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Sofia Ninnes and Julie Tolu contributed equally to this work.

Key Points:

- Pyrolysis-GC/MS yields detailed molecular information on lake organic matter sources and sediment preservation conditions
- Organic matter composition is highly dynamic throughout the Holocene and shows similar trajectories in the two adjacent boreal lakes

Supporting Information:

- Supporting Information S1
- Table S2
- Table S5

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Investigating molecular changes in organic matter composition in two Holocene lake-sediment records from central Sweden using pyrolysis-GC/MS

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Abstract Organic matter (OM) is a key component of lake sediments, affecting carbon, nutrient, and trace metal cycling at local and global scales. Yet little is known about long-term (millennial) changes in OM composition due to the inherent chemical complexity arising from multiple OM sources and from secondary transformations. In this study we explore how the molecular composition of OM changes throughout the Holocene in two adjacent boreal lakes in central Sweden and compare molecular-level information with conventional OM variables, including total carbon, total nitrogen, C:N ratios, δ^{13}C, and δ^{15}N. To characterize the molecular OM composition, we employed a new method based on pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS), which yields semiquantitative data on >100 organic compounds of different origin and degradation status. We identify large changes in OM composition after deglaciation (circa 8500 ± 500 B.C.), associated with early landscape development, and during the most recent 40–50 years, driven by degradation processes. With molecular-level information we can also distinguish between natural landscape development and human catchment disturbance during the last 1700 years. Our study demonstrates that characterization of the molecular OM composition by the high-throughput Py-GC/MS method is an efficient complement to conventional OM variables for identification and understanding of past OM dynamics in lake-sediment records. Holocene changes observed for pyrolytic compounds and compound classes known for having different reactivity indicate the need for further paleo-reconstruction of the molecular OM composition to better understand both past and future OM dynamics and associated environmental changes.

1. Introduction

The transport and fate of organic matter (OM) in lake systems are fundamental to many in-lake and global elemental cycles, including carbon (C), key nutrients such as nitrogen (N) and phosphorus, and (trace) metals that play critical roles in ecotoxicology, such as mercury [*Sloth et al.*, 1995; *van Luijn et al.*, 1999; *Tranvik et al.*, 2009; *Sunendra et al.*, 2015; *Bravo et al.*, 2017]. In boreal and subarctic lakes, OM is often the largest fraction of the sediment matrix on a dry weight basis and commonly in the range of 20 to 60% [e.g., *Bigler and Hall*, 2002; *Chmiel et al.*, 2015]. This is followed or equaled by biogenic silica (e.g., 0.2–62% in surface sediments from 94 Swedish lakes [*Meyer-Jacob et al.*, 2014]), with the remainder of the sediment consisting of detrital mineral matter, authigenic minerals, and elements bound to OM. OM in lake systems is a mixture of molecules deriving from plant, algal, animal, fungal, and bacterial residues. The quality, or molecular composition, of lake-sediment OM varies, depending not only on the source but also on the extent of biotic and abiotic processing [*Tranvik and Bertilsson*, 2001; *Kothawala et al.*, 2014; *Kellerman et al.*, 2015; *Bravo et al.*, 2017]. The molecular composition strongly influences a range of biochemical reactions, for example, phosphorus cycling [*Kleeberg*, 2013], speciation of aluminum [*Hagvall et al.*, 2015], and bacterial growth and production [*Gudasz et al.*, 2012], the last of which in turn affect the extent of methylmercury production [*Bravo et al.*, 2017].

Empirical studies on ongoing environmental changes, such as recovery from soil acidification and climate change, have shown that the quantity of OM in lake water is increasing [e.g., *Freeman et al.*, 2001; *Monteith et al.*, 2007], and there is considerable uncertainty regarding future trajectories and effects on lake ecosystems [*Solomon et al.*, 2015]. Paleolimnological reconstruction of past OM dynamics in lake systems is key to improving our understanding of how environmental changes impact the OM fraction in lake sediment.

So far, reconstructions have mainly relied on well-established analyses such as loss on ignition to estimate the total OM content (cf. the citation record of *Heiri et al.* [2001]), total organic carbon (TOC) and nitrogen (TN) contents as well as their ratio (C:N), and stable isotopic compositions (δ^{13}C and δ^{15}N) [e.g., *Hu et al.*, 2001; *Hammarlund et al.*, 2004; *Finney et al.*, 2012; *Mackay et al.*, 2012; *Ilyashuk et al.*, 2013; *Finkenbinder et al.*, 2014; *Rantala et al.*, 2015a, 2015b]), which we hereafter refer to as "conventional OM variables." However, interpreting changes in C:N, δ^{13}C, and δ^{15}N in natural samples is often difficult due to overlapping signatures for OM sources [*Meyers and Ishiwatari*, 1993] and degradation processes [*Gälman et al.*, 2008, 2009], and due to isotopic depletion as a result of the last 150 years' atmospheric emissions [*Friedli et al.*, 1986; *Keeling et al.*, 1989; *Holtgrieve et al.*, 2011]. A few studies have complemented these parameters with an OM characterization using "Rock-Eval" pyrolysis [*Wohlfarth et al.*, 2004] or infrared spectroscopy [*Rosén and Hammarlund*, 2007; *Rosén et al.*, 2011; *Michelutti et al.*, 2010; *Bragée et al.*, 2015]. In other studies, mass spectrometry-based methods, requiring fastidious, time-consuming, and compound-specific extractions, have been used to identify a limited number of organic molecules (biomarkers), such as lignin oligomers for the identification of terrestrially derived OM [*Moingt et al.*, 2014; *Chmiel et al.*, 2015], and *n*-alkanes for estimation of terrestrial and aquatic OM source inputs [*Bragée et al.*, 2013].

In this study, we characterize the molecular composition of OM in the Holocene sediment records from two adjacent boreal forest lakes, Lång-Älgsjön and Dragsjön, located in south central Sweden, using a newly optimized pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) method [*Tolu et al.*, 2015]. We then compare these results to trends in total carbon (TC) and TN contents, C:N ratios, δ^{13}C, and δ^{15}N. Beyond the fast analysis and data treatment, and the small sample mass required (200 μg), our Py-GC/MS method yields semiquantitative data on $>$100 organic compounds belonging to different organic compound classes (e.g., lignin oligomers, chlorophylls, carbohydrates, and N compounds) and reflecting different origins and degradation states [*Tolu et al.*, 2015]. Our two study lakes are located only 700 m apart and are both characterized by floating *Sphagnum* mats along most of their shorelines and by adjoining peatlands. Given the short distance between the lakes, which minimizes differences in geology, climate, vegetation, and land use histories, and their comparable lake characteristics (catchment, size, and water depth), we expect similar trajectories for changes in OM composition in both lakes over time. A recent study of the sediment record from Lång-Älgsjön using biological (pollen and diatoms) and inorganic geochemical proxies provided information about the natural Holocene baseline conditions and human impacts on the landscape at the catchment scale [*Meyer-Jacob et al.*, 2015], allowing for a comprehensive interpretation of our Py-GC/MS data.

Our specific objectives are to (i) provide a characterization of the changes in the molecular composition of sedimentary OM in two boreal lakes in south central Sweden throughout the Holocene and (ii) compare the changes in the sedimentary molecular OM composition with those recorded by conventional OM variables (TC, TN, C:N ratios, δ^{13}C, and δ^{15}N), in order to assess how the information obtained from the two approaches affects the identification and interpretation of long-term changes in OM dynamics.

2. Materials and Methods

2.1. Site Description

The two study lakes Lång-Älgsjön (435 m above sea level, 60°24′18″N, 15°07′21″E) and Dragsjön (432 m above sea level, 60°23′41″N, 15°07′16″E) are situated 700 m apart in the boreal forest of south central Sweden (Figure 1). The lakes have similar surface areas (4.4–4.6 ha) and have maximum depths of 12 and 6 m, respectively, and the shorelines of both lakes are lined with floating mats of *Sphagnum*. The catchment of Lång-Älgsjön extends over ~70 ha and drains to the north. Extensive peatlands are found in the eastern and southwestern parts of the lake's catchment, covering approximately 33% of the catchment, and border approximately half of the lake's shoreline. Two smaller lakes draining the southwestern catchment are located upstream of Lång-Älgsjön. Dragsjön has a slightly larger catchment, ~90 ha, and drains to the south. Peatlands cover approximately 14% of the catchment, though direct connection with Dragsjön is limited to the southern shoreline. Surrounding soils are predominately shallow ($<$1 m) and developed on blocky glacial till [*Geological Survey of Sweden*, 2016]. In this region, human land use in the form of forest grazing and haymaking on mires extends back to A.D. 900–1500 [*Segerström and Emanuelsson*, 2002; *Bindler et al.*, 2011; *Meyer-Jacob et al.*, 2015]. There is evidence for past charcoal production, in the form of relict charcoal kilns, and timber harvesting within the general study area [*Länsstyrelsen Kopparbergs län*, 1971], but the

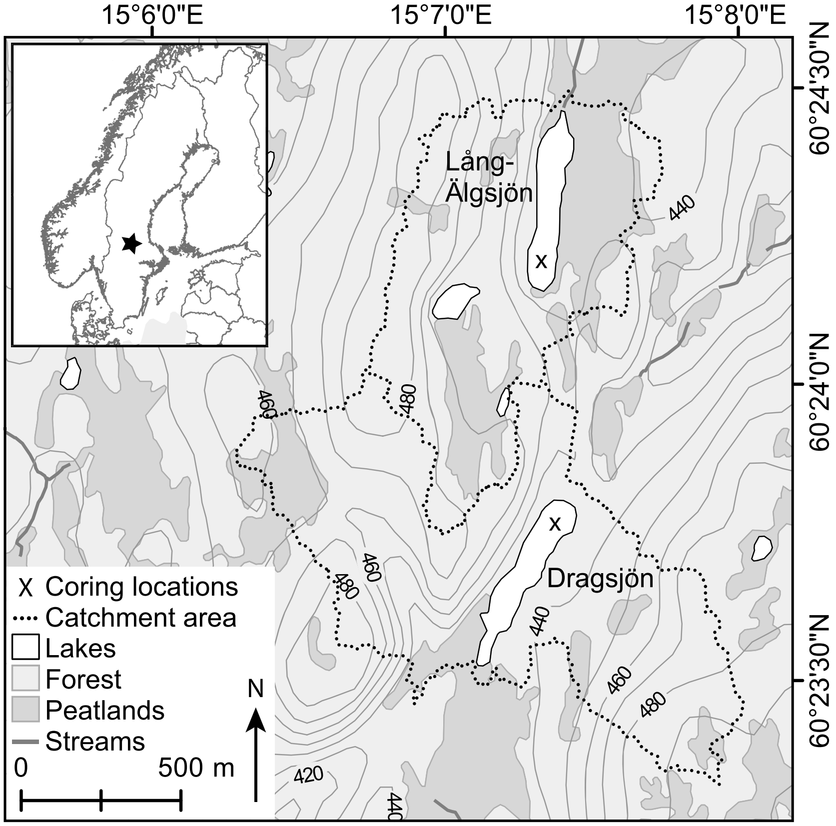

Figure 1. Map of Lång-Älgsjön and Dragsjön showing the coring locations, lake catchment areas, topography, and present-day land cover. Inset: location of study area in Scandinavia.

timing and extent of these activities within the catchments of Lång-Älgsjön and Dragsjön are uncertain. The study area is within the low atmospheric N deposition zone of northern Sweden, with a mean wet deposition of 3.8 kg N ha^{-1} yr^{-1} during the period of 1995–2001 [*Bergström et al.*, 2005].

2.2. Sample Recovery and Dating

A 2.9 m long sediment profile was collected at 5.8 m depth in the northern part of Dragsjön in 2014 and consisted of a gravity core (0–54 cm) and a series of overlapping Russian peat cores (1 m long, 8 cm diameter). From Lång-Älgsjön, a 3.4 m long profile was collected in 1998, also employing a series of overlapping Russian peat cores but using a freeze corer for the top 25 cm of sediment [*Meyer-Jacob et al.*, 2015]. Cores were recovered from the southern basin at a depth of 10.8 m and stored frozen or in the cooler at 4°C until analysis in 2012/2013. All sediment samples were freeze-dried and finely ground before further analysis. A total of 61 samples were analyzed from Dragsjön and 30 samples from Lång-Älgsjön.

The age-depth model for Lång-Älgsjön has been previously published by *Meyer-Jacob et al.* [2015]. Briefly, the model was established with a combination of spheroidal carbonaceous fly ash particles age markers (upper 10 cm), correlation of stable lead isotopes ratios (^{206}Pb/^{207}Pb) from Lång-Älgsjön (upper 120 cm) with the varved sediment record from Kalven, 56 km SE [*Bindler et al.*, 2011] and two accelerator mass spectrometry (AMS) ^{14}C ages from the lower part of the profile (111–236.5 cm). The basal age was set to 10500 ± 500 calendar years (cal years) B.P. (1950) based on the estimated time of deglaciation for the area. For Dragsjön, the age-depth model was constrained by three AMS ^{14}C dated terrestrial macrofossils complemented by three ages from the last 760 years that were obtained from matching of the Pb records for Dragsjön and Lång-Älgsjön, as well as the varve-based chronology from Kalven [*Bindler et al.*, 2011; *Meyer-Jacob et al.*, 2015] (Figure S1 and Table S1 in the supporting information). One carbon age was corrected for a 200 year reservoir effect based on the expected timing of establishment of *Picea abies* (L.) H. Karst. ([*Giesecke and Bennett*, 2004; *Giesecke*, 2005], Text S1 in the supporting information). Similar to the age-depth model for Lång-Älgsjön, the basal age was set to 10,500 ± 500 cal years B.P. (1950) [*Geological Survey of Sweden*, 2016]. The age-depth model was produced using CLAM 2.2 [*Blaauw*, 2010] and the IntCaL13-14C calibration curve [*Reimer et al.*, 2013].

The reliability of the timing of changes between the cores and their correspondence with established trajectories for landscape development has been evaluated by comparison of pollen curves for Lång-Älgsjön [*Meyer-Jacob et al.*, 2015], Dragsjön, and Holtjärnen, 30 km NW [*Giesecke*, 2005; *European Pollen Database*, 2016]. Pollen samples from Dragsjön were prepared and analyzed using standard methods as described by *Barber* [1976]. At least 500 terrestrial pollen grains were counted per sample, and the pollen data are expressed as percentages of total terrestrial pollen. Pollen curves for *Alnus*, *Tilia*, and *Picea* indicate an overall good agreement between these records and with trajectories for regional vegetation changes (Figure S2). However, because the lower halves of the profiles are poorly constrained, the basal ages are associated with large (±500 years) uncertainties.

Table 1. Certified Standard Reference Materials (SRMs) Used for Calibration of $\delta^{13}C$ and $\delta^{15}N$ Analyses[a]

SRM	$\delta^{13}C$, ‰ VPDB	$\delta^{15}N$, ‰ Air
IAEA-600	−27.771	+1.0
IAEA-CH-6	−10.449	–
IAEA-N-2	–	+20.3
USGS40	−23.389	−4.5
USGS41	–	+47.6

[a] Measurements of $\delta^{13}C$ are referenced to Vienna Peedee belemnite (VPDB) and $\delta^{15}N$ to air (0‰),

2.3. Conventional OM Variables and Molecular Characterization by Py-GC/MS

Total C and N contents were determined with a Flash 2000 Organic Elemental Analyzer (Thermo Fisher Scientific), interfaced with an isotope ratio mass spectrometer (DeltaV, Thermo Fisher Scientific) for the isotope analyses, at the Swedish University of Agricultural Sciences (SLU) in Umeå. Sample sizes ranged from 1.9 to 11.0 mg depending on an estimated range of carbon content for each sample. For determination of $\delta^{13}C$ a two-point linear normalization was used and for $\delta^{15}N$ single-point anchoring with a control. Laboratory standards were maize ($^{13}C = -11.0$‰, $^{15}N = 1.9$‰) and wheat ($^{13}C = -24.7$‰, $^{15}N = 3.9$‰) flour calibrated against certified standard reference materials (Table 1). Samples for $\delta^{13}C$ and $\delta^{15}N$ are referenced to Vienna Peedee belemnite (VPDB) and AIR standards, respectively. Analytical errors were ≤0.15‰ for isotope determination and ≤2% for TC and TN.

The molecular composition of OM was determined by Py-GC/MS following the method developed by *Tolu et al.* [2015]. Briefly, pyrograms were measured for 200 ± 20 μg sediment using a FrontierLabs PY-2020iD oven (450°C) connected to an Agilent 7890A-5975C GC/MS system. Peak integration and identification were performed using a data processing pipeline under "R" computational environment [*R-Development-Core-Team*, 2011], the software "NIST MS Search version 2.0" containing the library "NIST/EPA/NIH 2011" [*National Institute of Standards and Technology*, 2011] and additional spectra from published studies [*Faix et al.*, 1991; *Nguyen et al.*, 2003; *Meredith et al.*, 2008; *Buurman et al.*, 2009; *Chen et al.*, 2009; *Schellekens et al.*, 2009; *Gupta and Cody*, 2011; *Fabbri et al.*, 2012; *Sessions et al.*, 2013; *Schellekens et al.*, 2014]. Peaks extracted by the data processing pipeline were 492 and 617 for the sediment records of Dragsjön and Lång-Älgsjön, respectively. Over these extracted peaks, 152 common pyrolytic organic compounds (hereafter noted Py compounds) could be identified, altogether representing 38 ± 3% and 40 ± 4% of total extracted peak areas for the two lakes, respectively. The remaining 60% may correspond to background signals from unavoidable sample bleed after pyrolysis or to unknown pyrolytic products of natural OM compounds/structures. Details about the peak identification procedure and its accuracy are given in *Tolu et al.* [2015]. Our list of 152 identified Py compounds is highly similar to lists of compounds identified in soil, peat, and sediment samples in other Py-GC/MS studies [e.g., *Peulvé et al.*, 1996; *Buurman et al.*, 2005; *Schellekens et al.*, 2009; *Carr et al.*, 2010; *Micić et al.*, 2011]. A detailed list containing information on the molecular mass and structure, and reference for mass spectra for all 152 compounds is given in Table S2. For each identified Py compound, the peak area was normalized by setting the sum of the identified peak areas (total identified peak area) for each sample to 100%.

2.4. Statistical Analyses

A cluster analysis was performed on each sediment record separately using all the identified Py compounds in order to distinguish periods with different OM molecular composition. For this purpose, a hierarchical agglomerative cluster analysis with Wards linkages [*Ward*, 1963] and squared Euclidean distances was employed. Bivariate correlations between total identified peak area and TC were performed using the Spearman rank correlation test. All statistical analyses were performed using the "SPSS software package PASW, version 22.0" [*IBM Corporation*, 2013].

3. Results and Discussion

3.1. Identified Pyrolytic Organic Compounds and Information About Their Sources and Degradation Status

Of the 152 identified compounds, 151 were grouped into 12 pyrolytic organic compound classes (hereafter Py-compound classes, e.g., carbohydrates, N compounds, lignin oligomers, and chlorophylls) based on similarities in molecular structure and on studies that have explored the pyrolysis products of different OM sources and biochemical classes. [e.g., *Faix et al.*, 1990; *Gupta et al.*, 2007; *Fabbri et al.*, 2012]. The smallest compound, acetic acid (~2–3% of the total identified peak area), was excluded from this grouping due to the limited value as a diagnostic biomarker (potentially released during pyrolysis by different types of compounds). For both records, whole-core averages of the relative abundances (% total identified peak area) of the 12 Py-compound classes follow the order: carbohydrates (30–35%) $>$ *n*-alkanes (12–13%) ≈ *n*-alkenes (~12%) ≈ N compounds (10–12%) ≈ phenols (11–13%) $>$ chlorophylls (~5%) $>$ lignin oligomers (4–5%) ≈ steroids (3–4%) $>$ alkan-2-ones (2–3%) ≈ hopanoids (2–3%) ≈ (poly)aromatics (2–3%) $>$ tocopherols (0.5–0.6%).

Changes in the relative abundances of these Py-compound classes, and of subgroups within the Py-compound classes (specific biomarkers), can provide information about changes in OM sources and degradation status. The carbohydrates derive mainly from the pyrolysis of polysaccharides and their degradation products [*Faix et al.*, 1990; *Schellekens et al.*, 2009], although can also include microbially derived carbohydrates [*Buurman et al.*, 2005]. Carbohydrates is the dominant class of organic compounds, but plants are well known to contain much higher proportions of carbohydrates and polysaccharides compared to algae and microorganisms—the algae instead being richer in N compounds [*Bianchi and Canuel*, 2011]. Among the carbohydrates, the levosugars are pyrolysis products of polysaccharides [*Faix et al.*, 1990], an important fraction of lake sediment OM, and are thus not a proxy of fire events as when determined by chemical extraction and LC/MS. Levosugars are a reliable proxy for nondegraded OM, while the (alkyl)furans represent mainly the degradation products of polysaccharides and bacterial carbohydrates [*Schellekens et al.*, 2009]. The lignin oligomers are specific of vascular plants [*Meyers and Ishiwatari*, 1993], while phenols may derive from both nonvascular (e.g., *Sphagnum*) and vascular plants [*Faix et al.*, 1990; *Schellekens et al.*, 2009]. Among the phenols, isopropenylphenol marks the presence of *Sphagnum* [*Stankiewicz et al.*, 1997; *Schellekens et al.*, 2009]. Among the N compounds, the 2,5-diketopiperazines are specific pyrolysis products of proteins [*Fabbri et al.*, 2012], which are known to be rapidly degraded [*Nguyen et al.*, 2003]. In contrast, the (alkyl)pyrroles mainly represent degradation products of proteins and chlorophylls [*Sinninghe Damsté et al.*, 1992; *Jokic et al.*, 2004]. Similar to N compounds, chlorophylls are typically found in larger quantities in algae than in plants [*Bianchi and Canuel*, 2011] and chlorophyll content is commonly used as a proxy of algal production in aquatic ecosystems [e.g., *Peulvé et al.*, 1996; *Bianchi and Canuel*, 2011]. Of the two types of chlorophyll-derived compounds we identified, the phytadienes are more readily degraded than the pristenes [*Nguyen et al.*, 2003].

The *n*-alkanes originate from lipids of plants, algae and bacteria, each source distinguished by the C chain-length number or by a predominance of odd or even C number (see below). However, in Py-GC/MS, the specificity of these biomarkers is strongly affected by the formation of *n*-alkene/*n*-alkane doublets during pyrolysis of biomacromolecules, such as suberin, cutin, or algaenan, and by the decarboxylation reaction of carboxylic acids [*Sáiz-Jiménez*, 1994]. Both lake records contain a series of *n*-alkene/*n*-alkane doublets from C12 to C28, which means that only the identified *n*-alkanes C29, C31, and C33 can be inferred as deriving from plant lipids. Therefore, we use the sum of *n*-alkanes and *n*-alkenes as proxies for resistant and degraded OM, considering that these aliphatic compounds, especially the short-chain compounds, are also formed during OM degradation [*Schellekens et al.*, 2009]. The sum of (poly)aromatics is used as a proxy for resistant and degraded OM, given that most of the identified compounds within this class are alkyl-benzenes, which may result from cyclization of aliphatic compounds during pyrolysis or indicate polycondensation of OM, which occurs during diagenesis [*Burdige*, 2007]. The alkan-2-ones may arise with oxidation of *n*-alkanes

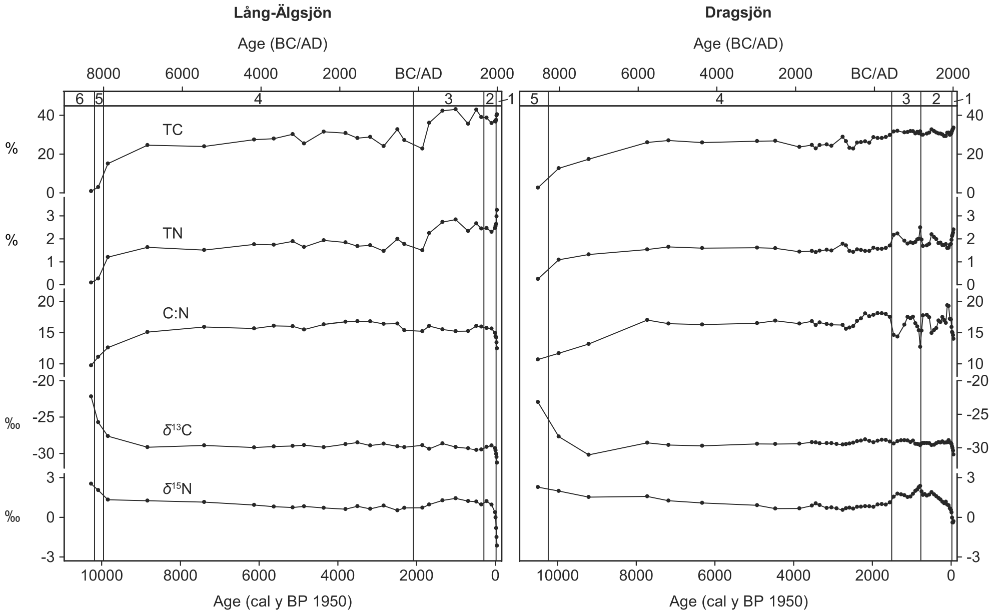

Figure 2. Holocene changes in trends for conventional OM variables (TC, TN, C:N, δ^{13}C, and δ^{15}N) for the sediment records of (left) Lång-Älgsjön and (right) Dragsjön. The numbers above indicate clusters (1–6).

[*Zheng et al.*, 2011] but are also specific biomarkers for plants living in humid environments, such as peatland plants and aquatic macrophytes, with alkan-2-ones C23–25 being more specific to *Sphagnum* and C27–C33 being more specific to vascular plants [*Baas et al.*, 2000; *Hernandez et al.*, 2001; *Nichols and Huang*, 2007].

Steroids are abundant in most organisms but have rarely been reported in previous Py-GC/MS studies, especially not for aquatic matrices. However, within this Py-compound class, the sterol forms are a useful proxy for OM degradation status because of the high susceptibility to degradation [*Mackenzie et al.*, 1982]. Hopanoids are known to derive from the cell membranes of prokaryotes, especially bacteria [*Meredith et al.*, 2008; *Sessions et al.*, 2013], but have not been determined directly with Py-GC/MS and are rarely reported [*Buurman et al.*, 2005]. Similarly, the tocopherols are abundant in most photosynthetic organisms, because of their fundamental role in the photosynthetic process [*Maeda and DellaPenna*, 2007]. Due to the limited value as diagnostic biomarkers and the very low abundances in our lake sediment records, data on hopanoids and tocopherols are only presented in Tables S1–S3 and S5. These data will not be further discussed in this study because the aim here is to provide a first characterization of the molecular OM composition and a first comparison between conventional OM variables and molecular OM composition over the Holocene, rather than a detailed paleo-reconstruction of factors and processes driving past OM dynamics.

3.2. Holocene Trends in OM Molecular Composition

To identify periods with different OM molecular composition during the Holocene, we performed a cluster analysis for each sediment record using the relative abundances of the 152 identified Py compounds. The output of this statistical analysis is a grouping of sediment samples into clusters based on similarities and differences in OM molecular composition. The operator specifies the number of clusters, and, having evaluated the outputs for 5–10 clusters (data not shown), we decided to present the results using six clusters for Lång-Älgsjön and five clusters for Dragsjön. This means presenting the 5–6 groups of sediment samples that show the greatest similarities (within clusters) and differences (between clusters) in molecular OM composition. Groupings are then interpreted together with trends for conventional OM variables (TC, TN, C:N, δ^{13}C, and δ^{15}N; Figure 2), Py-compound classes (Figure 3), and specific biomarkers (Figure 4). Changes in therelative abundances of OM classes and specific biomarkers between clusters are described and discussed based on averages ±1 standard deviation (SD). Average relative abundance and associated SD of conventional OM variables, Py-compound classes, and specific biomarkers for each cluster are given in Tables S3 and S4, and for each sample in Table S5.

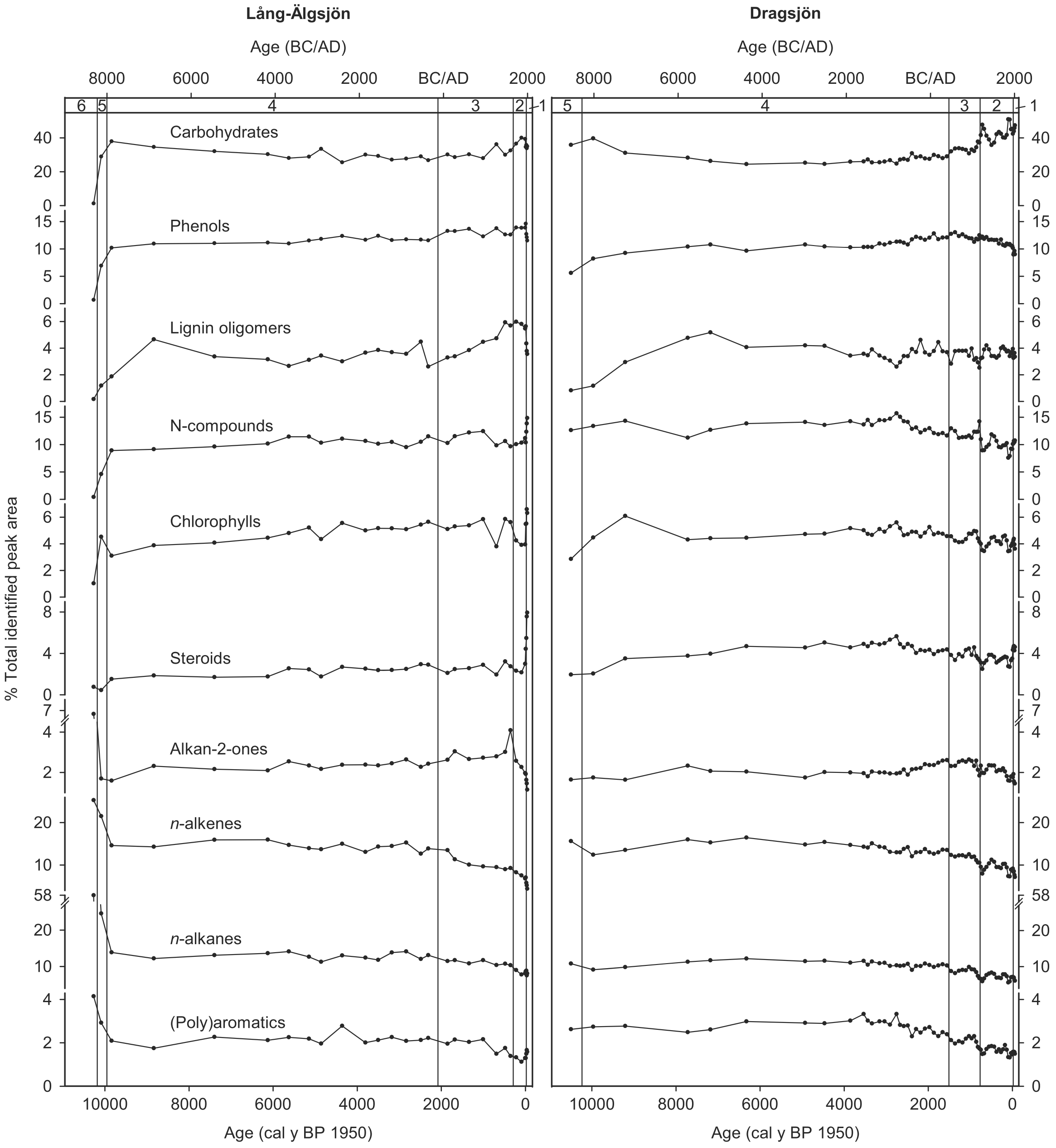

Figure 3. Holocene changes in relative abundances (% total identified peak area) of Py-compounds classes for the sediment records of (left) Lång-Älgsjön and (right) Dragsjön. The numbers above indicate clusters (1–6).

3.2.1. Post-Glacial, >7900 B.C.

For Lång-Älgsjön, the sediment samples deposited before circa 7900 B.C. are separated into cluster 6 (C6; 1 sample; circa 8300 B.C.) and C5 (1 sample; circa 8100 B.C.) and one sample is included in C4 (14 samples, 8000–130 B.C.). For Dragsjön, sediments aged >7900 B.C. are represented in C5 (1 sample, circa 8500 B.C.) and sediments aged 8000 B.C. to A.D. 440 grouped into C4 (27 samples). The conventional OM variables are in good agreement with the outputs of the cluster analyses, which are based on the molecular OM composition (Figure 2). Sediments of C6 and C5 for Lång-Älgsjön and C5 for Dragsjön present the lowest TC (<3%), TN (<0.3%) and C:N (<10), and the highest δ^{13}C (−22.2 to −23.2‰). For Lång-Älgsjön, TC and TN increase from 0.9 to 3% and from 0.1 to 0.3%, respectively, from circa 8300 B.C. (C6) to circa 8100 B.C. (C5). TC and TN increase further to 15% and 1.2%, respectively, by circa 7900 B.C. Over the same time period (8300 to 7900 B.C.) C:N increases from 10 to 13 and δ^{13}C and δ^{15}N decline by 5.4‰ and 1.2‰,

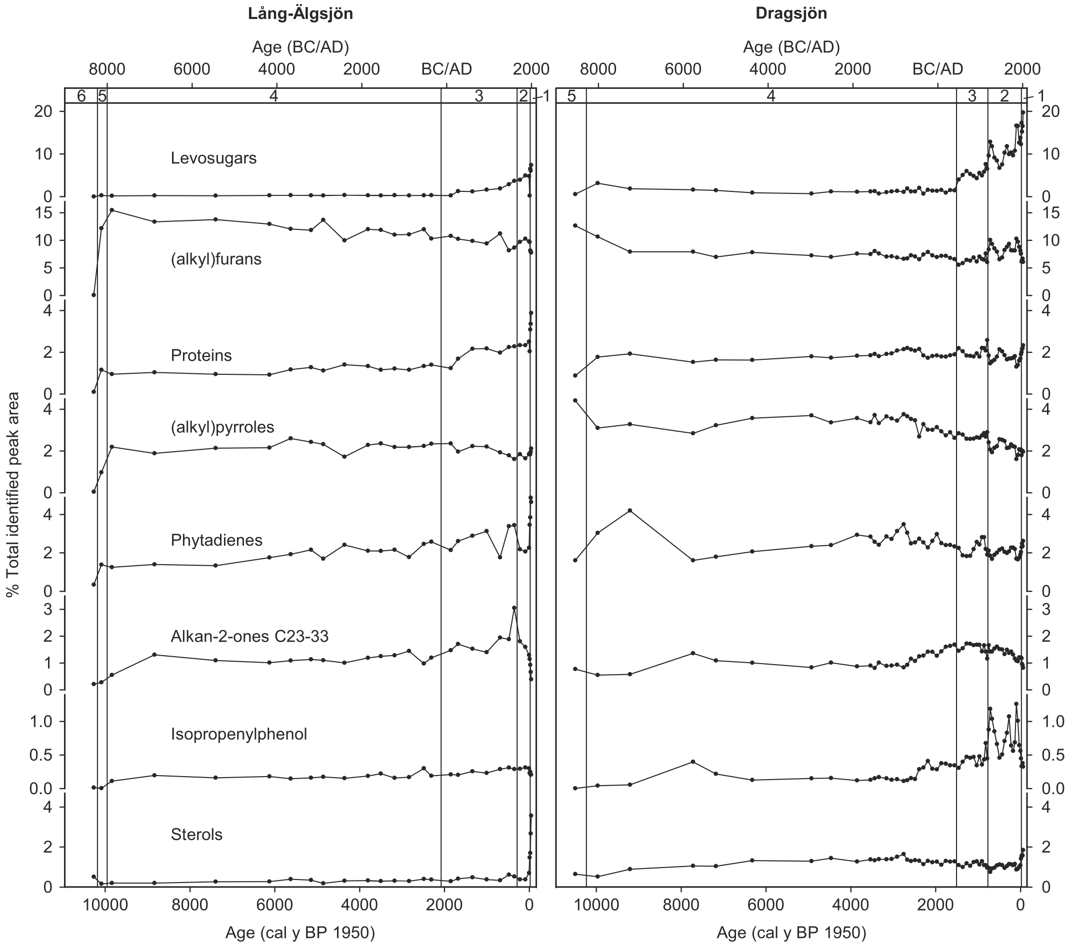

Figure 4. Holocene changes in relative abundances (% total identified peak area) of specific biomarkers for the sediment records of (left) Lång-Älgsjön and (right) Dragsjön. The numbers above indicate clusters (1–6).

respectively. For Dragsjön, the TC and TN contents at circa 8500 B.C. (C5; 2.7 and 0.3%, respectively) are more similar to the contents in sediments deposited at circa 8100 B.C. than at circa 8300 B.C. for Lång-Älgsjön, but TC and TN increase to 13 and 1.1%, respectively, by circa 8000 B.C., which is similar to TC and TN contents found at circa 7900 B.C. in Lång-Älgsjön. In Dragsjön, from circa 8500 to 8000 B.C., C:N increases from ~11 to 12, while δ^{13}C and δ^{15}N decline by 5.1‰ and 0.3‰, respectively.

The differences in TC and TN before circa 8000 B.C. between Lång-Älgsjön and Dragsjön could be related to differences in OM inputs or preservation between the two lakes but are more likely due to age-depth model limitations for the early Holocene. The changes in relative abundances of Py-compound classes further indicate age-depth model limitations during this period because the changes in OM composition from C5 to C4 for Dragsjön are overall more similar to changes in Lång-Älgsjön occurring between C5 (circa 8100 B.C.) and circa 8000 B.C. than between C6 (circa 8300 B.C.) and C5 (circa 8100 B.C.) (Figure 3). For Lång-Älgsjön, relative abundances of carbohydrates, phenols, lignin oligomers, and N compounds increase 7–23 times from 8300 B.C. (C6) to circa 8100 B.C. (C5), followed by further increases in phenols, lignin oligomers, N compounds (2–3 times), and steroids (5 times) by circa 8000 B.C. For Dragsjön, phenols, lignin oligomers, chlorophylls, steroids increase 2–5 times from circa 8500 B.C. (C5) to circa 8000 B.C. Another difference between the lakes during this period is that increases in the relative abundances of intact molecules from plants (e.g., lignin oligomers and phenols) and algae (i.e., chlorophylls and N compounds) are accompanied by a substantial decrease of the degraded OM pool in Lång-Älgsjön, as shown by the relative abundances of *n*-alkanes, *n*-alkenes, alka-2-ones, and (poly)aromatics, while for Dragsjön the abundances of these Py-compound classes indicative of degraded OM remain stable.

Despite limitations of the age-depth models for the oldest sediment levels, both records show major shifts in all conventional OM variables $>$7900 B.C. With an estimated time of deglaciation of 8500 ± 500 B.C. [*Geological Survey of Sweden*, 2016], the development for the conventional OM variables is characteristic for recently deglaciated lakes [*Engstrom et al.*, 2000; *Fritz and Anderson*, 2013] and can be linked to the establishment and development of catchment vegetation, reduced catchment erosion, and increased in-lake productivity [e.g., *Reuss et al.*, 2010; *Ilyashuk et al.*, 2013; *Chmiel et al.*, 2015; *Meyer-Jacob et al.*, 2015; *Rantala et al.*, 2015b]. Declines in δ^{13}C may be the result of increased aquatic respiration and supply of δ^{13}C-depleated plant OM but can also represent a reduced influence of inorganic C (IC) from glacial debris [*Hammarlund*, 1993; *Wolfe et al.*, 1999]. The latter is, however, less likely, because carbonates are not known to occur in the area [*Geological Survey of Sweden*, 2016], and Fourier transform infrared spectroscopic measurements for the two sediment records show no absorbance-peaks in the wavelength ranges corresponding to IC, and thus, the samples are carbonate-free [*Rosén et al.*, 2010]. Additionally, TC contents are significantly positively correlated with the sum of the identified peak areas of the 152 identified Py compounds, with correlation coefficients of 0.78–0.81 ($p < 0.01$; Figure S3 and Text S2). This strongly suggests that variations in TC are mainly driven by variations in the OC content in our two study lakes. Overall, our two sediment records, like many other lake sediment records, demonstrate that the initial period after deglaciation was associated with large changes in environmental conditions and that these initial dynamics are well reflected by conventional OM variables. Molecular data on sediment OM obtained by our high throughput Py-GC/MS method corroborate conventional OM variables by the large changes in the molecular OM composition toward greater proportions of intact molecules from plants and algae, and for Lång-Älgsjön also the substantial decrease of the degraded OM pool.

3.2.2. Early to Early Late Holocene, <7900 B.C.–Circa A.D. 300

The sediments accumulated from circa 8000 to 130 B.C. in Lång-Älgsjön and from 8000 B.C. to A.D. 440 in Dragsjön were grouped together into a single cluster for each lake (C4; Table S3), suggesting that overall, the OM molecular composition of the sediments is similar during this period. The conventional OM variables display more stable trends during C4 compared to earlier and later time periods, even though there is some variability (Figure 2). From circa 7900 to 6900 B.C. for Lång-Älgsjön, and from 8000 to 5800 B.C. for Dragsjön, we observe substantial increases in TC (by 10–14%) and C:N (by 3–5). There are also small increases in TN (by 0.4–0.5%) and declines in δ^{13}C by ~1‰. These changes are more gradual for Dragsjön than Lång-Älgsjön and could indicate that the buildup of catchment and in-lake OM pools continues until 6900 and 5800 B.C. for Lång-Älgsjön and Dragsjön, respectively, but at increasingly slower rates [*Fritz et al.*, 2004]. The increase in C:N could also be interpreted as reflecting an increasing importance of terrestrial input relative to in-lake algal production [*Meyers and Ishiwatari*, 1993]. After 6900 B.C. for Lång-Älgsjön and 5800 B.C. for Dragsjön, TC, TN, C:N, and δ^{13}C do not show any specific trend, while for δ^{15}N we observe a slow, steady decline. With the generally warm and dry climatic conditions in Fennoscandia during the middle to early late Holocene [*Seppä et al.*, 2005; *Seppä et al.*, 2009], stable catchment conditions are often inferred for this period [*Reuss et al.*, 2010; *Rosén et al.*, 2011; *Rantala et al.*, 2015b].

From 7900 to circa 6900 B.C. in Lång-Älgsjön, the molecular OM composition shows increasing abundances of lignin oligomers (proxy of vascular plants), isopropenylphenol (proxy for *Sphagnum*), and alkan-2-ones C23–C33 (proxy for plant living in humid environments), while the proportions of algal-derived (N compounds and chlorophylls) and degraded OM (*n*-alkanes and *n*-alkenes) remain stable (Figures 3 and 4). The molecular OM composition thus indicates an increase in plant OM, which is in agreement with the conventional OM variables, and support the early development of peatlands at Lång-Älgsjön inferred from *Sphagnum* leaf counts [*Meyer-Jacob et al.*, 2015]. For Dragsjön, the abundances of lignin oligomers and phenols also clearly follow the increase in TC from 8000 to 5800 B.C. Isopropenylphenol and alkan-2-ones C23–C33 increase later, from circa 7300 B.C., while algal-derived organic compounds (N compounds and chlorophylls) increase from 8000 to 7300 B.C. and subsequently decrease until 5800 B.C. The differences in timing between the lakes may be due to age-depth model uncertainties but could also be related to divergence in early peatland development within the catchments, given current differences in peatland-lake connectivity.

While trends for TC, TN, C:N, and δ^{13}C remain relatively stable after 6900 B.C. and 5800 B.C. for Lång-Älgsjön and Dragsjön, respectively, a number of Py-compound classes and specific biomarkers, for example, lignin oligomers, phytadienes, and steroids, are highly variable in C4. If the number of clusters for each lake were increased by one cluster, C4 would be split into two periods: 8000–3900 B.C. and 3900–130 B.C. for Lång-Älgsjön and 8000–500 B.C. and 500 B.C.–A.D. 440 for Dragsjön. This highlights that the molecular OM composition is more dynamic than can be elicited from conventional OM variables alone. However, further studies using higher-resolution subsampling and complementary parameters, such as sediment geochemistry, are needed in order to discuss the environmental changes associated with these compositional changes. Based on the principle of hierarchical cluster analyses, the differences between these two additional clusters are less important than the differences between the 5–6 clusters presented and discussed in detail. This means that when considering all identified organic compounds, molecular OM composition is more stable during this early to early late-Holocene compared with earlier and later periods.

3.2.3. Late Holocene, Circa A.D. 300–Circa 1970

For both records, the late Holocene (until circa A.D. 1970) is separated into two clusters: C3 spans 130 B.C.–A.D. 1660 for Lång-Älgsjön and A.D. 440–1180 for Dragsjön and C2 A.D. 1660–1970 and A.D. 1180–1970, for each lake, respectively. These results suggest two periods with different OM composition during the late Holocene. The conventional OM variables display different trends (Figure 2). For Lång-Älgsjön, TC averages 28 ± 3% from 6900 B.C. to A.D. 100 increasing to 39 ± 3% from A.D. 100 to 1960, while TN increases from 1.7 ± 0.2% to 2.5 ± 0.2%, and the C:N ratio remains stable, averaging 16.0 ± 0.6 and 15.5 ± 0.5. For Dragsjön, TC and C:N start to increase at circa 400 B.C. and by A.D. 390 TC stabilizes. Overall, the change in TC is more gradual for Dragsjön than Lång-Älgsjön. From A.D. 390 to 1960 TN and, consequently, C:N fluctuate considerably. The δ^{13}C does not show any substantial variation with averages of -29.1 ± 0.3‰ for Lång-Älgsjön from 6900 B.C. to A.D. 1960 and -29.2 ± 0.2‰ for Dragsjön from 5770 B.C. to A.D. 1950. In contrast to δ^{13}C, δ^{15}N increases from circa A.D. 370 to A.D. 1900 and peaks at 1.4‰ in Lång-Älgsjön at A.D. 940 and at 2.4‰ in Dragsjön at A.D. 1160 (Figure 2). Therefore, while TC and TN point toward a change in OM content and δ^{15}N toward altered N cycling from circa 400 B.C.–A.D. 100, none of the conventional variables indicate a second change in OM composition before A.D. 1960 as suggested by the cluster analyses. Compared to the early to early late Holocene (C6–C4), the molecular OM composition in C3–C2 is characterized by (i) higher proportions of plant OM and (ii) higher proportions of nondegraded OM.

For Lång-Älgsjön, the abundance of alkan-2-ones C23–C33 increases from 1.2% at 360 B.C. to 1.7% at A.D. 270, and after a small decline, peaks at 3.1% at A.D. 1590 (Figure 4). Phenols increase from 11.5 to 13.6% from 360 B.C. to A.D. 610, then fluctuates between 12.3 and 14.6% until A.D. 1960 (Figure 3). Lignin oligomers show an increasing trend from 360 B.C. until A.D. 1470 and isopropenylphenol from A.D. 270 to 1260, after which abundances stabilize, averaging 5.8% from A.D. 1470 to 1960 and 0.3% from A.D. 1260 to 1940, respectively. Alongside increases in OM from both vascular and nonvascular (e.g., *Sphagnum* and other mosses) plants, abundances of levosugars, and proteins show that the proportion of nondegraded OM from plants and algae, respectively, is also increasing from A.D. 100. N compounds and chlorophylls are relatively stable until circa A.D. 940, after which N compounds decline by 3% to A.D. 1260 and chlorophylls fluctuate between 3.8 and 5.9%, whereas the abundances of *n*-alkanes, *n*-alkenes, and (poly)aromatics show that the proportion of degraded and resistant OM declines. These changes in the molecular OM composition occur concomitant to increases in TC and TN and are most likely linked to natural processes resulting in increased catchment OM inputs and enhanced preservation of lake sediment, such as expansion of adjacent peatlands and floating mats of *Sphagnum*/aquatic macrophytes along the shoreline [*Nichols and Huang*, 2007; *Ortiz et al.*, 2011]. These processes have been previously discussed by *Meyer-Jacob et al.* [2015] based on observations of an alteration of the diatom community structure and a decline in diatom production at circa A.D. 200 in Lång-Älgsjön. Expanding peatlands may increase OM freshness through a greater supply of organic plant residues, leading to more anoxic conditions at the sediment-water interface [*Kleeberg*, 2013] and subsequently lower rates of OM degradation [*Bastviken et al.*, 2004; *Isidorova et al.*, 2016]. The abundances of plant (lignin oligomers and isopropenylphenol) and nondegraded OM (levosugars and proteins) increase further from A.D. 1260 to 1960, while the proportion of degraded OM continues to decline. This change is concomitant to a decrease in alkan-2-ones C23–C33 after the peak at A.D. 1590, suggesting that this second change in OM composition is not linked to a new expansion of adjacent peatlands or *Sphagnum* mats. Continuous human disturbance at a regional level is indicated by the pollen record from circa A.D. 900 [*Segerström*, 1997; *Segerström and Emanuelsson*, 2002; *Bindler et al.*, 2011] and pollen from indigenous species generally favored by human disturbance increase from circa A.D. 1200 in Lång-Älgsjön [*Meyer-Jacob et al.*, 2015]. Higher proportions of plant and nondegraded OM in the sediments are likely to reflect rapid transfer of forest soil and peatland litter to the lakes due to the physical disturbance associated with the expansion of summer forest farms. This land use activity involved systematic forest clearing, forest grazing, haymaking on mires, and small-scale cultivation of cereal and was practiced near Lång-Älgsjön between circa A.D. 1450 to 1950 [*Meyer-Jacob et al.*, 2015].

For Dragsjön, the abundance of alkan-2-ones C23–C33 increases from circa 630 B.C. to circa A.D. 80 and show a general decline after circa A.D. 1770. Phenols follow a similar trend to alkan-2-ones C23–C33, and there is also a marked increase in isopropenylphenol from 540 B.C. After A.D. 1090 isopropenylphenol becomes highly variable, with large peaks at A.D. 1230, 1680, and 1850 and abundances that are consistently higher than before A.D. 1090. Levosugars increase from circa A.D. 290, largely driving the increase in carbohydrates, and continue to increase until A.D. 1960. In contrast to these compounds of plant origin, the N compounds and chlorophylls show declining trends from circa 400 B.C. Increases in alkan-2-ones C23–C33, isopropenylphenol, and TC from circa 600–400 B.C., and levosugars from A.D. 290, indicate that the natural processes of peatland and/or *Sphagnum*-mat expansion are also occurring at Dragsjön, but offset in timing by a few centuries as compared to Lång-Älgsjön. The decline in algal OM (N compounds and chlorophyll) may be related to reduced algal productivity due altered habitat availability in the lake during *Sphagnum*-mat expansion [*Meyer-Jacob et al.*, 2015]. Differences in N supply and preservation conditions between the lakes may have contributed to the increases in δ^{15}N in both lakes and to the contrasting behavior of the C:N ratios between the lakes. The lack of increase in lignin oligomers in Dragsjön, particularly after A.D. 1200, indicates that the input of OM from vascular plants was smaller at Dragsjön, and there are several possible explanations for this. The area near Dragsjön may not have been utilized for summer forest farming to the same extent as the area near Lång-Älgsjön due to the more inaccessible location in the middle, rather than at the northern edge, of the highland plateau on which the lakes are situated. It is further possible that the *Sphagnum* mats along the shoreline played a more important role in intercepting OM transported to the lake from the surrounding forests at Dragsjön than Lång-Älgsjön. Finally, and perhaps most importantly, the proportion of peatlands within a catchment directly influences the amount of dissolved OC in surface waters [*Kortelainen*, 1993; *Dillon and Molot*, 1997; *Kortelainen et al.*, 2006] and it appears likely that both the proportion of peatlands within the catchments and the area of peatlands in direct connection with lake shorelines differed between Lång-Älgsjön and Dragsjön already by circa A.D. 1200.

Overall these results show that the molecular OM composition is essential for understanding the processes linked to the trends in the conventional OM variables, such as the changes in TC in both lakes from circa 400 B.C–A.D. 100 and the behavior of C:N ratios and δ^{15}N after circa A.D. 400. In addition, molecular information enables identification of the impact of human catchment disturbance on the OM composition in Lång-Älgsjön from circa A.D. 1260, which would not have been identified using the conventional OM variables alone.

3.2.4. A.D. 1970 to Present

For both lake records, sediments deposited from circa A.D. 1970 to present are grouped into C1. From A.D. 1960 (sediments included in C2 for both lakes) to present (i.e., 1998 or 2014), TC increases from 36.8 to 40.5% for Lång-Älgsjön and from 31.0 to 33.6% for Dragsjön, and TN from 2.6 to 3.3% and from 1.9 to 2.4% for the two lakes respectively (Figure 5). In parallel, C:N ratios decline by ~2, δ^{13}C by 1.5–1.6‰ and δ^{15}N by 0.6–2‰. These changes may in part reflect changing land use activities, such as the cessation in summer forest farming [*Meyer-Jacob et al.*, 2015], or increases in atmospheric N deposition [*Holtgrieve et al.*, 2011] but can also be driven by OM degradation processes after sediment burial. Based on a series of varved sediment cores collected from a boreal lake in northern Sweden over a 30 year period, *Gälman et al.* [2008, 2009] reported that 23% and 35% of the initial sediment TC and TN concentrations, respectively, were lost after 30 years of sediment burial, and these losses were accompanied by increases in C:N by ~2 and δ^{13}C by 0.4–1.5‰ and declines in δ^{15}N by 0.3–0.7‰. For our sediment records, if we assume that preburial sediment concentrations of TC and TN were equal for all sediment deposited between A.D. 1960 and the present, the observed decreases in TC and TN down to 4.0 (Lång-Älgsjön) and 4.5 cm depth (Dragsjön) would correspond to losses in TC of 8–9% and TN of 19–21% over a period of 40–50 years. These assumed that values for degradation losses of TC and TN are lower than those reported by *Gälman et al.* [2008], while increases in C:N and δ^{13}C are of similar magnitude. The progressive enrichment of δ^{15}N for Lång-Älgsjön and Dragsjön from the surface down to 4.0–4.5 cm depth contrasts the declines in δ^{15}N reported by *Gälman et al.* [2009], but increases in δ^{15}N during N degradation in lacustrine systems have also been

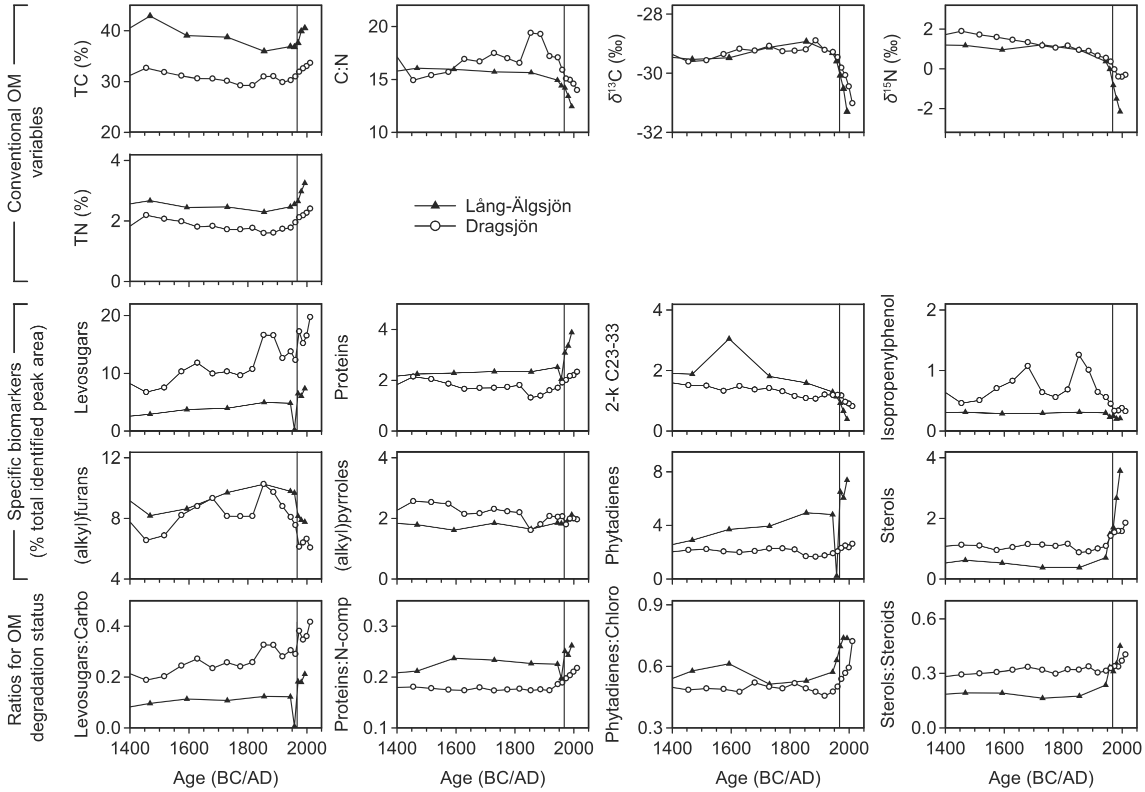

Figure 5. Changes in conventional OM variables (TC, TN, C:N, δ^{13}C, and δ^{15}N), specific biomarkers, and four ratios indicative of OM degradation status (levosugars: carbohydrates, proteins:N compounds, phytadienes:chlorophylls, and sterols:steroids) from A.D. 1400 to present. The samples to the right of the solid vertical line belong to cluster 1 (A.D. 1970–present).

reported [*Talbot*, 2001]. Also, the influence of factors leading to declines of δ^{15}N toward the surface sediments, such as atmospheric N deposition, cannot be ruled out [*Holtgrieve et al.*, 2011; *Brahney et al.*, 2014].

For Lång-Älgsjön, strong declining trends in several specific biomarkers are observed throughout C1, continuing down to 4 cm depth (circa 1960 A.D.), with levosugars declining from 7.4 to 0.2%, proteins from 3.9 to 2.1%, phytadienes from 4.7 to 3.5%, and sterols from 3.5 to 1.5%. C1 also has the highest average relative abundances for these four specific biomarkers as compared to earlier time periods (Table S4). For Dragsjön, only the levosugars show the highest relative abundance in C1 compared with earlier time periods, but declining trends from the surface sediment to down to 4.5 cm depth (circa 1960 A.D.) are observed for levosugars, from 19.7 to 12.3% and sterols from 1.8 to 1.4% (Figure 5). Relative abundances of proteins and phytadienes are in the range and variability of earlier periods. The impact of degradation processes can be assessed by normalizing these specific biomarkers, which are compounds known to be rapidly degraded, against each respective Py-compound class to obtain ratios for OM degradation status [*Schellekens et al.*, 2009]. Normalizing levosugars, proteins, phytadienes, and sterols highlights that the proportion of nondegraded OM within each of the four compound classes is exceptionally high in the most recently deposited sediment and shows strong declining trends with depth even for Dragsjön (Figure 5). The effects of OM degradation are arguably evident down to ~8–9 cm depth (A.D. 1860) in Lång-Älgsjön and ~9–10 cm depth (A.D. 1890) in Dragsjön, as shown by trends for these four ratios and for the conventional OM variables. Overall, both conventional OM variables and molecular data show that the magnitude of postburial degradation processes considerably complicates our ability to interpret the OM dynamics in the lake-sediment records for the most recent 40–50 years.

4. Conclusions

Using a new, high-throughput Py-GC/MS method optimized for lake sediments, this study demonstrates that the molecular composition of sediment OM in two adjacent boreal lakes in south central Sweden changed considerably throughout the Holocene. The overall consistency between the two Holocene lake-sediment records indicates that the data on OM molecular composition provide valuable information on past changes in OM sedimentation in response to natural and human-related environmental changes.

Our comparison between changes in the molecular OM composition determined using Py-GC/MS and conventional OM variables (TC, TN, C:N, δ^{13}C, and δ^{15}N) shows that both approaches adequately capture the early landscape development after deglaciation (>7900 B.C.), which is characterized by increasing OM contents through inputs of both plant and algal OM. The most stable trends for both conventional OM variables and for many Py-compound classes are observed from circa 7900 B.C. to circa A.D. 300, even though the OM composition remains dynamic. Sediments deposited during the last circa 1700 years are characterized by increasing OM contents and higher proportions of plant and nondegraded OM. The molecular OM composition indicates that peatland expansion may have been an import natural process affecting the OM composition, both in terms of OM sources and preservation conditions in the sediment. Additionally, for Lång-Älgsjön, some molecular changes can be clearly linked with intensified human disturbances within the catchment. Strong changes in the surface sediments, which cover the last circa 40–50 years, due to degradation processes are indicated by both conventional OM variables and the molecular OM composition and complicate the identification and interpretation of environmental changes over this period. Our study demonstrates that molecular proxies, as opposed to conventional variables, do give specific information on the sources of OM, the degradation status of the source material, and on preservation conditions in the sediment. Therefore, molecular proxies provide information on the mechanisms of change, rather than only composition, which is critical for understanding future trajectories in OM dynamics.

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