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## Non-Hydroxyl Radical Species Production during Dark Air Oxidation of Alluvial Soils

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2 **Non-hydroxyl radical species production during dark air-**  
3 **oxidation of alluvial soils**  
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5

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7 Alliot<sup>3</sup>, Alexandre Gélabert<sup>4</sup>, Valentine Rollot<sup>4</sup>, Elodie Guigon<sup>3</sup>, Jessica Brest<sup>1</sup>, Sylvie Nélieu<sup>5</sup>,  
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23

24 **ABSTRACT**

25 Natural environments subjected to hydrologically-driven redox fluctuations are regarded as  
26 propitious to contaminant degradation since they favor cyclic oxygenation of Fe(II)-minerals that  
27 produces oxidizing reactive species, such as the hydroxyl radical, OH•. However, the identity of  
28 these reactive species may vary as a function of physicochemical conditions and is still a matter of  
29 research. Here, using spin-trapping electron paramagnetic resonance (EPR) with 5,5-dimethyl-1-  
30 pyrroline *N*-oxide (DMPO) as spin trap, we show that a non-hydroxyl reactive species is produced in  
31 significant amount upon air-oxidation of alluvial soil suspensions (Seine River basin, France). Indeed,  
32 among the DMPO-OH•, DMPO-CO<sub>2</sub>•<sup>-</sup> and DMPO-alkyl• adducts observed, the latter one  
33 dramatically raised when adding ethanol or, to a lesser extent, *tert*-butanol, especially with phosphate  
34 buffer. This result revealed a dominant non-hydroxyl species we interpret as Fe(IV) since it is known  
35 to oxidize alcohols into alkyl• radicals and to be favored by phosphate ligands. With phosphate buffer  
36 and ethanol, the DMPO-alkyl• production correlated with the initial reduced-state iron pool in the  
37 samples determined using Fe *K*-edge X-ray absorption spectroscopy (XAS). Fe(II)-phyllosilicates,  
38 and Fe(0) in one soil, and to a lesser extent vivianite, were the most significantly oxidized upon soil  
39 oxygenation, pyrite appearing less reactive. Hence, we show that a significant reactive species,  
40 differing from OH•, forms upon oxygenation of soil Fe(II)-minerals, especially in the presence of  
41 soil-sourced phosphate. Our results may thus call for further direct identification of this putative  
42 Fe(IV) species and for investigating its ability to degrade organic contaminants in natural  
43 environments.

44

45 **KEYWORDS:** alkyl•, OH•, CO<sub>2</sub>•<sup>-</sup>, Fe(IV), phosphate, clays, EPR, XAS

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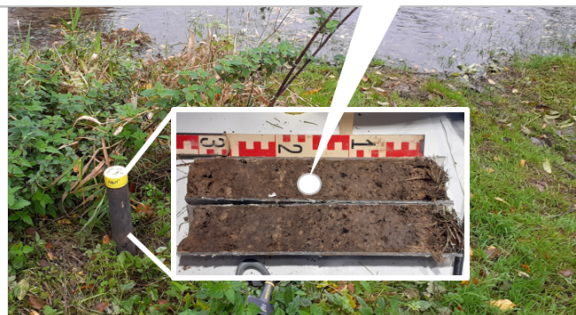
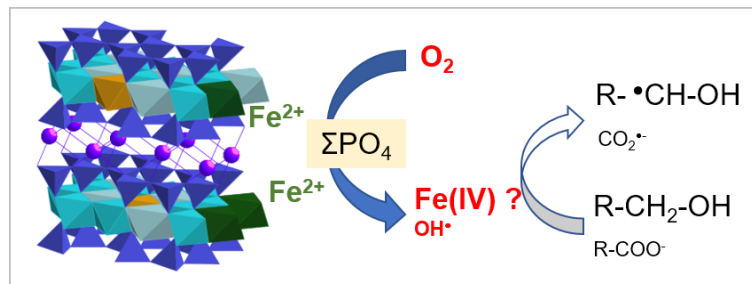
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50 **GRAPHICAL ABSTRACT (TOC)**

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## 56 INTRODUCTION

57 A wide diversity of advanced oxidation processes has been the subject of intense research for the  
58 last decades in order to help designing efficient remediation processes for organic pollutants in water  
59 and soils<sup>1-3</sup>. Among recent developments, particular interest has been devoted to investigate Fenton-  
60 based processes using iron-bearing compounds as catalysts and airborne O<sub>2</sub> as oxidant, especially in  
61 order to promote eco-compatible routes favoring circumneutral pH and avoiding strong oxidants<sup>4,5</sup>.  
62 For instance, various organic compounds have been reported to be degraded upon oxygenation of  
63 iron-rich solid phases such as zero-valent iron<sup>6</sup>, magnetite<sup>7,8</sup>, FeS<sup>9,10</sup>, pyrite<sup>11</sup> and clay minerals<sup>12-14</sup>.  
64 Moreover, some studies have provided promising results regarding the degradation of organic  
65 contaminants upon oxygenation of natural soils and sediments, in relation with the redox reactivity  
66 of Fe(II)-bearing soil components<sup>15-17</sup>. In these studies, organic contaminant degradation has been  
67 attributed to the oxidizing role of reactive oxygen species (ROS), particularly OH•, that have been  
68 reported to be produced upon oxygenation of reduced soils and sediments<sup>17-23</sup>. Some of these studies  
69 proposed that OH• production could be related to oxidation of iron minerals<sup>15-18</sup> and organic  
70 matter<sup>18,24-26</sup>. Nevertheless, in aqueous media that are relevant to this literature, the actual formation  
71 of OH• could be probed only using indirect approaches, due to the high reactivity and extremely short  
72 lifetime of this species (typically estimated to ~ 10<sup>-9</sup> s at 37°C in 1M linoleate <sup>27</sup>). Thus, OH•  
73 scavengers have been used to investigate the role of this radical species in pollutant degradation<sup>16</sup>.  
74 More generally, the hydroxylation of specific aromatic molecules by OH• has been rather used to  
75 obtain quantitative estimates of this short-lived species. In particular, the production rate of *p*-  
76 hydroxybenzoic acid (*p*-HBA) from benzoic acid (BA) has been often used to assess OH• production.  
77 This method was first established by Zhou & Mopper<sup>28</sup> and has been now commonly used in various  
78 contexts including in soils and sediments oxygenation experiments<sup>15,20,26,29,30</sup>. Similarly, the  
79 conversion of terephthalic acid (TPA) into hydroxyterephthalic acid (hTPA) is another method that  
80 has been used to quantify OH•<sup>18,19</sup> upon oxygenation of soils. However, the specificity of aromatic  
81 hydroxylation methods, especially the ability of the BA/*p*-HBA method to selectively quantify

82 aqueous OH• upon Fe(II)-mineral air-oxidation have been recently questioned<sup>31</sup>. In addition, the  
83 molecular-scale mechanisms of heterogeneous Fenton-like reaction using O<sub>2</sub> as the primary oxidant,  
84 remains an ongoing debate.

85 Besides, while it is commonly assumed that OH• is produced under such oxygenation conditions,  
86 spin-trapping electronic paramagnetic resonance (EPR) spectroscopy studies have revealed a wider  
87 variety of radicals species that can be produced upon oxygenation of soils or sediments, including  
88 alkyl radicals that can be formed upon oxidation of natural organic matter by reactive oxygen  
89 species<sup>32,33</sup>. Moreover, pioneering and recent spin-trapping EPR studies have suggested that another  
90 reactive species, the ferryl ion Fe(IV)=O<sup>2+</sup>, is formed upon oxygenation of Fe(II) at neutral and  
91 alkaline pH<sup>34-36</sup>. This was not confirmed by another indirect method involving the conversion of  
92 phenyl methyl/dimethyl sulfoxide (PMSO/DMSO) to phenyl methyl/dimethyl sulfone (PMSO),  
93 which was not observed upon oxygenation of aqueous iron complexes<sup>37</sup> or magnetite at neutral pH<sup>38</sup>,  
94 although this conversion is expected to occur in the presence of Fe(IV). In contrast in another study,  
95 the PMSO to PMSO<sub>2</sub> conversion was observed upon oxygenation of reduced smectites and rectorite<sup>39</sup>.  
96 Nevertheless, the selectivity of this latter method has been recently disputed<sup>40</sup>. Hence, although  
97 providing direct evidence for Fe(IV) in aqueous systems remains challenging<sup>41-43</sup>, EPR studies have  
98 given clues for the formation of abundant non-hydroxyl species upon homogeneous and  
99 heterogeneous oxygenation of Fe(II), especially in the presence of ligands such as phosphate<sup>34,36</sup>,  
100 which has been interpreted as possible ligand-promoted Fe(IV) formation<sup>35</sup>.

101 Nevertheless, natural environments subjected to hydrological fluctuations are particularly regarded  
102 as propitious to such contaminant degradation processes since they may favor cyclic oxygenation of  
103 Fe(II)-minerals. Indeed, due to fluctuations of the redox boundary in riverbanks, alluvial soils or  
104 coastal areas sediments<sup>23-25</sup>, ROS are expected to be produced during low-water periods from the  
105 oxidation of reduced-state iron substrates that may be regenerated via microbial reduction during  
106 high-water periods, thus contributing to ROS production at the next low-water period<sup>23,33,44</sup>.

107 According to these previous findings, the mechanisms of ROS production in soils subjected to  
108 redox fluctuation thus deserve further research. The two main objective of this work were to better  
109 characterize the reactive species involved in the air-oxidation of natural soils in darkness at neutral  
110 pH, using spin-trapping EPR spectroscopy, and to evaluate the role of Fe-bearing phases in the  
111 reactive species production, using X-ray absorption spectroscopy (XAS) as a probe for Fe-speciation.

112

## 113 **MATERIALS AND METHODS**

114 All samples were handled in a JACOMEX® glovebox under N<sub>2</sub> atmosphere (O<sub>2</sub> < 2 ppm, as  
115 measured using a JACOMEX® electro-galvanic oxygen sensor) to avoid oxidation of the alluvial soil  
116 samples before oxygenation experiments. When required, O<sub>2</sub>-free deionized water (18.2 mΩ.cm,  
117 Millipore® Milli-Q system) was prepared by bubbling N<sub>2</sub> gas at 75°C for 50 minutes, ensuring  
118 dissolved O<sub>2</sub> concentration in the 10<sup>-5</sup> mg.L<sup>-1</sup> range<sup>45</sup>. All experiments presented were conducted at  
119 room temperature except XAS analyses that were conducted at cryogenic temperature to limit beam-  
120 damage.

121 **Alluvial soils sampling and characterization procedures.** Alluvial soils were collected from  
122 two different locations (**Figure S1**, top). Two soil cores were collected in the Orgeval watershed, on  
123 the banks of the Avenelles river, on the edge of a cropped field (CRD3) and of a meadow (CRG1). A  
124 third alluvial soil core was collected in the Seine riverbank upstream from the Bassée alluvial plain  
125 (T1S1). At the Avenelles site, we used a PVC tube and a rubber hammer for coring. A manual steel  
126 corer with an inner PVC tube and a rubber hammer were used to core the muddy soil at the T1S1 site.  
127 The soils cores of about 30 cm length were immediately sealed in their PVC tube with taped plastic  
128 stoppers in order to limit contact with atmosphere and were transported in a passive cool box ( $\leq 5^{\circ}\text{C}$ )  
129 to the IMPMC laboratory within 24 hours. The cores within their PVC tubes were cut transversally  
130 in the glovebox and half-cores were subdivided into subsamples as a function of depth, according to

131 the difference of colors and textures of the horizons. Subsamples were then dried under vacuum in a  
132 desiccator within the glovebox.

133 Major elements concentrations in the dry soils samples were determined by Inductively Coupled  
134 Plasma - Optical Emission Spectrometry (ICP-OES), at SARM-CRPG (Nancy, France) after alkaline  
135 fusion and acid digestion (**Table 1**). Full chemical compositions are reported in **Table S1**. Total  
136 carbon, total organic carbon (TOC), and total inorganic carbon (TIC) calculated by subtraction (**Table**  
137 **1**), were determined in dried samples in three replicates by pyrolysis and element analysis using a  
138 Vario Isotope Select element analyzer (Elementar, Lyon, France) at ECOSYS, INRAE. Prior to the  
139 organic carbon measurements, inorganic carbon was eliminated from soils by acidic fumigation using  
140 HCl<sup>46</sup>.

141 For two selected samples, CRD3 20-30 cm and T1S1 0-10 cm, dissolved organic carbon (DOC)  
142 was measured in the filtered suspension after air-oxidation (please see next section for oxidation  
143 protocol) using a total organic carbon analyzer TOC-5050A (Shimadzu, Marne-La-Vallée, France).  
144 Uncertainties were estimated from two independent experiments. Phosphate concentration was  
145 measured by the molybdenum blue reaction with orthophosphate, by colorimetry at 710 nm,<sup>47</sup> in the  
146 filtered suspension before air-oxidation and uncertainties were estimated from triplicate experiments.

147 The mineralogy of the dried soil subsamples was determined using powder X-ray diffraction  
148 (XRD) and Scanning Electron Microscopy coupled to Energy Dispersive X-ray analysis (SEM-  
149 EDX). XRD data were collected using a PANalytical® Xpert Pro diffractometer in Bragg-Brentano  
150 geometry with Co-K $\alpha$  radiation, for 2h between 2 and 80° 2 $\theta$ -range in a continuous mode. For this  
151 purpose, soil samples were ground in the anoxic glove-box in an agate mortar in mixture with ethanol  
152 and were deposited on a zero-background silicon wafer before being placed into an anoxic chamber  
153 with Kapton® window during the XRD measurements. Mineral phases were identified using the  
154 HighScore Plus® software and the PDF-2 database (**Table 1**).

155 For scanning electron microscopy coupled to energy dispersive X-ray (SEM-EDX) spectroscopy  
156 analyses, ~50  $\mu$ m thick soil thin-sections were prepared on glass slides from soil powder embedded



157 in Epoxy resin. SEM observations were performed on a Zeiss Ultra55 SEM equipped with a FEG-  
158 Schottky electronic source operating at 15 kV and with a Bruker™ Si-drift detector for EDX. Semi-  
159 quantitative elemental analysis was performed on EDX spectra using the Esprit1.9® using a spectra  
160 database for standard materials (**Figure 1**).

161 **Air-oxidation procedure.** To avoid any photo-activation from natural light, the air-oxidation  
162 experiments were conducted within amber glass flasks. For all samples of the CRD3, CRG1 and T1S1  
163 soil cores, suspensions were prepared in an anoxic glove box. For this purpose, 100 mg of dried  
164 sample were mixed with 350  $\mu\text{L}$  phosphate buffer 1 M pH 7 (prepared from anhydrous  $\text{NaH}_2\text{PO}_4$  and  
165  $\text{Na}_2\text{HPO}_4$  salts), 16  $\mu\text{L}$  of 99.98% absolute ethanol, 160  $\mu\text{L}$  of  $\text{O}_2$ -free deionized water, and then 300  
166  $\mu\text{L}$  of DMPO 0.1 M (n° CAS: 3317-61-1;  $\geq 98.0\%$  for EPR-spectroscopy, Sigma-Aldrich®). Final  
167 concentrations in the mixture are 0.036 M, 0.42 M, 0.33 M for DMPO, phosphate and ethanol  
168 respectively. The suspensions were left equilibrating overnight before adding DMPO and sealing the  
169 flasks with butyl rubber stoppers. Air-oxidation was performed outside from the glove box, by  
170 injecting 200 mL of air over a two minutes period of time using a 50 mL syringe and needle through  
171 the butyl rubber stopper. The suspension is  $60\pm 5\%$  saturated with  $\text{O}_2$  after this 2 min air bubbling as  
172 determined with a WTW® 3630 IDS FDO Check probe for dissolved oxygen. The flask was then  
173 shaken for ten seconds and the liquid phase was extracted with a 5 mL syringe and needle and was  
174 then filtered through 0.2  $\mu\text{m}$  nylon filters before being transferred in an EPR liquid flat-cell for  
175 analysis. Besides, a control experiment without solid was also carried out in the same conditions and  
176 is referred to as blank.

177 In order to better decipher among various possible reactive species, specific experiments were  
178 conducted on the CRD3 20-30 cm and T1S1 0-10 cm samples, with or without adding 16  $\mu\text{L}$  of the  
179  $\text{OH}^\bullet$  scavenger, i.e. either ethanol (99.98%) or *tert*-butanol (99%). In addition, to assess the possible  
180 effects of ligands, the air-oxidation experiments were conducted with or without phosphate buffer,  
181 then replacing it by  $\text{O}_2$ -free deionized water. Removing the buffer did not significantly affect the pH

182 of the suspensions upon oxygenation since they were already buffered at pH 7.0-7.3 by the soil  
183 alkalinity and dropped to 6.7-6.8 after oxidation.

184 **Spin-trapping Electron Paramagnetic Resonance (EPR).** Immediately after the air-oxidation,  
185 shaking and filtration steps, an EPR spectrum was acquired every 5 min over a one-hour period, with  
186 the beginning of air-bubbling as the initial time reference ( $t = 0$  min). For these measurements, X-  
187 band EPR spectra were acquired at room temperature at the IMPMC laboratory over the 0.3460 –  
188 0.3560 Tesla magnetic field-range on a Bruker EMXplus<sup>TM</sup> EPR spectrometer, or at the LRS  
189 laboratory, over the 0.33204–0.34204 Tesla magnetic field-range on a JEOL® FA-300 spectrometer  
190 (**Figure S2**). Acquisition parameters are detailed in Supporting Information Section S1.

191 As in Morin et al. (2023)<sup>36</sup>, EPR spectra were least-squares fit using the EPRPLP code<sup>48</sup> in order  
192 to extract EPR parameters of the DMPO-radical adducts (**Table 2; Figure 2**) and scale factors  
193 proportional to the abundance of every adduct as a function of time. Typical time course series of  
194 EPR spectra collected for this spin-trapping kinetic EPR analysis are displayed in **Figure S3**. For all  
195 experiments, the time-course evolution of the scale factor for each adduct was fit by a combination  
196 of two first order kinetic laws, representing the adduct production and decay, which can be expressed  
197 as follows for a given DMPO-radical• adduct (**Figures S4 and S5 ; Table S2 and Table 3**):

198

$$199 \quad [\text{DMPO-radical}^\bullet](t) = [\text{DMPO-radical}^\bullet]_{\text{max}} \cdot \frac{k_{\text{prod}}}{(k_{\text{decay}} - k_{\text{prod}})} \cdot (e^{-k_{\text{prod}}t} - e^{-k_{\text{decay}}t}) \quad (1)$$

200

201 where  $k_{\text{prod}}$  and  $k_{\text{decay}}$  are rate constants and  $[\text{DMPO-radical}^\bullet]_{\text{max}}$  is the calculated maximum EPR  
202 intensity. This latter parameter was then used as an estimate of the amount of radical species produced  
203 in our air-oxidation experiments (**Table S2; Figures S6 and S7**). Triplicate experiments were  
204 especially conducted with phosphate buffer and EtOH for all samples (**Figure S8; Table 3**). As  
205 previously observed in a previous study<sup>36</sup> upon air-oxidation of pure iron substrates, a short radical  
206 production phase is observed ( $k_{\text{prod}}$ ) before decay ( $k_{\text{decay}}$ ) indicating that radicals are still produced in  
207 the filtered supernatant after the 2 min bubbling. This effect is related to the contribution of aqueous

208 Fe(II) species oxidation to radical production after filtration, in addition to surface Fe(II) species  
209 oxidized before filtration<sup>31,36</sup>.

210 **X-ray Absorption Spectroscopy (XAS).** Iron *K*-edge X-ray Absorption Near Edge Structure  
211 (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy data were collected  
212 on the soil core samples before and after the same 2 min air-oxidation protocol as that used for EPR  
213 analyses, but without DMPO. Following the bubbling step, samples were centrifuged for 20 seconds  
214 before being vacuum-dried into the anoxic glovebox. In the glove box, the samples were ground in  
215 agate mortar, weighted to ~30 mg to optimize edge-jump vs. total absorbance, pressed as pure pellets,  
216 sealed under Kapton® tape and mounted on samples holders. Those were then sealed within glass  
217 vials closed with butyl rubber stoppers and brought to the synchrotron beamline glove box. The  
218 sample holders were exposed to air for less than 20 seconds before being placed into the liquid  
219 nitrogen cryostat sample chamber that was then pumped down to ~10<sup>-6</sup> bar and cooled. The data on  
220 the CRD3 and T1S1 samples were collected at 80K in transmission detection mode using ionization  
221 chambers on the bending-magnet XAFS beamline at the ELETTRA synchrotron (Trieste, Italy).  
222 Energy was selected using a Si(111) double-crystal monochromator detuned for 30% in order to avoid  
223 the 3<sup>rd</sup> order harmonic. The data on the CRG1 samples were collected at 30K on the undulator LUCIA  
224 beamline at the SOLEIL synchrotron (Saint-Aubin, France) using a Si(111) double-crystal  
225 monochromator, and harmonic rejection mirrors. On this beamline, transmission and fluorescence  
226 (Si-drift detector) detection mode data were used for EXAFS and XANES, respectively. Energy was  
227 calibrated using a Fe foil analyzed in double-transmission setup, setting the first inflection point of  
228 the Fe *K*-edge at 7112 eV. Either two or three spectra were merged, normalized, background-  
229 subtracted, and deglitched if necessary, using the Athena software<sup>49</sup>.

230 A Principal Component Analysis (PCA) and Target Transform (TT) analysis (**Figure S9-S11**;  
231 **Table S3**), followed by Linear combination fit (LCF) (**Figures 3 and 4**; **Table 4**) was performed to  
232 assess iron speciation in the soil samples, before and after air-oxidation. PCA-TT was performed  
233 using the SIXPack software<sup>50</sup>, whereas XANES and EXAFS LCF was performed with a home-built

234 Fortran 90 code based on a Levenberg-Marquardt minimization algorithm used in previous studies<sup>51–</sup>  
235 <sup>55</sup>.

236 In this latter software, fit quality for XANES LCF is estimated with a R-factor,  $R_f = \frac{\sum [\mu_{\text{exp}} - \mu_{\text{fit}}]^2}{\sum \mu_{\text{exp}}^2}$ , where  $\mu$  is the normalized absorbance, and with a reduced chi-square,  $\text{Chi}_R^2 = \frac{N}{(N - N_p)}$   
237  $\frac{[\mu_{\text{exp}} - \mu_{\text{fit}}]^2}{\sum \mu_{\text{exp}}^2}$ , where  $N_p$  is the number of fitting components and  $N$  is the number of independent  
238 parameters corresponding to the energy range divided by the natural width of the Fe levels<sup>56</sup>. The  
239 uncertainty on each fitting parameter  $p$  was estimated to 99.7% confidence ( $3\sigma$ ) as  $3\sqrt{(\text{var}(p) \cdot \text{Chi}_R^2)}$ ,  
240 where  $\text{var}(p)$  is the variance of parameter  $p$  returned by the Levenberg-Marquardt routine for the  
241 lowest  $\text{Chi}_R^2$  value. The fit quality of EXAFS LCF was estimated by a reduced chi-square parameter  
242  $\text{Chi}_R^2 = \frac{N}{[(N - N_p) \cdot n \cdot \varepsilon^2]} \sum [k^3 \chi(k)_{\text{exp}} - k^3 \chi(k)_{\text{fit}}]^2$ , with  $N = (2\Delta k \Delta R) / \pi$ , the number of independent  
243 parameters,  $N_p$  the number of free fitting parameters,  $n$  the number of data points, and  $\varepsilon$  the root mean  
244 square of the data noise. This latter value was estimated as the Fourier back-transform of the data in  
245 the 15–25 Å R-range, following a method modified after Ravel and Newville<sup>43</sup>. The uncertainty on  
246 EXAFS fitting parameters was estimated to 95% confidence ( $2\sigma$ ) by  $2\sqrt{(\text{var}(p) \cdot \text{Chi}_R^2)}$ , where  $\text{var}(p)$   
247 is the variance of parameter  $p$  returned by the Levenberg-Marquardt routine for the lowest  $\text{Chi}_R^2$   
248 value. Fitting components were selected from our database using the results of TT analysis (**Table**  
249 **S3**) and were further screened by requiring uncertainties returned from the LCF procedure to be lower  
250 than the refined parameter values (**Table 4**). Applying this method, a consistent set of six fitting  
251 components, i.e. Fe(0), pyrite, vivianite, biotite, illite and goethite, was found to fit both XANES and  
252 EXAFS spectra of our whole set of soil cores samples, before and after air-oxidation. Calculated  
253 uncertainties revealed that vivianite and pyrite minor components, although observed by SEM, were  
254 significant in XANES fitting but not in EXAFS fitting (**Figure 4; Table 4**). In contrast, Fe(0) was  
255 required to fit both the XANES and EXAFS data of CRD3 samples (**Figure S12; Table S4**). This  
256 component may be attributed to steel or other metallic particles, some of which being identified by  
257 SEM-EDX observations (**Figure 1**). We infer that they could originate from incident anthropogenic  
258 inputs in the studied cropped fields, due for instance to soil tilling.

260 Thanks to lower uncertainties and reliable sum-of-component criteria, XANES spectroscopy was  
 261 more accurate at determining Fe redox state than EXAFS and was then used to evaluate the “reduced-  
 262 state iron” pool, calculated as the sum of Fe(0) and Fe(II) (**Table 4**). This observation obviously  
 263 results from the well-known sensitivity of the energy position of the Fe *K*-edge to oxidation state and  
 264 first-ligands, which allows accurate determination of Fe oxidation state in complex natural samples  
 265 using XANES LCF, provided that appropriate model compounds are available<sup>53,55,57–59</sup>.

266

## 267 RESULTS AND DISCUSSION

### 268 Chemical and mineralogical characterization of the alluvial soils

269 Major minerals determined by XRD analysis, i.e. quartz, feldspars, calcite and clay minerals  
 270 (**Table 1; Figure S1**) were in qualitative agreement with ICP-OES data (**Table 1 and S1**). Hence,  
 271 the samples from the Seine site (T1S1) were found to be more calcic than the siliceous soils from the  
 272 Avenelles site (CRD3 and CRG1).

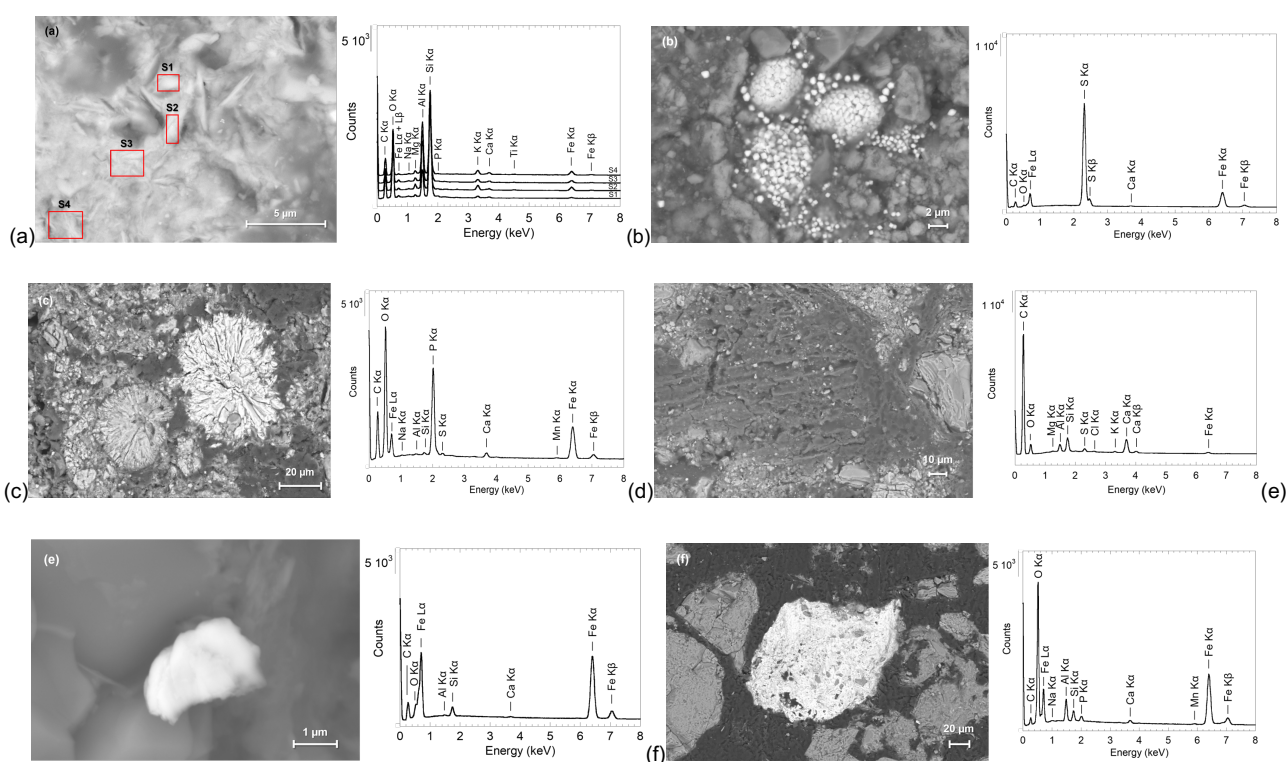
273 **Table 1.** Selected chemical and mineralogical data on the studied soil core samples, as determined  
 274 by ICP-OES (Fe and S concentrations refer to total concentrations of these elements), carbon analyser  
 275 (TOC, TIC), powder XRD (Qz: Quartz; Cal: Calcite; Feld: Feldspar; Clay: phyllosilicates; **Figure**  
 276 **S1**) and SEM-EDX (Viv: vivianite, Py: pyrite; Fe-Ox: iron oxyhydroxides; OM: organic matter;  
 277 Fe(0): metallic iron (**Figure 1**). Relative analytical uncertainties are  $\pm 10\%$ ,  $\pm 20\%$  and  $\pm 15\%$  for Fe,  
 278 S and P, respectively. Uncertainties ( $3\sigma$ ) on last digit are given under bracket for triplicate  
 279 measurements of TOC and TIC.

Sample	Fe (wt%)	S (wt%)	P (wt%)	TOC (wt%)	TIC (wt%)	Major minerals	Fe-bearing phases
CRD3 0-3 cm	0.67	0.03	< 0.044	1.4(2)	0.2(1)		
CRD3 3-10 cm	0.97	0.04	< 0.044	2.06(6)	0.12(1)	Qz, Cal,	Clays, Fe-
CRD3 10-20 cm	0.92	0.05	< 0.044	1.6(1)	0.3(2)	Feld, Clays	Ox, Fe(0)
CRD3 20-30 cm	1.02	0.04	< 0.044	4.2(1)	0.2(1)		
CRG1 8-14 cm	1.09	0.06	0.048	3.8(2)	0.3(2)		
CRG1 14-21 cm	0.79	0.04	< 0.044	2.2(4)	0.4(3)	Qz, Cal,	Clays, Fe-
CRG1 21-28 cm	1.23	0.07	0.057	3.9(1)	0.2(2)	Feld, Clays	Ox
CRG1 28-35 cm	1.18	0.07	0.052	5.4(3)	0.3(3)		
T1S1 0-10 cm	1.58	0.10	0.096	4.2(7)	5.7(7)		Clays, Fe-
T1S1 10-15 cm	1.59	0.07	0.096	4.1(7)	5.7(8)	Cal, Qz,	Ox, Viv, Py,
T1S1 15-24 cm	1.54	0.08	0.100	4(1)	6(1)	Clays	OM
T1S1 24-30 cm	0.92	0.07	0.061	2.2(2)	7.9(3)		

280

281 Complementary information on minor Fe-bearing phases below XRD detection limit was provided  
282 by SEM-EDX analysis (**Figure 1**). Fe-bearing phyllosilicates and iron-oxyhydroxides were identified  
283 as Fe-bearing phases in the CRD3 and CRG1 soil cores (**Figure 1**; **Table 1**) and metallic iron particles  
284 were observed in the former core (**Figure 1e**). In the T1S1 soils, Fe-bearing phyllosilicates and iron-  
285 oxyhydroxides were also observed, as well as iron associated to organic matter (**Figure 1d**),  
286 framboidal pyrite ( $\text{FeS}_2$ ) (**Figure 1b**) and vivianite ( $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ ) (**Figure 1c**).

287



288

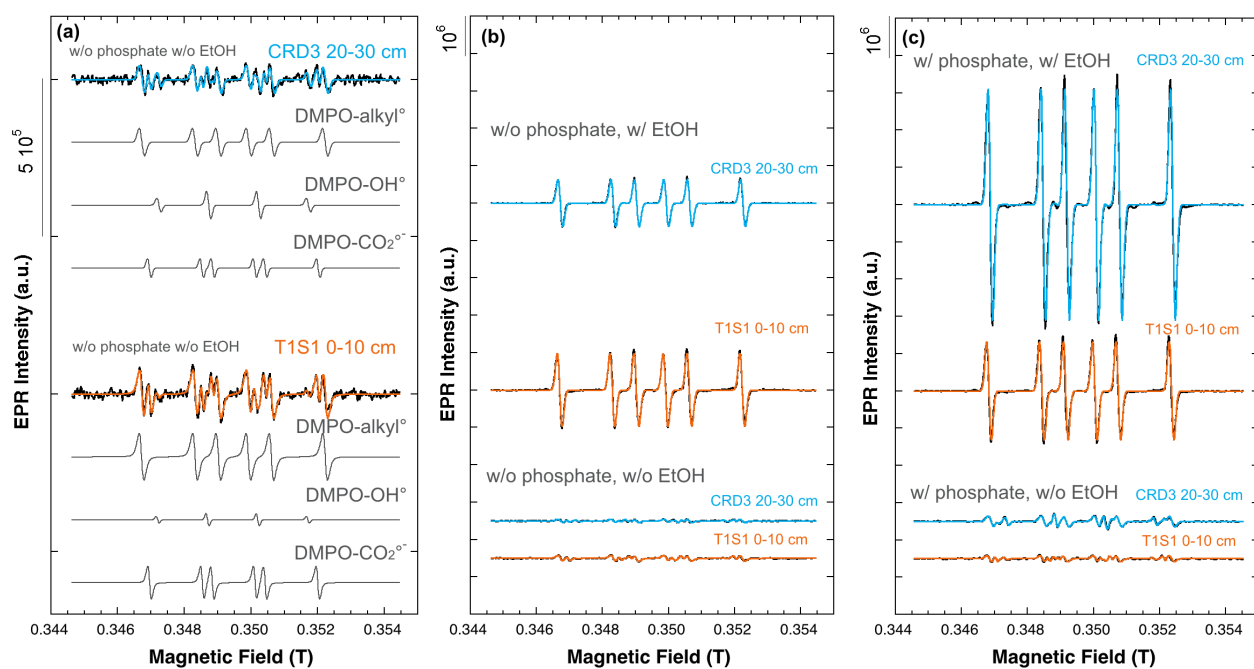
289

290 **Figure 1.** SEM images in backscattering mode (left) and corresponding EDX spectra (right) (a)  
291 phyllosilicate aggregate in CRD3 0-3 cm sample with spectra corresponding to the red tags, (b)  
292 framboidal pyrites in T1S1 24-30 cm sample ( $\text{Fe/S} = 0.50 \pm 0.05$  mol/mol) (c) vivianite grain in T1S1  
293 24-30 cm sample ( $\text{Fe/P} = 1.40 \pm 0.05$  mol/mol) (d) organic matter aggregate in T1S1 24-30 cm sample  
294 ( $\text{Fe/C} = 0.08 \pm 0.01$  mol/mol) (e) metallic iron grain in CRD3 20-30 cm sample (f) iron oxyhydroxide  
295 in CRD3 0-3 cm sample.

296

297 **Radical species produced upon air-oxidation of the alluvial soils.** Three DMPO adducts were  
298 produced upon air-oxidation of the soil suspensions particularly in the absence of alcohol and  
299 phosphate buffer, and were observed by EPR in the filtered soil suspensions, as shown in **Figure 2a**.

300 The first signal is the DMPO-OH• adduct, characterized by its quadruplet spectrum<sup>60,61</sup> (**Table 2**).  
 301 Accordingly, DMPO is known as an efficient spin trap for the hydroxyl radical OH• and the DMPO-  
 302 OH• adduct has been previously detected using EPR upon oxygenation of soils<sup>15,20</sup> and of Fe(II)-  
 303 bearing substrates such as FeS<sup>9</sup>. However, DMPO-OH• can be also formed by decomposition of  
 304 DMPO-O<sub>2</sub>•<sup>-</sup> with typically a few percent of this adduct being transformed into DMPO-OH• after a  
 305 few minutes<sup>62</sup>. Such origin for DMPO-OH• cannot be excluded in our experiments since the half-life  
 306 of the DMPO-O<sub>2</sub>•<sup>-</sup> adduct is as short as 1 or 2 min, and even shorter in the presence of Fe<sup>2+</sup><sup>62,63</sup>. This  
 307 adduct might then be overlooked by our first EPR spectrum that is taken at 5 min after the beginning  
 308 of the oxygenation.



309 **Figure 2.** EPR spectra taken at time  $26 \pm 2$  min after the start of 2 min air-oxidation of the CRD3 20-  
 310 30 cm or T1S1 0-10 cm samples suspensions. (a) without phosphate buffer and without EtOH added.  
 311 Experimental (black) and fitting curves (blue or orange) are displayed together with weighted  
 312 theoretical fitting components: DMPO-alkyl•, DMPO-OH• and DMPO-CO<sub>2</sub>•<sup>-</sup> adducts. (b) Without  
 313 phosphate buffer and without or with EtOH added. (c) With phosphate buffer and with or without  
 314 EtOH added. EPR parameters of the adducts are reported in **Table 2**.  
 315

316  
 317 Nevertheless, even though the hydroxyl radical could be directly produced by oxygenation of  
 318 Fe(II)-minerals at neutral pH, the intensity of DMPO-OH• EPR signal in our study, as well as in  
 319 previous reports, was found to be close to the background signal<sup>9,15,20</sup>. In contrast, based on aromatic

320 hydroxylation methods such as BA/*p*-HBA conversion, OH• has been assumed to be generated upon  
 321 oxygenation of soils and sediments<sup>17-23</sup>.

322 The second signal is a sextet with hyperfine parameters (**Table 2**) matching those of DMPO  
 323 adducts of alkyl radicals (RCH•R') or hydroxyalkyl radicals (RCH•OH) with R being an alkane or a  
 324 H atom<sup>61</sup>, which we will both refer to as DMPO-alkyl• adduct thereafter. Such adduct is typically  
 325 observed when a ROS scavenger, especially an alcohol, is present and reacts with the ROS before  
 326 being trapped by DMPO<sup>62</sup>. Hence, OH• scavengers such as methanol, ethanol or DMSO are used to  
 327 distinguish genuine DMPO-OH• from the same adduct resulting from the decomposition of DMPO-  
 328 O<sub>2</sub>•<sup>-</sup>, since the superoxide radical O<sub>2</sub>•<sup>-</sup> is not scavenged by alcohols nor DMSO<sup>60,62</sup>. In our  
 329 experiments, one may infer that the DMPO-alkyl• formation results from the scavenging of reactive  
 330 species by alkyl groups associated to dissolved organic matter in our soil suspensions (**Table 1**), and  
 331 their subsequent trapping by DMPO. Similar signal was indeed reported in the past upon oxygenation  
 332 of sediments<sup>15</sup>.

333

334 **Table 2.** EPR parameters of DMPO adducts of the hydroxyl radical (DMPO-OH•), carbon dioxide  
 335 anion radical (DMPO-CO<sub>2</sub>•<sup>-</sup>), hydroxyethyl radical (DMPO-EtOH•) and hydroxy*tert*-butyl radical  
 336 (DMPO-*t*-BuOH•), determined from the fitting of soil samples suspension data. Parameters include  
 337 the *g* factor of the (S=1/2) center and its hyperfine coupling constants to hydrogen (A<sub>H</sub>) and nitrogen  
 338 (A<sub>N</sub>) neighbors.

Adduct	<i>g</i>	<i>This study</i>		<i>Buettner (1987)</i> <sup>61</sup> *	
		A <sub>H</sub> (cm <sup>-1</sup> ) A <sub>H</sub> (Gauss)	A <sub>N</sub> (cm <sup>-1</sup> ) A <sub>N</sub> (Gauss)	A <sub>H</sub> (cm <sup>-1</sup> ) A <sub>H</sub> (Gauss)	A <sub>N</sub> (cm <sup>-1</sup> ) A <sub>N</sub> (Gauss)
DMPO-OH•	2.0055(2)	0.00138(6) 14.7(7)	0.00141(6) 15.1(7)	0.00140(3) 15.0(3)	0.00140(3) 15.0(3)
DMPO-CO <sub>2</sub> • <sup>-</sup>	2.0054(2)	0.00177(4) 18.9(4)	0.00149(2) 15.9(2)	0.00175(5) 18.7(5)	0.00146(4) 15.6(4)
DMPO-alkyl•	2.0054(1)	0.00217(4) 23.2(4)	0.00150(1) 16.0(1)	0.0022(2) 23.5(20)	0.00149(8) 15.9(8)

339 \* Mean values of hyperfine constants reported in Buettner (1987)<sup>61</sup> converted in cm<sup>-1</sup> unit using either *g* = 2.0054  
 340 or *g*-value reported therein. Only the values measured in water as solvent were kept for this calculation.

341



342 A third radical was observed, whose hyperfine constants matched those of DMPO-CO<sub>2</sub>•<sup>-</sup>  
343 adducts<sup>60,61</sup> (**Table 2**). The carbon anion radical CO<sub>2</sub>•<sup>-</sup> has been reported to be produced in the  
344 presence of formate HCOO<sup>-</sup> upon oxygenation of iron-bearing asbestos<sup>64</sup>. This radical was also  
345 detected in a Fe(II)-EDTA/H<sub>2</sub>O<sub>2</sub> system at pH 7.4 in the presence of formate<sup>65</sup>. More recently, it has  
346 been reported CO<sub>2</sub>•<sup>-</sup> formation upon photo-oxidation of formate<sup>66</sup>. Besides, CO<sub>2</sub>•<sup>-</sup> was recently  
347 detected upon Cr(VI) reduction in wastewaters<sup>67</sup>. According to these previous reports, the CO<sub>2</sub>•<sup>-</sup>  
348 radical that formed upon oxygenation of our soils suspension could likely result from the oxidation  
349 of carboxylate compounds that necessarily originated from soil-sourced organic matter.

350 As shown in **Figure 2a**, the three DMPO adducts of OH•, alkyl• and CO<sub>2</sub>•<sup>-</sup> were observed upon  
351 air-oxidation of alluvial soils samples from both sites, but with a higher intensity of alkyl• and CO<sub>2</sub>•<sup>-</sup>  
352 radicals for the T1S1 sample than for the CRD3 sample. Since we infer that these two radicals may  
353 be generated through ROS scavenging by alkyl and carboxylate groups from dissolved organic  
354 matter, the more than two-fold higher amount of DOC in the filtered suspension after oxygenation of  
355 the T1S1 0-10 cm sample (150±40 mg.L<sup>-1</sup>) compared to the CRD3 20-30 cm sample (65±20 mg.L<sup>-1</sup>)  
356 could be invoked to explain this difference in radical production.

357 **Effect of radical scavengers and phosphate.** EtOH used as scavenger is expected to convert OH•  
358 into the  $\alpha$ -hydroxyethyl radical, EtOH• and forms a DMPO-hydroxyethyl• adduct with a sextet EPR  
359 spectrum, typical of the DMPO-alkyl• adducts<sup>62</sup>. It can be then distinguished from the quadruplet  
360 spectrum of a DMPO-OH• adduct that could have potentially resulted from the decomposition of  
361 DMPO-O<sub>2</sub>•<sup>-62</sup>. In our experiments conducted in the absence of phosphate buffer, the addition of EtOH  
362 lead to a significant decrease of the DMPO-OH• signal (**Figure 2b and S6**), suggesting that the major  
363 fraction of the DMPO-OH• observed in the absence of both EtOH and phosphate buffer was related  
364 to the production of OH• upon air-oxidation of the soil samples. Since OH• is converted into alkyl•  
365 in the presence of EtOH, the amount of DMPO-alkyl• adduct would be expected to be in the same  
366 range as that of the DMPO-OH• adduct observed in the absence of EtOH, as observed in Fenton-like

367 oxidation experiments performed with H<sub>2</sub>O<sub>2</sub><sup>36</sup>. On the contrary, addition of EtOH led to a significant  
 368 increase of the DMPO-alkyl• sextet signal that was found about 50-fold higher than the DMPO-OH•  
 369 observed without EtOH (**Figure 2b** and **S6, Table S2**). Importantly, this strong DMPO-alkyl• signal  
 370 observed in the presence of added EtOH (**Figure 2b**) indicates that another non-hydroxyl species is  
 371 produced by air-oxidation of our soil samples and that it is able to oxidize EtOH into EtOH•. More  
 372 precisely, the relative proportions of this non-hydroxyl species and of the hydroxyl radical can be  
 373 estimated, as shown in **Figure S6**, from the amounts of DMPO-OH• and DMPO-alkyl• adducts  
 374 determined from our spin-trapping EPR kinetic analysis (**Table S2**), the trapping rate constants of  
 375 OH• by DMPO<sup>60</sup> and EtOH<sup>68</sup> and the known concentrations of DMPO, EtOH and DOC in our soil  
 376 suspensions. This estimation indicated that ~87 and ~99% of the DMPO-alkyl• adduct signal is due  
 377 to EtOH oxidation by a non-hydroxyl species upon air-oxidation of the CRD3 20-30 cm and T1S1 0-  
 378 10cm soil suspensions, respectively, in the presence of EtOH. In other words, the relative proportion  
 379 of non-hydroxyl species over hydroxyl species is estimated to 86 and 91% for the CRD3 20-30 cm  
 380 and T1S1 0-10cm soil suspensions, respectively, in these conditions (**Figure S6**). Previous evidences  
 381 for the formation of a non-hydroxyl species air-oxidation of aqueous Fe(II) species<sup>34,35</sup> and Fe(II)-  
 382 mineral phases<sup>36</sup> at near neutral pH have been reported from EPR spin-trapping analyses. In these  
 383 former studies, the authors proposed that the main reactive species produced in such conditions may  
 384 be a high-valent state of iron, the ferryl ion Fe<sup>IV</sup>O<sup>2+</sup>, since this species is known to oxidize EtOH into  
 385 EtOH• through hydrogen abstraction<sup>4,65,69,70</sup>. Indeed, the ferryl ion has been proposed as a possible  
 386 product of Fe(II) oxidation by H<sub>2</sub>O<sub>2</sub> in Fenton-like systems especially at neutral pH<sup>65,71-76</sup> and has  
 387 been also proposed to form upon oxygenation of Fe(II)<sup>34,35,77</sup> and zero-valent iron<sup>4,78</sup>. Based on these  
 388 findings, we hypothesize that, in our air-oxidation experiments in the presence of EtOH, the  
 389 hydroxyethyl radical EtOH• could have mainly formed from the following reactions<sup>36,70</sup> (**Figure 2b**):



392 while in the absence of EtOH, the low amount of observed alkyl radicals could have resulted from  
393 the oxidation of soils-sourced natural organic matter by both OH• and Fe(IV) (**Figure 2a**):



396 More detailed hypotheses on the mechanisms possibly underlying reaction (2) are especially  
397 reported in previous studies<sup>4,32</sup> and references therein. In the present study, support for this non-  
398 hydroxyl species is further provided by the results of air-oxidation experiments conducted in the  
399 presence of our concentrated phosphate buffer at pH 7 (**Figure 2c** and **S5**). Without ethanol, the  
400 overall EPR signal remained low but a slight increase could be observed compared to the experiments  
401 without phosphate buffer (**Figure 2b**), especially for the CRD3 20-30 cm (**Figure S6**). In the presence  
402 of ethanol, addition of the phosphate buffer lead to a greater increase of the DMPO-alkyl• adduct  
403 signal (**Figure 2c, S4a and S6**) than in the non-added phosphate experiments (**Figure 2b, S5a and**  
404 **S6**), especially for the CRD3 20-30 cm sample, indicating that phosphate favored the formation of  
405 the putative Fe(IV) species. More precisely, the amount of non-hydroxyl species, interpreted as  
406 Fe(IV), increased by factors of ~4 and ~2 for the CRD3 20-30 cm and T1S1 0-10 cm samples,  
407 respectively, when adding the phosphate buffer in the presence of EtOH (**Figure S6**). Furthermore,  
408 the relative proportion of putative Fe(IV) over hydroxyl radical species is estimated to 79 and 92%  
409 for the CRD3 20-30 cm and T1S1 0-10 cm soil suspensions, respectively, in the presence of added  
410 EtOH and phosphate buffer (**Figure S6**). Such effect of phosphate has been documented in previous  
411 studies<sup>34-36</sup> and is thought to be another hint pointing toward Fe(IV). Moreover, other specific iron  
412 complexing agents, such as EDTA, have been reported to favor the Fe(IV) pathway over the OH•  
413 pathway at neutral pH, both in Fenton systems<sup>65,72,73,79</sup> and in oxygenation experiments<sup>34-36</sup>. Hence,  
414 the increase in alkyl• radicals production observed in the presence of phosphate buffer (**Figure 2c**  
415 and **S6**) is consistent with the reported ability of phosphate to favor the formation of Fe(IV) over OH•  
416 upon oxygenation at neutral pH<sup>34-36</sup>. Addition of ethanol in our EPR-spin trapping experiments is  
417 then thought to reveal Fe(IV) through the formation of the DMPO-alkyl• adduct, due to the known

418 ability of this species to abstract an hydrogen atom to ethanol<sup>4,65,69,70</sup>, leading to an EtOH•  
419 radical<sup>34,36,62</sup>. Moreover, according to the excess of DMPO over DOC in our experiments, the higher  
420 amount of DMPO-alkyl• adduct than DMPO-OH• in the absence of ethanol (**Figure 2a**, **S4a**, and  
421 **S5a**) suggests that a significant fraction of the soil-derived dissolved organic molecules may be  
422 oxidized rather by Fe(IV)<sup>69</sup> than by OH• to form alkyl• radicals. Accordingly, owing to DOC  
423 concentrations measured in our soil suspensions, i.e., 65±20 and 150±40 mg.L<sup>-1</sup> for the T1S1 0-10  
424 cm and CRD3 20-30 cm samples, respectively, the relative proportion of non-hydroxyl species  
425 largely exceeds that of hydroxyl radical in the absence of EtOH as estimated in **Figure S6**.

426 Interestingly, the effect of added ethanol and phosphate buffer on the production of DMPO-alkyl•  
427 varied among the two selected soil samples studied (**Figure 2b**, **2c**, **S4**, **S5** and **S6**), which suggests  
428 that soil-derived aqueous species present in the soil suspensions, specifically DOC and phosphate,  
429 may have interfered in the putative production of Fe(IV) during air-oxidation. Indeed, the stronger  
430 DMPO-alkyl• signal observed in T1S1 0-10 cm than in CRD3 20-30 cm, in the absence of phosphate  
431 buffer (**Figure 2a**, **2b** and **S4a**; **Table S2**), could be explained by both the higher dissolved phosphate  
432 and higher dissolved organic carbon concentrations in the former sample suspension (2.1±0.1 mg.L<sup>-1</sup>  
433 <sup>1</sup>P as phosphate and 150±40 mg.L<sup>-1</sup> DOC) than in the latter (1.2±0.4 mg.L<sup>-1</sup> P as phosphate and 65±20  
434 mg.L<sup>-1</sup> DOC). Furthermore, assuming that CRD3 20-30 cm sample is more sensitive to air-oxidation  
435 than the T1S1 0-10 cm one, as it will be shown in the next section, the lower concentration of soil-  
436 sourced phosphate in CRD3 20-30 cm could help explaining why the addition of phosphate buffer  
437 has a larger effect on Fe(IV) production for this sample than for the T1S1 0-10 cm one, with and  
438 without EtOH (**Figure 2c**, **S5a** and **S6**; **Table S2**).

439 A supplementary result supporting the formation of Fe(IV), especially in the presence of  
440 phosphate buffer, is given by using *tert*-butanol (t-BuOH) instead of ethanol as radical scavenger  
441 (**Figure S7**). Indeed, whereas OH• is expected to oxidize t-BuOH as well as ethanol with fast  
442 kinetics<sup>80</sup>, we observe a significantly weaker DMPO-alkyl• adduct signal with t-BuOH than with  
443 ethanol, which is consistent with the lower reactivity of high-valent iron species toward the former

444 alcohol<sup>74,81</sup>. Our results thus suggest that a non-hydroxyl species, interpreted as a putative Fe(IV)  
 445 species, could be produced upon oxygenation of natural alluvial soil samples, which calls for further  
 446 examination of the role of Fe(II)-bearing phases in this process, as discussed in the next section.

447 **Role of the reduced-state iron pool in reactive species production.** Addition of ethanol and of  
 448 phosphate in excess in our experiments conducted with EtOH and phosphate buffer allowed us to  
 449 compare the soils samples reactivity to air-oxidation on a same basis and to evaluate the role of iron-  
 450 bearing phases in radical production. Indeed, under this excess phosphate and with the chosen ethanol  
 451 over DMPO ratio in our experiments, alkyl radicals are mostly produced via the oxidation of ethanol  
 452 into the  $\alpha$ -hydroxyethyl radical by a non-hydroxyl species as indicated by **Figure 2** and illustrated in  
 453 **Figure S6**, and we interpret these species as Fe(IV) as detailed in the previous section. In **Figure S8**,  
 454 intensities varied significantly from one replica to another likely because of soils samples  
 455 heterogeneity, as attested by the error bars representing the standard deviation within triplicate results.  
 456 However, particular samples with lower radical production could be easily distinguished, i.e. those  
 457 with the lowest iron content: CRD3 0-3 cm, CRG1 14-21 cm and T1S1 24-30 cm (**Table 1**).

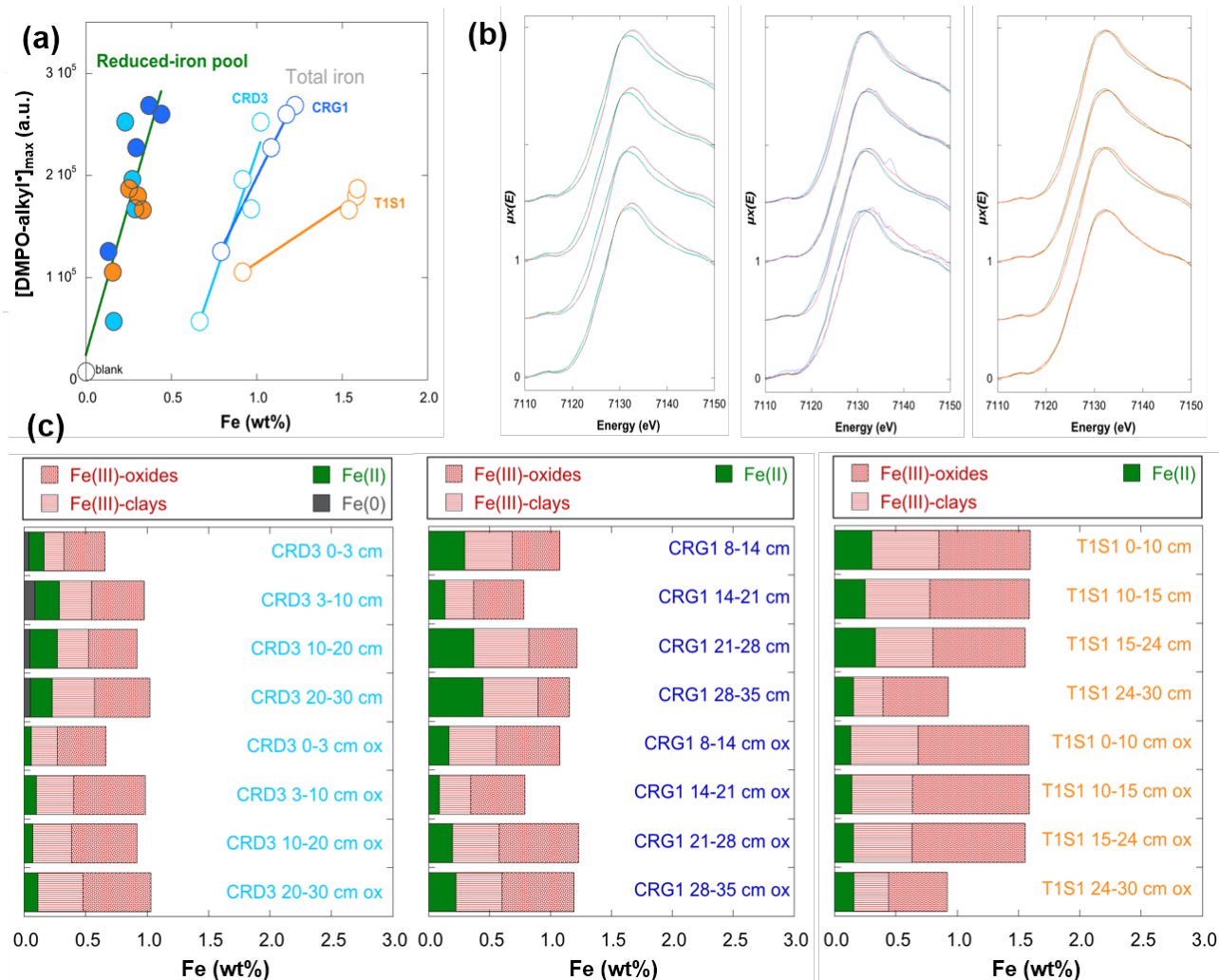
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459 **Table 3.** Kinetics parameters, namely  $[\text{DMPO-alkyl}^\bullet]_{\text{max}}$ ,  $k_{\text{prod}}$  and  $k_{\text{decay}}$  derived from the fitting to  
 460 Eq.1 (see text) of the time-course evolution of the DMPO-alkyl $^\bullet$  scale factor in the air-oxidation  
 461 experiments conducted in the presence of ethanol and 0.435 M phosphate buffer. Reported kinetic  
 462 parameters were obtained from the fitting of the average of triplicate experiments to Eq.1, as shown  
 463 in **Figure S8**. Uncertainties on  $[\text{DMPO-alkyl}^\bullet]_{\text{max}}$  values are reported under bracket for the last digit  
 464 and include mean quadratic error on triplicates together with fitting uncertainties to Eq 1.  
 465 Uncertainties on kinetic constants refer to fitting to Eq 1.

<i>DMPO-alkyl<math>^\bullet</math></i>	$[\text{DMPO-alkyl}^\bullet]_{\text{max}}$ $\mu\text{M}$	$[\text{DMPO-alkyl}^\bullet]_{\text{max}}$ (a.u.) $\times 10^5$	$k_{\text{prod}}$ ( $\text{min}^{-1}$ )	$k_{\text{decay}}$ ( $\text{min}^{-1}$ )	$\text{Chi}^2$ $\times 10^6$	<i>R</i>
CRD3 0-3 cm	14.5(17)	0.57(7)	0.22(6)	0.023(3)	109.0	0.956
CRD3 3-10 cm	42.5(23)	1.67(9)	0.35(2)	0.0125(3)	16.54	0.998
CRD3 10-20 cm	49.8(20)	1.96(8)	0.277(9)	0.0071(2)	21.37	0.996
CRD3 20-30 cm	64.0(30)	2.52(12)	0.274(2)	0.00985(4)	0.94	0.999
CRG1 8-14 cm	57.6(8)	2.27(3)	0.253(5)	0.0178(2)	8.25	0.999
CRG1 14-21 cm	31.9(8)	1.26(3)	0.24(2)	0.0113(7)	44.93	0.989
CRG1 21-28 cm	68.1(15)	2.68(6)	0.36(2)	0.144(3)	57.78	0.998
CRG1 28-21 cm	66.0(23)	2.60(9)	0.254(3)	0.0170(1)	5.47	0.999
T1S1 0-10 cm	45.7(20)	1.80(8)	0.283(4)	0.00792(9)	2.64	0.999
T1S1 10-15 cm	47.5(26)	1.87(10)	0.16(1)	0.0077(8)	116.0	0.977
T1S1 15-24 cm	42.2(23)	1.66(9)	0.221(5)	0.0051(2)	10.58	0.995
T1S1 24-30 cm	26.8(25)	1.06(10)	0.18(1)	1.06(3)	47.93	0.968

466

467 **Figure 3a** shows the maximal quantity of DMPO-alkyl• adduct, i.e. [DMPO-alkyl•]<sub>max</sub> (**Table 3**,  
 468 **Figure S8**), produced after 2 min air-oxidation of each soil sample as a function of total iron in the  
 469 sample. Positive correlations are observed for CRD3, CRG1 and T1S1 core samples, but with a lower  
 470 rate of radical production with respect to total iron for T1S1 compared to CRD3 and CRG1.



471  
 472 **Figure 3.** Role of the reduced-state iron pool in reactive species production upon air-oxidation. (a)  
 473 The quantity of DMPO-alkyl• adduct produced after 2 min air-oxidation is displayed as a function of  
 474 total iron concentration (open circles) and of the initial reduced-state iron pool (plain circle).  
 475 Uncertainties fall within the symbol size (**Table 3**). The reduced-state iron pool is calculated as  
 476 Fe(0)+Fe(II) species in the pristine soil samples, as determined from LCF of XANES data at the Fe  
 477 K-edge (**Figure 4**; **Table 4**) (b) Detail of the LCF in the edge region is displayed before and after air-  
 478 oxidation with fit curves displayed as as green and red curves, respectively, and overlap experimental  
 479 data displayed as light blue, blue and orange colors for CRD3, CRG1 and T1S1, respectively. Strong  
 480 overlap between fit and experiment relies to fit quality. (c) Iron speciation derived from XANES LCF  
 481 analysis of the soils core samples before and after 2 min air-oxidation is displayed as bar diagrams  
 482 scaled to total iron concentration. Additional details on XANES and EXAFS LCF procedures are  
 483 reported in Supporting Information.

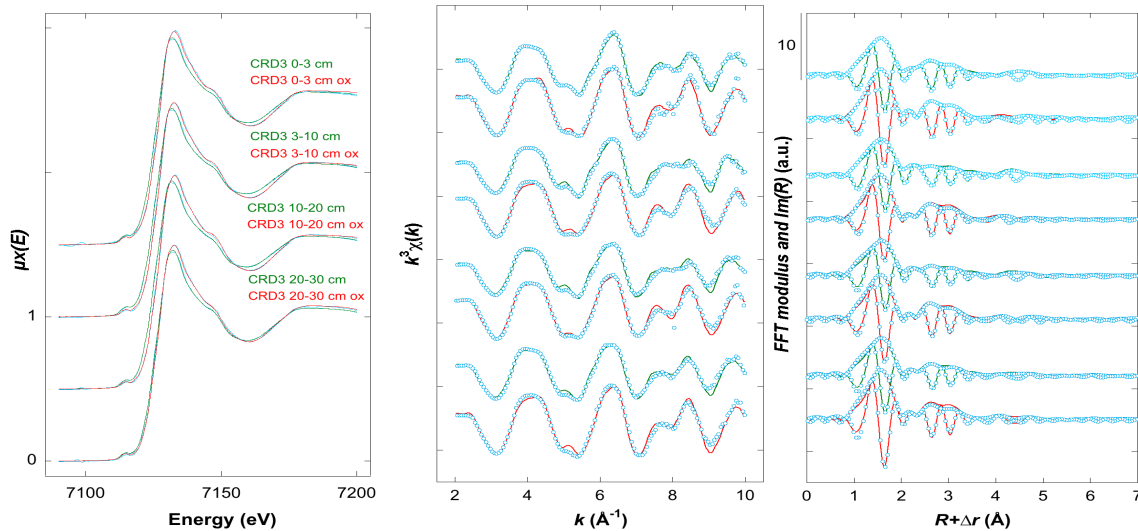
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485 Such positive but complex correlation between radical production and total iron content<sup>15</sup> or with  
486 Fe(II)<sup>18,20</sup> were previously observed in the past, which emphasizes the need for better identifying the  
487 driving factor for radical production, especially using spectroscopic methods<sup>17</sup>.

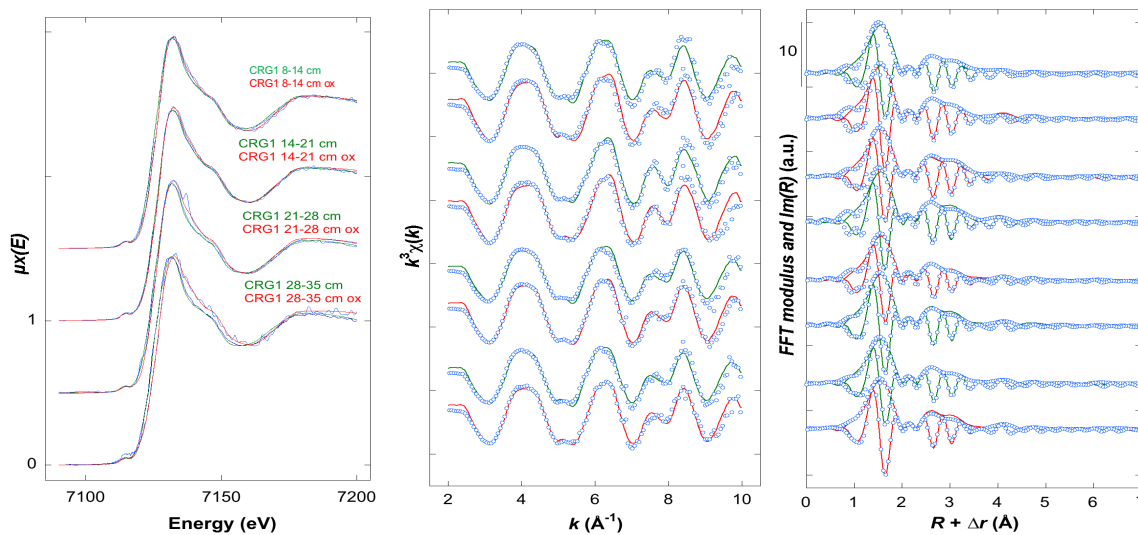
488 In our study, the differences in trend observed between the soils cores when considering total iron  
489 may be explained by differences in iron redox state as shown in **Figure 3b and 3c**. Indeed, the energy-  
490 shift of the Fe *K*-edge position before and after air-oxidation, is larger for most of the CRD3 and  
491 CRG1 samples than for the T1S1 ones (**Figure 3b**). This difference suggests that a larger proportion  
492 of total iron has been oxidized upon oxygenation in CRD3 and CRG1 than in T1S1. Accordingly, in  
493 the pristine samples, the proportion of initially reduced-state iron species over total iron is higher in  
494 CRD3 and CRG1 than in T1S1, as determined from LCF of Fe *K*-edge XANES data (**Table 4**).  
495 Hence, when scaling XANES LCF results (**Table 4**) to total iron (**Table 1**), the absolute “reduced-  
496 state iron” pool concentration in the pristine soil samples, i.e. Fe(0) + Fe(II) in CRD3 or Fe(II) in  
497 T1S1 and CRG1, ranges within similar values for the three soils cores (0.044 – 0.198 wt%) (**Figure**  
498 **3c**). It is then possible to compare this reduced-state iron pool in the pristine soil samples with the  
499 quantity of radical species produced upon their oxygenation and detected by EPR in the form of  
500 DMPO-alkyl• adducts (**Figure 3a**). The differences in radical production trends between the CRD3,  
501 CRG1 and T1S1 soils cores tend to vanish when considering the initial reduced-state iron pool instead  
502 of total iron. The fast and close-to-linear increase of radical species as a function of reduced-state  
503 iron pool ( $R = 0.85$  in **Figure 3a**) could then be interpreted as the initial rate of Fe(IV) production  
504 from highly reactive reduced-state Fe species.

505 The identity of the initial reduced-state iron pool species was further investigated by EXAFS LCF  
506 (**Figure 4; Table 4**). According to both EXAFS and XANES LCF results, structural Fe(II) in  
507 phyllosilicates largely contributed to the oxidizable fraction of iron since it systematically decreased  
508 after oxidation (**Figure 3c; Table 4**). Our proxy for the structural-Fe(II) clay component in the  
509 XANES and EXAFS LCF analysis is a Fe(II,III) biotite model compound (**Table 4**). Other  
510 phyllosilicates may actually host structural-Fe(II) and could match this proxy, especially smectites.

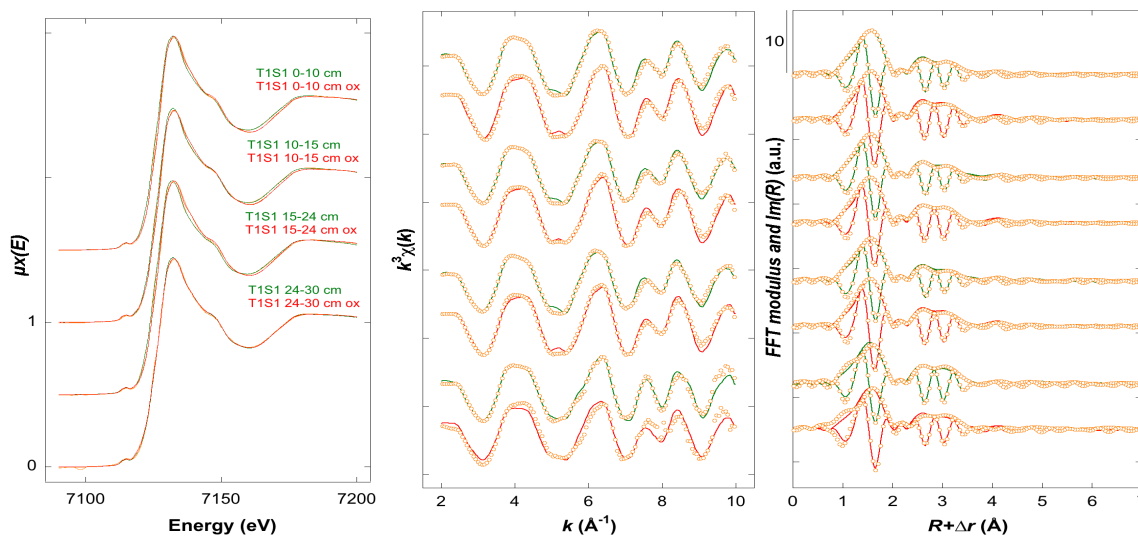
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514

515 **Figure 4.** Results of Fe K-edge XANES and EXAFS LCF for all samples studied. Experimental data  
 516 are plotted in light-blue, blue and orange colours for CRD3, CRG1 and T1S1 core samples,  
 517 respectively. Fitting curves are plotted in green and red curves for pristine and oxidized samples,  
 518 respectively



519 **Table 4.** Results of LCF analysis for Fe K-edge XANES and EXAFS data of alluvial soil samples from the  
520 Avenelles (CRD3 and CRG1 cores) and upstream-Bassée (T1S1 core) sites, before and after 2 min air-  
521 oxidation. Uncertainties on the last digit of reported component proportions are indicated under bracket to  
522 99.7% and 95% confidence ( $3\sigma$  and  $2\sigma$ ) for XANES and EXAFS, respectively (see text). Fit quality was  
523 estimated by a R factor (Rf) and a reduced  $\chi^2$  ( $\chi^2_R$ ) (see text). The proportion of “reduced-state Fe” over total  
524 iron is calculated as Fe(0)-metal + Fe(II)-pyrite + Fe(II)-vivianite + 0.7 x Fe(II,III)-biotite, based on the Fe-  
525 redox composition of our Fe(II,III)-biotite model compound (**Figure S9**).

XANES LCF Samples	Fe(0)- metal (%)	Fe(II)- pyrite (%)	Fe(II)- vivianite (%)	Fe(II,III)- biotite (%)	Fe(III)- illite (%)	Fe(III)- goethite (%)	Sum (%)	“reduced- state Fe” (%)	Rf $\times 10^4$	$\chi^2_R$ $\times 10^3$
CRD3 0-3 cm	6(2)	3(2)	7(2)	12(3)	21(5)	50(5)	100	24(2)	0.25	0.254
CRD3 0-3 cm ox	-	6(2)	-	4(3)	31(10)	59(10)	100	9(2)	1.06	1.077
CRD3 3-10 cm	9(1)	-	9(2)	17(3)	22(5)	44(5)	101	30(2)	0.27	0.270
CRD3 3-10 cm ox	-	3(1)	4(3)	5(5)	30(8)	60(8)	100	11(4)	0.63	0.641
CRD3 10-20 cm	5(2)	2(2)	10(2)	18(3)	22(5)	43(5)	100	30(2)	0.27	0.271
CRD3 10-20 cm ox	-	4(2)	4(1)	-	34(9)	58(9)	100	8(2)	0.76	0.757
CRD3 20-30 cm	5(1)	-	7(2)	15(3)	29(5)	44(5)	100	23(3)	0.27	0.271
CRD3 20-30 cm ox	-	2(2)	5(3)	6(5)	34(9)	54(9)	101	11(5)	0.75	0.774
CRG1 10-14 cm	-	-	13(3)	20(6)	30(10)	36(10)	99	27(5)	1.10	1.091
CRG1 10-14 cm ox	-	-	9(4)	9(7)	33(11)	48(10)	99	15(6)	1.16	1.147
CRG1 14-21 cm	-	1(1)	8(3)	11(5)	27(8)	52(7)	99	17(4)	0.57	0.563
CRG1 14-21 cm ox	-	2(2)	5(3)	6(5)	31(9)	56(9)	100	11(4)	0.76	0.767
CRG1 21-28 cm	-	2(2)	12(3)	23(6)	30(10)	32(10)	99	30(5)	0.95	0.942
CRG1 21-28 cm ox	-	-	16(2)	-	31(20)	53(19)	101	16(2)	4.13	4.128
CRG1 28-35 cm	-	-	18(5)	28(9)	30(15)	22(15)	99	38(8)	2.36	2.313
CRG1 28-35 cm ox	-	8(3)	11(2)	-	32(16)	50(16)	101	19(3)	2.64	2.660
T1S1 0-10 cm	-	1(1)	7(2)	16(3)	30(5)	47(5)	100	19(3)	0.23	0.229
T1S1 0-10 cm ox	-	2(1)	3(2)	5(4)	33(7)	57(7)	100	9(3)	0.46	0.461
T1S1 10-15 cm	-	1(1)	5(2)	14(4)	29(6)	51(6)	100	16(3)	0.33	0.337
T1S1 10-15 cm ox	-	4(1)	5(1)	-	31(7)	60(7)	100	9(1)	0.51	0.506
T1S1 15-24 cm	-	-	9(2)	18(3)	25(5)	49(5)	100	22(6)	0.28	0.281
T1S1 15-24 cm ox	-	2(1)	8(3)	-	31(8)	60(8)	101	10(2)	0.64	0.651
T1S1 24-30 cm	-	5(1)	5(2)	10(4)	23(7)	58(7)	99	17(4)	0.45	0.443
T1S1 24-30 cm ox	-	7(2)	6(3)	6(5)	29(9)	52(8)	99	17(4)	0.73	0.727

EXAFS data Samples	Fe(0)- metal (%)	Fe(II)- pyrite (%)	Fe(II)- vivianite (%)	Fe(II,III)- biotite (%)	Fe(III)- illite (%)	Fe(III)- goethite (%)	Sum (%)	“reduced- state Fe” (%)	Rf $\times 10^2$	$\chi^2_R$
CRD3 0-3 cm	5(2)	-	-	21(11)	30(12)	36(10)	91	20(7)	2.02	2.529
CRD3 0-3 cm ox	2(1)	-	-	-	69(8)	23(8)	94	2(1)	2.66	1.893
CRD3 3-10 cm	7(3)	-	-	33(16)	23(17)	31(14)	94	30(12)	2.55	5.119
CRD3 3-10 cm ox	-	-	-	-	56(19)	26(20)	82	0	3.17	11.80
CRD3 10-20 cm	5(3)	-	-	32(20)	27(21)	27(18)	90	27(15)	3.39	7.607
CRD3 10-20 cm ox	-	-	-	12(10)	52(11)	27(9)	92	8(6)	2.79	2.177
CRD3 20-30 cm	3(4)	-	-	30(24)	35(25)	24(22)	92	24(20)	3.00	11.59
CRD3 20-30 cm ox	3(3)	-	-	-	66(16)	24(17)	93	3(3)	3.41	8.339
CRG1 10-14 cm	-	-	-	25(15)	56(16)	19(13)	100	18(12)	7.93	4.682
CRG1 10-14 cm ox	-	-	-	-	73(13)	20(13)	93	0	6.61	5.427
CRG1 14-21 cm	-	-	-	19(11)	44(11)	39(9)	102	13(8)	5.63	2.330
CRG1 14-21 cm ox	-	-	-	-	59(12)	33(12)	92	0	9.93	4.415
CRG1 21-28 cm	-	-	-	21(19)	52(19)	17(16)	90	15(14)	7.60	7.033
CRG1 21-28 cm ox	-	-	-	13(9)	60(10)	23(8)	94	9(6)	4.76	1.703
CRG1 28-35 cm	-	-	-	27(12)	51(12)	17(10)	95	19(9)	6.07	2.721
CRG1 28-35 cm ox	-	-	-	13(9)	60(10)	23(8)	94	9(6)	4.76	1.703
T1S1 0-10 cm	-	-	-	31(20)	38(20)	31(17)	100	22(16)	2.15	7.645
T1S1 0-10 cm ox	-	-	-	-	54(20)	36(21)	90	0	2.64	13.62
T1S1 10-15 cm	-	-	-	27(13)	40(13)	29(11)	95	19(9)	1.85	3.138
T1S1 10-15 cm ox	-	-	-	-	52(16)	34(16)	85	0	2.44	8.409
T1S1 15-24 cm	-	-	-	33(12)	36(12)	27(10)	97	23(8)	2.41	11.37
T1S1 15-24 cm ox	-	-	-	-	58(18)	28(18)	86	0	2.67	10.51
T1S1 24-30 cm	-	-	-	27(18)	22(19)	49(16)	98	19(13)	4.36	6.779
T1S1 24-30 cm ox	-	-	-	20(18)	40(19)	27(16)	87	14(13)	10.3	6.555

527 This result is in line with other studies<sup>15,17</sup> proposing the Fe(II)-clay component as a major  
528 contributor to radical species production upon oxygenation of soils or sediments. In addition, our  
529 results suggest that Fe(0), likely from anthropogenic origin (**Figure 1e**), could also contribute to the  
530 oxidizable Fe fraction in the CRD3 samples since its proportion systematically decreases after  
531 oxidation (**Figure 3c; Table 5**). Vivianite (**Figure 1c**) could also contribute to oxidizable iron as  
532 indicated by a decrease of this component after air-oxidation (**Table 4**).

533 Alternative XANES and/or EXAFS LCF fit solutions could also be obtained, from sample to  
534 sample, by adding Fe(II)-polyphosphate or carboxylates fitting components, but with larger  
535 uncertainties (data not shown) than in **Table 4**, and resulted however in similar overall Fe(II)-pool  
536 quantities. Nevertheless, sorbed- or organic-Fe(II) species could also contribute to the Fe(II) pool and  
537 to radical production, as proposed in previous studies<sup>15,23,82,83</sup>. Because of such uncertainties on the  
538 identity of minor Fe(II) components, we have chosen in the present study to merge the Fe(II)  
539 components in the whole reduced-state iron pool, this latter estimate being accurately estimated by  
540 XANES LCF (**Table 3; Figure 3b and Figure 4**), and appearing relevant to be compared with the  
541 radical species production rate (**Figure 3a**). Finally, XANES LCF results do not reveal significant  
542 pyrite oxidation considering our experimental conditions, which is consistent with the results of  
543 previous laboratory experiments conducted under similar oxygenation conditions<sup>36</sup>.

544 Our results thus confirm that iron minerals are susceptible to play a major role in producing  
545 reactive species upon soil or sediment oxygenation<sup>15,17</sup>. For instance, a non-linear but positive  
546 correlation has been reported<sup>15</sup> between total iron content in river sediments and the amount of OH•  
547 produced upon oxygenation, as measured by BA/*p*-HBA method. In the same study, radical species  
548 production was found to increase with sediment sampling depth and after their reduction, thus  
549 suggesting that Fe(II) may be a major substrate for radical production. Structural and sorbed Fe(II)  
550 associated to clay minerals has been proposed as main contributors to radical production upon  
551 oxygenation, based on comparative air-oxidation experiments after selective chemical treatments<sup>15</sup>,  
552 and more recently using spectroscopic analyses<sup>17,39</sup>. Natural organic matter has been also proposed

553 to contribute in other studies<sup>18,24,25,33,84</sup>. The generation of re-oxidizable Fe(II) species in soils is  
554 typically attributed to microbial reduction of Fe(III)-minerals under anaerobic flooding conditions<sup>23-</sup>  
555 <sup>25</sup>, as those characterizing the alluvial soils studied here.

556 Beyond these previous findings, the present study show that Fe(II)-minerals, especially Fe(II)-  
557 bearing phyllosilicates play a key role in the production of non-hydroxyl reactive species in air-  
558 oxidation of riverbank soils. We also show that soil sourced and added phosphate favor these non-  
559 hydroxyl reactive species over OH• and that natural organic matter may be oxidized by these non-  
560 hydroxyl reactive species to form alkyl• and CO<sub>2</sub>• radical species.

561

## 562 **CONCLUSION**

563 Our results confirm that ferrous iron oxidation can be a major driver for the production of reactive  
564 species in soils and sediments upon air-oxidation<sup>15,17,23,82</sup>, which is actually recognized as a  
565 widespread process that may occur for instance in alluvial plains and coastal areas<sup>18,24,82,85</sup>. However,  
566 the identity of the various reactive species produced during iron-bearing minerals oxygenation may  
567 vary as a function of physicochemical conditions and are still a matter of research<sup>4,5,34,35,51,77,78</sup>. While  
568 it is widely assumed in the literature that OH• is produced, here we show by EPR spin-trapping  
569 analysis that another non-hydroxyl species is significantly produced upon air-oxidation of natural  
570 soils and sediments. Based on its differential reactivity toward tert-butanol and ethanol, and its  
571 enhancement by phosphate ligands, we hypothesize that this non-hydroxyl species could be  
572 interpreted as Fe(IV)<sup>4,34-36,65,69,70</sup>. Interestingly, the results of our air-oxidation experiments  
573 conducted without phosphate buffer show that this putative Fe(IV) species can be formed in natural  
574 soils suspensions, which could be explained by the presence of natural ligands favoring Fe(IV)  
575 formation in the soils, especially phosphate.

576

577

578 **ASSOCIATED CONTENT**

579 The supporting information file contains 4 tables (**Tables S1-S4**) and 12 figures (**Figure S1-S12**)  
580 including in particular XRD data, kinetics results on reactive species as derived from EPR data fitting,  
581 as well as PCA-TT analysis of Fe *K*-edge XANES and EXAFS data.

582

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597

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