



# Short-Term Effects of Wildfire Ash on Water Quality Parameters: A Laboratory Approach

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## Abstract

Climate change coupled with inappropriate burning practices has increased large-scale wildfires in Brazilian tropical savannahs (*Cerrado*). Considering that the effects of ash from wildfires on water parameters are scarcely known in tropical savannahs, this study investigated the chemical changes caused by ash in the soft water, commonly used for bioassays. To this end, ash samples were collected immediately following a fire in a *Cerrado* area (Federal District, Brazil) and put into water (1:10 ash:soft-water *m/v*) to check physical parameters under laboratory conditions. Major water-extractable elements ( $K^+$ ,  $SO_4^{2-}$ ,  $Ca^{2+}$ ,  $PO_4^{3-}$ ,  $Na^+$ ,  $Mg^{2+}$ ) from ash strongly altered water quality parameters: elevated total dissolved solids and conductivity levels as well as an increase in pH and decrease in dissolved oxygen concentration were reported over the course of the experiment (15 days) compared to control conditions. Our results point out relevant solubilized compounds from ashes which may potentially impact water quality in post-fire scenarios.

**Keywords** *Cerrado* biome · Fire · Ash · Water · Physicochemical parameters

Fire plays an important role in the circulation and exchange of nutrients among environmental compartments (Bodí et al. 2014), but human activities have strongly modified the natural fire regime throughout the world, which, in turn, may increase fire severity (Mann et al. 2017). Despite the use of modern technologies in agriculture in Brazilian tropical savannahs (Lapola et al. 2014), which discourages fire practices in graze lands, burning activities, as a way of land clearing, have still exerted strong impacts on the ecosystem structure and function, and threatened habitat connectivity of the remaining natural areas (Ferreira et al. 2012).

Intense fires can result in significant production of ash, which may also remain in the soil (Oliveira-Filho et al. 2018) or be carried by surface runoffs to aquatic ecosystems

during rainfall events (Silva et al. 2015). Several studies have shown that post-fire event, combined with rainfalls, lead to ash and top-soil flows into aquatic systems and pose complex impacts on water quality, such as increase in water turbidity, pH, conductivity and oxygen depletion (Bixby et al. 2015), with diverse and adverse effects on aquatic biota (Gonino et al. 2019). In spite of the world's recognition of Brazilian savannah, known as *Cerrado*, as one of the hotspots for biodiversity conservation (Myers et al. 2000), large-scale agriculture, grazing and deforestation of remaining natural areas has been occurring over the last decades (Sano et al. 2010) coupled with inappropriate burning practices, drive wildfire events resulting in negative effects on biota and aquatic ecosystem.

Most current studies investigating the impacts of fires on water resources are derived from fire prone regions in temperate areas (Dahm et al. 2015; Campos et al. 2016; Nunes et al. 2018), and studies about the effects of ash on tropical waterways are scarce (Brito et al. 2017; Oliveira-Filho et al. 2018; Gonino et al. 2019). To address this research gap, this study investigated the effects of ash from a burnt area on water quality (soft-water) over a short period (15 days). We carried out our study under controlled conditions, where physical parameters were controlled or manipulated for confounding effects, and then offered relevant data of ash-inputs

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on water systems. It is also noteworthy that these data are a continuation of larger laboratory-based studies of ash from different burnt areas in *Cerrado* regions (Brito et al. 2017; Oliveira-Filho et al. 2018).

## Materials and Methods

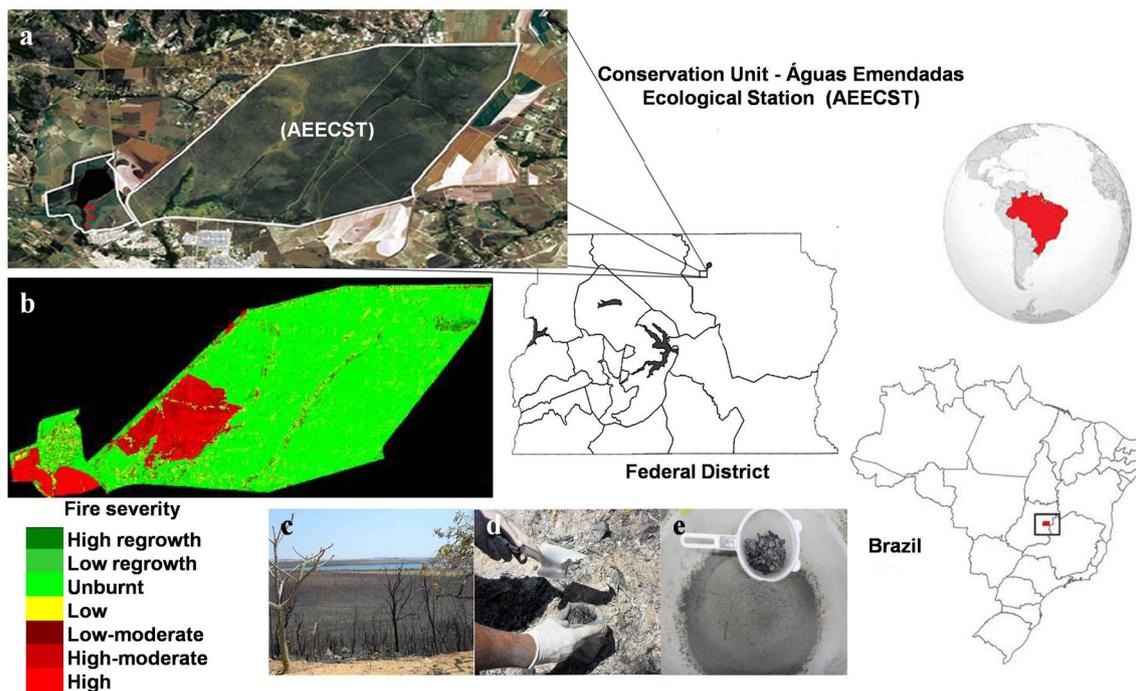
This study was carried out in a recently burnt area within a Conservation Unit (15°36'33,6"S and 47°43'09,1"W; Águas Emendadas Ecological Station-AEECST), located in the Federal District, in central Brazil (Fig. 1). The AEECST has a total area of 10,500 ha and the landscape varies from open grasslands to woody cover, besides gallery forests and swamp communities (*vereda*). The selected area was burnt by a wildfire in early September 2010, affecting an area predominantly covered by a transition area between palm swamp communities (*vereda*) and savannah fields (*campo cerrado*) and near the Bonita Lagoon. The wildfire was classified as high-moderate severity, according to the methodology described in Teobaldo and Baptista (2013). For assessing fire severity, remote sensing standard methods were used and fire severity classification is shown in Fig. 1 (Teobaldo and Baptista 2013).

The *Cerrado* is the second largest Brazilian biome and is the most threatened tropical savannah in the world; it

includes a complex vegetation ranging from grassland to tall woodlands (Ribeiro and Walter 2008). The regional climate is humid tropical-Aw (Köppen classification), with high precipitation in the summer (November-January) and a dry season in the winter (June-August). The average annual precipitation is between 1100 and 1700mm (September-April), and the soils of the study area were mapped predominantly as Rhodic Ferralsol.

Ashes are characteristic of burnt areas and are composed of organic and inorganic particulate residue remaining from organic matter combustion (Bodí et al. 2014). Samples of ashes were collected from five points defined the day after the fire was extinguished (Fig. 1d). Since the ashes are not homogeneously distributed in the study area, the five sampling points were selected in places with visually-assessed larger ash deposits, and covering the largest spatial diversity of the area near the Bonita Lagoon (Fig. 1a). Then, similar volumes of ashes (~ 3 L) were collected at each point, by using a small brush and spoon. The collected ash samples were placed into plastic bags and taken to the laboratory. The five ash samples from each point were likewise mixed into a single homogeneous composite of ash sample, which was sieved through 1 mm mesh, and then stored for preparation of the stock solution (Fig. 1e).

The stock solution was prepared by shaking the ash sample in 1:10 (*m/v*) ratio with soft water. Synthetic soft water



**Fig. 1** a Location map of the study area burnt by wildfire in *Cerrado* Biome (early September 2012, Federal District, Brazil). Left down: the study area and location of the ash five samplings (red stars). b Burnt area in the Conservation Unit with the fire severity classifica-

tion according to Teobaldo and Baptista (2013). c Ash sampling on the day immediately after the fire. d Photo of the study area was taken on the day of the ash sampling. e Preparation of ashes for the tests

(pH  $7.2 \pm 0.2$  and  $40 \text{ mg L}^{-1}$  of  $\text{CaCO}_3$ ) is commonly used in ecotoxicological assays (ABNT 2005). In order to assess the ash solubilisation over the exposure time, samples of the stock solution were placed in Erlenmeyer flasks and kept under agitation (on an orbital shaker at 150 rpm) for 30 days. Aliquots of samples were taken for chemical analyses at 4, 10, 15 and 30 days. The proportions of the stock-solution used here were based on ecotoxicological assessments of ashes and leachates (Brito et al. 2017).

The stock solution ( $100 \text{ g L}^{-1}$ ) sample was filtered through a cellulose ester filter ( $0.45 \mu\text{m}$ ) and maintained in a freezer ( $5^\circ\text{C}$ ) for determination of chemical analyses by Ion chromatography techniques (*Compact IC 761 Metrohm*), which was used for both cations [Lithium ( $\text{Li}^+$ ), Sodium ( $\text{Na}^+$ ), Ammonium ( $\text{NH}_4^+$ ), Potassium ( $\text{K}^+$ ), Calcium ( $\text{Ca}^{2+}$ ) and Magnesium ( $\text{Mg}^{2+}$ )] and anions: [Fluoride ( $\text{F}^-$ ), Chloride ( $\text{Cl}^-$ ), Nitrate ( $\text{NO}_3^-$ ), Nitrite ( $\text{NO}_2^-$ ), Bromide ( $\text{Br}^-$ ), Phosphate ( $\text{PO}_4^{3-}$ ) and Sulphate ( $\text{SO}_4^{2-}$ )] (Table 1) (EMBRAPA 1997). The cation and anion detection limits were  $0.001 \text{ mg L}^{-1}$  and we used standard IC ranging from  $0.02$  to  $50 \text{ mg L}^{-1}$  from Merck certified solutions ( $1000 \text{ mg L}^{-1}$ ).

The stock concentration ( $100 \text{ g L}^{-1}$ ) was diluted with soft-water in three sequence concentrations for the experiments ( $10$ ,  $25$  and  $50 \text{ g L}^{-1}$ ) and the control solution was composed of only soft-water. For general characterisation of water quality, the physicochemical parameters were daily measured. The dissolved oxygen (DO) was determined by using a *Thermo Orion 3 Star* bench oximeter, and temperature, pH, electrical conductivity (EC), and total dissolved solids (TDS) were analysed by a multiparameter *Hach Sension 156*.

**Table 1** Solubilisation of cations and anions ( $\text{mg L}^{-1}$ ) obtained from the stock solution samples (ash:soft-water 1:10 m/v), under agitation, at 4, 10, 15 and 30 days

Time (days)	4	10	15	30
Li	<DL	<DL	<DL	<DL
$\text{Na}^+$	43.4–54.3	55.4–61	55–56.3	51.7–68.7
$\text{NH}_4^+$	<DL	<DL	<DL	<DL
$\text{K}^+$	1690–1965	1994–2067	2058–2069	1658–2210
$\text{Ca}^{2+}$	64–174	93–116	116–145	5–17
$\text{Mg}^{2+}$	13–16	11–16	5–9	4–8
$\text{F}^-$	<DL	<DL	<DL	<DL
$\text{Cl}^-$	24–25	24–25	23–24	29–28
$\text{NO}_2^-$	<DL	<DL	<DL	<DL
$\text{Br}^-$	<DL	<DL	<DL	<DL
$\text{NO}_3^-$	<DL	<DL	<DL	<DL
$\text{PO}_4^{3-}$	50	52	50–54	48–49
$\text{SO}_4^{2-}$	314–318	312–318	308–317	302

<DL stands for below detection limit ( $<0.001 \text{ mg L}^{-1}$ )

An additional experiment was conducted to assess the physicochemical parameters of the stock solution under agitation (on an orbital shaker at 150 rpm) and without agitation, by keeping stock solution in 0.5 L-beakers uncapped inside an incubator at  $20^\circ\text{C}$  for short-term responses of water quality (15 days).

Normality of the datasets was assessed using the Shapiro–Wilk test. As the datasets were not normally distributed, non-parametrical statistics were used. Differences in physicochemical parameters of the ash concentration treatments (control,  $10 \text{ g L}^{-1}$ ,  $25 \text{ g L}^{-1}$ ,  $50 \text{ g L}^{-1}$  and  $100 \text{ g L}^{-1}$ ) were analysed by using the non-parametric Kruskal–Wallis (K-W) test. Spearman’s rank correlation coefficient ( $R$ ) was used to assess possible associations between physical parameters (pH, DO, TDS, and EC) and the exposure time. The statistical procedures were performed using the R software 2.15.3 version (R Core Team 2019) and the  $\alpha$  level was set at 0.05 for all tests.

## Results and Discussion

The water-soluble elements from the stock solution were assessed over time under continuous agitation, and  $\text{K}^+$  was the preponderant element in the ash-solution (Table 1). Chemical composition of our stock solution (1:10 ash:soft-water) had slight variations ( $\text{K}^+$ ,  $\text{PO}_4^{3-}$ , and  $\text{SO}_4^{2-}$ ), decreased strongly over time ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , corresponding to decreases of 90% and 72%, respectively) or maintained undetected ( $<0.001 \text{ mg L}^{-1}$ ), such as  $\text{Li}^+$ ,  $\text{F}^-$ ,  $\text{Br}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and  $\text{NO}_3^-$ . For  $\text{Na}^+$  and  $\text{Cl}^-$ , a slight increase at 30 days ( $\sim 20\%$ ) was recorded. We also observed 24–30  $\text{mg L}^{-1}$  for  $\text{Cl}^-$ , 302–318  $\text{mg L}^{-1}$  for  $\text{SO}_4^{2-}$ , and  $<0.001 \text{ mg L}^{-1}$  for  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Li}^+$ ,  $\text{Br}^-$  throughout the experiment (Table 1).

Wildfires release large amounts of elements from biomass combustion (Pereira et al. 2011), which may pose complex interactions in watercourses through runoffs (Dahm et al. 2015). The composition of ashes from wildfires is diverse and reflects the heterogeneous landscapes, depending on the vegetation, soil type, climate and fire severity (Bodí et al. 2014).

Using the stock solution (1:10 ash:soft-water) for ecotoxicological assessment, Brito et al. (2017) reported low metal concentrations ( $<1 \text{ mg L}^{-1}$ ) for P, Al, B, Sr, Cu and Fe and very low ( $<0.005 \text{ mg L}^{-1}$ ) metal concentrations for Mn and Zn in ash-solution after one-day exposure. The high levels of K, Si, Ca, S and Mg and the low availability of Al, Fe, and Sr were explained by the greater solubility and lower affinity to the organic matter.

Available nitrogen in ash-solution (ammonium, nitrate and nitrite) was not detectable (Table 1). In fact, nitrogen is very sensitive to fire temperatures and starts to volatilise

around 200°C. During wildfires, large amounts of N are lost through volatilization (Qian et al. 2009). Even though this nutrient element was not present in the ash-solution, we reported considerable nutrient levels for  $\text{PO}_4^{3-}$  (~ 50 mg  $\text{L}^{-1}$ ) throughout the exposure period.

The burning was not extremely severe in our studied area, because of the sulphate concentrations in the ash-solution (Table 1). The sulphate volatilises when the temperature reaches values in the order of 800°C (Shakesby and Doerr 2006).

The composition of surface runoffs from wildfires is highly variable over time (Campos et al. 2012), and the water-extractable elements increase over time and with the quantity of water used (Audry et al. 2014). Our results showed that the highest  $\text{K}^+$  levels were found between 10 and 15 days, the levels of  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  remained stable, while  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  levels decreased through the exposure period (Table 1). The decrease in metal levels in solution was likely due to the adsorptive capacity of carbonate phases in ash (Cerrato et al. 2016).

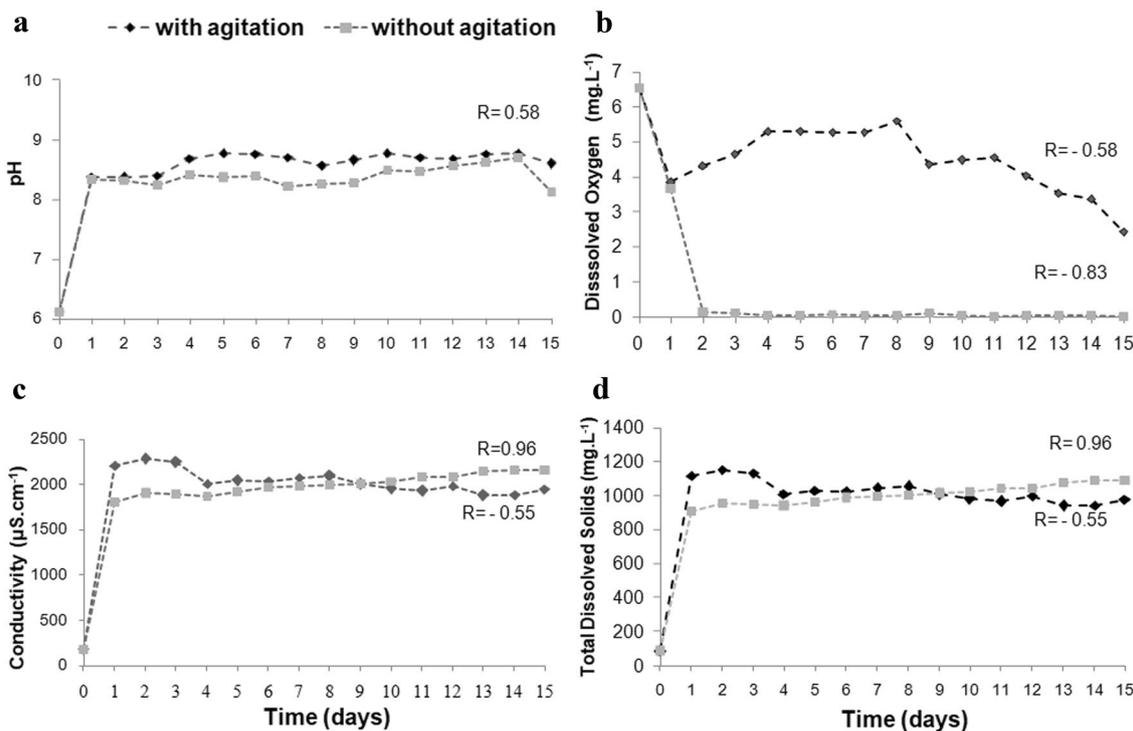
The water-soluble elements from ashes were mainly composed of  $\text{K}^+$  and  $\text{Ca}^{2+}$ , and this was also observed by Ulery et al. (1993) and Pereira et al. (2012). These preponderant cations occur because ash is very rich in both of these elements. In addition, these elements are easily soluble,

especially at favourable pH values (7 and 8) and are probably from dark ashes (Pereira et al. 2012).

Chemical analysis of stock solution clearly demonstrated that water-soluble elements, variations in major ions, namely  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , resulted in increased levels of EC, TDS and pH and decrease of DO levels (Fig. 2). In fact, this trend was observed for all the ash-concentrations used in comparison to the mean control levels with significant differences in the mean values of all physicochemical parameters (Kruskal-Wallis test,  $p < 0.05$ ) (Table 2).

Despite the relation between fire severity, pH and  $\text{CaCO}_3$  (Pereira et al. 2012), there is no direct relationship between ash water-extractable cations and fire severity (Úbeda et al. 2009). Significant differences in mean values of physicochemical water parameters have also been observed by Gonino et al. (2019) with sugarcane ash concentration treatment (2.0 g  $\text{L}^{-1}$ ) as compared to the control, but no significant differences were observed between low concentration (1.0 g  $\text{L}^{-1}$ ) and the control regarding these parameters.

Studies simulating fire effects under laboratory conditions and event-based studies have established that pH and  $\text{CaCO}_3$  levels in ashes increase with fire severity (Pereira et al. 2012). The alkaline pH from ash-solution is attributed to the mineralization of basic elements, creating oxides that are converted to high levels of carbonates



**Fig. 2** Water quality parameters (pH, Dissolved Oxygen, Electrical Conductivity and Total Dissolved Solids) obtained from the stock solution (100 g  $\text{L}^{-1}$ ) throughout 15 days with continuous agitation and without agitation. The lines (dark and grey) represent continu-

ous measurement and not any fitted function. Day zero refers to the data collected at the beginning of the experiment. Only correlations between the parameter and the exposure period significant at  $p < 0.05$  are shown

**Table 2** Physicochemical parameters (mean  $\pm$  SD) of the different ash concentration treatments measured throughout the exposure period (15 days)

Parameters	0 g L <sup>-1</sup>	10 g L <sup>-1</sup>	25 g L <sup>-1</sup>	50 g L <sup>-1</sup>	100 g L <sup>-1*</sup>	100 g L <sup>-1**</sup>
pH	6.19 $\pm$ 0.22 <sup>a</sup>	8.06 $\pm$ 0.13 <sup>b</sup>	8.4 $\pm$ 0.15 <sup>c,f</sup>	8.55 $\pm$ 0.1 <sup>d</sup>	8.65 $\pm$ 0.15 <sup>e</sup>	8.39 $\pm$ 0.2 <sup>f,c</sup>
Dissolved oxygen (mg L <sup>-1</sup> )	5.8 $\pm$ 0.8 <sup>a</sup>	4.35 $\pm$ 0.8 <sup>b,e</sup>	3.4 $\pm$ 0.86 <sup>c,d</sup>	3.29 $\pm$ 1 <sup>d,c</sup>	4.4 $\pm$ 0.9 <sup>e,b</sup>	0.3 $\pm$ 0.9 <sup>f</sup>
Conductivity ( $\mu$ S cm <sup>-1</sup> )	174.8 $\pm$ 4 <sup>a</sup>	390.47 $\pm$ 23 <sup>b</sup>	625.6 $\pm$ 23.3 <sup>c</sup>	984.2 $\pm$ 50 <sup>d</sup>	2035.53 $\pm$ 124 <sup>e,f</sup>	1998.7 $\pm$ 110 <sup>f,e</sup>
Total Dissolved Solid	83.7 $\pm$ 2.4 <sup>a</sup>	188.35 $\pm$ 12 <sup>b</sup>	301.3 $\pm$ 19.4 <sup>c</sup>	483.2 $\pm$ 26 <sup>d</sup>	1023.7 $\pm$ 65 <sup>e,f</sup>	1003.5 $\pm$ 57 <sup>f,e</sup>

Significant differences (Kruskal-Wallis test,  $p < 0.05$ ) between treatments for each parameter are represented by different letters

\*With agitation, \*\*without agitation

and hydroxides from the burnt biomass (Bodí et al. 2014; Cerrato et al. 2016). The EC and TDS levels, as well as pH, showed a pulse value on the first day (Fig. 2), mainly because of the immediate solubilisation of elements from ashes (Table 1).

The increase of pH values from ash-solution and the pH stabilisation in both situations (agitation and without agitation) may also be explained by the high TDS and EC levels (Fig. 2c, d). These parameters remained quite stable throughout the experiment, because the major elements did not have large variations in concentration over time (Table 1), suggesting that the effects from ashes may be not limited to the immediate post-fire period, mainly in small catchments. Post-fire effects, due to ash runoffs, can lead to changes in water turbidity and pH in rivers (Shakesby and Doerr 2006), posing risks to potable water supplies (Nunes et al. 2018). It is worth noting that although carbonate dissolved from ash can cause water pH increase in high alkalinity waters (e.g.: water sourced from carbonate lithologies), metal concentrations can cause a pH decrease in low-alkalinity waters (Cerrato et al. 2016).

In the stock concentration (100 g L<sup>-1</sup>), the EC levels were much higher (> fourfold increase) than the 175  $\mu$ S cm<sup>-1</sup> observed in the control solution (Table 2). The TDS levels were in the order of 100 mg L<sup>-1</sup> in the control solution, 2-fold for 10 g L<sup>-1</sup>, 3.5-fold for 25 g L<sup>-1</sup> and almost 6-fold for 50 g L<sup>-1</sup>. Mansilha et al. (2017) also reported an increase in conductivity in post-fire compared to pre-fire conditions and reference streams.

Even in the control solution, the DO level decreased considerably throughout the exposure period (from 7.6 to 4 mg L<sup>-1</sup>) (Table 1). Although the lowest DO level in the control solution is not lethal to some fish species (Bohlen 2003), it is likely due to unmeasured parameters (e.g., inorganic trace elements) or bacteria and algal growth in the solution.

The DO depletions in a stream water through surface runoff post-fire could be attributed to the chemical oxygen demand and biological oxygen demand stimulated by the ash-input, composed of organic matter, sulphides, reduced metals and black carbon (Marañon-Jiménez et al. 2013). In

general, these effects have a short duration and are limited to small streams (Rieman et al. 2012).

While the DO level decreased to 2.4 mg L<sup>-1</sup> in the stock solution test with agitation in the 15-day period (4.4  $\pm$  0.9 mg L<sup>-1</sup>), it decreased strongly to anoxia conditions in the stock solution test without agitation on the second day of the experiment (0.3  $\pm$  0.9 mg L<sup>-1</sup>) (Fig. 2b). The increased water volume and hydrological movements in lotic systems should considerably buffer physicochemical changes in water quality by ash runoffs. In addition, heavy rainfalls during the rainy season may contribute to water turbulence and oxygenation of the water. Overall, a greater runoff during rainfalls, associated with wildfire severity and the lack of riparian vegetation (a natural barrier to the runoffs) implies greater entry of ashes and soil sediment into watercourses.

## Conclusions

Our findings point out the role of wildfires in the mobilisation of several ash elements into the aquatic system. The water-soluble elements from ash-solution (K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, Ca<sup>2+</sup>, PO<sub>4</sub><sup>3-</sup>, Na<sup>+</sup> and Mg<sup>2+</sup>) resulted in increased TDS, conductivity (EC) and pH, in addition to decreased DO levels throughout the exposure period. The DO decreased to levels detrimental to the survival of aquatic organisms, even under continuous agitation. Further, variations in major ions took place, namely Ca<sup>2+</sup> and Mg<sup>2+</sup>.

While the interactions of ashes with water were assessed under controlled conditions, this study provides a further understanding of the physicochemical changes of ashes into water chemistry over a short period. It addresses field experiments across landscapes, considering temporal and catchment scales in tropical savannah regions for a further understanding of the ecological impacts of wildfires on aquatic resources.

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