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Comparing levoglucosan and mannosan ratios in sediments and corresponding aerosols from recent Australian fires

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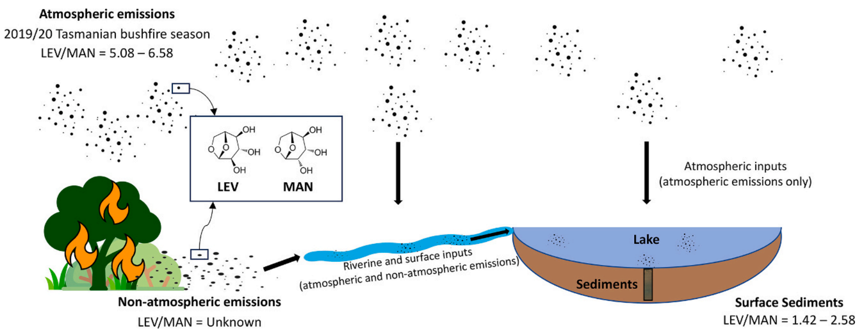
HIGHLIGHTS

- There are many uncertainties around the application of fire sugars in sediments.
- Fire sugar fluxes in freshwater sediments represent past fire events.
- Local and regional fires contribute to flux more strongly than distant fires.
- The isomer ratio (LEV/MAN) is lower in sediments than in corresponding aerosols.
- L/M ratios in sediments may not be indicative of the type of vegetation burnt.

GRAPHICAL ABSTRACT



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ABSTRACT

The monosaccharide anhydrides levoglucosan, mannosan, and galactosan are known as 'fire sugars' as they are powerful proxies used to trace fire events. Despite their increasing use, their application is not completely understood, especially in the context of tracing past fire events using sediment samples. There are many uncertainties about fire sugar formation, partitioning, transport, complexation, and stability along all stages of the source-to-sink pathway. While these uncertainties exist, the efficacy of fire sugars as fire tracers remains limited. This study compared high-resolution fire sugar fluxes in freshwater sediment cores to known fire records in Tasmania, Australia. Past fire events correlated with fire sugar flux increases down-core, with the magnitude of the flux inversely proportional to the distance of the fires from the study site. For the first time, fire sugar ratios

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(levoglucosan/mannosan, L/M) in aerosols were compared with those in sediments from the same time-period. The L/M ratio in surface sediments (1.42–2.58) were significantly lower than in corresponding aerosols (5.08–15.62). We propose two hypotheses that may explain the lower average L/M of sediments. Firstly, the degradation rate of levoglucosan is higher than mannosan in the water column, sediment-water interface, and/or sediment. Secondly, the L/M ratio of non-atmospheric emissions during fires may be lower than that of atmospheric emissions from the same fire. Due to the uncertainties about transport partitioning (atmospheric versus non-atmospheric emissions) and fire sugar degradation along all stages of the source-to-sink pathway, we advise caution when inferring vegetation type (e.g. softwood, hardwood, or grasses) based purely on fire sugar ratios in sediments (e.g. L/M ratio). Future investigations are required to increase the efficacy of fire sugars as a complimentary, or standalone, fire tracer in sediments.

1. Introduction

Fire is an extremely important global phenomenon that is not yet fully understood (Bowman et al., 2009). Fire impacts many aspects of vegetation, climate, and human life, all of which are closely interlinked. The full extent of its impacts have been explored and listed elsewhere, but include economic, climate, carbon cycling, primary production, ecosystem, vegetation, habitat, and health impacts (Bowman et al., 2009; Bowman et al., 2011)(and references therein). To better predict how fire regimes may be changing in the future due to climate change, we need to fully understand historical fire events at a geological scale. Fire records in sediments can be studied alongside climate and vegetation reconstructions to better understand the intricate links between them.

Fire tracing in sediments has traditionally been done using charcoal quantification (Whitlock and Larsen, 2001). Charcoal is formed by the incomplete combustion of organic material between 280 and 500 °C, and is resistant to oxidation and microbial activity, meaning it can remain in sediments for long time periods (Herring, 1985; Braadbaart and Poole, 2008; Mooney and Tinner, 2011). Typically, charcoal is categorised into two broad classes, 'microscopic' charcoal (pieces <200 μm in diameter) and 'macroscopic' charcoal (>200 μm in diameter). Microscopic charcoal has the potential to travel long distances (20–100 km) from the fire plume and thus represents regional fire history, whereas macroscopic charcoal is more likely to remain within 1 km of the burnt area and thus represents local fires (Clark, 1988; Whitlock and Larsen, 2001; Conedera et al., 2009; Mooney and Tinner, 2011). A drawback of charcoal quantification is that it may miss signals from low intensity (<280 °C) fires, such as controlled burns.

Levoglucosan, mannosan, and galactosan (also called fire sugars) are alternate, and complimentary, fire tracers. Fire sugars are produced during the pyrolysis of cellulose (producing levoglucosan, 1,6-anhydro-β-ᴅ-glucopyranose) and hemicellulose (producing mannosan, 1,6-anhydro-β-D-mannopyranose and galactosan, 1,6-anhydro-β-ᴅ-galactopyranose) between 150 and 350 °C, meaning that they are produced during wild fires (Simoneit et al., 1999; Kuo et al., 2008). Fire sugars are predominantly produced by biomass burning, however, lignite and low-grade coal burning, food cooking, fireworks, and the burning of municipal/industrial waste can also produce fire sugars, meaning that it is important to consider these sources in certain study cases or locations (Fabbri et al., 2009; Bi et al., 2010; Cheng et al., 2014; Wu et al., 2021; Marynowski and Simoneit, 2022). Levoglucosan and microscopic charcoal are both suggested to be regional/distant fire proxies, meaning that their concentrations should correlate throughout a sedimentary record (Simoneit et al., 1999). However, fire sugar concentrations, specifically levoglucosan concentrations, only sometimes correlate with charcoal counts in past sediment studies. Levoglucosan concentrations have correlated strongly with microscopic charcoal counts in sediment cores from the Amazon basin (Elias et al., 2001) and Lake Allom, Brisbane, Australia (Schreuder et al., 2019), and partially with macroscopic charcoal in the Maya Lowlands in Guatemala (Schüpbach et al., 2015). Whereas almost no correlation was found between levoglucosan and microscopic charcoal in sediment cores from New Zealand (Sikes et al., 2013) and the Mediterranean (Norström et al., 2021).

The ratio between the fire sugars (e.g., levoglucosan/mannosan, L/M) can provide information on the type of biomass that burnt (Engling et al., 2006; Bhattarai et al., 2019). This is due to the different proportion of cellulose and hemicellulose in different biomass types. The burning of hardwoods were reported to have L/M ratios between 10 and 30, whereas softwoods were reported to have L/M ratios between 2.5 and 10 (Fabbri et al., 2009; Xu et al., 2019; Marynowski and Simoneit, 2022). However, this is strongly species dependent and there are many exceptions. Furthermore, combustion conditions (smouldering vs flaming), or part burnt (such as roots, leaves, or needles) can also affect the L/M ratio (Mkoma et al., 2013; Sullivan et al., 2014; Vicente and Alves, 2018). Knowing the type of biomass burnt provides vital information that can aid past fire and vegetation reconstructions.

The application of fire sugars as fire tracers is the subject of many studies in recent decades, typically focussing on aerosol samples (Bhattarai et al., 2019; Marynowski and Simoneit, 2022). The analysis and interpretation of fire sugars in freshwater sediments is less common. Existing freshwater sediment studies focus on identifying climate and vegetation shifts based on fire sugar concentration variations and fire sugar isomer ratios (Sikes et al., 2013; Schüpbach et al., 2015; Kirchgeorg et al., 2014; Battistel et al., 2016; Schreuder et al., 2019; Dietze et al., 2020b; Norström et al., 2021; Callegaro et al., 2018; Argiriadis et al., 2018). Fire sugar data are often accompanied by other climate or vegetation proxies like drought/aridity index, pollen records, or charcoal records to help make accurate reconstructions. These studies tend to focus on longer time scales (thousands of years) compared to that of this study (hundreds of years). Despite the dozen or so studies analysing fire sugars in freshwater sediments, there remain many uncertainties about the formation, transport, and stability of fire sugars measured in such samples, limiting the accuracy of historical reconstructions and the resulting environmental interpretations (Suciu et al., 2019). The major uncertainties include specifics about fire sugar production and partitioning during pyrolysis, degradation along the source-to-sink pathway, and the applicability of fire sugar ratios (e.g., L/M) in sediments.

The specifics about fire sugar production during pyrolysis are not completely understood (Suciu et al., 2019). While the majority of fire sugar production occurs around 300 °C and is emitted as volatile compounds, there is a secondary, higher temperature production around 600 °C due to the depolymerization of polymeric products (Shafizadeh and Sekiguchi, 1984; Schkolnik and Rudich, 2006; Kawamoto et al., 2003). This secondary source may interact with aromatic substances, stabilizing fire sugars in the char (Hosoya et al., 2006). During fires, fire sugars are predominantly emitted during smouldering combustion but can also be emitted during other stages of pyrolysis/combustion (Suciu et al., 2019). This means that fire sugars may be released in the gas phase, particle phase, or as charcoal. However, the partitioning between these phases is unknown, resulting in a large knowledge gap. Further study needs to be undertaken to gain an understanding about the fraction of fire sugars emitted via the atmosphere (aerosol emissions) versus the land (henceforth referred to as 'non-atmospheric emissions'). Non-atmospheric emissions are fire sugars adsorbed to macroparticles or residual charcoal in the soil that can be translocated through the environment (Suciu et al., 2019).

Degradation along the source-to-sink pathway, particularly in the water column, water-sediment interface, and sediment, are not well understood. Fire sugar degradation is well characterised in the atmosphere, with lifetimes dependent on physical (dry and wet deposition), chemical (homogeneous and heterogeneous oxidation), and indirect (gas-particles partitioning, hydrophobic/hydrophilic conversion, particle growth, and cloud condensation nuclei) processes/factors (Petters et al., 2006; Hennigan et al., 2010; Hoffmann et al., 2010; Vakkari et al., 2014; Suciu et al., 2019). Depending on these factors, levoglucosan remains preserved in the atmosphere at a scale of minutes to days. The degradation rates (and influencing conditions) in the water column, water-sediment interface, and sediment are less understood. There are only a few studies measuring fire sugar degradation in water, and most of these are focussed on the dissolved form of the fire sugars. Dissolved levoglucosan was found to have a half-life of 3–4 days in river water (Norwood et al., 2013), and the degradation of the three isomers in wastewater samples after 28 days was 85 % (± 6.6 %), 86 % (± 8.5 %) and 44 % (± 17.9 %) for levoglucosan, mannosan, and galactosan, respectively (Kirchgeorg, 2015). Both studies identified a lag time between the beginning of the test and the start of biodegradation, likely related to the complex and slow assimilation and metabolization by fungi or yeast (Kitamura et al., 1991; Nakahara et al., 1994; Xie et al., 2006). The dissolved form of the fire sugars may degrade more readily than particle-bound fire sugars like that which may exist in the environment after biomass burning. Schreuder et al. (2018) found that levoglucosan did not substantially degrade in the marine water column, potentially due to adsorption to biogenic particles, which protected it from biodegradation. Similarly, the identification of fire sugars (specifically levoglucosan) in sediments over long time periods, such as 430,000 years in North-Eastern Siberia (Dietze et al., 2020b) and 130,000 years in South-Eastern Australia (Lopes dos Santos et al., 2013), shows that, under certain conditions, they can be preserved. Better understanding of the degradation of fire sugars at the sediment-water interface and under different sedimentary conditions (e.g., anoxic versus oxic, or varying sedimentation rates) requires further study.

The applicability of fire sugar ratios in sediments is also not well understood. Due to the uncertainties about fire sugar production and partitioning during pyrolysis, their transport into lakes/lagoons, and their stability at all stages of their source-to-sink pathway, the ratios between the isomers (e.g., L/M) in sediments may not accurately reflect the type of biomass burnt. It is possible that each isomer is affected differently along the source-to-sink pathway, meaning that the ratios identified in sediments may not be comparable to the ratios identified in aerosol and source burning studies. This would affect vegetation reconstructions.

To address these knowledge gaps, this study:

1) Compares a high-resolution sedimentary record of fire sugar fluxes to known local, regional, and distant fire history to better understand fire sugar sources.
2) Compares the fire sugar ratios (L/M) in sediment samples to the ratios in corresponding aerosol samples collected approximately 100 km away and showing the same fire period (2018/19 bushfire season in Tasmania, Australia), to identify if fire sugar ratios in sediments are comparable to those in aerosols, and are therefore representative of the type of biomass burnt.

2. Methods

2.1. Sediments

2.1.1. Study site

Little Pine Lagoon (LPL) and Penstock Lagoon were both created as water storage reservoirs for use within the hydroelectric power scheme in Tasmania. These lagoons are 17 km apart, although reside in different catchments. LPL was created in 1954 by flooding several natural lagoons fed by the Little Pine River (Hydro 1999). Penstock Lagoon was created as an artificial water storage in 1916 (Hydro, 1999). Prior to damming, it is unknown how often the regions were submerged underwater. As dammed reservoirs, these sites have higher sedimentation rates than natural lakes or lagoons (Kondolf et al., 2014; Stevens et al., 2024), thus providing better resolution for assessing recent sedimentary changes.

These lagoons are situated in the Central Highlands of Tasmania, Australia. This area has experienced many fires at local, regional, and national scales in the past two centuries. Furthermore, many of the fires occurring in the past century have been well documented, allowing for the comparison between fire records and fire sugar records. For example, major fires occurred in the 2018/19 summer period in Tasmania. Between December 2018 and February 2019, 210,311 ha (approximately 2.9 % of land area) burnt across Tasmania, including 95,000 ha of Tasmanian Wilderness World Heritage Area (Keating, 2021). Four major fire complexes were responsible for 184,008 ha of area burnt (87 % of total area burnt). These four complexes are outlined in Fig. 1 and detailed in Table S1. The most common vegetation burnt includes buttongrass moorland, wet eucalyptus forest, and dry eucalyptus forest (Table S1).

Buttongrass moorland is typically dominated by ‘buttongrass’, *Gymnoschoenus sphaerocephalus*, with accompaniment from other sedge (Cyperaceae family), cord rushes (Restionaceae family), herbs, or shrub species (Jarman, 1988). Wet eucalypt forests are dominated by Eucalypt species such as *Eucalyptus delegatensis*, *Eucalyptus nitida*, and *Eucalyptus obliqua*, with various different understoreys including rainforest, broadleaf shrubs, or *Leptospermum* (Kitchener, 2013). Dry eucalypt forests are also dominated by eucalypt species (commonly *Eucalyptus coccifera, Eucalyptus delegatensis*, *Eucalyptus obliqua*, and *Eucalyptus amygdalina*), however the understorey is made up primarily of dry shrubs, heath, or grasses (Kitchener, 2013).

2.1.2. Sample collection

In May 2021, two sediment cores were collected from the Central Highlands of Tasmania, Australia. One 24 cm sediment core was taken from the centre of Little Pine Lagoon (42°00′9″ S, 146°35′59″ E) and one 32 cm sediment core was taken from the centre of the southern end of Penstock Lagoon (42°05′62” S, 140°46′11″ E) (Fig. 1). The cores were collected in polycarbonate tubes using a Uwitec gravity corer. Care was taken when coring to ensure straight, undisturbed cores were collected. The Little Pine Lagoon core was sectioned at 0.5 cm intervals in the top 10 cm and 1.0 cm intervals for the remainder (36 samples total). The Penstock Lagoon core was sectioned at 0.5 cm intervals in the top 5 cm, and 1.0 cm for the remainder (34 samples total). All samples were stored in a freezer at −18 °C, before being freeze dried and then ground using a Retsch mixer mill 200 (25/s for 60 s).

2.1.3. ^{210}Pb dating

The two cores were dated at the Australian Nuclear Science and Technology Organisation (ANSTO) by ^{210}Pb dating, following standard methods for alpha spectrometry described by Appleby (2002). All samples were digested on a hot plate according to ANSTO Method I-3331 (Lead-210 dating sample preparation). Each sample was further prepared using Method I-3329 (Polonium Chemical Isolation) and I-3330 (Radium Chemical Isolation). Polonium fractions were autodeposited onto silver disks, radium fractions were co-precipitated with $BaSO_4$ and collected on fine resolution filter papers ready for spectroscopy analyses. The filter samples containing ^{133}Ba and ^{226}Ra were first analysed by gamma ray spectroscopy to measure ^{133}Ba activities and determine the ^{226}Ra recoveries. Finally, each prepared sample was analysed for ^{210}Po and ^{226}Ra activities using alpha particle spectroscopy. ^{210}Po is the granddaughter of ^{210}Pb and is in secular equilibrium with ^{210}Pb, allowing the activity of total ^{210}Pb to be determined. ^{226}Ra is the grandparent of ^{210}Pb which can be used as the proxy of supported ^{210}Pb. Unsupported ^{210}Pb activity was calculated by subtracting the supported from the total ^{210}Pb activity for each sample. Using the determined unsupported ^{210}Pb activities, the constant rate of supply (CRS) model,

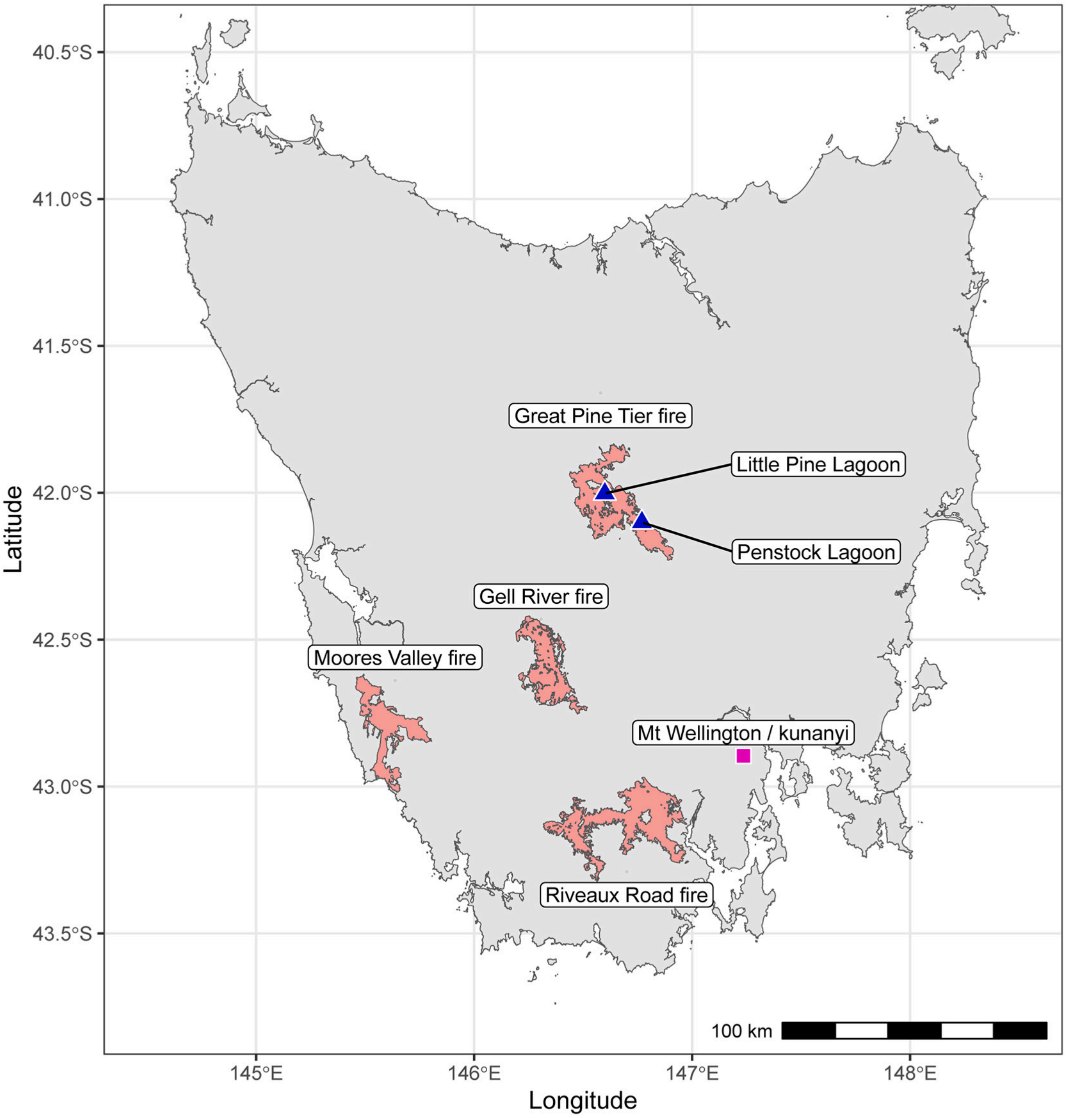

Fig. 1. Map of Tasmania, Australia. Blue triangles = sediment core sampling locations. Magenta square = aerosol sampler location. Red shaded areas represent the four major fires of the 2018/19 summer bushfire season in Tasmania.

which assumes a constant atmospheric flux of ^{210}Pb and variable influx rate of sediments, was applied (Appleby and Oldfield, 1978). The CRS model was validated using an independent age marker (fallout radionuclides).

2.1.4. Fallout radionuclides

Fallout radionuclides were used as an independent age marker to support the ^{210}Pb derived ages and the use of the CRS model (Smith, 2001; Appleby, 2002). ^{239}Pu, ^{240}Pu, ^{241}Pu, and ^{236}U were measured in 30 samples (15 from each core). Sample preparation was based on previously published methodology (Child et al., 2008). In short, approximately 0.75 g of each sample was weighed out and calcined at 800 °C for 8 h to destroy organics. ^{233}U and ^{242}Pu tracers were added to samples before drying and subsequent digestion by aqua regia and HNO_3 additions. Samples were dried down, dissolved in 2 M HNO_3, and pumped through stacked TEVA/UTEVA ion exchange columns for purification, resulting in separate uranium and plutonium fractions. These fractions were then separately co-precipitated with iron hydroxide, dried, and calcined to iron oxide for accelerator mass spectrometry (AMS) analysis. AMS analysis was performed using the Vega AMS system at ANSTO, using methods described by Hotchkis et al. (2019). The plutonium and uranium isotopes were measured relative to the respective ^{242}Pu and ^{233}U tracers in each of the Pu and U sample sets. From these measurements the isotope concentrations and isotopic ratios were derived.

2.1.5. Fire sugar extraction and quantification from sediment

Details about chemicals and standards, extraction method, instrumental method, and analytical performance validation can be found in Stevens et al. (2023). In short, 1.0 mL of de-ionised water (DIW) was added to 0.05 g of sediment before sonication for 60 s at 70 % amplitude using an ultrasound probe (Branson 450 Digital Sonifier). Samples were centrifuged (8 min at 4400 rpm) and filtered through syringe filters (0.22 μm polyethersulfone membrane) into 2 mL polypropylene autosampler vials. Internal standard (carbon-13-labelled levoglucosan) was added before analysis by suppressed ion chromatography with electrospray – triple-stage quadrupole tandem mass spectrometry (IC-TSQ-MS).

A Thermo Scientific Dionex ICS-5000+ Reagent-Free IC system coupled to a Thermo Scientific TSQ Quantiva triple-stage quadrupole mass spectrometer in heated-electrospray ionisation mode were used for the quantification. After sample treatment, 50 μL of sample were injected via an AS-AP autosampler into a Dionex Amino-Trap column (10 μm, 2 × 50 mm) coupled with a CarboPac PA-1 analytical column (10 μm, 2 × 250 mm). The fire sugars separation was performed in 8 min at 30 °C using a KOH eluent in gradient mode, at a flow rate of 0.250 mL/min. Before entering the mass spectrometer, 0.5 mM of lithium chloride in methanol solution was added using a second auxiliary pump at a flow rate of 0.02 mL/min into the IC eluent stream via a mixing tee. Detection of fire sugars was achieved in positive electrospray ionisation and selected reaction monitoring acquisition mode. Samples were measured in singlicate. The method limit of detection was 0.37 and 0.51 μg/L for levoglucosan and mannosan, respectively. The instrumental limit of detection was 0.10 and 0.12 μg/L for levoglucosan and mannosan, respectively (Stevens et al., 2023). The instrumental limit of quantification was 0.30 and 0.36 μg/L for levoglucosan and mannosan, respectively. The instrumental set-up and method was adopted from previous work using the same IC-TSQ-MS instrument which was earlier optimised for atmospheric aerosol analysis (Sanz Rodriguez et al., 2020).

2.2. Aerosols

2.2.1. Study site and collection

Atmospheric aerosol samples were collected quasi-continuously from a high-volume air sampler (HiVol 3000, Ecotech) located on the top of kunanyi/Mount Wellington, Hobart, Tasmania, Australia (Fig. 1). The air sampler operated at a flow rate around 56.7 m^3 h^{-1} and total suspended particles were collected on acid-washed Whatman 41 cellulose filters. Further details can be found in Perron et al. (2022). This study uses data from aerosol samples collected between the 3rd Jan 2019 and 3rd Feb 2020, capturing both the 2018/19 and 2019/20 Australian bushfire seasons. Four major Tasmanian fires from the 2018/19 bushfire season have been outlined in Fig. 1 and are between 35 and 120 km away from the aerosol sampling site.

2.2.2. Fire sugar extraction and quantification from aerosols

A 41 mm circular sub-section of each aerosol filter was processed for fire sugar quantification. Each sub-section was folded and placed within a 10 mL polypropylene vial containing 6 mL of DIW and 100 μg/L of carbon-13-labelled levoglucosan (internal standard). Samples were ultrasonicated for 20 min in an ultrasonic bath at 20 °C. The solution was then filtered through syringe filters (0.22 μm polyethersulfone membrane) into 2 mL polypropylene autosampler vials for analysis by IC-TSQ-MS. Instrumental details are identical to the details mentioned for sediment samples in Section 2.1.5, except for the Dionex Amino-Trap column, which was replaced with a CarboPac PA-1 guard column (10 μm, 2 × 50 mm) for the analysis of aerosol samples. Additional details about sample extraction and quantification can be found in Sanz Rodriguez et al. (2020).

2.2.3. HYSPLIT modelling during the Tasmanian 2018/19 bushfire season

The HYSPLIT model simulates the dispersion and trajectory of substances through the atmosphere, over local to global scales (Stein et al., 2015; Rolph et al., 2017). The HYSPLIT model was used to calculate back trajectories for air parcels arriving at the aerosol sampler on kunanyi/Mount Wellington (1271 m asl, −42.90, 147.24) for the respective aerosol sample dates (Table 1) to determine the source of fire sugars collected from each sample. The Global Data Assimilation System (0.5°, global, 09/2007–06/2019) meteorology model was the model selected within HYSPLIT to calculate backward trajectories. Total run time for each trajectory was 6 h, and a new trajectory was started every 4 or 6 h (maximum number of trajectories permitting). Resulting trajectory plots were overlain over Fig. 1 to identify how many trajectories passed over the area burnt from each fire and the contribution of each fire was calculated for each time period and rounded to the nearest percent (Fig. S7 and S8). Contribution calculations assume that 100 % of fire sugars in any given aerosol sample arise solely from the four major ongoing fires during the 2018/19 bushfire season. The contribution calculations do not consider the amount of time between the source (fire) and the aerosol sampler (dependent on distance travelled and wind speed), which may affect the extent of fire sugar degradation. However, almost all air parcels reached the kunanyi/Mount Wellington aerosol sampler within 6 h (Fig. S7 and S8), meaning that degradation in the atmosphere is likely minimal and comparable between all four fire locations.

Table 1
Fire sugar concentrations in aerosol samples taken between 3rd January – 11th February 2019 (2018/19 bushfire season) and 27th November 2019 – 3rd February 2020 (2019/20 bushfire season), collected from the aerosol sampler at kunanyi/Mount Wellington, Tasmania, Australia.

Date	Levoglucosan (ng/m^3)	Mannosan (ng/m^3)	L/M
03–05/01/2019	2981	452.9	6.58
05–10/01/2019	192.5	34.06	5.65
10–17/01/2019	112.1	19.50	5.75
17–22/01/2019	473.2	93.05	5.08
22–24/01/2019	2855	511.7	5.58
24–29/01/2019	5534	904.8	6.12
29–31/01/2019	7910	1502	5.27
31/01–04/02/2019	751.8	142.2	5.29
04–06/02/2019	34.06	6.17	5.52
06–11/02/2019	39.98	6.66	6.00
27/11–05/12/2019	0.43	0.03	15.62
05–11/12/2019	7.16	0.46	15.61
11–17/12/2019	0.98	0.07	14.16
17–23/12/2019	47.48	3.88	12.25
23/12/2019–06/01/2020	19.43	1.41	13.82
06–10/01/2020	74.71	5.12	14.59
10–15/01/2020	283.4	20.36	13.92
15–17/01/2020	218.4	14.78	14.77
17–22/01/2020	3.17	0.23	14.00
22–29/01/2020	0.46	0.06	8.19
29/01–03/02/2020	1.78	0.25	7.20

3. Results

3.1. Sediment dating

LPL and Penstock Lagoon both exhibited decreasing unsupported ^{210}Pb concentrations down the core, indicating that the sediments were intact and undisturbed (Fig. S1 and S2). In Penstock Lagoon, the unsupported ^{210}Pb profile was not monotonic however, indicating that the CRS model would be more reliable than the constant flux constant sedimentation (CFCS) model. The use of the CRS model was supported by the fallout radionuclide data (Fig. 2).

Using the CRS model, LPL was dated to 1851 ± 15 at 20.5 cm depth, and Penstock Lagoon was dated to 1868 ± 18 at 8.5 cm depth. LPL had a much higher sedimentation rate compared to Penstock Lagoon, with LPL averaging 1.67 mm/yr post damming, and Penstock averaging 0.63 mm/yr post damming.

The LPL total Pu concentration ranged from 1.57×10^{-4}–0.237 pg/g, with the maximum occurring at 7.5–8.0 cm sediment depth (Fig. 2). The Penstock Lagoon total Pu concentration ranged from 1.61×10^{-3}–0.126 pg/g, with the maximum occurring at 3.5–4.0 cm sediment depth.

3.2. Sediment fire sugar concentrations

No samples fell below the method limit of quantification for levoglucosan, and two samples (Penstock Lagoon CRS year 1961 and 1868) fell below the limit of quantification for mannosan (but were above the limit of detection). Galactosan partially co-eluted with another compound of the same mass-to-charge ratio, identified as 1,6-anhydro-beta-D-glucofuranose by the analysis of a standard (Sanz Rodriguez et al., 2020). This partial co-elution is problematic because it can cause inaccurate quantification of both compounds. However, initial tests on LPL and Penstock Lagoon sediments revealed very low amounts of galactosan and/or 1,6-anhydro-beta-D-glucofuranose, always below the

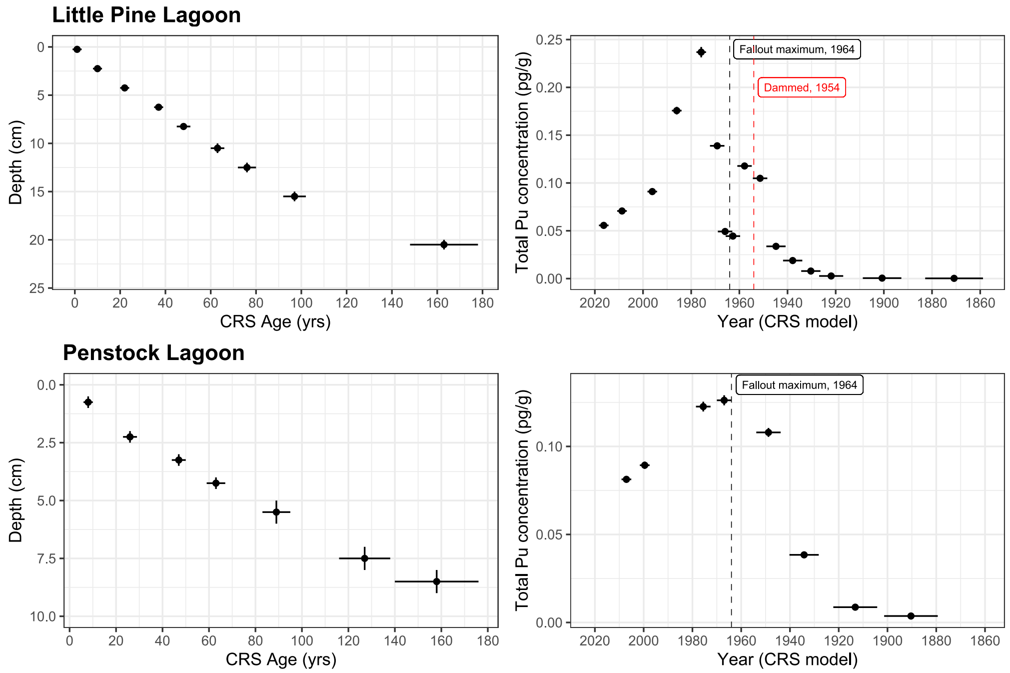

Fig. 2. Left-hand side: ^{210}Pb age approximation using CRS model, plotted against depth. Right-hand side: Independent age marker, total Pu concentration, plotted against calculated CRS age. Little Pine Lagoon top row. Penstock Lagoon bottom row.

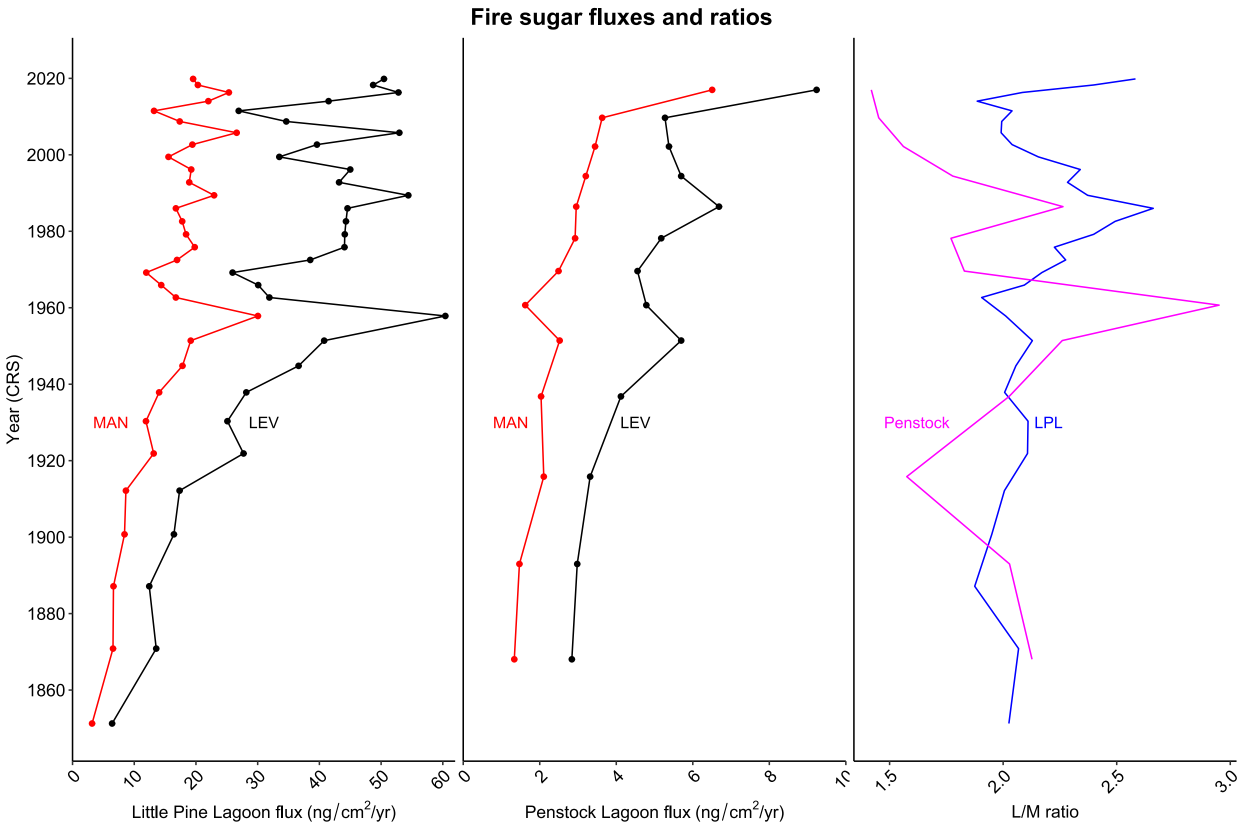

Fig. 3. Fire sugars fluxes and ratios down core. Leftmost column: Little Pine Lagoon fire sugar fluxes. Levoglucosan (LEV) in black, and mannosan (MAN) in red. Middle column: Penstock Lagoon fire sugar fluxes. Rightmost column: down-core L/M ratios in both LPL (blue) and Penstock Lagoon (magenta).

limits of quantification, and hence are not reported further in this study.

Fire sugar (levoglucosan and mannosan) fluxes (ng/cm^2/yr) were calculated to account for sedimentation fluctuations throughout the study period, and to more accurately reflect the input of fire sugars into the waterbody (Schreuder et al., 2019; Chen et al., 2023; Tan et al., 2023). Fluxes were calculated according to the formula:

$$Flux\ (ng/cm^2/yr) = fire\ sugar\ concentration\ (ng/g)^*\ dry\ bulk\ density\ (g/cm^3)^*\ sedimentation\ rate\ (cm^2/yr).$$

Where, dry bulk density was assumed to be 1 g/cm^3.

In Little Pine Lagoon, during the 1851 to 2021 period, the levoglucosan flux ranged from 6.41 to 60.4 ng/cm^2/yr, with an average of 35.87 ng/cm^2/yr (Fig. 3). The mannosan flux ranged from 3.17 to 30.04 ng/cm^2/yr, with an average of 16.54 ng/cm^2/yr. The Levoglucosan to mannosan ratio (L/M) ranged from 1.88 to 2.66, with an average of 2.15. In Penstock Lagoon, during the 1868 to 2021 period, the levoglucosan flux ranged from 2.84 to 9.24 ng/cm^2/yr, with an average of 5.06 ng/cm^2/yr. The mannosan flux ranged from 1.33 to 6.51 ng/cm^2/yr, with an average of 2.79 ng/cm^2/yr. The Levoglucosan to mannosan ratio (L/M) ranged from 1.42 to 2.95, with an average of 1.93.

3.3. *Aerosol fire sugar concentrations*

Levoglucosan concentrations ranged from 0.43 to 7910 ng/m^3 over the 2018/19 and 2019/20 bushfire seasons (Table 1). Samples above 10 ng/m^3 of LEV were identified as 'fire-impacted aerosols' (Perron et al., 2022), meaning that all samples across the 2018/19 bushfire period were 'fire-impacted samples'. Mannosan concentrations were consistently lower, ranging from 0.03 to 1502 ng/m^3. In the 2018/19 bushfire season, the L/M ratio ranged from 5.08 to 6.58, with a weighted average of 5.72 ($n = 10$). In the 2019/20 bushfire season, the L/M ratio ranged from 7.20 to 15.62, with a weighted average of 13.87 ($n = 11$).

4. Discussion

4.1. *Fallout radionuclides*

The LPL total Pu concentration profile did not exhibit the expected shape for fallout radionuclides in the environment (Fig. 2). The expected shape is a single curve, beginning with a low background concentration, a gradual increase after 1945, a maximum around 1964 (at the peak of global nuclear weapons testing), and a decline towards the surface as nuclear weapons testing became less frequent (Jaakkola et al., 1983; Hancock et al., 2011). The LPL total Pu concentration profile included a large dip in concentration around 1964 (Fig. 2). The dip in Pu concentration at ^{210}Pb age of 1964 may be caused by drastically increased sedimentation rates which 'diluted' the radionuclide signal. Such an event may be the damming of LPL, occurring in 1954, which drastically increased the sedimentation rate. Unfortunately, this concealed the expected Pu maximum peak around 1964, as seen in Fig. 2. The same dilution was absent in the ^{210}Pb data because the depths 8.0–8.5 and 10.0–11.0 cm were selected for ^{210}Pb analysis, but 9.0–9.5 and 9.5–10.0 cm were selected for fallout radionuclide analysis. The absence of the Pu maximum peak makes it difficult to support the CRS model, however the identification of an influx event (likely associated with damming) provides its own event to help support chronology. The influx event occurred somewhere between the 9.5 cm (1964 ± 3) to 11 cm (1955 ± 3) bracket. Damming occurred in 1954, and water levels would have increased shortly after this date. This falls within the estimated CRS age profile and supports the use of the CRS model. The LPL ^{236}U (Table S2) profile matched the plutonium closely, as expected considering that ^{236}U and plutonium have the same origin in global weapons test fallout. The ^{240}Pu/^{239}Pu ratios (Table S2) show some variation with depth, with an average ratio (0.164 ± 0.028) consistent with the global fallout value.

Penstock Lagoon was dammed in 1916, meaning that the Pu fallout maximum (around 1964) was not obscured and was visible in Fig. 2. The total Pu concentration peak (1964) occurred somewhere between the 3.5 cm (1971 ± 4) to 4.5 cm (1953 ± 4) bracket, meaning that the use of the CRS model was supported. Like LPL, the Penstock Lagoon ^{236}U (Table S3) profile matched the plutonium closely, and the ^{240}Pu/^{239}Pu average ratio (0.176 ± 0.011, Table S3) is consistent with the global fallout value.

4.2. *Fire sugar fluxes*

The range of fire sugar fluxes in the LPL and Penstock Lagoon sediment samples were comparable to the ranges found in other sediment studies (Table 2). The range found in other studies varied considerably (0.061–151.21 ng/cm^2/yr levoglucosan), potentially influenced by the individual study sites, or the different extraction and quantification methods utilised. Fluxes were approximately five-fold greater throughout LPL sediments compared to Penstock Lagoon sediments (Fig. 3), which is surprising given their proximity to each other (17 km). The greater flux in LPL is partially explained by the increased sedimentation rate at that site, with an approximate 2.7 times increase in sedimentation rate post-damming (Table S4). The increased sedimentation rate in LPL may be related to the greatly increased flushing rates

Table 2

Fire sugar fluxes and levoglucosan / mannosan ratios in freshwater sediment cores studies since 2012 (Kirchgeorg et al., 2014; Schüpbach et al., 2015; Shanahan et al., 2016; Argiriadis et al., 2018; Callegaro et al., 2018; Schreuder et al., 2019; Dietze et al., 2020b; Norström et al., 2021; Tan et al., 2023).

Reference	Sample location	Levoglucosan flux (ng/cm^2/yr)	Mannosan flux (ng/cm^2/yr)	L/M range
This study	Little Pine Lagoon, Tasmania, Australia	6.41–60.40	3.17–30.04	1.88–2.66
This study	Penstock Lagoon, Tasmania, Australia	2.84–9.24	1.33–6.51	1.42–2.95
(Tan et al., 2023)	Wei River, China	13.04–151.21	12.76–170.49	0.88–2.53
(Norström et al., 2021)	Agios Floros fen, Peloponnese, Greece	–	–	1.4 average
(Dietze et al., 2020b)	Lake El'gygytgyn, northeast Siberia	–	–	0.1–2.0
(Schreuder et al., 2019)	Lake Allom, Fraser Island, Australia	0.1–7.2	0.03–2.2	2.0–8.0
(Callegaro et al., 2018)	Paru Co Lake, Tibetan Plateau	–	–	0.6–100
(Argiriadis et al., 2018)	Lake Kirkpatrick and Lake Diamond, New Zealand	–	–	0.1–7.0
(Shanahan et al., 2016)	Lake Bosumtwi, Ghana	0.1–5.0	–	N/A
(Schüpbach et al., 2015)	Lake Petén Itzá, northern Guatemala	LOQ – 2.0	LOQ – 0.9	0.4–11
(Kirchgeorg et al., 2014)	Lake Kirkpatrick, New Zealand	–	–	0.9–2.4

of LPL compared to Penstock Lagoon. The average, yearly flushing rate of LPL (between 1959 and 2023) was 6.32 days (SD = 1.28), whereas in Penstock Lagoon the flushing rate (between 2001 and 2023) was 122.68 days (SD = 64.57, Table S5). The further flux difference is likely related to other factors, such as geographical (e.g. LPL and Penstock reside in different catchments), physical (e.g. catchment area, average water depth), or sedimentary (e.g. grain size, organic matter content, redox state, dry bulk density) factors. Physical factors are comparable between the lakes however, with an approximate depth of 1 m in both lagoons, and catchment areas of 214.26 and 329.50 km^2 for LPL and Penstock Lagoon, respectively. This means geographical or sedimentary factors are likely contributing to the flux difference between the sites. Despite the differences in flux magnitudes between the sites, many of the trends and features of the down-core flux profile were the same (Fig. 3). This, and the similar L/M ratios throughout both profiles, indicates that the source of the fire sugars is likely the same, or very similar, between the two sites.

4.3. *Levoglucosan fluxes and past fire events*

Down-core levoglucosan fluxes were compared to known fire records for Tasmania and Australia (Fig. 4). Fires were classed into ‘local’, ‘regional’, and ‘distant’ fires based on distance away from the study site and the size of the fire, with the assumption that as distance increases, smaller fires are less likely to significantly impact the study site due to dilution. Local fires represented fires that burnt over 250 ha and were within 20 km of the study site. Regional fires represented fires that burnt over 30,000 ha and were 20–200 km away from the study site. Distant fires represented fires that burnt over 200,000 ha and were 200–1000 km away from the study site. Distant fire records begun in 1890, whereas local and regional fire records began in 1930 (Johnson and Marsden-Smedley, 2002; LISTmap, 2024).

Upon visual inspection, levoglucosan fluxes appear to correspond well with past fires in both study sites (Fig. 4). Regression analyses were performed on the two lagoons to identify if levoglucosan flux was related to the distance to the nearest fire or the area of the fire. In Little Pine Lagoon, there was a significant negative trend between levoglucosan flux and the distance to the nearest fire, with flux decreasing by 0.115 % with every 1 % increase to the distance to the nearest fire (Fig. S3 and Table S6). There was no trend between levoglucosan flux and fire area in Little Pine Lagoon. In Penstock Lagoon, there was a significant negative trend between levoglucosan flux and the distance to the nearest fire, with flux also decreasing by 0.115 % with every 1 % increase to the distance to the nearest fire (Fig. S4 and Table S6). There was a significant (but weaker) positive trend between levoglucosan flux and fire area, with flux increasing by 0.059 % for every 1 % increase to fire area (Table S6).

Overall, local and regional fires influence the levoglucosan flux more strongly than distant fires, with levoglucosan flux negatively correlated with the distance of the fires from the study site. This is likely for two main reasons. Firstly, fire sugars from distant fires would experience more degradation in the atmosphere compared to local or regional fires because of the increased travel time. Secondly, distant fires are more reliant on wind-direction, meaning there is a higher chance of past, distant fires not appearing in the fire sugar record because of unfavourable wind directions at the time of the fire. There are also multiple uncertainties that need to be considered. There are uncertainties about the degree of bioturbation or vertical mixing in these lagoons, which may dilute or shift the fire sugar flux peaks and valleys. There are uncertainties about sedimentary factors that may affect fire sugar concentration (e.g. grain size or organic matter) that may have likely changed throughout time and thus indirectly altered the down-core fire sugar flux.

4.4. *Comparison of fire sugar ratios (L/M) between sediment and aerosols*

The L/M ratios identified in surface sediments (1.42–2.58) were lower than expected, given the type of biomass burnt and the L/M ratios of aerosol samples taken during the 2018/19 and 2019/20 bushfire seasons (5.08–15.62, Table 1). The 2018/19 bushfire season was Tasmania's largest fire event since 1967 (Keating, 2021). LPL and Penstock

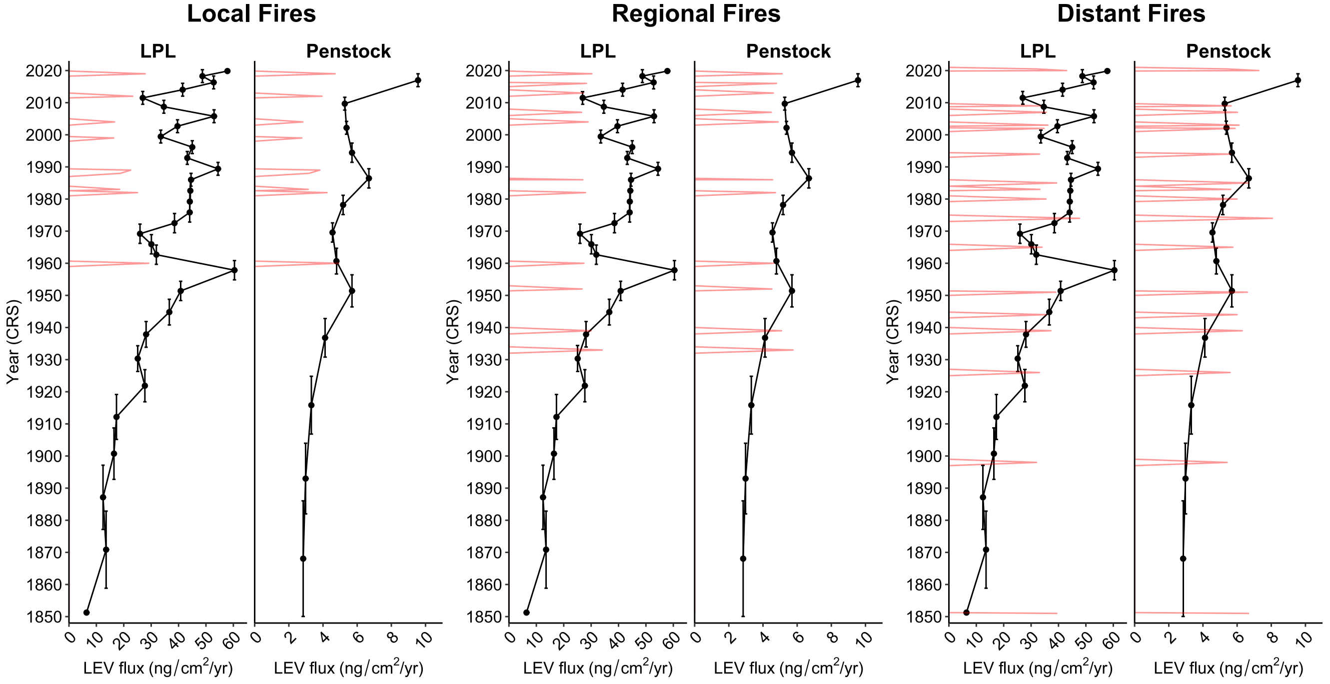

Fig. 4. Little Pine Lagoon and Penstock Lagoon down-core levoglucosan fluxes (black line) compared to past, recorded fires (red line). Left panel: local fires (>250 ha burnt and within 20 km). Middle panel: regional fires (>20,000 ha burnt and 20–200 km away). Right panel: distant fires (>200,000 ha burnt and 200–1000 km away). Past fire peak height is based on area burnt (logarithmic scale in the Penstock Lagoon plots and a custom scale to match in the LPL plots).

Lagoon were both surrounded by the Great Pine Tier fire, the second largest fire of the season (Fig. 1 and Table S1). Fire sugar fluxes in the surface sediments of both cores were relatively high, with Penstock Lagoon receiving the maximum flux of levoglucosan and mannosan (Fig. 3). This flux increase was likely related to the Great Pine Tier fire event but also may be related to other regional fires during 2018/19 (Fig. 1) or major, distant fires in the 2019/20 bushfire season that burnt approximately 18.6 million ha of mainland Australia (Table 1). The L/M ratios of the surface sediment samples were extremely low, with 2.58 in LPL and 1.42 in Penstock Lagoon - the lowest value throughout the profile. According to source burning studies, a L/M ratio between 2.5 and 10 indicates that softwoods, or certain grass species, are the dominant biomass burnt (Fabbri et al., 2009; Xu et al., 2019; Marynowski and Simoneit, 2022). Whereas a L/M ratio between 10 and 30 is indicative of hardwood species dominating biomass burnt. The Great Pine Tier fire burnt predominantly dry eucalypt forest (64 %, Table S1), which contained many hardwood eucalypt species, as well as smaller shrubs and grasses. The L/M ratio from this biomass would be expected to be higher than 2.5 because it is a mixture of hardwoods, softwoods, and grasses.

To estimate the L/M ratio of the emissions from the Great Pine Tier fire, HYSPLIT back trajectory models were used to estimate the contributions (%) of the four major fires to each kunanyi / Mount Wellington aerosol sample collected during the 2019/20 bushfire season period (Table 3). The Great Pine Tier fire was never the sole contributor to any of the collected aerosol samples, meaning that the L/M ratio is not accurately known. However, across all the collected aerosol samples, the L/M range was small (5.08–6.58), despite the various contributions from each of the four fires, including several samples influenced by the Great Pine Tier fire (Table 3). This indicates that the vegetation burnt across each fire was comparable, and yielded L/M ratios around 5–7. This is more in-line with the expected value given the type of biomass burnt (a combination of hardwoods, softwoods, and grasses).

The L/M ratios identified in aerosol samples during the 2018/19 Australian bushfire season also were much higher than those identified in the surface sediments. Kunanyi / Mount Wellington aerosol samples taken during December 2019 and January 2020 showed elevated levoglucosan and mannosan concentrations (Table 1) and sampling notes for the most elevated sample indicated that intense smoke haze from mainland fires was visible at the time of sampling. The elevated samples had an average L/M of 13.87 ± 1.00 (Table 1), much higher than the 2.58 and 1.42 identified in LPL and Penstock Lagoon surface sediments.

These results suggest that the L/M ratio found in sediments is not comparable to that found in aerosols. This is assuming that the fire sugars in surface sediments (L/M = 2.58 and 1.42) were derived from local or regional fires during the 2019/20 Tasmanian bushfire season (L/M = 5.08–6.58), or distant Australian fires during the 2019/20 bushfire season (L/M = 13.87 ± 1.00). Therefore, the L/M ratio found in these sediments is likely not representative of the type of biomass burnt.

The finding that L/M ratios are lower in sediments than in corresponding aerosol samples is potentially not limited to Tasmanian sediments. Past sediment studies also identify extremely low L/M ratios. Four out of nine sediment core studies in Table 2 found L/M ratios below 2.53 for the entirety of the down-core profile. Only two of the nine studies ever found a L/M ratio above 10 (11 maximum in Lake Petén Itzá, northern Guatemala (Schüpbach et al., 2015) and 100 maximum in Paru Co Lake, Tibetan Plateau (Callegaro et al., 2018). Similarly, six of the studies identified ratios below 1 (indicating a higher proportion of mannosan than levoglucosan), which is extremely rare in aerosol measurements. A compilation of ambient aerosol data from different land covers throughout the world showed that the L/M ratios ranged from 2.2 to 26.0, $n = 31$ (Bhattarai et al., 2019)(and references therein). A compilation of the L/M ratios of various biomass species burnt in a controlled setting (predominantly fireplace, stove, chamber, and open chamber combustion) showed that almost all measured softwood and hardwood species fell between their expected ranges (2.5–10) and (10−100), respectively (Cheng et al., 2013) (and references therein). However, needles and duffs (decaying plant litter) had very low L/M ratios, with needles ranging from 1.42 to 6.53 and duffs ranging from 0.99 to 2.43 (Sullivan et al., 2008). This is nearing the ratios commonly identified in sediments samples. The lowest L/M ratio identified in the literature was 0.3 in charred pine cones from Alberta, Canada (Otto et al., 2006). This data highlights how uncommon low L/M ratios are for aerosol studies, with only two examples exhibiting an L/M below 1. Conversely, over half of the freshwater sediment studies since 2012 consistently identify L/M ratios below 1 in sediment samples (Table 2). This is circumstantial evidence, but it does warrant future investigation into the understanding and use of fire sugars in freshwater sediments.

We propose two hypotheses to explain the phenomenon of low L/M ratios in sediments:

Degradation rates vary between levoglucosan and mannosan in different mediums. Specifically, levoglucosan breaks down more rapidly than mannosan in either the water column, the sediment-water interface, or in the sediments, leading to decreased L/M ratios in sediments compared to those identified in aerosols. Degradation rates likely vary with physical and chemical factors (e.g. redox conditions or organic matter content). The vastly different degradation rates between dissolved galactosan (44 % degraded after 28 days) and the other isomers (85 % and 86 % degraded after 28 days) in wastewater samples found in initial tests by Kirchgeorg (2015) highlights that these isomers can behave different chemically, despite their structural similarities.

During pyrolysis, fire sugars are emitted via atmospheric and non-atmospheric pathways. Fire sugars associated with non-atmospheric pathways may have a lower, average L/M ratio than those associated with atmospheric pathways. This may be due to the types of particles that are associated with non-atmospheric emissions (likely larger particles) or the different formation temperatures during pyrolysis.

Exploring these hypotheses should be the focus of future work. Schreuder (2018) found significant degradation of levoglucosan in the sediment-water interface. This may be the key site of fire sugar degradation, rather than deep in the sediment core due to post-depositional processes, although this needs to be explored further. Fig. 5 shows the fire sugar concentrations for five different sediment cores, taken from four different sites, and representing three different time periods.

There are minor trends observed between sediment age and fire

Table 3

Fire plume contribution to each kunanyi/Mount wellington aerosol sample in 2019, based on HYSPLIT backward trajectories for the respective time period. HYSPLIT conditions and contribution calculation methodology are detailed in Section 2.2.3.

Aerosol sample period	3 – 5th Jan	5 – 10th Jan	17 – 22nd Jan	22 – 24th Jan	24 – 29th Jan	29 – 31st Jan	31st Jan – 4th Feb	4 – 6th Feb	6 – 11th Feb
Levoglucosan (ng/m^3)	2981	192.52	473	2855	5534	7910	752	34	40
L/M ratio	6.58	5.65	5.08	5.58	6.12	5.27	5.29	5.52	6.00
	Contribution (%) of each fire plume to the collected aerosol sample								
Great Pine Tier	0	0	0	20	0	11	14	33	0
Gell River	100	100	17	0	92	56	36	0	44
Riveaux Road	0	0	28	40	0	33	29	0	13
Moores Valley	0	0	55	40	8	0	21	67	44

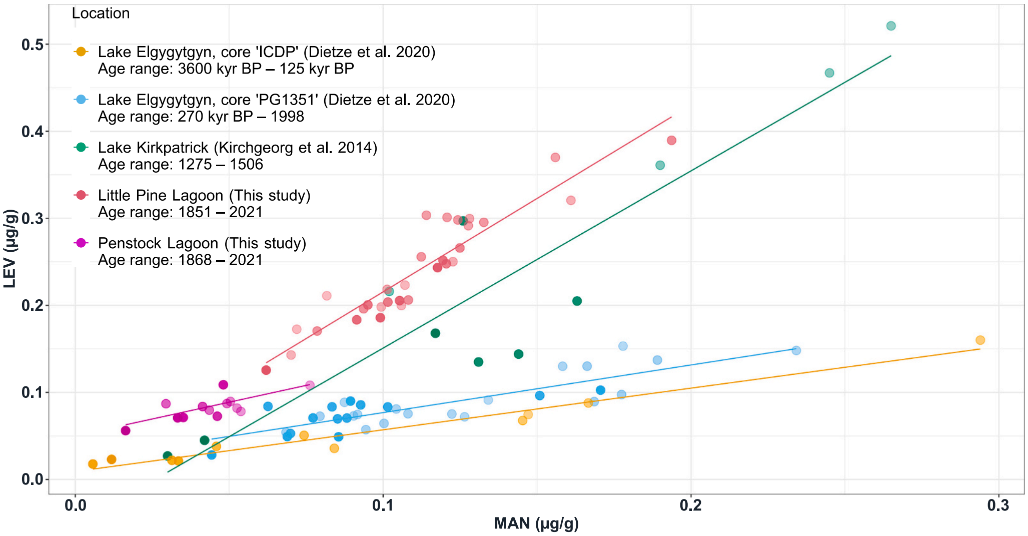

Fig. 5. Levoglucosan (LEV) versus mannosan (MAN) concentrations (µg/g) in sediment samples from five different sediment cores (Kirchgeorg et al., 2014; Dietze et al., 2020a). Each core is portrayed using a different colour (yellow, blue, green, red, magenta). Points represent individual samples, and lines represent the linear trendline (average L/M ratio) for the respective core. The transparency of each point varies with depth, with the most transparent point indicating the surface-most sample for the respective core, and the least transparent point indicating the deepest sample for the respective core.

sugar concentrations, with both levoglucosan and mannosan concentrations decreasing with increasing age, in all cores (Fig. 5, Fig. S5, and Table S7). Although statistically significant in most cases, the rates of degradation are extremely low, with levoglucosan concentrations decreasing between 3.53×10^{-6}–1.35×10^{-1} µg/g per 100 years and mannosan concentrations decreasing between 5.76×10^{-6}–5.46×10^{-2} µg/g per 100 years (Table S7). It is important to note that this does not consider the source of the fire sugars changing over time, which may impact concentration values. A larger sample size is required to further explore the trends between fire sugar concentrations and sediment age, but it appears that levoglucosan and mannosan both degrade slowly over time in sediments.

There are no consistent trends between L/M ratio and sediment depth (Fig. 5 and Fig. S6), indicating that the fire sugar isomers are degraded (or not degraded) at equal rates. This indicates that L/M ratios in sediments are altered due to either degradation in the water column or sediment-water interface, or due to non-atmospheric emissions contributing to the total fire sugar pool. However, further research is required because fire sugar degradation due to post-depositional processes may vary depending on sedimentary conditions (e.g., redox conditions or organic matter content).

Until fire sugar partitioning into atmospheric and non-atmospheric emissions during pyrolysis, and the degradation along the source-to-sink pathway and in sediments is more comprehensively understood, we recommend caution around interpretations of vegetation type based on fire sugar ratios (specifically L/M) in sediments.

5. Conclusion

Fire sugars have the potential to be extremely useful fire tracers given they are almost exclusively formed by biomass burning. In aerosols, they are well understood, and as a result they are effective tracers of biomass burning as well as useful indicators of the types of biomass burnt (via the isomer ratios). In sediments and ice cores however, fire sugars remain not fully understood. Key knowledge gaps include fire sugar production and partitioning during pyrolysis, and complexation and degradation along the source-to-sink pathway and within the sediment itself. These gaps limit the efficacy of fire sugars as fire tracers and as indicators of the types of biomass burnt. Fire sugars in freshwater sediments appear to be useful historical fire tracers, with levoglucosan flux increases often coinciding with past fires, however, the relative contribution from different fires (local, regional, and distant) is likely site specific and depends on many factors (such as wind direction). This is evident through the findings from this study, and the findings of other studies that identified various degrees of fire sugar correlation with microscopic and macroscopic charcoal.

For the first time, L/M ratios have been measured in sediments and corresponding aerosols to compare L/M ratios from the same source, within different mediums. L/M ratios are consistently lower in sediments compared to corresponding aerosols, with this study, and many previous sediment studies, identifying extremely low L/M ratios in sediments. Common ranges of L/M ratios in aerosol source burning studies are 2.5–10 for softwoods, 10–30 for hardwoods, and 30+ for grasses, with exceptions. Common ranges of L/M ratios in past sediment studies are typically lower, with six of nine past freshwater sediment studies since 2012 identifying L/M ratios below 1 in down-core sediment samples. We propose two hypotheses for the lowered L/M in sediments: 1) Degradation rates of levoglucosan are higher than that of mannosan in either the water column, sediment-water interface, or sediments; 2) Fire sugars emitted via atmospheric and non-atmospheric pathways during pyrolysis may have intrinsically different L/M ratios and therefore the L/M identified in sediments (made-up of fire sugars from both pathways) is different to that in atmospheric aerosols, even for the same source vegetation.

Therefore, until better understood, fire sugars should be used as complimentary tracers, to be measured alongside other fire tracers such as micro- or macroscopic charcoal, or polycyclic aromatic hydrocarbons. Furthermore, we recommend caution around interpretations of vegetation type based solely on fire sugar ratios (specifically L/M) in sediments.

CRediT authorship contribution statement

Harrison Stevens: Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis, Conceptualization. **Leon A. Barmuta:** Formal analysis, Supervision, Resources. **Zanna Chase:** Writing – review & editing, Supervision. **Krystyna M. Saunders:** Writing – review & editing, Validation, Supervision. **Atun Zawadzki:** Resources, Investigation. **Andrew R. Bowie:** Writing – review & editing, Resources, Investigation. **Morgane M.G. Perron:** Writing – review & editing, Investigation. **Estrella Sanz Rodriguez:** Writing – review & editing, Resources, Methodology, Investigation.

Brett Paull: Writing – review & editing, Resources. **David P. Child:** Resources, Investigation. **Michael A.C. Hotchkis:** Resources, Investigation. **Bernadette C. Proemse:** Writing – review & editing, Supervision, Resources, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.174068.

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