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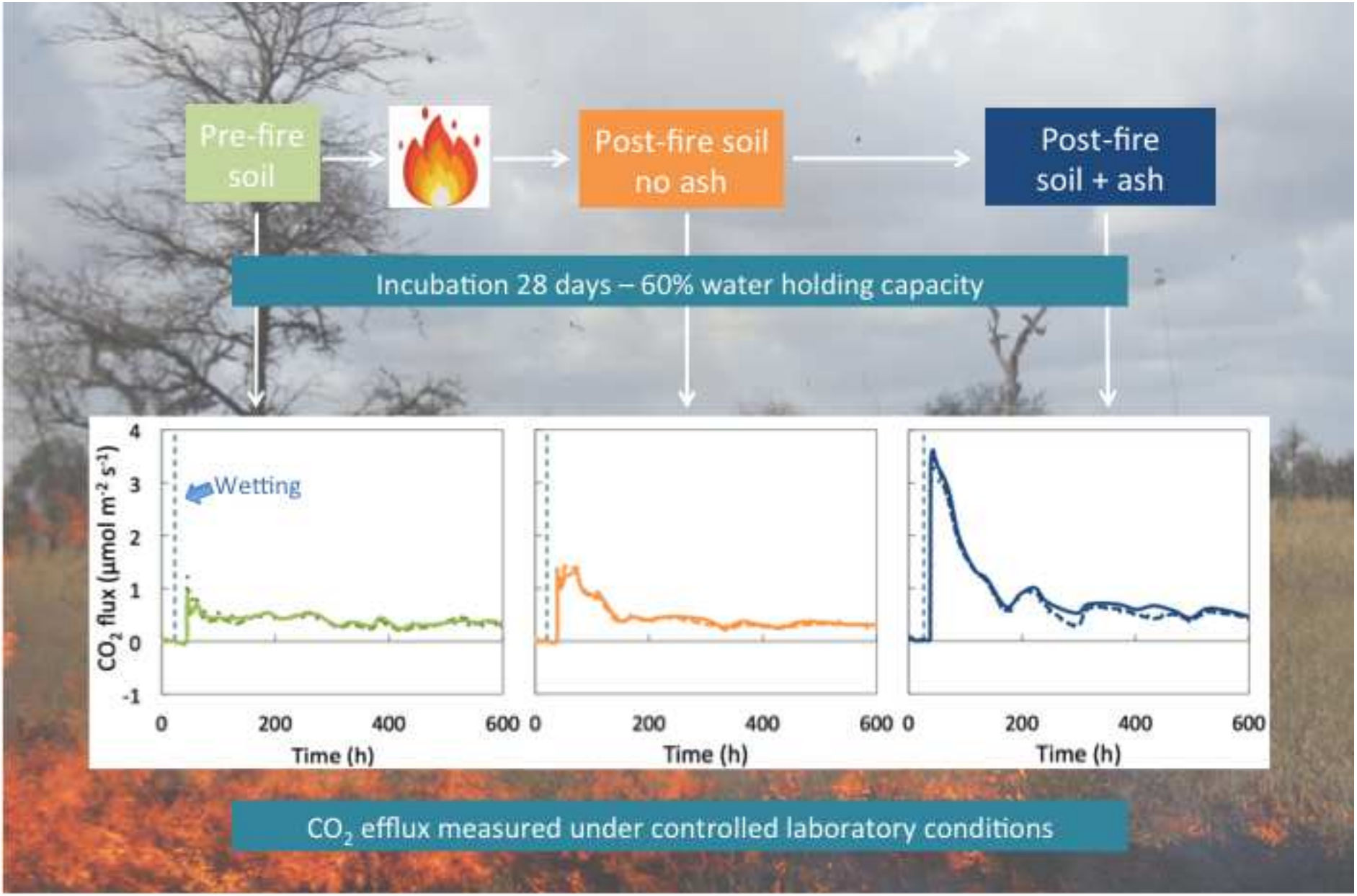

- Wildland fire ash enhanced CO_2 flux compared to pre and post-fire soil without ash.
- The addition of wildland fire ash accelerated the recovery of post-fire soil respiration.
- A large fraction of total carbon released occurred shortly after wetting of dry samples.
- Wildland fire ash is a significant player in post-fire carbon fluxes in African savannahs.

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Wildland fire ash enhances short-term CO_2 flux from soil in a Southern African savannah

Keywords: vegetation fire; ash; savannah; CO_2 flux; carbon emissions; pyrogenic carbon.

Abstract

Savannah fires are the largest contributor to global carbon (C) emissions from vegetation fires as a result of their high frequency and the large area burnt each year. Fires not only emit CO_2 during the combustion process, they can also lead to enhanced CO_2 fluxes from affected soils and vegetation, especially during the initial post-fire recovery period. Wildland fire ash is a ubiquitous product of vegetation fires known to enrich the nutrient content and pyrogenic C (PyC) of the underlying soil. However, the role of ash in post-fire soil C fluxes has rarely been examined. We address this research gap by investigating the effects of fire and wildland fire ash on CO_2 fluxes from fire-affected savannah soils. Soil and ash material were sampled from three different sites in an African savannah in the Kruger National Park (South Africa) before and immediately after experimental fires. CO_2 fluxes from homogenised natural soils and ash were continuously monitored for 28 days in a laboratory incubation experiment under controlled conditions (20 °C, 60% water-holding capacity). Wildland fire ash enhanced CO_2 emissions by up to 3 times compared with pre- and post-fire soils (without ash), likely as a result of the high content of readily available nutrients in the ash. Our results also show that as much as 40% of the total C released over 28 days occurred during a short-lived burst of CO_2 (lasting between 20 and 61 h) following wetting of the post-fire soil with ash samples. This study, although based on homogenised soil and ash material, shows that not considering wildland fire ash during post-fire soil C observations will likely

misrepresent natural conditions and might lead to underestimations of short-term post-fire C fluxes. The large differences observed between the post-fire soil with ash, and both the pre- and post-fire soil without ash, clearly suggest that ash is a key player in C fluxes and should be taken into account in post-fire C cycling studies. Our results also highlight the importance of high frequency observations during the short-term period following wetting of fire-affected soils, since bursts of CO_2 upon wetting of burnt soil can comprise a substantial fraction of total C emissions from burnt savannah soil.

1. Introduction

Fires in savannahs currently represent ~62% of the total global CO_2 emissions from vegetation fires. This is due to their high frequency and the large area burnt annually that these extensive ecosystems exhibit (van der Werf et al., 2017). Fire is a recurrent intrinsic ecological driver in African savannahs and considering that they cover half of the continent, understanding the role of fire in carbon (C) dynamics in these fire-prone ecosystems is essential (Bird et al., 2000; Shackleton & Scholes, 2000).

Soils store the largest pool of terrestrial C of which approximately two-thirds is soil organic C (SOC; Stockmann et al., 2013). Fire can directly alter the soil C pool by SOC combustion or by modifying SOC characteristics and composition. Indirectly, it can alter processes that affect the fluxes and composition of C, like post-fire changes in vegetation cover and soil erosion (Coetsee et al., 2010; Santín and Doerr, 2018). During a fire some of the burnt biomass is converted into recalcitrant forms of C (known as pyrogenic C, PyC) and can represent a C sink (Santín et al., 2015).

49 The CO_2 flux from soils is the largest C flux to the atmosphere from terrestrial ecosystems
50 (Longdoz et al., 2000). Fire can influence soil CO_2 fluxes by reducing microbial activity via
51 heat damage, or by altering soil chemical properties essential for microbial functioning such
52 as nutrient pools (Jensen et al., 2001; Matáix-Solera et al., 2009). Increases in CO_2 fluxes
53 from burnt savannah soils compared with unburnt ones have been observed in response to
54 precipitation events when sufficient soil moisture reactivates microbial activity (Andersson
55 et al., 2004; Castaldi et al., 2010; van Straaten et al., 2019).
56
57 It is widely assumed that ash deposition stimulates soil respiration due to its fertilization
58 effect by supplying readily available nutrients (e.g. Matáix-Solera et al., 2009). Enhanced soil
59 CO_2 fluxes in laboratory-based studies have been reported after the addition of lab-
60 produced ash to burnt soils (Badía & Marti, 2003; Raison & McGarity, 1980) and after the
61 soil fertilization with wood-ash (Fritze et al., 1994; Perkiömaki et al., 2003; Zimmermann &
62 Frey, 2002). In a recent field and laboratory study in a burnt eucalyptus and pine stand in
63 central Portugal we observed a larger increase in the CO_2 flux following wetting of burnt soil
64 in which a surface ash layer was intact compared with burnt soil in which the ash layer had
65 been experimentally removed, but the specific contribution of the ash layer to CO_2 fluxes
66 could not be isolated from other factors such as vegetation cover or soil texture (Sánchez-
67 García et al., 2020). In addition, the ash layer often contains PyC which is relatively resistant
68 to environmental degradation acting as a long-term C sink (Bodí et al., 2014; Santín et al.,
69 2016). Globally, savannah fires are the largest source of PyC because of their high fire
70 frequency (Jones et al., 2019). However, rapid degradation of some forms of PyC has been
71 previously reported from both wildfire-produced PyC (Bird et al., 1999; Zimmermann et al.,
72 2012) and after the application of laboratory-produced PyC to soil (Hilscher et al., 2009;
73 Jones et al., 2011). In some cases, PyC addition has been also observed to have a priming
74 effect in SOC decomposition (Maestrini et al. 2015).

Although ash is a ubiquitous direct product of vegetation fires, its role in post-fire soil C fluxes has scarcely been considered. This is primarily because of its rapid disappearance from the burnt areas prior to the initiation of most field studies due to its incorporation into the soil or redistribution or loss by wind and water erosion (Bodi et al. 2014; Santín et al., 2012). In addition, differences in the production conditions between naturally-produced ash (thereafter termed 'wildland fire ash') and artificially-produced ash (thereafter termed 'lab ash'), such as the duration of laboratory pyrolysis experiments or oxygen availability, can result in ash of different physico-chemical characteristics (Santín et al., 2017). In this study we refer to 'wildland fire ash' as the particulate ash residue naturally produced during experimental landscape fires (Bodí et al., 2014). To our knowledge, only two previous studies have investigated the input of naturally-produced ash on soil CO_2 fluxes. Enhanced CO_2 fluxes after the input of wildland fire ash were reported from African savannah soils by Andersson et al. (2004); whereas García-Oliva et al. (1999) observed a reduction in CO_2 fluxes from soils with added wildland fire ash from a tropical deciduous forest in Mexico suggesting that chemical changes induced by the input of ash inhibited microbial activity.

Therefore, evidence of the role of wildland fire ash on post-fire C fluxes is sparse and the response of soil CO_2 fluxes to the input of wildland fire ash remains poorly understood. Here we address this knowledge gap and aim at better understanding the effects of savannah fires on CO_2 fluxes from soils. The objective of the study was to investigate the fundamental effects of soil heating and wildland fire ash on CO_2 fluxes from savannah soils. We hypothesised that: I) the input of wildland fire ash to post-fire savannah soil will stimulate CO_2 fluxes, and II) soil heating from the fires will limit biological activity, thus reducing soil CO_2 flux when compared with pre-fire soil.

2. Research design and methods

2.1. Study sites

The study comprises a series of CO_2 flux incubation experiments on homogenised natural soil and ash materials (< 2 mm fraction) conducted under controlled laboratory conditions. Samples were collected hours before (pre-fire soils) and after (post-fire soils and ash) large-scale experimental fires conducted in the Kruger National Park (KNP; South Africa) in August 2018, in the middle of the dry season. The locations used for the study are part of the ongoing long-term experimental burn plots (EBPs) at KNP established in 1954 to study the impact of different fire regimes across representative South African savannah landscapes (Biggs et al., 2003). Three plots were selected for the study. Two of the plots were located in the Pretoriuskop area (mean annual rainfall of 705 mm), a Lowveld Sour Bushveld landscape on sandy granitic soils, which included one plot burnt annually (hereafter known as PB1; lat./long.: 25° 08' 24''S; 31° 12' 26''E) and a second plot burnt triennially (hereafter known as PB3; lat./long.: 25° 08' 06''S; 31° 12' 24''E). The dominant grass species were *Hyperthelia dissoluta*, *Themeda triandra* and *Setaria sphacelata*. The main tree species were *Dichrostachys cinerea* and *Terminalia sericea*. The third plot was located in the Mopani area (mean annual rainfall of 451 mm), a *Colophospermum mopane* shrubveld on clayey basaltic soil, which has been burnt annually (hereafter known as MB1; lat./long.: 23° 33' 48''S; 31° 27' 24''E). The dominant grass species was *Bothriochloa radicans* and the dominant tree species was *Colophospermum mopane*.

2.2. Experimental fires and soil and ash sampling

For soil and ash sampling and fire behaviour monitoring, a 30 x 30 m subplot was selected within the experimental burn plot at both PB1 and PB3 (Fig. 1c). These subplots were located more than 20 m from the edge of the burn plots to avoid edge effects (Smit & Asner,

126 2012). Locating a subplot with enough fuel continuity to ensure a successful burn was
127 challenging in MB1, therefore, a smaller subplot of 20 x 20 m with sufficient fuel was
128 selected (Fig. 1c). Before conducting the fires, three parallel transects were established
129 within each plot, 30 m long and 15 m apart in PB1 and PB3, and 20 m long and 5 m apart in
130 MB1. To monitor temperatures during the fire, K-type thermocouples with dataloggers
131 (Lascar, Easylog) were installed along each transect at four sampling points, at 9 m intervals
132 in PB1 and PB3 and 5 m intervals in MB1. At each sampling point (n = 12 per plot: Fig. 1c),
133 one thermocouple was placed in the grass, 3 – 5 cm above the ground, and another in the
134 mineral soil at ~1 cm below the surface. In addition, between the three sampling transects,
135 two 'control' transects were used for taking soil samples before the fire without disrupting
136 the post-fire sampling transects (Fig. 1c). A couple of hours before the fire, the top 0 - 1 cm
137 soil layer was sampled along these 'control' transects at 3 m intervals in PB1 and PB3 and
138 1 m intervals in MB1 (n = 20), using a 20 x 20 cm sampling frame and after removal of the
139 grass. The same day of the fire, the ash layer was brushed off the surface and the top 0 –
140 1 cm soil layer was sampled along the three sampling transects at the same points where
141 the thermocouples had been placed (n = 12) also using a 20 x 20 cm frame. At each plot,
142 three composite ash samples were also taken, based on material collected from several
143 locations within each burnt plot (approximately 500 g per sample). All samples were air
144 dried and stored in dry conditions in the laboratory. The fire characteristics are given in
145 Table 1. [Fig. 1 and Table 1 should be near here]
146
147 ## 2.3. Laboratory experiments and analysis
148 ### 2.3.1. CO_2 flux
149 For the laboratory experiments, the following sample materials were used from each of the
150 three burn plots: a) a pre-fire composite soil sample per site formed by combining equal

151 weights of the samples collected before the fire from each site (n = 20); b) a post-fire
152 composite soil sample per site formed by combining equal weights of the samples collected
153 after the fire from each sampling location (n = 12) and c) a composite ash sample per site
154 formed by combining the three ash samples. All air-dried soil and ash samples were sieved
155 to < 2 mm to remove larger debris. To study the effect of fire and the impact of naturally-
156 produced ash (wildland fire ash) on CO_2 fluxes, we used the following treatments: pre-fire
157 soil (PreF), post-fire soil without ash (PostF) and post-fire soil with added ash (PostF_wA).
158 We included three replicates of these three treatments from each site (PB1, PB3 and MB1),
159 resulting in 27 separate samples for flux measurement. The 70 g of soil material for the PreF
160 and PostF treatment were carefully placed into gas-tight plastic containers of 9 cm diameter
161 and 11 cm height. For the post-fire soil with added ash (PostF_wA), 7 g of ash was mixed
162 with 70 g of post-fire soil from their respective plots to create homogeneous samples. The
163 ash load (1051 g m^{-2}) was substantially higher than that observed in the field (~90 g m^{-2},
164 unpublished data), but selected in order to be comparable with other PyC/ash-soil
165 incubation studies (e.g. Gómez-Rey et al., 2012; Smith et al., 2010; Whitman et al., 2016).
166 The CO_2 flux measurements were conducted by connecting each soil container to an infrared
167 CO_2 gas analyser system (IRGA) (Li-8100A, Li-COR Inc., Lincoln, NE, USA) via a multiplexer (Li-
168 8150, Li-COR Inc., Lincoln, NE, USA) to allow an automated measurement of the CO_2 flux
169 from each sample every hour. Ambient air was continuously flushed between
170 measurements to prevent high CO_2 concentrations from developing in the containers. The
171 measurement of the CO_2 concentration in each container lasted 2 min with an additional
172 30 s for pre- and post-purge. The measurements of the soil CO_2 flux for the first 24 h started
173 with air-dried samples. The initial soil moisture in the air-dried samples (i.e. 1.3%, 1.7% and
174 2% gravimetric SWC for the PB1, PB3 and MB1 respectively) was lower than that typically
175 observed under field conditions during the dry season, when soil moisture typically ranges
176 between 3 – 5% across the KNP (Table 1 and Khosa et al., 2020). The samples were then

177 wetted to 60% of water-holding capacity (WHC) to ensure moisture availability while
178 avoiding saturation. The wetting was achieved by spraying deionised water from above. The
179 CO_2 flux monitoring was continued for 28 days. Soil moisture (60% WHC; i.e. 10% and 18%
180 volumetric soil water content for the PB and MB1 soils, respectively) and temperature
181 (~20 °C) were maintained throughout the observations, with any minor moisture loss caused
182 by evaporation being adjusted daily according to the weight difference in the samples from
183 the previous day. A small number of shoots that germinated from the soil during the
184 incubations were quickly removed by clipping to eliminate any root and shoot respiration.
185
186 The CO_2 concentration data over time was fitted exponentially, excluding the initial 30 s. Any
187 CO_2 flux data (µmol m^{-2} s^{-1}) with a coefficient of $R^2 \leq 0.95$ was discarded. This applied to < 3%
188 of the total measurements, which correspond predominantly to dry soil before wetting
189 where the CO_2 flux was 0, or close to 0. Therefore, discarding these values does not affect
190 the results. The cumulative flux (µmol m^{-2}) was calculated as the total CO_2 flux emitted
191 during the whole duration of the observations (28 d). Carbon respired was calculated by
192 converting cumulative flux (µmol m^{-2}) to g C m^{-2}.
193

194 ### 2.3.2. Chemical Analysis

195 The pH and electrical conductivity (EC) of soil and ash samples were determined in water at
196 a soil/ash-to-water mass ratio of 1:2.5 after stirring and waiting for 10 min (Buurman et al.,
197 1996). pH was measured with a Crison micropH 2000 pH meter, with buffer solutions of pH
198 4, 7 and 9. EC was measured with a Crison GLP 31 apparatus, calibrated with 0.1 and 0.01 M
199 potassium chloride (KCl) solutions (12.88 mS cm^{-1} and 1413 µS cm^{-1}, respectively).
200

Total Nitrogen (TN) and carbon (TC) concentrations were determined using a Leco TruSpec CHN. The total concentration of aluminium (Al), calcium (Ca), cobalt (Co), cromiun (Cr), copper (Cu), iron (Fe), magnesium (Mg), manganese (Mn), nickel (Ni) and zinc (Zn) were determined in extracts obtained by acid digestion (HNO_3/HCl, ratio v/v 3:1; at 180 °C for 45 min in an Ethos Easy Milestone Microwave) and measured by Atomic Absorption in a PerkinElmer PinAAcle 500 Atomic Absorption Spectrometer. Total phosphorus (P) was measured in the same extracts by colourimetry in a Jasco V360 spectrophotometer.

Water-soluble elements were extracted following the leaching test method described in Hageman (2007). Two g of sample were weighed into 50 ml bottles. Then, 40 ml ultrapure water (sample:water ratio 1:20) was added and the bottles were capped and shaken for 5 min. After shaking, the contents were allowed to settle for 10 min. The supernatants were vacuum-filtered through 0.45 µm cellulose nitrate membranes. Water-soluble organic carbon (WSOC), phosphate (PO_4^{-3}) and ammonium (NH_4^+) were then measured by colourimetry in a Jasco V360 spectrophotometer. Water-soluble nitrate (NO_3^{-2}) was quantified by liquid ion chromatography (Dionex Series 4500i Chromatographer).

2.3.3. TG-DSC analysis

Thermogravimetry-Differential Scanning Calorimetry (TG-DSC) was performed in order to examine thermal recalcitrance in the soil and ash material. The analyses were conducted in a simultaneous Thermal Analyzer (STA) 6000 PerkinElmer. Ground samples (50-70 mg) were placed in a ceramic crucible and heated under dry air (under O_2 flux; flow rate, 50 mL^{-1}) with increasing temperature from 50 to 600 °C at a heating rate of 10 °C min^{-1} while continuously monitoring the combustion rate and sample mass change rate. For each DSC thermograph, the area in the 150 - 600 °C region, where the combustion of organic matter (OM) occurs,

was divided into three temperature sections representing different levels of resistance to thermal oxidation (Merino et al., 2015): labile OM, mainly comprising carbohydrates, proteins and other labile aliphatic compounds (150 < T1 < 375 °C); recalcitrant OM, such as lignin or other polyphenols (375 < T2 < 475 °C); and highly recalcitrant OM, such as polycondensed aromatic forms (475 < T3 < 600 °C). The resulting partial heats of combustion, representing these three regions were calculated as Q1, Q2 and Q3, respectively.

2.4. Data analysis

The non-parametric Mann-Whitney U-test was used to test for statistical differences in the CO_2 fluxes (accepted at $p < 0.05$) between the incubation treatments and to test for differences in chemical composition and thermolability. The Spearman's rank correlation coefficient (rho) was used to test for linear correlations between the CO_2 flux and chemical properties (significance level set at $p < 0.05$). The tests were performed with Microsoft Excel 2011. The correlation tests amongst the thermogravimetry indicators and CO_2 fluxes were not performed since thermogravimetry data for the PostF_wA treatment were not available, as these were only obtained for the post-fire soil and the ash samples individually.

3. Results

3.1. CO_2 flux evolution with time

For all samples, the CO_2 flux before wetting was below 0.1 µmol m^{-2} s^{-1}. Following wetting, the CO_2 flux increased in all samples (i.e. PreF, PostF and PostF_wA) after a lag phase of 14 to 23 h in the PB1 and PB3 soils and ~29 h in the MB1 soil (Fig. 2). With the addition of ash to the post-fire soil (PostF_wA) the lag phases in the PB1, PB3 and MB1 soils were 8, 9 and 25 h

250 shorter than in the pre-fire soil, respectively. After the lag phase the CO_2 fluxes quickly
251 reached a peak (between 1 and 29 h) in all samples, except in the MB1 PreF soil where no
252 distinct peak was detected (Fig. 2). The CO_2 pulse in pre-fire (PreF) soils was low (mean ≤ 1 ±
253 0.18 µmol m^{-2} s^{-1}), while post-fire (PostF) soils had a significantly higher pulse ($p < 0.001$)
254 with the mean ranging between 1.5 ± 0.08 and 2.5 ± 0.24 µmol m^{-2} s^{-1} in the PB1 and PB3
255 soils, respectively (Fig. 2). [Fig. 2 should be near here]
256
257 The addition of ash to the post-fire soils (PostF_wA) resulted in an even higher pulse in all
258 samples ($p < 0.001$), reaching a mean of 4.5 ± 0.8 µmol m^{-2} s^{-1} in the MB1 soil and 3.5 ± 0.19
259 and 3.3 ± 0.14 µmol m^{-2} s^{-1} in the PB1 and PB3 soils (Fig. 2). The size of the pulse in the PB1
260 and PB3 PostF_wA soils was triple that of the PreF and nearly 11 times higher in the MB1
261 PostF_wA than in the PreF. The CO_2 fluxes decreased quickly after reaching their peak and
262 the pulse was over within the following 34 to 130 h. The CO_2 fluxes remained low thereafter
263 (< 0.5 µmol m^{-2} s^{-1}) in all soils until the end of the observations, 27 d after the beginning of
264 wetting (Fig. 2).
265

266 ### 3.2. Cumulative CO_2 flux and respired C

267 The cumulative CO_2 flux in the PreF soils ranged between 594 and 869 mmol m^{-2} in the PB3
268 and MB1 soil, respectively (Fig. 3). In the PostF soils, the cumulative flux was 25, 36 and 97%
269 higher than in the PB1, MB1 and PB3 PreF soils, respectively ($p < 0.001$; Fig. 3). The addition
270 of ash to the post-fire soils (PostF_wA) doubled the cumulative flux of the PreF soils in the
271 PB1 and MB1 (mean 1707 ± 98 and 1718 ± 66 mmol m^{-2}, respectively) and trebled PreF
272 values in the PB3 soil (mean 1772 ± 56 mmol m^{-2}; $p < 0.001$). The total C released from the
273 PostF_wA soil comprised 3 - 5% of the total carbon (TC) present in the sample (soil + ash)
274 (Table 2). [Fig. 3 and Table 2 should be near here]

The cumulative flux released during the pulse only comprised up to 23% of the total cumulative flux in the PreF soils (up to 1% of the TC) (Table 2). Up to 36 and 41% of the total cumulative flux was released during the pulse in the PostF and PostF_wA respectively, accounting for up to 3% of TC in the PostF soil and up to 2% of TC in the PostF_wA soil (Table 2).

The cumulative flux was positively correlated to dissolved organic carbon (DOC) and total carbon (TC; Fig. 4). The size of the CO_2 pulse was significantly correlated to cumulative CO_2 flux, TC, DOC and NH_4^+. TC was significantly correlated to TN and PO_4^{-3}, and TN was significantly correlated to NO_3^{-2} (Table 3). [Fig. 4 and Table 3 should be near here]

3.3. Chemical properties of soil and ash

Statistically significant differences were observed between PreF and PostF soils in the three studied sites in pH, electrical conductivity (EC), dissolved organic carbon (DOC), water-soluble ammonium (NH_4^+), nitrate (NO_3^{-2}), phosphate (PO_4^{-3}), total chromium (Cr), copper (Cu) and phosphorus (P). After the fire, a significant increase was found in both pH (from 6.5 to 7.5) and water-soluble PO_4^{-3} (from 0.4 to 2.3) in the PB3 soil (Table 4). With regards to DOC, a significant increase was detected in all PostF soils, which was particularly prominent in the MB1 soil where DOC values were 5 times higher than PreF ones (8.4 to 13.7 mg kg^{-1} in the PB1 soil, 5.0 to 27.2 mg kg^{-1} in the PB3 soil and 5.7 to 19.4 mg kg^{-1} in the MB1 soil, Table 4). While the concentration of water-soluble NH_4^+ was significantly enhanced after the fire in the PB3 soil (from 0.1 to 0.6 mg kg^{-1}); the concentration of water-soluble NO_3^- increased (from 0.4 to 0.8 mg kg^{-1}) and decreased (1.5 to 0.9 mg g^{-1}) significantly in the PB1 and MB1 soil after fire, respectively (Table 4). [Table 4 should be near here]

Regarding the ash samples, pH values were consistently around 10 (Table 4). The TC ranged between 20,900 and 28,600 mg kg^{-1} in the PB3 and MB1 sites respectively. The TN in the MB1 ash was nearly half that in the PB1 ash and around a third lower than in the PB3 ash (Table 5). Regarding inorganic N, both the concentrations of water-soluble NH_4^+ and NO_3^{-2} were significantly higher in the PB1 and PB3 soils than in the MB1 soils. The concentration of water-soluble PO_4^{-3} was especially high in the ash from the MB1 site with an average of 149 mg kg^{-1} compared with 6.7 and 6.2 mg kg^{-1} in the PB1 and PB3 sites (Table 4). [Table 5 should be near here]

3.4. Differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis

The DSC thermographs of the pre-fire samples revealed a first peak ($T1_Q$) in the range of 346 – 353 °C and a second, less prominent peak ($T2_Q$) at 376 – 399 °C (Fig. S1). In the pre-fire samples the majority of the energy was released in the Q1, which represents the labile OM category (Table 6; Campo & Merino, 2016). [Table 6 should be near here]

The thermograms of the soils sampled after the fire maintained the shape of the pre-fire samples with a peak at 341 – 346 °C (Fig. S1). $T50_Q$ rose slightly but not significantly in both the PB1 and PB3 soil after the fire (371 - 388 °C in the PB1 soil and 304 - 355 °C in the PB3 soil), and did not differ from pre-fire values in the MB1 soil (Table 6). The Q1 thermolability remained the most dominant category for all three soils (Table 6).

The DSC thermograms of the ash samples showed a prominent peak at much higher temperatures than in the soil samples, around 438 – 464 °C (Fig. S1). Most of the OM in the ash samples was classified into the Q2 category (43 - 56%), representing recalcitrant OM,

with only 21 - 29% of the DSC thermogram´s area in the labile Q1 category. The ash from the PB1 site showed the highest thermolability (Q1 = 29% and Q3 = 15%) while the lowest thermolability was observed in the MB1 site (Q1 = 21% and Q3 = 25%; Table 6). Detailed values of the TG-DSC analysis are shown in Table S2.

4. Discussion

4.1. CO_2 flux responds to ash input but not to soil heating

The post-fire soils showed an increase in CO_2 flux for all samples within 3 to 29 h after the start of the wetting. The additional input of wildland fire ash stimulated this CO_2 release by 2 to 3 times compared with the pre-fire and post-fire soils (without ash; Fig. 3). Therefore, we accept our first hypothesis that the input of wildland fire ash to fire-affected savannah soil stimulates soil CO_2 flux. Enhanced CO_2 fluxes following wetting of fire-affected soils have been previously reported either during rainfall simulation experiments (e.g. Pinto et al., 2002; Castaldi et al., 2010), or after actual rainfall events (e.g. Pinto et al., 2002; van Straaten et al., 2019). In a previous field study we also observed a rapid increase in the CO_2 flux following a rainfall simulation in a recently burnt pine and eucalyptus stand in Portugal, and larger CO_2 fluxes in plots with ash compared with those in which the ash layer was removed, although the specific effect of ash could not be isolated from that of vegetation cover and soil texture (Sánchez-García et al., 2020). Enhanced soil CO_2 fluxes with the experimental addition of ash have also been observed in previous incubation studies (e.g. Badía and Marti, 2003; Raison and McGarity, 1980; Hogg et al., 1992). For example, in the incubation experiment by Badía & Marti (2003), a 10% increase in respiration was observed with the addition of laboratory-produced ash to artificially-burnt soils from NE-Spain. Our results are in line with Andersson et al. (2004) who, to our knowledge, conducted the only previous study isolating the effects of wildland fire ash on C fluxes. They reported higher CO_2

fluxes in burnt loamy soils with added wildland fire ash than in burnt-only soils from African savannah woodland during a field experiment.

Ash is rich in organic C and soluble nutrients readily available for mineralization, like N and P (Tables 4 and 5; Bodí et al., 2014). The high pH commonly observed in ash (~10 in this study) can reduce soil acidity and enhance nutrient availability (Jensen et al., 2001; Perkiömaki et al., 2003). This can boost microbial activity resulting in higher respiration rates (Fritze et al., 1994; Zimmermann & Frey, 2002). Although carbonates present in the ash can contribute to the rapid CO_2 release upon wetting (Serrano-Ortiz et al., 2010), the addition of hydrochloric acid to the ash from this study showed no presence of carbonates. Therefore, we expect the contribution from carbonates in the ash to CO_2 fluxes here to be negligible.

It is important to note that for our results to be replicable we produced homogeneous samples of the post-fire soil with ash. However, under natural conditions the effect of ash can be spatially heterogeneous since some ash will be redistributed by wind and water and likely accumulate preferentially in depositional areas in the landscape, or be incorporated in the soil by bioturbation or percolating rainfall (Bodí et al., 2014).

Our results indicate that heating from the fire had little direct impact on the soil as supported by the slight and non-significant differences in thermal recalcitrance between pre- and post-fire soils (Table 6) and the generally low temperatures registered in the soil surface during the fires (Supplementary Table 1). Thus, we can reject our second hypothesis that heating of savannah soil reduces CO_2 flux when compared with pre-fire soil. Lower CO_2 fluxes were emitted from the post-fire soils without ash than from post-fire soils with ash, but the former were still significantly higher than those emitted from the pre-fire soils. This

375 is likely a result of some residual ash being incorporated in the post-fire mineral soil surface
376 sampled after the removal of the ash layer (Fig. 1).
377
378 The average CO_2 fluxes observed in the post-fire soil with wildland fire ash are similar to
379 those in unburned savannahs reported by Zepp et al. (1996), who observed mean fluxes
380 (measured for 30 min per day) of ~1 g C m^{-2} d^{-1} after light *in-situ* wetting of the soil in a semi-
381 arid savannah also from the Kruger National Park. Our daily flux in the post-fire soil with
382 added ash averaged 0.8 g C m^{-2} d^{-1}. In contrast, the CO_2 flux reported in our post-fire soil
383 with wildland fire ash is lower than those reported by Castaldi et al. (2010) (10 g C m^{-2} d^{-1},
384 fluxes measured 5 times over a two-week period) and Pinto et al. (2002) (3.7 g C m^{-2} d^{-1},
385 fluxes measured 3 times during one month); both during *in-situ* observations in a grass and
386 shrub savannah in the region of Congo (central Africa) and in a Brazilian savannah (central
387 Brazil), respectively. When compared with other arid and semi-arid ecosystems the mean
388 CO_2 flux observed in our post-fire soil with added ash is similar to those reported by Vargas
389 et al. (2012) (between 0 and 1 µmol m^{-2} s^{-1}) following a wildfire in an arid grassland in New
390 Mexico (USA) receiving 20 mm per month of rainfall. In wildfire-burnt semi-arid mixed
391 conifer and ponderosa pine stands in Oregon, Meigs et al. (2009) and Irvine et al. (2007)
392 reported higher annual CO_2 fluxes (~300 g C m^{-2} y^{-1} in both cases), but in the same order of
393 magnitude as those estimated for this study. In contrast, double the mean CO_2 fluxes (~2 g
394 CO_2 m^{-2} d^{-1}) as those observed in this study (~0.8 g C m^{-2} d^{-1}) were reported by Wüthrich et
395 al. (2002) over the month following an experimental fire in a sweet chesnut forest in
396 southern Switzerland.
397
398 From all the analysed chemical parameters total CO_2 released from the samples was only
399 positively correlated to TC and DOC (Table 3). Similar relationships with TC and DOC were
400 reported by Dicen et al. (2020) and Badía and Marti (2003), respectively, in their laboratory

401 incubation studies using artificially-burnt soil. Ash is a very good source of easily
402 mineralizable C (Table 4) and it is likely that microorganisms initially rely on the DOC, since
403 this C pool can be accessed immediately (Jones et al., 2011), after which microbes will utilise
404 more stable forms of C (Hilscher et al., 2009). However, the DOC in our samples (≤ 0.002 g C
405 in all cases, data not shown) is an order of magnitude lower than the total C respired (Table
406 2). Another explanation could be that microorganisms do not directly mineralize the labile C
407 in the ash, but use the nutrients in the ash to mineralize C from the native soil organic
408 matter (priming effect) (Maestrini et al., 2015).
409
410 The organic carbon in vegetation fire ash is mostly present in the form of PyC (Santín et al.,
411 2020). Even though PyC is considered highly resistant to microbial degradation, it has a labile
412 component (relatively large in our samples, between 21 and 29%, as indicated by the Q1% in
413 Table 5) which can undergo fairly rapid degradation during the initial stages of
414 mineralisation (Santín et al., 2016). High wildfire PyC degradation rates have previously been
415 reported in savannah soils from Zimbabwe (Bird et al., 1999) and Australia (Zimmerman et
416 al., 2012). Similarly, during a laboratory incubation experiment, Hilscher et al. (2009)
417 observed a complete consumption of the PyC's labile fraction (lab-produced) within the
418 initial 30 days of the incubation.
419
420 The results from this study clearly show that examining post-fire soil without ash is unlikely
421 to reflect natural conditions except for those patches in which ash has been lost by wind or
422 water erosion. It is important to highlight that the ash load applied in this study was
423 substantially higher than that generated from the experimental burns in the field in order to
424 allow comparison with previous PyC/ash-soil incubation studies. The outcomes should thus
425 be seen as indicative only, and we expect the CO_2 flux response to be less pronounced under
426 field conditions due to this factor and post-fire ash redistribution.

427

428 ## 4.2. Ash accelerated the CO_2 flux recovery after fire

429 The CO_2 pulse observed after wetting was preceded by a lag phase of very low CO_2 flux
430 lasting between 14 to 29 h (Fig. 2). Rewetting of dry soils is associated with a large flush of
431 CO_2 from the soil, known as the Birch effect (Birch, 1958), and has been extensively
432 observed in burnt and unburnt soils (Jarvis et al., 2007; Sánchez-García et al., 2020; Thomas
433 et al., 2014). In burnt soils the duration of the lag phase (i.e. the microbial activity recovery
434 time after the fire) is linked to heat exposure, since soil temperatures > 80 °C may kill many
435 microorganisms with most of them disappearing completely at 115 – 150 °C (Matáix-Solera
436 et al., 2009). During the experimental fires in this study only a few points registered T_{max} >
437 80 °C (Supplementary Table 1); therefore, considering that our studied samples were
438 composite samples, we expect that heating did not lead to high rates of microbial mortality
439 in our soils. This suggests that the lag phase is likely a consequence of the dry conditions
440 before wetting. These observations are in line with Pinto et al. (2002) and Zepp et al. (1996)
441 who also observed very low or neglible effects of fire on CO_2 fluxes. The length of the lag
442 phase observed in this study is in line with those reported following wetting of dry unburnt
443 soil (e.g. Meisner et al., 2017; Göransson et al., 2013).

444

445 Shorter lag phases were observed in all the post-fire soils with added ash; likely in response
446 to the input of readily available nutrients from the ash (Fig. 2). An exceptionally short lag
447 phase of only 3 h was observed in the MB1 post-fire soil with ash along with a higher CO_2
448 pulse than in the other two soils. The MB1 soil exhibited higher nutrient content than both
449 PB soils (Table 4 and 5) which could lead to a quicker recovery of microbial activity. Yet no
450 differences in the duration of the lag phase were observed amongst the pre- and post-fire
451 soil without ash in this soil. The very short lag phase in the MB1 post-fire soil with ash may

have been a response to the high available P in the ash from this site (i.e. water soluble PO_4^{-3}; Table 5). P is one of the most limiting nutrients in savannahs (Feig, 2004). Large inputs of P can result in its adsorption to soil particles and the desorption of bonded OM, which can increase the amount of DOC within 1 h after the addition of P and contribute to the larger CO_2 pulse (Meisner et al., 2015; Spohn & Schleuss, 2019). The increase in available P might also accelerate the reactivation of heterotrophic bacteria in soil which generally recovers quickly after a fire (Matáix-Solera et al., 2009) and could be a contributing factor for the quick and large CO_2 pulse in the MB1 soil after the addition of ash.

4.3. The importance of capturing the CO_2 flux response to wetting

The high-temporal resolution of our observations shows that up to 40% of the total C respired from post-fire soils with ash occurred within hours after the wetting. In African savannahs the CO_2 flux emitted during pulses in response to rainfall is estimated to account for up to a fifth of the annual CO_2 flux from soils (Fan et al., 2015) and soil moisture is one of the main CO_2 flux controllers in these semi-arid ecosystems (Zepp et al., 1996). In this study the burst of CO_2 following wetting of fire-affected soil was highly enhanced by wildland fire ash. After a fire the first wetting mobilises soil nutrients from both the soil and ash, reactivates microbial activity and facilitates the release of stored CO_2 in the soil pores resulting in a short, yet intense, mineralisation period which would explain the large CO_2 flush observed in this study (Matáix-Solera et al., 2009; Sánchez-García et al., 2020).

It is unlikely that under field conditions soil moisture would remain constant for long periods of time following wetting of burnt soil (e.g. Vargas et al., 2012). Instead another period of dry weather might follow with subsequent fluctuation in the CO_2 fluxes after each drying-wetting cycle. Capturing these “hot moments” of CO_2 release after a wildfire, and while the

layer of ash is still on the soil surface, is challenging but missing these large spikes in CO_2 flux can lead to unrealistic estimates of post-fire C dynamics and highlights the need to (i) increase the frequency of observations and (ii) for models to reflect this high variation in CO_2 fluxes. This becomes especially relevant in ecosystems with high fire frequency, like savannahs, which contribute most to global CO_2 emissions from vegetation fires each year (van der Werf, et al., 2017), and where fire occurrence is already being altered by climate change (Zubkova et al. 2019; Wei et al., 2020).

In summary, this study indicates that ash plays a quantitatively important role in post-fire C emissions. We expect a similar response of soil C fluxes to the presence of wildland fire ash in other post-fire environments, but the magnitude of this response, which we anticipate will depend on factors including fire charateristics, vegetation and soil types, and climatic conditions during the post-fire period, needs to be assessed by future studies.

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Table 1. Experimental fire characteristics including atmospheric conditions (wind speed, air temperature (Air T) and relative humidity (RH)), pre-fire soil water content (SWC), maximum temperature range (Tmax) registered in the soil surface and grass (n = 12), temperature residence times > 300 °C, and details of fire impacts on vegetation. Full details of temperatures reached during the experimental fires and their residence times in the soil surface and grass are provided in Supplementary Table 1.

		Atmospheric conditions				T max (°C)		T residence time > 300 °C (s)*		
Site	Date	Wind speed (m s^{-1})	Air T (°C)	RH (%)	SWC (% grav.)	Soil surface	Grass	Soil surface	Grass	Fire impacts on vegetation
PB1	19/08/18	1.8 – 2.7	26	41	3.6 ± 0.7	40 - 225	484 – 744	0	23 ± 20	In both PB1 and PB3 the fire burnt the entire experimental plot with complete combustion of fine fuels and no unburnt grass left. Woody fuels were mostly unaffected and wood on the ground (down wood) and bark from standing trees remained uncharred.
PB3	19/08/18	1.8 – 2.7	31	30	5.1 ± 1.9	40 - 182	651- 918	0	54 ± 38	
MB1	23/08/18	2.2 – 3.1	31	41	2.0 ± 0.3	40 - 498	452 - 850	15 ± 24	51 ± 40	Most (> 90%) of the fine fuels on the ground were burnt. Coarser woody fuels remained largely unaffected, whereas most of the green and brown leaves of the shrubs were consumed.

* Reported as this is the temperature threshold above which organic materials tend to transform into more aromatic and recalcitrant forms (Santín et al., 2016).

Table 2. Carbon (C) respired as CO_2 (CO_2-C; g C m^{-2}) during the 28-day observation period and during the CO_2 pulse (lasting 34 - 130 h) in g of C and as a percentage of the total C (TC). Values are the arithmetic mean (n = 3) with standard deviation.

		Total CO_2-C released - entire observation (g C m^{-2})	CO_2-C released - entire observation (g)	CO_2-C released - pulse only (g)	CO_2-C released - entire observation (% of TC)	CO_2-C released - pulse only (% of TC)
PB1	PreF	9.8 ± 0.6	0.065 ± 0.004	0.007 ± 0.001	7.9 ± 0.4	0.8 ± 0.1
	PostF	12.3 ± 0.4	0.082 ± 0.002	0.029 ± 0.002	7.8 ± 0.3	2.8 ± 0.2
	PostF_wA	20.5 ± 1.2	0.136 ± 0.008	0.056 ± 0.006	5.4 ± 0.3	2.2 ± 0.2
PB3	PreF	7.4 ± 0.3	0.049 ± 0.002	0.011 ± 0.001	4.5 ± 0.2	1.0 ± 0.1
	PostF	14.6 ± 0.3	0.097 ± 0.002	0.032 ± 0.004	6.4 ± 0.1	2.1 ± 0.3
	PostF_wA	21.3 ± 0.7	0.142 ± 0.004	0.043 ± 0.002	4.8 ± 0.2	1.4 ± 0.1
MB1	PreF	9.5 ± 0.2	0.063 ± 0.001	0.010 ± 0.001	3.1 ± 0.1	0.5 ± 0.1
	PostF	12.9 ± 0.8	0.086 ± 0.005	0.021 ± 0.004	3.8 ± 0.2	1.0 ± 0.2
	PostF_wA	20.6 ± 0.8	0.137 ± 0.005	0.032 ± 0.001	3.3 ± 0.1	0.7 ± 0

Table 3. Spearman's rank correlation (Spearman's rho) between CO_2 flux (size of the pulse and cumulative flux) and selected characteristics of the PreF, PostF and PostF_wA samples in mg kg^{-1} (total C and N, and dissolved organic carbon (DOC), NH_4^+, NO_3^{-2} and PO_4^{-3}; n = 9). Values with an asterisk show significant differences (at $p < 0.05$).

	Size of CO_2 pulse (µmol m^{-2} s^{-1})	Cumulative CO_2 flux (mmol m^{-2})	TC (g kg^{-1})	TN (g kg^{-1})	DOC (mg kg^{-1})	NH_4^+ (mg kg^{-1})	NO_3^{-2} (mg kg^{-1})	PO_4^{-3} (mg kg^{-1})
Size of CO_2 pulse (µmol m^{-2} s^{-1})	1.000							
Cumulative CO_2 flux (mmol m^{-2})	0.917*	1.000						
TC (g kg^{-1})	0.667*	0.767*	1.000					
TN (g kg^{-1})	0.350	0.433	0.85*	1.000				
DOC (mg kg^{-1})	0.833*	0.95*	0.633	0.317	1.000			
NH_4^+ (mg kg^{-1})	0.717*	0.600	0.133	-0.133	0.617	1.000		
NO_3^{-2} (mg kg^{-1})	0.067	0.017	0.500	0.717*	-0.167	-0.083	1.000	
PO_4^{-3} (mg kg^{-1})	0.583	0.667*	0.867	0.714	0.733	0.150	0.283	1.000

Table 4. Chemical properties of the pre-fire (PreF) and post-fire (PostF) soils and of the ash. Values are the arithmetic mean (n = 3) with standard deviation. Values with an asterisk show significant differences (at $p < 0.05$) between pre- and post-fire soil.

		pH	EC (µS cm^{-1})	DOC (mg kg^{-1})	NH_4^+ (mg kg^{-1})	NO_3^{-2} (mg kg^{-1})	PO_4^{-3} (mg kg^{-1})
PB1	PreF	6.4 ± 0.2	60.2 ± 25.8	8.4 ± 3.4	0.2 ± 0	0.4 ± 0.1	0.5 ± 0.3
	PostF	7.0 ± 0.5	99.7 ± 24.9	13.7* ± 1.5	0.7 ± 0.4	0.8* ± 0.2	1.2 ± 0.7
	Ash	9.8 ± 0.2	5543.3 ± 605.8	100.4 ± 36.1	0.5 ± 0.1	4.7 ± 1.3	6.7 ± 2.7
PB3	PreF	6.7 ± 0.1	68.9 ± 39	5.0 ± 3.1	0.1 ± 0	0.7 ± 0.2	0.5 ± 0
	PostF	7.5* ± 0.5	206.4* ± 37.1	27.2* ± 9.3	0.6* ± 0.2	0.4 ± 0.2	2.3* ± 0.3
	Ash	10.0 ± 0.1	4776.7 ± 631.7	84.4 ± 12.2	0.4 ± 0	3.2 ± 0.4	6.2 ± 1.7
MB1	PreF	7.9 ± 0.1	139.4 ± 22.2	5.7 ± 1.9	0.1 ± 0	1.5 ± 0.4	2.0 ± 0.5
	PostF	7.6 ± 0.4	258.0* ± 43.7	19.4* ± 5	0.2 ± 0.1	0.9* ± 0.1	2.4 ± 0.6
	Ash	9.9 ± 0	2877.7 ± 965.3	50.3 ± 2.2	0.2 ± 0	1.6 ± 0.3	149.3 ± 29.9

Table 5. Elemental concentrations (mg kg^{-1}) for the pre-fire (PreF) and post-fire (PostF) soil and the ash. Values are the arithmetic mean (n = 3) with standard deviation. Values with an asterisk show significant differences (at $p < 0.05$) between pre and post-fire soil.

		C:N	TC	TN	Al	Ca	Co	Cr	Cu	Fe	Mg	Mn	Ni	P	Zn
PB1	PreF	16 ± 3	11797 ± 5100	750 ± 400	14449 ± 2821	481 ± 337	4 ± 1	40 ± 3	6 ± 1	14732 ± 1766	356 ± 96	193 ± 42	2 ± 1	97 ± 34	11 ± 2
	PostF	16 ± 4	14963 ± 1000	943 ± 200	14643 ± 1530	723 ± 93	4 ± 0	25* ± 1	8* ± 0	18219 ± 2672	393 ± 64	218 ± 3	2 ± 1	125 ± 31	11 ± 1
	Ash	39 ± 2	248267 ± 45700	6287 ± 1000	9852 ± 1530	34226 ± 1262	19 ± 1	51 ± 13	32 ± 1	6551 ± 1521	7373 ± 420	1297 ± 58	8 ± 1	3902 ± 272	164 ± 13
PB3	PreF	16 ± 0	15730 ± 6000	990 ± 400	12601 ± 3703	999 ± 662	5 ± 2	59 ± 3	7 ± 1	10656 ± 954	397 ± 105	244 ± 34	8 ± 3	128 ± 19	11 ± 2
	PostF	19 ± 3	21543 ± 13300	1147 ± 600	10867 ± 668	1419 ± 607	4 ± 1	41* ± 6	8 ± 1	9735 ± 1646	482 ± 64	246 ± 13	8 ± 1	149 ± 22	9 ± 3
	Ash	50 ± 3	208967 ± 16800	4203 ± 600	9917 ± 2709	43281 ± 4976	8 ± 11	65 ± 17	29 ± 9	7256 ± 2007	8936 ± 1026	1435 ± 252	14 ± 3	4687 ± 515	182 ± 27
MB1	PreF	15 ± 0	29050 ± 1100	1977 ± 100	36248 ± 1406	17700 ± 666	37 ± 1	353 ± 15	75 ± 1	57773 ± 1277	20740 ± 651	949 ± 3	348 ± 8	1217 ± 84	78 ± 1
	PostF	16 ± 1	31850 ± 5500	2047 ± 400	35153 ± 2200	16606 ± 1126	38 ± 1	353 ± 8	77 ± 4	57298 ± 945	21135 ± 192	941 ± 29	349 ± 8	1437* ± 71	164 ± 13
	Ash	93 ± 5	286133 ± 6500	3080 ± 100	3695 ± 329	17870 ± 2724	4 ± 1	57 ± 1	22 ± 1	6125 ± 430	6872 ± 590	252 ± 21	44 ± 2	5861 ± 1040	129 ± 15

Table 6. Main TG-DSC parameters for the pre-fire (PreF) and post-fire soil (PostF) and in the ash. $T50_Q$: temperature at which the sample released half of its total stored energy; Q1, Q2 and Q3: percentage of heat released in each group of thermal oxidation (150 – 375 °C; 375 – 475 °C; 475 – 600 °C respectively). Values are the arithmetic mean (n = 3) with standard deviation.

Site	Treatment	$T50_Q$ (°C)	Q1 (%)	Q2 (%)	Q3 (%)
PB1	PreF	371.3 ± 25.9	44.9 ± 12.6	31.7 ± 6.6	23.3 ± 9.5
	PostF	387.7 ± 27.1	42.1 ± 10.3	34.7 ± 7.7	23.2 ± 18
	Ash	414.3 ± 2.6	29.4 ± 1.4	55.9 ± 1.1	14.6 ± 1.9
PB3	PreF	304.0 ± 133.5	40.9 ± 0.7	35.9 ± 8	23.2 ± 7.7
	PostF	355.0 ± 35.5	53.0 ± 12.4	35.2 ± 9.8	11.8 ± 4.1
	Ash	419.0 ± 3.2	26.3 ± 2.6	56.4 ± 0.2	17.3 ± 2.5
MB1	PreF	342.0 ± 1.7	53.6 ± 2.6	33.2 ± 1.6	13.1 ± 4.3
	PostF	343.0 ± 3.6	53.3 ± 2.8	33.7 ± 0.4	13.0 ± 2.9
	Ash	433.8 ± 4.4	21.2 ± 2.6	53.4 ± 1.6	25.4 ± 3.5

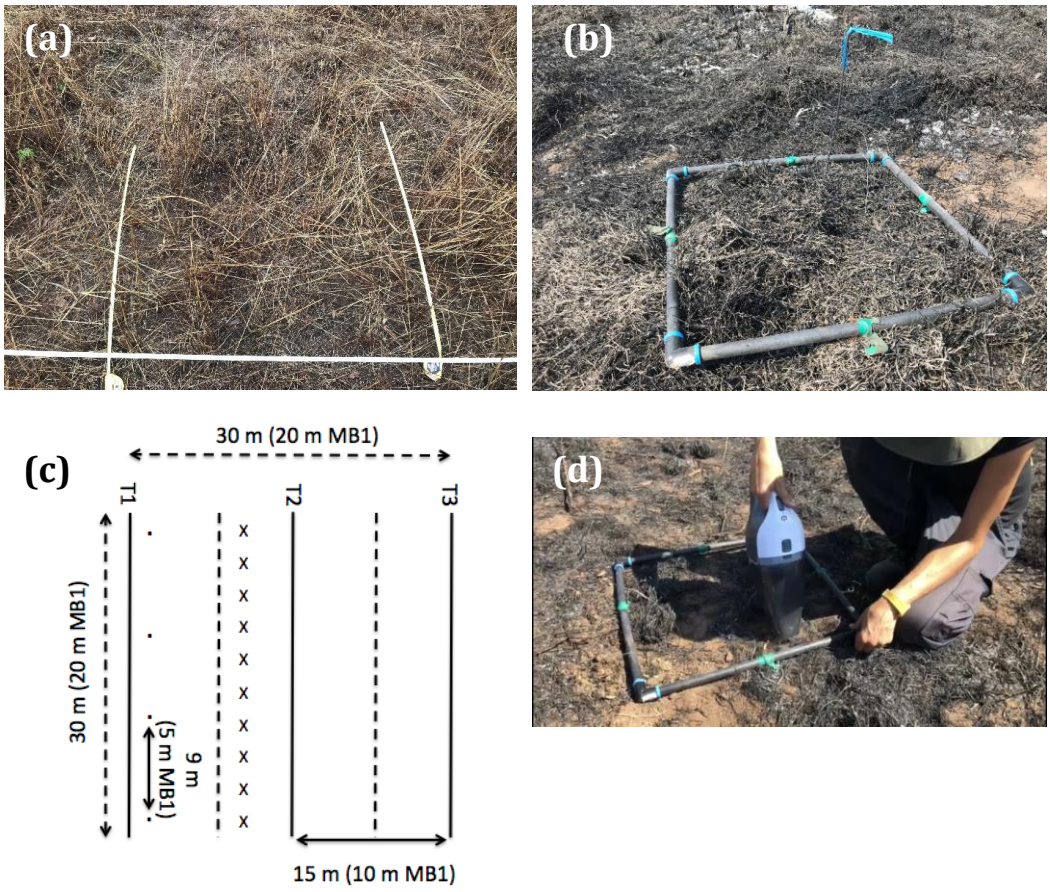

Fig. 1. **(A)** Grass in the PB3 site before the fire. **(B)** Burnt grass in the MB1 site after the fire. **(C)** Experimental plot diagram for PB1 and PB3 plots, and dimensions for the MB1 plot in brackets. Solid lines represent the experimental transects and dashed lines represent the control transects. Dots along the experimental transects represent the locations of the thermocouples and crosses along the control transect represent soil sampling locations before the fire. **(D)** Sampling the ash layer in the MB1 site after the fire.

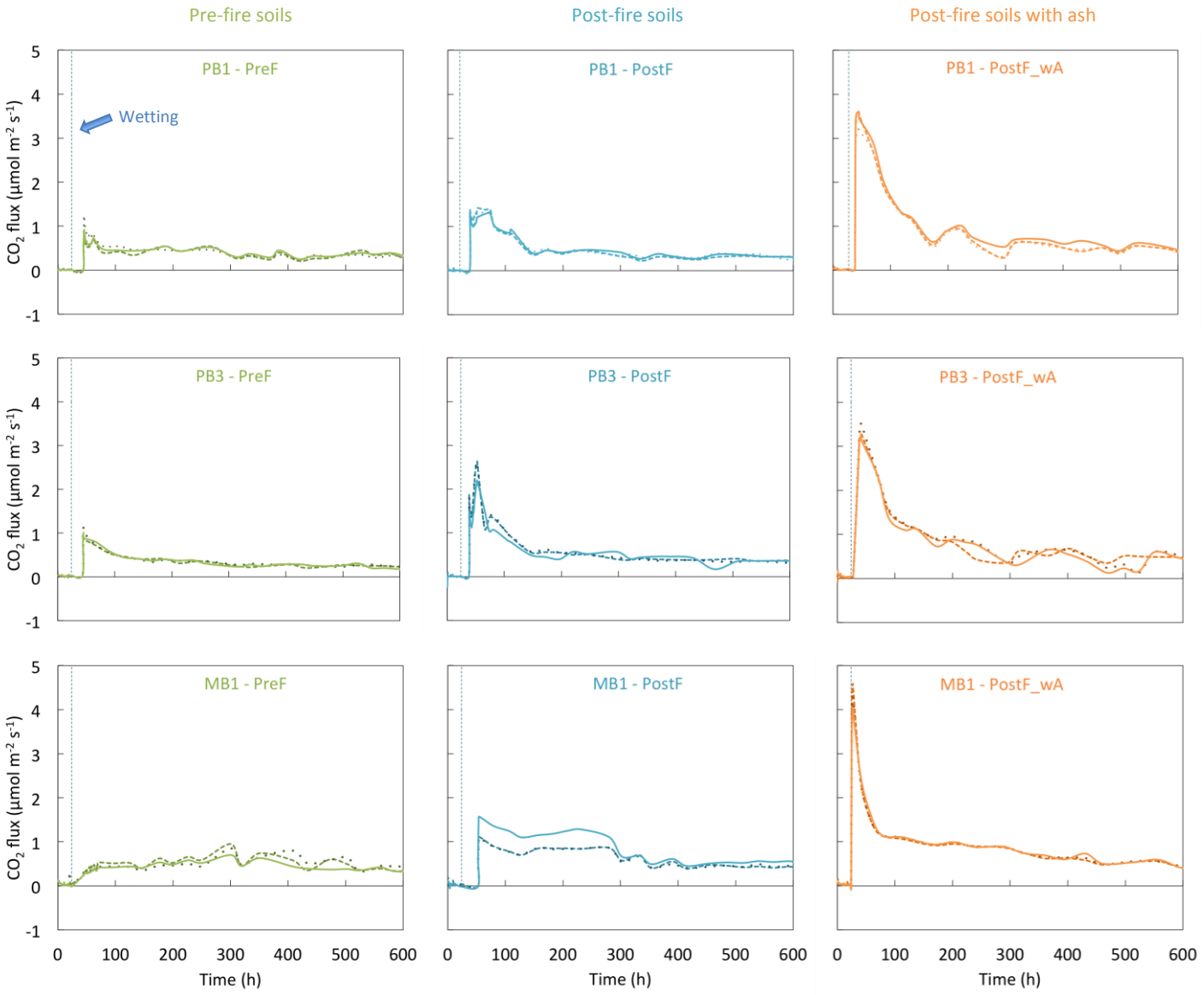

Fig. 2. Response of CO_2 flux to wetting of pre- (PreF) and post-fire soils (PostF) and post-fire soils with added ash (PostF_wA). Solid, dotted and dashed lines represent the three replicates. The blue dashed vertical line represents the start of the wetting, 24 h after the start of measurements.

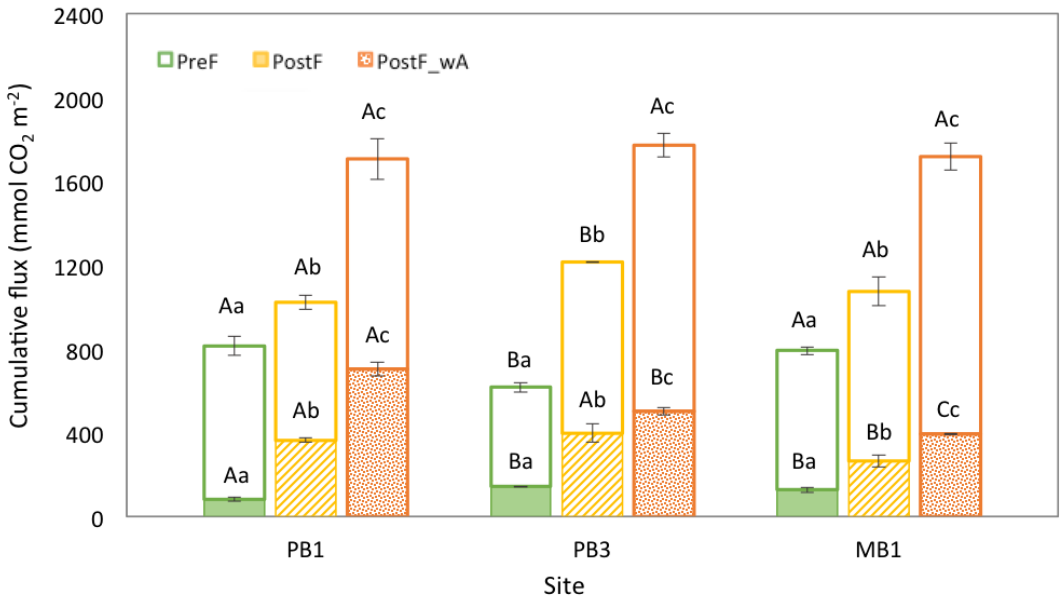

Fig. 3. Cumulative flux for the duration of the observations (28 d) (total columns) and proportion of the cumulative flux released only during the CO_2 pulse (24 – 130 h) (filled columns) in the pre-fire (PreF) and post-fire soils (PostF) and in the post-fire soils with added ash (PostF_wA). Values represent the mean (n = 3) with standard deviation bars. Different lowercase letters (a – c) within the same site indicate significant differences between incubation treatments and different uppercase letters (A – C) indicate significant differences between sites for each treatment at $p < 0.05$. Letters above the unfilled columns represent differences between the total cumulative flux and letters above the filled columns represent differences between the cumulative flux released during the CO_2 pulse.

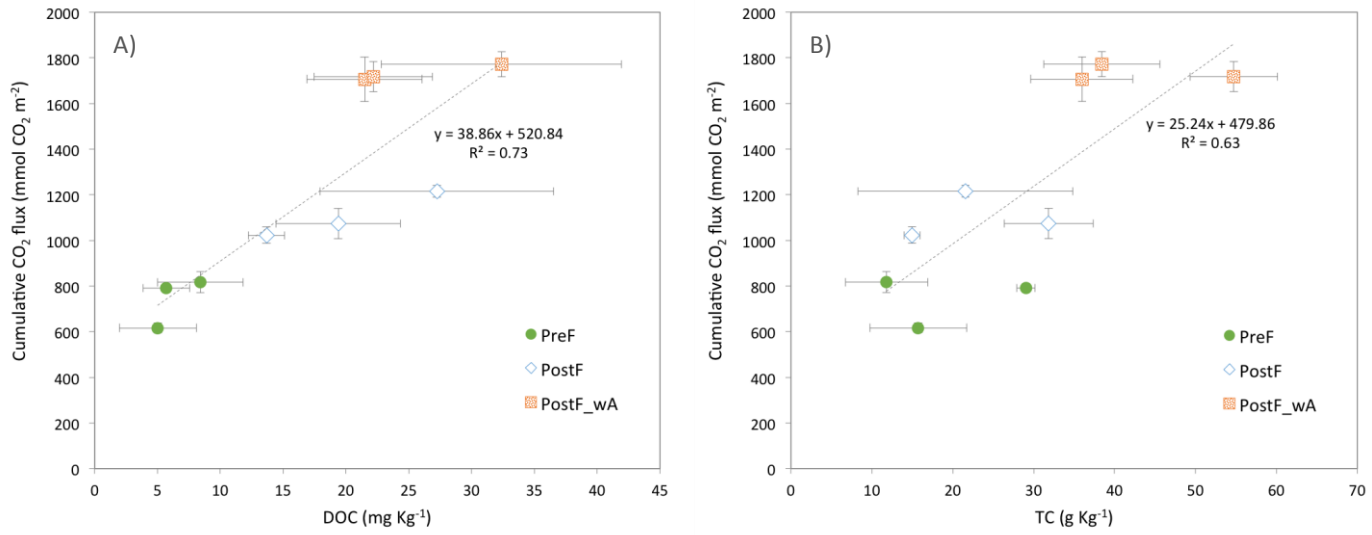

Fig. 4. A) Relationship between cumulative CO_2 flux and dissolved organic carbon (DOC) ($p < 0.001$) and B) relationship between cumulative CO_2 flux and total carbon (TC) ($p < 0.05$) in the pre-fire (PreF) and post-fire soils (PostF) and in the post-fire soils with added ash (PostF_wA). Values are the arithmetic mean (n = 3) with standard deviation bars.

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Conflict of interest statement

The authors have no conflict of interest to declare.