The sediment fluorescence - trophic level relationship: using water-extractable organic matter to assess past lake water quality in New Zealand

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Abstract

Lake sediments are the physical remnants of past allochthonous and autochthonous carbon and mineral inputs and therefore have the potential to illuminate both past terrestrial carbon cycling and within-lake biological productivity. However, there are currently no robust, rapid, and inexpensive methods to chemically characterise the organic matter (OM) components in lake sediments, which limits their utility for reconstructing past soil carbon export trends or trophic status. This study explores the use of 3D excitation-emission matrix (EEM) fluorescence spectroscopy of water extractable dissolved organic matter (WEDOM) from lake sediments as a method for reconstructing past soil dissolved organic matter (DOM) export and past lake water quality. Using contemporary lake sediments from eleven New Zealand lakes, we demonstrate that both overall WEDOM fluorescence and protein-like fluorescence intensity are strong functions of trophic status across lakes. We also demonstrate that protein-like fluorescence is a function of sedimentary total nitrogen concentrations in palaeo-sediments from a pristine, high-altitude lake (Adelaide Tarn). This approach has applications in the evaluation of the trophic status of infrequently monitored lakes and in paleolimnology.

1. Introduction

In the last few decades, the literature on terrestrial carbon cycling has increased in parallel to the literature on water quality science and eutrophication (Abell *et al*. 2019; Battin *et al.* 2009; Cole *et al.* 2007; Smith, 2003). Both topics share dissolved organic matter (DOM) (including carbon) as central themes, and in both fields the debate over contemporary changes has led scientists to turn to environmental archives like lake sediments to provide longer-term perspectives (Meyer-Jacob *et al*. 2015). This approach allows us to establish pre-human (or pre-industrial land-use) ecological baselines (Abell *et al*. 2019), and to assess the relationship between concentrations and characteristics of DOM and environmental changes. In this study, we develop a rapid and inexpensive method for differentiating organic matter in New Zealand lakes based on fluorescence spectroscopy.

1.2 DOM in relation to the eutrophication of inland waters

Aquatic DOM contains a heterogeneous mixture of organic compounds, and is either allochtonous or autochtonous. Allochtonous DOM is produced outside of a waterbody, and transported into it (e.g. from plant material or soil in the surrounding catchment), while autochtonous DOM is produced within the waterbody (e.g. by algae). Humic-like DOM is generally derived from plant material and soil, and largely consists of phenolic and carboxylic moieties, although a number of functional groups are often present. Protein-like DOM is associated with microbial products and includes amino acids such as tryptophan and tyrosine.

DOM is ubiquitous in aquatic systems, including lakes. DOM is involved in the transport of nutrients (Yang *et al.* 2013), lowering of light penetration (Rae *et al.* 2001; Ask *et al.* 2009), altering lake mixing depths (Fee *et al.* 1996), and serves as a substrate for heterotrophs (Tranvik, 1988). DOM may also undergo biogeochemical alteration, be mineralised to CO_2 or CH_4, or be stored within sediments (Figure 1).

In natural waters, DOM is often the predominant form of C, N, and P (Findlay & Parr, 2017). Total nitrogen and total phosphorus are important indicators of water quality (Burns *et al.* 2000), and concentrations of these elements have increased in New Zealand water bodies due to human activities (Abell *et al*. 2010). Because DOM is closely linked to nutrient transport (Findlay & Parr), DOM is likewise a major factor in contemporary lake water quality decline.

As well as DOM, particulate organic matter (i.e., OM with a particle size greater than 0.45 μm) is also found in lakes. Sediment particles may remain in suspension in the water-column, but can also settle on the lake bottom. Prior to, and after deposition, particulate organic matter may be subject to bacterial decomposition, potentially leading to mineralisation and release of CO_2 and other greenhouse gases.

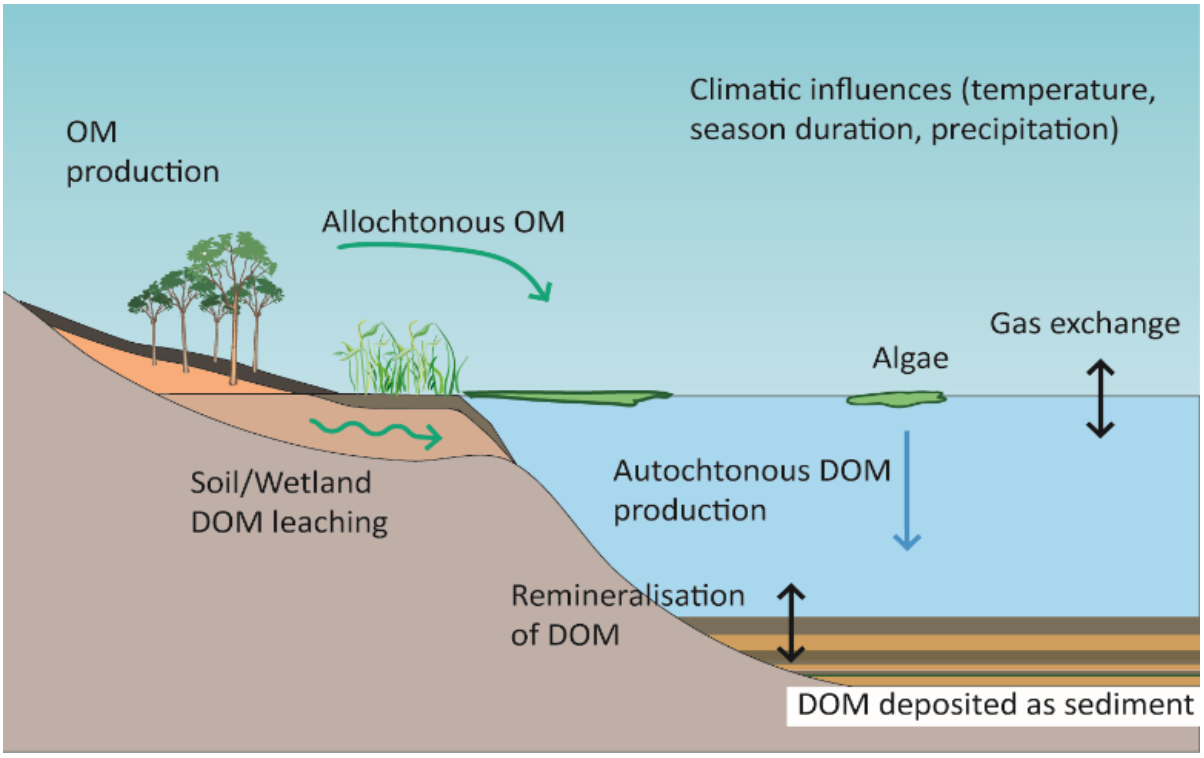

Figure 1 DOM can enter a lake from the surrounding landscape or be produced/altered within the waterbody itself. Lacustrine DOM can be deposited in the sediment, where it may be stored or remineralised. DOM may be lost from the waterbody as CO_2.

1.3 DOM fluorescence and environmental monitoring

A small, yet representative fraction of DOM is fluorescent and is typically described as chromophoric dissolved organic matter (CDOM). DOM fluorescence occurs when light energy (photons) excites loosely held electrons in the molecular orbitals of DOM (Fairchild & Baker, 2012). As the electrons return to their original ground state, energy is lost as fluorescence (emission of photons). Thus, DOM concentration can be measured by assessing fluorophore intensity, whilst constituents can be determined by observing the wavelengths at which excitation and emission occur. For example, protein-like fluorescence (produced by molecules including tryptophan and tyrosine) occurs at different wavelengths (ex 270–280 nm; em 330–368 nm) to the fluorescence signal produced by humic-like fractions (ex 320–360 nm; em 420–460 nm) (Coble *et al.* 1990; Coble *et al.* 1998; Fellman *et al.* 2010).

Three-dimensional (3D) excitation emission matrix (EEM) fluorescence is a rapid (> 100 samples per day) and cost-effective method which requires minimal sample preparation (filtration only) (Coble, 1996; Stedmon and Bro, 2008). Because fluorescence methods can be used to distinguish the constituents of DOM, information on the source and biological activity of the analyte can also be gained (Mladenov *et al.* 2008; Fellman *et al.* 2010). The relationship between humic-like fluorescence and TOC concentrations is well-established (Cumberland & Baker, 2007), whilst protein-like fluorescence has been used to determine water quality (Baker & Inverarity, 2015), and to indicate waste-water contamination (Hartland *et al.* 2011; Sgroi *et al.* 2017). Despite the significance of DOM in freshwater environments, and the ease and low cost of analysis, fluorescence methods have been under-utilised in New Zealand.

In New Zealand, trophic level index (TLI) is used to assess lake water quality (Burns *et al.* 2000). TLI is calculated from the measurement of total nitrogen (TN), total phosphorus (TP) and chlorophyll *a* (Chl*a*) concentrations, as well as Secchi disc depth (SDD). Measurements of TN, TP and Chl*a* concentrations require chemical preparation. SDD is designed to measure the transparency of lake water; however, water transparency can be influenced by several independent factors (e.g., suspended sediment, cloud cover). To address these problems, several studies have suggested that water quality characterisation should incorporate the nutrient-colour paradigm (which includes spectroscopic analysis of CDOM) (Webster *et al.* 2008; Zhang *et al.* 2018). Indeed, Zhang *et al*. (2018) observed a strong correlation between CDOM optical properties and trophic gradients in 800 surface water samples from 22 Chinese lakes, thus demonstrating that fluorescence methods may complement conventional water quality monitoring.

1.4 Lake sediments as archives of DOM

Lakes act as sediment sinks, accumulating ecological, physical, biological, and chemical information that can inform us about past environmental changes (Lowe & Walker, 2014). Of the organic carbon that is deposited into sediments, a proportion will be remineralised as CO_2, and the remainder will be incorporated and buried (Gudasz *et al.* 2010). However, lakes are also subject to hydrological and geomorphological influence, and therefore correlations between lake sediment properties and climatic

and environmental change may be non-linear, and variable between individual lakes (Fritz, 2008). Nevertheless, lake sediments can inform questions of past lake productivity and catchment DOM influxes.

1.6 Aims of study

This study aims to highlight 3D EEM fluorescence as a method that may complement the trophic level index paradigm used to assess water quality in New Zealand lakes. However, rather than using lake surface water samples, this research focuses on sedimentary water-extractable dissolved organic matter (WEDOM), to demonstrate that water quality and sedimentary DOM are related, and that DOM sources from the past may be reconstructed using sedimentary WEDOM fluorescence.

We establish this relationship by comparing WEDOM fluorescence to water quality parameters from contemporary monitoring data from eleven lakes in New Zealand. To assess the potential of 3D EEM fluorescence analysis of WEDOM over longer time-scales and in a pristine environment, this study also analysed 3D EEM fluorescence of ten WEDOM samples (with an age range of 270-13,234 cal. year BP) from Adelaide Tarn, a small, sub-alpine lake. In Adelaide Tarn, these analyses are compared to sedimentary Fourier transform infrared spectroscopy (FTIRS) inferred TOC measurements and conventional total carbon and total nitrogen measurements.

We also present an NZ-specific calibration for the determination of total organic carbon (TOC) by Fourier-transform infrared spectroscopy (FTIRS) (sample n= 141) of conventionally measured non-purgeable organic carbon (NPOC) concentrations from modern sediments in 13 lakes. FTIRS has been successfully deployed to reconstruct past lacustrine TOC concentrations elsewhere (Rosén *et al.* 2010; Meyer-Jacob *et al.* 2014).

2. Materials and Methods

2.1 Lake sediment WEDOM training set

Surface sediments (maximum depth 4 cm) were sampled from eleven New Zealand lakes to build a fluorescence training dataset (Figure 2; Supplementary Table 1). Lakes in the training set are monitored by their respective regional councils, with data compiled by LAWA (Land Air Water Aotearoa). These

lakes cover a latitudinal gradient spanning approximately 7.7° and are characterised by differing climate, land-use regimes, and trophic levels. A survey of New Zealand lake (112 lakes) water quality (2005–2009) (Verburg *et al.* 2010) revealed that the highest water quality is found in alpine lakes in catchments with high native vegetation cover, whilst poor water quality (eutrophy) is associated with warmer lakes in catchments dominated by pastoral land use (Verburg *et al.* 2010). To capture the widest range of trophic levels, the training set includes lakes from all points along this continuum.

Lakes Rotoiti (mesotrophic), Rotorua (eutrophic), Rotoehu (mesotrophic), Rotomahana (mesotrophic), Taupō (oligotrophic) and Tarawera (oligotrophic) are in the Central Volcanic Plateau of the North Island (Figure 2). These lakes (most notably Rotomahana) are of volcanic origin, and several are influenced by geothermal inflows (Mazot *et al.* 2014). Anthropogenic activities (predominantly urbanisation and agriculture) also affect several of these lakes, especially Rotorua. Lake Rotorua's catchment land use is 39% forest, 52% pasture, and 8% urban, and includes the city of Rotorua (Verburg *et al.* 2014). The nearby catchments of Okataina, Rotoehu, Rotoiti, Tarawera and Rotomahana have predominantly native vegetation (Verburg *et al.* 2010). Within the catchment of Lake Taupō, there is a mixture of native vegetation and pastoral land, as well as a town located on its northern shore. Lakes Aviemore and Benmore (both oligotrophic) are man-made reservoirs created in the 1960s in Canterbury, South Island, and their catchment land-use is principally pastoral (Verburg *et al.* 2010). Lake Ohau is a microtrophic glacial lake, located in Canterbury, which is fed by rivers with sources on the Southern Alps. Ohau's catchment contains low intensity pasture and native vegetation. Lake Pearson's catchment (Canterbury) has a mix of low intensity pasture and native vegetation.

Sediments from Aviemore, Benmore, Ohau and Pearson were collected in the deepest part of each lake using a gravity corer in November 2011. Core samples from Lakes Rotorua and Rotoehu were collected using a gravity corer in 2016. Sediments from Lake Okataina, Rotomahana, Tarawera and Taupō were collected using a gravity corer in multiple years between 2006 and 2011. All samples were freeze-dried prior to storage.

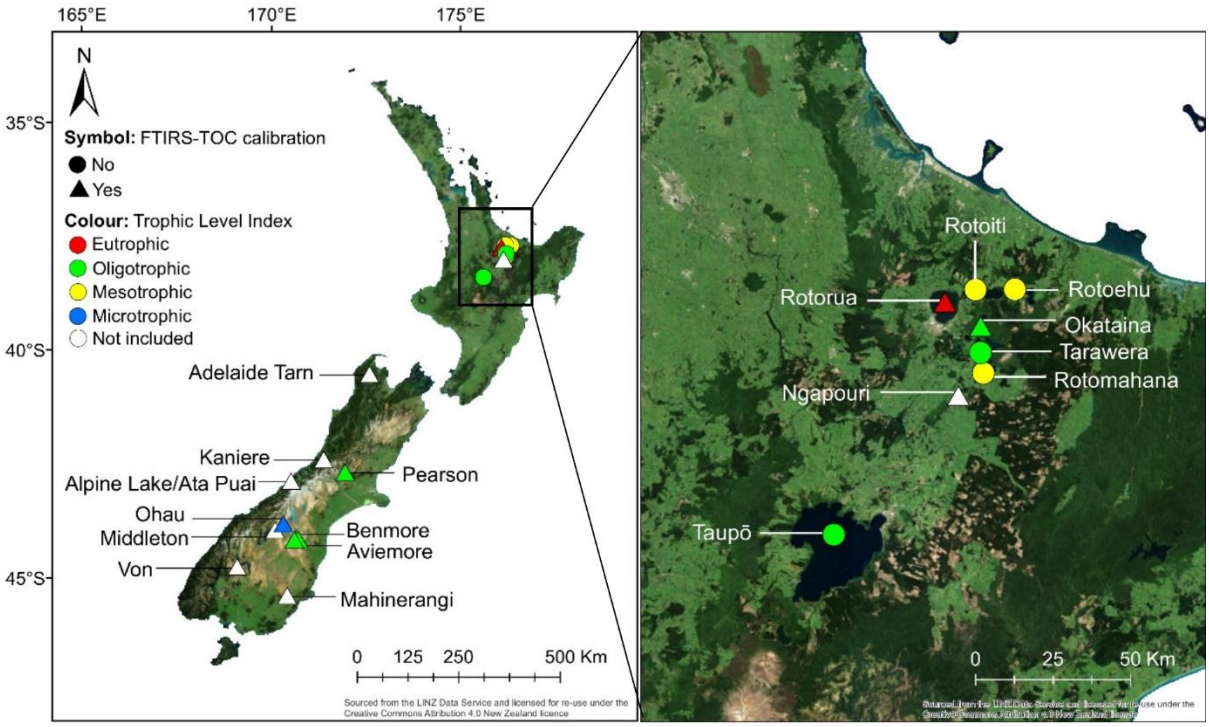

Figure 2 Locations of lakes. Lakes that were used in the FTIRS-TOC calibration are shown with triangle symbols. Lake trophic status is indicated by colour, and lakes that were not included in the TLI calibration (but were included in the FTIRS-TOC calibration are indicated by white symbols.

2.2 Adelaide Tarn- a pristine lake with a palaeo-environmental archive

Adelaide Tarn (Lat: -40.941; Long: 172.544) is a small (0.06 km^2, maximum depth 7.6 m) low-alpine lake (1250 m altitude) with one inlet and one outlet, located in the Douglas Range of the Tasman Mountains, NW Nelson Region, on New Zealand's South Island (Figure 2) (Jara *et al.* 2015). The lake is situated in a glacial cirque (3.8 km^2) with steep slopes and thin soil and was formed when permanent ice retreated from the catchment around ~16,100 cal. years BP (Jara *et al.* 2015). Adelaide Tarn is currently located above the treeline, although nearby forest is dominated by mountain beech (*Fuscospora cliffortioides*) with low-shrub species including *Coprosma* and *Griselinia* spp. forming the sub-canopy. The low alpine ground cover is mainly herbaceous flora including *Astelia*, *Uncinia*, Apiaceae, Plantaginaceae, and Asteraceae. Adelaide Tarn has an estimated mean annual temperature of 6.2 °C and annual precipitation of 2,500 mm (Leathwick *et al.* 2010).

Two overlapping sediment cores (AT 1115 and AT 1116) were collected from an anchored platform using a 5 cm diameter square-rod piston corer (Wright, 1967) from the deepest part (7.6 m) of the tarn. Both cores consist of multiple overlapping 1 m length core sections. A gravity core was taken to collect the water-sediment interface. A single composite succession was constructed by cross correlating common stratigraphic units (Jara *et al.* 2015). The age model was reported previously by Jara *et al.* (2015), and the sedimentary chronology was constructed from 16 accelerator mass spectrometer (AMS) radiocarbon dates and calibrated using the SH Cal13 dataset (Hogg *et al.* 2013).

2.3 Water quality monitoring data

Monitoring data were collected by the respective regional councils and compiled by LAWA (Land Air Water Aotearoa; LAWA, 2014). The TLI score can be calculated via two different techniques, either as TLI3 or TLI4. TLI4 is calculated from log-transformed values of four variables: total phosphorus (TP), total nitrogen (TN), chlorophyll *a* (Chl-*a*) and Secchi disc depth (SDD) (a measure of water clarity), whilst TLI3 ignores SDD. Each lake is assigned a TLI score between 1 and 7, where the lower the number, the higher the water quality. This study used the TLI3 method, as SDD data are not available for every lake in the training set.

To characterise each lake, mean TN, TP, Chl-*a* and TLI values for the three years prior to core extraction were calculated from the LAWA database. The number of measurements, the number of within-lake sampling sites and the number of years of measurements used in this study are listed in the supplementary information (Supplementary Table 1). Total nitrogen is the sum of all inorganic and organic forms (NO_3, NO_2, NH_4, amino acids and plant tissues). Total phosphorus includes dissolved reactive phosphorus, orthophosphate and organic P bound to sediments. Chlorophyll *a* is measured to estimate the biomass of phytoplankton suspended in the water column.

2.4 Water extraction of sedimentary OM

A water extraction protocol commonly used in soil analysis (Guigue *et al.* 2014) was used to remove DOM (as WEDOM) for fluorescence analysis. Briefly: 10 mg of freeze-dried, homogenised sediment was added to 7 mL of distilled-deionised (18 MΩ) water in a polypropylene tube and shaken vigorously

for 60 minutes, before being centrifuged for 30 minutes at 3600 rpm. Traditionally, assessments of water extractable OM are limited to alkaline extractions from sediments (Corvasce *et al.* 2006). However, Lehmann and Kleber (2015) suggested that analysis should focus on water-soluble (and therefore bioavailable) OM, since an alkaline treatment at pH 13 ionises compounds that would never dissolve in a natural pH range (pH 3.5 to pH 8.5).

Freeze-drying prior to WEDOM extraction for fluorescence analysis has rarely been reported in the literature but is known to alter pore structure and to cause stress to the microbial community within the sample (Zsolnay, 2003). However, air drying can eliminate interesting differences in DOM quality and quantity (Zsolnay, 2003). For this reason, freeze-drying was undertaken in sample preparation.

2.5 3D EEM fluorescence measurements of water extractable dissolved organic matter (WEDOM)

3D EEM fluorescence is a routine approach to assessing water quality in lakes and rivers (Baker *et al.* 2004; Hudson *et al.* 2007). The wavelengths at which fluorescence excitation and emission occurs allow the biochemical characteristics and sources of DOM to be distinguished (Fellman *et al.* 2010). Following water extraction, supernatants were filtered through 0.45 μm cellulose acetate syringe filters (Microanalytix Pty Ltd, Australia). The extracts were then analysed using a Horiba Jobin Yvon Aqualog® fluorescence spectrometer with a 0.5 sec integration time, a step-size of 3 nm, and a measurement range of 240–600 nm excitation and 245–800 nm emission. To correct for instrument specific biases (Stedmon & Bro, 2008), each matrix was corrected for inner-filter effects, scatter lines were Rayleigh masked, and spectra were then Raman normalised to the mean Raman peak area of distilled de-ionised water.

2.6 PARAFAC (parallel factor analysis) of components of WEDOM fluorescence

Fluorescence data in this study were processed using parallel factor analysis of components (PARAFAC) using the N-way toolbox (Andersson & Bro, 2000), a multivariate modelling technique developed in MATLAB® 2013. PARAFAC provides multi-way analysis through which fluorescence signals can be distinguished and separated into statistically valid independent components. PARAFAC

thus provides estimates of the relative contribution of each component to the total fluorescence signal and can quantify common fluorophores present in natural samples as statistical components (Fellman *et al.* 2010). The model was validated using the drEEM toolbox (Stedmon & Bro, 2008).

2.7 FTIRS (Fourier transform infrared spectroscopy)

FTIRS spectra from New Zealand lake sediments (Figure 2, Supplementary Table 2) were related to conventionally measured TOC using a PLSR (partial least square regression) approach (Rosén *et al.* 2011). Many FTIRS-TOC studies have established local/regional calibrations, and these can differ substantially depending on local variations in sediment character (Meyer-Jacob *et al.* 2014). For conventional TOC measurement, samples first underwent acid pre-treatment to remove carbonates, followed by catalytic combustion (900°C, O_2) and separation, before analysis in a thermal conductivity detector (Elementar Analyser). Splits of the same samples were also analysed via FTIRS using a Perkin-Elmer Spectrum 100 spectrometer. Prior to analysis, samples were freeze-dried overnight, ground and homogenised using a pestle and mortar. Aliquots of 2 mg (+/-2.5 %) of each sub-sample were extracted, mixed, and homogenised with 1 g of oven-dried (100°C) KBr, before being compressed to form translucent discs. Discs were kept in desiccators prior to analysis. After recording a blank (no disc in the cell), the discs were measured under controlled conditions, with blank measurements taken every 15 measurements to avoid possible spectral drift. The absorption of infrared (IR) light with wavenumbers of 3750–400 cm^{-1} was recorded through 64 scans per sample.

3. Results

3.1 Fourier transform infrared spectroscopy (FTIRS)-TOC calibration

Partial-least squares regression (PLSR) modelling of FTIRS data vs conventionally measured TOC resulted in a 5-component model, with an R^2 value of 0.88 (Figure 3). Higher TOC values (>10 %) are less accurately estimated by this model due to the underrepresentation of this sample type in the FTIRS-TOC training set. The regression line has the equation y= 0.9375x + 0.3774. In subsequent discussion and presentation of results we have used this equation to calculate TOC concentrations from FTIRS measurements.

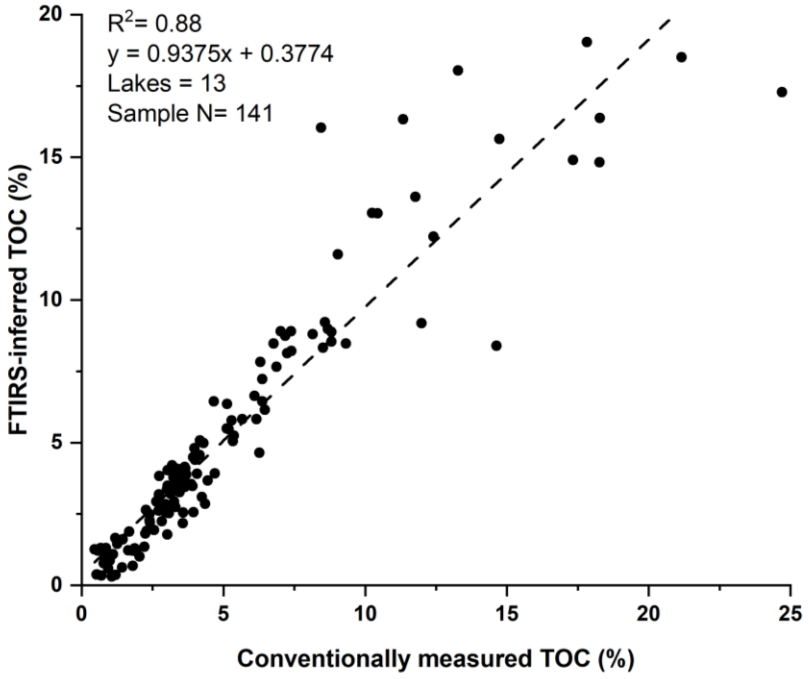

Figure 3 FTIRS-TOC calibration for thirteen New Zealand lakes based on PLSR.

3.2 3D EEM fluorescence of WEDOM

Figure 4 shows that most of the lake sediments exhibit C, A, and T fluorescence peaks (Coble, 1996), and that the intensities of each peak vary considerably between lakes. Peaks C and A are commonly associated with humic-like fluorescence from higher plant matter and soil (Fellman *et al.* 2010), whilst peak T is associated with protein and biomolecules containing amino acids (Baker & Inverarity, 2004).

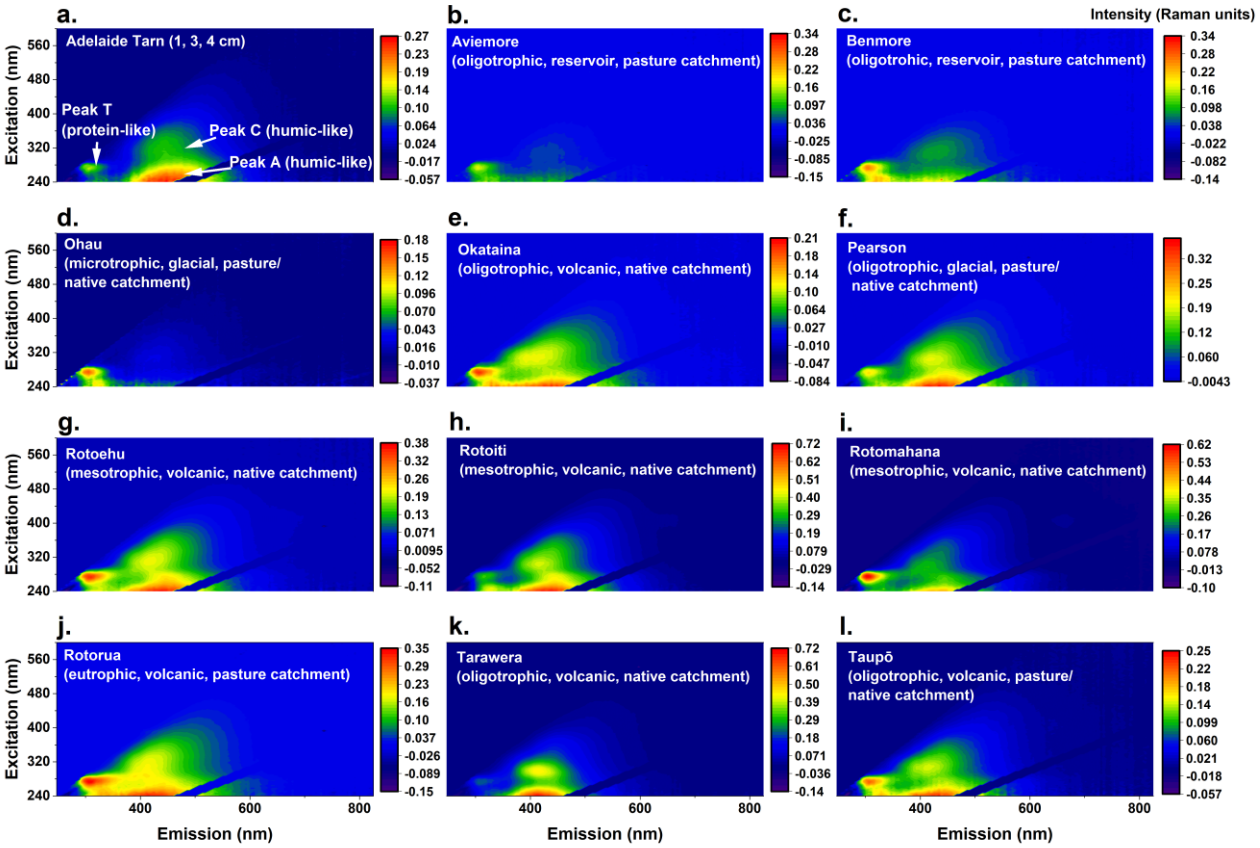

Figure 4 3D EEM contour plots illustrate that WEDOM characteristics and concentrations vary considerably across the dataset.

Figure 5 shows the first three components from a PARAFAC model that included all WEDOM samples.

Components 1 and 2 are both humic-like but are atypical in shape. Typically, maximum fluorescence intensities for humic-like peaks occur at wavelengths of Ex: 237-260; Em: 400–500 nm (peak A), or Ex: 300–370; Em: 400–500 (peak C) (Coble, 1996). The unusual peak shape of Components 1 and 2 is explained by the diverse range of fluorescence peak shapes at the different sites, which the components are fitted to. Given that the main focus of this study is the quantification of autochtonous vs allochthonous contributions to the lake carbon reservoir, and given that two humic-like peaks have overlapping properties, we henceforth consider humic-like components 1 and 2 together (described as "Total humic-like fluorescence").

If a two-component model was generated, then a protein-like peak was not produced. However, for the three-component model, the third component was clearly protein-like. This component spans a

relatively wide range of emission wavelengths, consistent with red shifting (exhibiting emission at longer wavelengths) of this peak due to the variety of conjugated biomolecules found at different sites.

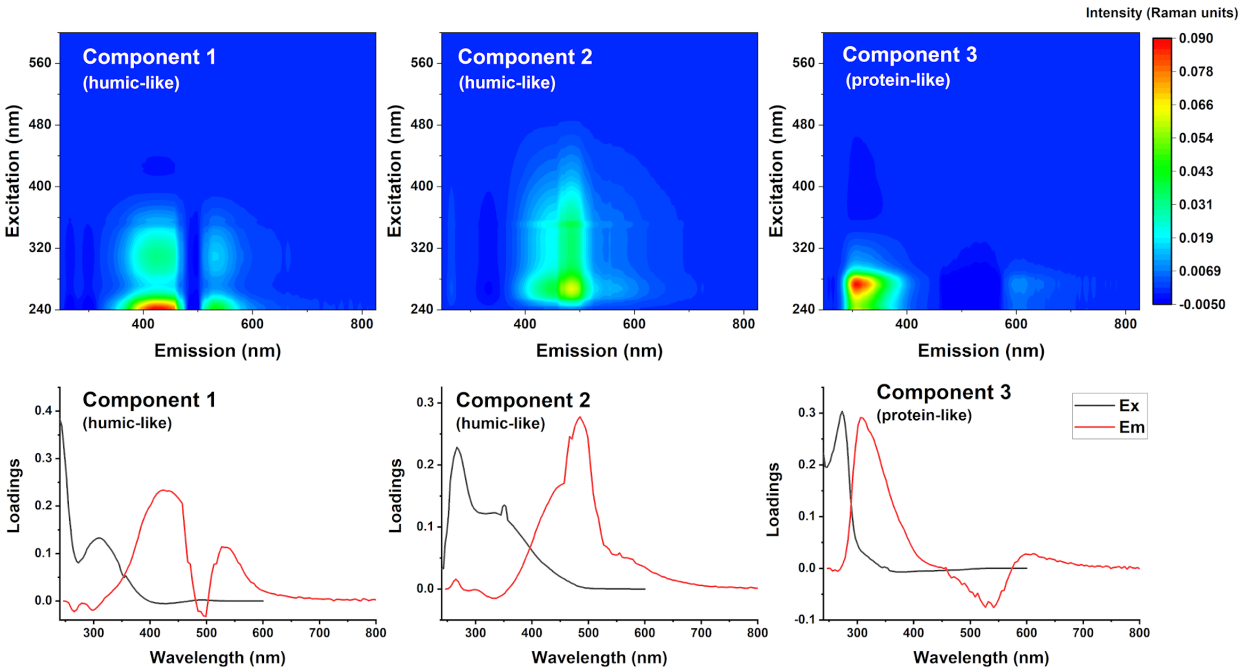

Figure 5 A three-component model combining New Zealand calibration data from 11 lakes. Components 1 and 2 are atypical but clearly humic-like, whilst component 3 is a typical protein-like component.

3.3 Comparing trophic level index scores and parameters against WEDOM fluorescence intensity

Figure 6 shows correlations between various measures of lake water quality, sedimentary FTIRS-TOC, and sedimentary WEDOM fluorescence. All fluorescence components are strongly positively correlated with each other and with FTIRS-TOC, indicating that increases in allochthonous input are not independent of increases in autochthonous production.

Regression values and statistics for fluorescence components vs trophic level indicators are reported in Table 1 and the regression of protein-like fluorescence vs TLI is shown in Figure 7. Residuals for Figure 7 passed the Shapiro-Wilk test (Shapiro & Wilk, 1965) for homoscedasticity with a p-value of 0.445. The relationships between humic-like fluorescence and Chl-a, TN and TP are not statistically significant at the $p < 0.05$ level. The relationship between humic-like fluorescence and TLI is statistically significant but explains a relatively low proportion of the variation. Protein-like fluorescence has a

statistically significant relationship ($p < 0.05$) with all trophic level indicators, and particularly with TLI and TP, and a relatively high R^2 in all cases (again, especially TLI and TP). This indicates that TLI is the trophic level indicator that can be most usefully predicted by WEDOM fluorescence measurements. Although both humic-like and protein-like fluorescence have statistically significant relationships with TLI, these variables are highly collinear.

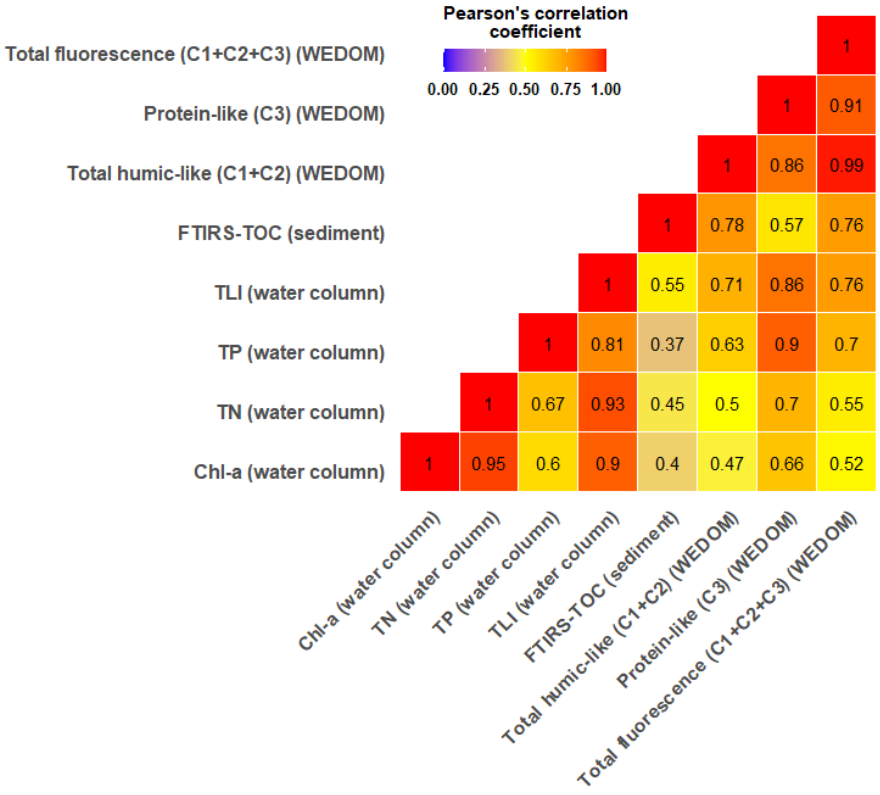

Figure 6 Pearson correlation matrix of averaged monitoring water-column data and fluorescence intensities for WEDOM total humic-like fluorescence (C1 + C2), total protein-like fluorescence (C3) and total fluorescence (C1 + C2 + C3). Chl-a = chlorophyll *a*, TN = total nitrogen, TP = total phosphorus from the training set of New Zealand lakes.

Table 1 Regression statistics (multiple R^2) for WEDOM fluorescence components vs water-column trophic level indicators in the training-set lakes.

3D EEM fluorescence components signal	Chl-*a*		Total nitrogen		Total phosphorus		Trophic level index score		TOC	
	R^2	p-value	R^2	p-value	R^2	p-value	R^2	p-value	R^2	p-value
Total humic-like	0.22	0.148	0.25	0.1209	0.49	0.0171	0.57	0.007122	0.57	0.04

Protein-like	0.43	0.0273	0.49	0.0159	0.81	0.0001745	0.74	0.0007375	0.25	0.07

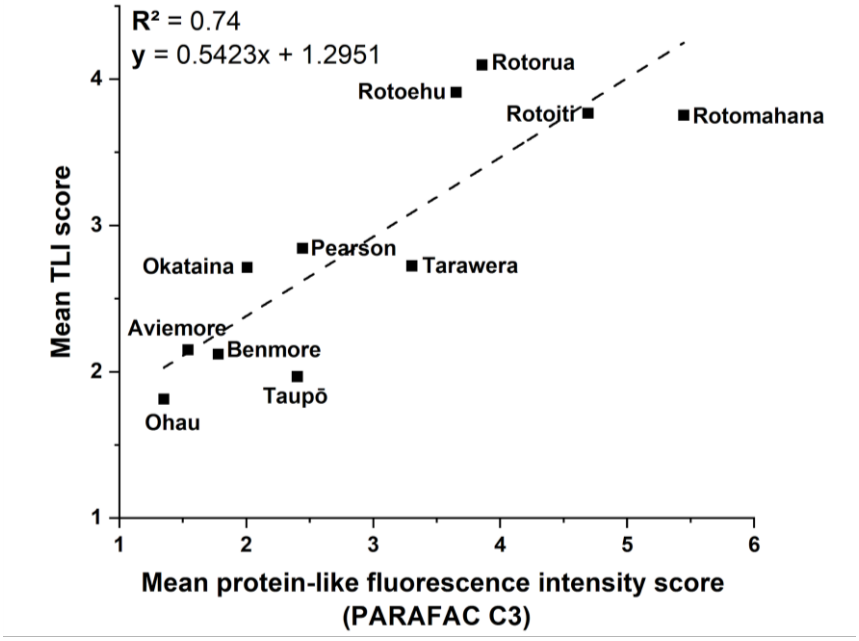

Figure 7 Regression of trophic-level index (water-column) against protein-like fluorescence intensity (WEDOM) for the 10 training-set New Zealand lakes. See Table 2 for regression values and statistics.

3.4. Fluorescence and sedimentary OM in Adelaide Tarn

Table 2 gives the results of conventional and optical measurements of OM characteristics in the ten subsamples from the Adelaide Tarn core. Figure 9 shows correlations between the conventional and optical measurements for these subsamples. Protein-like fluorescence is positively correlated with total nitrogen (0.93), total carbon (0.86), and TC/TN (0.64). Total humic-like fluorescence is also positively correlated with total carbon (0.73) and total nitrogen (0.84). FTIRS-TOC is positively correlated with each fluorescence component but has the strongest correlations with protein-like fluorescence (0.79) and total humic-like fluorescence (0.74).

Table 2 Conventional measurements of sediment organic carbon and optical measurements of WEDOM from 10 subsamples from the Adelaide Tarn core.

Depth (cm)	Age (Cal.	Sediment Total	Sediment Total	Sediment C:N ratio	Sediment FTIRS-	WEDOM PARAFAC C1 score	WEDOM PARAFAC C2 score	WEDOM PARAFAC	WEDOM PARAFAC

	year BP)	nitrogen (%)	carbon (%)		inferred TOC (%)	(humic-like)	(humic-like)	C1 + C2 score (total humic-like)	C3 score (protein-like)
4	**276**	0.44	5.83	13.28	6.0	2.94	3.69	6.63	1.29
44	**1,306**	0.52	7.66	14.66	7.2	2.90	3.40	6.3	1.26
97	**2,756**	0.58	8.39	14.49	10.9	4.63	5.14	9.77	1.50
204	**5,992**	0.58	8.98	15.58	7.1	5.23	6.15	11.38	1.61
257	**8,410**	0.66	11.59	17.45	11.7	5.33	4.54	9.87	1.55
299	**9,674**	0.74	13.61	18.42	14.9	7.69	5.90	13.59	2.01
338	**10,869**	0.80	13.03	16.38	12.6	10.49	10.72	21.21	2.10
366	**11,858**	0.59	9.22	15.58	9.7	5.97	5.01	10.98	1.56
395	**12,726**	0.61	8.80	14.39	9.5	5.31	5.34	10.65	1.69
417	**13,234**	0.58	8.47	14.53	9.8	6.23	7.34	13.57	1.65

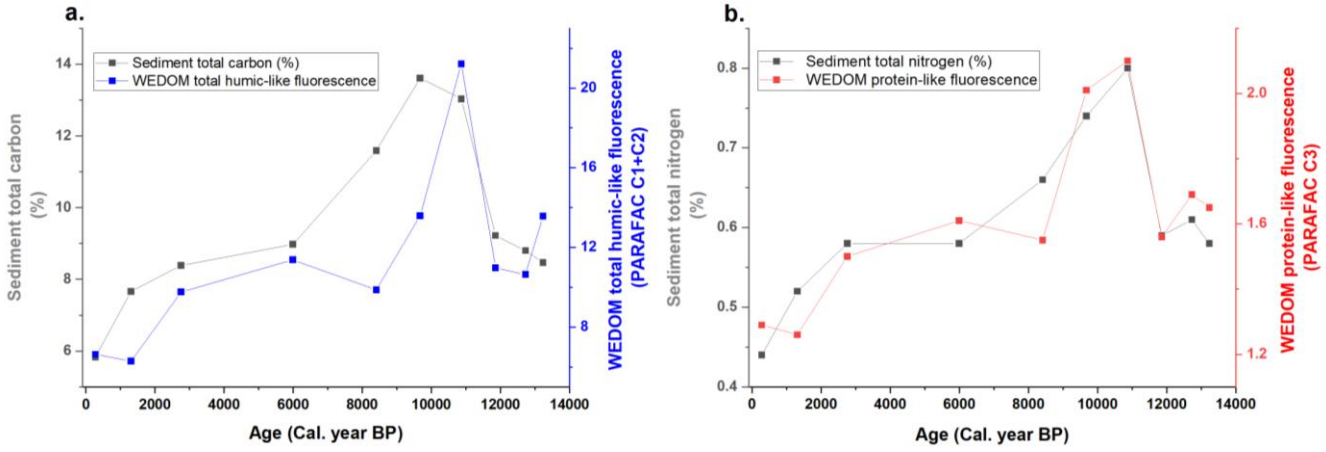

Figure 8 (a.) Sediment total carbon and WEDOM total humic-like fluorescence through the Adelaide Tarn sedimentary record **(b.)** Sediment total nitrogen (%) and WEDOM protein-like fluorescence through the Adelaide Tarn sedimentary record.

Table 3 Regression statistics (multiple R^2) for WEDOM fluorescence components vs sedimentary geochemical measurements in Adelaide Tarn.

Adelaide Tarn 3D EEM fluorescence components signal (WEDOM)	**TC (Sediment)**		**TN (Sediment)**		**TC:TN (Sediment)**		**FTIRS-TOC (Sediment)**	
	R^2	**p-value**	**R^2**	**p-value**	**R^2**	**p-value**	**R^2**	**p-value**
Total humic-like	0.53	0.02	0.73	0.02	0.21	0.18	0.64	0.06
Protein-like	0.75	0.001	0.86	0.0001	0.43	0.04	0.4	0.053

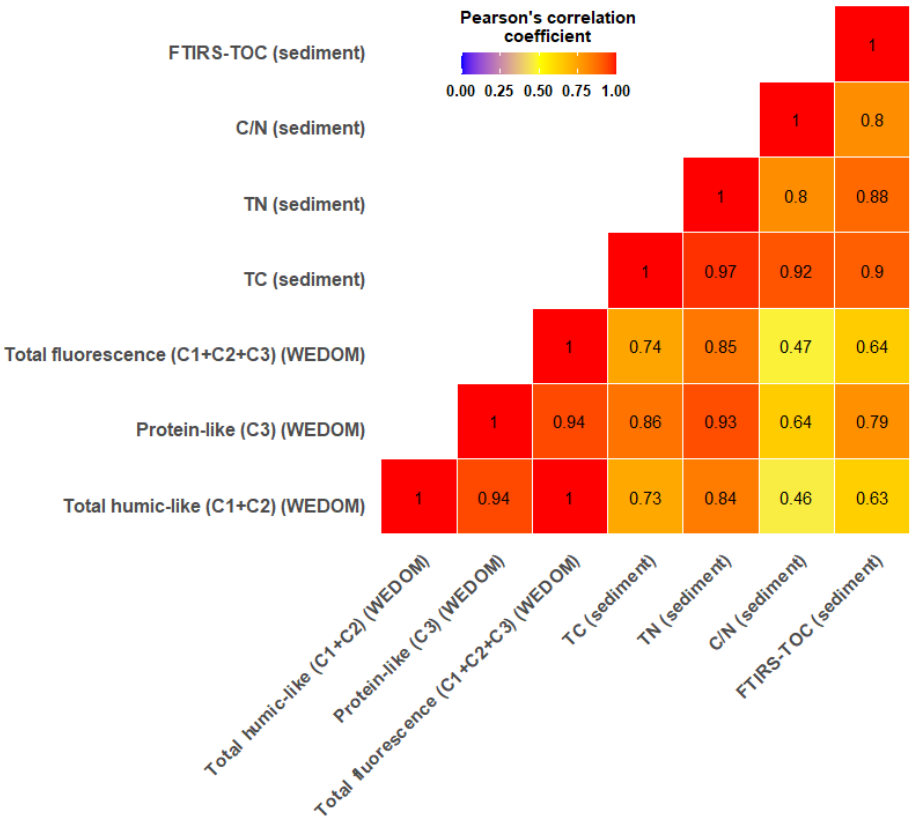

Figure 9 Pearson correlation matrix of conventional sediment measurements and optical WEDOM measurements from 10 Adelaide Tarn sediment sub-samples (Table 2).

4. Discussion

4.1 The relationship between WEDOM fluorescence components and TLI parameters

Protein-like fluorescence is very strongly correlated with total nitrogen, total phosphorus, trophic level index, and chlorophyll *a* (Figure 6). All these correlations are statistically significant ($p < 0.05$; Table 1). Conversely, humic-like fluorescence (indicating allochthonous OM) is significantly less correlated to indicators of trophic level, and the correlation with TN and chlorophyll *a* is not statistically significant at $p < 0.05$. This indicates that, although both parameters can tell us something about lake trophic state, the sedimentary protein-like fluorescence signal is more useful in this regard (Figure 6).

The detailed relationships between trophic level indicators and fluorescence components are consistent with the hypothesis that protein-like fluorescence is a faithful proxy for the trophic level of the lake. Chlorophyll *a* is a proxy for algal biomass (Boyer *et al*. 2009), and therefore the significant relationship between protein-like fluorescence and chlorophyll *a* indicates that sedimentary protein-like

fluorescence is sensitive to autochtonous productivity. Meanwhile, the lack of a significant correlation between chlorophyll *a* and sedimentary humic-like fluorescence indicates that humic-like fluorescence is not directly related to within-lake productivity. Similarly, total nitrogen is affected by the source of OM. Carbon-nitrogen ratios are higher in allochthonous than in autochthonous OM, so in a mixed system, changes in the amount of autochthonous input will have a greater effect on total nitrogen than changes in the amount of allochthonous input. The relationships shown in Figure 6 and Table 1 thus provide support for the use of protein-like fluorescence from sedimentary WEDOM as a measure of lake trophic state.

The relationships between the different fluorescence components and FTIRS-TOC tell a different story. In this case, humic-like fluorescence is significantly and strongly correlated with FTIRS-TOC, while the correlation between protein-like fluorescence and FTIRS-TOC is weak and not statistically significant (Figure 6; Table 1). Overall, protein-like fluorescence has relatively low absolute values and variance across lakes, while in all but the microtrophic Lake Ohau, humic-like fluorescence has higher absolute values and variance (Supplementary Figure 1). This indicates a generally greater contribution of allochthonous OM to the overall lacustrine OM pool in these lakes, and thus explains the strong and significant correlation between humic-like fluorescence and FTIRS-TOC, as well as the lack of significance in the relationship between protein-like fluorescence and FTIRS-TOC. Thus, even in a set of lakes where autochthonous OM input plays a relatively minor role in between-lake carbon-cycle variability, protein-like fluorescence can still be used to predict trophic level.

The fluorescence components are strongly positively correlated with each other, indicating that increases in allochthonous input are not independent of increases in autochthonous production (Figure 6). This is to be expected, as nutrients associated with allochthonous DOM can stimulate lake productivity (Karlsson *et al.* 2009). One shortcoming of our data is the under-representation of mesotrophic and (especially) eutrophic lakes.

Monitoring data in New Zealand has demonstrated that TLI has a moderate negative correlation with the percentage of native/alpine vegetation cover (R^2= -0.55) (Verburg *et al.* 2010), and lakes in very cold climates had the lowest median TLI score (2.3: oligotrophic) compared to lakes from other

climate regimes in New Zealand. Verburg *et al.* (2010) extrapolated their findings to suggest that New Zealand lakes are mesotrophic on average, and alpine lakes with native vegetation are typically microtrophic or oligotrophic (Verburg *et al.* 2010), being representative of pre-human lake conditions in New Zealand (Abell *et al.* 2019). Because even low-TLI lakes are likely to experience increased DOM loads due to changes in catchment land cover (Rae *et al.* 2001), and because sedimentary protein-like fluorescence appears to be sensitive to trophic level changes even at low levels of productivity, a fluorescence-based investigation into recent and ongoing perturbations of DOM might be fruitful in detecting subtle shifts in lake trophic status in New Zealand's still pristine lake systems.

4.2 A comparison of sediment fluorescence to geochemical data in Adelaide Tarn

We do not have information about total phosphorous or chlorophyll *a* in Adelaide Tarn sediments. The only measure of productivity corresponding to the indicators used for the training set lakes is total nitrogen. Notably, the values reported here are of total *sedimentary* nitrogen, not of nitrogen in the water column. Furthermore, the Adelaide Tarn dataset represents *within*-lake variability, while the modern lakes dataset represents *between*-lake variability. Having said this, the pattern observed is similar to that seen in the modern lakes: while both humic-like and protein-like fluorescence are statistically significantly correlated with total nitrogen at $p < 0.05$, protein-like fluorescence both shows a stronger correlation and a lower p-value than humic-like fluorescence. Protein-like fluorescence is also significantly correlated to carbon-nitrogen ratio, a measure of the contribution of aquatic OM to the overall carbon pool (Meyers & Benson, 1988), although in this case the correlation is only moderate. Humic-like fluorescence does not have a statistically significant relationship with carbon-nitrogen ratio at $p < 0.05$ (Table 3). This pattern of correspondences supports the hypothesis that protein-like fluorescence can be used as a proxy for lake productivity in ancient as well as modern lake sediments.

In terms of measures of total carbon in Adelaide Tarn, the picture is somewhat mixed. While both humic-like and protein-like fluorescence show statistically significant correlations to both conventionally measured total carbon (TC) and FTIRS-TOC, the strength and significance of the correlation varies depending on which measure of total carbon is used. Protein-like fluorescence is

399 more strongly correlated with TC, while humic-like fluorescence is more strongly correlated with
400 FTIRS-TOC. The reason for this discrepancy is not clear. However, as with our modern lakes, the fact
401 that both fluorescence measures correlate with both measures of total carbon is likely due to the fact
402 that nutrients associated with or transported by allochthonous DOM (primarily humic-like) can
403 stimulate autotroph productivity (Karlsson *et al.* 2009) and thus drive elevated protein-like
404 fluorescence.

405 In Adelaide Tarn, a simple catchment with limited anthropogenic influence, changes in
406 allochthonous inputs must be associated with natural environmental change. Indeed, the impacts of
407 future climate change on lakes are expected to be most pronounced at high elevations (Bradley *et al.*
408 2004), where treeline advancement and vegetation change has occurred due to temperature and
409 precipitation changes (Roush *et al.* 2007).

410 One possible issue with using protein-like fluorescence to reconstruct past changes in
411 productivity is the question of how faithfully sediments preserve autochthonous OM. Because
412 autochthonous OM is less refractory on average than allochthonous OM, it is more likely to be
413 respired and therefore there is likely to be a preservation bias against autochthonous OM.
414 Furthermore, preservation may vary with climate, with warmer conditions leading to increased rates
415 of respiration and therefore reduced preservation of protein-like fluorophores, obscuring the signal of
416 productivity changes. However, there is evidence that even in highly degraded OM, organic
417 components can survive in sufficient quantities to allow reconstruction of past productivity changes
418 (Sobek *et al.* 2009).

419 In Adelaide Tarn, the intensity of protein-like fluorescence ranges from 1.26 to 2.1
420 fluorescence units, with a median value of 1.59. This median falls at the lower end of the range of
421 protein-like fluorescence values shown in the modern lakes. Specifically, it is close to values shown
422 by Lake Aviemore (1.54) and Lake Benmore (1.78) (both oligotrophic), and higher than the value
423 shown by Lake Ohau (1.35) (microtrophic). Presently, Adelaide Tarn is microtrophic/oligotrophic,
424 and has never been subject to high levels of anthropogenic nutrient input. The downcore protein-like
425 fluorescence scores are consistent with protein-like fluorescence as an indicator of past trophic level.

Only two protein-like fluorescence scores fall outside of the range of scores shown by modern oligotrophic/microtrophic lakes, and these are the most recent samples which would be expected to have undergone the least degradation. There is therefore no evidence of significant degradation of the proteinaceous OM in the Adelaide Tarn samples.

A further piece of evidence supporting protein-like fluorescence as a proxy for past lake productivity is the observed downcore pattern of variability in protein-like fluorescence at Adelaide Tarn (Figure 8 b). Notably, the highest protein-like fluorescence intensities correspond to an interval ~10.8–9.7 kyr BP. These sediments were deposited during the Holocene climatic optimum (HCO, 10.5–9 kyr BP), when climate was inferred to be 1.5-2 °C warmer than the intervening period (Barrows *et al.* 2007). If preservation of proteinaceous DOM was not uniform in time, we would expect that preservation would be lower under warmer conditions due to enhanced respiration of DOM, and thus we would see a decrease in protein-like fluorescence at the HCO. High protein-like fluorescence suggests that protein-like fluorescence signals in sediment archives can be faithful indicators of productivity changes.

5. Implications and recommendations for future research

This study makes the first link between New Zealand lake systems and the large body of international research on fluorescence and water quality. We demonstrate a strong and coherent link between protein-like fluorescence and within-lake productivity via the TLI indicator for modern lakes, and find evidence that sedimentary fluorescence may also be a faithful recorder of palaeo-productivity and trophic status in more ancient lake sediments.

The application of water quality indices in contemporary monitoring is somewhat flawed, as the indices are constructed using independent variables that may not co-vary (e.g., TN concentration may increase, but TP may decline), potentially resulting in similar TLI scores representing quite different ecosystem properties. There is potential for further investigation into the potential of fluorescence measurements to improve water quality measurements in such situations.

Further research should continue to test the relationship between 3D EEM fluorescence in contemporary water samples and in recently deposited sediments and/or suspended sediments. Microbial reworking of OM during sinking and early sedimentation may diminish the total OM concentration whilst replacing many primary organic compounds with secondary ones, and therefore the DOM contained in sediment may be altered compared to DOM contained in the surface waters (Meyers & Ishiwatari, 1993).

Water extraction of DOM may also have limitations in its power to delineate stratigraphic differences in a sediment core. The extraction of DOM will always be incomplete; even in NaOH extractions, 50–70 % of the OM is left unextracted (Lehmann & Kleber, 2015). Post-deposition, DOM mobility and degradation is poorly understood, however, the vigorous shaking required to extract CDOM (after freeze-drying) indicates that the WEDOM was strongly bound to the sediment particles (Meyers & Ishiwatari, 1993). The consistent results from Adelaide Tarn provide suggest that WEDOM analyses have stratigraphic integrity, but this finding should be investigated further.

6. Conclusions

This study demonstrated that protein-like sedimentary WEDOM fluorescence is related to water quality indicators (particularly TP and TLI in modern lake sediments, and TN in Adelaide Tarn), whilst humic-like WEDOM fluorescence corresponds with TOC concentrations. This approach may compliment reconstructions of past trophic status and provide a means of evaluating the contemporary water quality of more remote and/or infrequently monitored lake systems.

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8. Disclosure statement

The authors have nothing to disclose regarding financial interests, conflicts of interests or other benefits from this research.

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613

SUPPLEMENTARY INFORMATION

The sediment fluorescence - trophic level relationship: using water-extractable organic matter to assess past lake water quality in New Zealand

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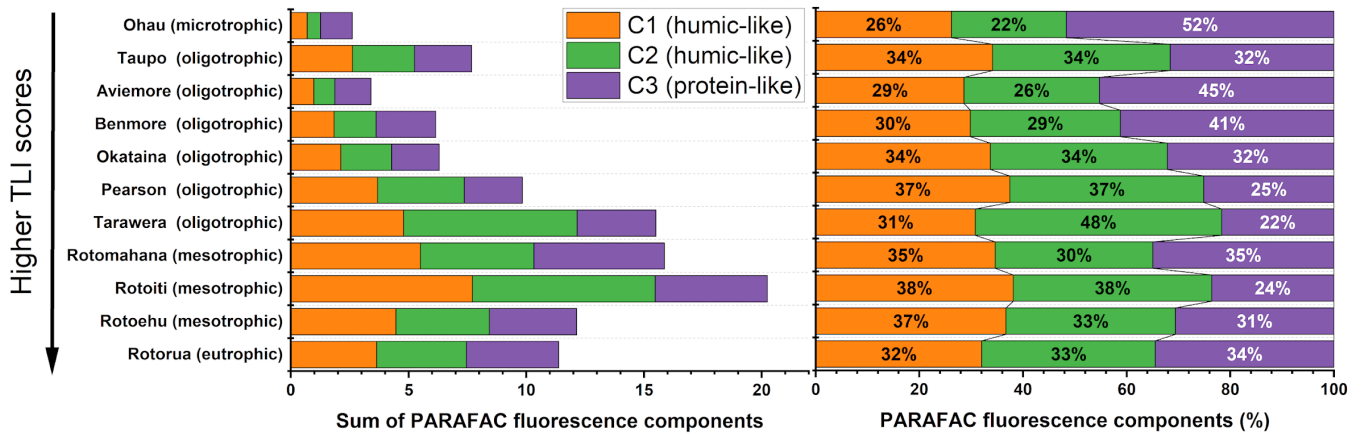
626 **Supplementary Table 1** Information on lakes used in the training-set of fluorescence measurements of modern lake
627 sediments.

Lake	Trophic state (based on average of annual TLI scores 3-years prior to sampling)	Average TLI score [59]	TLI data years[59]	Lake size (ha.)	Max. water depth (m)	N. of modern samples (N. of cores)	Location	Altitude (m)	Co-ordinates	Geomorphic type	Dominant land cover[56]
Aviemore	Oligotrophic	2.2	2010-2011	2900	unknown	2(1)	Canterbury, S. Island	268	Lat: -44.619; Long: 170.305	reservoir	pasture
Benmore	Oligotrophic	2.1	2009-2011	7585	120	1(1)	Canterbury, S. Island	361	Lat: -44.525; Long: 170.076	reservoir	pasture
Ohau	Microtrophic	1.8	2009-2011	5927	129	4(1)	Canterbury, S. Island	410	Lat: -44.235; Long: 169.850	glacial	native
Okataina	Oligotrophic	2.7	2009-2011	1080	78.5	4(2)	Bay of Plenty, N. Island	284	Lat: -38.134; Long: 176.407	volcanic	native
Pearson	Oligotrophic	2.8	2009-2011	202	17	2(1)	Canterbury, S. Island	616	Lat: -43.116; Long: 171.781	glacial	native
Rotoehu	Mesotrophic	3.9	2013-2015	810	13.5	8(3)	Bay of Plenty, N. Island	289	Lat: -38.024; Long: 176.528	volcanic	native
Rotoiti	Mesotrophic	3.8	2009-2011	3400	126	3(3)	Bay of Plenty, N. Island	277	Lat: -38.029; Long: 176.384	volcanic	native
Rotomahana	Mesotrophic	3.8	2009-2011	900	125	5 (2)	Bay of Plenty, N. Island	339	Lat: -38.270; Long: 176.424	volcanic	native
Rotorua	Eutrophic	4.1	2013-2015	17980	45	11(4)	Bay of Plenty, N. Island	386	Lat: -38.068; Long: 176.273	volcanic	pasture
Tarawera	Oligotrophic	2.7	2009-2011	4130	87.5	4(3)	Bay of Plenty, N. Island	282	Lat: -38.211; Long: 176.411	volcanic	native
Taupō	Oligotrophic	2 (1.9-2)	2009-2011	62200	162.8	5(5)	Waikato, N. Island	360	Lat: -38.751; Long: 175.793	volcanic	native

628



Supplementary Figure 1 (a.) Sum of PARAFAC components for each lake **(b.)** PARAFAC Component (%) for each lake.

Supplementary Table 2 Information on lakes used in the FTIRS-TOC calibration.

Lake	Mean FTIR-TOC (%) (range)	Mean NPOC measurement (%) (range)	Lake size (ha.)	Max. depth (m)	N. of modern samples	Region	Altitude (m)	Co-ordinates	Geomorphic type	Dominant land cover
Aviemore	0.9 (0.5-1.1)	0.9	2900	unknown	4	Canterbury, S. Island.	268	Lat: -44.619; Long: 170.305	reservoir	pasture
Adelaide Tarn	10 (6.0-14.9)	9.6 (5.8-13.6)	6	7.6	10	Tasman, S. Island	1250	Lat: -40.941; Long: 172.544	glacial	native
Alpine Lake/ Ata Puai	23.6 (10.1-29.8)	24 (6.8-29.6)	61.5	20	8	West Coast, S. Island	101	Lat: -43.286; Long: 170.137	glacial	native
Benmore	0.9 (0.5-1.1)	1.1 (0.6-1.2)	7585	120	13	Canterbury, S. Island	361	Lat: -44.525; Long: 170.076	reservoir	pasture
Kaniere	4.4 (3.3-5.2)	3.1 (2.6-3.9)	2200	195	3	West Coast, S. Island	72	Lat: -42.830; Long: 171.145	glacial	native
Mahinerangi	17.3 (6.2-28.3)	15.0 (8.9-20.4)	15	unknown	4	Otago, S. Island	398	Lat: -45.833; Long: 169.887	reservoir	pasture and

										tussock grassland
Middleton	8.7 (7.8-9.0)	8.6 (6.2-8.7)	118	unknown	5	Canterbury, S. Island	523	Lat: -44.277; Long: 169.849	glacial	native
Ngapouri	5.8 (4.8-6.2)	6.2 (5.2-7.8)	991	24.5	8	Waikato, N. Island	475	Lat: -38.338; Long: 176.334	volcanic	native
Ohau	0.6 (0.4-0.9)	0.4 (0.3-0.4)	5927	129	5	Canterbury, S. Island	410	**Lat:** -44.235; **Long:** 169.850	glacial	native
Okataina	3.3 (1.1-7.1)	3.0 (1.2-5.8)	1080	78.5	55	Bay of Plenty, N. Island	284	Lat: -38.134; Long: 176.407	volcanic	native
Pearson	3.6 (2.6-6)	4.2 (3.2-6.4)	202	17	12	Canterbury, S. Island	616	Lat: -43.116; Long: 171.781	glacial	native
Rotorua	3.9 (3.2-4.1)	5 (4.8-5.1)	17980	45	3	Bay of Plenty, N. Island	386	Lat: -38.068; Long: 176.273	volcanic	pasture
Von	12.7 (10.4-15.7)	15.6 (9.2-19)	0.87	15	10	Otago, S. Island	303	Lat: -45.139; Long: 168.358	glacial	native

Further details on the lakes studied are available via www.lawa.org.nz

Supplementary Table 3 TLI classification descriptions in New Zealand (LAWA, 2014).

Trophic level index score	Lake water quality
<2	Microtrophic (very good water quality)
2-3	Oligotrophic (good water quality)
3-4	Mesotrophic (average water quality)
4-5	Eutrophic (poor water quality)
5-7	Supertrophic (very poor water quality)