RESEARCH ARTICLE

Key Points:
- High contribution of terrestrially derived organic matter to lake sediments
- Dominance of autochthonous C in settling matter in summer but not in sediments
- Lakes as sequesters of terrestrially derived C in the boreal landscape

Preferential sequestration of terrestrial organic matter in boreal lake sediments

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Abstract The molecular composition and origin has recently been demonstrated to play a critical role in the persistence of organic matter in lake water, but it is unclear to what degree chemical attributes and sources may also control settling and burial of organic matter in lake sediments. Here we compared the annual contribution of allochthonous and autochthonous sources to the organic matter settling in the water column and present in the sediments of 12 boreal lakes. We used the fluorescence properties and elemental composition of the organic matter to trace its origin and found a consistent pattern of increasing contribution of terrestrial compounds in the sediments as compared to the settling matter, with an annual average allochthony of ~87% and ~57%, respectively. Seasonal data revealed a predominance of in-lake-produced compounds sinking in the water column in summer. Yet only a slight concurrent decrease in the contribution of terrestrial C to lake sediments was observed during the same period, and sediment allochthony increased again to high levels in autumn. Our results reveal a preferential preservation of allochthonous matter in the sediments and highlight the role of lakes as sequesters of organic carbon primarily originating from the surrounding landscape.

1. Introduction

Organic carbon (OC) sequestration in the sediments of freshwater ecosystems, and of lakes in particular, represents a significant sink in the global carbon cycle. For instance, larger amounts of OC are buried on an annual basis in lake and reservoir sediments as compared to the ocean floor [*Cole et al.*, 2007; *Tranvik et al.*, 2009] despite the fact that these lacustrine ecosystems occupy a much smaller area of the Earth's surface (~1% as compared to the world's oceans, 71%) [*Downing et al.*, 2006; *Verpoorter et al.*, 2014]. In fact, recent studies have shown that the role of lakes as burial sites of OC has been increasing significantly over the past century, in part driven by human activities [*Anderson et al.*, 2013; *Chmiel et al.*, 2015; *Heathcote et al.*, 2015]. Lake sediments do not only capture and trap OC, however, but also act as reactors mineralizing OC into CO_2 and CH_4, which contribute to the gas dynamics and metabolic balance of the system. Thus, of the sinking organic particles that settle onto the sediment surface, only a fraction will be buried on geological timescales. In this regard, understanding the balance between remineralization and burial in lake sediments may improve our understanding not only of the mechanisms leading to OC burial but also of the role and importance of lakes as long-term sequesters of OC.

The source of OC, and its chemical attributes, may strongly regulate the persistence of OC in both the water column [*Kellerman et al.*, 2015; *Kothawala et al.*, 2014] and after it settles onto sediments [*Burdige*, 2007; *Westrich and Berner*, 1984]. In the water column of boreal lakes, terrestrially derived (or allochthonous) dissolved organic carbon (DOC) dominates [*Kothawala et al.*, 2014; *Wilkinson et al.*, 2013]. In the sediments, the particulate organic carbon (POC) pool cannot be fully accounted for by the transport of particles from the watershed or by aquatic primary production. Instead, sediments are largely the result of flocculation of allochthonous DOC in the water column making it susceptible to gravitational settling [*von Wachenfeldt and Tranvik*, 2008]. Once allochthonous OC reaches the sediments, it has been hypothesized that it would be preferentially preserved and buried due to the recalcitrant nature of terrestrial compounds and slower decomposition under anoxic regimes [*Gudasz et al.*, 2012; *Sobek et al.*, 2009]. This view of a high allochthony in lake sediments, although conflicting reports exist [*Dean and Gorham*, 1998; *Gorham et al.*, 1974], has in fact been long ingrained in the limnological literature based on mass balance [*Molot and Dillon*, 1996] or

paleolimnological observations [*Brunskill et al.*, 1971; *Cranwell*, 1981; *Mackereth*, 1966]. However, current evidence remains mainly circumstantial. For instance, paleolimnological records focus on the OC accumulating in lake sediments and thus provide little insight into whether sediment composition is simply a reflection of the material being deposited or if it rather results from the selective removal and preservation during early diagenesis of specific compounds of different origin. In fact, knowledge on the sources of the OC sinking and being preserved in lake sediments has recently been identified as one of the major gaps in our understanding of lake C cycling [*Cole*, 2013], and in current lake C budgets and models [*Hanson et al.*, 2014a].

Past studies have relied on tracers such as the $\delta^{13}C$ isotopic signature of settling and sedimentary matter to assess origin, but the reliability of these tracers has been questioned due to their susceptibility to diagenetic alteration [*Meyers and Ishiwatari*, 1993]. In addition, isotopes provide very limited insight into the chemical changes underpinning OC burial. The fluorometric characterization of the dissolved organic matter (DOM) pool has been shown to be a useful and reliable tracer of composition and origin in multiple waterbodies [*Fellman et al.*, 2010; *Hudson et al.*, 2007] and has been applied to the interstitial waters of coastal [*Burdige et al.*, 2004; *Klapper et al.*, 2002; *Wolfe et al.*, 2002] and stream [*Larsen et al.*, 2015] sediments. Here we used an approach similar to that of *Wolfe et al.* [2002], which consists in extracting OC from solid sediments for spectrofluorometric analysis. We then combined the obtained fluorescence spectra with parallel factor analysis (PARAFAC) [*Stedmon et al.*, 2003] to identify the chemical composition and origin of the OC settling in the water column, as well as that present in the upper sediment layers of 12 boreal lakes in Sweden. Because the relative contribution of autochthonous versus allochthonous sources is likely to vary with seasonal patterns in temperature, light, and ice cover, the investigation was conducted over an annual cycle. We tested the hypothesis that allochthonous OC is less susceptible to degradation compared to the fresher or diagenetically less transformed autochthonous OC [*Guillemette et al.*, 2013] and should thus be preferentially buried in boreal lake sediments [*Cole*, 2013]. By comparing the fluorescence characteristics of the settling OC collected in sediment traps to that of surface sediments, we provide support to this hypothesis by demonstrating that specific fractions of allochthonous OC are preferentially sequestered during early sediment diagenesis.

2. Materials and Methods

2.1. Study Lakes and Sampling Strategy

The fluorescence characteristics of the extracted organic matter from sediment traps and sediments were measured in 12 low to moderately productive boreal lakes of southeast Sweden (chlorophyll *a* concentrations between 0.7 and 9.4 $\mu g\ L^{-1}$) with annual average DOC content ranging from 3.7 to 30.0 mg C L^{-1} (supporting information Table S1). In addition to scattered mires, the watersheds of the lakes sampled are similarly dominated by coniferous forest typical of boreal landscapes with dominant tree species being Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), and to a lower extent deciduous species such as birch (*Betula* spp.) and alder (*Alnus glutinosa*).

A detailed description of the methodology used to collect the sinking particles, as well as sinking rates, has been described elsewhere [*von Wachenfeldt and Tranvik*, 2008]. Briefly, sediment traps were deployed in the deepest part of the lake and harvested after 21 days over four seasons in 2004–2005. The organic matter from each sediment trap, consisting of brown organic flocs with no apparent larger material such as needles or litter, was transferred to a sterile polypropylene tube and stored in the dark at 4°C until extraction. In parallel, sediment samples were taken with a core sampler after the sediment traps were harvested to avoid capturing resuspended sediments in the traps. Here we targeted the upper 3 cm of each core, which corresponds to about 10 years of sediment accumulation [*Sobek et al.*, 2009]. In this way, we focus on comparing settling particles with sediments under early diagenesis and avoid comparison with deeper layers deposited long ago (~100 years) since environmental conditions might have been quite different then. Each core was sliced, transferred into an acid-washed vial, and stored at 4°C until further analysis within 2 weeks.

2.2. Lake Water Analysis

Samples for DOC were filtered (0.2 μm, Gelman Supor) with acid rinsed equipment, and analyzed on a Shimadzu TOC-5000 total organic carbon analyzer. Lake water chlorophyll *a* (Chl *a*) concentration

was determined spectrophometrically following overnight extraction with 95% ethanol [*Jespersen and Christoffersen*, 1987]. Lake water absorbance was measured at 250 nm with a Perkin Elmer Lambda 40 UV-visible light spectrometer spectrophotometer and converted to Naperian absorption coefficient (a_{250}, m^{-1}) [*Hu et al.*, 2002].

2.3. Optical Characterization of Sediment Trap and Sediment Matter

Sediment and sediment trap matter was first solubilized following the procedure of *Wolfe et al.* [2002]. Ten milliliters of 0.5 *M* NaOH was added to vials containing sediment trap material or freeze-dried sediment (0.1 g dry weight) with a N_2 headspace to prevent oxidation. The extraction with NaOH was performed for 24 h with continuous agitation followed by centrifugation (10 min at 3000 rpm), and filtration (1.2 μm, Whatman GF/C) of the supernatant. The extracted dissolved organic matter (DOM) samples were neutralized to pH 7 with 1 N HCl and diluted with Milli-Q water to DOC concentrations of 1.8–17.5 mg C L^{-1}. There was no difference in extraction efficiency between the sediment trap (33.9% ± 13.1) and sediment (34.4% ± 13.2; *t* test, *P* = 0.86) samples in terms of the resulting DOC concentrations of the extracts as compared to the C content of the original freeze-dried trap or sediment material.

Absorbance spectra (200–600 nm) were generated using the same spectrophotometer as used for lake water. We derived two spectral slopes measured at 275–295 nm and 350–400 nm ($S_{275-295}$ and $S_{350-400}$, respectively) and divided the former by the latter to calculate the spectral slopes ratio (S_R) [*Helms et al.*, 2008]. Specific ultraviolet absorbance (SUVA) was calculated by dividing the absorption coefficient at 254 nm by DOC concentration [*Weishaar et al.*, 2003]. Fluorescence intensity of corresponding extracted DOM samples from the sediments and traps was measured the same day. Excitation and emission matrices (EEMs) were generated on a SPEX FluoroMax-2 (Horiba Jobin Yvon) fluorescence spectrophotometer and corrected for lamp intensity [*Cory et al.*, 2010], inner filter effects [*Kothawala et al.*, 2013], and normalized to Raman units (R.U.) [*Stedmon et al.*, 2003]. All corrections were performed using the FDOMcorr toolbox version 1.6 [*Murphy*, 2011].

EEMs were analyzed with parallel factor analysis (PARAFAC) using the procedure described in *Murphy et al.* [2013] and revealed four humic-like components (C1, C2, C3, and C5; ex/em: 310/432, 280/522, 335/436, and 270/466, respectively), one microbial-like component (C4; ex/em: 315/384), and one tryptophan-like fraction (C6; ex/em: 280/354). The model was validated using core consistency diagnostic and a split-half validation procedure (supporting information Figure S1). Pretreatment of the EEM data set and PARAFAC analysis were performed with MATLAB 8.1 (Mathworks Inc., Natick USA). Finally, we calculated the fluorescence index (FI) [*Cory et al.*, 2010], freshness index (Fresh) [*Parlanti et al.*, 2000], and humification index (HIX) [*Ohno*, 2002; *Zsolnay et al.*, 1999].

2.4. Elemental Composition of Sediment Trap and Sediment Material

Sediment trap matter was filtered onto preweighed glass fiber filters (1.2 μm, Whatman GF/C) and freeze-dried. Filters and ~0.25 g of sediment (dry weight) from sediment cores were packed in tin capsules prior to elemental composition (C and N atoms only) determination using a NA 1500 elemental analyzer (Carlo Erba instruments).
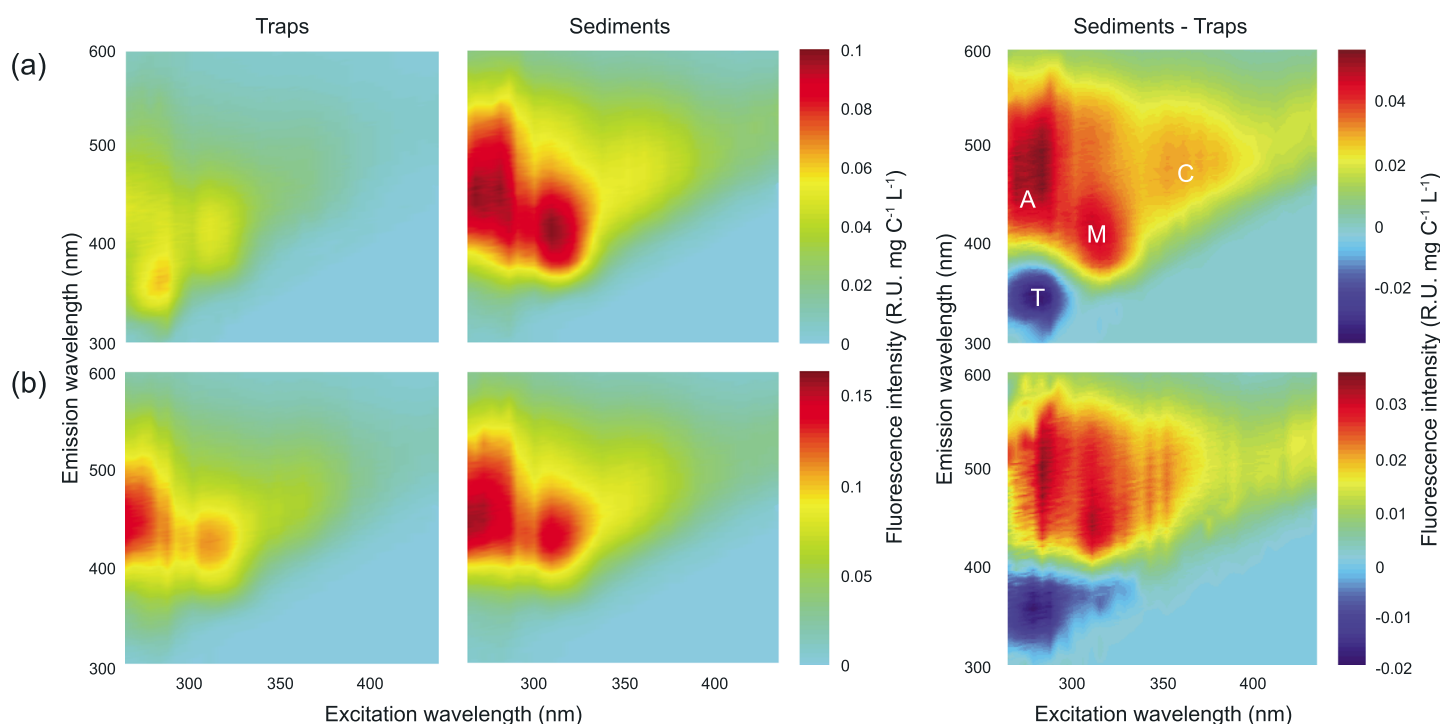
2.5. Sediment Trap and Sediment Organic Matter Allochthony

The relative contribution of aquatic versus terrestrial precursors to the sediment trap and the sediment organic matter (OM) was estimated using the FI [*McKnight et al.*, 2001] and further compared to the C:N elemental ratio (expressed hereby as N:C according to *Perdue and Koprivnjak* [2007]) and corresponding two-source mixing equations:

$$FI_{Trap/Sediment\,OM} = f_1 FI_{Aquatic} + f_2 FI_{Terrestrial} \tag{1}$$

$$N:C_{Trap/Sediment\,OM} = f_1 N:C_{Aquatic} + f_2 N:C_{Terrestrial} \tag{2}$$

$$f_1 + f_2 = 1 \tag{3}$$

Figure 1. Example of fluorescence scans of the organic matter collected in sediment traps and surface sediments. Fluorescence spectra of (a) a low DOC clear water lake (Klintsjön) and (b) a high DOC, humic lake (Stora Skärsjön) in summer. Fluorescence intensity was normalized to the DOC concentration of the extracted material for comparison purpose. Also shown (right column) is the change in fluorescence spectra from sediment traps to surface sediment. Letters in the top right panel refers to fluorescence regions named after *Coble* [1996] and corresponds to fulvic-like (peak A), humic-like (peak C), microbial-like (peak M), and tryptophan-like (peak T) fluorescence.

where $FI_{Trap/Sediment}$ OM and $N:C_{Trap/Sediment}$ OM correspond to the fluorescence index and the nitrogen-to-carbon ratio of the sediment trap and sediment OM, respectively, and f_1 and f_2 are the relative contribution of aquatic and terrestrial C sources. Here we assumed terrestrial and aquatic (microbially) derived end-member FI values of 1.21 and 1.55, respectively, according to *Cory et al.* [2010]. Similarly, the average C:N values previously reported for terrestrial (44.8 ± 24.5) and aquatic (7.3 ± 0.03) derived sources [*Hedges and Oades*, 1997; *Redfield*, 1963; *Sun et al.*, 1997; *Thornton and McManus*, 1994] were first considered as end-members. However, while the aquatic FI and C:N end-members have been shown to be fairly well constrained and invariant in previous studies, recent advances in soil biogeochemistry have revealed a more microbial character of soil OM composition than previously thought [*Kaiser and Kalbitz*, 2012; *Kleber and Johnson*, 2010; *Marín-Spiotta et al.*, 2014], which may result in higher FI and lower C:N values of terrestrial OM than expected a priori. Thus, additionally, we ran the mixing models using a terrestrial FI value of 1.32 which corresponds to the average FI of small streams draining mixed mire-forest catchments in boreal Sweden [*Kothawala et al.*, 2015], and a terrestrial C:N ratio of 15 recently reported in forest soils [*Marín-Spiotta et al.*, 2014]. Below, we report the average estimated contribution of terrestrial OM to the sediment traps and lake sediments from the two model runs for each tracer as well as the range as a measure of uncertainty associated to the terrestrial end-member.

2.6. Statistical Analyses

Relationships between optical characteristics of the sediment trap and sediment matter were explored using principal component analysis (PCA). Data were log transformed to achieve normality. Differences in the means of fluorescence properties of sediment trap and sediment material were assessed with independent Student's *t* tests or analysis of variance (ANOVA). Differences in the relationships between the optical properties of sediment trap and sediment OM and environmental variables were assessed using analysis of covariance (ANCOVA). All statistical analyses were considered significant at $\alpha \leq 0.05$ and were performed using JMP 10 statistical software (SAS Institute).
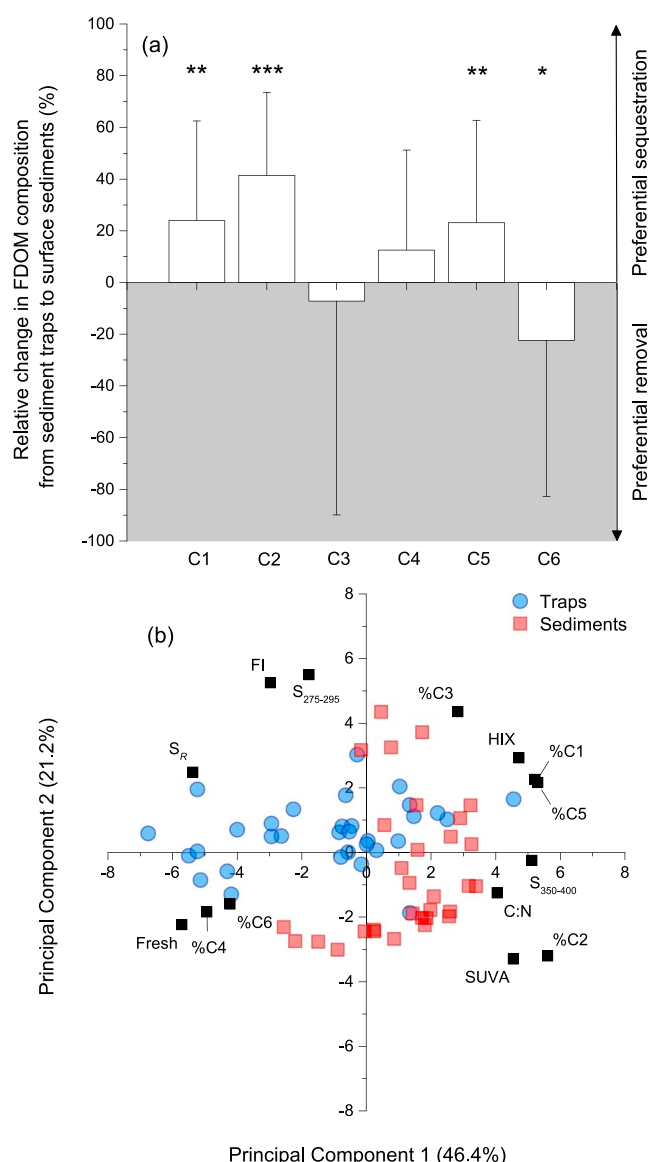
Figure 2. (a) Relative change from sediment trap matter to surface sediment of the six fluorescence components identified in this study. Positive values indicate higher values in the sediments than in the traps, i.e., preferential sequestration, whereas negative values indicate net removal (shaded area). The bars represent annual averages ±SD. Asterisks denote significance levels of independent t tests (*: $P < 0.05$, **: $P < 0.01$, and ***: $P < 0.001$). (b) Principal component analysis of the optical characteristics of the settling matter collected in sediment traps and surface sediments. The percent explained variation of the two first components is shown in brackets. See section 2.3 for acronyms.

3. Results

3.1. Patterns in Traps Versus Sediments Organic Matter Chemical Composition

Figure 1 shows representative C-normalized fluorescence spectra of the sediment traps and the surface sediments of a clear water lake (Klintsjön, Figure 1a) and a humic lake (Stora Skärsjön, Figure 1b) in summer. The different fluorescence spectra showed broad fluorescence regions previously associated to humic-like (peaks A, C, and M) and protein-like (peak T) fluorophores [*Coble*, 1996] (Figure 1). While the overall C-normalized fluorescence intensity associated with the sediment trap and surface sediment matter was lower in the clear versus the humic lake, when we examined the difference between spectra (sediments-traps) there was a general increase in fluorescence intensity of the humic peaks A, C, and M, and a decrease in protein-like fluorescence (peak T) in the surface sediments of both lakes (Figure 1, middle column), compared to the corresponding sediment traps (Figure 1, left column).

Changes in the chemical composition during early sediment diagenesis were also revealed by multivariate PARAFAC analysis with distinct fluorescent components located within these broad regions. On average, the contribution of humic-like components C1, C2, and C5 to total fluorescence significantly increased by 24%, 41%, and 23% in the sediments compared to settling matter, whereas a net decrease (22%) in the protein-like component C6 (peak T) was noted (Figure 2a). The microbial-like component C4 (peak M) and one
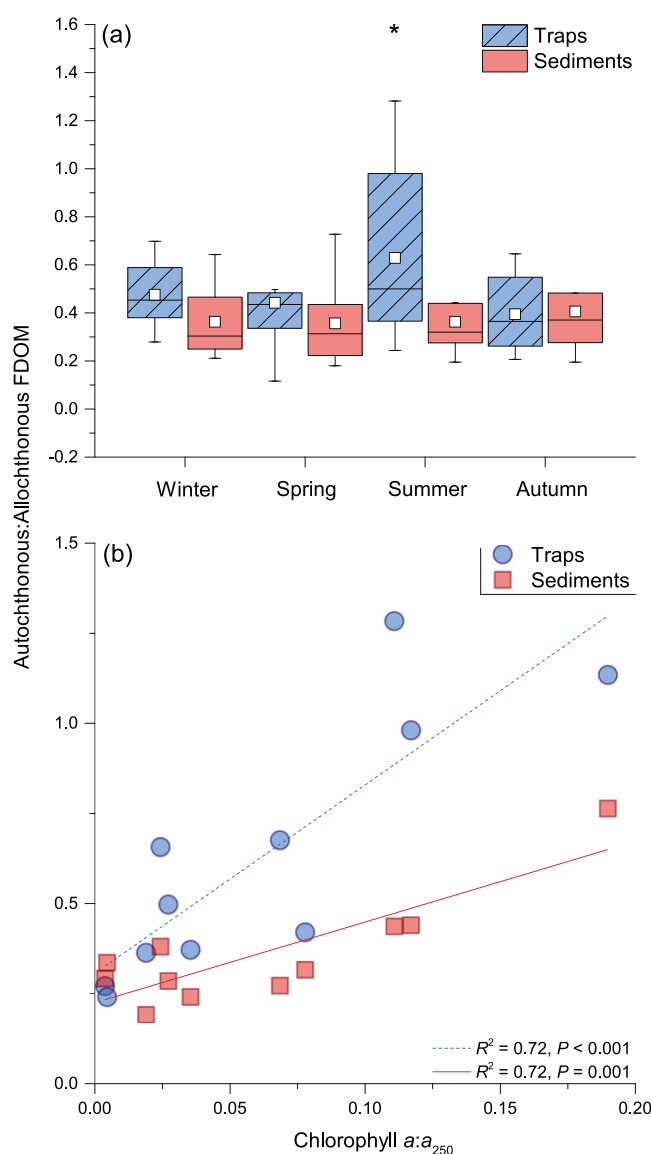
humic-like component (C3; peak A) exhibited high variability among samples and no clear pattern (Figure 2a). We further performed a PCA analysis using the combination of absorbance and fluorescence characteristics, and the C:N ratio of the settling and sediment matter. There was a clear distinction between groups of variables associated with a more aromatic or humified state on the right side, such as the SUVA and HIX indices, the humic-like components C1, C2, C3, and C5, and a higher C:N elemental ratio (Figure 2b). On the other hand, variables associated with a fresher state (Fresh) or to protein-like (C6) and microbial-like (C4) compounds of low molecular weight (S_R) typical of autochthonous matter correlated negatively with the first axis (Figure 2b). A similar separation was found between the trap and sediment samples, where samples

Figure 3. (a) Box-and-whisker plot depicting the seasonal variation in the ratio of autochthonous (C4 + C6) versus allochthonous (C1 + C2 + C3 + C5) FDOM components of the collected matter in the traps (dashed blue) and surface sediments (open red). The asterisk denotes averages that are statistically different (ANOVA, $P < 0.001$). (b) The relationships between the ratio of autochthonous versus allochthonous FDOM components of the organic matter in traps (blue circles; $y = 0.22 + 2.24x$, $R^2 = 0.72$, $P < 0.001$) and in surface sediments (red squares; $y = 0.31 + 5.23x$, $R^2 = 0.72$, $P = 0.001$), and the ratio of chlorophyll a to a_{250} in summer. Slopes of the relationships are significantly different (ANCOVA, $P < 0.001$), but not the intercept.

collected from the traps were skewed toward the left-hand side of the PCA along with indicators of autochthonous OC (high values of FRESH, C4, C6, and S_R). In contrast, sediment samples were distributed toward the right (Figure 2b) along with indicators of allochthonous OC (high values of SUVA, HIX, C1, C2, C3, and C5, and C:N). Interestingly, however, the settling material collected in sediment traps showed large variation along the first axis of the PCA (Figure 2b). Hence, there may have been shifts in the chemical composition of settling organic material, and likely in the relative contribution of the different sources, that occurred across lakes and seasons in the settling matter but not in the sediments.

3.2. Seasonality of Traps Versus Sediments Organic Matter Chemical Properties

To investigate the variability across lakes and seasons further, we first looked at the ratio of autochthonous (C4 + C6) versus allochthonous (C1 + C2 + C3 + C5) fluorescence associated with the settling matter collected in the traps and the surface sediments across seasons. This ratio was lowest in the surface sediments (Figure 3a) and did not vary among seasons (ANOVA, $P > 0.05$). Similarly, we observed low and constant values in the sediment traps, except in summer where significantly higher ratios of autochthonous to allochthonous fluorescence were observed (ANOVA, $P < 0.001$). The drastic increase in the contribution of autochthonous components C4 + C6 to total fluorescence in summer was not uniform across lakes but rather reached the highest values in lakes with high Chl a to water color (a_{250})

ratios (Figure 3b). A concurrent yet much lower increase in the autochthonous to allochthonous fluorescence ratio was also noted in the sediments along a similar gradient (ANCOVA, $P < 0.001$; Figure 3b). However, these patterns disappeared during the following autumn in all lakes, when the autochthonous versus allochthonous ratio of the settling matter shifted towards lower values.
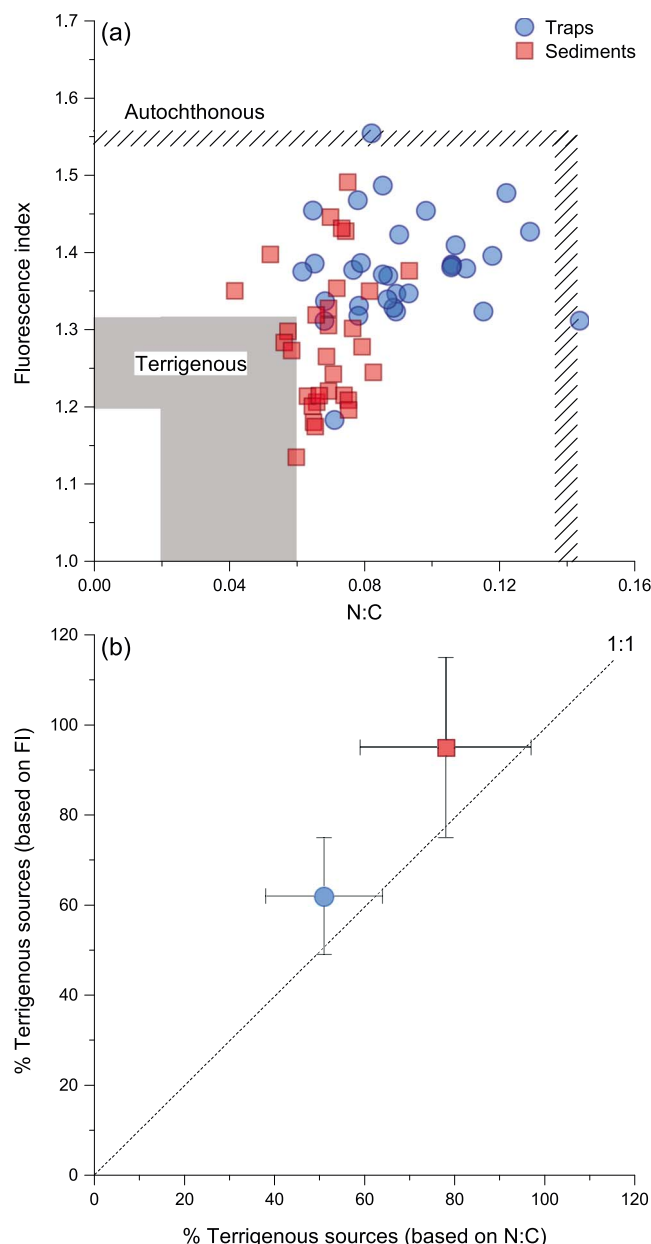
3.3. Patterns in Traps Versus Sediments Allochthony

Finally, we apportioned the relative contribution of autochthonous versus allochthonous precursors to the settling and the surface sediment OM using the FI and N:C ratio as proxies for OM origin and mixing

Figure 4. (a) Biplot of the fluorescence index versus the nitrogen-to-carbon ratio of the traps (blue circles) and surface sediments (red squares) organic matter. Also shown is the range of likely values of the fluorescence index and N:C ratio of terrigenous (shaded area), and autochthonous (dashed area) organic matter. Any data point falling within these areas can be considered as being 100% terrestrial or autochthonous. (b) Biplot of the estimated fraction of terrigenous sources in the collected material in sediments traps (blue circle) and in surface sediments (red square). Note that these estimates represent weighted averages, which account for difference in sampling effort across the different seasons (supporting information Table S1). Also shown is the range of estimated allochthony accounting for uncertainties in the terrestrial end-member FI and N:C values. See section 3.3 for details. The dashed line is the 1:1 line.

models (equations (1)–(3)). Values of FI and N:C values were closer to the terrestrial end-member in the surface sediments and approached the autochthonous endpoint in the sediment trap samples (Figure 4a). As a result, the estimated terrestrial contribution was higher in the surface sediments than in settling material regardless of the tracer used, with average values (and range associated to uncertainties in the terrestrial end-member FI and N:C values) of 95% (75–115) and 62% (49–75; FI), and 78% (59–97) and 51% (38–64; N:C) for the surface sediment and the sediment trap organic matter, respectively (Figure 4b). These estimates represent weighted averages, which account for difference in sampling effort across seasons (supporting information Table S1).

4. Discussion

This study shows that the preservation in sediments of autochthonous and allochthonous OC sinking in the water column of boreal lakes differs substantially. While in-lake and terrigenous matter contributed roughly equally to the OC in sediment traps (grand average of 57%), we observed higher allochthony in the sediments of all lakes on average (~87%; Figure 4b). These findings agree with previous studies suggesting that terrestrial OC is an important component of the settling matter pool [*Teodoru et al.*, 2013; *von Wachenfeldt and Tranvik*, 2008], and of lake sediments [*Chmiel et al.*, 2015; *Gudasz et al.*, 2012; *Sobek et al.*, 2009]. Because we directly compared the changes in chemical character and origin of the settling matter to that of the surface sediments, not only were we able to demonstrate that allochthonous matter is preferentially buried in lake sediments in line with our initial hypothesis but also that specific fractions of terrestrial OC were more prone to gravitational settling and burial.

Our results further revealed a significant increase in the relative contribution (20–40%, on average; Figure 2a) of the fulvic- and humic-like components C1, C2, and C5 to the total fluorescence in surface sediments as compared to the settling matter. These components have a fluorescence signature associated with terrestrial environments as observed in previous studies [*Fellman et al.*, 2009; *Stedmon et al.*, 2003]. In addition, the positive correlations between these fluorescence components with SUVA, the HIX index, and the C:N ratio are also coherent with the expected composition of terrigenous precursors such as lignin and cellulose (high aromaticity and C:N ratios >20) [*Sun et al.*, 1997; *Weishaar et al.*, 2003]. Moreover, two recent studies using high-resolution mass spectrometry found that these fluorescent components correlates with vascular plant-derived polyphenols and other condensed aromatic molecules [*Kellerman et al.*, 2015; *Stubbins et al.*, 2014], and we thus conclude that these humic-like OM constituents are of terrestrial origin. However, our results further suggest that these terrestrially derived fractions are not equally prone to burial; the relative contribution of component C2 to total fluorescence was twice as high as components C1 and C5 in the sediments compared to the settling matter. Interestingly, a terrestrial fluorescent fraction similar to component C2 was found to correlate strongly with vascular plant-derived polyphenolic compounds in a recent study using high-resolution mass spectrometry [*Kellerman et al.*, 2015] and to be rapidly lost with increasing water residence times of lakes in a recent nationwide lake survey in Sweden [*Kellerman et al.*, 2015; *Kothawala et al.*, 2014]. This component is known to be photodegraded by sunlight in the water column of lakes, which would explain why it is less abundant in the sediment traps than in surface sediments [*Lapierre and del Giorgio*, 2014; *Mostovaya et al.*, 2016]. In addition, this loss is also likely driven by flocculation due to the high aromatic and hydrophobic character of this component (positive correlation with SUVA; Figure 2b), its high apparent molecular weight [*Kellerman et al.*, 2015], and ability to bind with metals [*Tipping*, 1981]. Here we can only speculate on the propensity of component C2 to form flocs, although previous studies give credence to this scenario [*Kellerman et al.*, 2015; *Kothawala et al.*, 2014]. Regardless, our results suggest that once flocculated and settled, this specific fraction of terrestrial OC is likely to be sequestered in lake sediments.

Along with the increase in terrestrially derived, humic-like compounds in the sediments, we observed a concurrent decrease in the protein-like component C6 (Figure 2a). The fluorescence signature of this particular component resembles that of the amino acid tryptophan [*Coble*, 1996] and has been shown to be derived from algal or autochthonous microbial processes [*Lønborg et al.*, 2009; *Romera-Castillo et al.*, 2010]. Furthermore, this component has been shown to be more aliphatic and nitrogen rich [*Kellerman et al.*, 2015; *Stubbins et al.*, 2014] and thus considered to be bioreactive in freshwaters [*Cammack et al.*, 2004; *Guillemette and del Giorgio*, 2011], which is in agreement with our observed preferential removal of component C6 in lake sediments. In addition to being autochthonous, protein-like DOM in lake water may also be of terrestrial origin [*Lapierre and del Giorgio*, 2014] but is then preferentially degraded by bacteria in lakes [*Guillemette and del Giorgio*, 2012]. In this regard, we cannot exclude the possibility that the disappearance of the protein-like C6 might also reflect the removal of a fraction of the terrestrially derived DOM flocculating in the aquatic environment.

The high and similar contribution of allochthonous compounds to the sediments across lakes is remarkable. On one hand, our results clearly show an increased contribution of autochthonous compounds to the sinking pool of particles in more productive lakes in summer (Figure 3a). Yet we observed a much lower similar increase in surface sediments within the same period (Figure 3b). It is plausible that a combination of extensive sunlight (up to 20 h in Sweden by midsummer) and increased temperature may have stimulated pelagic and benthic primary production enough to dilute temporarily the overwhelming terrestrial signature of the sediments, which accumulated for over ~10 years, in the more productive lakes. In the fall, the pattern disappeared, suggesting that the autochthonous OC pool settling is either removed in transit in the water column or short-lived in the sediments (about 16 days in lake sediments according to *Baines et al.* [1994]). These results are in agreement not only with the high lability associated with the protein-like fractions as mentioned previously but also with the rapid turnover of autochthonous OC in general compared to the low degradation rates typically observed for terrestrial OC exported from boreal catchments [*Berggren et al.*, 2007; *Catalán et al.*, 2016; *Koehler et al.*, 2012], and the strong increase of lake sediment remineralization in summer [*Gudasz et al.*, 2012]. In this regard, the pattern of a high and constant level of allochthony in lake sediments regardless of the productivity of the system or season is perhaps not surprising but nonetheless highlights the ability of boreal lakes to retaining land-born OC in line with previous reports [*Chmiel et al.*, 2015; *Wolfe et al.*, 2002].

As independent indicators of the sources of OC in settling matter and surface sediments, we used the FI index and C:N ratios and found higher allochthony in lake sediments than in the sediment traps (Figure 4b). Although this pattern is significant and systematic across lakes and seasons, our estimates of allochthony depend (1) on the ability of these two independent approaches to trace terrestrial OC in settling matter and lake sediments and (2) on constraining the terrestrial and aquatic end-members. The FI has been shown to be insensitive to diagenetic changes in long-term lake water incubations [*Kothawala et al.*, 2012] and therefore to successfully trace allochthony in sediments as shown in previous studies [*Klapper et al.*, 2002; *Wolfe et al.*, 2002]. However, we cannot exclude the possibility that the accumulation of some fulvic and humic-like fluorescence components observed here may also reflect the accumulation of bacterial by-products in the sediments. For example, it has been shown that microbial processes may induce the formation of compounds fluorescing in the peak C region similar to our components C1 and C5 in lake water incubations [*Kothawala et al.*, 2012], with rates increasing with lake trophy [*Guillemette and del Giorgio*, 2012]. As a consequence, our estimates based on FI should be viewed as the upper limit of allochthony in the settling and sediment matter, especially in the more productive systems. Similarly, the use of the C:N ratio as an indicator of OC origin can be biased by factors such as preferential degradations of either carbon or nitrogen-rich compounds [*Meyers and Teranes*, 2001] or the settling and preservation of low C:N bacterial biomass [*Lehmann et al.*, 2002]. However, these alterations are not extensive enough to overprint the large difference existing between the terrestrial versus aquatic elemental signature [*Meyers and Teranes*, 2001], and as such this approach has also been used successfully in previous studies to trace sediment OC origin [*Gudasz et al.*, 2012; *Meyers and Ishiwatari*, 1993; *Wolfe et al.*, 2002].

We estimated the relative contribution (and uncertainties) of the aquatic versus terrestrial sources to the settling matter and lake sediments based on two alternative scenarios of the terrestrial end-member FI and C:N ratio: (1) the most commonly used approach, based on plant tissue and litter composition [*Hedges and Oades*, 1997; *Sun et al.*, 1997] and (2) alternative values adjusted to reflect the recent paradigm shift in soil biogeochemistry that recognizes the extensive contribution of microbial by-products to the soil OM pool (higher FI and lower C:N) [*Kaiser and Kalbitz*, 2012; *Kleber and Johnson*, 2010; *Marín-Spiotta et al.*, 2014]. Both these approaches yielded similar overall patterns (Figure 4). While the C:N-based estimates were fairly well constrained by the terrestrial end-member values used, the estimated allochthony exceeded 100% in some lake sediment samples using the alternative end-member constant. These samples had lower FI values (~1.20) than the terrestrial "microbial" end-member (second scenario) with a FI of 1.32 based on small streams draining mixed forest-mire watersheds [*Kothawala et al.*, 2015]. This may reflect a higher contribution of OC from mires to the organic pool settling pool in these lakes with reported values as low as 1.15 [*Kothawala et al.*, 2015] or may be due to the removal of microbially derived OC during transit in the water column as suggested by the disappearance of proteinaceous material observed between the settling and sediment matter (Figure 2a), or both.

Regardless, both the FI and C:N agree well with the spatial and temporal patterns revealed by the PARAFAC fluorescent components and yielded similar degrees of allochthony (Figure 4b), suggesting that the FI and elemental ratio may be a useful tracer of origin in sediments and that the patterns in allochthony we described are robust. In this regard, our study fills an important gap in current lake C budgets, which is to quantify the relative contribution of terrestrially derived and in-like produced organic matter delivered and buried in lake sediments [*Hanson et al.*, 2014b]. The lakes sampled in this study represent unproductive lakes typical of the boreal biome, i.e., one of the most abundant lake types globally [*Benoy et al.*, 2007; *Verpoorter et al.*, 2014]. Similar preferential preservation of terrestrially derived compounds may also occur in more productive systems where terrestrial inputs become extensively diluted with autochthonous derived OC.

5. Conclusions

Allochthonous organic matter, previously demonstrated to be an important precursor of sediments via flocculation of DOC [*von Wachenfeldt and Tranvik*, 2008; *von Wachenfeldt et al.*, 2008], contributes strongly to the organic matter that is settling in boreal lakes, and, due to the preferential preservation shown in this study, even more so to the organic matter that is sequestered in sediments. These results may have important implications regarding the role of lakes as sinks of OC [*Cole et al.*, 2007; *Tranvik et al.*, 2009] in the context of increased delivery of terrestrial OC to lakes observed in northern aquatic systems [*Roulet and Moore*, 2006].

The magnitude and causes of this increase are under debate [*Erlandsson et al.*, 2008; *Evans et al.*, 2006; *Monteith et al.*, 2007], but this added OC flux from land to lakes may well be sustained in northern systems by increased production in the catchment [*Larsen et al.*, 2011] and/or precipitation and runoff [*Eimers et al.*, 2008; *Hongve et al.*, 2004] in response to a changing climate. In addition, the burial of OC has been increasing over the last century, likely driven by human activities [*Anderson et al.*, 2013; *Chmiel et al.*, 2015; *Heathcote et al.*, 2015]. Our results suggest that these activities may have increased OC burial primarily by modulating the amount of terrestrial OC delivered to the aquatic network, and only secondarily by stimulating in-lake primary production through an increase in nutrient inputs as we show that this autochthonous substrate is preferentially degraded in lake sediments. Thus, considering (1) the role of DOC for sedimentation in boreal lakes [*von Wachenfeldt and Tranvik*, 2008], (2) the substantial carbon storage in boreal lake sediments [*Kortelainen et al.*, 2004], and (3) the preferential burial of allochthonous OC demonstrated here, the increasing terrestrial OC delivery to unproductive boreal lakes may be dampened not only due to enhanced mineralization of terrestrial OC [*Lapierre et al.*, 2013] but also through the preferential in-lake sequestration of OC of allochthonous origin.

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