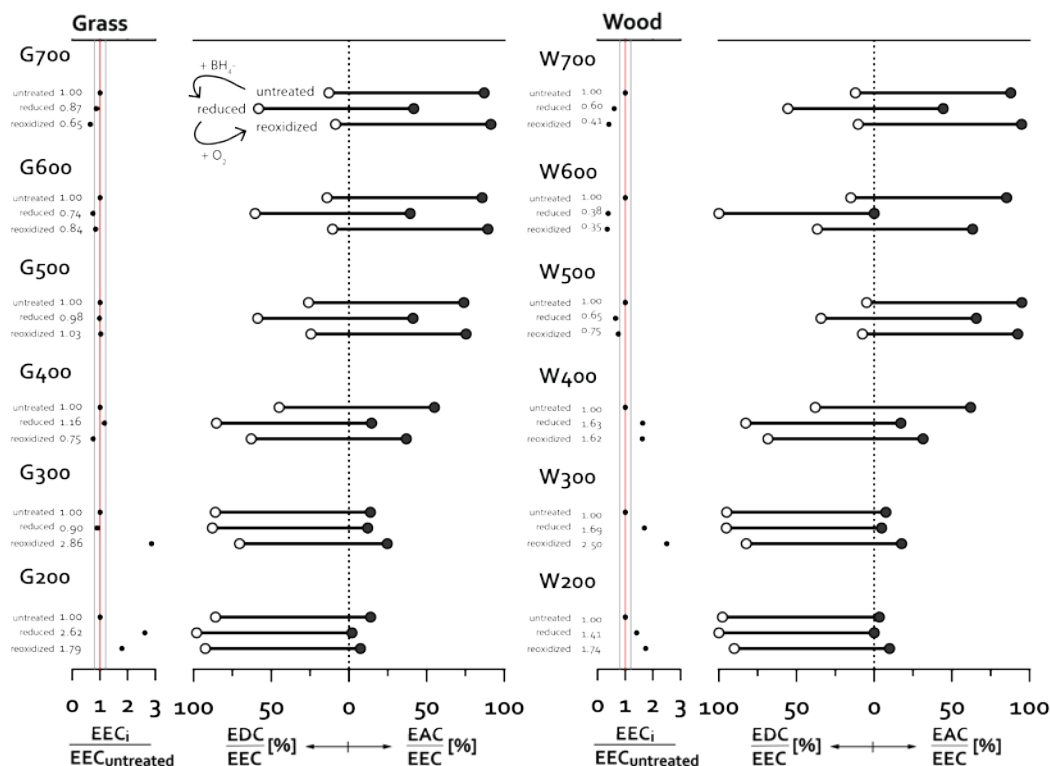
312 **Figure 2. a,b.** Changes in the electron accepting capacities (EACs) (black solid
 313 symbols), electron donating capacities (EDCs) (grey open symbols), and the electron
 314 exchange capacities (EECs) (black bars) as a function of the heat treatment
 315 temperature (HTT) for the thermosequence chars prepared from grass (GX) and wood
 316 (WX), where X denotes the charring temperature in °C. The corresponding carbon-
 317 normalized EAC, EDC, and EEC values are provided in the SI. **c,d.** Changes in the
 318 relative contributions of EAC and EDC values to the total EEC values as a function
 319 of HTT (grey and black lines and symbols) and changes in the average carbon
 320 oxidation states, C_{ox}, with HTT (green crosses and dashed lines). Error bars in all
 321 panels represent standard deviations from triplicate electrochemical analyses. EAC
 322 and EDC values normalized to ash-content corrected char mass and to g C are shown
 323 in **Figure S2**.

324 *Effects of charring conditions on char redox properties.* To assess pyrolysis
325 effects other than HTT on the redox properties of chars, we quantified the EAC and
326 EDC values of an additional six chars formed at HTT of 400/450° C and 700°C and
327 from different feedstock. **Figure S3** shows that the six additional chars also accepted
328 and donated electrons under the used electrochemical conditions, suggesting that the
329 presence of reducible and oxidizable moieties is a common feature of chars. At the
330 same time, chars formed under comparable HTT exhibited a large range in EEC
331 values (i.e., from EEC= 0.34 mmole-/g for DF400 to 2.28 mmole-/g for CW450).
332 RS450 and CW450, which showed the highest EEC values of all tested chars, were
333 both pyrolysed significantly longer (5h for RS450 and CW450) than the other chars
334 tested (e.g., 1h for the thermosequences). **Figure S3** also shows large differences in
335 the EEC values of chars produced at comparable HTT and from similar feedstock but
336 in different pyrolysis systems (e.g., wood as feedstock in CW450 and W450). These
337 findings suggest that factors other than HTT and feedstock have large effects on the
338 redox properties of the chars. These factors may include feedstock processing prior to
339 pyrolysis, the rate and extent of oxygen supply during charring, and the exposure
340 time at a given HTT.^{76,77}

341 *Reversibility of electron transfer to chars.* We separately assessed the
342 reversibility of electron transfer to the chars by quantifying their changes in EAC and
343 EDC over a borohydride reduction and O₂-reoxidation cycle. We chose BH₄⁻ as the
344 chemical reductant because it reduces quinones to hydroquinones (i.e., ketones and
345 aldehydes to alcohols),^{78,79} it was previously used to reduce electron accepting
346 moieties in carbon blacks⁶² and natural organic matter,^{80,81} and it is oxidized to
347 borate,⁷⁸ which is electro-inactive in the subsequent mediated electrochemical

348 analysis and therefore does not interfere with the EAC and EDC measurements of the
349 chars.

350 The EAC, EDC, and the corresponding EEC values for all untreated, reduced, and
351 re-oxidized chars are provided in **Table S4**. The EEC values of the low-HTT chars
352 (i.e., G200, G300, W200, W300, and W400) increased during the redox cycling. This
353 increase is shown in **Figure 3** as the ratio of the EEC values of the untreated,
354 reduced, and re-oxidized specimen to the (original) EEC of the untreated specimen.
355 The relative increases rather than the absolute increases in EEC are shown in the
356 Figure to aid comparisons among the different chars. The increases in EEC values in
357 the low-HTT chars were mainly caused by an increase in the EDC values (**Table S4**),
358 suggesting that new electron donating moieties were formed. It is possible that the pH
359 increase during BH_4^- treatment resulted in reactions of OH^- with activated aromatic
360 moieties in the chars, leading to the formation of new electron-donating phenolic
361 moieties. However, even though the EEC values of the low-HTT chars increased,
362 they remained smaller than the EEC values of chars formed at $\text{HTTs} \geq 400^\circ\text{C}$. As
363 compared to the low HTT chars, redox cycling had a much smaller effect on the
364 absolute EEC values of the chars formed at intermediate HTT of 400 to 550 °C
365 (shown for both thermosequences in **Figure 3** and for HZ400, HZ550, DF400,
366 RS450, and CW450 in **Figure S4**). The small changes in the EECs of these chars
367 demonstrate that the chemical reduction and O_2 re-oxidation steps had little effects on
368 the total number of redox-active moieties in these chars. Finally, redox cycling
369 resulted in a decrease in the EEC values of the high HTT-chars ($\text{HTT} \geq 600^\circ\text{C}$), as
370 shown for G600, G700, W600, and W700 in **Figure 3** and for DF700, and HZ700 in
371 **Figure S4**.



372
373

374 **Figure 3.** Changes in the electron exchange capacities (EECs), electron accepting
 375 capacities (EACs) and electron donating capacities (EDCs) of the grass (G) and wood
 376 (W) thermosequence chars during redox cycling. Changes in the EECs during redox
 377 cycling are expressed relative to the EEC of the untreated chars (i.e., $EEC_i/EEC_{untreated}$
 378 where i corresponds to the untreated, the borohydride (BH_4^-)-reduced and the O_2
 379 re-oxidized char specimen). The $EEC_i/EEC_{untreated}$ values are shown both in numbers and
 380 as black dots on the left of each thermosequence. The red line corresponds to
 381 $EEC_i/EEC_{untreated}$ of 1, and the outer lines correspond to ratios of 0.8 and 1.2 (i.e.,
 382 deviations of 20% from the initial EECs). Changes in the relative redox states of the
 383 char specimen are expressed as the relative contributions of EAC and EDC values to
 384 the total EEC value of each sample (i.e., EAC/EEC and EDC/EEC).
 385

386 Because redox cycling altered the total number of redox active moieties of some
 387 chars, it is difficult to use absolute EAC and EDC values to assess the effects of
 388 redox cycling on the redox states of the chars. Changes in the redox states are more
 389 apparent when comparing the relative contributions of EAC and EDC to the total
 390 EEC value of the untreated, reduced, and re-oxidized chars: the EAC/EEC and
 391 EDC/EEC ratios are direct measures of the relative extents of reduction and oxidation
 392 of the char specimen, respectively. **Figures 3** and **S4** show that BH_4^- -treatments

393 decreased the EAC/EEC and increased the EDC/EEC ratios of all tested chars,
394 consistent with the reduction of the electron accepting moieties in the chars.
395 Subsequent O₂-exposure of the reduced chars resulted in their re-oxidation, as
396 evidenced by increasing EAC/EEC and decreasing EDC/EEC ratios. The finding that
397 the redox states of all chars responded to changes in the external redox conditions
398 demonstrates that chars may act as redox buffers. Furthermore, electron transfer to
399 and from the intermediate-HTT chars was also largely reversible, as evidenced from
400 only small variations in their EEC values over the reduction and re-oxidation cycle.

401 *Nature of redox-active moieties in the chars.* In principle, the redox properties of
402 chars may originate from both organic and inorganic constituents. To assess possible
403 contributions of redox active metal species, we quantified Fe and Mn contents in the
404 thermosequence chars by acid digestion and subsequent ICP-OES analysis. The Fe
405 and Mn contents of all thermosequence chars were too small to explain the measured
406 EEC values (**Table S5**). Consequently, organic electron accepting and donating
407 moieties dominated the char redox capacities.

408 There are two possible explanations for the pronounced increase in the EEC values
409 from the low to the intermediate-HTT chars (i.e., 200 & 300°C versus 400 & 500°C):
410 either redox-active organic moieties present in the feedstock (and the low-HTT chars)
411 were accumulated relative to other constituents during charring with increasing HTT
412 or new redox-active moieties were formed in the charring process. We evaluated
413 these two possibilities by relating the changes in EEC values to the respective
414 charring yields (**Table S6**). As detailed in the Supporting Information, this analysis
415 revealed that the EEC increases from low to intermediate-HTT chars were too large
416 to be explained by a relative accumulation of redox active groups. The EEC increases
417 with increasing HTT therefore had to result from neoformation of a large number of

418 electron accepting moieties, which was partly counterbalanced by a decrease in the
419 number of electron donating moieties (as detailed in the Supporting Information).

420 The neoformation of electron accepting moieties is directly supported by an
421 increase in the average carbon oxidation state, C_{ox} , from the low to intermediate-HTT
422 chars that paralleled the increase in the EAC/EEC ratio of these chars (**Figure 2 c,d**).

423 C_{ox} was calculated as

$$424 \quad C_{ox} = \frac{2[O]-[H]-k[N]-m[S]}{[C]} \approx \frac{2[O]-[H]-k[N]}{[C]} \quad \text{Eq. 2}$$

425 where [Y] is the content of element Y in the char [$\text{mmol Y (g}_{\text{char}})^{-1}$] (**Table 1**), and
426 k and m are stoichiometric factors that depend on the oxidation states of N and S in
427 the char.⁷⁴ Assuming small sulfur contents, C_{ox} was estimated by the right term in Eq.
428 2. Varying k between the extreme values of +5 and -3 for fully oxidized and reduced
429 N, respectively, resulted in slight changes in the C_{ox} values for the grass but not for
430 the wood thermosequence chars (**Figure S5**). More importantly, however, variations
431 in k did not affect the overall trend of increasing C_{ox} of the chars from both
432 thermosequences with increasing HTT. **Figure 2c,d** shows that the carbon in the low
433 HTT-chars was most reduced (i.e., C_{ox} was most negative with -0.5 and -0.38 for
434 G300 and W200, respectively), consistent with the prevalence of electron donating
435 (i.e., reducing) moieties. We note that C_{ox} for the low HTT-chars was similar to
436 values calculated for lignin (i.e., -0.41, based on published sum formulas for lignin⁸²).

437 The intermediate HTT-chars showed a much higher accepting than donating capacity,
438 consistent with the more oxidized carbon (i.e., less negative C_{ox} values) in these
439 chars. C_{ox} values gradually increased with HTT to the highest values of -0.14 and -
440 0.11 for G700 and W700, respectively, and therefore approached $C_{ox} = 0$, the
441 expected value for chars composed of only carbon in condensed aromatic sheets.

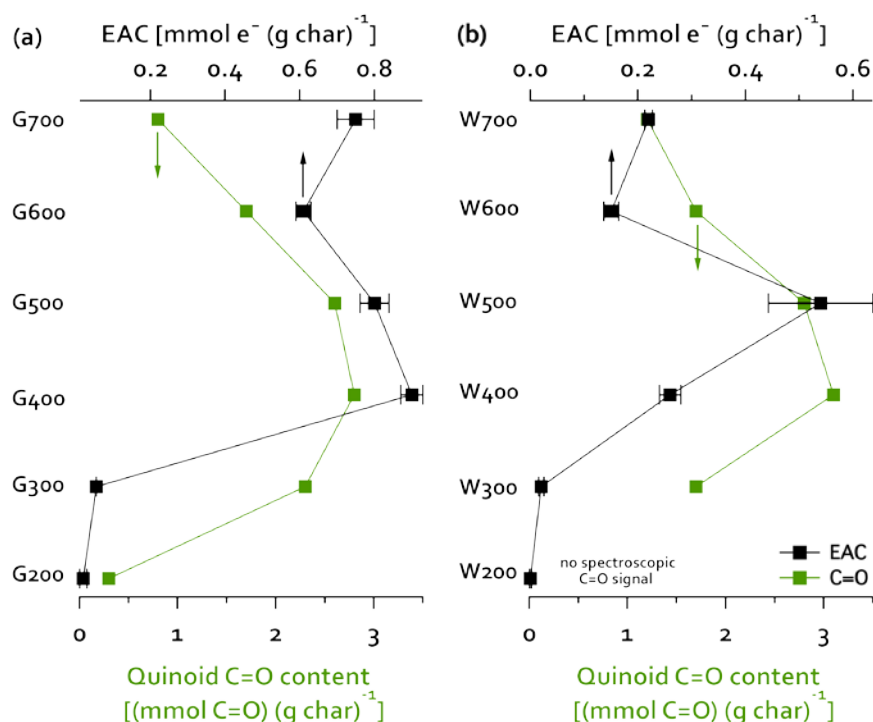
442 As detailed in the following, we propose that the pool of redox-active moieties
443 was dominated by electron-donating, phenolic moieties in the low-HTT chars, by
444 newly-formed electron accepting quinone moieties in intermediate-HTT chars, and
445 by electron accepting quinones and possibly condensed aromatics in the high-HTT
446 chars. A plausibility analysis revealed that O was sufficiently abundant in the
447 thermosequence chars to account for the measured EAC and EDC values: assuming
448 that all redox active moieties contained oxygen, as is the case for quinones and
449 phenols, the fraction of O that had to be electroactive ranged between 0.1 - 33% for
450 the EAC and 0.4-6.7% for the EDC of the grass thermosequence chars and between 0
451 - 6% for the EAC and 0.3 - 1.5% for the EDC of the wood thermosequence chars
452 (**Figure S6**).

453 A predominance of phenolic, electron-donating moieties in the low-HTT chars is
454 consistent with these materials being composed of only slightly processed
455 constituents of the feedstock, including lignin, cellulose, and hemicellulose. Lignin is
456 a polyphenolic macromolecule characterized by high EDC and low EAC values, as
457 demonstrated by MER and MEO measurements (**Figure S7**). The redox capacities of
458 lignin agree with the EDC and EAC values in the low-HTT chars. The higher lignin
459 content in wood than grass^{83,84} may explain the slightly larger EDC values of W200
460 than G200. We note that cellulose showed only very small current responses in MER
461 and is not electroactive in MEO (**Figure S7**).

462 Intermediate HTT of 400-500°C yield pyrogenic amorphous grass and wood chars
463 which are composed of lignin- and cellulose derived transformation products.³⁶ While
464 the O contents decrease from low to intermediate-HTT grass and wood chars, the
465 intermediate HTT-chars have higher quinoid C=O contents (**Table 1, Figure 4**).
466 These contents were estimated from C 1s NEXAFS spectra of the thermosequence

467 chars reported in ref. 36, as detailed in the Supporting Information. The higher
 468 quinoid C=O contents support quinone moieties as major electron acceptors in the
 469 intermediate HTT-chars. A predominance of quinones in these materials is consistent
 470 with their reversible electron transfer behavior (**Figure 3**).

471 HTTs of 600 and 700°C further decreased the absolute O contents of the grass and
 472 wood chars (**Table 1**). More importantly, the quinoid C=O contents also decreased
 473 from intermediate to high HTT. **Figure 4** shows strikingly similar trends of both
 474 EAC values and the quinoid C=O contents with HTT: both properties had maxima at
 475 intermediate HTTs (around 400 to 500 °C).



476

477 **Figure 4.** Effect of the heat treatment temperature (HTT) on the estimated quinoid
 478 C=O contents, determined from C=O absorption peaks in C 1s NEXAFS spectra
 479 from reference³⁶ (green, lower x-axis) and the electron accepting capacities (EACs;
 480 black, upper x-axis) for grass (G; panel a) and wood (W; panel b) thermosequence
 481 chars. Quinoid C=O content and EAC show comparable trends with HTT.

482

483 The ratios of the EAC to the estimated quinoid C=O contents increased with
 484 increasing HTT from 0.2 and 0.1 mol e⁻ (mol C=O)⁻¹ for G300 and for W300,

485 respectively, to 0.94 and 0.19 mol e⁻ (mol C=O)⁻¹ for the G700 and W500
486 thermosequence chars (**Figure S8**). This suggests that quinone moieties were
487 sufficiently abundant to explain the measured EAC values. The combined
488 electrochemical and spectroscopic data therefore strongly support quinones as major
489 electron accepting moieties.

490 The high ratios of EAC to quinoid C=O contents for the high HTT chars (and
491 particularly a ratio of close to unity for G700) may signify an increasing contribution
492 of non-quinoid structures, such as conjugated Π -electron systems, to the EAC with
493 increasing HTT. The formation of polycondensed aromatic structures at high HTT is
494 supported by increasing double bond equivalents, DBE, and the aromaticity index
495 values, AI, from the intermediate to high-HTT chars (**Figure S9**). The DBE and AI
496 values are estimates of char aromaticity and were calculated from the elemental
497 composition data of the chars (Supporting Information). Compared to the DBE, the
498 AI is a more conservative estimate for aromaticity as it accounts for the fact that
499 double bonds of heteroatoms do not necessarily contribute to aromaticity, ring
500 formation or condensation.⁷⁵ The high-HTT chars have AI values above the
501 condensation threshold of AI= 0.67, and therefore must contain condensed aromatic
502 structures. Such aromatic clusters were previously reported for a 700°C char.⁵⁸

503

504 **Implications**

505 The results of this work suggest that redox-activity is a general functionality of
506 chars and that chars may be more important as redox-active organic phases in the
507 environment than previously recognized. There are both fundamental biogeochemical
508 and applied engineering implications of this insight. Given that chars are redox
509 active, they are immediate candidates for environmental engineering applications that

510 require or involve controlled and catalytic transfers of electrons. Such applications
511 include reductive pollutant transformations in sediments and the mitigation of nitrous
512 oxide emissions from soils. Of particular interest is the possibility to adjust the
513 electrochemical properties of chars for very specific applications through the choice
514 of pyrolysis conditions (HTT controlling the absolute magnitude of EEC) and
515 feedstock. HTT may be varied to engineer chars that favor either conductance via
516 sheets or redox buffering by quinone/hydroquinone functionalities.

517 The electrochemical properties of chars may further have consequences in a
518 broader biogeochemical context. For example, the presence of char black carbon in
519 many sediments^{7,8} raises the question as to whether microbes in these systems can use
520 chars as terminal electron acceptors in anaerobic respiration. A particularly intriguing
521 consequence of our findings pertains to the fundamental question why natural organic
522 matter around the globe is so good at 'shuttling' electrons.⁸⁵⁻⁸⁷ Our results raise the
523 question whether "humic substances" typically employed as proxies in investigations
524 of electron shuttling phenomena may have developed this capacity not as a result of
525 what used to be called "humification" processes,⁸⁸ but because the operational humic
526 extraction procedure includes significant proportions of electrochemically active char
527 components.

528 Our work clearly demonstrates that chars are electroactive in a quantitatively
529 meaningful dimension. This evidence can be combined with the insight that char
530 admixtures are ubiquitous in soil ecosystems worldwide (e.g.,⁸⁹⁻⁹¹). More support for
531 a general contribution of char constituents to the electrochemistry of natural organic
532 matter comes from our observation that the charring temperatures of 400-500°C, that
533 resulted in chars with the highest redox capacities, corresponded to temperatures
534 reported for biomass burning in wildfires.^{92,93} Roden et al.⁴³ used electron energy-

535 loss spectroscopy to demonstrate that electron shuttling 'solid-phase humic
536 substances' were almost purely aromatic – a molecular property that is hard to
537 rationalize as the result of hypothetical, biotic or abiotic "humification" processes.
538 Admittedly, quinones, phenazines and other electron shuttling moieties may originate
539 from diverse sources. While engineering applications for electrochemically active
540 chars and their residues appear to be obvious, our results also strongly suggest chars
541 may play a larger role in biogeochemically relevant electron transfer reactions than
542 previously recognized.

543 **Associated content**

544 *Supporting information.* This material is available free of charge via the Internet at
545 <http://pubs.acs.org>.

546 **Author information**

547 *Corresponding author.*

548 Michael Sander

549 **Acknowledgements.** LK and MS thank the Swiss National Science Foundation for
550 funding (Project 200021_135515) and Samuel Abiven for helpful comments. Markus
551 K. was partially supported by a research fellowship from the Institute of Soil
552 Landscape Research, Leibniz-Center for Agricultural Landscape Research (ZALF),
553 15374 Müncheberg, Germany

554

555 **References**

- 556 1. Schmidt, M. W. I.; Noack, A. G.; Black carbon in soils and sediments:
557 Analysis, distribution, implications, and current challenges. *Global Biogeochemical*
558 *Cycles* **2000**, *14*, (3), 777-793.
- 559 2. Dickens, A. F.; Gelinas, Y.; Masiello, C. A.; Wakeham, S.; Hedges, J. I.;
560 Reburial of fossil organic carbon in marine sediments. *Nature* **2004**, *427*, (6972),
561 336-339.
- 562 3. Kuhlbusch, T. A. J.; Black carbon and the carbon cycle. *Science* **1998**, *280*,
563 (5371), 1903-1904.

- 564 4. Masiello, C. A.; New directions in black carbon organic geochemistry.
565 *Marine Chemistry* **2004**, *92*, (1-4), 201-213.
- 566 5. Masiello, C. A.; Druffel, E. R. M.; Black carbon in deep-sea sediments.
567 *Science* **1998**, *280*, (5371), 1911-1913.
- 568 6. Schmidt, M. W. I.; Biogeochemistry - Carbon budget in the black. *Nature*
569 **2004**, *427*, (6972), 305-+.
- 570 7. Middelburg, J. J.; Nieuwenhuize, J.; van Breugel, P.; Black carbon in marine
571 sediments. *Marine Chemistry* **1999**, *65*, (3-4), 245-252.
- 572 8. Gustafsson, O.; Gschwend, P. M.; The flux of black carbon to surface
573 sediments on the New England continental shelf. *Geochimica Et Cosmochimica Acta*
574 **1998**, *62*, (3), 465-472.
- 575 9. Kuzyakov, Y.; Subbotina, I.; Chen, H. Q.; Bogomolova, I.; Xu, X. L.; Black
576 carbon decomposition and incorporation into soil microbial biomass estimated by C-
577 14 labeling. *Soil Biology & Biochemistry* **2009**, *41*, (2), 210-219.
- 578 10. Liang, B.; Lehmann, J.; Solomon, D.; Sohi, S.; Thies, J. E.; Skjemstad, J. O.;
579 Luizao, F. J.; Engelhard, M. H.; Neves, E. G.; Wirrick, S.; Stability of biomass-
580 derived black carbon in soils. *Geochimica Et Cosmochimica Acta* **2008**, *72*, (24),
581 6069-6078.
- 582 11. Skjemstad, J. O.; Taylor, J. A.; Smernik, R. J.; Estimation of charcoal (char)
583 in soils. *Communications in Soil Science and Plant Analysis* **1999**, *30*, (15-16), 2283-
584 2298.
- 585 12. Sander, M.; Pignatello, J. J.; Characterization of charcoal adsorption sites for
586 aromatic compounds: Insights drawn from single-solute and Bi-solute competitive
587 experiments. *Environmental Science & Technology* **2005**, *39*, (6), 1606-1615.
- 588 13. Accardi-Dey, A.; Gschwend, P. M.; Reinterpreting literature sorption data
589 considering both absorption into organic carbon and adsorption onto black carbon.
590 *Environmental Science & Technology* **2003**, *37*, (1), 99-106.
- 591 14. Allen-King, R. M.; Grathwohl, P.; Ball, W. P.; New modeling paradigms for
592 the sorption of hydrophobic organic chemicals to heterogeneous carbonaceous matter
593 in soils, sediments, and rocks. *Advances in Water Resources* **2002**, *25*, (8-12), 985-
594 1016.
- 595 15. Gustafsson, O.; Haghseta, F.; Chan, C.; MacFarlane, J.; Gschwend, P. M.;
596 Quantification of the dilute sedimentary soot phase: Implications for PAH speciation
597 and bioavailability. *Environmental Science & Technology* **1997**, *31*, (1), 203-209.
- 598 16. Koelmans, A. A.; Jonker, M. T. O.; Cornelissen, G.; Bucheli, T. D.; Van
599 Noort, P. C. M.; Gustafsson, O.; Black carbon: The reverse of its dark side.
600 *Chemosphere* **2006**, *63*, (3), 365-377.
- 601 17. Cornelissen, G.; Haftka, J.; Parsons, J.; Gustafsson, O.; Sorption to black
602 carbon of organic compounds with varying polarity and planarity. *Environmental*
603 *Science & Technology* **2005**, *39*, (10), 3688-3694.
- 604 18. Cornelissen, G.; Gustafsson, O.; Bucheli, T. D.; Jonker, M. T. O.; Koelmans,
605 A. A.; Van Noort, P. C. M.; Extensive sorption of organic compounds to black
606 carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for
607 distribution, bioaccumulation, and biodegradation. *Environmental Science &*
608 *Technology* **2005**, *39*, (18), 6881-6895.
- 609 19. Beesley, L.; Marmiroli, M.; The immobilisation and retention of soluble
610 arsenic, cadmium and zinc by biochar. *Environmental Pollution* **2011**, *159*, (2), 474-
611 480.

- 612 20. Uchimiya, M.; Klasson, K. T.; Wartelle, L. H.; Lima, I. M.; Influence of soil
613 properties on heavy metal sequestration by biochar amendment: 1. Copper sorption
614 isotherms and the release of cations. *Chemosphere* **2011**, *82*, (10), 1431-1437.
- 615 21. Beesley, L.; Moreno-Jimenez, E.; Gomez-Eyles, J. L.; Harris, E.; Robinson,
616 B.; Sizmur, T.; A review of biochars' potential role in the remediation, revegetation
617 and restoration of contaminated soils. *Environmental Pollution* **2011**, *159*, (12),
618 3269-3282.
- 619 22. Choppala, G. K.; Bolan, N. S.; Megharaj, M.; Chen, Z.; Naidu, R.; The
620 Influence of Biochar and Black Carbon on Reduction and Bioavailability of
621 Chromate in Soils. *Journal of Environmental Quality* **2012**, *41*, (4), 1175-1184.
- 622 23. Park, J. H.; Choppala, G. K.; Bolan, N. S.; Chung, J. W.; Chuasavathi, T.;
623 Biochar reduces the bioavailability and phytotoxicity of heavy metals. *Plant and Soil*
624 **2011**, *348*, (1-2), 439-451.
- 625 24. Joseph, S. D.; Camps-Arbestain, M.; Lin, Y.; Munroe, P.; Chia, C. H.; Hook,
626 J.; van Zwieten, L.; Kimber, S.; Cowie, A.; Singh, B. P.; Lehmann, J.; Foidl, N.;
627 Smernik, R. J.; Amonette, J. E.; An investigation into the reactions of biochar in soil.
628 *Australian Journal of Soil Research* **2010**, *48*, (6-7), 501-515.
- 629 25. Mochidzuki, K.; Soutric, F.; Tadokoro, K.; Antal, M. J.; Toth, M.; Zelei, B.;
630 Varhegyi, G.; Electrical and physical properties of carbonized charcoals. *Industrial &*
631 *Engineering Chemistry Research* **2003**, *42*, (21), 5140-5151.
- 632 26. Kemper, J. M.; Ammar, E.; Mitch, W. A.; Abiotic degradation of hexahydro-
633 1,3,5-trinitro-1,3,5-triazine in the presence of hydrogen sulfide and black carbon.
634 *Environmental Science & Technology* **2008**, *42*, (6), 2118-2123.
- 635 27. Xu, W. Q.; Dana, K. E.; Mitch, W. A.; Black Carbon-Mediated Destruction of
636 Nitroglycerin and RDX By Hydrogen Sulfide. *Environmental Science & Technology*
637 **2010**, *44*, (16), 6409-6415.
- 638 28. Yu, X. D.; Gong, W. W.; Liu, X. H.; Shi, L.; Han, X.; Bao, H. Y.; The use of
639 carbon black to catalyze the reduction of nitrobenzenes by sulfides. *Journal of*
640 *Hazardous Materials* **2011**, *198*, 340-346.
- 641 29. Oh, S. Y.; Son, J. G.; Lim, O. T.; Chiu, P. C.; The role of black carbon as a
642 catalyst for environmental redox transformation. *Environmental Geochemistry and*
643 *Health* **2012**, *34*, 105-113.
- 644 30. Oh, S. Y.; Son, J. G.; Chiu, P. C.; Biochar-mediated reductive transformation
645 of nitro herbicides and explosives. *Environmental Toxicology and Chemistry* **2013**,
646 *32*, (3), 501-508.
- 647 31. Oh, S. Y.; Son, J. G.; Hur, S. H.; Chung, J. S.; Chiu, P. C.; Black Carbon-
648 Mediated Reduction of 2,4-Dinitrotoluene by Dithiothreitol. *Journal of*
649 *Environmental Quality* **2013**, *42*, (3), 815-821.
- 650 32. Xu, W. Q.; Pignatello, J. J.; Mitch, W. A.; Role of Black Carbon Electrical
651 Conductivity in Mediating Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
652 Transformation on Carbon Surfaces by Sulfides. *Environmental Science &*
653 *Technology* **2013**, *47*, (13), 7129-7136.
- 654 33. Cayuela, M. L.; Sanchez-Monedero, M. A.; Roig, A.; Hanley, K.; Enders, A.;
655 Lehmann, J.; Biochar and denitrification in soils: when, how much and why does
656 biochar reduce N₂O emissions? *Scientific Reports* **2013**, *3*.
- 657 34. Harter, J.; Krause, H.-M.; Schuettler, S.; Ruser, R.; Fromme, M.; Scholten, T.;
658 Kappler, A.; Behrens, S.; Linking N₂O emissions from biochar-amended soil to the
659 structure and function of the N-cycling microbial community. *The ISME Journal*
660 **2013**, 1-15.

- 661 35. Cayuela, M. L.; van Zwieten, L.; Singh, B. P.; Jeffery, S.; Roig, A.; Sánchez-
662 Monedero, M. A.; Biochar's role in mitigating soil nitrous oxide emissions: A review
663 and meta-analysis. *Agriculture, Ecosystems and Environment* **2013**.
- 664 36. Keiluweit, M.; Nico, P. S.; Johnson, M. G.; Kleber, M.; Dynamic molecular
665 structure of plant biomass-derived black carbon (biochar). *Environmental Science &*
666 *Technology* **2010**, *44*, (4), 1247-1253.
- 667 37. Heymann, K.; Lehmann, J.; Solomon, D.; Schmidt, M. W. I.; Regier, T.; C 1s
668 K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy for
669 characterizing functional group chemistry of black carbon. *Organic Geochemistry*
670 **2011**, *42*, (9), 1055-1064.
- 671 38. Emmerich, F. G.; Rettori, C.; Luengo, C. A.; ESR in heat treated carbons
672 from the endocarp of babassu coconut. *Carbon* **1991**, *29*, (3), 305-311.
- 673 39. Scott, D. T.; McKnight, D. M.; Blunt-Harris, E. L.; Kolesar, S. E.; Lovley, D.
674 R.; Quinone moieties act as electron acceptors in the reduction of humic substances
675 by humics-reducing microorganisms. *Environmental Science & Technology* **1998**, *32*,
676 (19), 2984-2989.
- 677 40. Aeschbacher, M.; Sander, M.; Schwarzenbach, R. P.; Novel electrochemical
678 approach to assess the redox properties of humic substances. *Environmental Science*
679 *& Technology* **2010**, *44*, (1), 87-93.
- 680 41. Aeschbacher, M.; Vergari, D.; Schwarzenbach, R. P.; Sander, M.;
681 Electrochemical Analysis of Proton and Electron Transfer Equilibria of the Reducible
682 Moieties in Humic Acids. *Environmental Science & Technology* **2011**, *45*, (19),
683 8385-8394.
- 684 42. Dunnivant, F. M.; Schwarzenbach, R. P.; Macalady, D. L.; Reduction of
685 substituted nitrobenzenes in aqueous solutions containing natural organic matter.
686 *Environmental Science & Technology* **1992**, *26*, (11), 2133-2141.
- 687 43. Roden, E. E.; Kappler, A.; Bauer, I.; Jiang, J.; Paul, A.; Stoesser, R.; Konishi,
688 H.; Xu, H. F.; Extracellular electron transfer through microbial reduction of solid-
689 phase humic substances. *Nature Geoscience* **2010**, *3*, (6), 417-421.
- 690 44. Zhang, C. F.; Katayama, A.; Humin as an Electron Mediator for Microbial
691 Reductive Dehalogenation. *Environmental Science & Technology* **2012**, *46*, (12),
692 6575-6583.
- 693 45. Matsumura, Y.; Hagiwara, S.; Takahashi, H.; Automated potentiometric
694 titration of surface acidity of carbon black. *Carbon* **1976**, *14*, (3), 163-167.
- 695 46. Garten, V. A.; Weiss, D. E.; The quinone-hydroquinone character of activated
696 carbon and carbon black. *Australian Journal of Chemistry* **1955**, *8*, (1), 68-95.
- 697 47. Tarasevich, M. R.; Bogdanovskaya, V. A.; Zagudaeva, N. M.; Redox
698 reactions of quinones on carbon materials. *Journal of Electroanalytical Chemistry*
699 **1987**, *223*, (1-2), 161-169.
- 700 48. Studebaker, M. L.; Huffman, E. W. D.; Wolfe, A. C.; Nabors, L. G.; Oxygen-
701 containing groups on the surface of carbon black. *Industrial and Engineering*
702 *Chemistry* **1956**, *48*, (1), 162-166.
- 703 49. Langley, L. A.; Fairbrother, D. H.; Effect of wet chemical treatments on the
704 distribution of surface oxides on carbonaceous materials. *Carbon* **2007**, *45*, (1), 47-
705 54.
- 706 50. Kongkanand, A.; Kamat, P. V.; Interactions of single wall carbon nanotubes
707 with methyl viologen radicals. Quantitative estimation of stored electrons. *Journal of*
708 *Physical Chemistry C* **2007**, *111*, (26), 9012-9015.

- 709 51. Kongkanand, A.; Kamat, P. V.; Electron storage in single wall carbon
710 nanotubes. Fermi level equilibration in semiconductor-SWCNT suspensions. *Acs*
711 *Nano* **2007**, *1*, (1), 13-21.
- 712 52. Xie, Q. S.; Perezcordero, E.; Echegoyen, L.; Electrochemical detection of
713 C60- and C70- - Enhanced stability of fullerenes in solution. *Journal of the*
714 *American Chemical Society* **1992**, *114*, (10), 3978-3980.
- 715 53. Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J.; Electrochemical
716 detection of fullerene and highly reduced fullerene (C₆₀(5-)) ions in solution.
717 *Journal of the American Chemical Society* **1991**, *113*, (20), 7773-7774.
- 718 54. Krishnamurthy, S.; Lightcap, I. V.; Kamat, P. V.; Electron transfer between
719 methyl viologen radicals and graphene oxide: Reduction, electron storage and
720 discharge. *Journal of Photochemistry and Photobiology a-Chemistry* **2011**, *221*, (2-
721 3), 214-219.
- 722 55. Lightcap, I. V.; Kosel, T. H.; Kamat, P. V.; Anchoring Semiconductor and
723 Metal Nanoparticles on a Two-Dimensional Catalyst Mat. Storing and Shuttling
724 Electrons with Reduced Graphene Oxide. *Nano Letters* **2010**, *10*, (2), 577-583.
- 725 56. McBeath, A. V.; Smernik, R. J.; Variation in the degree of aromatic
726 condensation of chars. *Organic Geochemistry* **2009**, *40*, (12), 1161-1168.
- 727 57. McBeath, A. V.; Smernik, R. J.; Schneider, M. P. W.; Schmidt, M. W. I.;
728 Plant, E. L.; Determination of the aromaticity and the degree of aromatic
729 condensation of a thermosequence of wood charcoal using NMR. *Organic*
730 *Geochemistry* **2011**, *42*, (10), 1194-1202.
- 731 58. Cao, X. Y.; Pignatello, J. J.; Li, Y.; Lattao, C.; Chappell, M. A.; Chen, N.;
732 Miller, L. F.; Mao, J. D.; Characterization of Wood Chars Produced at Different
733 Temperatures Using Advanced Solid-State C-13 NMR Spectroscopic Techniques.
734 *Energy & Fuels* **2012**, *26*, (9), 5983-5991.
- 735 59. Nishimiya, K.; Hata, T.; Imamura, Y.; Ishihara, S.; Analysis of chemical
736 structure of wood charcoal by X-ray photoelectron spectroscopy. *Journal of Wood*
737 *Science* **1998**, *44*, (1), 56-61.
- 738 60. Rhim, Y.-R.; Zhang, D.; Fairbrother, D. H.; Wepasnick, K. A.; Livi, K. J.;
739 Bodnar, R. J.; Nagle, D. C.; Changes in electrical and microstructural properties of
740 microcrystalline cellulose as function of carbonization temperature. *Carbon* **2010**, *48*,
741 (4), 1012-1024.
- 742 61. Bauer, M.; Heitmann, T.; Macalady, D. L.; Blodau, C.; Electron transfer
743 capacities and reaction kinetics of peat dissolved organic matter. *Environmental*
744 *Science & Technology* **2007**, *41*, (1), 139-145.
- 745 62. Matsumura, Y.; Takahashi, H.; Potentiometric redox titration of quinone in
746 carbon black with NaBH₄ and I₂. *Carbon* **1979**, *17*, (2), 109-114.
- 747 63. Peretyazhko, T.; Sposito, G.; Reducing capacity of terrestrial humic acids.
748 *Geoderma* **2006**, *137*, (1-2), 140-146.
- 749 64. Struyk, Z.; Sposito, G.; Redox properties of standard humic acids. *Geoderma*
750 **2001**, *102*, (3-4), 329-346.
- 751 65. Graber, E. R.; Tschansky, L.; Cohen, E.; Reducing capacity of water extracts
752 of biochars and their solubilization of soil Mn and Fe. *European Journal of Soil*
753 *Science* **2013**, *asap*.
- 754 66. Aeschbacher, M.; Graf, C.; Schwarzenbach, R. P.; Sander, M.; Antioxidant
755 Properties of Humic Substances. *Environmental Science & Technology* **2012**, *46*, (9),
756 4916-4925.
- 757 67. Gorski, C. A.; Aeschbacher, M.; Soltermann, D.; Voegelin, A.; Baeyens, B.;
758 Fernandes, M. M.; Hofstetter, T. B.; Sander, M.; Redox Properties of Structural Fe in

759 Clay Minerals. 1. Electrochemical Quantification of Electron-Donating and -
760 Accepting Capacities of Smectites. *Environmental Science & Technology* **2012**, *46*,
761 (17), 9360-9368.

762 68. Gorski, C. A.; Klupfel, L.; Voegelin, A.; Sander, M.; Hofstetter, T. B.; Redox
763 Properties of Structural Fe in Clay Minerals. 2. Electrochemical and Spectroscopic
764 Characterization of Electron Transfer Irreversibility in Ferruginous Smectite, SWa-1.
765 *Environmental Science & Technology* **2012**, *46*, (17), 9369-9377.

766 69. Gorski, C. A.; Kluepfel, L.; Voegelin, A.; Sander, M.; Hofstetter, T. B.;
767 Redox properties of structural Fe in clay minerals: 3. Relationships between smectite
768 redox and structural properties. *Environmental Science & Technology* **2013**, *47*, (23),
769 13477-13485.

770 70. Fulton, W.; Gray, M.; Prah, F.; Kleber, M.; A simple technique to eliminate
771 ethylene emissions from biochar amendment in agriculture. *Agronomy for*
772 *Sustainable Development* **2013**, *33*, (3), 469-474.

773 71. Kaal, J.; Schneider, M. P. W.; Schmidt, M. W. I.; Rapid molecular screening
774 of black carbon (biochar) thermosequences obtained from chestnut wood and rice
775 straw: A pyrolysis-GC/MS study. *Biomass and Bioenergy* **2012**, *45*, (C), 115-129.

776 72. Hammes, K.; Smernik, R. J.; Skjemstad, J. O.; Herzog, A.; Vogt, U. F.;
777 Schmidt, M. W. I.; Synthesis and characterisation of laboratory-charred grass straw
778 (*Oryza saliva*) and chestnut wood (*Castanea sativa*) as reference materials for black
779 carbon quantification. *Organic Geochemistry* **2006**, *37*, (11), 1629-1633.

780 73. Hammes, K.; Smernik, R. J.; Skjemstad, J. O.; Schmidt, M. W. I.;
781 Characterisation and evaluation of reference materials for black carbon analysis using
782 elemental composition, colour, BET surface area and C-13 NMR spectroscopy.
783 *Applied Geochemistry* **2008**, *23*, (8), 2113-2122.

784 74. Masiello, C. A.; Gallagher, M. E.; Randerson, J. T.; Deco, R. M.; Chadwick,
785 O. A.; Evaluating two experimental approaches for measuring ecosystem carbon
786 oxidation state and oxidative ratio. *Journal of Geophysical Research* **2008**, *113*, (G3),
787 G03010.

788 75. Koch, B. P.; Dittmar, T.; From mass to structure: an aromaticity index for
789 high-resolution mass data of natural organic matter. *Rapid Commun. Mass Spectrom.*
790 **2006**, *20*, (5), 926-932.

791 76. Soucemarianadin, L. N.; Quideau, S. A.; MacKenzie, M. D.; Bernard, G. M.;
792 Wasylshen, R. E.; Laboratory charring conditions affect black carbon properties: A
793 case study from Quebec black spruce forests. *Organic Geochemistry* **2013**, *62*, 46-55.

794 77. Cantrell, K. B.; Hunt, P. G.; Uchimiya, M.; Novak, J. M.; Ro, K. S.; Impact of
795 pyrolysis temperature and manure source on physicochemical characteristics of
796 biochar. *Bioresource Technology* **2012**, *107*, 419-428.

797 78. Chaikin, S. W.; Brown, W. G.; Reduction of aldehydes, ketones and acid
798 chlorides by sodium borohydride. *Journal of the American Chemical Society* **1949**,
799 *71*, (1), 122-125.

800 79. Johnson, M. R.; Rickborn, B.; Sodium borohydride reduction of conjugated
801 aldehydes and ketones. *Journal of Organic Chemistry* **1970**, *35*, (4), 1041-&.

802 80. Ma, J. H.; Del Vecchio, R.; Golanoski, K. S.; Boyle, E. S.; Blough, N. V.;
803 Optical Properties of Humic Substances and CDOM: Effects of Borohydride
804 Reduction. *Environmental Science & Technology* **2010**, *44*, (14), 5395-5402.

805 81. Thorn, K. A.; Pettigrew, P. J.; Goldenberg, W. S.; Covalent binding of aniline
806 to humic substances .2. N-15 NMR studies of nucleophilic addition reactions.
807 *Environmental Science & Technology* **1996**, *30*, (9), 2764-2775.

- 808 82. Adler, E.; Lignin chemistry—past, present and future. *Wood Science and*
809 *Technology* **1977**, *11*, (3), 169-218.
- 810 83. Demirbaş, A.; Relationships between lignin contents and heating values of
811 biomass. *Energy conversion and management* **2001**, *42*, (2), 183-188.
- 812 84. Fahmi, R.; Bridgwater, A. V.; Darvell, L. I.; Jones, J. M.; Yates, N.; Thain, S.;
813 Donnison, I. S.; The effect of alkali metals on combustion and pyrolysis of Lolium
814 and Festuca grasses, switchgrass and willow. *Fuel* **2007**, *86*, (10-11), 1560-1569.
- 815 85. Lovley, D. R.; Coates, J. D.; BluntHarris, E. L.; Phillips, E. J. P.; Woodward,
816 J. C.; Humic substances as electron acceptors for microbial respiration. *Nature* **1996**,
817 *382*, (6590), 445-448.
- 818 86. Sposito, G., Electron Shuttling by Natural Organic Matter: Twenty Years
819 After. In *Aquatic Redox Chemistry*, Tratnyek, P. G.; Grundl, T. J.; Haderlein, S. B.,
820 Eds. 2011; Vol. 1071, pp 113-127.
- 821 87. Kluepfel, L.; Piepenbrock, A.; Kappler, A.; Sander, M.; Humic substances as
822 fully regenerable electron acceptors in recurrently anoxic environments. *Nature*
823 *Geoscience* **2014**, *accepted*.
- 824 88. Essington, M. E., *Soil and Water Chemistry: An Integrative Approach*. CRC
825 Press: 2003.
- 826 89. Skjemstad, J. O.; Reicosky, D. C.; Wilts, A. R.; McGowan, J. A.; Charcoal
827 carbon in US agricultural soils. *Soil Science Society of America Journal* **2002**, *66*, (4),
828 1249-1255.
- 829 90. Ohlson, M.; Dahlberg, B.; Okland, T.; Brown, K. J.; Halvorsen, R.; The
830 charcoal carbon pool in boreal forest soils. *Nature Geoscience* **2009**, *2*, (10), 692-695.
- 831 91. Rodionov, A.; Amelung, W.; Peinemann, N.; Haumaier, L.; Zhang, X. D.;
832 Kleber, M.; Glaser, B.; Urusevskaya, I.; Zech, W.; Black carbon in grassland
833 ecosystems of the world. *Global Biogeochemical Cycles* **2010**, *24*.
- 834 92. Alexis, M. A.; Rasse, D. P.; Rumpel, C.; Bardoux, G.; Péchot, N.; Schmalzer,
835 P.; Drake, B.; Mariotti, A.; Fire impact on C and N losses and charcoal production in
836 a scrub oak ecosystem. *Biogeochemistry* **2007**, *82*, (2), 201-216.
- 837 93. Gimeno-Garcia, E.; Andreu, V.; Rubio, J. L.; Spatial patterns of soil
838 temperatures during experimental fires. *Geoderma* **2003**, *118*, (1-2), 17-38.
- 839