The potential acidity of montane peatlands in the Greater Blue Mountains World Heritage Area: What might this mean for waterways downstream?

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Key points

- Montane peatlands in the Greater Blue Mountains World Heritage Area can experience sulfidisation.
- Field pH was mildly acidic (4.5 – 5.5 pH units) and mean chromium reducible sulfur was 0.03%.
- Potential acidity was highest in the transition zone between 40 – 60 cm (maximum of 0.07% sulfides).
- Potential oxidation of sulfides poses an environmental concern in the face of climatic regime changes.
- Droughts, bushfires and erosion may contribute to oxidation, releasing stored acidity downstream.

Abstract

Peatlands are naturally acidic environments due to the decomposition of organic material, with porewater and subsequent outflow typically ranging from 4 – 6 pH units. However, the potential acidity of peatlands can be increased by the presence of sulfides, particularly pyrite (FeS_2), which releases acidity when oxidised. There is the risk that if peat soils that contain appreciable sulfides were to become oxidised the buffering capacity may be overwhelmed, releasing acidity into downstream environments. This research investigated the potential acidity of a montane peatland in the Greater Blue Mountains World Heritage Area and possible risks posed to downstream ecosystems. Peat cores were examined at Mount Banks peatland, and this site was found to be mildly acidic (4.5 – 5.5 pH units), with mean chromium reducible sulfur values of 0.03% (in line with Australian trigger guidelines for acid sulfate soils). Sulfide formation places montane peatlands at risk of acidity generation in the event of landscape dehydration and oxidation. This is of particular concern as south-eastern Australia is subject to extreme climatic events, including droughts and bushfires. Acidity released downstream can alter metal bioavailability and significantly impact biotic communities (including vegetation, aquatic species, and microbial communities). Mount Banks peatland may not be strictly classified as containing acid sulfate soils however, the current landscape reflects sulfide retention. Whilst these conditions are not expected to be common in the Blue Mountains, this study highlights the importance of maintaining natural peatland hydrology and considering the potential acidity of peatlands in the face of changing climatic regimes.

Keywords

Peatlands, water chemistry, soil chemistry, sulfur, extreme events, acidity

Introduction

Peatlands are recognised to be naturally acidic environments due to the decomposition of organic material and release of organic acids associated with peat development (Boman et al., 2023). This organic acidity is generally localised within the peat material under saturated conditions and lowers the pH of porewater and any subsequent outflow from peatlands to values typically between pH 4 and 6 (Hope et al., 2012; Boman et al., 2023). Surface peat is rich in partially decomposed organic matter, including humic and fulvic acids (Shotyk, 1988), which naturally release protons under slightly toxic or neutral pH conditions. This acidity is common across peat soils and connected surface water worldwide (Yakovlev et al., 2021; Boman et al., 2023), across south-eastern Australia (Hope et al., 2012), and in the Blue Mountains region (Carroll et al., 2022). The production of acidity in peat systems can be buffered by inputs of alkalinity provided by groundwater or surface water supplies from the surrounding catchment (Shotyk, 1988).

Whilst organic acidity is typically dominant in peatlands, the presence of inorganic sulfur mineral phases (such as pyrite; FeS_2) can also influence the potential acidity of peat soils (Fitzpatrick, 2020; Boman et al., 2023). This is of interest as the oxidation of sulfides upon exposure to atmospheric conditions generates acidity, and the export of this acidity can have a deleterious impact on the surrounding environment (Pons, 1973; Sammut et al., 1995; Boman et al., 2023). The characteristics and implications of acidity release from peat soils that contain oxidised sulfides may be considered to behave as acid sulfate soils under specific conditions (Fitzpatrick, 2020). Acid sulfate soils refer to conditions whereby the exposure of sulfide minerals (such as pyrite) to atmospheric conditions results in the formation of acidity with a resultant pH decrease to below pH 4 (Pons, 1973; Sammut et al., 1995; Boman et al., 2023). However, despite the presence of sulfides being reported in peatland environments (such as Fitzpatrick, 2020; Dear et al., 2023), the definition of an organic acid sulfate soil in soil taxonomy is debated (Boman et al., 2023). The presence of sulfides in naturally acidic peatlands increases the potential acidity of these systems, which may exceed the buffering capacity of the organic substrate. There is the risk that if peat soils that contain appreciable sulfide levels were to become oxidised, the buffering capacity of the organic substrate may be overwhelmed, resulting in the release of acidity into downstream environments (Fitzpatrick, 2020; Dear et al., 2023).

Changing climatic conditions and altered hydrology significantly threaten Australian peatlands (Carroll et al., 2023). Altered climatic regimes have been shown to exacerbate the effects of acid sulfate landscapes (Pons, 1973; Åström et al., 2010; Mosley et al., 2022). Whilst previous studies investigating sulfur loads in peatlands have been dominated by studies on coastal landscapes (Fitzpatrick, 2020; Vithana et al., 2022; Boman et al., 2023; Andersson & Hansen, 2024), the occurrence of elevated sulfur loads has also been reported within freshwater peat and wetland systems (Hall et al., 2006; Smolders et al., 2006; Creeper et al., 2013). In the face of altered climatic regimes and extreme climatic events such as bushfires, droughts, and erosion, the risk of the oxidation of acid sulfate soils poses a concern (Åström et al., 2010). Climatic changes can also contribute to the oxidation of peat, which poses additional challenges when sulfides are present (Fitzpatrick, 2020). Therefore, further examination of the role of sulfides and their retention in peat soils is of interest. There is limited reporting on montane peat soils whereby soil development is impacted by sulfur loading. A detailed study of the link between potential acidity and the microbial community in the Blue Mountains was undertaken and is outlined in Carroll et al., (2025). This research will focus on the potential acidity of a montane peatland in the Greater Blue Mountains World Heritage Area and investigate the possible risks this stored acidity may pose to downstream ecosystems in the event of release.

Methodology

Mount Banks peatland (33°35'12.9"S 150°22'14.6"E) consists of a broad basin, headwater peatland covering 5.7 ha at 835 m above sea level (Figure 1). A detailed summary of the site is provided in Carroll et al., (2025). The site has a temperate climate, with mean temperatures ranging from 8.1 – 16.9°C and mean annual precipitation of 1411.4 mm (Bureau of Meteorology, 2023). Geology of the region reflects a basalt cap, overlying Permo-Triassic quartz sandstone and inter-bedded claystone of predominantly Narrabeen Group Hawkesbury Sandstone and Banks Wall sandstone (Pickett & Alder, 1997). Soil is classified as Organosols, containing greater than 40 cm of organic materials in the upper 80 cm with seasonal waterlogging along the drainage line and increasingly sandier, unconsolidated materials on the outer margins (Isbell et al., 2021), and the peat layers are underlain by basal clays (Carroll et al., 2025).

The site was divided into a lower downstream basin of shallow peat materials (H1 – H3) and an upper basin of deeper peat materials (H4 – H6) based on the depth of the peat interval (Figure 1; further outlined in Carroll et al., 2025). Peat cores were collected using a Russian D-section corer following the central drainage line. Cores were divided using peat texture with the loose, fibric layer (oxidised zone 0 – 20 cm) overlying dense sapric peat (40 – 60 cm transition zone) and the natural water table, overlying the basal peat layer (reduced zone 60 – 150 cm). The pH of field moist samples was measured using a calibrated TPS AQUA-Cond-pH meter. The D-section corer was thoroughly cleaned between samples with deionised water followed by ethanol to minimise contamination. Samples (~50 g per depth) were collected using sterilised stainless-steel spatulas, placed in sterile, plastic jars, and stored on ice in the field (for less than five hours) before being placed at -80°C.

Soil samples were analysed using standard methods for Acid Sulfate Soil (Sullivan et al., 2018). The analysis included exchangeable acidity (pH_{KCl}), acid extractable sulfate (including S_{HCl} and S_{KCl}; as mg/kg), mean potential acidity as chromium reducible sulfur (CRS; mg/kg), titratable actual acidity (TAA; moles of hydrogen per tonne (mol H^+/t)), retained acidity (RA; estimated using the Net Acid Soluble Sulfur (%S_{NAS}) method based on the difference between S_{HCl} and S_{KCl}), and net acidity (mol H^+/t; calculated as the sum of CRS, TAA, and RA values). RA was not calculated for samples where exchangeable acidity was greater than 4.5 pH units as per Sullivan et al., (2018). Soil organic carbon (LECO) was assessed following standard methods (Rayment & Lyons, 2011). Values below detection limits are indicated as half of the detection limit.

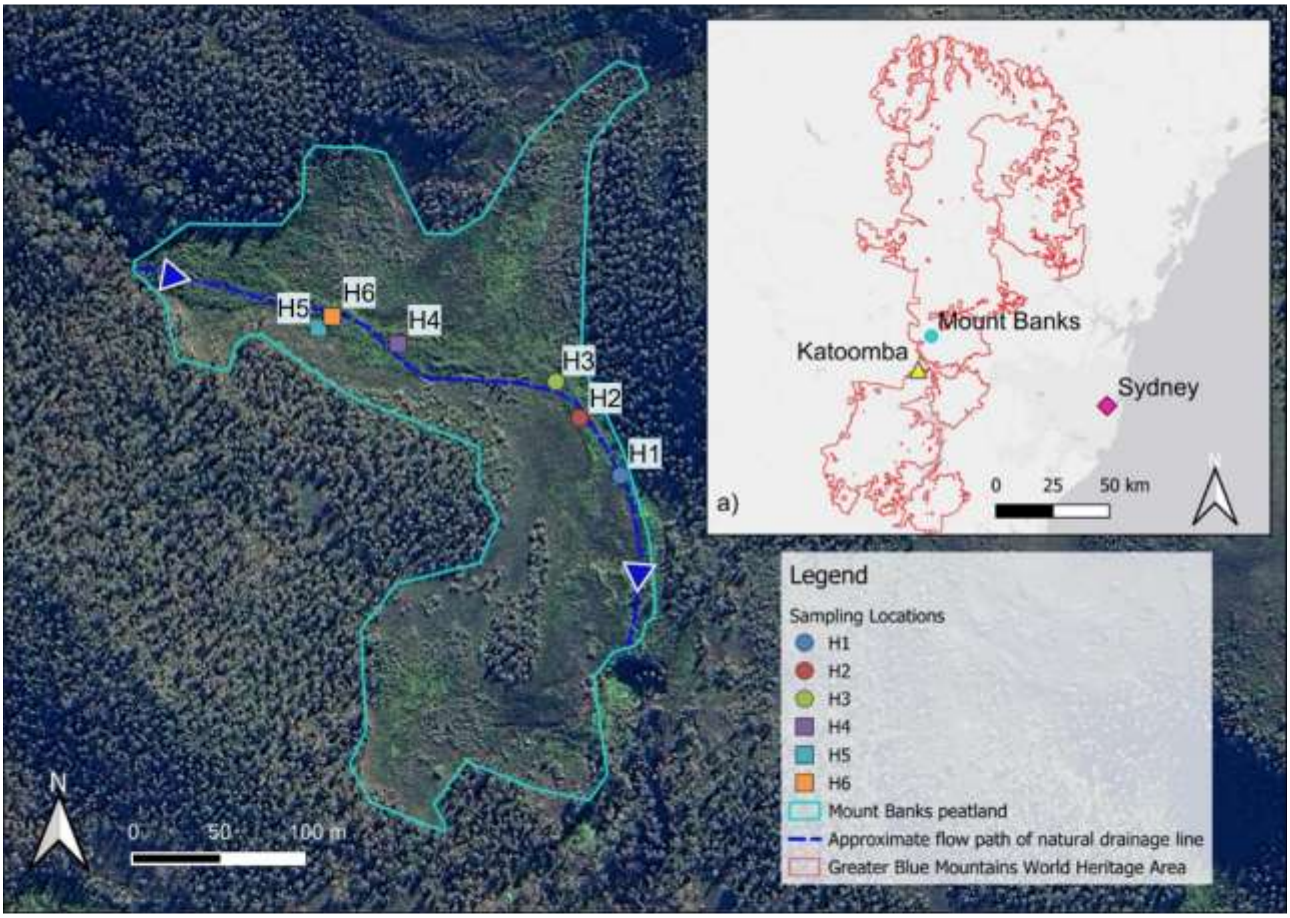

Figure 1 Mount Banks peatland (within the Greater Blue Mountains World Heritage Area (outlined in red), west of Sydney, New South Wales shown in a) and sampling locations (circles indicate lower basin and squares indicate upper basin sites). The approximate drainage line (dashed with arrows showing flow direction) are outlined. Satellite imagery source: QGIS v 3.24.3. Produced as part of Carroll et al., (2025)

Results

The Mount Banks peatland is comprised of three distinct layers: the surficial, oxidised peat layer (0 – 20 cm), which contained poorly decomposed organic materials; the transition zone at 40 – 60 cm where peat was saturated with moderately to well decomposed organic material present; followed by a sapric peat layer (depth of 70 cm at H3 to greater than 150 cm at H4). Below the sapric peat, a transition to the basement layer (excluding at H4, where the basement layer was not reached) occurred as basal clays. Mean total organic carbon was 14.7% (Table 1), which is in line with expectations of peat soils in Australia (between 12 – 18% based on Isbell et al., (2021)). Carbon content declined with depth in the lower basin (H1 – H3) and was consistent in the upper basin (H4 – H6). Field pH in the lower basin (at H3) ranged from 5.05 – 5.28 pH units, and the upper basin (at H6) ranged from 4.91 – 5.66 pH units (Figure 2). The exchangeable acidity (pH_{KCl}) had a mean of 4.38 in the upper basin and 4.95 in the lower basin (Table 1).

Soil acidity levels differed between the upper (H4 – H6) and the lower (H1 – H3) basin (Table 1). The mean potential acidity (CRS) for the Mount Banks site was 0.03%. There was spatial variability in stored acidity, with a mean of 0.02% CRS in the lower basin, and 0.04% CRS in the upper basin (Table 1). Net acidity (NA) was highest in the oxidised zone with the maximum value at H5 0 – 20 cm (344 mol H^+/t). Total actual acidity (TAA) was highest in all surface samples and decreased with depth. Mean TAA in the oxidised zone of the upper basin was 259 mol H^+/t and 200 mol H^+/t in the lower basin and is driven by the decomposition of organic matter. There was zero Retained Acidity (RA) in the lower basin samples (for the transition and reduced zones at H1 and H2, and all three zones at H3), as the pH_{KCl} was greater than 4.5 (as per Sullivan et al., 2018). The upper basin had a mean RA value of 423.51 mg/kg and was highest in the oxidised zone at H5 of the upper basin (862.2 mg/kg), however, maximum RA was recorded at 0 – 20 cm at H1 (1073.2 mg/kg).

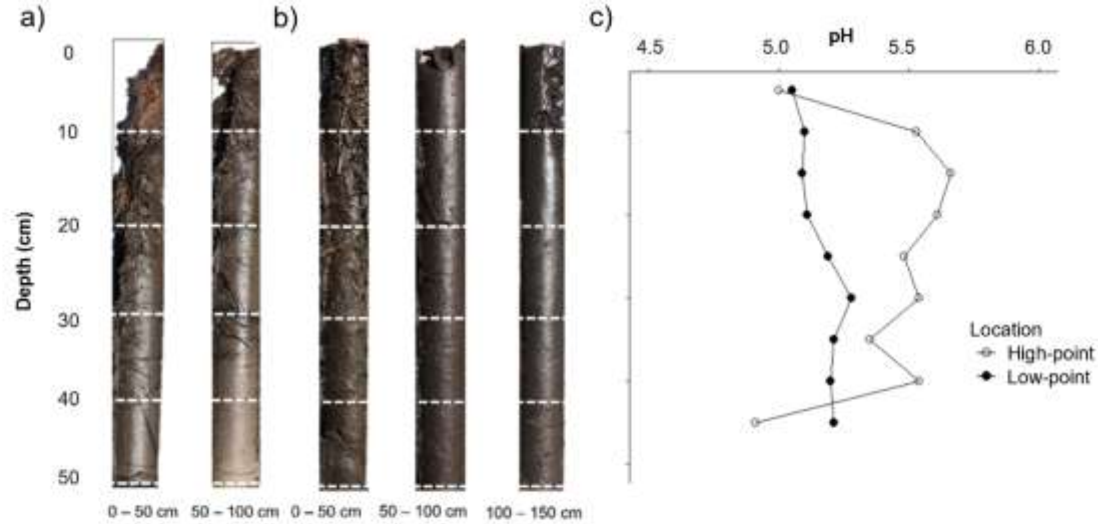

Figure 2 Peat cores from the Mount Banks lower basin (H3; a) and upper basin sites (H4; b) in October 2023. Depth from the surface is indicated as 0 – 50 cm, 50 – 100 cm, and 100 – 150 cm. Note that the black outlined rectangle symbolises the missing humic peat material that did not always adhere to the coring device, shown in a). Field pH from in situ samples is shown in c) for the lower basin (low-point; closed circles) from site H3 measured in June 2022, and upper basin (high-point; open circles) from site H6 derived from the mean for November 2021 and June 2022 sampling

Discussion

This research at Mount Banks peatland highlights the potential for sulfide imprinting to occur in freshwater, montane peat soils in south-eastern Australia, with CRS levels in line with recognised acid sulfate soils (Dear et al., 2023). However, the occurrence of sulfide retention in peat soils is not well documented or understood, and there is debate as to the classification of organic soils with sulfides present (Boman et al., 2023). The implications of the release of this stored acidity into downstream environments is also not well understood.

The potential acidity of Mount Banks peatland

Sulfide is suggested to be present in the profile at Mount Banks peatland, peaking in the transition zone (40 – 60 cm) and being retained in the reduced zone. Within Australia (for coastal and inland areas), the trigger guideline for acid sulfate soils for sands, loamy sands, and peaty soils in Australia is 0.03% sulfur (for 1 – 1000 t of material) (Dear et al., 2023). Based on the acid sulfate soils trigger values, the Murray Darling Basin Authority (2010) derived net acidity threshold risk ratings, which include low (0.03% sulfur), moderate (<0.1% sulfur), and high net acidity risk (≥ 0.1% sulfur). All samples from Mount Banks peatland had a net acidity threshold risk rating of low to moderate, excluding at depth in the lower basin (60 – 150 cm) and at the surface in the upper basin (0 – 20 cm). This highlights that whilst peat soils, such as those observed at Mount Banks, may not meet the definition of an acid sulfate soil, the potential for oxidation and release of acidity remains a concern and this highlights the need for detailed acid sulfate soils assessment to better understand this occurrence on montane peat systems.

The differences in CRS, TAA, and RA values between the upper (H4 – H6) and lower (H1 – H3) basin cores indicated sulfide formation and retention in the upper basin peats. Observed CRS and NA values are not dissimilar to surface soils from coastal peatlands in Australia (Grealish et al., 2014; Fitzpatrick, 2020) but did not show the same levels of acidity at depth when compared to Australian and international examples of coastal peatlands and acid sulfate soils (Vithana et al., 2022; Nyman et al., 2023). The detection of sulfidic materials within freshwater peat and wetland systems has previously been observed (Hall et al., 2006; Smolders et al., 2006; Creeper et al., 2013). Peat soils at Mount Banks further highlight that a montane, freshwater peat system with sulfidic materials risks becoming a hyposulfidic organic soil due to increasing climatic pressures (drought, bushfire, and erosion).

Table 1 Mount Banks peatland soil chemistry results (mean for lower basin (H1 – H3) and upper basin sites (H4 – H6)) for the oxidised zone (0 – 20 cm), transition zone (40 – 60 cm), and reduced zone (60 – 150 cm). Retained acidity (RA; S_{NAS} mg/kg) was not calculated when exchangeable acidity was greater than 4.5 pH units as per Sullivan et al., (2018), indicated as -. CRS refers to chromium reducible sulfur (potential acidity; %), TAA refers to titratable actual acidity (mol H^+/t), NA refers to net acidity (mol H^+/t), and TOC refers to total organic carbon (%). Standard error (±) of the mean is shown. Extract from Carroll et al., (2025)

Site	Depth (cm)	CRS (%)	pH_{KCl}	TAA (mol H^+/t)	RA (S_{NAS} mg/kg)	NA (mol H^+/t)	TOC (%)
Lower Basin	0-20	0.03 ± 0.01	4.53 ± 0.11	200.00 ± 27.43	908.10 ± 165.10	247.33 ± 37.11	16.77 ± 1.03
	40-60	0.03 ± 0.01	4.97 ± 0.05	82.67 ± 4.54	-	98.00 ± 7.44	9.44 ± 1.16
	60-150	0.02 ± 0.01	5.36 ± 0.02	32.67 ± 5.89	-	39.00 ± 8.95	2.08 ± 0.76
Upper Basin	0-20	0.02 ± 0.002	4.33 ± 0.09	258.67 ± 26.45	574.00 ± 173.41	301.33 ± 33.05	21.50 ± 0.65
	40-60	0.05 ± 0.01	4.39 ± 0.04	219.33 ± 25.18	399.07 ± 78.58	267.33 ± 33.71	18.87 ± 2.09
	60-150	0.04 ± 0.004	4.41 ± 0.05	99.00 ± 44.37	297.47 ± 61.85	135.67 ± 47.42	19.60 ± 0.91

The Blue Mountains is not typically recognised as having acid sulfate soils (NSW DPE, 1998), therefore, it could be assumed that acid sulfate soil conditions are not common in peatlands in this region. In addition, if conditions were favourable, sulfides would take extended time periods to build up, demonstrated at Mount Banks peatland as the peak sulfide value occurs in the transition zone at 40 – 60 cm. The source of sulfides at this site is expected to be naturally occurring due to the chemistry of the local geology and groundwater. The Blue Mountains montane peatlands are broadly characterised as freshwater systems with groundwater estimated to contribute an average of 51% of water (ranging from 28 – 82%) (Cowley et al., 2019). Mount Banks peatland occurs at the uppermost topography of the catchment, just below the peak of Mount Banks (approximately 1,062 m asl). Therefore, groundwater contributions are expected to be low with inputs from precipitation and surface runoff. Groundwater from the underlying Hawkesbury sandstone is high in iron and sulfate, ranging from 0.01 – 13.6 mg/L for iron and 1.1 – 21.2 mg/L for sulfate in the Kulnura–Mangrove Mountain region of NSW (Cendón et al., 2014), a mean of 9.0 – 27.3 mg/L for iron and 3 – 41 mg/L for sulfate at sites located in the Upper Nepean and Western Sydney region (McLean & Rose, 2009), to 0.06 – 0.57 mg/L of iron and <1.0 – 2.7 mg/L for sulfate in swamps of the Newnes Plateau region of the Greater Blue Mountains World Heritage Area (Centennial Coal, 2013). The source of the sulfides contributing to acidity is predicted to be natural and not an artefact of human disturbance that has impacted groundwater. However, human disturbance and extreme climatic events may play a role in exacerbating acidity release from peat soils.

Implications for downstream environments

The oxidation of sulfide minerals (such as observed in acid sulfate soils) can result in high acidity and this can lead to potential ecological implications, including altered bioavailability and negative impacts on biotic species (Pons, 1973; Sammut et al., 1995; Fitzpatrick, 2020; Boman et al., 2023). The harsh conditions experienced in acid sulfate soils contribute to a distinct microbial community that utilises sulfur (Johnson et al., 2023; Carroll et al., 2025), and as the decomposition of organic material by microbes is crucial for peat formation, this may have implications for these ecosystems. More acidic pH values also influence the bioavailability of metals, for example aluminium and heavy metals, and may increase the mobility of these to toxic levels for aquatic biota (Grealish et al., 2013; Dear et al., 2023). For example, elevated metal concentrations can contribute to fish kills and loss of aquatic and riparian vegetation (Sammut et al., 1995). This is a concern within the Greater Blue Mountains World Heritage Area, as water quality in this region is naturally acidic and dilute, with low buffering capacity (Carroll et al., 2022). Montane peat deposits predominantly form in catchment headwaters in this region. Therefore, changes to peatland outflows may play an important role in influencing pH buffering for biogeochemical processes downstream (Silvester, 2009). The timeframe and scale of peat oxidation is also of concern. For example, in 2019/2020 severe wildfires following prolonged drought resulted in a significant loss of peat from the Greater Blue Mountains region within a rapid timeframe (Fryirs et al., 2021; Carroll et al., 2023). If peat oxidation were to occur rapidly within a landscape exhibiting sulfide retention, this may lead to an acidic pulse being released downstream.

Future monitoring and management of montane peatlands

In south-eastern Australia, climatic changes are predicted to lead to an increase in the severity and frequency of extreme climatic events, such as prolonged droughts, more intense and frequent bushfires, and more intense rainfall events contributing to flooding and erosion (CSIRO & BOM, 2022). These conditions contribute to the oxidation or desiccation of peat, which can increase risk of burning during fire events and loss due to wind or intense rainfall, and in turn can lead to the lowering of the water table, loss of peat-forming vegetation communities, and shrub encroachment (Clarke et al., 2015). Reducing the risk of oxidation of peatlands and the maintenance of frequent, saturated conditions is crucial to allow for accumulation of organic material under anaerobic conditions and to minimise fire and erosion risks that can occur if peat becomes severely desiccated during drought conditions. The importance of water in the landscape has been recognised in peatlands subject to land use change worldwide (Wilkinson et al., 2023). Preservation of natural peat hydrology is essential, and rewatering strategies assist to promote the maintenance of water within these systems. Retention structures such as coir logs or haybales seek to maintain natural hydrology, by serving as sediment traps and allowing for the capture and spread of surface water to rewet desiccated peat (Freidman & Fryirs, 2015).

Whilst sulfur derived acidity may not be widespread in montane peatlands of the Greater Blue Mountains or south-eastern Australia, it is important to consider this when assessing risks posed to downstream waterways due to changing climatic regimes and the implications of peat desiccation. This study demonstrates the importance of incorporating assessment of sulfides and potential acidity when analysing peatland condition. Field pH is suggested as the initial test to examine peatland acidity. The use of hydrogen peroxide (as per IUSS Working Group WRB, 2022) is recommended as a follow-up step in order to conduct a preliminary investigation to determine the potential acidity of peat soils. If pH falls below or close to 2.5 pH units following 24 hours in 6% hydrogen peroxide, then it is recommended that a chip tray incubation experiment is conducted to provide a greater understanding of pH changes that could occur naturally over time in a real-world system. This would entail monitoring changes to pH in field moist samples placed in a chip tray for a minimum of nine up to 19 weeks (in line with Creeper et al., (2013), Sullivan et al., (2018) and Boman et al., (2023)). If incubation pH falls to below 4 pH units, is between 4.0 – 4.5 pH units or drops by greater than 0.5 pH units (Boman et al., 2023) at the end of the incubation period, then detailed analysis of acid sulfate soil properties, including CRS (Sullivan et al., 2018) is recommended to provide absolute determination of the upper limit of peat potential acidity and acid sulfate soil classification. This approach would assist in identifying target sites for further analysis and increase understanding of the role of sulfur in peatland systems.

Conclusions

Peatlands are naturally acidic environments. Whilst peatlands in the Greater Blue Mountains World Heritage Area are not typically associated with acid sulfate soil conditions, there is the potential for the formation of sulfides to occur within peat deposits. Mount Banks peatland is a montane freshwater system that exhibits a significant store of acidity in the form of sulfides within the peat, predominantly within the transition and reduced zones. The dehydration of these environments due to alterations to the hydrologic regime may result in the oxidation of sulfides. This places this landscape at increasing risk of enhancing acidity under oxidising conditions, which may result in significant impacts on the surrounding environment if exported. This research highlights an example of a subtle change to peat conditions that may pose a significant risk to downstream environments. Findings from Mount Banks peatland also reinforce the complexity of acidic peat systems and the difficulties in differentiating between organic derived acidity and sulfide retention in these landscapes. In the face of predicted extreme climatic conditions and widespread human impacts, the risk of peat oxidation highlights the importance of further considering the potential acidity of montane peatlands.

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