Traces of sunlight in the organic matter biogeochemistry of two shallow subarctic lakes

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Abstract  Global environmental change alters the production, terrestrial export, and photodegradation of organic carbon in northern lakes. Sedimentary biogeochemical records can provide a unique means to understand the nature of these changes over long time scales, where observational data fall short. We deployed in situ experiments on two shallow subarctic lakes with contrasting light regimes; a clear tundra lake and a dark woodland lake, to first investigate the photochemical transformation of carbon and nitrogen elemental (C/N ratio) and isotope (δ13C, δ15N) composition in lake water particulate organic matter (POM) for downcore inferences. We then explored elemental, isotopic, and spectral (inferred lake water total organic carbon [TOC] and sediment chlorophyll a [CHLa]) fingerprints in the lake sediments to trace changes in aquatic production, terrestrial inputs and photodegradation before and after profound human impacts on the global carbon cycle prompted by industrialization. POM pool in both lakes displayed tentative evidence of UV photoreactivity, reflected as increasing δ13C and decreasing C/N values. Through time, the tundra lake sediments traced subtle shifts in primary production, while the woodland lake carried signals of changing terrestrial contributions,
indicating shifts in terrestrial carbon export but possibly also photodegradation rates. Under global human impact, both lakes irrespective of their distinct carbon regimes displayed evidence of increased productivity but no conspicuous signs of increased terrestrial influence. Overall, sediment biogeochemistry can integrate a wealth of information on carbon regulation in northern lakes, while our results also point to the importance of considering the entire spectrum of photobiogeochemical fingerprints in sedimentary studies.

**Keywords** Global change · Paleo-optics · Particulate organic matter · Photobiodegradation · Sediment biogeochemistry · Subarctic

### Introduction

Sunlight governs fundamental biotic and abiotic processes in shallow northern lake ecosystems including those tightly connected to the aquatic carbon balance. Visible wavelengths of the solar spectrum fuel the conversion of inorganic carbon into organic forms through photosynthesis while light, particularly in the ultraviolet (UV) range, also disintegrates organic matter resulting either in partial photodegradation or complete photomineralization (Bertilsson and Tranvik 2000; Chen and Jaffé 2016; Cory and Kling 2018). Carbon sourced both from lake production and from the surrounding terrestrial environment contribute to the aquatic carbon cycle, while their reactivities and pathways within lakes often differ (Kellerman et al. 2015). Growing global human pressures, including warming but also changes in atmospheric deposition chemistry, are increasingly affecting the production, terrestrial export and processing of carbon in shallow northern lakes. These changes reshape underwater optical environments alongside the cycling of carbon (Fig. 1), carrying a threat of amplifying climate feedbacks parallel to cascading ecological regime shifts (Smol et al. 2005; Solomon et al. 2015).

Among the most prominent symptoms of Arctic warming are widespread decreases in the length of the snow and ice cover period (Magnuson et al. 2000; Callaghan et al. 2010; Griffiths et al. 2017) promoting the transfer of solar energy into aquatic ecosystems (Fig. 1). The ensuing increase in photosynthetically active radiation (PAR) intertwined with nutrient and habitat stimuli are often found to increase the productivity of aquatic communities (Michelutti et al. 2005; Smol and Douglas 2007; Rantala et al. 2017) and may enhance photosynthetic carbon sequestration. There is, however, an ecological tradeoff to improved light availability, as concomitant increases in incident UV radiation may begin to impede algal growth through photoinhibition (Marwood et al. 2000; Vincent et al. 2007). Furthermore, increased UV irradiance can intensify photochemical processing of organic matter, inciting changes in the reactivity of lake organic carbon pools (Berggren et al. 2018) and increasing carbon dioxide (CO₂) outgassing (Koehler et al. 2014). In addition to shaping internal carbon flows in lakes, global change is altering material transport from surrounding land areas (Fig. 1) with impacts on underwater light regimes and fundamental ecosystem functions (Solomon et al. 2015). Whether through changes in climate or alterations in atmospheric deposition chemistry, affecting the size and mobility of terrestrial carbon stocks, global change is increasing the flow of land-derived organic matter into northern waters (Finstad et al. 2016; Meyer-Jacob et al. 2019; Fig. 1). Colored terrestrial organic carbon is the predominant light attenuating medium in unproductive lakes (Laurion et al. 1997; Nevalainen et al. 2015) diminishing photosynthesis through shading (Karlsson et al. 2009; Ask et al. 2012) while reducing UV stress on aquatic biota (Williamson et al. 2016). Concurrent increases in terrestrial nutrient inputs may further reduce the adverse effects of increased shading and stimulate aquatic productivity (Rantala et al. 2016; Vasconcelos et al. 2018). Simultaneously, increased concentration or photoreactivity of land-derived organic matter may enhance rates of photochemical degradation (Lapierre et al. 2013; Cory and Kling 2018). These myriad environmental drivers often overlap, interact and incite threshold responses in northern lakes challenging predictions of the broad scale effects of global change on their carbon cycling. While the causes and consequences of changing aquatic production and terrestrial carbon export have been the focus of considerable research efforts over the past decades, uncertainties prevail due to the overlapping effects of climate change and other global human disturbances (Meyer-Jacob et al. 2019) and the heterogeneity of consequent lake responses, as
discussed below. As yet, few studies have sought to understand the repercussions of global change on photochemical degradation in shallow northern lakes despite its well-established importance in the aquatic carbon cycle (Cory et al. 2014; Sulzberger et al. 2019).

The impacts of warming are often exacerbated in northern lakes where snow and ice moderate biological activity through much of the year and even modest changes in the cryosphere can result in disproportionate ecological consequences. The effects are further aggravated by the continuous daylight of the summer months, high solar irradiance, and the often small and shallow character of the lake basins linking them tightly to the terrestrial carbon cycle (Rautio et al. 2011). The often nutrient-poor waters can also be considered highly sensitive to climate-mediated increases in nutrient input or atmospheric nitrogen deposition (Wolfe et al. 2006). In spite of these broadly unifying features, the sensitivity and responses of circumpolar lakes to climate change and atmospheric pollution begin to rapidly depart at regional and local spatial scales. Here the underwater optical environment may be considered as a gauge of environmental change (Williamson et al. 2014) but also as the backdrop for external perturbations. For instance, clear water lakes situated in barren tundra landscapes may be considered particularly vulnerable to changes in UV irradiance because of their low background organic carbon levels (Laurion et al. 1997; Rose et al. 2009) as opposed to wetland and thaw lakes brimming with light attenuating colored carbon (Wauthy et al. 2018). Other local scale features, such as hydrological connection to the surrounding catchment, will further modify the prevalent environmental drivers and the ecosystem response they trigger (Bogard et al. 2019). Moreover, the patterns and
controls of lake carbon cycling are unlikely to advance linearly through time as the environmental backdrop is in constant change. The apparent heterogeneity of environmental drivers, rivaled only by the complexity of ensuing lake responses, underscores the need for a spatially and temporally comprehensive assessments of aquatic carbon regulation in northern lakes. Such assessments are severely hampered by the scarce, scattered and discontinuous monitoring data from remote northern environments that can, however, be supplemented with paleoenvironmental data obtained from lake sediments (Smol and Douglas 2007; Smol and Schelske 1998; Wolfe et al. 2006) and terrestrial carbon export (Talbot 2001). Where frequently used to trace pathways in lake ecosystems (Meyers and Teranes 2003; Schmitt-Kopplin et al. 2003; Schmitt-Kopplin et al. 1998) of the residual organic matter. Photobiogeochemistry of particulate organic matter (POM) has been much less studied despite its role as a critical intermediate pool between lake water and sediments. Notwithstanding, POM is considered similarly sensitive to photodegradation (Vähätalo 2009) and there are indications of corresponding light-induced elemental and carbon isotope effects as those observed for DOM (Mayer et al. 2009). Overall, the elemental and isotopic composition of organic matter archived in lake sediments could thus integrate information of past variations in some of the most fundamental elements of aquatic carbon cycling in shallow northern lakes (Fig. 1).

Building on this notion, we investigated the biogeochemistry of lake water and sediment organic matter in two shallow lakes at the subarctic Fennoscandian treeline to elucidate the effects of global change on aquatic primary production, terrestrial carbon flows, and photodegradation in this sensitive lake environment. A clear mountainous tundra lake and a dark woodland lake were chosen for the analysis, both of which are typical of the region but represent contrasting carbon and underwater light regimes. Our first objective was to assess whether and how UV photodestruction might contribute to shaping the elemental (C/N) and isotopic ($\delta^{13}C$, $\delta^{15}N$) composition of lake water particulate organic matter (POM) in the lakes, for potential downcore applications. To this end, we employed in situ experiments on both lakes over four weeks to identify signals of photochemical degradation in the biogeochemistry of lake water POM. We expected to find increases in $\delta^{13}C$ and declines in C/N of POM in treatments exposed to UV radiation, and further hypothesized that these signals could also be applied in the multiproxy sedimentary context to trace past trends in underwater light and photodegradation rates. Next, we examined elemental (C/N ratio) and isotopic ($\delta^{13}C$, $\delta^{15}N$) fingerprints in the lake sediments, searching for signals of both changing carbon source (pelagic and benthic aquatic production, terrestrial carbon export) and photochemical processing under natural climate fluctuations and ongoing global change. As the varied source and processing signals often overlap, reflectance spectroscopy was used to depict temporal trends in sediment chlorophyll a (CHLa) and lake water total organic carbon (TOC) concentrations as independent indices of changing aquatic primary production, water transparency, and terrestrial carbon input. We expected to find distinct but disparate signals of environmental change in connection to growing global human influence in the studied lakes. The tundra lake, with its extensive ice cover and low availability of organic substrate in the surrounding catchment, was suspected to be most vulnerable to direct climate impacts on lake ice regimes, and the increases in PAR
and UV radiation associated with the lengthening of the ice free season. The dark woodland lake was expected to be more prone to catchment-mediated climate impacts increasing terrestrial carbon export into the lake (for instance, via catchment greening or wetland carbon mobilization). We also suspected that potential increases in the length of the ice free period driven by anthropogenic warming may have increased rates of photodegradation in the lakes. The results are expected to shed light on processes controlling carbon flows in shallow subarctic lakes over decadal to centennial time scales, and to advance the use of sedimentary paleo-optics in the study of lake carbon cycling in the face of growing human influence.

Material and methods

Study region

The study was conducted in northwestern Finnish Lapland (Fig. 2) on two lakes that share characteristics typical of lakes in the subarctic region and the circumpolar north more broadly (shallow waters, low productivity) but represent contrasting carbon and underwater light regimes. A tundra lake (Lake Iso-Jehkas, unofficial name) situated ~ 300 m above the mountain birch treeline at an elevation of 925 m.a.s.l. was chosen to portray alpine clear water lakes with low concentrations of organic carbon in the water column and high underwater light exposure. Solar irradiance and the UV radiation dose on the lake are further increased by the high elevation (Rose et al. 2009). To represent a more organic-rich system with low light penetration and UV exposure, we selected a brown colored woodland lake (Lake Mukkavaara, unofficial name) situated at an elevation of 545 m.a.s.l. in the mountain birch woodlands. Rocky outcrops surrounding the tundra lake support mainly lichens, mosses and small shrubs, while the woodland lake is surrounded by patches of mountain birch, low growing dwarf birch and willow, shrubs, and water-logged soils at the lake margin. Climate in the region is continental, with mean annual air temperature of −2.0 °C, mean July air temperature of 11.8 °C and mean annual precipitation of 530 mm. The growing season length is approximately three months. The lakes are small (~ 1 ha) with catchment areas of approximately ~ 7 ha. Both lakes are hydrologically isolated with no permanent inlets or outlets. The tundra lake has ultraoligotrophic (total phosphorus 2.2 μg L⁻¹, mean of measurements performed in July and August 2018 from surface waters at ~0.5 m depth) and oligohumic waters with DOC concentrations of 1.6 mg L⁻¹, while the woodland lake is characterized by oligotrophic (6.7 μg L⁻¹) and polyhumic waters with DOC of 8.0 mg L⁻¹. Both lakes have circumneutral waters, with pH values of 6.7 (mean of July and August measurements) in the tundra lake and 7.0 in the woodland lake. Colored dissolved organic matter (CDOM) absorption at 320 nm ($a_{320}$), tightly coupled to underwater light attenuation (Nevalainen et al. 2015), is high in the woodland lake (~ 21 m⁻¹) and low in the tundra lake (~ 2 m⁻¹). The difference in underwater light conditions is also visibly distinct, as the bottom of the slightly deeper tundra lake (maximum depth ~ 4 m) was clearly visible, while that of the woodland lake (~ 1.2 m) was not. Iron concentrations were low (below the detection limit of 0.04 mg L⁻¹) in both lakes and are not expected to carry large influence on underwater light attenuation. Detailed limnological characterizations of the lakes are provided in Nevalainen et al. (2020a).

Experimental approach

An experimental analysis was first undertaken to assess whether and how the elemental and isotope biogeochemistry of lake water POM, part of which eventually settles to form lake sediment, displays sensitivity to photochemical alteration in the studied lakes. The experiments were performed in small mesocosms deployed directly onto the lakes to mimic the natural physicochemical and biological environment and ambient fluctuations in sunlight intensity and spectral composition. The experiments accordingly incorporate the effects of both photochemical and biological degradation that are intrinsically coupled in natural waters (Moran et al. 2000; Cory and Kling 2018). Nine treatments were performed on both lakes, comprising triplicate treatments under ambient sunlight (UV + PAR), sunlight without UV wavelengths (PAR), and no light (DARK) as a dark control. Vinyl acetate containers (Insinööritoimisto Haikonen Oy, Paippinen, Finland) with a volume, length and diameter of 340 L, 1.2 m and 0.6 m, respectively, were filled with lake surface water and set afloat on the lakes.
from early July to early August in summer 2018. In the woodland lake, the enclosures effectively covered the entire water column and in the tundra lake approximately one-third of the depth of the water column. The containers were wrapped in a double layer of thick white plastic allowing light penetration only through the surface while maximizing the reflection of sunlight. The UV + PAR enclosures were covered with acetate foil (Aclar®; Honeywell, Charlotte, USA) transmitting 90–93% of UV (280–390 nm) and 93% of PAR. PAR enclosures were covered with UV blocking foil (no. 311413, Roscolab Ltd, London, UK) transmitting 82% of radiation > 390 nm while screening wavelengths < 390 nm. Dark controls were covered with two layers of thick black plastic. The foils were set up on convex aluminum netting allowing contact with air and preventing condensation on their surface. Wind mixing of the experimental waters was largely inhibited in the enclosures. The experiments were carried out during the Arctic summer exposing the enclosures to continuous daylight, although the highest irradiance period in the region occurs earlier, around mid-June. The incubation time was set at four weeks, estimated sufficient to produce detectable biogeochemical changes based on earlier studies examining isotopic transformation of the DOM pool (Ophsall and Zepp 2001; Chomicki 2009), while trying to minimize disparities between the experimental and natural system growing with time. Water residence time in the closed lake basins is much longer than the duration of the experiments, and the exposure of organic matter to light before burial is likely further promoted by the clear waters in the tundra lake (light reaching the surface sediments) and shallow depth of 

Fig. 2  a Location of the studied lakes in northwestern Finnish Lapland and characteristics of the landscape surrounding the b woodland lake (68.91°N, 21.00°E) and c tundra lake (69.07°N, 20.88°E)
the woodland lake (increasing potential for sediment resuspension). In both lakes, efficient water column mixing is likely to increase the exposure of organic matter to photochemical processing. Direct scaling of the exposure time between the experimental waters and lake sediments is therefore limited, though neither critical as the primary focus here is on the direction of the elemental and isotopic transformations and on potential differences in their amplitude between the studied tundra and woodland lake.

Following the four week incubation period, the enclosures were sampled for lake water collected into opaque 5 L containers from the surface waters at ~ 0.5 m depth. Concurrent with the installation of the experimental pools in July and collection of the samples in August, lake water was further sampled as reference of pretreatment conditions and natural biogeochemical succession in the lakes. Lake water particulate organic matter (POM) was filtered onto pre-combusted (450 °C for 2 h) GF/F filters. Terrestrial and aquatic vegetation were further sampled on both sites to estimate initial origins of the lake water organic matter pool. To assess changes in the size of the particulate organic carbon pool, we used total and dissolved organic carbon (TOC and DOC) to calculate concentrations of particulate organic carbon (POC) in the lake water and the experimental enclosures, and chlorophyll a concentrations to evaluate changes in the photosynthetic production of POM in the light treatments. Analytical details for the limnological and optical measurements are presented in Nevalainen et al. (2020a) investigating UV effects on the limnological, optical and pigment properties of the dissolved organic matter (DOM) pool in the same experiments.

All samples were kept under cold and dark conditions until further treatment and analysis. The lakes are situated on non-carbonate bedrock and, overall, any influence of carbonate precipitation by photosynthesis in these soft, circumneutral and oligotrophic waters can be considered minor. No measures were therefore taken to remove inorganic carbon since acid treatments can cause nonlinear deviations in δ13C and C/N values (Brodie et al. 2011; Schlacher and Connolly 2014). While we thus cannot rule out entirely the influence of carbonates on the elemental and carbon isotope composition of the experimental samples, this should mainly be considered when comparing the absolute values among lakes, whereas our analysis was focused on variability between the treatments. Elemental and isotope analyses were performed on a Delta V Plus continuous flow isotope ratio mass spectrometer linked to a Flash 2000 elemental analyzer with a MAS 200 R autosampler (Thermo-Fisher Scientific, Bremen, Germany) at the NIWA Environmental and Ecological Stable Isotope Facility (Wellington, New Zealand). The isotope ratios are expressed in delta (δ) notation as per mill (‰) difference relative to international standard. The reference standards used were Vienna Pee Dee Belemnite for carbon and atmospheric nitrogen. The effects of sunlight on the biogeochemical composition of POM were calculated as respective differences in δ13C, δ15N and C/N between the different treatments, with particular focus on variability between the two light treatments (PAR and UV + PAR). Changes in POC concentrations were assessed in a similar manner. Notably, both visible and UV radiation contribute to photochemical reactions in the water column, while the UV wavelengths are generally considered as primary driver of organic matter photodegradation. The two were isolated here to better extract the effects of photodegradation from those related to photosynthetic production. Significance of the changes between treatments were tested with one-way analysis of variance (ANOVA) followed by Tukey’s pairwise comparison where needed.

Sedimentary approach

Paleolimnological analyses were subsequently undertaken on the lake sediments to search for biogeochemical evidence of centennial scale variations in aquatic primary production, terrestrial carbon export and photochemical processes. Short sediment cores (15 cm in length) were retrieved with a Limnos gravity corer in July 2018 following the deployment of the experimental enclosures on the lakes. The cores were retrieved from the deepest parts of the morphometrically simple small lake basins. Subsampling was performed in the field at 1 cm intervals and the samples were stored under cold and dark conditions prior to freeze drying and homogenization for elemental and isotope analysis. Radiometric techniques were used to obtain age estimates for the sediment cores, including radiocarbon analysis of sedimentary macrofossils in the deeper sediments and 137Cs analysis of the surface sequences (topmost 0–10 cm). For 137Cs, 1-cm thick samples (6–12 g)
were analyzed by direct gamma assay at the Geological Survey of Finland (Espoo, Finland) using a fully digital BrightSpec bMCAUSB pulse height analyzer coupled to a well-type NaI(Tl) detector. The activity concentrations were normalized with sample weights. Radiocarbon analysis was carried out at Beta Analytic (Miami, Florida, USA) on two terrestrial plant macrofossils found at sediment depths of 5 and 12 cm in the woodland lake, and on two moss fragments at depths of 7 and 14 cm in the tundra lake where other suitable plant macro remains were not found. In soft and well-mixed waters, mosses can, however, be considered appropriate for radiocarbon dating (Wolfe et al. 2004; Oswald et al. 2005). Elemental and isotope analyses were performed on freeze dried and homogenized sediment samples at the NIWA Environmental and Ecological Stable Isotope Facility (Wellington, New Zealand) similar to the experiment samples. Visible near-infrared (VNIR) spectroscopic analyses for the inference of past trends in lake water total organic carbon (TOC) and chlorophyll a (CHLa) concentrations were performed on freeze dried and sieved (125 μm) sediment samples. VNIR spectra were analyzed with a Model 6500 series Rapid Content Analyzer (FOSS NIRSystems Inc.) at the Paleocological Environmental Assessment and Research Laboratory (Kingston, Canada). Scanning was performed through the base of glass vials in diffuse reflectance mode. Measurements were carried out over the wavelength range 400–2500 nm with each obtained spectra representing the mean of 32 scans at 2 nm resolution. Quantification of sediment chlorophyll a concentrations was done following Michelutti et al. (2010) using the peak area between 650 nm and 700 nm. The measurements capture both primary chlorophyll a and its main degradation products making the inferences less sensitive to diagenetic effects (Michelutti and Smol 2016; Rydberg et al. 2020). Lake water TOC estimates were based on a partial least squares regression (PLSR) model between VNIR spectra of surface sediments and corresponding modern surface water TOC concentrations following Meyer-Jacob et al. (2017). A subset of 138 lakes from the universal lake water TOC model for northern lakes (Meyer-Jacob et al. 2017) was used for past lake water TOC inferences in this study. This subset consists of lakes from northern Fennoscandia that are located within < 300 km of the studied lakes and cover a TOC gradient of 0.5 to 14.9 mg L⁻¹. The resulting 3-component PLSR model had a cross-validated coefficient of determination of 0.62 and root mean square error of 1.6 mg L⁻¹. Pairwise correlations were used to examine interconnection between the sediment biogeochemical indices (C/N ratio, δ¹³C, δ¹⁵N, TOC, CHLa), applying false discovery rates with Bonferroni correction to account for multiple comparison (q = 0.05).

Results

Transformation of lake water POM biogeochemistry

The elemental and isotopic composition of POM measured from lake water in July and August in both lakes suggests mixed origins with contributions from pelagic and benthic aquatic production and terrestrial sources (Fig. 3). Mean δ¹³C_{POM} and δ¹⁵N_{POM} values were slightly lower in the tundra lake (−27.5 ± 0.7 SD / −0.3 ± 0.0 SD) compared to the woodland lake (−27.0 ± 1.2 SD), / 1.6% ± 1.7 SD) where, in turn, C/N values were slightly lower (8.4 ± 1.2 SD) relative to the tundra lake (8.9 ± 1.5 SD). Between the three treatments, the elemental and isotopic composition of POM was distinctly different in both lakes following the four-week incubation under no light (DARK), light without the UV wavelengths (PAR), and full sunlight (UV + PAR). No statistically significant differences were found based on ANOVA attributable to the relatively large variability among treatment replicates, however, some consistent and conspicuous patterns were observed. In the woodland lake, lowest δ¹³C_{POM} values were found in the DARK enclosures (mean −29.7 ± 1.2 SD) increasing towards the PAR treatment (−29.4 ± 0.6 SD) and finally UV + PAR (−28.4 ± 0.3 SD) (Fig. 4). In the tundra lake, δ¹³C patterns were more erratic, however; an increase in δ¹³C_{POM} was observed between PAR (−28.0 ± 0.9 SD) and UV + PAR (−27.4 ± 0.0 SD) consistent with the trend in the woodland lake. δ¹⁵N_{POM} showed lowest and highest values in the DARK treatments in the woodland (−0.0 ± 0.5 SD) and tundra (2.0 ± 1.0 SD) lake, respectively, but no conspicuous and consistent patterns were found between the two light treatments. Both in the woodland and tundra lake, C/N_{POM}
declined from DARK (8.4 ± 0.6 and 7.3 ± 0.6, respectively) to PAR (8.1 ± 0.9 and 6.7 ± 0.3, respectively) and UV + PAR (7.6 ± 0.3 and 6.3 ± 0.2, respectively). UV exposure had a more conspicuous effect on POM composition than concentrations both in the tundra and woodland lake, as
suggested by the minor variability in POC concentrations (Supplementary Fig. 1) between PAR (0.22 mg L$^{-1}$ ± 0.0 SD and 0.46 mg L$^{-1}$ ± 0.3 SD, respectively) and UV + PAR (0.22 mg L$^{-1}$ ± 0.0 SD and 0.39 mg L$^{-1}$ ± 0.1 SD, respectively) treatments. Changes in DOC concentrations were similarly very small (Supplementary Fig. 1; Nevalainen et al. 2020a) suggesting little transfer between the particulate and dissolved organic carbon pools during the experiments, although we did not quantify the production of new POC or loss of DOC via mineralization that could mask some of the variability. We focused primarily on changes between the three treatments rather than on changes from the initial values (i.e., before the incubation) as those could be influenced by the experimental setting. Briefly, without convective mixing, part of the more resistant POM fractions may have settled at the bottom of the enclosures over the four weeks. Second, the mixed lake water is likely to incorporate a stronger benthic signal relative to the stagnant experimental waters. Thus, signals of photochemical processing could partially mix with signals of changing organic matter source. Indeed, there was a shift towards more negative $\delta^{13}$C$_{POM}$ in the enclosures in both lakes consistent with a relative increase in pelagic contribution (Figs. 3 and 4), even though chlorophyll $a$ concentrations indicated lowered productivity (Nevalainen et al. 2020b, Supplementary Fig. 1). In keeping with the carbon isotope values, $\delta^{15}$N$_{POM}$ in the tundra lake enclosures shifted towards a typical pelagic signal (Kivilä et al. 2020) relative to initial values before incubation.

Centennial patterns in sediment biogeochemistry

Radiometric measurement yielded three age estimates for both lakes, with one from each deemed unreliable. Data for the four dates used in the study are presented in Table 1 and displayed in Figs. 5 and 6. Both lakes displayed relatively low $^{137}$Cs activities (Supplementary Fig. 2) with a single peak attributed to the nuclear weapons testing peaking in the 1960s. In this environment, the Chernobyl fallout (1986) is less likely to leave a distinct peak as the lakes are located >700–800 km north of the highest fallout area in central southern Finland (Arvela et al. 1990). The effect of post-fallout re-deposition from the catchment is probably minor in the closed lake basins, however, diffusion (Ojala et al. 2017) may have affected the

| Lake     | Depth (cm) | Radionuclide | Estimated age range   |
|----------|------------|--------------|-----------------------|
| Tundra   | 7          | $^{14}$C     | 530–452 cal BP        |
| Tundra   | 14         | $^{14}$C     | 982–904 cal BP        |
| Woodland | 5          | $^{137}$Cs   | ~ 1960s               |
| Woodland | 12         | $^{14}$C     | 1290–1220 cal BP      |
$^{137}$Cs profile of the tundra lake. Specifically, $^{137}$Cs concentrations in the tundra lake peaked at 7 cm inconsistent with the radiocarbon date at the same depth and at 14 cm (Table 1), as well as with age estimates from a long sediment core obtained from the same lake (Nevalainen et al. 2020b). For reference, most of the Holocene history (~ 10 500 years) of the lake was encompassed in a 73-cm sediment sequence, as could be expected for such a sedimentation environment. Mixing of sediment can occur in shallow lake basins, however, this was not supported by the gradual development patterns in the biogeochemical proxies (Fig. 5) and the radiocarbon dating of the long sediment core indicating a stable sedimentation environment for the Holocene (Nevalainen et al. 2020b).

The elevated organic content in the uppermost sediments combined with slow accumulation rates in turn may have promoted downward diffusion that could explain the deep (and broad) $^{137}$Cs peak in the lake. In the woodland lake, radiocarbon analysis gave an age estimate of 5130 yr BP for the sample at depth 6 cm possibly related to redeposition of older material (Wolfe et al. 2004). The age is broadly inconsistent with the other age estimates from the profile (Table 1) and dating results from a long sediment core from the same lake (unpublished results). The $^{137}$Cs date at 7 cm for the tundra lake and the $^{14}$C date for the woodland lake were hence rejected. As our work focuses on dynamic relationships between the sedimentary indices, we did not attempt age-depth modelling for either of the cores but use the obtained point in time estimates to provide a coarse chronological framework for the sedimentary inferences.

Through time, variations in sediment biogeochemical proxies were relatively small but largely synchronous throughout the two sediment records (see Supplementary Fig. 3 for pairwise comparisons). Chlorophyll $a$ and inferred lake water TOC were generally lower and showed smaller variability in the tundra lake (mean 0.04 mg g$^{-1}$ ± 0.01 SD and
2.5 mg L$^{-1}$ ± 0.3 SD, respectively) relative to the woodland lake (0.09 mg g$^{-1}$ ± 0.05 SD and 7.8 mg L$^{-1}$ ± 0.9 SD, respectively). δ$^{13}$C were slightly more negative in the tundra lake (−24.7% ± 0.3 SD) compared to the woodland lake (−24.0% ± 0.5 SD), while C/N values were very similar between the lakes (11.7 ± 0.8 and 11.8 ± 0.9 SD, respectively). In the tundra lake (Fig. 5), changes in sediment chlorophyll $a$ were positively correlated to variations in inferred lake water TOC (R = 0.73, p = 0.003) and negatively correlated to sediment C/N (R = −0.77, p = < 0.001) and, to lesser extent, to changes in δ$^{15}$N (R = −0.67, p = 0.007). Variations in δ$^{13}$C were more erratic and displayed no conspicuous connections to the other variables. Both chlorophyll $a$ and lake water TOC showed a very subtle increasing trend (by +0.007 mg g$^{-1}$ and +0.3 mg L$^{-1}$, respectively) across the lower half of the sediment sequence matched by declining (−0.5) C/N values.

At around 6 cm, chlorophyll $a$ and TOC showed a synchronous decline (−0.009 mg g$^{-1}$ and −0.8 mg L$^{-1}$, respectively) followed by a more pronounced increase (+0.03 mg g$^{-1}$ and +1.2 mg L$^{-1}$, respectively) near the surface. These trends were mirrored by C/N, though with a barely discernible increase (up to +0.3) after 6 cm and a more distinct surface decline (−1.5). In the woodland lake (Fig. 6), inferred lake water TOC, sediment C/N ratio and δ$^{13}$C showed similar patterns, though only the latter two variables were significantly negatively correlated (R = −0.76, p = 0.001) after correction for multiple comparisons. A transient increase in lake water TOC and C/N (+2.1 mg L$^{-1}$ and +2.3, respectively) coupled to a decline (−0.8%) in δ$^{13}$C occurred between around 6 and 7 cm. Below, TOC (mean 8.1 mg L$^{-1}$) and C/N (12.0) were generally more elevated and δ$^{13}$C (−24.0%) more negative compared to the section above (6.9 mg L$^{-1}$, 11.0% and −23.6%).
respectively), although inferred lake water TOC displayed an increasing trend in the topmost 3 samples (+ 1.1 mg L\(^{-1}\)). Chlorophyll \(a\) showed little change in the lower half of the sediment sequence followed by an increasing (+ 0.1 mg g\(^{-1}\)) trend towards the surface initiated at around 5 cm.

**Discussion**

UV photoalteration of lake water POM biogeochemistry

Our understanding of the control of carbon transformation and mineralization in lake ecosystems has shifted over recent years upon recognition of the key importance of photodegradation in shaping the pathways and fate of organic matter in northern waters (Cory et al. 2014; Sulzberger et al. 2019). However, comparatively little research has been carried out on the effects of photoalteration on lake water POM despite its inherent connection to the sediment carbon pool. Results from our four week experiments suggest that the elemental and carbon isotopic composition of lake water POM in both of the studied subarctic lakes may be sensitive to UV-driven photochemical degradation. Although generally consistent with our expectations, the shifts were comparatively small and should therefore be considered tentative. The experiments were conducted on natural waters for a more accurate depiction of the natural environment, yet with less control over the multiple interacting ecosystem processes that likely account for the scatter between treatment replicates. Whatever combination of processes underlie the observed changes, the direction of the shifts in \(\delta^{13}C\) and C/N of lake water POM in both lakes is consistent with the earlier experimental works. Accordingly, the observed enrichment of the organic matter \(\delta^{13}C\) signature under UV exposure in both lakes (Fig. 4) concurs with the previously observed preferential degradation of the \(^{12}C\) fraction of carbon under sunlight (Ophsal and Zepp 2001; Vähätalo and Wetzel 2008).

Similarly, the decline in C/N conforms with the anticipated faster loss of carbon relative to nitrogen under light exposure (Schmitt-Kopplin et al. 1998; Buffam and McGlathery 2003; Chomicki 2009). These changes have been attributed to the loss of high molecular weight aromatic compounds such as terrestrial lignins (Ophsal and Benner 1998; Vähätalo et al. 1999; Mayer et al. 2009) depleted in \(^{13}C\) and enriched in carbon (Benner et al. 1987). The process appears plausible also here considering the apparent terrestrial component in the POM pool of both lakes (Fig. 3) corroborated by the spectral characteristics of the lake water DOM (Nevalainen et al. 2020a).

Importantly, the observed changes in POM biogeochemistry between the two light treatments do not depict an isolated signature of photochemical processing but also of tightly coupled biological processes. Although the extent and direction of their influence on elemental and isotopic ratios may be more erratic, there is an element of predictability linked to the origin and biogeochemical characteristics of organic matter. Where primarily autochthonous organic substrate can transform into more biorefractory compounds under light exposure (Benner and Biddanda 1998; Tranvik and Bertilsson 2001), photodegradation generally renders terrestrial organic matter more labile (Moran et al. 2000; Cory and Kling 2018) thereby promoting biodegradation. Consistently, previous research suggests that photoexposure is likely to increase overall microbial activity in clear water and humic oligotrophic lakes due to the low availability of labile carbon produced within-lake (Tranvik and Bertilsson 2001). Bacteria preferentially remove autochthonous organic carbon over lignin and other aromatic terrestrial compounds (Benner et al. 1987) entailing that the effect of photodegradation on organic matter biogeochemistry could in effect be partially muted by the biotic interaction. DOM fluorescence components indicated a considerably stronger microbial signal in the woodland lake (~ 55%) relative to the tundra lake (~ 15%; Nevalainen et al. 2020b), in keeping with earlier research suggesting that biodegradation dominates organic matter processing in dark colored lakes (Berggren et al. 2018). In accordance, the low \(\delta^{13}C\) and elevated C/N dark control values (Fig. 4) imply that coupled bacterial processing could be dampening the photochemical signal in the woodland lake. The elevated dark control \(\delta^{13}C\) and C/N in the tundra lake in turn resemble those of the initial lake water POM, suggesting weaker photobiological interaction. Biodegradation aside, we observed lowered chlorophyll \(a\) concentrations in the enclosures exposed to full sunlight (Supplementary Fig. 1) potentially related to UV photoinhibition of algal production (Nevalainen et al. 2020a). Reduced demand for inorganic carbon
results in higher photosynthetic discrimination against $^{13}$C (Hodell and Schelske 1998) and could thus contribute to diminishing the UV effect on carbon isotope signatures. Overall, the consistent shifts towards more enriched $\delta^{13}$C values and lowered C/N under UV exposure suggest that the coupled biotic interactions may weaken but not entirely diminish the signal of photochemical processing in the studied lakes, conforming to earlier research considering photochemical and coupled microbial effects on DOM isotope biogeochemistry (Ophsal and Zepp 2001).

Irrespective of their distinct carbon and underwater light regimes, the amplitude of the changes in $\delta^{13}$C and C/N between the two light treatments (PAR and UV + PAR) (Fig. 4) did not differ markedly between the studied lakes. In the tundra lake, mean $\delta^{13}$C increase under UV exposure was lower ($+0.6\%$) compared to the woodland lake ($+1\%$); however, the decline in C/N was slightly larger ($−0.6\%$ vs. $−0.3\%$). The lack of clear distinction between the lakes may relate to confounding biological processes, such as microbial degradation in the woodland lake negating the effects of photodegradation, but also to tradeoffs between substrate lability and availability, and light exposure (Cory et al. 2015). In particular, the effects of photodegradation could be delimited in the woodland lake by the rapid attenuation of light in the dark water column (Williamson et al. 1996; Nevalainen et al. 2015) confining photodegradation to the surface layer, and in the tundra lake by the low availability of photolabile organic matter (Nevalainen et al. 2020a).

It should also be noted that, in both lakes, the organic matter has been exposed to natural photochemical and biological processing already prior to the incubation, which is likely to partially account for the small amplitude of the observed biogeochemical changes. Notably, while the results are not directly comparable due to differences in experimental design and environment, our results correspond well, both in direction and extent, with the results of Mayer et al. (2009) examining photolytic transformation of riverine and coastal suspended sediments. The changes in $\delta^{13}$C observed by the authors ranged from $+0.4\%$ to $+0.5\%$ and the declines in C/N from $−0.7$ to $−1.3$, following 70 h of constant irradiation by strong light (corresponding to mid-day subtropical sun). This was the only earlier study we found investigating the photolytic transformation of the elemental and isotopic composition of POM precluding further comparisons. For reference, the amplitude of the $\delta^{13}$C shifts observed here is at the lower range of variation found in earlier experimental works studying DOM transformation under light exposure (Osburn et al. 2001; Ophsal and Zepp 2001; Väätäinen and Wetzel 2008; Chomicki 2009). Further comparative experiments are evidently needed to decipher the extent to which photochemical and coupled biological processing may contribute to the elemental and isotopic transformation of lake water POM in different lake environments. Although the results from our pioneering study are tentative and do not directly scale with the sediment organic matter that may have been exposed to sunlight for much longer periods of time in the closed lake basins and well-mixed waters, they nevertheless suggest that photodegradation could be a relevant driver of POM biogeochemistry that should not be overlooked in sedimentary studies.

Tracing solar biogeochemical fingerprints through time

In closed lake systems, the fraction of POM not reduced to the dissolved phase and mineralized settles at the bottom of the lake to form a record of its past origins and of subsequent biotic and abiotic alterations. The relative importance of each type of source and alteration varies broadly between lake ecosystems and may vary through time under environmental transitions, whether of natural or human origin. In the studied tundra lake, the most prominent long-term patterns in organic matter biogeochemistry were associated with changes in aquatic primary production, as indicated by the tightly correlated trends in sediment chlorophyll $\alpha$, C/N ratio and inferred lake water TOC (Fig. 5). Prevalence of the subtle productivity signal in the ultraoligotrophic waters indicates that, in the context of the late Neoglacial climate regime, the lake has remained largely isolated from shifts in terrestrial carbon cycling. Besides recent warming, the sediment sequence covers the Medieval Warm Period (~900–1300 CE) and the following cold period referred to as the Little Ice Age (prevailing until the twentieth century in northern Finland; Luoto et al. 2017) that have left distinct imprints in paleoenvironmental records across the region (Weckström et al. 2006; Kivilä et al. 2020). Although we cannot pinpoint the exact timing of the changes due to
chronological constraints, our record suggests that these earlier climate phases have not driven marked changes in the productivity of the lake. The slight chlorophyll \( a \) increase towards the sediment surface may suggest a recent increase in aquatic production potentially linked to the observed lengthening of the ice-free season over the past century in subarctic Fennoscandia (Callaghan et al. 2010), possibly coupled with atmospheric nitrogen deposition given the declining \( \delta^{15}N \) at the surface (Wolfe et al. 2004). Trends near the sediment surface must, however, always be considered with some caution due to potential diagenetic overprinting. Even though spectral chlorophyll \( a \) inferences also incorporate degradation products of chlorophyll \( a \) and are therefore less sensitive to post-depositional alteration (Michelutti et al. 2010; Rydberg et al. 2020), some chlorophyll \( a \) loss can still occur within the first years after deposition. For example, Rydberg et al. (2020) showed up to 24–45% losses before chlorophyll \( a \) levels stabilized 10–15 years after initial sediment deposition in a boreal lake in Sweden. The near-surface declines in sediment \( C/N \) (~ 2 units) and \( \delta^{15}N \) (~ 1.5‰) (Fig. 5) could also be partially related to the progressive loss of nitrogen and \( ^{14}N \) with time (Talbot et al. 2001; Gälman et al. 2008). We therefore interpret these recent changes with some caution.

Increases in PAR denote also increasing UV stress (Fig. 1) that can carry cascading effects extending from the cellular level to entire ecosystem functioning (Vincent et al. 2007). UV influence may be considered particularly pronounced in clear and shallow alpine lakes where the underwater light spectrum inclines towards the UV range (Laurion et al. 1997), the thinner atmosphere increases solar exposure (Rose et al. 2009), low temperatures and nutrient deficiency impair photoprotective pigmentation and cellular repair (Beardall et al. 2014), and the shallow waters and continuous summer daylight further limit behavioral adaptations to UV stress. Although primary production in the tundra lake may thus be considered highly sensitive to photoinhibition, the benefits of improved resource availability still appear to have exceeded the adverse effects of UV, even if the potential increase in production was very small. Neither did we detect concomitant opposing patterns in organic matter \( ^{13}C \) and \( C/N \) values that could have carried indications of enhanced photoprocessing over the recent period, nor earlier in the sediment sequence. It could be that the recorded environmental variability is too subtle to drive changes in photoprocessing rates, however, photodegradation could also be insensitive to increased light in the system due to substrate limitation. In clear waters, already short exposure to UV can rapidly deplete photolabile organic matter fractions (Cory et al. 2015) and thus long-term variability in the rates of photodegradation could be primarily sensitive to changes in the concentrations (or photoreactivity) of terrestrial organic carbon.

In the woodland lake, centennial patterns in sediment biogeochemistry appeared to be linked to varying contributions of terrestrial carbon to the lake water, as indicated by the coeval shifts in sediment \( ^{13}C \) values, \( C/N \) ratio, and inferred lake water TOC (Fig. 6). Interestingly, while the transient upward shift in \( C/N \) and decline in \( ^{13}C \) towards typical terrestrial values (~ 28‰, Fig. 3, Kivilä et al. 2020) with increasing lake water TOC plausibly reflect increased catchment-derived carbon inputs, the experimental results, corroborated by the earlier research (Ophsal and Zepp 2001; Buffam & McGlathery 2003; Mayer et al. 2009), suggest that lowered photochemical processing could contribute towards a similar elemental and isotopic shift. Correspondingly, \( ^{13}C \) enrichment together with lowered \( C/N \) and TOC earlier in the sequence and particularly over the past decades could either point to reduced terrestrial influence or enhanced photodegradation rates. In light of the landscape context and limnological characteristics of the lake, both processes are equally conceivable. For one, carbon flows from the surrounding marshy soils may be expected to be sensitive to changing temperatures and hydrology (Tranvik and Jansson 2002), and we also cannot rule out potential effects of acidification and subsequent recovery on carbon fluxes (Meyer-Jacob et al. 2019) over the past few decades. Unlike in the tundra site, photodegradation in the dark woodland lake is likely to be light limited (Cory et al. 2015) meaning that the rates of photoalteration are more likely to accelerate under increased light than changing concentrations of terrestrial organic carbon. Increased UV exposure under lengthened growing season could thereby either drive or contribute to the generally lowered TOC and prevalent autochthonous signal over the past decades. Unfortunately, we cannot confidently link the earlier transitions in sediment biogeochemistry with the preceding climate phases due to chronological constraints. Additional
sedimentary proxies are also needed to extract the individual or synergistic contributions of changing source (terrestrial influence) and processing (photodegradation rates) on the temporal patterns. Notwithstanding, the results point to a potentially overlooked role of photodegradation in controlling sediment biogeochemical patterns.

Sediment biogeochemistry in the woodland lake carried a strong benthic signature (Fig. 3) in accordance with the shallow and nutrient-poor water column. Benthic primary production is often strongly light limited (Vadeboncoeur et al. 2008; Karlsson et al. 2009) and therefore vulnerable to changes in the concentration of colored terrestrial organic carbon (Ask et al. 2012). At low DOC concentrations (Seekell et al. 2015) or optical depths (Vasconcelos et al. 2018), concurrent nutrient stimuli may, however, override the adverse effect of shading on aquatic biota. In effect, earlier research from northern Lapland indicated that terrestrial nutrients may continue to promote primary production in similar shallow (<2 m) and dark (a320 > 20 m\(^{-1}\)) lakes despite the apparent low light penetration (Rantala et al. 2016). In the woodland lake, the centennial shifts in lake water TOC, whether related to changes in terrestrial carbon transport or photoprocessing, displayed an ambiguous connection to aquatic primary production. This may be attributed to the dual role of terrestrial organic carbon as a nutrient subsidy and shading agent (Fig. 1), as well as to relative changes in allochthonous and autochthonous contributions to the lake water TOC pool. For one, the transient increase in allochthonous TOC (\(\sim 2 \text{ mg L}^{-1}\)) mid-core was little reflected in chlorophyll \(a\) concentrations suggesting either that the related shading and nutrient effects were cancelling one another out, or that neither was sufficiently large to influence aquatic production. On the other hand, the increase in TOC (\(\sim 1 \text{ mg L}^{-1}\)) in the topmost three samples coincided with clearly elevated chlorophyll \(a\) and could indicate either increased catchment material fluxes, adding allochthonous TOC and promoting lake production, or higher autochthonous contribution to the TOC pool. The latter appears more plausible here in light of the elevated \(\delta^{13}\text{C}\) and low C/N values near the surface, although simultaneous increase in aquatic production could be partially masking allochthonous signals. Diagenetic effects could contribute to the chlorophyll \(a\), \(\delta^{13}\text{C}\) and C/N shifts towards the surface but should not account for the trends sustained over several decades as diagenetic effects on chlorophyll \(a\) (Rydberg et al. 2020), carbon and nitrogen elemental concentrations (Gålman et al. 2008), and carbon isotope composition (Gålman et al. 2009) should primarily take place within the first few years after deposition.

Aquatic carbon cycling under global change

Mounting evidence shows that the role of northern lakes in the biogeochemical carbon cycle has changed in response to growing human pressure and will continue to transform under global change (Tranvik et al. 2009). Whether this change will be towards increasing carbon sequestration or release is yet difficult to resolve. A prevalent uncertainty here relates to the complex effects of increased productivity and browning of northern waters (Fig. 1) that often tend to push aquatic carbon balances in opposite directions (Ask et al. 2012). Our analyses depicted disparate controls for lake carbon cycling above and below the subarctic treeline under natural climate fluctuations, yet under global change both of the studied lakes displayed a uniform pattern of increasing aquatic primary production (Figs. 5 and 6) in common to numerous other small and shallow lakes spread across the circumpolar north (Michelutti et al. 2005; Kivilä et al. 2020). The change was, however, very subtle in the tundra lake possibly related to the high elevation of the lake that may delay climate impact on productivity (Griffiths et al. 2017). Although several of the multitudinous effects of global change are simultaneously promoting the browning of northern lakes (Creed et al. 2018; Wauthy et al. 2018), we found no evidence of distinct recent increases in terrestrial carbon loading in either of the lakes. While different in many aspects, the two lakes share certain regional and local features that may contribute to their common deviance from the widespread circumpolar pattern. For one, it may be that no substantial catchment greening (Larsen et al. 2011; Finstad et al. 2016) has occurred around the lakes, as suggested by a recent study from the region (within \(\sim 100 \text{ km}\) of the studied lakes) demonstrating conspicuous plant species shifts over the past four decades across the treeline transect, but no clear expansion in trees nor tall shrubs (Vuorinen et al. 2017). Furthermore, earlier studies have proposed that hydrologically isolated lakes could be less prone to growing terrestrial influence (Bogard
et al. 2019) and therefore rather reflect more sensitively changes occurring within-lake. Hydrological disconnectedness could thereby also contribute to the uniform response of these two contrasting lakes. Irrespective of causes, the results illustrate how lake responses to global change may not always align with expectations based on landscape position and lake water carbon regime. This corroborates the importance of identifying key environmental factors shaping lake vulnerability and directing their responses to human perturbation within and across regions, for rigorous global upscaling (Seekell et al. 2018; Bogard et al. 2019). Moreover, our study underscores the utility of the long-term sedimentary perspective that can help us identify ecosystem-level responses to growing human pressures and assess the nature and extent of ongoing changes against background variability prior to anthropogenic influence (Smol 2019). Finally, while ambiguities remain as regards the contribution of photodegradation to the elemental and isotopic patterns, the results suggest that we could be overlooking a relevant driver of organic matter biogeochemistry in sedimentary studies. This can be considered a caveat for the already complex elemental and isotopic carbon indices but also an opportunity for paleo-optical research, and either way calls for further experimental research on POM photobiogeochemistry. In regard to lake sediments, additional techniques such as those drawing on molecular biogeochemistry (Ninnes et al. 2017) for better differentiation of terrestrial influence, or paleopigment applications (Nevalainen and Rautio 2014) shedding further light on underwater UV regimes, will be needed to enable a better distinction of the role of photodegradation. Despite the complexity of intertwined environmental signals, biogeochemical archives retained in lake sediments hold valuable information of aquatic carbon regulation in northern lake ecosystems increasingly exposed to global human perturbation.

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Author contributions Liisa Nevalainen, Marttiina Rantala, Henriikka Kivilä and Tomi Luoto lead the conception of the study and carried out the experimental and sediment material acquisition. All authors contributed to sample processing and analyses, in relation to limnological, elemental and isotopic analyses (Marttiina Rantala, Henriikka Kivilä, Tomi Luoto, Liisa Nevalainen), spectral analyses (Carsten Meyer-Jacob, John Smol), and radiometric dating (Antti Ojala). Marttiina Rantala prepared the first draft of the manuscript that was critically reviewed and commented on by all authors. All authors have read and approved the final manuscript.

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Data availability All data generated during this study are included in this published article and its supplementary information files.

Code availability Not applicable.

Declarations

Conflict of interest The author’s declare no conflicts of interest.

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