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Black and White Fire Ash Alters Greenhouse Gas Emissions and Temporarily Reverses Carbon Source-Sink Status in Aquatic Mesocosms

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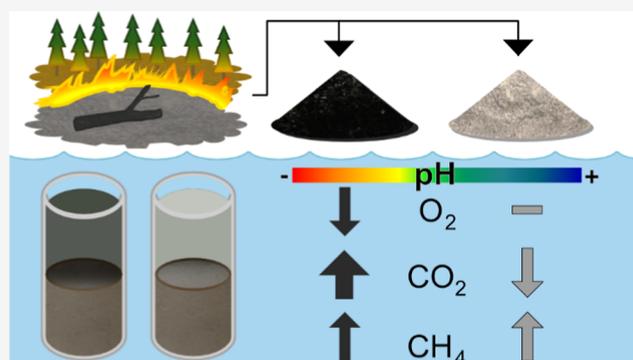
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Supporting Information

ABSTRACT: Wildfire ash is transported in large quantities to receiving water bodies, where it may exert strong chemical controls on ecosystem function. To assess the role of fire ash in altering CO₂ and CH₄ fluxes in aquatic sediments, we designed three mesocosm experiments that compared the changing fluxes of these gases and water quality parameters under different loads and types of ash. Black ash (char) caused substantial drops in pH and increased CO₂ and CH₄ emissions through abiotic and biotic mechanisms, while white ash dramatically increased pH and enhanced CH₄ emissions, possibly due to inhibition of methanotrophy. White ash-driven increases in pH also instigated CO₂ uptake. If this abiotically driven CO₂ uptake could interact with ash-driven nutrient fertilization to synergistically enhance biotic CO₂ uptake in surface waters after a fire, these initial increases in pH may represent an important priming effect. Our findings suggest that strong ash flows following fires may trigger substantial pulses of heterotrophic or abiotically driven greenhouse gas emissions or uptake in recipient lentic aquatic ecosystems, which—although they may be overshadowed by autotrophic responses—may nonetheless be central to altered lake or wetland carbon balance following a fire.

KEYWORDS: fire, ash, wetlands, greenhouse gas, carbon dioxide, methane, black carbon, mesocosm, biochar



1. INTRODUCTION

Wildfires create massive loads of pyrogenic products that are readily transported to adjacent ecosystems,^{1–5} delivering large quantities of nutrients, metals, and other substances that can profoundly influence soil or water chemistry.^{2,6–9} One of these products that impacts recipient ecosystems is ash. However, the ephemeral nature and varied composition of ash have limited both the quantity and scope of studies.¹⁰ Of the studies that do exist, the effects of ash transport and deposition in aquatic systems are less well studied compared to terrestrial ecosystems, and particularly so for ponds, lakes, or wetlands compared to streams.⁷

Ash production in fires varies broadly in terms of quantity, typification, and deposition^{10–13} and is dependent on physical factors such as fuel moisture, maximum temperature, duration of burning, and density of fuel as well as chemical factors such as oxygen availability and fuel composition.^{10,13} These factors interact at multiple scales—from microscopic to landscape level—to create spatially heterogeneous ash loads and types.

Differential combustion produces two main types of ash. Hotter and sustained combustion in the presence of oxygen

volatilizes organic components of fuel, leaving behind a gray to white material that is rich in inorganic carbonates, oxides, silicates, and metals.^{10,11,14} Ash of this type is produced in small quantities relative to fuel loads, as these constituents represent the trace inorganic components of a primarily organic fuel.¹² Cooler burns or oxygen-limited burns, such as those occurring within soil layers or large pieces of fuel (e.g., coarse woody debris), typically undergo incomplete combustion and pyrolysis, whereby organic compounds are partially volatilized, forming black carbon deposits and polycyclic aromatic hydrocarbons.^{15,16} Black ash forms in larger quantities than white ash due to mass-efficient conversion from fuel and the ability to form within soils. Since it is only partially mineralized, black ash

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contains many structural and chemical remnants of its organic fuel and is extremely diverse and often difficult to characterize. Both ash types can vary in composition according to fuel characteristics (species, tissue type, woody versus herbaceous, etc.)^{10–12,17} but can generally be classified into these two product types.

Ashes are naturally transported away from burn sites by wind and water.^{1,4,10,17,18} The former is especially likely during intense fires, which create updrafts that can carry ash particles,¹⁹ while the latter occurs during postfire precipitation events.⁷ While both white and black ash can be hydrologically transported, white ash is considerably more soluble than black ash and may be disproportionately represented in ash flows despite being formed in lesser quantities than black.^{11,12} Lentic aquatic ecosystems (e.g., lakes, reservoirs, and wetlands) serve as storage pools in which ash additions may endure and exert strong chemical controls on ecosystem parameters.^{9,12}

Fire ash is known from a few studies to impact aquatic ecosystem chemical properties,^{9,12,20} and it is notable for its strong potential to impact pH. While many studies have shown that wood ash can increase pH, it is important to note that the degree of combustion and speciation into black and white ashes determine the directionality of that pH shift.^{10,21} Black ash may also be either acidic or basic, depending on burn and fuel characteristics,¹⁵ and natural black carbon sources are known to contain extractable acidic material and various forms of dissolved organic matter (DOM).^{22,23} White ash leachate is also a strong source of macronutrients such as Mg, Ca, K, and P, as well as micronutrients such as Fe and Mn.^{8,10,12} Aquatic systems receiving an influx of ash may therefore experience a pH- or nutrient-driven fertilization effect and alteration to community structure and function.^{1,18,24,25}

Lentic aquatic ecosystems can serve as net sources or sinks of carbon dioxide (CO₂) and are usually net sources of methane (CH₄).^{26,27} Fluxes of these gases from sediments are partially determined by interactions between methanotrophs and anaerobic methanogens. Methanogens generally experience peak function at a neutral pH, and so a shift toward alkaline with the addition of ash may be expected to decrease emissions of CH₄.^{28,29} However, since many common methanotrophic lineages favor neutral or acidic conditions, a shift toward alkaline could enhance emissions of CH₄ by negatively impacting methane oxidation to a greater degree than methane production.³⁰ Additionally, increasing pH converts dissolved inorganic carbon (DIC) from carbonic acid and toward bicarbonate and carbonate, therefore increasing the dissolution of atmospheric CO₂ into water, decreasing net emissions, and potentially instigating uptake. Through these mechanisms, alterations to pH are expected to impact net ecosystem GHG flux.

Relatively few studies have directly manipulated ash inputs to an aquatic ecosystem (See literature review in Supporting Information, Section 3), and those that do often focus on the role of ash in affecting aquatic organism survival or fitness,^{31–33} water quality, or heavy metal mobilization.^{34,35} Few studies also have examined the role of ash in influencing ecosystem function, though there are a few which have demonstrated potentially altered nitrate or sulfate reduction³⁶ and some which have observed altered carbon cycling or methane emission in burned wetlands.^{37–39} However, identification of mechanisms of these alterations as well as the specific contributions of ash produced under different conditions (black ash via pyrolysis and white ash

via combustion) to nonautotrophic GHG fluxes remain underexplored.

To investigate the effects of both black and white ash on GHG emissions in lentic systems, we implemented three mesocosm experiments. These experiments assessed the effects of different loads and combinations of black ash, activated charcoal, and white ash on pH and CO₂ and CH₄ flux. We utilized laboratory mesocosm experiments to achieve sufficient replication and control while investigating this underexplored phenomenon. This approach more tightly controlled factors that might influence our results (primary production, sediment type, temperature, etc.), so that we could better delineate the effects of these two differently mobilized and chemically characterized “extremes” of a continuum of ash products. We predicted that black ash would increase both CO₂ and CH₄ emissions by supplying a labile organic material and decreasing the pH and dissolved oxygen (DO). We predicted that white ash would decrease the level of CO₂ emissions through a pH-mediated shift in DIC away from carbonic acid. We also predicted that white ash would decrease CH₄ emissions by raising pH above the tolerable range for methanogenesis.²⁹

2. METHODS

We collected the sediment used in the establishment of experimental mesocosms from flooded ditches near Wageningen University and Research, The Netherlands (51.988384 N, 5.653297 E). The sediment was filtered through a 1 mm sieve and homogenized using a hand-drill and propeller attachment before allocation to 1.5 L glass mesocosms (height 20 cm). We filled each mesocosm with sediment to a depth of 10 cm and topped each with 9 cm of overlying 63 μm mesh-filtered pond water. Subsequent settling of sediment resulted in a slight decrease in sediment height over the experimental period to heights of around 9 cm. We maintained mesocosms for a period of 2 weeks before the experimental addition of ash and kept all mesocosms in a temperature-controlled water bath (19.58 ± 0.028°; 95% CI) with negligible levels of photosynthetically active radiation for the duration of the experiment.

To test the relative contributions of ash types, we produced black and white ash via low-temperature pyrolysis and combustion, respectively, in a laboratory muffle furnace at 300 and 600 °C from *Fraxinus* sp. wood (See Supporting Information). These temperatures were selected based on the volatility and speciation of elemental constituents of ash, which influence factors of solubility and nutrient availability, reviewed by Bodí et al.¹⁰ During the production of each ash type, target temperatures were maintained for 3 h. We selected the mass of ash treatments using conservative estimates of ash deposition per unit area from published field observations¹⁰ (See Supporting Information, Section 2). This ash was utilized in both the first and second of the three experiments.

In the first experiment, black and white ash treatment levels were created from equivalent masses of fuel but generated different amounts of material per ash type; we burned 1.288, 12.878, and 38.634 g of *Fraxinus* sp. wood to produce 0.165, 1.645, and 4.9357 g of black ash and 0.009, 0.0857, and 0.257 g of white ash in “low”, “medium”, and “high” treatment levels ($n = 5$ each, Table S1). Mesocosms for the second experiment received 1 g of the same black or white ash ($n = 5$ each; Table S2). For the third experiment, we used activated black charcoal produced from *Fagus* sp. wood via high-temperature pyrolysis (produced by BoomLab.nl). A subset of this material was secondarily burned in the presence of oxygen at 600° to convert

Table 1. Elemental Analysis Results for the Four Ash Types^a

	Ca	Fe	Mg	P	S	C	N
black ash	4481	41	1008	649	330	604,700	4600
white ash	98,953	589	20,382	13,627	7135	58,400	300
activated char	12,938	1332	778	394	357	795,300	4400
white char	215,095	24,419	18,457	8063	12,236	65,900	100

^aBlack and white ash is produced by the lab combustion of *Fraxinus* sp. wood fuel at 300 and 600°, respectively. Activated char represents industrially sourced *Fagus* sp. activated charcoal, and white char represents the same charcoal re-combusted at 600° in the presence of oxygen. These values represent means of ash samples of each ash type. All units are in mg kg⁻¹.

it to white ash. These ashes were combined in ratios of 100:0, 75:25, and 50:50. Mesocosms in the third experiment received one of the five ratios of ash, each totaling 0.53 g ($n = 3$ for each ratio; Table S3).

Immediately before each flux measurement, we measured temperature, DO, pH, salinity, total dissolved solids, and conductivity in each mesocosm using digital probes (WTW, CellOx325, sentITx41, tetraCon 325, and Multimeter 3630 IDS). We then measured CO₂ and CH₄ fluxes in each mesocosm using a portable greenhouse gas analyzer (LGR-ICOS, GLA-132 series) 2 days before ash addition, seconds after ash addition, and at 1-, 3-, 5-, and 7 days following addition. The analyzer was connected to a gastight flux chamber that nested on glass mesocosms via a silicone-lubricated gasket. The headspace above the water surface varied from 1 to 2 cm depending on the water height. We submerged the gas outlet tube from the analyzer into mesocosm water columns to “strip” dissolved gases through agitation from the water as an estimate of potential sediment-to-water flux, (or fluxes from air to water, in the case of CO₂).^{40,41}

At the conclusion of the sampling period, we used optical oxygen and pH sensors (Unisense) mounted on a micro-manipulator to measure oxygen and pH above and below the sediment–water interface from a randomly selected mesocosm of each treatment. These data were used to create profiles of pH and DO for each ash type and to assess the depth of sediment penetration of ash effects on pH and DO (Figure S1). We sampled sediments from mesocosms at the conclusion of the study for deriving the organic matter content. Ash and activated charcoal samples were analyzed using ICP-OES with an aqua regia digestion for Ca, Fe, Mg, P, and S concentrations and total C and N using LECO–CN928 with combustion (Table 1).

2.1. Statistical Analysis. Data were analyzed with eight two-way repeated-measures ANOVAs: one for each of black and white ash for the response variables CO₂ and CH₄ flux in experiment 1 and one for each gas flux for each of the other two experiments. We treated the effect of treatment and day as explanatory variables with mesocosms treated as a random effect to account for repeated sampling. To address violations of sphericity encountered through Mauchly’s Test, we applied a Greenhouse-Geisser correction to relevant tests. We conducted posthoc analyses on planned contrasts between treatment levels on each day and between days for the same treatment level using estimated marginal means. All tests were performed using R with RStudio.^{42,43} All data were prepared, visualized, and tested using the dplyr, emmeans, ez, ggplot2, ggpubr, lubridate, and rstatix packages.^{44–50}

To determine the relative importance of environmental factors explaining the variable effects of ash types on CO₂ and CH₄ flux, we compared multiple linear mixed effects models using Akaike’s Information Criterion adjusted for small sample size (AICc) and an information theoretic approach.⁵¹ We

employed this approach to identify and model some of the primary drivers that contribute to our results. Parameters initially selected for possible inclusion in multiple regression models were pH (both at the time of measurement and a lagged effect from the previous measurement date [pH_{*t*-1}]), temperature (°C), dissolved oxygen (mg L⁻¹), days after ash addition (including decimal days), and binary predictor variables for ash type (black = 0, white = 1) and whether white ash was produced from wood or activated charcoal (wood = 0, activated = 1). When necessary, dependent variables were log-transformed to satisfy the assumptions of normality, homogeneity of variance, and linearity. We tested explanatory variables for multicollinearity with Pearson’s correlation coefficient (r) matrices and variance inflation factors (VIF), and any two variables with $r \geq 0.60$ were not included in the same model. We used AICc to select the most parsimonious and plausible model (lowest AICc) among all possible combinations of parameters and their interactions within $\Delta\text{AICc} < 10$ and then further selected from among that set by choosing the model with the best predictive ability. We determined the predictive abilities of models with k -fold ($k = 10$) cross-validation and comparison of root-mean-squared error (RMSE). Briefly, 1/10th of the data was randomly set aside, and parameter estimates (β values) from each model were generated from the remaining 9/10ths of the data. These were then used to predict the response variable for each line of withheld data (1/10th of the data set), and RMSE was calculated from the regression of observed vs predicted CO₂ or CH₄ flux. This procedure was repeated 100 times for each model, and an average value of RMSE was calculated. Lower RMSE indicates improved predictive power. All analyses were conducted in R software.⁴⁵

3. RESULTS AND DISCUSSION

Our results show that wildfire ash inputs, primarily via shifts in pH and other physical conditions, may substantially impact key processes of carbon cycling in aquatic environments. White ash, by rapidly raising pH and driving an influx of atmospheric carbon, reduces emissions and may instigate the uptake of CO₂ in larger quantities. Black ash inputs have the opposite effect by causing a large release of CO₂ due to drops in pH and a potential increase in respiration as it may be a partially bioavailable material. However, both white and black ash enhance CH₄ fluxes immediately after a fire, likely via different mechanisms. Substantial increases in pH (pH > 10) after an influx of white ash may enhance CH₄ fluxes from sediments, while inputs of black ash may substantially lower pH and DO, thereby benefiting methanogens in the short term, while an influx of organic substrates (less abundant in white ash) may enhance methanogenesis in the longer term after a fire.

3.1. Carbon Dioxide. Effects of ash on CO₂ fluxes were immediate (Figures 1, 2 and 3A), with a significant interaction between treatment and time in all three experiments ($p < 0.001$,

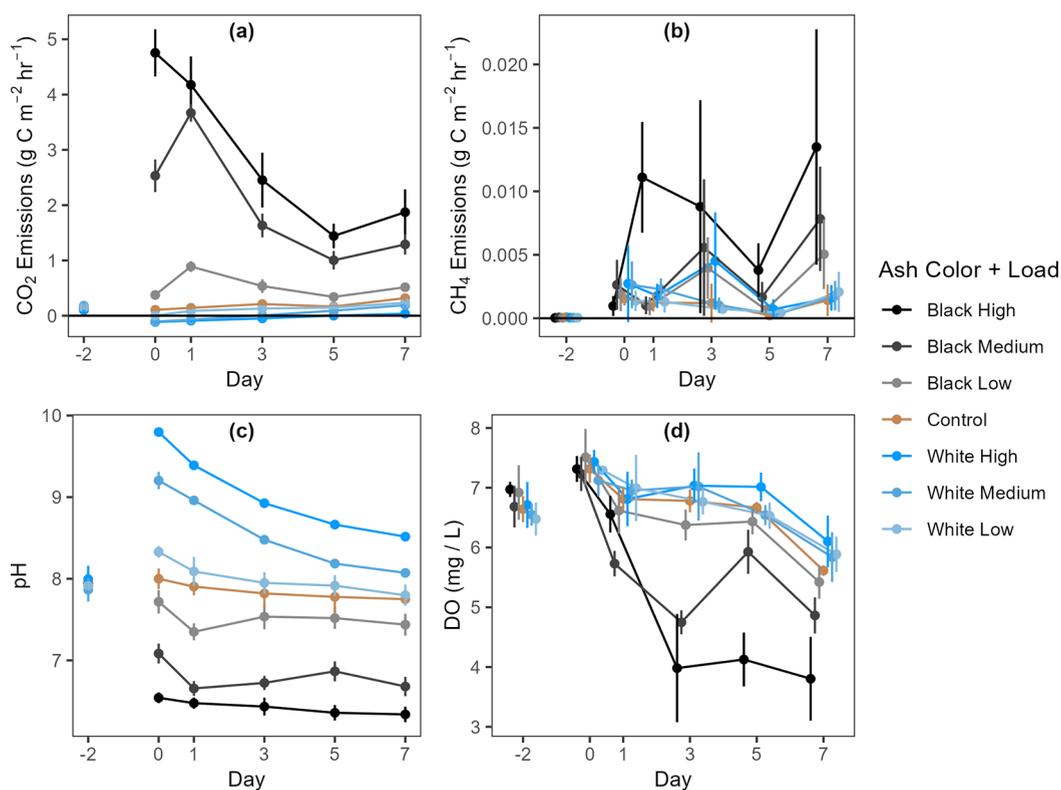


Figure 1. Mean CO₂ (a) and CH₄ (b) fluxes and corresponding pH (c) and DO (d) for experiment 1: equal fuel masses. Mesocosms received low, medium, or high loads of either black or white ash, derived from *Fraxinus* sp., administered seconds before flux measurements on day 0 (Table S1). White high, medium, and low treatments received 0.257, 0.0857, and 0.00857 g of ash, respectively. Black high, medium, and low treatments received 4.94, 1.65, and 0.165 g of ash, respectively. Error bars represent 95% confidence intervals. Disconnected points at Day -2 correspond with premanipulation values measured 2 days prior. Points are jittered for clarity. In panels (a,b), values greater than 0 indicate emissions, and negative values indicate gas uptake.

Table S4). White ash additions generally reduced CO₂ fluxes or caused CO₂ uptake, and black ash additions enhanced emissions. Since day 0 fluxes were measured within seconds of ash addition, initial CO₂ fluxes in these experiments are likely abiotic and attributable to ash-driven shifts in pH that altered the solubility of CO₂. The direction and magnitude of flux correlated to immediate and lingering pH shifts (Table 2), though the impact of pH on the CO₂ flux does diminish with time, particularly for black ash (Figure 4).

Decreased fluxes or enhanced uptake of CO₂ was observed throughout the three experiments in mesocosms receiving white ash, with effects enduring longest in those which received the most white ash and experienced the greatest shifts in pH (maximum pH = 10.86) (Figures 1–3). An interaction between pH and time since ash addition explained 92% of the variability in the CO₂ flux in white ash mesocosms (Table 2). The increase in solubility of CO₂ was not confined to the water column, as pH shifts extended into the sediment layer to different degrees according to the amount of ash administered (Figure S1). Our uptake rates were slightly higher than rates of uptake in some eutrophic reservoirs (fluxes in our white ash treatments averaged $-0.114 \text{ g C m}^{-2} \text{ h r}^{-1}$ in high loads immediately after ash inputs in experiment 1 (Figure 1), compared to $-0.058 \text{ g C m}^{-2} \text{ h r}^{-1}$ documented by Golub et al.⁵²), highlighting the potential magnitude of a pH-shift-induced uptake in our study.

High loads of black ash significantly enhanced CO₂ emissions immediately after ash addition (mean = $4.65 \text{ g C m}^{-2} \text{ h r}^{-1}$ in highest ash loads), corresponding to substantial drops in pH, but CO₂ fluxes subsided over time despite persistent effects on pH

(Table 2 and Figure 4). Aqueous abiotic oxidation of black ash may be partially responsible for the instantaneous CO₂ response,^{53–55} and comparably lower respiratory CO₂ fluxes may have been overshadowed by larger pH-driven fluxes in the sampling period. Given that fluxes between black ash treatments and controls failed to converge, the enhanced CO₂ emissions documented in our study may be persistent, but that will need to be documented in longer-term studies. Though a recent field-based study identified high dissolved CO₂ concentrations in temperate lakes following fires,⁵⁶ our CO₂ emissions were greater than typical daytime fluxes in natural systems (average emissions in our control mesocosms were $0.181 \text{ g C m}^{-2} \text{ h r}^{-1}$, around 10 times greater than the maximum average of rates for small lentic bodies reviewed by Holgerson and Raymond, 2016²⁶). However, our average emissions in our controls were much lower than nighttime fluxes in some systems (up to $4.2 \text{ g C m}^{-2} \text{ h r}^{-1}$ in some studies,⁵⁷ comparable to emissions immediately after black ash addition in our first experiment: $4.754 \text{ g C m}^{-2} \text{ h r}^{-1}$ (Figure 1)).

Through these mechanisms, substantial CO₂ pulse emissions or capture may occur in aquatic systems following fires. Since these two distinct pyrogenic products (black and white ash) may drive CO₂ flux in opposite directions, knowing the relative amount of black and white ash being formed and transported is crucial to predicting the net flux of CO₂ within receiving aquatic ecosystems. Given the relative persistence of black ash compared to white ash in water,¹² as well as the relative magnitudes of response between ash types (Figures 1–3), it is possible that the net effect of mixed ash loads reaching aquatic systems is

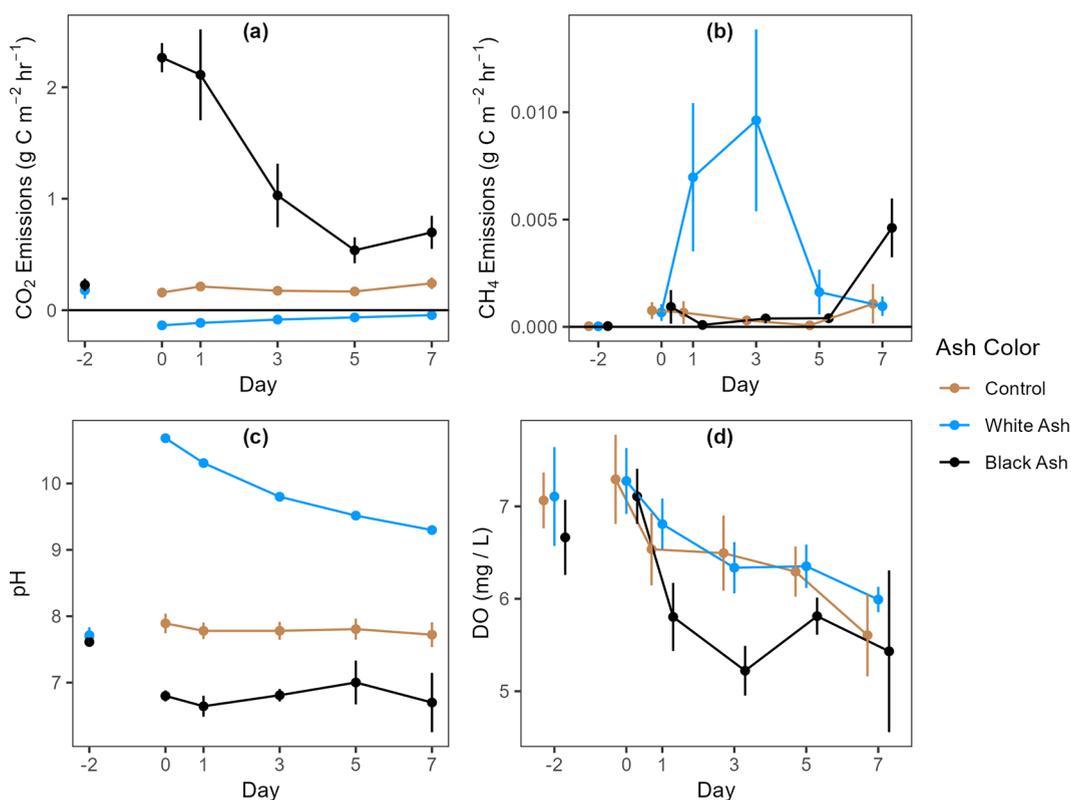


Figure 2. Mean CO₂ (a) and CH₄ (b) fluxes and corresponding pH (c) and DO (d) for experiment 2: equal ash masses. Mesocosms received 1 g of either black or white ash, sourced from *Fraxinus* sp. wood, seconds before flux measurements on day 1 (Table S2). Error bars represent 95% confidence intervals. Disconnected points at day −2 correspond with premanipulation values measured 2 days prior. Points are jittered for clarity. In panels (a,b), values greater than 0 indicate emissions, and negative values indicate gas uptake.

enhanced CO₂ emissions—if largely insoluble black carbon particles can be mobilized and transported far enough. Conversely, the solubility, small particle size, and potentially greater mobility of white ash may result in its overrepresentation in ash flows.¹² For example, following a moderately sized wildfire in 2013 in New South Wales that produced an estimated 181,000 tons of ash, minimal redistribution of black ash was observed, though authors did notice a depletion of gray and white ash with time,^{9,58} suggesting that those ash types had been mobilized.

White ash inputs, by rapidly raising pH and driving a concurrent influx of atmospheric CO₂, may prime conditions for the nutrients in ash to enhance phytoplankton production in surface waters after a fire, especially so in systems which may be relatively carbon-limited.^{59,60} Past studies have demonstrated that aerosol and ash plume fertilization by wildfires can generate massive marine phytoplankton blooms, capturing enough carbon to rival wildfire emissions.^{3,5} Because our study intentionally minimized primary producer responses via low levels of photosynthetically active radiation, our findings suggest that abiotically enhanced availability of CO₂, in combination with fertilization by macro- and micronutrients from ash, has the potential to synergistically drive rapid carbon assimilation by autotrophs to a greater extent than either enhanced CO₂ or nutrient availability alone.

3.2. Methane. The addition of both combusted white ash and pyrolyzed black ash augmented sediment CH₄ emissions on different time scales and presumably through different mechanisms, with a significant interaction between treatment and time for all three experiments (Table S4). Neither ash type

had immediate (day 0) effects on CH₄ flux, but CH₄ emissions were eventually significantly greater than those of controls in most treatments.

High loads of white ash induced peak methane fluxes midway through all three experiments (Figures 1–3b and Tables 1 and 2), but we had predicted the opposite: that an ash-driven increase in pH would exceed the optimal range of methanogenesis and reduce CH₄ fluxes. Instead, by enhancing alkalinity in both the water column and sediments (Figure S1), white ash additions may have diminished the activity of methanotrophs, of which most lineages experience optimal metabolic activity at a neutral or slightly acidic pH.^{28–30} The difference in CH₄ emissions between high and low ash loads, as well as the difference between the relatively cationically enriched white ash made from activated charcoal and our *Fraxinus* ash (Tables 1 and 2), suggests that these treatments may have exceeded a pH threshold great enough to inhibit methanotrophy. Moreover, the delay between pH shifts and onset of elevated emissions supports the notion of a biotic mechanism like diminished methanotrophy (Table 2), sustained perhaps only while the pH exceeded this methanotrophic suppression threshold (Figure 2C). Although we did not directly isolate the activity of either functional group in the sediment community, CH₄ flux is the net effect of methanotrophic and methanogenic activity,⁶¹ and it has been demonstrated that many methanotrophs function optimally at a pH of 6.6–6.8²⁹.

Black ash increased CH₄ emissions in experiments 1 and 2 in all treatment levels at different times, but fluxes varied over time (Figures 1 and 2). The magnitude of emissions compared to that of controls corresponded not only to the amount of material

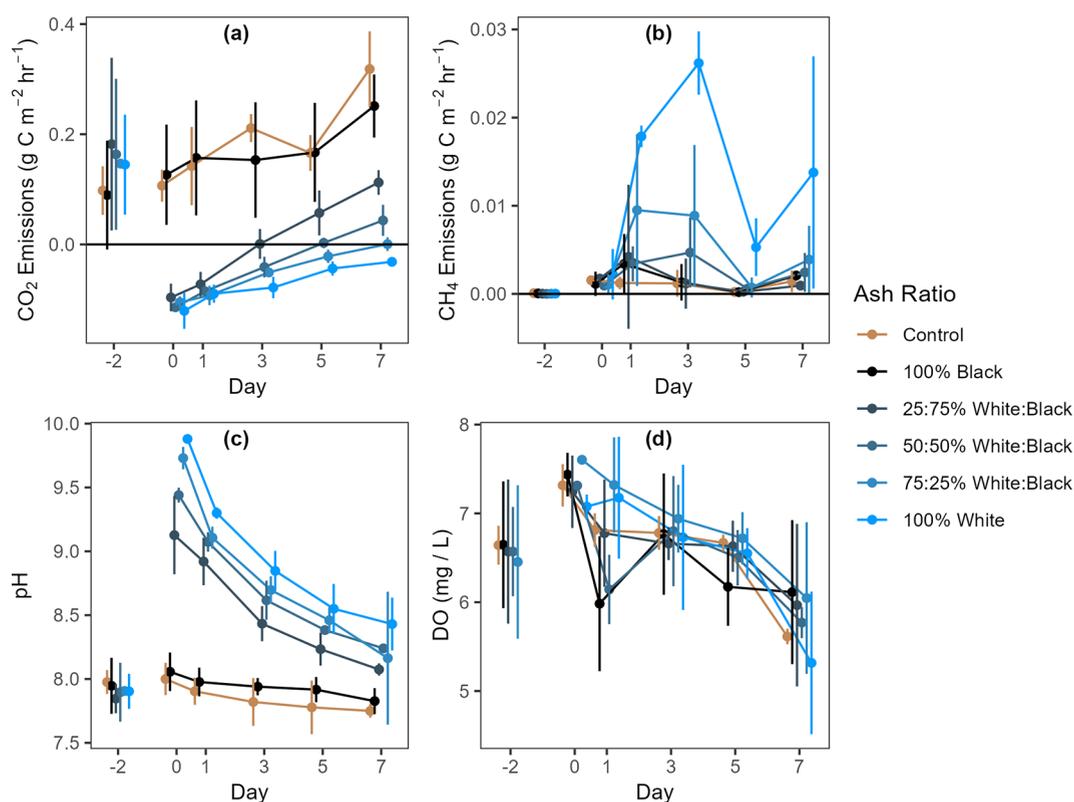


Figure 3. Mean CO₂ (a) and CH₄ (b) fluxes and corresponding pH (c) and DO (d) for experiment 3: mixed ash ratios with activated charcoal (black) produced via pyrolysis from the wood of *Fagus* sp., and the same activated charcoal combusted at high temperature in the presence of oxygen (white). Mesocosms received 0.53 g of a mixed ratio of black and white ash seconds before flux measurements on day 0 (Table S3). Error bars represent 95% confidence intervals. Disconnected points at day −2 correspond with premanipulation values measured 2 days prior. Points are jittered for clarity. In panels (a,b), values greater than 0 indicate emissions, and negative values indicate gas uptake.

administered but also to apparent oxygen demand, as methanogenesis occurs in anoxia. While we did not directly monitor oxygen demand, DO decreasing with time in black ash treatments compared to controls explained 40% of the variability in control-adjusted CH₄ emissions. Due to the open top of mesocosms combined with periodic agitation during flux sampling, some degree of oxygen replenishment was likely. Differentially affected activity of methanogens or methanotrophs (not directly measured) may again be the most plausible explanation for the observed rise in CH₄ flux following black ash additions⁶¹ (Figures 1B and 2B), possibly due to enhanced methanogenesis in acidic conditions. The delayed effect of pH ($t-1$) was a strong predictor of CH₄ flux for both black and white ash, predicting 42% and 54% variability, respectively (Table 2). Additionally, decreases in DO and pH are partially linked as oxidation of black ash, whether biotic or abiotic, will consume oxygen and release CO₂, decreasing pH with carbonic acid. The strong collinearity between pH and DO prevented the inclusion of both factors in the same model (Figure 5).

As CH₄ emissions increased both with alkalinity in white ash treatments and with acidity in black ash treatments (Figure 5), it is reasonable to predict augmented CH₄ production in lentic systems downstream of fires regardless of the mixture of ash types in inputs. Past mesocosm studies have demonstrated moderate increases in other anaerobic processes such as nitrate and sulfate reduction with the addition of pyrogenic materials,³⁶ and Levine et al. documented enhanced CH₄ emissions in Florida wetlands following controlled burns.⁶² However, in some field studies, fires had no measurable effect on aquatic CH₄

concentrations.⁶³ Differences in antecedent factors among lentic ecosystems—including differences in sediment organic matter, nutrient availability (our system was relatively nutrient-rich, Table S13), ecosystem productivity, and amount and timing of ash input—may modulate ash effects on CH₄ fluxes. These factors interplay: nutrient availability could dictate a receiving system's latent productivity, influencing the ability of ash to affect ecosystem processes. Additionally, the timing of postfire measurements may affect perceived CH₄ emissions—we measured fluxes within a few days of ash addition, but this may not be feasible for many natural fires. Our results suggest that accounting for chemical characteristics and quantity of ash entering the system, as well as time since ash deposition and physical parameters of the water column (e.g., pH), is crucial to building more comprehensive mechanistic models of ash impacts on aquatic methane fluxes.

3.3. Fuel Sources. The inclusion of activated charcoal in the mixed-ash analysis (experiment 3) highlights stark differences in chemical speciation and the effects of black carbon compounds. Compared to our lab-created black ash, this charcoal did not significantly alter CO₂ or CH₄ emissions (Figures 3 and S3–S10), and had little effect on pH or DO (Figure 3). Likely representing a more completely pyrolyzed product, this charcoal was relatively enriched in C and depleted in N and P compared to our black ash (Table 1), and likely lacked surface functional groups which might have impacted pH or allowed for microbial utilization.^{15,64} These differences underscore a need to better characterize pyrogenic black carbon in natural systems, as its composition may be as varied as its production.¹⁵ Given the

Table 2. Comparison of Candidate Linear Mixed Effects Models^a

	<i>k</i>	<i>C_p</i>	cond. <i>R</i> ²	AICc	Δ_i	<i>w_i</i>	RMSE	% diff
full data set—ln CO ₂								
pH (−1.311)/days (−0.545)/pH*days (0.0635)	5	243	0.95	246.4		1	0.3174	
full data set—CH ₄								
pH _{t-1} (−0.0033)/ash type (−0.0468)/pH _{t-1} *ash type (0.0059)	5	−2490	0.48	−2489.6		1	0.003815	
white ash—CO ₂								
pH (−0.0935)/days (0.1352)/pH*days (−0.0153)/activated (−0.0782)	3	−721	0.92	−660.1		1	0.003598	
black ash—CO ₂								
pH (−2.49)/days (−2.2870)/pH*days (0.2905)	5	271	0.86	262.3		1	0.5004	
white ash—CH ₄								
pH _{t-1} (−0.0016)/activated (−0.0313)/pH _{t-1} *activated (0.0040)	5	−1847	0.57	−1732.0		0.96	0.003089	
pH _{t-1} (0.0027)	3	−1801	0.54	−1725.5	6.48	0.04	0.003270	−5.8
black ash—CH ₄								
pH _{t-1} (−0.0033)	3	−1299	0.42	−1223.2		0.60	0.003598	−5.9
O ₂ (−0.0015)	3	−1298	0.40	−1222.4	0.84	0.40	0.003577	

^aThese models explain variation in CO₂ and CH₄ fluxes in mesocosms receiving black or white ash, with corresponding conditional coefficients of determination (cond. *R*²). Parameter estimates are provided in parentheses after each parameter and give the relative strength and direction of the parameter's effect. *K* is the number of model parameters (including *y*-intercept and a random effect of mesocosm ID), *C_p* is Mallows' *C_p* (a measurement of model error), AICc is Akaike's Information Criterion corrected for small sample size, Δ_i is the difference between the candidate and best model's AICc, *w_i* is the relative strength of evidence for each model in the set (between 0–1), and RMSE is the root-mean-square error (model predictive ability) generated via *k*-fold cross validation (*k* = 10). %diff is the percentage difference between each model's validation RMSE and that of the top model, with + or − indicating increased or decreased predictive ability. %diff values may be assessed with the following criteria: <10 = not substantial, 10–19 = somewhat substantial, 20–29 = substantial. All models with Δ_i < 10 and % difference in RMSE < 10 are shown. The term "ash type" denotes white or black ash, "activated" = whether white ash was produced from wood or activated charcoal, "days" = days since addition of ash, "pH_{t-1}" = a lagged effect of pH from the previous measurement date, and O₂ = dissolved oxygen.

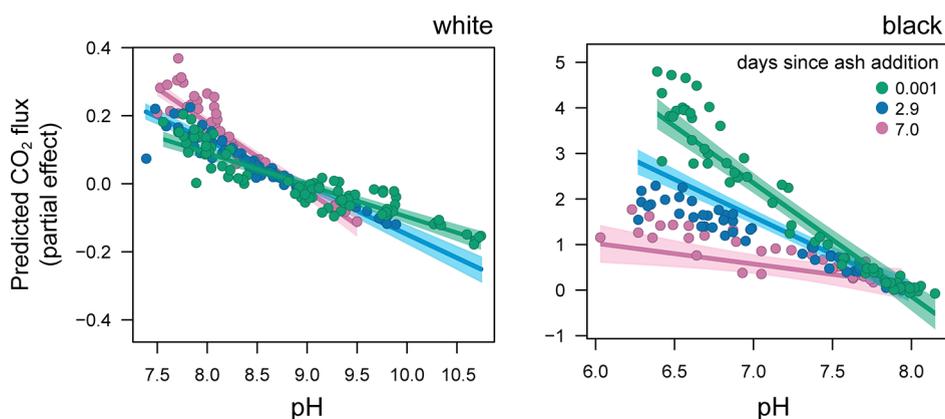


Figure 4. Parameter effect plots for pH in the top model (selected according to lowest AICc and RMSE) explaining variability in CO₂ emissions after addition of white (for experiments 1–3) and black ash (for experiments 1 and 2), showing an immediate impact of pH on CO₂ emissions (0.001 days), which becomes less pronounced over time, particularly after additions of black ash. Note the differences in scales of axes.

number of published studies employing black carbon and biochar, it is critical that the characteristics and language used to identify these varied materials become more standardized and descriptive.

While our experiments demonstrated diverse chemical or ecological effects of different forms of black ash, our results suggest a chemical homogenization of white ash derived from different fuel sources. The effects of white ash derived from two fuel types (activated charcoal and *Fraxinus* wood) on CO₂ and CH₄ fluxes, pH, and DO were similar. This implies a homogenization of ash composition and chemical effects with recombustion as differing organic constituents are volatilized to produce similar inorganic products and effects. The relative reactivity of white ash in experiment 3 in comparison to its black counterparts indicates recombustion as one pathway for the transformation of natural black carbons, whose large-scale methods of natural degradation are inferred but not wholly

accounted for.¹⁵ This enhanced reactivity returns relatively inert black carbon from a slowly cycling pool to the fast carbon cycle, potentially representing a risk to weigh against the efficacy of biochar soil amendments as a carbon storage method, especially in light of predicted increases in frequency of large fires in the 21st century.^{65,66}

3.4. Limitations and Future Directions. The findings of this study demonstrate some of the effects of ash on lentic GHG cycling and may implicate the role of ash in temporarily affecting the activity of sediment microbial communities, but there are many challenges in expanding this study to the ecosystem scale. Although our CH₄ emissions were similar to other reported rates [our control average throughout the experiment was 7.2×10^{-4} g C m⁻² h r⁻¹, within the range of emissions (3×10^{-5} to 1.1×10^{-3}) for small lentic bodies reviewed by Holgersson and Raymond²⁶, different ecosystems can exhibit widely different rates.⁶⁷ Our mesocosms were not flushed by inflows or outflows

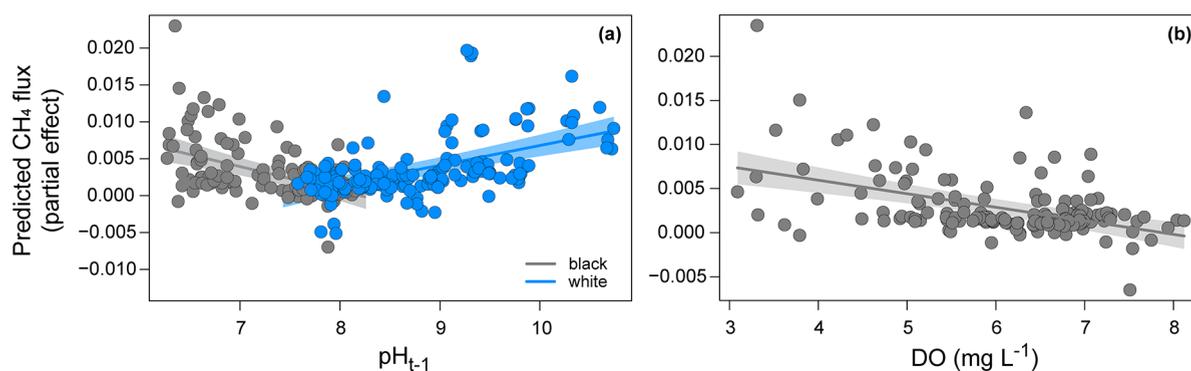


Figure 5. Parameter effect plots for (a) lagged effects of pH (pH_{t-1}) and (b) dissolved oxygen in the top model (selected according to lowest AICc and RMSE), explaining variability in CH_4 emissions after addition of white or black ash for the full data set. Data for white ash include experiments 1–3, while data for black ash are for experiments 1 and 2 (activated charcoal excluded). The effect of dissolved oxygen on CH_4 flux after black ash additions (panel b) was as plausible as a model containing lagged pH alone in the case of black ash. Note the differences in scales of axes.

of water and therefore had essentially infinite residence times. Observational or experimental ecosystem-scale studies should test for the occurrence and persistence of these processes in situ, where variable residence times may determine the persistence of the effects.

Our mesocosm sediments, collected from a peri-urban agricultural area, were low in organic matter ($0.66\% \pm 0.28\%$), likely due to fine particulate loss during sediment sieving. If methanogenesis was energy-limited in these sediments, then the addition of black ash may have enhanced the activity of a previously substrate-deprived sediment microbial community, thereby instigating GHG emissions by supplying labile organic material. However, increases in sediment GHG emissions with the addition of organic-matter-depleted white ash show that the microbial community was functional, despite possible organic substrate limitation. Future work should compare the ways that different sediment types across lentic systems influence the magnitude and persistence of altered GHG fluxes.

Although mesocosm experiments can control conditions to elucidate ash effects that may be obscured in larger, more variable natural systems, they may not account for all of the parameters that could influence experimental outcomes. Many parameters, such as water level, temperature, light, and nutrient availability, fluctuate seasonally, and future work should investigate how these seasonal changes may alter the effects of ash on aquatic GHG emissions and uptake. System-specific hydrology may determine ash residence times, but the timing of fire coincidence with seasonal changes in precipitation or discharge could also determine relative amounts of ash delivered to a waterbody.¹² These interacting drivers may modulate the effects of fire on aquatic carbon cycling, and lack of accounting for these environmental factors may contribute to the lack of consensus in the few published studies on fire effects on aquatic CO_2 and CH_4 fluxes or pH shifts.^{37–39,56,63,68} Field-based studies should build on these findings by carefully monitoring chemical, hydrological, and seasonal parameters and include descriptive chemical data from both ash loads and pre-existing sediments. This would allow future studies to isolate parameter effects in controlled laboratory experiments or to model processes using comprehensive field-derived data.

Our experiments were conducted in a laboratory with negligible levels of photosynthetically active radiation in an effort to minimize the effects of primary producers, thereby demonstrating the ability of ash or other pyrogenic products to influence lentic GHG flux in ways that may otherwise have been

masked by strong autotrophic responses. However, ash heavily impacts physical and chemical properties of aquatic systems—turbidity, DIC, pH, nutrients and other fire exports are known to affect phytoplankton blooms and alter producer community composition.^{24,25} The coincidence of ash inputs with seasonal dominance of phytoplankton groups may also impact the persistence and magnitude of altered fluxes^{69,70}—nitrogen-fixing and rapidly growing cyanobacteria may be more common in warmer months and disproportionately fertilized by phosphorus in ash compared to diatoms or green algae,^{69,70} influencing carbon budgets through photosynthesis and organic matter export to sediments. Additionally, the increase in solubility of CO_2 with high loads of white ash may compound with fertilization and elevated photosynthesis in natural systems to greatly increase carbon capture and potentially alter carbon source-sink status, especially considering white ash's evident ease of mobilization.^{9,10,12}

Our experiment only lasted 7 days, but the longer-term effects of ash intrusion may be inferable from chemical data. Being considerably more soluble and reactive, white ash may not persist long either on the landscape or in recipient ecosystems, particularly if they are well-flushed.^{8,12,58} In natural systems, pH-driven effects of white ash may become overshadowed by a potentially delayed input of black ash and a medium-term increase in soil-derived DOM mobilized by erosion often seen following fires.^{10,71} Any observable increase in CO_2 uptake due to DIC speciation or by fertilization of primary production may be observable primarily on short time scales, supported by field measurements of pH and nutrient concentrations in recipient waters.^{10,63} The long-term effects of black ash on aquatic GHG emissions may diminish with time as surface functional groups of black carbon particles are mineralized by microbial activity.^{15,72} However, black ash-augmented CH_4 emissions may also linger for some time as potentially delayed delivery due to larger or denser particles—and persistence due to lower solubility—may temporarily increase organic carbon delivery and retention in lentic sediments.¹² Future field studies should attempt to capture the full ontogeny of ash effects on the pH, CH_4 , and CO_2 . These may diminish with time (Figures 1–4), although some studies have found that fires can have lasting impacts on aquatic ecosystem chemistry long after occurrence,^{63,73} and that potential decreases in allochthonous inputs after repeated fires may lower lentic productivity or sediment accumulation of organic matter.⁷⁴ Given that wildfires often represent enduring and repeated disturbance events in fire-prone areas, it is

necessary to collect more robust field-based data to determine the long-term and cumulative role of ash inputs to lentic sediment systems/communities, especially given the potential role these sediments play in contributing to GHG emissions.^{26,27}

Though some ash-driven factors like pH or DIC may be short-lived in many aquatic ecosystems (Figures 1–3), long-term mesocosm or field studies could determine whether repeated ash additions result in accumulation of more strongly retained components of ash such as phosphate⁷⁵ or black carbon⁷⁶ through sediment core samples. These studies should monitor how accumulating ash components shape the physiochemistry and biota of those systems with successive inputs on time scales reflective of natural burns, while mesocosm-based approaches can identify the roles of these constituents in shaping ecosystem processes.

Our mesocosm approach isolated and compared the effects of two types of ash (black and white) produced from different fuels on GHG fluxes in recipient aquatic ecosystems. These two classes of pyrogenic products, while naturally found together in ash flows,¹⁰ represent extreme ends of a larger spectrum of ash products which may dramatically and somewhat oppositely influence ecosystem processes and which are differentially mobilized, a delineation which has yet to be factored into manipulative studies of this kind. This study shows that inputs of ash can play a large role in aquatic chemistry without autotrophic influence and implicates a role of ash in affecting GHG fluxes and sediment microbial activity, which should be explored more directly in future research through metagenomic sequencing techniques. Emissions and community structure may also change with time, as possible feedback loops between methanogenesis and methanotrophy occur. Additionally, microbial communities in acidic sediments may be especially impacted by alkaline ash inputs compared to communities in already alkaline waters.^{28,30} As CH₄ fluxes are at least partially driven by differences in activity of methanogens and methanotrophs, it is important to characterize community shifts in ash-affected aquatic sediments as has been done in terrestrial soils, where depletion of organic matter, short-term nutrient pulses, or pH shifts may differentially affect the activity or abundances of various groups.^{39,77–79} Future work should also strengthen the characterization of either lab-produced or field-sampled ash to better understand the relative contributions of white and black ash to the mixed, exported product as well as how chemical differences among ashes produced from fuels of different species or types may influence these findings. Finally, we selected our phenomenological analyses to demonstrate a plausible mechanism, which has yet to be fully explored in the literature but which future studies may statistically explore more causally to create robust models of ash-affected systems.

There have been studies demonstrating the ability of ash, smoke, or other pyrogenic materials to influence carbon budgets of aquatic systems through their effects on microbial activity³⁹ or increased primary production,^{24,80,81} and these altered carbon fluxes can even rival that of fires themselves.^{3,5} However, little work has been done to investigate the ultimate fate of potential fixed carbon in these systems. Ash-driven fertilization combined with an influx of abiotic uptake of atmospheric carbon may initiate strong bottom-up effects in aquatic food webs, and it may be that much of this ash- and aerosol-induced carbon capture and primary production is ephemeral—eventually consumed and counteracted by lagging respiration and emissions.

While studies have recently begun to characterize the effects of ash on downstream and downwind ecosystems, much is still

unknown about rates of production, deposition, and transport of ash and char in natural systems, as reviewed by Bodí et al.¹⁰ and Paul et al.^{7,82} While detailed field measurements occasionally accompany large fires, the relatively ephemeral nature of these substances has precluded much standardization of measurement of transport and downstream deposition.⁸ Inasmuch as this and other studies have considered the role fires play on aquatic systems in both short and long-term,^{18,20,83} accurate field measurements of ash and char production and transport are critically needed to enable a rapidly expanding and crucial field of research.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.4c10046>.

Ash production and allocation methodology, pH and DO profiles, statistical results, and literature search (PDF) (XLSX)

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Notes

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