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Method for the determination of specific molecular markers of biomass burning in lake sediments

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ABSTRACT

Fire has an influence on regional to global atmospheric chemistry and climate. Molecular markers of biomass burning archived in lake sediments are becoming increasingly important in paleoenvironmental reconstruction and may help determine the interaction between climate and fire activity. Here, we present a high performance anion exchange chromatography–mass spectrometry method to allow separation and analysis of levoglucosan, mannosan and galactosan in lake sediments, with implications for reconstructing past biomass burning events. Determining mannosan and galactosan in Lake Kirkpatrick, New Zealand (45.03°S, 168.57°E) sediment cores and comparing these isomers with the more abundant biomass burning markers levoglucosan and charcoal represents a significant advancement in our ability to analyze past fire activity. Levoglucosan, mannosan and galactosan concentrations correlated significantly with macroscopic charcoal concentration. Levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) ratios may help determine not only when fires occurred, but also if changes in the primary burned vegetation occurred.
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1. Introduction

Human activity has influenced fire regimes by changing fire ignition rate, the fuel, land use and land cover for millennia (Bowman et al., 2009). Data from natural archives, including sediment and ice cores, can help understand past fire activity over longer temporal and spatial scales. Charcoal data from lake sediment cores represent a well known proxy for biomass burning and are used to reconstruct past fire activity on a local scale to a regional scale (e.g. Whitlock and Larsen, 2001). Molecular markers of biomass burning archived in lake sediments are increasingly important in paleoenvironmental reconstruction and may help determine the interaction between climate and fire activity.

One group of biomass burning markers is the monosaccharide anhydrides (MAs) levoglucosan (1,6-anhydro-*β*-D-glucopyranose), mannosan (1,6-anhydro-*β*-D-mannopyrose) and galactosan (1,6-anhydro-*β*-D-galactopyranose), which are specific indicators of fire activity. In contrast to polycyclic aromatic hydrocarbons, MAs are only generated by biomass burning at temperatures > 300 °C (Simoneit, 2002) and are present in combustion residues from biomass containing cellulose and hemicellulose. Due to their relatively low volatility they tend to be ab-/adsorbed to aerosols in the atmosphere.

Several studies have used MAs as specific markers for biomass burning in atmospheric aerosols (Simoneit and Elias, 2000; Jordan et al., 2006). While a proportion of levoglucosan can be degraded in the atmosphere, these compounds are still able to undergo long range atmospheric transport due to their stability and the significant emissions of levoglucosan during biomass burning (Fraser and Lakshmanan, 2000; Hoffmann et al., 2010). Snow pit and aerosol studies from remote Arctic regions demonstrate the applicability of levoglucosan as a fire activity tracer up to thousands of km from potential sources (Kehrwald et al., 2012; Zangrando et al., 2013). Zennaro et al. (2014) demonstrated the stability and suitability of levoglucosan as a proxy for biomass burning by analyzing a Greenland ice core covering the last two millennia.

In contrast to ice core and aerosol studies, the stability of MAs in lake sediments is not well known. Only in one laboratory

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experiment was an aquatic half-life of 3–4 days for dissolved levoglucosan determined (Norwood et al., 2013). The capability of MAs to remain in lake and marine sediments for timescales as along as 20,000 yr (Elias et al., 2001; Kuo et al., 2011a; Hopmans et al., 2013) suggests that, at a minimum, the levoglucosan entrapped in particles deposited on the lake surface should be stable in the aquatic phase and incorporated into sediments (Elias et al., 2001).

The literature demonstrates methods for determining MAs in different matrixes using gas chromatography–mass spectrometry (GC–MS) based on derivatization (Schkolnik and Rudich, 2006; Medeiros and Simoneit, 2007), high performance anion exchange chromatography (HPAEC) with amperometric detection, mass spectrometry (MS) or MS/MS (Engling et al., 2006; Saarnio et al., 2010; Piot et al., 2012) and high performance liquid chromatography tandem mass spectrometry (HPLC–MS/MS; Gambaro et al., 2008; Hopmans et al., 2013). Only a few of these methods have been applied to sediments (Elias et al., 2001; Kuo et al., 2011a; Hopmans et al., 2013) and to the best of our knowledge only levoglucosan data have been published from sediment cores.

The aim of this study was to develop a method for analyzing all three MAs in lake sediment cores based on the existing HPAEC methods used for other matrices (Saarnio et al., 2010; Piot et al., 2012). The method has the advantage of not requiring derivatization, which is necessary for GC–MS. The selectivity and sensitivity of the HPAEC–MS method are better than for amperometric methods and HPAEC results in better separation of the three isomers than HPLC (Gambaro et al., 2008; Hopmans et al., 2013). A major benefit of analyzing all three isomers is the possibility of calculating the emission ratios of levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) that might help determine changes in burned vegetation. Laboratory burning experiments and smoke analysis demonstrated characteristic emission ratios of the three isomers depending on the type of vegetation burned (Fabbri et al., 2009). For method validation we applied the new method to 12 selected samples from a Lake Kirkpatrick (New Zealand) sediment core and compared our MA results with the known charcoal concentration in the samples.

2. Material and method

2.1. Material

Levoglucosan was from Sigma Aldrich (St. Louis, USA), and mannosan and galactosan (> 99%) were from Molecula (Shaftesbury, UK). $^{13}C_6$-levoglucosan (> 98%) was from Cambridge Isotope Laboratories Inc. (Andover, MA, US). MeOH (Ultrapure) was from Romil LTD (Cambridge, UK) and NH_4OH (Fluka, 25%) from Sigma Aldrich. Ultra-pure water was produced by PURELAB Pulse and PURELAB Flex (ELGA LabWater, Marlow, UK). He and N_2 of purity 5.0 was from SIAD (Bergamo, Italy).

2.2. Samples

The test samples ($n = 12$) with known macroscopic charcoal concentration (> 125 μm) originated from a sediment core drilled by the Montana State University research team at Lake Kirkpatrick (South Island, New Zealand; 45.03°S, 168.57°E, 570 m above sea level) in 2009. This small lake (ca. 3.5 ha) is characterized by a small catchment area (< 10 km^2) with a relatively closed basin with no significant surface inflow. The counted macroscopic charcoal was assumed to originate from local aerosols (< 1–3 km^2), eolian deposition from airborne particles and surface erosion. The samples were from a depth of 75–129 cm. Those from 119–129 cm originated from 1240–1311 A.D. and those between 75 and 88 cm from 1479–1533 A.D. Charcoal concentration in the samples was between 0 and 64.8 pieces/cm^3 (Table 1). Relative to the overall charcoal variation at Lake Kirkpatrick, samples between 5.6 and 64.8 pieces/cm^3 were indicated as samples with high charcoal values, significantly influenced by local biomass burning. Samples with charcoal concentration between 0 and 0.4 pieces/cm^3 were assumed to be low charcoal samples. Detailed information regarding the drilling site and charcoal measurements are available from McWethy et al. (2009). Samples were shipped from Montana State University to Venice in 2013.

2.3. Sample preparation and extraction

Wet samples were freeze-dried, milled and homogenized. Prior to extraction the samples were spiked with 100 μl of internal standard (1 ppm in MeOH) containing ^{13}C labeled levoglucosan. The freeze-dried sediment (ca. 0.2 g) was extracted using pressurized solvent extraction (PSE; PSEone, Applied Separations, Hamilton, USA) with MeOH (2 cycles of 5 min each, 100 °C at 100 bar). The sample was filtered (0.2 μm, PTFE), evaporated under a stream of N_2 to dryness (Turbovap, Biotage, Uppsala, Sweden), dissolved in 0.5 ml ultra-pure water and sonicated to avoid any adsorption to the walls of the evaporation glass. Finally, the sample was centrifuged (5 min, 14,000 rpm) and transferred to the measurement vials. A blank was extracted with each batch of 5 samples.

2.4. Instrumental analysis and quantification

Separation of levoglucosan, mannosan and galactosan was performed with an ion chromatography (IC) instrument (Dionex ICS 5000, Thermo Scientific, Waltham, US) equipped with a CarboPac PA1™ column and a CarboPac P10™ column (Thermo Scientific, each 2 mm × 250 mm). In addition, we used a CarboPac PA 10™ guard column (2 × 50 mm) and an AminoTrap column (2 × 50 mm) to trap amino acids. The three MAs were detected with a single quadrupole mass spectrometer (MSQ Plus™, Thermo Scientific) after IC separation. The injection volume was 25 μl.

NaOH was produced as a carrier solvent by an eluent generator (Dionex ICS 5000 EG, Thermo Scientific). The gradient was: 20 mM (0–15 min), 100 mM (15–40 min; column cleaning), 20 mM (40–60 min; equilibration). The flow was 0.250 ml/min. The NaOH was removed by a suppressor (ASRS 300, 2 mm, Thermo Scientific) before entering the MS source. For the protection of the MS instrument during the cleaning step, the flow was switched to waste after a total run time of 15 min. MeOH/NH_4OH was added post-column (0.02 ml/min) to improve ionization of the aqueous eluent. Ultrapure water for eluent generation and the MeOH mixture for the post-column infusion were kept under a He atmosphere to avoid external contamination and pressure fluctuation.

The MS instrument was equipped with an electrospray ionization (ESI) source used in negative ionization mode. Due to the post-column injection of MeOH/NH_4OH, we slightly modified the MS parameters from those described by Saarnio et al. (2010), to improve performance. The source temperature was reduced to 350 °C, the needle voltage was −3.5 kV and the cone voltage −50 V. Levoglucosan, mannosan and galactosan were analyzed using m/z 161, where m/z 101 and 113 were used as qualifiers when sufficient concentrations were present. The ^{13}C labeled internal standard was determined using m/z 167.

Samples were quantified using the response factor of levoglucosan, mannosan and galactosan vs. the ^{13}C labeled internal standard. The advantage of using an internal standard is the ability to correct potential analyte loss during extraction and handling. A Chromeleon 6.8 Chromatography data system (Thermo Scientific) was used for data acquisition and elaboration.

Table 1
Levoglucosan, mannosan, and galactosan concentrations (ppb dry wt. sediment), macroscopic charcoal counts (> 125 μm pieces/cm^3) and the ratios of levoglucosan/mannosan (L/M) and levoglucosan/(mannosan + galactosan) [$L/(M+G)$] in lake sediment samples vs. depth (cm).

Depth (cm)	Levoglucosan (ppb)	Mannosan (ppb)	Galactosan (ppb)	Charcoal (pieces/cm^3)	L/M	$L/(M+G)$
75	1109	509	295	64.8	2.2	1.4
76	521	265	129	17.4	2.0	1.3
78	467	245	138	15.6	1.9	1.2
80	361	190	103	5.6	1.9	1.2
83	216	102	76	10.0	2.1	1.2
119	205	163	41	0.2	1.3	1.0
120	135	131	52	0.2	1.0	0.7
121	144	144	43	0.0	1.0	0.8
122	297	126	68	0.4	2.4	1.5
127	168	117	69	0.0	1.4	0.9
128	27	30	31	0.4	0.9	0.4
129	45	42	31	0.2	1.1	0.6

3. Results and discussion

3.1. Sample extraction

Sonic bath, shaking and PSE techniques have been discussed as potential extraction methods for MAs from filters, soil or sediments (Saarnio et al., 2010; Piot et al., 2012; Hopmans et al., 2013). We applied PSE using MeOH (cf. Hopmans et al., 2013). Multiple extractions led to only a low MA concentration in the second extract (< limit of quantification; LOQ) and third (< limit of detection; LOD) extract. We therefore only used one PSE extraction with 2 extraction cycles as described above in order to keep the volume of MeOH as small as possible. The samples were evaporated to dryness and dissolved in water prior to injection.

3.2. Chromatographic separation

The suitability of CarboPac™ columns for the separation of levoglucosan, mannosan and galactosan has been discussed recently (Saarnio et al., 2010; Piot et al., 2012). Initially we used a CarboPac™ PA 10 column with an AminoTrap column and achieved a similar separation to Saarnio et al. (2010). However, due to the complex matrix of the samples some co-eluting compounds interfered with MA separation. Changing NaOH concentration in the eluent did not improve the separation from the matrix. The retention time of levoglucosan was not significantly affected by changing NaOH concentration between 0.1 mM and 20 mM. However, the introduction of a second column (CarboPac™ PA 1) in series with the CarboPac™ PA 10 column improved the separation substantially (Fig. 1D).

Retention time was 4.8 min, 6.4 min and 9.1 min for levoglucosan, mannosan and galactosan, respectively. We achieved baseline separation of levoglucosan and mannosan when both columns were used in series, thereby resolving the separation problem in the method of Saarnio et al. (2010) and increased the separation of the isomers (Fig. 1A) compared with Piot et al. (2012). In addition, we were able to separate levoglucosan from the complex background matrix (Fig. 1B–D), where Fig. 1D demonstrates the improved separation when using both columns vs. the CarboPac PA 10™ column only.

To further reduce matrix influence, we tested smaller injection volumes of 10 μl and 25 μl, compared with published ones of 50 μl for HPAEC–MS (Saarnio et al., 2010) or 449 μl for HPAEC–MS/MS (Piot et al., 2012). Both resulted in reduced matrix effects, so we used 25 μl due to the potentially low concentration of the analytes in lake sediment samples.

Due to the use of two columns, a long cleaning and reconditioning step was required after each sample injection, leading to a 60 min run time for a single analysis. The cleaning was necessary to remove all residual sugars in order to avoid carryover effects, as MAs can be generated in the ESI source > 300 °C if other sugars are present (Saarnio et al., 2010).

3.3. Analytical performance

We examined linearity via a 7 point response factor calibration with concentrations of levoglucosan, mannosan and galactosan from 25 to 500 ppb, with r^2 0.99 for all three MAs. The LOD and LOQ were calculated for the standard solution from signal/noise 3 (LOD) and 10 (LOQ), affording LOD and LOQ of 0.9–1.8 ppb and 3.2–5.8 ppb, respectively. These values are in the same range as in other studies (Saarnio et al., 2010), although we reduced the injection volume and introduced a second column. Using a 0.2 g sediment aliquot, which is less than the amount of sediment or soil analyzed using GC–MS (Elias et al., 2001) or HPAEC–MS/MS (Piot et al., 2012), corresponded to a LOD between 2.3 and 4.5 ppb and a LOQ between 8 and 14.5 ppb.

Instrumental precision was tested by a ten fold analysis of low (25 ppb) and high (300 ppb) concentration standards of levoglucosan, mannosan and galactosan, resulting in a relative standard deviation (RSD) of 3.8% and 6.6%, 3.2% and 2.3%, and 3.7% and 2.8% for the low and high concentration standard of levoglucosan, mannosan and galactosan, respectively.

Standard reference materials for MAs in lake sediments were not available, so we tested the method with the NIST reference material for urban dust SRM 1649b. MAs in this urban dust standard have been analyzed (Louchouarn et al., 2009), with reported concentrations (standard deviation in brackets) of 160.5 (± 5.0), 16.7 (± 0.7) and 4.8 (± 0.2) ppm for levoglucosan, mannosan and galactosan, respectively. Due to these high concentrations we only used a small aliquot (0.01 mg) and had to dilute the sample after extraction. We obtained concentrations of 168 (± 4.5), 15.7 (± 0.7) and 5.0 (± 0.2) ppm. Although levoglucosan and galactosan concentrations were slightly higher and mannosan concentration lower than the values in the literature, our results agree with the published values. The method accuracy based on the relative recovery of the MAs from spiked blank samples ($n = 5$), was 99.8% (± 1.3%) (levoglucosan), 97.7% (± 6.4%) (mannosan) and 94.1% (± 7.6%) (galactosan). The estimated overall method uncertainty was 4.7%, 9.9% and 8.7% for levoglucosan, mannosan and galactosan, respectively. The increased uncertainty for mannosan and galactosan compared with levoglucosan may be due to the lack of internal standards for mannosan and galactosan.

We also performed parallel extractions of sediment samples, resulting in concentrations of 348 and 333 ppb, 163 and 145 ppb and 70 and 80 ppb for levoglucosan, and mannosan and galactosan, respectively. In addition, we performed a second parallel extraction of sediment samples from 76 cm and 119 cm, respectively.

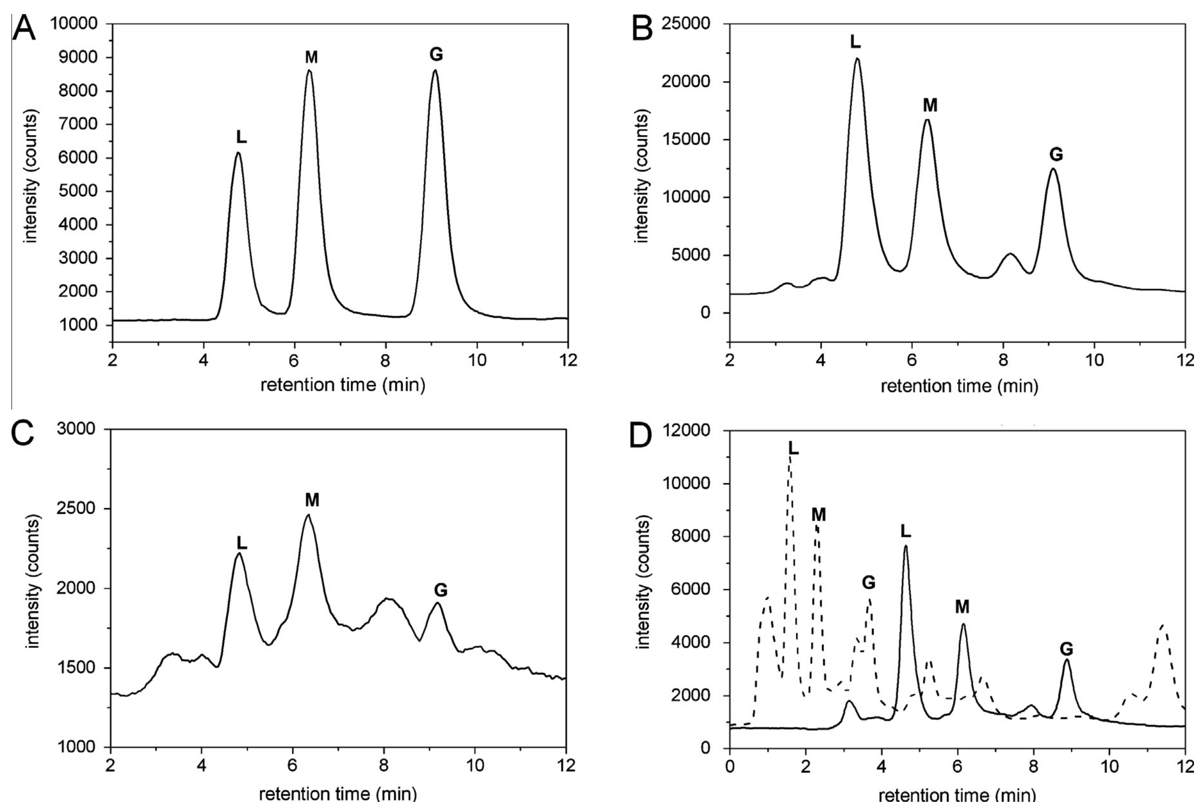

Fig. 1. (A) chromatogram (SIM) of a standard mixture (all 100 ppb) of levoglucosan (*L*), mannosan (*M*) and galactosan (*G*). The retention times are 4.8, 6.4 and 9.1 min, respectively. (B) chromatogram (SIM) of the three compounds in a New Zealand lake sediment sample with high charcoal concentration. (C) chromatogram (SIM) of the three compounds in a New Zealand lake sediment sample with low charcoal concentration. (D) comparison of the separation using only one column (dashed line) and the current method using two columns applied to a real sample. Note the different dimensions of the *y*-axis.

We extracted the second set of samples 3 weeks after the first set. The concentrations of levoglucosan, mannosan and galactosan were 521 and 512 ppb, 265 and 256 ppb and 129 and 117 ppb for the 76 cm sample, and 205 and 199 ppb, 163 and 157 ppb, and 41 and 44 ppb for the 119 cm sample, respectively. All parallel extractions demonstrated good method reproducibility and the variation was in the range of the estimated method uncertainty.

We measured blanks ($n = 3$) by treating them as real samples and also analyzed blanks within the different batches of five samples. The blank concentrations for these replicates ($n = 3$) were 10 ± 6, 2 ± 4 and 2 ± 3 ppb for levoglucosan, mannosan and galactosan, respectively The average blank concentrations during real sample analyses were between 15 ± 1 ppb for levoglucosan, 8 ± 7 ppb for mannosan and 4 ± 6 ppb for galactosan, thereby slightly higher. We corrected all sample concentrations using the blank values for the corresponding batch.

3.4. Sediment sample concentration

The method was tested and validated by analyzing lake sediment samples and comparing the results with the charcoal concentration of the samples. The samples were treated in random order to avoid any trend in the data that could possibly be influenced by the extraction or measurement procedures. In addition, we analyzed three blanks subjected to the same treatment as the samples.

The concentrations of levoglucosan, mannosan and galactosan in samples with charcoal counts between 5.6 and 64.8 pieces/cm^3 were 216–1109, 102–509 and 76–295 ppb, respectively. The concentrations of the three MAs in the samples with low charcoal counts (0–0.4 pieces/cm^3) were 27–297, 42–144 and 31–69 ppb. An overview of the concentrations is given in Table 1 and plotted in Fig. 2B. All concentrations were blank corrected.

Reports of levoglucosan concentration in lake sediments are rare, so we used the limited published data as an initial estimate of the Lake Kirpatrick MAs concentration range even if the studies covered different time periods and sampling regions. Two marine cores from the main basin of Puget Sound (USA), had a comparable concentration to the present study, with values of 60–782 ppb (1700–2000 A.D.; Kuo et al., 2011a). Levoglucosan concentration from the present study was lower than values from a New Zealand marine sediment core record (9 ppm and 1045 ppm) covering a period from 9116 to 26,066 yr B.P. (i.e. before 1950 A.D.; Sikes et al., 2013) and lake sediment cores from the Southern Serra dos Carajás, Brazil, covering a period from 100–7000 yr B.P. (0.1–41.4 ppm; Elias et al., 2001). All previous studies used GC–MS. To the best of our knowledge, this is the first study reporting mannosan and galactosan concentrations in a sediment core.

3.5. Comparison of MAs with charcoal

Charcoal in sediment is a biomass burning marker and laboratory studies have demonstrated the occurrence of levoglucosan in low temperature charcoal (Kuo et al., 2008). Therefore a comparison between levoglucosan, mannosan and galactosan with associated charcoal in the same core is essential. The literature demonstrates a relationship between charcoal and levoglucosan in sediments (Elias et al., 2001; Kuo et al., 2011a). Our Lake Kirkpatrick levoglucosan data correlated strongly (r^2 0.89, $p < 0.01$) with charcoal counts in samples from the same depth (Fig. 2A). Mannosan and galactosan concentrations displayed a similar trend (r^2 0.84 and 0.93, $p < 0.01$) to the levoglucosan and charcoal concentrations (Fig. 2A). The high

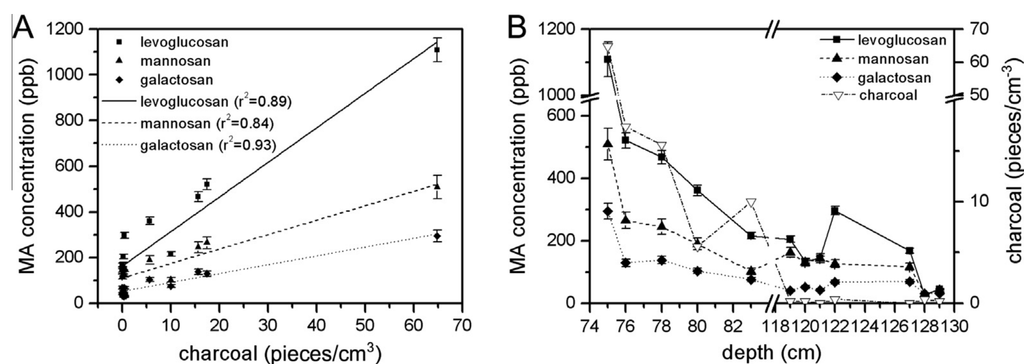

Fig. 2. (A) MA concentrations (dry wt. concentration in ppb) related to macroscopic (> 125 μm) charcoal concentration (pieces/cm³). Lines represent linear fits of the data. Error bars represent the estimated method uncertainty (B) MA concentration (dry wt. concentration in ppb) and charcoal concentration (pieces/cm³) related to sample depth (cm). Note the axis breaks.

value of the sample from 75 cm influenced the correlation and the exclusion of this sample led to a weaker correlation (r^2 0.65, 0.47 and 0.76), demonstrating that MAs in lake sediments are not only imported by macroscopic charcoal. This relationship may explain why MAs were also detected in samples without any macroscopic charcoal (> 125 μm).

Microscopic (< 50 and > 50 μm) charcoal was analyzed and detected in the core including samples from 75, 80 and 121 cm (McWethy et al., personal communication). Previous studies demonstrated that levoglucosan, mannosan and galactosan were detected in the aerosol size fractions PM 2.5 and PM 10 in the atmosphere, and burning experiments demonstrated levoglucosan concentration maxima in the coarser fractions (> PM 10) and the ultrafine fraction (< 0.49 μm; Jordan et al., 2006; Engling et al., 2009). These aerosols may be deposited in lake sediments and these fine particle fractions were not included in the charcoal analysis. Thus, analysis of MAs in lake sediments is an additional tool for reconstructing biomass burning. The present data suggest that the MAs in sediment reflect not only local the impact of biomass burning, but also record regional fire activity, since fine aerosol fractions survive long distance transport.

3.6. Comparison with MA emission ratios

Pollen analysis of the core demonstrate a change in the primary vegetation from beech (*Nothofagus* spp.) and podocarp forests in the samples from 119–129 cm to beech (*Nothofagus* spp.) and podocarp forests with increasing amounts of bracken (*Pteridium*), native grasses (*Poaceae)* and shrubs (*Coriaria* and *Coprosma* spp.) in the samples from 75–83 cm (McWethy et al., personal communication). The correlation of levoglucosan, mannosan and galactosan with each other ($p < 0.01$; Spearman rank correlation) indicates a similar transport and deposition behavior of all three isomers. If we further assume that all three isomers are equally stable in the atmosphere and in lake sediments, levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) ratios may be a tool for determining changes in vegetation at the source regions of the aerosol particles. The average ratios of levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) in the samples from 119–129 cm were 1.3 ± 0.5 and 0.9 ± 0.3 and for the samples from75–83 cm 2.0 ± 0.1 and 1.3 ± 0.1 (see Table 1). The different ratios may reflect the change in the primary vegetation, corresponding with the Lake Kirkpatrick pollen data (McWethy et al., personal communication).

However, the differences are not significant and the greater standard deviation for the deeper samples (119–129 cm) is due to the ratio for the 122 cm sample, which is more similar to the ratios of the upper samples. The 122 cm sample had the highest levoglucosan concentration in the 119–129 cm section and may be impacted by relatively distant sources as discussed above.

In addition, the ratios are in the range of published (Fabbri et al., 2009 and references within) emission ratios of (levoglucosan/mannosan and levoglucosan/(mannosan + galactosan) for different types of vegetation, such as softwood (0.6–13.8, 0.4–6.1), hardwood (3.3–22, 1.5–17.6) and grass (2.0–33.3, 1.7–9.5). The wide range in ratios for the same type of vegetation might be a result of different combustion conditions, which yield different emission ratios (Kuo et al., 2011b). This influence on the emission of MAs may further limit the use of the ratios to track back to specific vegetation.

If the MA ratios for lake sediment cores can be used to reconstruct specific burned vegetation and not only demonstrate general changes, burning experiments with the primary local vegetation would be necessary and should be compared with MAs in sediment cores over longer timescales. In the present study we analyzed only selected samples to validate the analytical method and, thus, the small dataset limits a deeper evaluation of the suitability of these ratios. However, the results are promising, with evidence that a change in primary vegetation may influence MA ratios in sediment cores.

4. Conclusions

The molecular markers levoglucosan, mannosan and galactosan in sediment samples were successfully separated and determined using high performance anion-exchange chromatography–mass spectrometry. All three markers correlated with charcoal, a local marker for biomass burning. However, the MA records may also have been influenced by more distant sources than charcoal. To the best of our knowledge the data are the first record of the three MAs from lake sediment samples. Therefore, some uncertainty exists, which may bias the new records, including multiple burned vegetation types, different combustion conditions, distance to potential sources and stability of the compounds in water and sediment. Future work should examine whether post-depositional effects such as degradation or redistribution change the ratios to the point that they no longer represent specific source emission ratios. The analysis of molecular markers in sediment cores is a fairly new but developing field with the possibility of addressing fundamental assumptions and unknowns in fire science.

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– "EARLYhumanIMPACT". This is EARLYhumanIMPACT contribution #9. The authors would like to thank the two anonymous referees for valuable comments, which helped improve the manuscript. We also thank C. Whitlock for providing samples and scientific discussions and R. Zangrando for fruitful discussions, as well as A. Hofer and B. Pavoni for freeze-drying the samples. Finally, we would like to thank Thermo Fisher Scientific for MSQplus support.

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