Can ash from smoldering fires increase peatland soil pH?

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ABSTRACT

Peatland wildfire frequency and severity are increasing globally owing to climate change. The direct risk of elevated greenhouse gas emissions from peat burning receives much attention, yet the risks to vegetation composition or peat decomposition from alkaline ash inputs are poorly understood. We explored whether ash produced during smoldering increases peatland topsoil (~0–25 cm) pH through field observations and laboratory experiments. We assessed spatial patterns of smoldering and ash presence, and measured soil and ash pH after a peatland wildfire in the Netherlands. Additionally, a peat smoldering experiment was conducted to compare freshly produced ash pH with aged ash pH collected 2 months following the wildfire. Additionally, we assessed the amount of ash needed to increase soil pH. Results showed that ash inputs at the field site were insufficient to increase pH of the acidic peatland after the wildfire. Incubation experiments showed that a ≥3 cm ash layer (ash load 163 t ha^{-1}) would be required to increase soil pH by at least 1 unit. Given that aged ash was slightly acidic and fresh ash was alkaline, leaching and neutralisation of ash after wildfire is likely, suggesting that elevated soil pH from ash input may be transient rather than long term.

Keywords: alkalisation, ash, nature recovery, peatlands, smoldering, soil, The Netherlands, wildfire.

Introduction

Peatlands globally receive much attention owing to their carbon storage function (e.g. Turetsky et al. 2015) and store an estimated ~600 Gt of carbon (Yu et al. 2010; Page et al. 2011). However, the carbon storage can become compromised when peatlands become degraded or disturbed (van der Velde et al. 2021), for example by changes in land-use and climate (Leifeld and Menichetti 2018). Moisture stress or lowering water levels can cause shifts in the peatlands' carbon sink functionality (Salimi et al. 2021), and potentially shift the system from a net sink to a net source of carbon (e.g. Evans et al. 2021). The combined stressors of drainage and suboptimal water management leading to drier surface conditions, the increased occurrence of invasive plant species that are more susceptible to wildfire, and more extreme weather conditions and warming trends will increase wildfire risk in peatlands (e.g. Flannigan et al. 2009; Kettridge et al. 2015). Given the increased risk of more frequent and severe wildfires and the associated risk of further destabilising carbon stores (Kasischke and Turetsky 2006; Flannigan et al. 2009; Bourgeau-Chavez et al. 2020), it is essential to understand peatland resilience to such disturbances and perturbations (Limpens et al. 2008).

Both above- and below-ground fires can potentially cause long-lasting consequences for the physical and ecological structure of the landscape. Generally, an increase in nutrient availability and a decrease in water availability after wildfire promote expansion of vascular plants (Limpens et al. 2003; Dieleman et al. 2015). Fires have the potential to accelerate recruitment of woody species in peatlands, which could set in motion a positive feedback loop, increasing dry woody vegetation at the cost of wet peat-forming vegetation (Weltzin et al. 2003; Waddington et al. 2015; Nelson et al. 2021), thus increasing fuel load and fire risk. Although many studies focus on the direct risk of peat consumption and carbon release following wildfires (Che Azmi et al. 2021), very little attention is given to the potential effects of fire-produced ash on soil chemistry in peatland systems (Khanna et al. 1996; Noble et al. 2017).

Peat typically burns via smoldering combustion, which is characterised by slow, low-temperature, flameless combustion of organic matter, and can spread horizontally and vertically, reaching deep into the soil layers (Rein 2013). Smoldering combustion can destroy peat layers that have taken centuries to accumulate (Benscoter *et al.* 2005), potentially reducing them to ash (Maltby *et al.* 1990). Additionally, burn residuals, such as ash consisting of mineral materials and charred organic components (Bodí *et al.* 2014), can pose a threat to peatlands. The deposited ash layer may be incorporated into the soil or redistributed by water and thus has the potential to alter the pH or nutrient content of peatlands (Prat-Guitart *et al.* 2011).

Wildfire ash produced in peatland-dominated landscapes can have a high pH, with values ranging between 8.5 and 11 (Thomas and Wein 1990; Emmerton *et al.* 2020) owing to the high concentration of carbonates in ash (Ulery *et al.* 1993; Úbeda *et al.* 2009; Bodí *et al.* 2014). Many studies have found that ash washed into soil can cause an increase in soil pH in a wide range of ecosystems (Bodí *et al.* 2014). However, this period of elevated soil pH is variable, and the time it takes to return to pre-fire conditions ranges from 1 year to almost one decade following fire (Strømgaard 1992; Costa *et al.* 2014; Alcañiz *et al.* 2016). In peatlands, smoldering fires can produce large quantities of ash and therefore have the potential to increase the pH of the peat (Jeong *et al.* 2009; Noble *et al.* 2017). Changes in peat soil pH could stimulate microbial decomposition (e.g. Andersson and Nilsson 2001; Evans *et al.* 2012) and force vegetation succession away from peat-forming *Sphagnum* mosses (Robroek *et al.* 2009), thus decreasing the carbon sequestration abilities of the system (Waddington *et al.* 2010).

To our knowledge, no study has specifically studied the interaction of ash and peat in terms of pH. Here, we explored if wildfire ash input can increase the pH of peat topsoil by combining both field observations from a burned peatland in the south of the Netherlands and laboratory experiments. The direct impacts of smoldering on peat loss, ash production and potential damage of *Sphagnum* mosses (e.g. Noble *et al.* 2019), and the indirect impacts of alkaline ash addition raised concerns from local land managers at our field site given ongoing nature restoration efforts. Thus, our study has direct relevance to aspects of peatland restoration and protection efforts in the Netherlands (e.g. Limpens *et al.* 2016) and peatlands globally (e.g. Granath *et al.* 2016; Humpenöder *et al.* 2020).

The objectives of the present study were to: (1) assess the spatial distribution of smoldering within a recently burned peatland; (2) assess ash presence and peat pH; and (3) explore how much ash is needed to increase peat soil pH and the potential impacts of ash input on peat pH. We expected that (1) smoldering frequency would increase with elevation and distance from water and drainage canals; (2) ash would be more abundant in locations that had smoldered compared with those that had not smoldered

and have a high pH; and (3) peat samples collected from smoldered patches in the field would have a higher pH due to input of alkaline ash. To address these objectives, we conducted field observations approximately 2 months after the wildfire to determine the locations and percentage of the area that had smoldered (Objective 1). This was expanded with pH measurements of soil and ash collected from the field, and the pH of freshly produced ash from an experimental smoldering box (Objective 2). Incubation and titration experiments untangle the extent of the potential impact of ash addition on peatland soil pH (Objective 3).

Materials and methods

Study area

The field observations for this research were conducted at the Deurnsche Peel (sometimes referred to as Deurnese Peel), a 1400-ha raised bog peatland reserve, in the south of the Netherlands (Fig. 1). The Deurnsche Peel is owned and managed by the Dutch Forest Service (hereafter: Staatsbosbeheer). The site has been a Natura2000 protected peatland reserve since 1994. It is surrounded by land of former and current intensive agricultural land use but is hydrologically isolated from the influx of eutrophic drainage water from surrounding farmland. Peat covers the entire study area, although the surface is uneven and consists of canals, dry ridges, and wet day pits due to former large-scale peat extraction in the area. Average peat thickness of the sampling area is 75 cm and ranges from 12 to 152 cm (Wageningen Environmental Research 2014). Podzol soils occur in isolated patches in the subsoil throughout the area but they still have a thin layer of peat covering them. In our earlier unpublished studies in 2014, topsoil pH in the study area was measured and found to vary between 3.4 and 3.7.

The irregular microtopography results in average water table depths ranging from 31 to 71 cm below surface with seasonal fluctuations (Knotters *et al.* 2008). Variability in surface wetness distribution typically aligns with the patterns of the canals, ridges and day pits, with water pooling in lower depressions and concave surfaces. Vegetation at the study site consists of *Sphagnum* mosses, which cover ~6% of the study area. Sundew (*Drosera*), bladderwort (*Utricularia*) and common heather (*Calluna vulgaris* and *Erica tetralix*) comprise ~2% of the area. In the deteriorated peat areas, species such as purple moor grass (*Molinia caerulea*) and eagle fern (*Pteridium aquilinum*) are found, comprising ~11% of the area. Forested parts, containing mainly birch trees (*Betula* spp.) comprise ~4% of the study area.

The wildfire at Deurnsche Peel began on 20 April 2020. At the time of the wildfire, the vegetation and peat were exceptionally dry with 6 mm rainfall in the past month and a precipitation deficit three times larger than normal conditions (82 mm) (data recorded at the Deurne weather station,
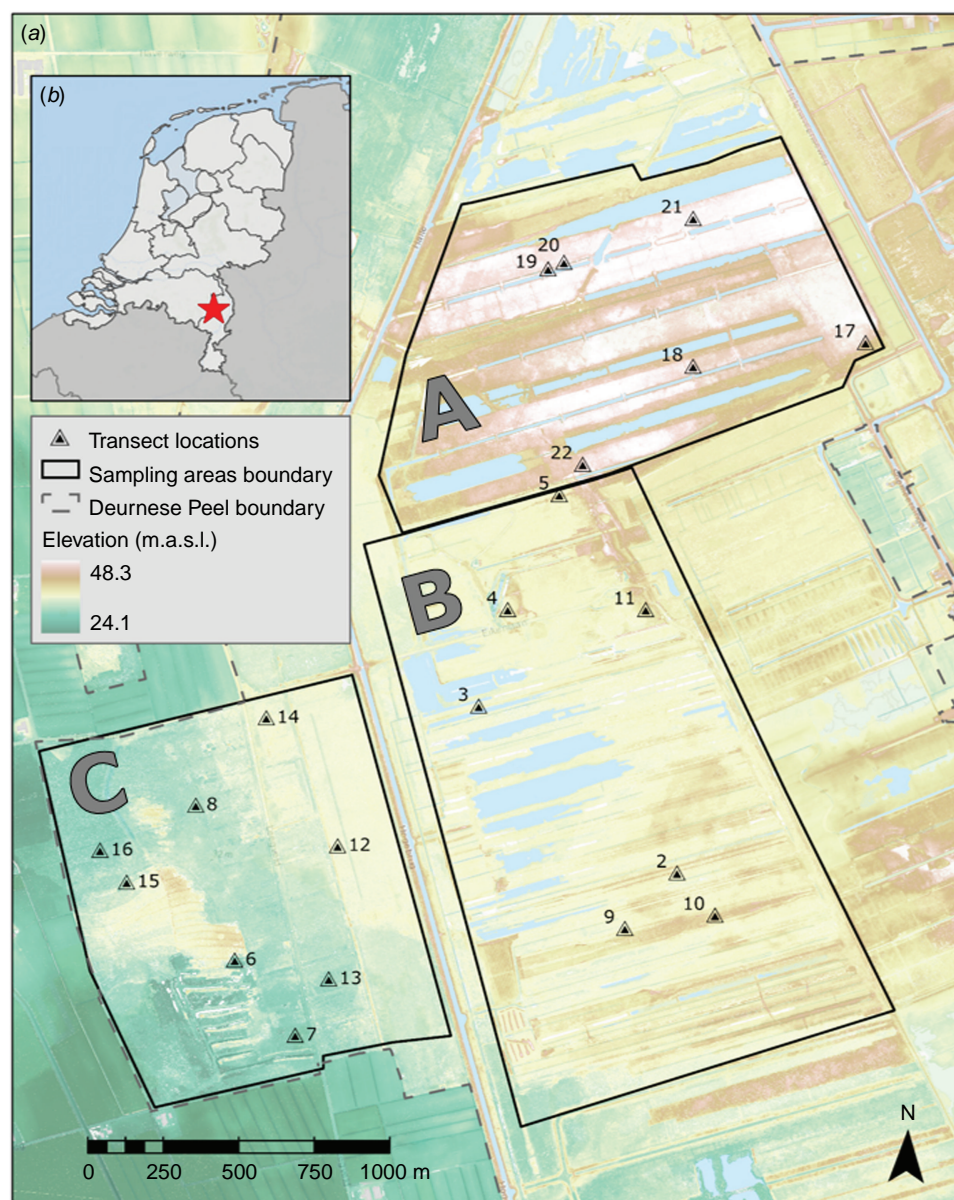
Fig. 1. (*a*) Overview and digital elevation model (DEM) of sampling sections at Deurnsche Peel, with the three sampling sections denoted by grey-coloured A, B, and C. Sampling transects are indicated with a small black triangle. (*b*) Inset map showing the Netherlands and the location of the Deurnsche Peel indicated with a red star. DEM data courtesy of Actueel Hoogtebestand Nederland (AHN). (masl: meters above sea level)

located 7 km northwest of the study area (KNMI (Koninklijk Nederlands Meteorologisch Instituut) 2020)). Aerial photographs and ground surveys conducted by Staatsbosbeheer indicate that the surface fire impacted nearly the entire study area, and varying degrees of smoldering occurred within the burned perimeter (Stoof *et al.* 2020), which consumed peat and locally created large amounts of ash. The above-ground flaming fire lasted 3–4 days and burned ~60% of the Deurnsche Peel. Peat continued to smolder for two months (Stoof *et al.* 2020). Efforts to suppress the peat smoldering hotspots consisted of localised insertion of water into the

ground, combined with digging in some locations. During the smoldering phase, 88 mm of precipitation was recorded, and in the time between smoldering and field work, 76 mm of precipitation was recorded at the Deurne weather station.

Site selection and field sampling procedures

Field work was conducted in the first two weeks of August 2020, approximately two months after the end of the smoldering phase (22 June 2020). This time period was expected to be sufficiently long enough for alkaline

compounds in the ash leachate to reach the soil column (Steenari *et al.* 1999), but not long enough for soil pH to recover to pre-fire conditions (Strømgaard 1992; Costa *et al.* 2014; Alcañiz *et al.* 2016). Field work was structured using a stratified random sample design by dividing the burned area into three sampling sections (Sections A–C) based on differences in micro-topography, drainage patterns and vegetation (Fig. 1*a*), seen from aerial photographs and initial field surveys, and based on already existing divisions of the area given the canals and walking trails. Unburned portions of the Deurnsche Peel were not included in the field sampling because the environmental conditions were not representative of the rest of the field site, nor were conditions suitable for access at the time of field work. In some locations in the middle of Section B, we observed ground disturbance from fire suppression efforts and ash compaction from large vehicles driving through the area. Those locations were excluded from the sampling. Impacts of fire suppression efforts were not observed in Sections A or C.

In each sampling section, 10 random points were generated in ESRI ArcGIS Pro (Environmental Systems Research Institute, California, USA). From the 10 points, six to eight points were selected as sampling points based on accessibility of the area at the time of field work. A 50 m-long transect was placed from each of the random points, with four 10 m-long transects extending perpendicular to the original main transect at 10-m intervals (Supplementary Fig. S1). We walked both the 10 and 50 m lengths of the transects using a TopCON dGPS (Topcon Corporation, Tokyo, Japan) while continuously registering at 1 m intervals the occurrence of smoldering, which was identified visually on the ground surface, to estimate the area that had smoldered for each sampling section (Supplementary Fig. S2). The smoldered surface area was visually mapped on paper for the 50 × 20 m area covered by the transect with an accuracy of ~0.5 m (Supplementary Fig. S1). Two random sampling points were subsequently located in the smoldered area and two random sampling points in the non-smoldered area (described in Supplementary Material). These data were also later used in analyses to determine if environmental variables or elevation differences could predict occurrence of smoldering in the area (description of analyses in Supplementary Material, Appendix B).

We surveyed a total of 21 transects and a total 82 sampling points. At each sampling point, a mini-soil pit of ~25 cm was dug and peat samples were collected at depths of 0–5, 5–10 and 20–25 cm to measure the soil pH in a depth gradient and compare pH of soil in smoldered and non-smoldered sampling locations. We collected 235 soil samples. Out of the 235 soil samples, 10 samples at the depth of 20–25 cm were mineral podzol soils that were beneath the peat layers. Given the small amount of podzols, the entire soil column was considered together in data analyses.

We collected ash samples to measure the pH of the ash, and to define its colour to determine if there are pH differences amongst the range of ash colours. Ash was often present on the ground surface at sampling points that had smoldered and it appeared to be intact at the time of sampling. Ash was present at only two burned sampling points where no peat smoldering occurred and these were considered together with the rest of the ash pH dataset analysis. In total, we collected 32 ash samples for pH measurements and further analyses. Ash colour was determined using a Munsell colour chart (Munsell Color 2009), and categorised into three colour classes for data analysis: dark (2.5Y 3/1, 5YR 2.5/1, 5Y 656 3/1, 7.5YR 4/1), light (10YR 5/1, 10YR 6/1, 10YR 5/2, 5Y 5/1, 2.5Y 4/2, 2.5Y 5/2) and tan (10YR 7/4, 10YR 6/4, 2.5Y 5/4, 2.5Y 6/4). Ash thickness was measured to determine if the thickness of the layer related to the amount of smoldering along a sample transect. Ash thickness data were also used to set up the incubation experiments, which are described later. When possible, ash thickness was measured at five equally spaced intervals along a 1-m ruler to capture spatial variability in thickness (Bodí *et al.* 2014) around the area of the sampling point.

Lab work and experiments

Experimental smoldering box

To determine the alkalinity of ash immediately post smoldering and compare it with aged ash, we created an experimental smoldering reactor (Rein *et al.* 2008; Prat-Guitart *et al.* 2016; Christensen *et al.* 2019), herein smolder box, to create 'fresh ash'. Because ash samples were collected from the area ~1.5 months following the completion of the smoldering phase, these ash samples are therefore called 'aged ash' because compositional changes may have occurred before sampling (Santín *et al.* 2015).

We collected a large peat block from the field for the smolder box experiments. The undisturbed peat block collected from the field (~40 × 40 × 40 cm in size) was air-dried until no further weight loss occurred. Air drying the block, rather than oven drying, limits the risk of chemical changes to the peat block that could occur with drying (Dettmann *et al.* 2021). The initial pH of the peat block was 3.95, measured in a demineralised water slurry using a 1:10 peat-to-water ratio.

Each smoldering box was 20 × 20 × 10 cm in size, constructed with insulating Superwool HT fiberboard (RS Components Ltd) (Fig. 2*b*). An undisturbed subsample from the peat block was placed in the smoldering box, rather than homogenised and mixed, to better replicate the natural spread of smoldering through the peat layers (Rein *et al.* 2008). The surface moss and litter layer also remained on the top of the peat block in the smolder box. The peat was ignited with a 5 cm-long electric resistance coil delivering 100 W for 30 min to begin the smoldering front. Five K-type thermocouples (1.5 mm, TC-direct, Nederweert, the Netherlands) connected to data loggers (EL-USBTC, Lascar Electronics, UK) were placed around the sides of the smoldering box at 5 cm depth
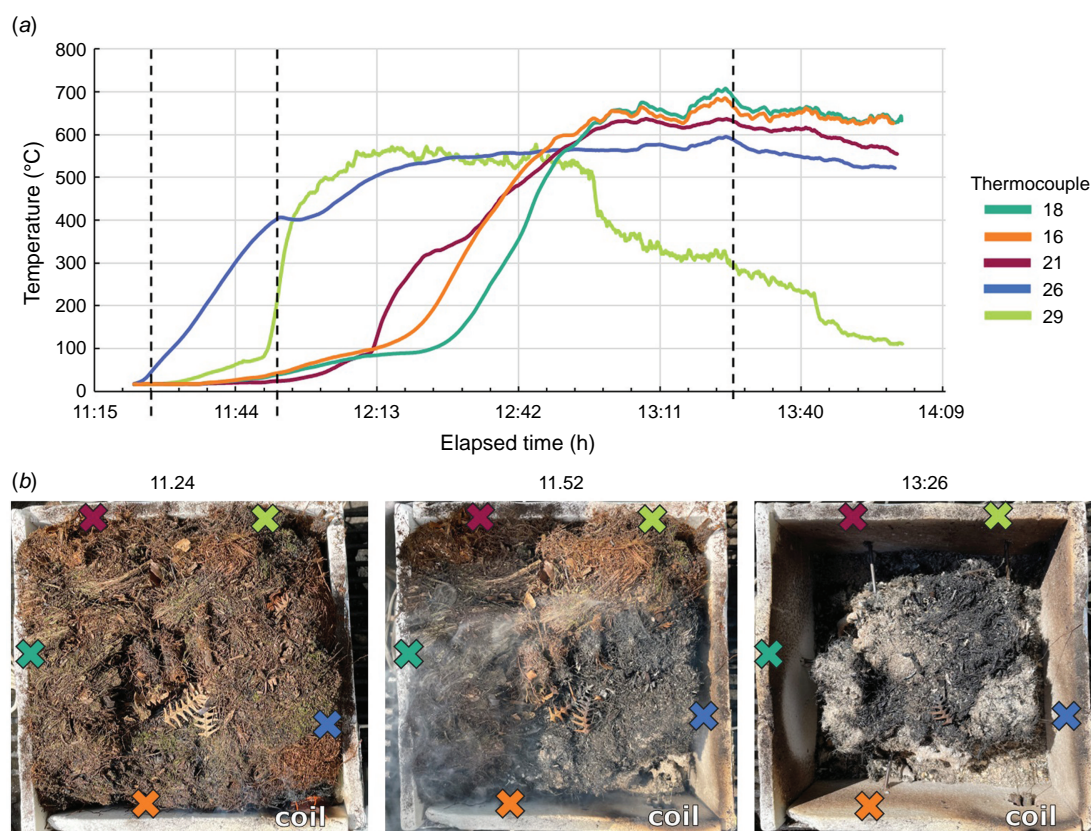
Fig. 2. (*a*) Temperatures reached during smolder box Rep 1 experiment, recorded by the thermocouples. The numbers and colours on the right side correspond to the colours of the lines on the graph, which represent the temperature measured. The black dotted lines indicate the time of each photograph below; (*b*) the photographs each show a different phase of the smoldering. The position of the coil (white text) and the thermocouples are identified with a coloured X, which corresponds to the temperature data (*a*). The coil and thermocouples were inserted around the perimeter of the peat block at a depth of 5 cm.

to record temperatures of the smoldering phase. We conducted two smolder box experiments in total using the top and bottom portions of the peat block, hereafter Rep 1 and Rep 2. Peak temperatures during the smoldering box experiment of Rep 1 ranged from ~500 to 700°C (Fig. 2*a*) and peak temperatures of Rep 2 ranged from ~400 to 600°C. The peat block became smaller during the smolder experiments and the thermocouples could no longer remain in the peat block; thus, temperatures were not recorded after ~2.5 h of the smolder box experiment. We collected one composite sample of light-coloured ash and one composite sample of dark-coloured ash from each smolder box once the smoldering was presumed to have stopped (i.e. no longer smoking or producing heat). The light-coloured ash from Rep 2 was used in this study's experiments because it had the highest pH value (pH 10.5), thus best representing a worst-case scenario of alkaline ash impacts.

Incubation and titration experiments

Incubation experiments were conducted with varying quantities of calcium carbonate ($CaCO_3$), aged ash and fresh ash added to peat to determine the effect on the measured soil pH and to quantify the potential liming effect of ash on the soils in a standardised manner. First, realistic application rates were estimated. The bulk density of the top 0–20 cm is ~0.2 t m^{-3} (Beuving 1984), which corresponds to a mass of 400 t ha^{-1}. Under normal conditions, there is almost no liming application of peat soils in the Netherlands. Rates in arable land, grassland and forested areas vary but are typically below 10 t ha^{-1}, which corresponds to a liming application ratio of 0.025 g $CaCO_3$ g^{-1} dry peat. This was considered to be a realistic ratio for the incubation experiments.

Ash layer thickness varied considerably throughout the study area at the time of field work, and could be as thick as ~6.5 cm in few severely and preferentially smoldered locations, such as on some ridges and around trees bases and exposed tree roots. However, ash layers were on average 1.3–3.6 cm thick (Supplementary Fig. S5). We used 3.75 cm of fresh ash produced from smolder box Rep 2 to represent a maximum average ash thickness value in our calculations of ash bulk density and an estimated total ash production.

The bulk density of the ash used in the experiments was $\sim 0.54 \, t \, m^{-3}$ based on calculations of ash thickness layer of a composite sample in a sample beaker. The calculated bulk density of the ash corresponds to an estimated total ash production of $375 \, m^3 \, ha^{-1} \times 0.54 \, t \, m^{-3} = 204 \, t \, ha^{-1}$, which equates to a ratio of $0.51 \, g$ ash g^{-1} dry peat. The respective $CaCO_3$ and ash ratios were used to select appropriate $CaCO_3$ and ash additions for the incubation experiments.

We conducted six incubations experiments using $CaCO_3$, fresh ash and aged ash using 50 g of field moist peat (corresponding to $\sim 10 \, g$ of dry peat) and an incubation time of 14 days. Peat used in the incubations was from the same sample in order to keep initial peat pH conditions as stable as possible. For the $CaCO_3$ incubations, we added 0, 0.05, 0.10, 0.15, 0.20 and 0.25 g (calculated maximum amount, 0.25 g, corresponding to an application of $10 \, t \, CaCO_3 \, ha^{-1}$) in the different treatments. Addition of $CaCO_3$ was to represent addition of an alkaline carbonate substance to the peat, and $CaCO_3$ is often a constituent of wildfire-produced ash (Bodí *et al.* 2014). For the incubation of fresh and aged ash, we added 0, 1, 2, 3, 4 and 5 g (calculated maximum amount corresponds to an ash layer $\sim 3.75 \, cm$, based on field measurements) in the different treatments. Each treatment was conducted in two replicates. All samples with $CaCO_3$ or ash addition were mixed with the peat in closed sample containers and stored at room temperature. After 14 days, the pH was measured using a 1:14 peat/water ratio following the same procedures described for measuring pH of ash and peat samples.

The potential liming effect of ash was estimated with a single addition titration of soil (Dunn 1943) and ash (Cerrato *et al.* 2016). Titrations were performed on peat samples using 1 M NaOH to determine the amount of an alkaline solution addition to peat needed to increase pH by 1 unit. The 1-unit pH increase is based on the average peat pH at our site (pH ~ 3.5), and a 1-unit increase to pH ~ 4.5 given that peatlands characteristically require a low pH (≤ 4.5) (Rydin and Jeglum 2013). Two replicates of 50 g of field moist sample (corresponding to $\sim 10 \, g$ of dry peat) mixed with 80 mL of demineralised water were used for the titrations. The 1 M NaOH was added in increments of 1 mL and the mixture was allowed to stand for 5 min; then, the pH was measured.

Titrations of fresh ash were conducted with 1 M HCl to determine the amount of acidic solution addition needed to decrease ash pH to an acidic end point. Two replicates consisting of 2 g of fresh ash mixed with 20 mL of demineralised water were used for the titrations (1:10 ash/water ratio). 1 M HCl was added to the slurry in 0.1 mL increments, the mixture was left to stand for 10 min after each addition, and then the pH was measured.

Measurement of ash and peat pH

The pH of aged ash, four fresh ash samples and all soil samples was measured. The pH measurements of peat were done on field moist samples rather than oven-dried samples because drying may alter the pH of organic-rich soils such as peat (Dettmann *et al.* 2021) and rewetting of dried samples may cause a decrease in soil pH (Erich and Hoskins 2011). The moisture content for each peat sample was determined by drying a sub-sample at 105°C for 24 h. The moisture content was then used to calculate how much field moist peat and additional demineralised water was needed for each slurry in order to keep the peat-to-water ratio consistent. Measurements with ash and peat samples were done in a demineralised water slurry using a 1:10 ash- or peat-to-water ratio. A 1:2.5 soil-to-water ratio was used for mineral soils. Samples were shaken manually for 1 min and allowed to settle for 30 min. This was repeated four times. After the fourth shake, the sample sat for 1 h to settle in order to have a fairly clear superfluent to measure pH in the unfiltered leachate, using a handheld multimeter calibrated with standard buffer solutions of pH 4.0 and pH 7.0.

Data analyses

Smoldering patterns and occurrence

Smoldering was recorded at the 21 transects during the time of field sampling, for a total transect length of 90 m. The surveys indicated locations along the transect that had smoldered. From that, we calculated the percentage smoldered for each sampling section and subsequently an area-weighted average for the total area smoldered. Using the sampling points of areas that smoldered and those that did not, we did two additional analyses of smoldering occurrence at our study site in order to establish a possible link to environmental parameters, which is further described in Supplementary Material Appendix B.

Ash pH and impact on soil

Summary statistics for aged ash pH values were calculated on the basis of the three sampling sections and the general ash colour value of dark, light, or tan. A significance test for ash pH was not conducted owing to the small ash dataset. Soil pH between smoldered and non-smoldered sampling points was compared using a student *t*-test. This was selected assuming unequal variances of the data. The effect of smoldering and ash input on soil pH may be disturbed by initial pre-fire differences in soil pH throughout the study area. To minimise this effect, an additional *t*-test was conducted comparing soil pH of the population of samples that were collected from transects with two sampling points having smoldered and two not having smoldered rather than the entire population of samples. This consisted of 10 transects: five from Section A, one from Section B and four from Section C.

The soil pH buffering capacity and lime requirement are calculated and expressed as Lime Buffering Capacity (LBC) (Barouchas *et al.* 2013). We used results of the incubations and titrations to determine the LBC, which is calculated

from the slope of the linear relationship between soil pH and the amount of CaCO₃ and both fresh and aged ash required to increase the pH by 1 unit per kilogram of soil (Kissel *et al.* 2007). The difference between LBC values of the fresh and aged ash is the potential alkalinity lost in the time between the end of the smoldering phase and field sampling. In calculations of the LBC from fresh ash titrations, the slope in reaching a pH of 6.0 was used in the calculations, rather than end-point pH, because a pH of 6.0 is considered a high pH value that could impact peat and *Sphagnum* health (Jeong *et al.* 2009).

Results

Area and patterns of smoldering in the field

Out of the total 82 sampling points from field work, 25 were at locations that smoldered and 57 were at locations that did not. We found that 14% of the total sampled area had smoldered and the percentage that had smoldered differed considerably between the sampling sections, with 11% having smoldered in Section A, 21% in Section B, and 7% in Section C (Table 1).

In the field, we observed that smoldered patches were often in a mosaic pattern of varying sizes and occurred in an apparently spatially random distribution at our sampling transects (Fig. 3). Smoldering locally existed along the edges of ridges that were slightly higher in elevation (~1 m) than the rest of the peatland, and sometimes

Table 1. The average percentage of smoldering in each of the sampling areas is shown below, in addition to the calculated drainage density of each of the sampling sections.

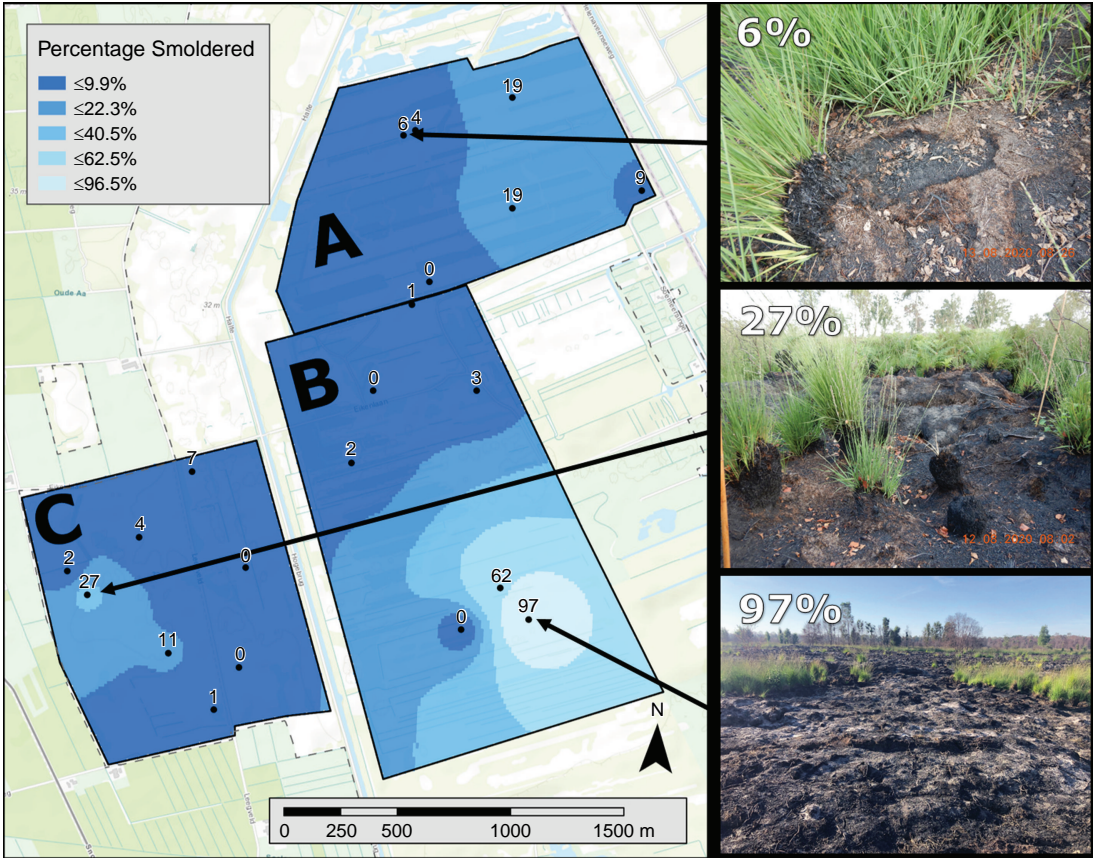| Section	Drainage density	Total smoldering (%)		Area (ha)
		Average	s.d.	
A	High (17%)	11	7	136
B	Intermediate (10%)	21	37	219
C	Low (1%)	7	9	131
All		14	21	486

Fig. 3. Map of smoldering occurrence (average percentage at each transect) at the Deurnsche Peel, created using Inverse Distance Weighting (IDW) with a power of 2 and a variable search radius, up to 12 points. Light blue indicates transects with the most smoldering and darker blue indicates less smoldering. The photos on the right side indicate different degrees of smoldering and the black arrow points to the respective transect. Photos were taking during field work ~2 months after the smoldering phase ended.

preferentially around tree roots, yet these patterns were not consistent throughout the entire study area.

The analyses that explored if smoldering occurred at higher elevations throughout the study area and if environmental variables could predict and identify preferential conditions of areas where smoldering may be more likely to occur showed no significance. Results are further explained in Supplementary Appendix B.

pH of ash and peat

Throughout the entire study area, the aged ash (collected ~ 2 months after the end of the smoldering phase) had an average pH of ~6 (Table 2). There was also no clear trend in pH differences amongst the different colours of aged ash (i.e. dark vs. light vs. tan). When comparing the three sampling sections, the overall average aged ash pH was highest in Section C (pH 6.6), and the lowest average pH of aged ash was in Section B (pH 5.8) despite it having the highest percentage of area that smoldered (Table 1). Spatial patterns of average thickness and aged ash pH at each transect show that these factors did not increase in areas with high amounts of smoldering (see maps in Supplementary Appendix C). At one transect in Section B, 97% of the area of the transect had smoldered (Fig. 3), and the average pH of aged ash at that transect was the most alkaline in Sampling Section B (pH 6.6). Conversely, the transect immediately north of that transect had 62% smoldered (Fig. 3) and the average pH of aged ash at that transect was acidic (pH 4.7; Supplementary Fig. S4).

We found that the pH of fresh ash was higher than the aged ash pH. The average pH of the light- and dark-coloured fresh ash created in the smolder box Rep 1 was 9.7 and 9.3, respectively. The average pH of the light- and dark-coloured fresh ash created in the smolder box Rep 2 was 10.5 and 9.5,

respectively. The light-coloured fresh ash was slightly more alkaline than the dark-coloured fresh ash produced from the smolder box experiments. The pH measurements of aged ash from the field provide an indication of the spatial variation in pH of the aged ash in the study area. The difference between fresh and aged ash pH is considered to be a measure of the alkalinity that is lost from the ash and leached to the underlying soil, potentially resulting in a pH increase of the soil.

The average soil pH values in locations that had not smoldered ranged from 3.5 to 3.6 and average soil pH values in smoldered locations ranged 3.2–3.3. On average, the pH was significantly higher ($P = 0.0007$) in peat samples collected from non-smoldered sampling points compared with the pH of peat from smoldered sampling points nearby (Table 3). The average pH of peat from non-smoldered points was also higher when analysed separately for each section (Table 3), as well when each sampling layer (0–5, 5–10 and 20–25 cm) is considered, with the exception of Section C in the 5–10 cm layers. Although on average the pH is higher in locations that did not smolder than those that smoldered, the variation amongst the average pH values is relatively small (Table 3). The *t*-test analysis of soil pH within transects with two smoldered points and two non-smoldered points shows that the average pH of all the non-smoldered sampling points was higher than that of smoldered location points in all three sampling sections.

Potential impact of ash on soil

Peat pH after 14 days of incubation with $CaCO_3$ ranged from a lowest average pH value of 4.2 (0.05 g $CaCO_3$ added) to a highest of pH 5.4 (0.25 g $CaCO_3$ added) (Fig. 4), and showed a clear trend in increasing pH with greater $CaCO_3$ addition. Peat pH values after 14 days of incubation with *fresh* ash

Table 2. Average calculated pH values of aged ash, and average pH values of the soil calculated for each of the three sampling sections.

	Ash measurement:	pH (all)	pH (dark)	pH (light)	pH (tan)	Ash thickness (cm)
All sampling sections	Mean	6.3	6.2	6.3	6.3	2.0
	Variance	0.74	0.70	0.77	0.75	0.70
	Observations	32	13	14	5	21
A	Mean	6.2	6.2	6.2	6.1	2.7
	Variance	0.47	0.16	0.92	0.09	0.62
	Observations	17	7	7	3	8
B	Mean	5.8	5.4	6.1	n.d.	1.7
	Variance	0.96	0.36	1.16	n.d.	0.45
	Observations	5	2	3	0	5
C	Mean	6.6	6.8	6.6	6.5	1.6
	Variance	0.88	1.34	0.05	1.62	0.34
	Observations	10	4	4	2	8

n.d. = no data was collected.

Table 3. Average pH values of soil at each different sampling depth, and average pH values of the soil calculated for each of the three sampling sections.

Peat layers:		0 cm		5 cm		20 cm	
		No smolder	Smolder	No smolder	Smolder	No smolder	Smolder
All Sections	Mean	3.6*	3.3	3.5*	3.3	3.5*	3.2
	Variance	0.05	0.13	0.05	0.26	0.08	0.07
	Observations	55	23	55	24	55	23
A	Mean	3.6*	3.2	3.5*	3.2	3.4*	3.2
	Variance	0.02	0.05	0.02	0.06	0.01	0.01
	Observations	12	9	12	9	12	9
B	Mean	3.8*	3.4	3.6*	3.4	3.7*	3.2
	Variance	0.08	0.01	0.08	0.06	0.14	0.02
	Observations	19	4	19	4	18	4
C	Mean	3.6	3.55	3.6	3.6	3.5	3.3
	Variance	0.04	0.25	0.03	0.67	0.07	0.19
	Observations	20	8	20	8	21	8

Significant at $P = 0.05$, indicated with *.
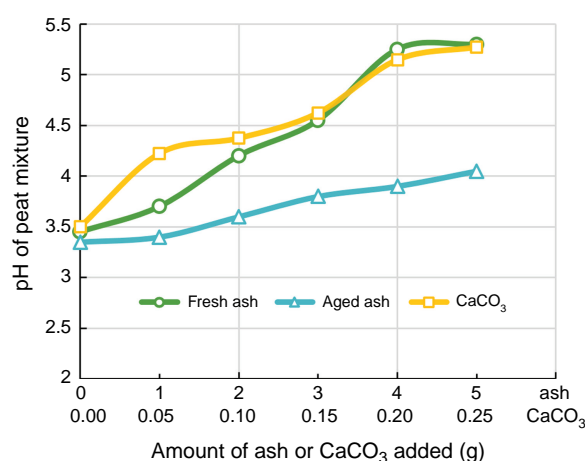
Fig. 4. The effect of varying amounts of fresh ash (green line with circles), aged ash (light-blue line with triangles), and $CaCO_3$ (yellow line with squares) addition to peat after 14 days of incubation. The figure approximately shows a calcium carbonate ($CaCO_3$) equivalence of 0.10 g $CaCO_3$ g^{-1} ash.

ranged from pH 3.7 (1 g ash added) to 5.3 (5 g ash added), and showed a clear trend of increasing pH with fresh ash addition. Peat pH values after 14 days of incubation with *aged* ash ranged from 3.4 (1 g ash added) to 4.1 (5 g ash added; Fig. 4). There is also increasing peat pH with more aged ash addition; however, the increase is not as rapid in comparison with that from the $CaCO_3$ and fresh ash incubations. The pH values for the titration of peat increased in small increments of <1 pH unit with each aliquot of NaOH added (Fig. 5a). The pH values resulting from the fresh ash titrations decreased by almost 2 pH units with each aliquot of HCl addition; however, at the cumulative concentration of 0.3 mL of HCl addition, the

pH remained nearly the same (6.1–5.9) before decreasing with the next HCl aliquot addition (Fig. 5b).

The LBC calculations from incubation results show that 0.23 mmol OH$^-$ per pH unit per g fresh ash was needed to cause a 1-unit increase in pH. However, it is important to consider that the rate may vary at different stages along the curve, with the pH ranging from ~3.5 to ~5.5 (Fig. 4). The fresh ash LBC was 1.12 mmol OH$^-$ per pH unit per g peat and the aged ash was 0.43 mmol OH$^-$ per pH unit per g peat. The difference between the LBC of the fresh ash and the aged ash LBC is 0.70 mmol g^{-1}, indicating that OH$^-$ or alkalinity was leached from the ash in the time following the fire, which could have resulted in a lower aged ash pH by the time of sample collection.

The slope of the value from the fresh ash titration to reach a pH of 6.0 was used in the calculations, rather than the entire dataset shown in Fig. 5b. The LBC calculated from the peat titration was 0.04 mmol OH$^-$ per pH unit per g peat, and the LBC calculated from the fresh ash titration was 0.06 mmol H$^+$ per pH unit per g fresh ash. These values are much lower than the outcomes for the incubations (0.23 for peat, and 1.12 for fresh ash), indicating that the rapid single addition titration procedures performed in this study are not suitable to predict the liming rate and increase in peat soil pH at our study site.

Discussion

Area and patterns of smoldering

We hypothesised that smoldered patches would occur at higher elevations – for example, on ridges – and that
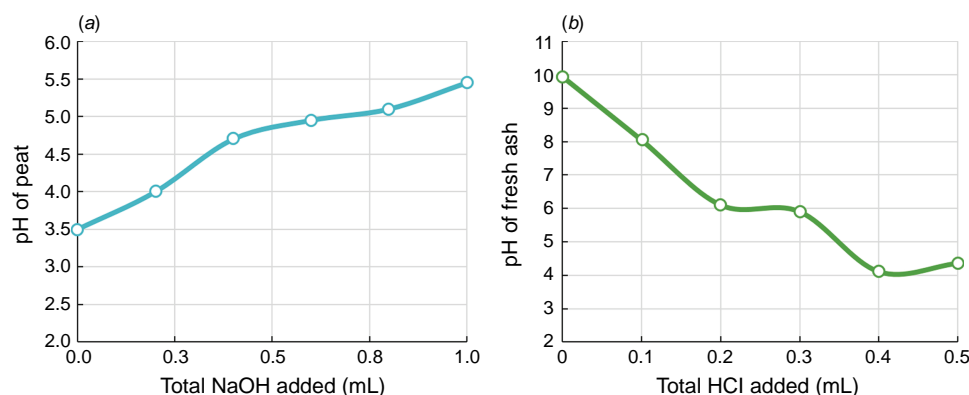
Fig. 5. (*a*) Titration with NaOH addition to peat shows increasing pH of the peat; (*b*) titration with HCl addition to fresh ash shows a decreasing pH. Note that slope to reach a pH of 6.0, rather than the end point, was used in the LBC calculations.

lower-elevation spots would be wetter owing to drainage and better connectivity with the water table and thus be less susceptible to smoldering. However, our analyses demonstrated that none of the environmental variables predicted the occurrence of smoldering throughout the area (Supplementary Table S1). Smoldered sampling points also did not occur more frequently at high elevations compared with non-smoldered sampling points (Supplementary Fig. S3). This is surprising given that many studies suggest that the severity and location of smoldering are related to microtopography, vegetation structure and surficial geology (Devito *et al.* 2012; Wilkinson *et al.* 2019). These environmental factors can influence water drainage and connectedness to the water table (Oosterwoud *et al.* 2017), in turn creating areas within the peatland that are vulnerable to smoldering (Hokanson *et al.* 2018). Soil profile scale characteristics such as peat depth (Wilkinson *et al.* 2020), peat bulk density (Mack *et al.* 2011), peat moisture (Davies *et al.* 2013; Prat-Guitart *et al.* 2016) and above-ground vegetation structure may also influence combustion and burn severity (Benscoter *et al.* 2011; Davies *et al.* 2016; Bourgeau-Chavez *et al.* 2020). The vegetation structure's influence on smoldering occurrence aligns with our qualitative field observations where peat smoldering sometimes occurred preferentially around tree roots, which may have encouraged localised rather than widespread smoldering (Turetsky and Wieder 2001). Davies *et al.* (2013) observed that soil consumption decreased with distance from trees, which could be related to moisture distribution (Rein *et al.* 2008); however, that does not explain our results or visual observations of all sample locations that had smoldered. This suggests that environmental differences may control smoldering occurrence at smaller spatial scales than at the landscape scale that we sampled.

We found that smoldered patches only occurred in a relatively small part (14%) of the study area (i.e., locations where peat had disappeared owing to smoldering), and the smoldered area differed between the sampling sections (Table 1). Conversely, Stoof *et al.* (2020) indicate that smoldering was widespread throughout much of the field site. Our present study focuses on the occurrence of smoldered patches, thus the differences between our findings and

Stoof *et al.* (2020) could be due to the scale of the area surveyed in each study. Our analysis indicates that the greatest amount of smoldering occurred in Section B. This aligns with qualitative observations during field work where we saw large continuous swaths of smoldered peat in that section, whereas smoldering occurrence did not appear to be as spatially continuous or widespread in Section C. This may be due to podzol deposits that occur under a thin (<25 cm) peat layer. The presence of a mineral soil layer may hamper the combustion process (Frandsen 1987) or influence spread of smoldering by serving as a natural fire break beneath the peat layers (Lin *et al.* 2021).

Given the complexity of interacting individual factors in peat smoldering combustion, the spatial variability in smoldering patterns at the Deurnsche Peel thus cannot be adequately explained without further research into these interacting roles of landscape and spatio-temporal factors. Because smoldering contributes to the loss of *Sphagnum*-forming peat layers (Davies *et al.* 2013), a better understanding of smoldering potential in a range of peatlands can improve proactive wildfire management and peatland restoration efforts.

Presence and alkalinity of ash

Ash was present at nearly all smoldered samplings locations, and only at two non-smoldered sampling locations (i.e. locations that only experienced burning of above-ground vegetation). This aligns with our hypothesis that ash will be more abundant in locations that smoldered compared with those that did not. Contrary to our initial expectations, the thickness of the ash layer at the time of field work was not related to the extent of smoldering. Although we observed that the ash layers at our field site were intact, it is possible that ash could have been redistributed via wind or water (Bodí *et al.* 2014; Pereira *et al.* 2015; Santín *et al.* 2015), or potentially incorporated into the soil column (Stoof *et al.* 2016). Variation in the thickness and spatial continuity of ash pockets, and possibility of redistribution, may explain the lack of ash samples present at non-smoldered sampling sites. Ash resistance to redistribution is related to its physical and

chemical properties, and by the influence of weather (i.e. precipitation and wind; Bodí *et al.* 2014), but these factors were not considered in our present study.

The pH values of aged ash samples were not as alkaline as originally hypothesised given the range of wildfire fresh ash pH values reported in the literature from peatland areas (pH ~8.5–11; Thomas and Wein 1990; Emmerton *et al.* 2020). The average pH values of aged ash were primarily neutral (Table 2); however, the pH values range from 4.3 to 8.6, representing both acidic and alkaline conditions. In contrast, the fresh ash produced from the smolder box was alkaline (pH ~9–10). This suggests that ash pH decreases during the process of ageing, likely owing to leaching losses or alkaline neutralisation (Plumlee *et al.* 2007). This finding aligns with other studies that have reported lower ash pH values (pH ~5–6) when sampling did not occur immediately after a wildfire (Costa *et al.* 2014; Santín *et al.* 2015). Smoldering hot-spot suppression efforts and rainfall events in the time leading up to field sampling also likely contributed to leaching losses, yet this is not reflected in the pH of the underlying peat layers (Table 3).

Fire suppression efforts, both at our field site and at other wildfire-impacted landscapes, may affect the quantity and properties of the ash produced (Bodí *et al.* 2014). Although it is most likely that the low aged-ash pH in our study is the result of the aging process, the duration and range of temperatures reached during the smoldering phases may also influence pH. Smoldering typically occurs at peak temperatures ranging from ~400 to 600°C (Rein *et al.* 2008), and studies have reported a higher pH of ash produced from soil and vegetation litter at such temperatures (i.e. pH ~9–12, Quintana *et al.* 2007; Úbeda *et al.* 2009). The range of peak temperatures from the smolder box experiment (Fig. 2*a*) and resulting fresh ash pH values (9.3–10.5) demonstrate that producing ash under varying temperatures may result in a different pH. Other studies have also noted ash pH differences produced by different temperatures (Úbeda *et al.* 2009; Balfour and Woods 2013), as well as a temperature thresholds that impact physical and chemical characteristics (Bodí *et al.* 2014). Stoof *et al.* (2020) reported that contractors did large-scale fire suppression in the middle portions of Section B; however, we did not sample in the locations within Section B that appeared to be disturbed. This suppression could have altered the burning patterns or caused the smoldering phase to end earlier than in other sections, as well as earlier than we observed from our study's smolder box experiments. Thus, it is conceivable that the fresh ash from the smolder box has an inherently higher pH than the pH of the wildfire-produced ash from our field site.

Potential impact of ash on soil pH

Our incubation experiments show that the aged ash collected during field sampling originally had the potential to increase the pH of the peat (i.e. from average field measured soil pH ~3.5–4.5) but likely became less alkaline during the time between the fire and field sampling. Based on the incubation experiments, a soil pH increase to 4.5 was achieved with 3 g of fresh ash addition. This corresponds to a 3 cm-thick layer of ash (or ash load of 163 t ha^{-1}). The ash thickness in the field at time of sampling ranged from 0.75 cm (ash load 41 t ha^{-1}) to a maximum of 6 cm (ash load 327 t ha^{-1}) at two sampling points, but the average thickness was ~1–3 cm. However, the thickness was highly variable in both depth and spatial continuity, even along the 1-m measurement transect at sampling points, and thus a 1-unit pH increase of peat pH would likely only occur in a few thicker ash patches throughout the area. As such, our results suggest that an ash load of ≥163 t ha^{-1} is needed to increase the pH of the soil at our field site by at least 1 pH unit. An addition of ash and increase in peat soil pH (up to pH ~6) may also negatively impact *Sphagnum* growth given that the species typically needs highly acidic and nutrient-poor conditions in order to out-compete vascular plants (van Breemen 1995).

We found that the topsoil in smoldered sampling locations did not have a high pH, which goes against our initial hypothesis that peat in smoldered locations would be alkaline owing to ash input. Rather, soil pH was higher in locations that had not smoldered compared with those that had. Our findings align with a study from Clara Bog, a peatland in Ireland, that reported that soil pH in a burned area became significantly lower than the soil pH of an unburned control area (pH 4.60 vs. 5.14, respectively) (Tomassen *et al.* 2003). Santín *et al.* (2015) also reports a higher pH of unburnt subsurface soils (pH 5.5) compared with burnt subsurface soils (pH 5.2) from the 2013 Balmoral wildfire in Australia. We therefore postulate that the time in which peat pH returns to pre-fire conditions after addition of ash is faster than reported for other soils and ecosystems (Strømgaard 1992; Costa *et al.* 2014; Alcañiz *et al.* 2016).

Our results suggest that the pH of the peat in this peatland ecosystem was well buffered from changes from alkaline ash input in the time period following the fire. This may also indicate that there was not enough ash present at the field site to change the peat pH, especially given the dilution and aging of the ash that occurred. In other studies, however, sensitivity to change in pH may be impacted by acidic strength and exchangeable acidity within the peat layers or porewater, as well as the degree of acidic dissociation given the addition of a base constituent and the amount of peat exchangeable complexes (McLaughlin and Webster 2010). The ability of ash to affect soil pH depends on the initial acidic strength of the peat, as well as the amount of ash added into the soil (Alauzis *et al.* 2004), either physically incorporated into the soil column or via leaching of ash extracts. Ash redistribution can potentially cause dilution of ash constituents (Clay *et al.* 2010; Ferrer *et al.* 2021). Ash has the ability wash into soil pores and be retained in porous media (Stoof *et al.* 2016); thus, infiltration of all ash

leachates into the soil column may not immediately occur, or may occur at different rates across the peatland landscape (Holden *et al.* 2013). As such, this demonstrates the complexity in smoldering patterns and ash production, and the resulting spatio-temporal impact of ash on peatlands.

Although our study focuses specifically on the amount ash needed to impact peat soil pH, future work should aim to include spatial heterogeneity of peat characteristics and burn severity when quantifying ash production and properties, and the spatio-temporal impacts on peatland soil pH dynamics. The incubation experiments in this study only accounted for a time period of two weeks. We recommend that future studies account for a longer time duration that encompasses more frequent monitoring of the soil pH, which could be until it recovers to pre-fire values. Given the probable base neutralising capacity of the peat, as well as the low pH of the aged ash (Table 2) and the pH of the soil (Table 3), this indicates a fairly quick recovery time of the peat pH to pre-fire conditions is likely at our field site. This has promising implications for post-fire recovery, and peatland protection and restoration at our field site (Stoof *et al.* 2020) as well as degraded peatlands globally (Grandgirard *et al.* 2002; Granath *et al.* 2016; Humpenöder *et al.* 2020).

Conclusion

This study presents results of pH measurements of soil and ash from a post-burn raised bog landscape in the Netherlands in order to determine if the input of wildfire-produced ash can cause an increase in peat soil pH. Ash sampled during fieldwork ∼2 months following the wildfire ('aged ash') had an average pH of ∼6, whereas fresh ash produced in an experimental smolder box was alkaline (pH ∼9–10). We also found that soil pH in both smoldered and non-smoldered sampling locations was acidic (pH ∼3–4), even in locations where ash was present at the time of sampling. Field measurements and observations of locations that smoldered suggest that smoldering was not widespread throughout the area, and instead was spatially variable in terms of size and extent.

Given that fresh ash had a high pH, and considering the results of the incubation and titration experiments, we do expect that ash addition to the peat likely caused a transient increase in soil pH immediately after the wildfire. However, alkaline components were likely quickly leached from the ash or neutralised by organic acids in the peat and porewater in the 2 months following the peatland wildfire; thus, it is reasonable to assume that there are no long-term changes to the soil pH due to ash input. This suggests that leaching and neutralisation of ash after a wildfire limit the duration of elevated soil pH, which potentially restricts soil microbial activity associated with liming effects and connected peatland carbon release after a wildfire.

Supplementary material

Supplementary material is available online.

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