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The potential power and pitfalls of using the X-ray fluorescence molybdenum incoherent: Coherent scattering ratio as a proxy for sediment organic content

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ABSTRACT

Changes in organic matter concentration in sediment cores from natural archives such as lakes and wetlands can be a valuable tool in paleoenvironmental studies. The molybdenum incoherent: coherent scattering ratio (moly ratio) from the Itrax core scanner offers the potential to measure down core changes in sediment organic content. The analysis is rapid, high resolution and does not destroy samples. We built upon previous studies of the power and potential pitfalls of using the moly ratio as a proxy for organic content in sediments. An important difference between our study and previous work is that we accounted for the total mass of moisture and organic content in the sediment using loss on ignition. This had the advantage over total organic carbon measurement of being able to account for all light elements (H, C, N, and O) that would affect the moly ratio. We used redundancy analysis to determine that both organic and moisture content can have large, independent, and variable effects on the moly ratio. It is therefore critical that moisture and organic content have a constant relationship with each other in a core. Samples with higher moisture to organic content ratios can over predict organic content and vice versa. The effect of moisture only accounted for 30% of the prediction error for the moly ratio in our study. We argue that a large part of remaining error reflects sample heterogeneity. XRF core scanning and organic content determination from sub-samples can show different results because the mean sediment composition is different. We recommend that calibration sub-samples are large (≥ 2 cm^3) in potentially heterogeneous sediments, authors should report the sample size used for calibration purposes, and multiple scans of the core may be needed. If organic content is an important proxy for an environmental reconstruction, we recommend calibration of the moly ratio and confirming a constant relationship between moisture and organic content. Thoughtful selection of sub-samples for this purpose could mean that calibration can be performed with a minimum of extra effort.

1. Introduction

Changes in organic matter concentration in sediment cores from natural archives such as lakes and wetlands can serve as a valuable tool in paleoenvironmental studies. Down-core changes in sedimentary organic content can be used to cross correlate sediment stratigraphy from multiple cores taken at the same site (Gale et al., 1995; Woodward et al., 2014a). Sediment organic content can also be used as a proxy for environmental changes, such as variation in aquatic productivity due to climate change (Meyers and Lallier-Vergés, 1999) and/or eutrophication (Meyers, 2003). A decrease in sediment organic content may also be used to indicate the influx of inorganic material due to catchment disturbance events such as forest clearance (Woodward et al., 2014a, Woodward et al., 2014b), earthquakes (Woodward et al., 2018), or tsunamis in coastal wetlands (Chagué-Goff et al., 2016).

There are two common methods that can be used to directly analyse the organic content of sediments; but these are destructive, can be expensive, and require sediment sub-sampling. The carbon and nitrogen content of sediments can be analysed using a CHN elemental analyser that uses the principle of the Dumas method. This method involves combustion, separation of combustion products by a chromatographic column and detection by a thermal conductivity detector (Shah et al., 1956). Loss on ignition (LOI) uses the drying of sediment at 60 °C (to remove water) then combustion at 550 °C to remove organics (Dean, 1974; Heiri et al., 2001; Santisteban et al., 2004). The resolution possible with these methods is determined by the limits of precise sediment sub-sampling. This is usually ∼2 mm resolution for wet sediments in our experience. Higher resolution may be desirable, especially when

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working on laminated sediment deposits (Lotter et al., 1997).

X-ray fluorescence (XRF) core scanners such as the Itrax (Croudace et al., 2006) have the potential to provide rapid, high resolution (< 1 mm) measurements of sediment organic content. This method is also non-destructive as far as most sediment properties are concerned (Davids et al., 2009). There are two main proxies that are commonly used for sediment organic content from XRF core scanners; bromine (Ziegler et al., 2008) and the molybdenum incoherent: coherent scattering ratio (Liu et al., 2013; Sáez et al., 2009; Chawchai et al., 2016). Bromine has been commonly used as a proxy for organic content in marine cores (Ziegler et al., 2008). Although it has been used as a proxy for organic content in freshwater settings (Fedotov et al., 2015; Fletcher et al., 2015), there has not been a systematic investigation of the relationship between bromine and organic content.

The molybdenum incoherent: coherent scattering ratio (hereafter referred to as the moly ratio) has been more thoroughly investigated as a proxy for organic content in freshwater settings (Liu et al., 2013; Saez et al., 2009; Chawchai et al., 2016). The moly ratio is the ratio of Compton (incoherent) scattering to Rayleigh (coherent) scattering detected by the XRF core scanner. For conventional XRF, where samples are dried and homogenised, the moly ratio will principally be affected by the mean atomic number of the elements in a sample (Duvauchelle and Babot, 1999). Compton scattering occurs when the energy of the incident X-rays (photons) is much greater than the energy binding electrons to the atom nucleus (Duvauchelle and Babot, 1999). The energy binding the electron to the nucleus of the atom tends to be lower in elements with lower atomic weight (Duvauchelle and Babot, 1999). Collision of incident X-rays (photons) with low energy electrons results in the Compton effect. The Compton effect is a loss of energy from the incident photon, a reduction in wave frequency of the reflected X-rays, and ultimately a change in photon momentum.

In sediment cores we would expect high values of the moly ratio in horizons where elements with low atomic numbers (e.g. H, C, N, and O) are abundant. This will occur when sediments are wet (contain abundant H_2O) and/or organic (contain abundant H, C, N, and O). However, there are also other factors to consider with on-line XRF core scanning that could affect the energy of emitted photons and hence the moly ratio. Water content will attenuate X-ray energy and affect Compton scattering because of the abundance of light elements (H and O). Other factors that can affect the moly ratio with in-line XRF core scanning include grain-size variability, surface roughness and changes in core surface elevation (Weltje and Tjallingii, 2008).

XRF core scanner measured moly ratio is commonly used as a proxy for organic content in unconsolidated sediments (Thomson et al., 2006; Guyard et al., 2007; Burnett et al., 2011; Giralt et al., 2011; Jouve et al., 2013), but there have only been a few studies that have thoroughly investigated the potential power and pitfalls of using the moly ratio to predict sediment organic content (Liu et al., 2013; Saez et al., 2009; Chawchai et al., 2016). Results so far show that the strength of the correlation between the moly ratio and organic content is quite variable, with an R ranging from 0.19 to 0.92 (Table 1). The poorest relationship between the moly ratio and organic content (R = 0.19–0.59) was reported by Chawchai et al. (2016) from highly organic (LOI > 40%) sediments collected in Thailand (Table 1). Chawchai et al. (2016) therefore concluded that the moly ratio is of limited use as an indicator for variations in organic content in peat or peaty gyttja.

In this paper we expand on the work of Liu et al. (2013), Saez et al. (2009) and Chawchai et al. (2016) by exploring the influence of moisture and organic content on the moly ratio. We wanted to determine if there are useful guidelines that can be established to assess the quality of moly ratio organic content reconstructions, and improve the methods that we use to calibrate the moly ratio. We chose to use loss on ignition as a measure of organic content so we could account for the entire mass of organic material in the core (not just carbon) and also calculate the entire mass of elements with low atomic numbers in sediment sub-samples. This way we could fully account for the effect of moisture and organic content on the moly ratio. Some previous studies have assessed the apparent effect of moisture and organic content on the moly ratio separately (Fortin et al., 2013). However, we are not aware of any studies that have quantitatively assessed how these two properties may independently affect the moly ratio. We also chose to focus on fine-grained sediments that do not contain carbonates, so we could easily assess the influence of moisture and organic content on the moly ratio.

2. Materials and methods

2.1. Core collection

2.1.1. Core collection methods

Cores were available from four sites; Lake Mary, Little Llangothlin Lagoon, Lake Chappa'ai, and Blue Lake (Figs. 1 and 2). These cores contain a large variation in sediment composition and organic content so are ideal for this study. A description of core collection methodology for the Little Llangothlin Lagoon and Chappa'ai cores is provided in Woodward et al. (2014a) and Woodward et al. (2018) respectively. The most important details relevant to this paper are that the Little Llangothlin Lagoon core did not require stabilisation in the field with sodium polyacrylate. Sodium polyacrylate stabilises wet sediment and allows the transport of cores without sediment mixing. The upper unconsolidated sediments from Chappa'ai required stabilisation with sodium polyacrylate following the protocol outlined in Tomkins et al. (2008). Cores from Lake Mary and Blue Lake were collected using a Universal Corer using the same protocol followed for the collection of the Chappa'ai (Woodward et al., 2018). Cores from these sites were also stabilised in the field using sodium polyacrylate.

2.1.2. Description of study sites

Lake Mary (Fig. 2A) is a small (0.02 km^2), shallow (< 1 m deep) freshwater (conductivity = 64 $\mu S\,cm^{-1}$), supertrophic (Chlorophyll *a* up to 13 $\mu g\,L^{-1}$) lake at an altitude of 590 m with a catchment area of 8.9 km^2. The bedrock comprises low-grade metamorphosed mudstones and sandstones. Details of the climate, catchment land cover, morphology, geology and limnology for Little Llangothlin Lagoon can be found in Woodward et al. (2014a) and Woodward et al. (2017), for Blue Lake in Raine (1982), Stanley and De Deckker (2002) and Chang et al. (2015), and for Lake Chappa'ai in Woodward et al. (2018). Little Llangothlin Lagoon (Fig. 2B) is a shallow (< 2 m maximum depth) supertrophic (Chlorophyll *a* up to 30 $\mu g\,L^{-1}$), freshwater (conductivity < 300 $\mu S\,cm^{-1}$) 1.2 km^2 lake at an altitude of 1350 m. The 3.2 km^2 catchment has a predominantly basalt and granite bedrock. Blue Lake (Fig. 2C) is a deep (max depth = 28 m), freshwater (conductivity < 10 $\mu S\,cm^{-1}$), oligotrophic (Chlorophyll *a* < 1 $\mu g\,L^{-1}$) 0.14 m^2 cirque lake at an altitude of 1890m. The Blue Lake catchment is 1.9 km^2 and the bedrock is granite and Ordovician metamorphosed shales. . Lake Chappa'ai (Fig. 2D) is a small (0.02 km^2), freshwater (conductivity = 20 $\mu S\,cm^{-1}$), oligotrophic (Chlorophyll *a* = 1 $\mu g\,L^{-1}$) cirque lake at an altitude of 1470 m with a maximum depth of 6.8 m and a catchment area of 0.15 km^2. The bedrock in the Lake Chappa'ai catchment is low-grade metamorphosed mudstones and sandstones.

2.2. Itrax XRF geochemistry

All the cores were scanned using Cox Analytical Systems Itrax core scanner based at Australian Nuclear Science and Technology Organisation (ANSTO). The surfaces of all the cores were cleaned prior to obtaining optical images. The cores were then covered with Ultralene foil prior to the X-Radiograph and XRF scans. The XRF scans were performed using a Mo tube at 500 μm resolution. Most XRF settings were the same except the voltage was 5 kV higher for the Little Llangothlin core (Table 2). This will have negligible effect on this study as there is little variation in excitation for most elements for the Mo

Table 1
Summary of studies which have tested the correlation between the moly ratio and organic content. Grey highlighted entries indicate the most organic sediments from Chawchai et al. (2016). These had an organic content (LOI) > 30%. Chawchai et al. (2016), Liu et al. (2013), Sáez et al. (2009).

Authors	Site	Core section	Measure of organic conent	Carbonates?	Relationship	Correlation (R)
This Study	Little Llangothlin Lagoon	Whole core	LOI	N	Exponential	0.95
	Little Llangothlin Lagoon	LOI > 40%	LOI	N	Exponential	0.90
	Lake Mary	Whole core	LOI	N	Exponential	0.95
	Blue Lake	Whole core	LOI	N	Exponential	0.92
	Chappa'ai	Whole core	LOI	N	Exponential	0.89
Chawchai et al. (2016)	Lake Kumphawapi	Whole core	LOI	N	Linear	0.87
	Lake Kumphawapi	Unit 1a	LOI	N	Linear	0.62
	Lake Kumphawapi	Unit 1b	LOI	N	Linear	0.63
	Lake Kumphawapi	Unit 2a	LOI	N	Linear	0.80
	Lake Kumphawapi	Unit 2b	LOI	N	Linear	0.21
	Lake Kumphawapi	Unit 3a	LOI	N	Linear	0.27
	Lake Kumphawapi	Unit 3b	LOI	N	Linear	0.27
	Lake Kumphawapi	Whole core	TOC	N	Linear	0.80
	Lake Kumphawapi	Unit 1a	TOC	N	Linear	0.65
	Lake Kumphawapi	Unit 1b	TOC	N	Linear	0.69
	Lake Kumphawapi	Unit 2a	TOC	N	Linear	0.76
	Lake Kumphawapi	Unit 2b	TOC	N	Linear	0.19
	Lake Kumphawapi	Unit 3a	TOC	N	Linear	0.23
	Lake Kumphawapi	Unit 3b	TOC	N	Linear	0.20
	Lake Nong Leng Sai	Whole core	LOI	N	Linear	0.89
	Lake Nong Leng Sai	Unit 1	LOI	N	Linear	0.79
	Lake Nong Leng Sai	Unit 2	LOI	N	Linear	0.37
	Lake Nong Leng Sai	Unit 2, LOI >40%	LOI	N	Linear	0.30
	Lake Nong Leng Sai	Unit 3	LOI	N	Linear	0.78
	Lake Nong Leng Sai	Whole core	TOC	N	Linear	0.92
	Lake Nong Leng Sai	Unit 1	TOC	N	Linear	0.84
	Lake Nong Leng Sai	Unit 2	TOC	N	Linear	0.59
	Lake Nong Leng Sai	Unit 2, LOI >40%	TOC	N	Linear	0.55
	Lake Nong Leng Sai	Unit 3	TOC	N	Linear	0.87
Liu et al. (2013)	Lake Malawi	Whole core	TOC	Y	Linear	0.70
	Lake Qinghai	Whole core	TOC	Y	Linear	0.89
Sáez et al. (2009)	Raraku Lake	Whole core	TOC	Y	Linear	0.7

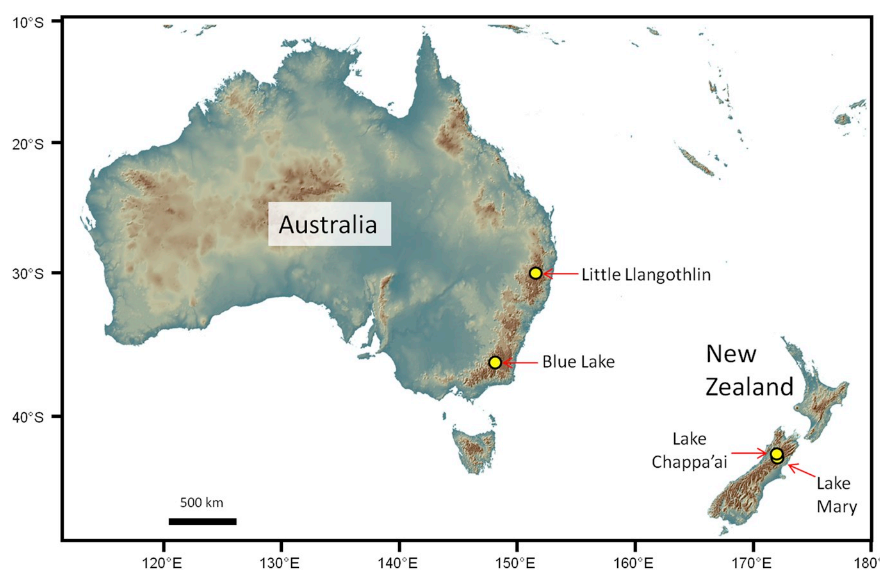

Fig. 1. The location of the sites where cores were collected for this study.

tube above 20 kV (Jarvis et al. (2015). The measuring spot size for the Itrax scans was 0.5 × 4 mm. Only the moly ratio was used from the Itrax data for the purpose of this paper. The moly ratio was calculated as the ratio between incoherent and coherent scattering values output from the Itrax (moly ratio = incoherent scattering/coherent scattering). Itrax data was then averaged to match the resolution of the LOI data, since the Itrax samples were higher resolution than the LOI samples.

2.3. Sediment organic and moisture content

Core sub-samples were collected using a scalpel to cut out approximate 1 cm^3 samples. Cores samples represented 1 cm or 0.5 cm thick intervals. The Little Llangothlin core was sampled continguously at 0.5 cm intervals, the Lake Mary core was sampled contiguously at 1 cm intervals. The Blue Lake and Lake Chappa'ai cores were not sampled

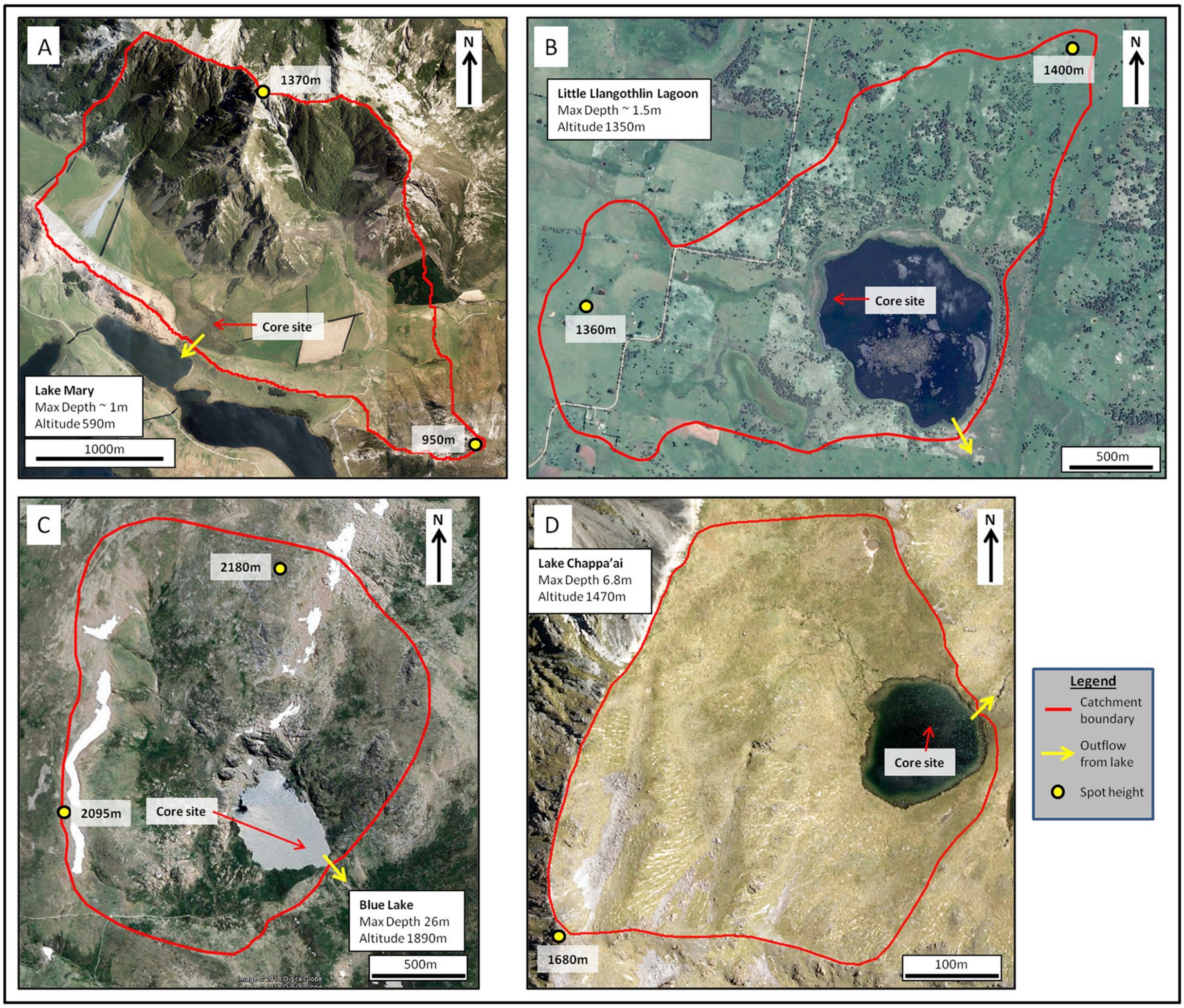

Fig. 2. Satellite images of the four study lakes and their catchments. A. Lake Mary, B. Little Llangothlin, C. Blue Lake, D. Lake Chappa'ai. Catchment boundaries are delineated by red lines, core sites are indicated by red arrows, and lake outflows are indicated by yellow arrows. Spot heights in the catchments are marked with yellow circles. Maximum depth and altitude of each lake is provided. More details on limnology and lake catchments is provided in section 2.1.2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2
Itrax XRF settings used to scan the cores in this study. Settings are provided for current (mA), voltage (kV), sample resolution (μm) and exposure time (s).

Core Name	XRF Settings		Resolution	Exposure Time
	mA	kV	μm	s
Little Llangothlin	55	35	500	10
Blue Lake	55	30	500	10
Lake Chappa'ai	55	30	500	10
Lake Mary	55	30	500	10

contiguously. Samples represented 0.5 cm intervals for Blue Lake and 1 cm intervals for Lake Chappa'ai. We used loss on ignition (LOI) at 550 °C as a measure of sediment organic content. We followed the protocol outlined in Heiri and Lotter (2001). Sediment samples were weighed wet in pre-weighed crucibles then dried overnight at 60 °C in a drying oven. Samples were then re-weighed to allow the calculation of moisture content using the formula:

Moisture content (%) = ((wet weight - dry weight)/wet weight) x 100

Samples were then combusted in a muffle furnace at 550 °C for 24 h and the combusted mass was determined. Organic content was calculated using the formula:

Organic content (%) = ((dry weight - combusted weight)/dry weight) x 100

It is important to consider that there are possible pitfalls to using LOI as a measure of sediment organic content. These are discussed in Santisteban et al. (2004). Santisteban et al. (2004) found that there was a strong correlation ($r^2 = 0.97$) between LOI and organic content in a core from Spain with diverse lithology. Santisteban et al. (2004) used total organic carbon content measured by a CHN analyser as a proxy for organic content. We agree with Santisteban et al. (2004) that de-watering of clays in inorganic samples (Loss on ignition < 5%) can lead to an over-estimation of organic content. We would like to highlight that there are also issues with using carbon as a sole measure of organic content. Organic matter is composed of carbon, nitrogen, oxygen, and hydrogen and the proportions of each component can vary widely; depending on the source of the organic matter and post burial diagenesis (Kuivila and Murray, 1984). Even though down-core trends in C, N, O and H are probably highly correlated; variations in the proportions of these elements will lead to an overestimation of the predictive error of LOI. Few studies measure C, N, O, and H is sediment samples. Klavins et al. (2008) measured C, N, O, and H in peat samples from Latvia and this serves to illustrate the potential variability in carbon content. Although all the samples measured by Klavins et al. (2008) had an LOI of ~94%, the carbon content varied from 41% to 54%. There was a smaller variation in the total C, H, N, and O content, which varied between 95 and 100%.

We therefore chose to use LOI as a measure of sediment organic content for our study as we could account for the total mass of organic and moisture content. As we mentioned in the introduction, the moly ratio will reflect the proportion of elements lighter than magnesium and this will be influenced by organic content (mainly H, C, N, O) and water content (H and O). The water content will also attenuate X-ray energy which will also influence Compton scattering. In the discussion, results, and figures, we use the term organic content to refer to organic content as a percentage of dry mass, determined by loss on ignition at 550 °C. When we refer to moisture + organic content, we refer to the total organic and moisture content as a percentage of the wet weight of the sediment samples.

2.4. Numerical analysis

The main aim of the numerical analyses was to explore the ability of the moly ratio to predict the sediment organic content. We also wanted to explore the effect of other variables that might influence the ability of the moly ratio to accurately predict sediment organic content. This required four main groups of analyses: (i) we performed a redundancy analysis to determine the influence of sediment properties (organic content and moisture content) on the moly ratio; (ii) we used regression analysis to explore the relationship between organic content and the moly ratio, moisture + organic content vs the moly ratio, and moisture vs organic content; (iii) redundancy analysis was then used to explore the influence of sediment properties on the predictive errors for organic content by the moly ratio; (iv) finally we used regression analysis to explore trends in predictive errors for organic content by the moly ratio.

2.4.1. Redundancy analysis of sediment properties and the moly ratio

We tested the explanatory power of organic and moisture content for the moly ratio using a series of redundancy analyses (RDAs) in CANOCO 4.5 (ter Braak and Šmilauer, 2002). All variables were log transformed to achieve normality except for the moly ratio which was already normally distributed. Separate RDAs were used to test the explanatory power of LOI and moisture content. Partial RDAs were then used to determine the effect of partialling out the effect of all other variables.

2.4.2. Regression analysis of sediment properties and the moly ratio

Regression analyses were performed on all data from each core and a separate dataset from a highly organic section (LOI > 40%) from the Little Llangothlin core (Fig. 3). We first explored which trend line would best explain the relationship between un-transformed variables. Trend lines were fitted to the data from each core so as to provide the highest r^2 value. Once a trend line was fitted in Excel, we used the equation for the selected function to determine predicted values residual values, and calculate the root mean squared error (RMSE). When the relationship between variables was an exponential or logarithmic function, we log-transformed the x variable so we could use the Regression function in the Excel Analysis Toolpak to determine the significance of the correlation (p - value).

We performed a regression analysis of moisture + organic content vs the moly ratio in Excel. Both variables did not require log transformation. We predicted that there would be a single, universal relationship between moisture + organic content and the moly ratio. The variable moisture + organic content should account for all elements with low atomic numbers (H, C, N, O) and also account for increased Compton scattering due to X-ray attenuation.

We expected that moisture content would have a large effect on the moly ratio. We therefore thought a deviation from a constant relationship between moisture and organic content in a core would affect the moly ratio. A deviation from a constant relationship may lead to over- or under-prediction of organic content by the moly ratio. We performed a regression of moisture content vs organic content to explore the relationship between these two variables in the cores used in this study.

2.4.3. Redundancy analysis of the effect of sediment properties on predictive errors

We tested the effect (explanatory power) of several variables on the predictive error of the moly ratio using a series of redundancy analyses (RDAs) in CANOCO 4.5 (ter Braak and Šmilauer, 2002). Changes in predictive error were expressed as residual (predicted – observed) values for the regression of organic content vs the moly ratio. We tested the explanatory power of four variables for the predictive error of the moly ratio. Residuals from the regression of moisture content vs organic content were used to test the effect of a deviation from a constant relationship between moisture and organic content. We expressed the residuals as observed - predicted for the regression of moisture content vs organic content. This way the residuals would express wetter than normal or drier than normal samples as positive and negative numbers respectively. We also explored the effect of organic content, moisture content and moisture + organic content on the predictive error. We wanted to see if there was a tendency for higher or lower predictive errors in wet sediments or highly organic sediments. Moisture content, organic content and organic + moisture content required log transformation to achieve normality.

2.4.4. Regression analysis of the effect of sediment properties on predictive errors

We performed a regression of the residuals from organic content vs the moly ratio (y) with all variables (x) that had a significant effect on the predictive errors of the moly ratio in the redundancy analyses (see section 2.4.3). This enabled us to quantify the effect of the individual variables on the predictive error of the moly ratio. Regression analyses were performed in Excel using the Regression function in the Data Analysis Toolpak.

3. Results

3.1. Core stratigraphy, moly ratio, moisture and organic content

Itrax optical images, x-radiographs and plots of organic content, averaged moly ratio, full high resolution moly ratio, moisture content and total moisture + organic content for each core are depicted in Fig. 3. In the following section we will discuss the main trends in core stratigraphy with reference to changes in lithology, moly ratio, organic content and moisture content.

3.1.1. Lake Mary

The Lake Mary core is 60 cm long (Fig. 3) and comprises organic (LOI ~ 20%) sediments occasionally interrupted by thin (< 5 cm thick) less organic clay layers. Sediments between 45 cm and 60 cm are light brown lake sediments (gyttja) containing abundant unidentified plant fragments. The sediments between 15 cm and 45 cm are mainly dark brown organic sediments containing abundant macrofossils, including bryophyte and *Myriophyllum* (water milfoil) fragments and seeds and oospores from aquatic plants (e.g. *Myriophyllum*, *Potamogeton* (pond weed), *Eleocharis* (a sedge) and Characeae (stone worts)). The sediments between ~ 7 cm and 12 cm are similar to the basal (45 cm–60 cm) sediments. The upper 7 cm comprised light green gyttja. The stratigraphic plot of the moly ratio appears similar to the plot of organic content. The trend of the moisture content plot also appears to follow that of organic content. More organic (LOI > 15%) sediments are wetter (moisture content = 80–90%), while inorganic sediments (LOI < 15%) are drier (moisture content = 40–70%).

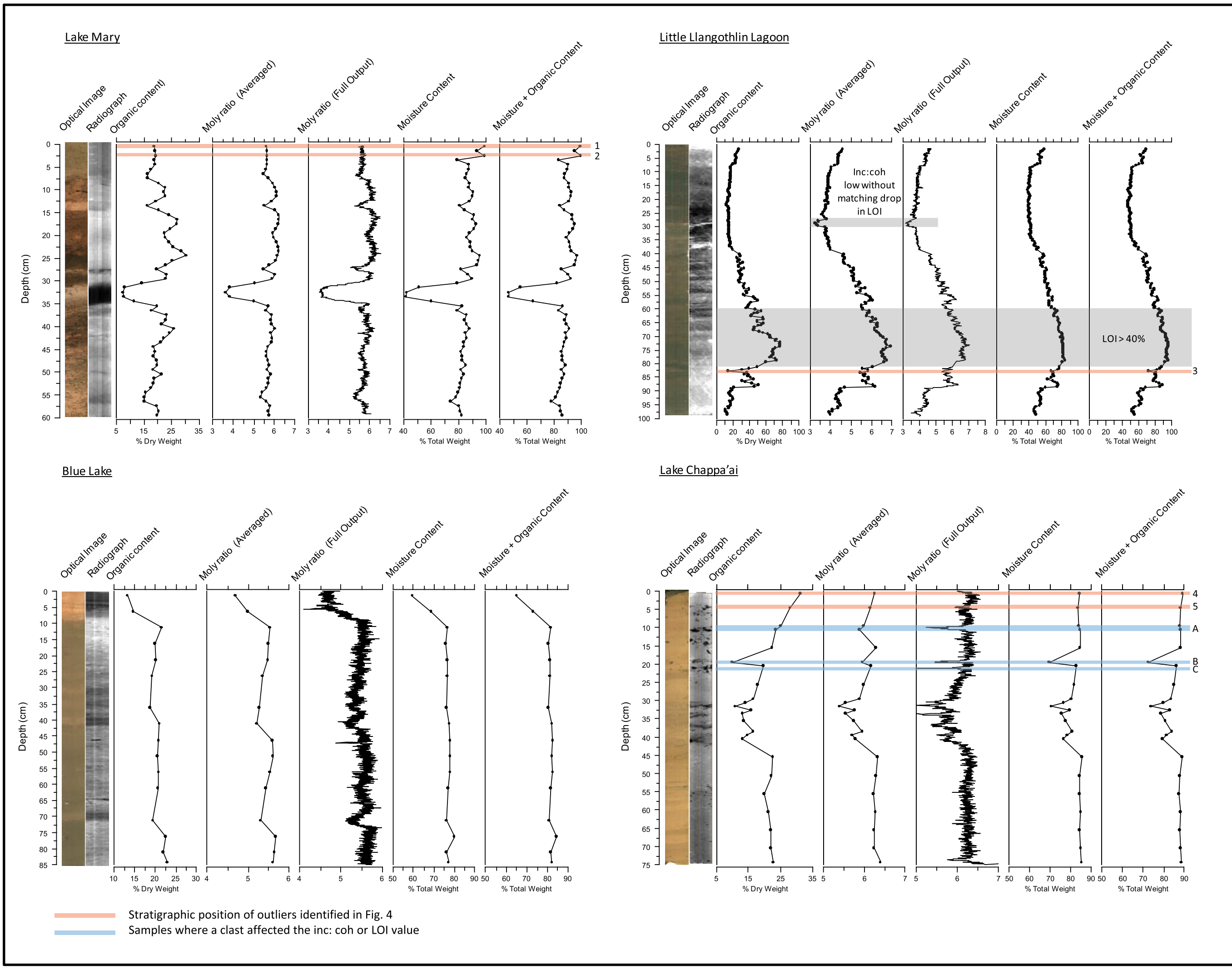

Fig. 3. Stratigraphic plots showing optical and x-radiograph images, and down-core variations in organic content (loss on ignition (LOI) at 550 °C), moly ratio averaged to match the resolution of LOI (Moly ratio (Averaged)), the high resolution output of the moly ratio (Moly ratio (Full Output)), moisture content, and the total % contribution of moisture and organic content to sediment wet weight (Moisture + Organic Content). Red lines and numbers indicate the position of outliers identified in XY plot in Fig. 4 that are also discussed in the text. Blue lines labelled A, B, and C indicate the position of samples in the Lake Chappa'ai core where sample heterogeneity had a large effect on the calibration samples or Itrax data. The upper grey bars in the Little Llangothlin Lagoon plot indicates the position of a section with a low moly ratio that is discussed in section 4.4.1. The lower grey box indicates the position of highly organic (loss on ignition (LOI) > 40%). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

3.1.2. *Little Llangothlin Lagoon*

A detailed description of the stratigraphy of the Little Llangothlin Lagoon core is provided in Woodward et al. (2014a) and Woodward et al. (2017). In summary, the core is ~100 cm long and comprises four main units (Fig. 3). The basal section (90 cm–100 cm) comprises slightly organic (LOI ~ 15%) sediments. This is overlain by organic sediments (LOI > 40%) between 40 cm and 90 cm. There are abundant macrofossils in this section including seeds and oospores from aquatic plants (e.g. *Myriophyllum*, *Potamogeton*, *Eleocharis* and Characeae). This is overlain by less organic sediments (LOI ~ 15%) between 7 cm and 40 cm which contains unidentified plant fragments. Woodward et al. (2014c) performed macroscopic charcoal analysis on the Little Llangothlin Lagoon core. The sediments between 7 cm and 40 cm contain lower concentrations of charcoal than the rest of the core. Macroscopic charcoal and plant fragments are absent from between 27 cm and 32 cm. There is no significant drop in the LOI between 27 cm and 32 cm, but there is a significant drop in the moly ratio (Fig. 3). The upper ~7 cm of the core is slightly more organic than the preceding section, with LOI ~20%. The upper section also contains abundant oospores from Characeae. Apart from the departure between 27 cm and 32 cm, the plot of moly ratio is appears quite similar to the plot of organic content. There is also an inorganic (LOI ~ 10%) layer at about 82 cm that is not detected in the moly ratio (labelled as 3 in Fig. 3). The overall trend in moisture content follows that of the organic content and moly ratio, except there is less variation in moisture content between 40 cm and 90 cm where the organic content is quite variable (Fig. 3).

3.1.3. *Blue lake*

The 85 cm Blue Lake core (Fig. 3) comprises two main units. The basal (10 cm - 85 cm) unit comprises dark brown organic sediments (LOI ~ 25%). There is some variation in this unit with occasional clay rich layers. These are represented by a decrease in the moly ratio and an increase in sediment density. The increase in sediment density is indicated in the x-radiograph by darker horizons. The upper 10 cm of the Blue Lake core comprises yellow-brown, silty sediments with a much lower organic content than the underlying sediments (LOI < 15%). The overall trend in moisture content appears similar to that of the moly ratio and organic content (Fig. 3). More organic sediments (LOI ~ 20%) have higher moly ratios (> 5) and higher moisture content (> 75%). More inorganic sediments (LOI < 15%) have lower moly ratios (< 5) and lower moisture content (< 70%).

3.1.4. Lake Chappa'ai

A detailed description of the sediment stratigraphy for the 75 cm Lake Chappa'ai core is provided in Woodward et al. (2018). The core comprises organic light brown sediments with frequent diamict layers containing clasts ranging from very coarse sand (1 – 2 mm) to coarse pebbles (16–32 mm) (Fig. 3). The basal section (42 cm–75 cm) contains one diamict horizon at ~ 55 cm and a low (< 20%) sand content. There is a major increase in the sand content above 42 cm. The section between 22 cm and 42 cm contains a high proportion (20–60%) of sand. This is reflected in the drop in organic content and a decrease in the moly ratio. There are also four diamict units in this sandy section between 30 cm and 42 cm. There is a decrease in the sand content above 22 cm with an increase in the total organic content towards the top of the core (Fig. 3). There are five main diamict horizons in the upper 22 cm. The overall trends in organic content, moly ratio and moisture content appear quite similar (Fig. 3). More organic sediments (LOI > 15%) have a higher moly ratio (> 6) and moisture content (> 80%). Less organic sediments (LOI < 15%) have lower moly ratios (< 6) and lower moisture content (< 80%). There are significant drops in the moly ratio (labelled as A, B, and C in Fig. 3) that correspond to the presence of clasts in the diamict layers. This drop in the moly ratio corresponds to the scanning of a clast on the surface of the core. The presence of clasts in the diamict layers also affected the results for LOI for one of these horizons (labelled B in Fig. 3). These three samples (A, B, and C) were excluded from the numerical analyses as the LOI and moly ratios were not representative of the entire sediment content for these horizons.

3.2. Numerical analyses

3.2.1. Redundancy analysis of sediment properties vs the moly ratio

All variables explain a significant ($p < 0.01$), independent amount of the variation in the moly ratio for the data from Little Llangothlin Lagoon and Lake Mary (Table 3). The total amount of variation explained by organic content and moisture is 95.8% for Little Llangothlin Lagoon. Organic content and moisture content independently explain 34.6% and 44.5% of the variation in the moly ratio for the Little Llangothlin Lagoon core respectively. This leaves 16.7% of the total variation of the moly ratio that is explained by the interaction between organic content and moisture content for the Little Llangothlin Lagoon core. The total amount of variation explained by organic and moisture content is 93.5% for the Lake Mary core. Organic and moisture content explain 61.3% and 22.1% of the variation in the moly ratio respectively. This leaves 10.1% of the total variation of the moly ratio that is explained by the interaction between organic content and moisture content for the Lake Mary core. The total amount of variation explained by organic content and moisture is 94% for the Chappa'ai core. Organic content is not significant after the effect of moisture is partialled out. Moisture still explains a significant amount of the variation in the moly ratio after the effect of organic content is partialled out. The total amount of variation explained by organic content and moisture is 86% for the Blue Lake core. Neither organic or moisture content remained significant when the other variable was partialled out for the Blue Lake core.

3.2.2. Regression analysis of sediment properties and the moly ratio

An exponential function best explains the relationship between organic content (y) and moly ratio (x) when data from the entire core is analysed (Fig. 4A and C). The exponential functions explaining the relationship between organic content and moly ratio, and their performance statistics (r^2 and RMSE) are provided in Table 4. Focussing the regression analysis on the highly organic (LOI > 40%) section from Little Llangothlin Lagoon (Fig. 3) resulted in a slightly poorer correlation between organic content and the moly ratio (Table 4). The r^2 dropped from 0.92 (for the entire core) to 0.82 (for the organic section). There was a slight increase in the RMSE from 4.2% for the entire core to 4.5% for the highly organic section. The relationship between organic content and the moly ratio for the organic section of the Little Llangothlin Lagoon core was best explained by a linear function (Table 4).

The relationship between moisture + organic content (y) and the moly ratio (x) is best explained by a linear function ($y = 16.095x - 9.2783$, $r^2 = 0.93$) (Fig. 4D). This linear function explains the relationship between moisture + organic content (y) and the moly ratio (x) for all cores. There are three obvious outliers from the linear trend. There are two samples from near the top of Lake Mary where the moly ratio would under predict the moisture + organic content. These samples are labelled as 1 and 2 in Fig. 4. There is one sample from Little Llangothlin Lagoon where the moly ratio would over predict the moisture + organic content. This sample is labelled as 3 in Fig. 4.

A logarithmic function best explains the relationship between moisture content (y) and organic content (x) (Fig. 4F). The logarithmic functions explaining the relationship between moisture content and organic content are provided in Table 4. Focussing the regression analysis on the highly organic (LOI > 40%) section from Little Llangothlin Lagoon (Fig. 3) resulted in a slightly poorer correlation between moisture content and organic content (Table 1). The r^2 dropped from 0.91 (for the entire core) to 0.77 for the organic section. However, there was a decrease in the RMSE from 4.26% for the entire core to 1.68% for the highly organic section. The relationship between moisture content and organic content for the organic section of the Little Llangothlin Lagoon core was best explained by a linear function (Table 4).

3.2.3. Redundancy analysis of the effect of sediment properties on predictive errors

The residual from the regression of moisture vs organics and organic content were the only variables to explain an independent ($P < 0.01$) portion of the variation in the predictive error of the moly ratio (Table 5). Partialling out the effect of other variables did not reduce the explanatory power of the residual from the regression of moisture vs organics and organic content. Both of these variables explained a total of 42.5% of the variation in the residuals from the regression of organic content vs the moly ratio. The residual from the regression of moisture vs organics explained 29.2% of the variation in the predictive error of the moly ratio. Organic content explained 13.3% of the variation in the predictive error of the moly ratio. Moisture content was not significant and moisture + organics became insignificant after the effect of organic content was partialled out (Table 5).

3.2.4. Regression analysis of the effect of sediment properties on predictive errors

The relationship between the residuals from the regression of organic content vs the moly ratio and moisture content vs organic content is best explained by a linear function ($y = 0.4611x - 0.2942$, $r^2 = 0.3$, $p < 0.0001$) (Fig. 5). When samples are wetter than usual (positive residuals on the x-axis) there is a tendency for the moly ratio to over-predict the organic content. When samples are drier than usual (negative residuals on the x-axis) the moly ratio tends to under-predict the organic content. The relationship between the residuals from the regression of organic content vs the moly ratio and log transformed organic content was best explained by a linear function ($y = -6.0169x + 7.9739$, $r^2 = 0.13$, $p < 0.0001$) (Fig. 5). There is a tendency for the moly ratio to more severely under-predict the organic content with increasing organic content.

Table 3
Results from partial redundancy analyses (RDA) to test the exaplanatory power of different sediment composition variables for the moly ratio for the four sites. Moly ratio was used as species data with organic and moisture content used as variables and co-variables. P-values significant to $P < 0.001$ are shown in bold.

Variable	Co-variable	% Moly ratio variation explained	F ratio	Eigen1/Eigen2	p-value
Little Llangothlin					
Organic content	None	92.4	2280.8	12.16	**0.0001**
Organic content	Moisture	34.6	98.4	0.52	**0.0001**
Moisture	None	93.6	2723.4	14.63	**0.0001**
Moisture	Organic content	44.5	149.4	0.81	**0.0001**
Organic content + Moisture[a]	None	95.8	4239.7	22.81	**0.0001**
Lake Mary					
Organic content	None	91.6	636.6	10.90	**0.0001**
Organic content	Moisture	61.3	90.1	1.58	**0.0001**
Moisture	None	83.2	287.3	4.95	**0.0001**
Moisture	Organic content	22.1	16.2	0.28	**0.0001**
Organic content + Moisture[a]	None	93.5	819.0	14.38	**0.0001**
Chappa'ai					
Organic content	None	81.0	80.9	4.26	**0.0001**
Organic content	Moisture	5.9	1.1	0.07	0.3147
Moisture	None	93.7	281.0	14.87	**0.0001**
Moisture	Organic content	68.7	39.5	2.18	**0.0001**
Organic content + Moisture[a]	None	94.0	284.1	15.67	**0.0001**
Blue Lake					
Organic content	None	85.5	82.9	5.90	**0.0001**
Organic content	Moisture	39.2	8.4	0.65	0.0144
Moisture	None	76.9	46.6	3.33	**0.0001**
Moisture	Organic content	2.8	0.4	0.03	0.5414
Organic content + Moisture[a]	None	86.0	79.6	6.14	**0.0001**

[a] Note this is the combined effect of organic content (% dry mass) and moisture content (% total or wet mass). This is not to be confused with moisture + organic content which is the sum of both components as a percentage of the total or wet mass.

4. Discussion

4.1. The effect of sediment heterogeneity on Itrax XRF results and calibration

The Itrax outputs for the Lake Chappa'ai core (Fig. 3) highlight a potential issue during core scanning, calibration and interpretation of the results. We should consider heterogeneity of the sediment during the scanning process, and how representative the data from the scan will be of the core sediment. The same issue can apply to sediment sub-samples taken for calibration. Both effects can result in an apparent reduction in the performance statistics for the calibration. In short, we should be comparing like with like during the calibration process. The sediment composition of the scanned samples should be the same as the composition of the sub-samples taken for calibration.

In the case of the Lake Chappa'ai core, the presence of clasts (inorganic material) along the path of the Itrax scan caused a severe reduction in the moly ratio. This is apparent for samples labelled A, B and C in Fig. 3. In one instance (sample B in Fig. 3) the organic content was much lower than expected. We observed a large clast in the residue after combustion and this would cause a reduction on the organic content. For the calibration of the Lake Chappa'ai moly ratio, we were able to exclude the erroneous samples manually before numerical analysis. This may not always be possible and measures should therefore be taken to reduce the possible effect of sample heterogeneity (MacLachlan et al., 2015). This can be achieved during the scanning process by performing multiple scans of the same core. This would add time (and cost) to the analysis, but may be justified if it is important to get a high resolution, accurate Itrax based inference of sediment organic content. Sample heterogeneity should also be considered for sediment sub-samples taken for determination of organic content. Sample size for determination of LOI and TOC was not mentioned in (Liu et al., 2013; Saez et al., 2009; Chawchai et al., 2016), so we cannot assess if this might have an effect on their results. We do note however, that sample heterogeneity may also have an effect on highly organic sediments and could partially explain the poor explanatory power of the moly ratio in the study by Chawchai et al. (2016) (Table 1). Chawchai et al. (2016) argued that the moly ratio is a poor predictor of organic content in peaty (LOI > 40%) sediments. Peaty sediments could also be heterogeneous if they contain macrofossils. Macrofossils such as plant foliage and seeds could have a higher organic content than the surrounding matrix and could lead to high sample heterogeneity.

With the common practice of multiproxy studies in palaeoecology (Reed, 2013) sediment supply is usually strictly rationed. We do however, recommend taking large (e.g. $\geq 2\,cm^3$) samples for analysis of organic content by LOI or TOC if this is an important aspect of a study. We also recommend reporting the quantity of sediment used in the analysis so that readers can assess how representative the sub-samples may be of the average sediment composition from the sampled horizon.

4.2. The power of the moly ratio as a proxy for sediment organic content

After removing samples from Chappa'ai that were not representative of the average organic content, there was a high ($r^2 > 0.8$) correlation

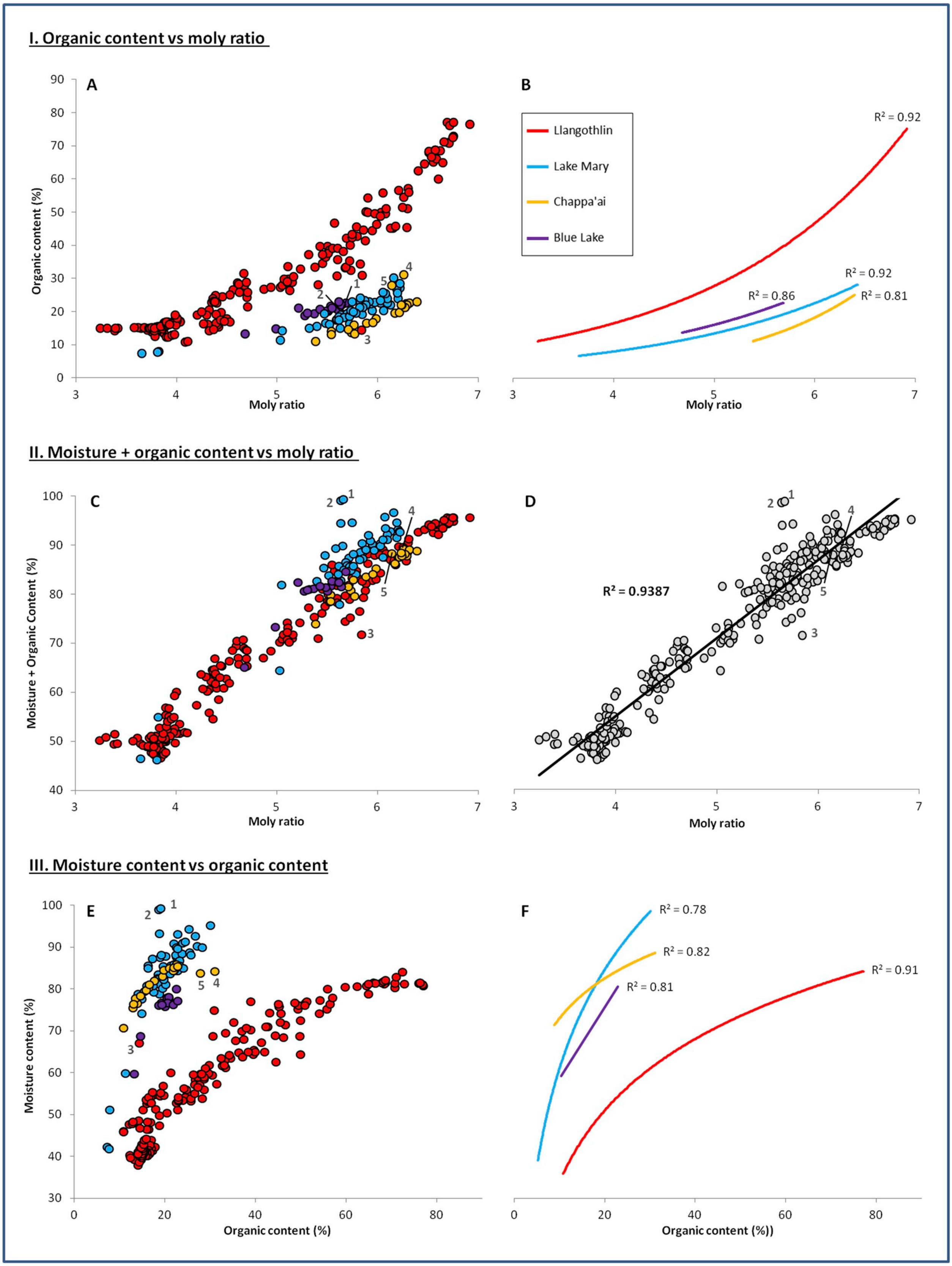

Fig. 4. XY plots of (A, B) organic content vs the moly ratio, (C, D) moisture + organic content vs the moly ratio and (E, F) moisture content vs organic content. Colour coding (red, blue, orange, purple) indicates the source of each sample in the four cores. Numbers indicate the position of outliers that are discussed in the text. Right hand panels (B and F) show models fitted to explain the relationship between x and y for each core. Each line is colour coded to indicate which core the model applies to. The linear model fitted in D is used to explain the relationship between moisture + organics the moly ratio for all sites combined. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 4
Functions and performance statistics for regression analyses.

	Organic content (y) vs moly ratio (x)	Moisture content (y) vs organic content (x)
Site		
Little Llangothlin (Whole core)	y = 2.0660e0.5198x, r^2 = 0.92, RMSE = 4.20%	y = 24.633ln(x) - 22.814, r^2 = 0.91, RMSE = 4.26%
Little Langothlin (Section where LOI > 40%)	y = 29.375x - 126.71, r^2 = 0.82, RMSE = 4.50%	y = 0.2911x + 60.881, r^2 = 0.77, RMSE = 1.68%
Lake Mary	y = 1.0072e0.5185x, r^2 = 0.92, RMSE = 1.64%	y = 34.110ln(x) - 17.584, r^2 = 0.78, RMSE = 4.96%
Chappa'ai	y = 0.1465e0.8043x, r^2 = 0.81, RMSE = 2.72%	y = 13.787ln(x) + 41.208, r^2 = 0.82, RMSE = 1.71%
Blue Lake	y = 1.3005e0.5030x, r^2 = 0.86, RMSE = 1.03%	y = 30.808ln(x) - 16.389, r^2 = 0.86, RMSE = 1.75%

e = Euler's number (~2.7182).
RMSE = Root mean squared error of prediction.
All results are significant to $p < 0.001$.

between sediment organic content and the moly ratio for the four cores in our study (Fig. 4, Table 4). There was a unique relationship between sediment organic content and the moly ratio for each site (Table 4). The moly ratio will predict a lower organic content in wetter cores and a higher organic content in drier cores (Fig. 4A and B). For example a moly ratio of 6 for Lake Chappa'ai would predict an organic content of 18%, while a moly ratio of 6 for Little Llangothlin would predict an organic content of 46% (Fig. 4B). The moisture content in the Lake Chappa'ai core is greater than 70%, while the moisture content in the Little Llangothlin core ranges from ~40% to 85% (Fig. 4E). We therefore follow the recommendation of Liu et al. (2013) that prediction of organic content using the moly ratio requires calibration on each core separately.

The reason for the difference in the relationship between organic content and the moly ratio in each core is the effect of water on the moly ratio. The moly ratio is the ratio of incoherent to coherent scattering. Incoherent scattering is inversely related to the mean atomic number of the elements, while coherent scattering is positively correlated to the abundance of elements with high atomic numbers (Rothwell and Croudace, 2015). The incoherent scattering value will therefore be dependent on the relative abundance of substances that contain elements with low atomic numbers, including organic content (which contains H, C, N, and O) and water (which contains H and O). Water content will also affect Compton scattering and hence the moly ratio via attenuation of X-ray energy (Weltje and Tjallingii, 2008). The contribution of both water and organic content is clearly demonstrated in the partial RDAs (Table 3) and the correlation between moisture + organic content and the moly ratio in Fig. 4C and D. We discuss the implications of these results for the effect of water on the moly ratio in the following sections.

4.3. Potential pitfalls: the effect of water content on the moly ratio

The partial RDAs (Table 3) support the idea that both water and organic content will have an influence on the moly ratio. Organic content and moisture content have an independent significant effect on the moly ratio for Little Llangothlin and Lake Mary. The influence of moisture content is slightly higher (44.5%) than organic content (34.6%) in the Little Llangothlin Lagoon core. The influence of organic content is much higher (61.3%) than moisture content (22.1%) in the Lake Mary core. We place less weight on our interpretation of the redundancy analysis from the Lake Chappa'ai and Blue Lake cores as these are small datasets (n = 21 and n = 16 respectively). The complete loss of explanatory power for organic content in the Lake Chappa'ai core and moisture in the Blue Lake core could be due to the small sample size. However, these datasets still indicate that both organic content and moisture can have a strong and variable effect on the moly ratio in different cores.

Because both moisture and organic content can have a strong effect on the moly ratio, we argue that it is important for there to be a consistent relationship between organic content and moisture content in the core. This consistent relationship is necessary for the moly ratio to work as a proxy for organic matter.

Fortunately there is a strong relationship ($r^2 > 0.7$) between moisture content and organic content in the cores that we studied (Fig. 4F, Table 4). Avnimelech et al. (2001) also observed that organic content and water content are highly correlated ($r^2 = 0.7$) in sediments from aquatic settings (rivers, lakes etc.). Avnimelech et al. (2001) used total organic carbon as a proxy for sediment organic content in samples from Israel, North America, Egypt and New Zealand. Avnimelech et al. (2001) proposed that this relationship exists because organic matter in aquatic sediments is highly hydrated. Even though organic matter accounts for a small fraction of the total wet weight of the sediment when dried, in reality hydrated organic matter can be a large component of the sediment composition. Our data reveals that we still must be cautious as there are circumstances when there is not a consistent relationship between moisture content and organic content.

The redundancy analysis (Table 5) Indicates that a deviation from a

Table 5
Assessment of the explanatory power of different sediment variables for the residuals from the regression of organic content vs the moly ratio P-value sin bold are significant to $p < 0.05$.

Variable	Co-variable	% Moly ratio variation explained	F ratio	Eigen1/Eigen2	p-value
Residual Moisture vs Organics + Organic content	None	42.4	208.528	0.736	**0.0001**
Residual Moisture vs organics	None	29.2	116.9	0.412	**0.0001**
Residual Moisture vs organics	Organic content	33.6	143.4	0.507	**0.0001**
Residual Moisture vs organics	Moisture	34.3	147.5	0.521	**0.0001**
Residual Moisture vs organics	Moisture + Organic content	35.6	156.4	0.553	**0.0001**
Organic content	None	13.3	43.4	0.153	**0.0001**
Organic content	Residual Moisture vs organics	18.7	65.2	0.231	**0.0001**
Organic content	Moisture	13.8	45.1	0.159	**0.0001**
Organic content	Moisture + Organic content	12.3	39.7	0.140	**0.0001**
Moisture	None	0.8	2.2	0.008	0.1392
Moisture + Organic content	None	2.4	6.9	0.025	**0.0074**
Moisture + Organic content	Residual Moisture vs organics	11.2	35.8	0.127	**0.0001**
Moisture + Organic content	Organic content	1.3	3.7	0.013	0.0546
Moisture + Organic content	Moisture	13.2	42.9	0.152	**0.0001**

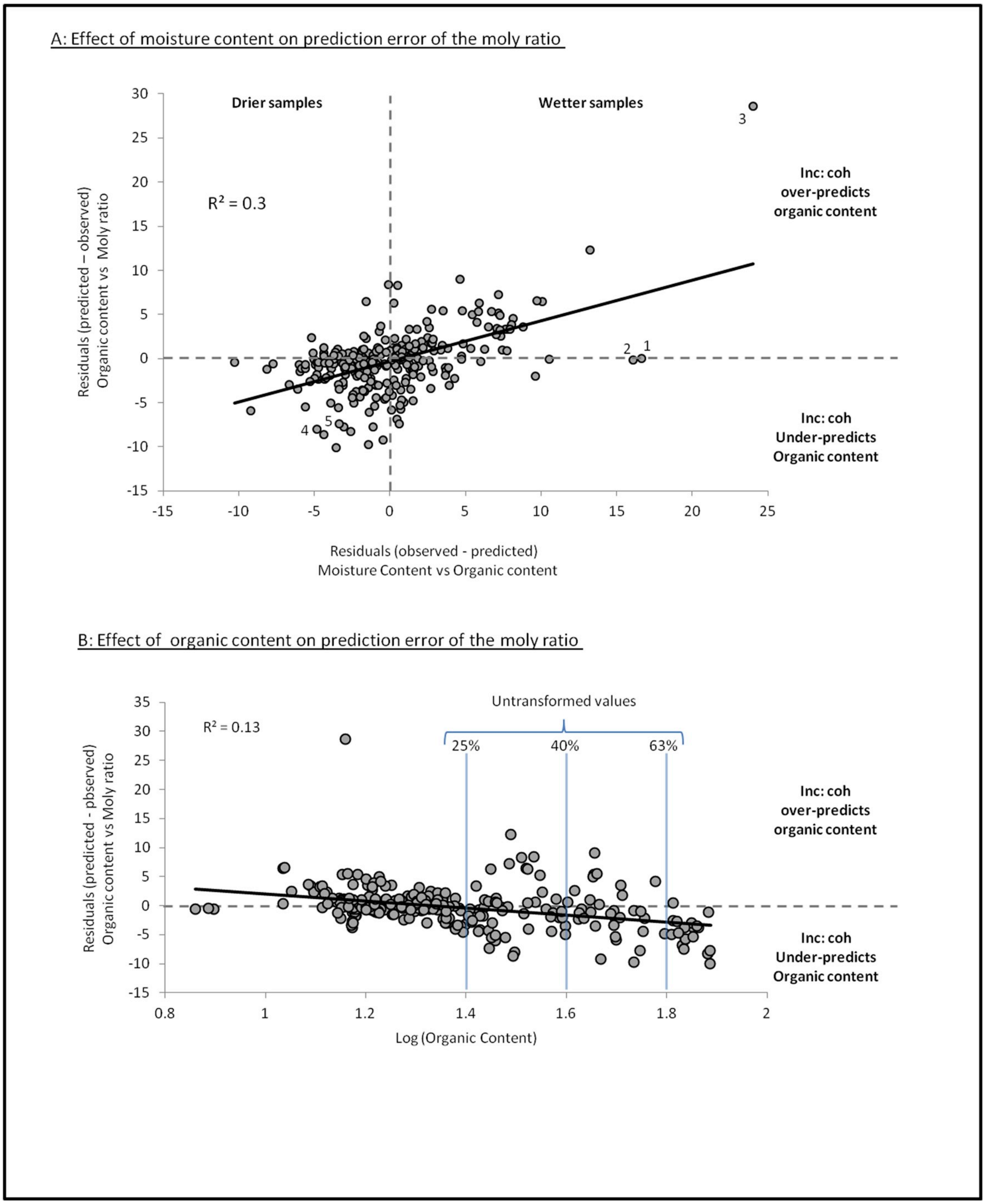

Fig. 5. A. Regression comparing errors on prediction of organic content by the moly ratio (y axis) and variation in the relationship between moisture content and organic content (x axis). The black line shows a linear line of best fit with an associated r^2. Numbers indicate the position of the outliers that are labelled in Fig. 4 and discussed in the text. The tendency is for samples that are wetter than usual (high x axis values) to over predict the organic content and vice versa. B. Regression comparing errors on prediction of organic content by the moly ratio (y axis) and organic content (log of loss on ignition (LOI). There is a tendency for the moly ratio to under predict organic content in more organic cores. This appears to be a result of model selection and can be alleviated by using a polynomial function.

constant relationship between moisture content and organic content explains ~ 30% of the error in the prediction of organic content by the moly ratio. Two different outputs demonstrate the possible effect of a deviation from a consistent relationship between moisture and organic content in a core. These outputs are: (i) the outliers in the regression of organic content vs moisture content ((samples 3, 4, and 5 in Fig. 4E); (ii) the regression of the residuals from organic content vs the moly ratio and moisture content vs organic content (Fig. 5A). There is a tendency for the moly ratio to over predict organic content for samples that are wetter than usual and to under-predict organic content for samples that are drier than usual (Fig. 5A).

4.3.1. *Under-prediction of organic content*

Samples 4 and 5 from Lake Chappa'ai (Figs. 3, 4 and 5A) are an example of the under prediction of organic content by the moly ratio since samples are drier than usual. By drier than usual, we mean that the moisture content is much lower than we might expect for a sediment sample with this organic content in this core. This means that the moly ratio under-predicts the organic content by ~10% at the top of the Chappa'ai core (Fig. 5). The moly ratio also fails to capture the sustained increase in organic content that is detected above 15 cm in the core (Fig. 3). We believe that the use of sodium polyacrylate to preserve the sediment water interface has de-watered the upper sediments in the core resulting in them being drier than usual. Sodium polyacrylate absorbs water due to a high osmotic pressure between the sodium polyacrylate powder and the surrounding water. Water will be absorbed by the sodium polyacrylate until the concentration of sodium ions is balanced between the inside and outside of the sodium polyacrylate polymer structure.

We followed the protocol of Tomkins et al. (2008) for the preservation of the sediment water interface using sodium polyacrylate. The lake water was drained until approximately 2 cm of water remained on top of the sediment water interface. Sodium polyacrylate was then sprinkled in to the water until it formed a solid gel. Tomkins et al. (2008) suggest continuing to sprinkle more sodium polyacrylate on top of the gel for up to one week prior to core transport. The sodium polyacrylate will continue absorb water from the top of the sediment at the same time as it absorbs the lake water. To some extent this might be desirable as it would stabilise the otherwise sloppy sediment at the sediment water interface and prevent mixing during transport. However, this also appears to affect the ability of the moly ratio to predict organic content at the top of the core. This does not appear to be an issue for the Lake Mary and Blue Lake cores (Fig. 3) and the effect of the sodium polyacrylate on the moisture content could be dependent on how much sodium polyacrylate powder is added. Adding more sodium polyacrylate powder to a core may make it more stable, but will result in severe de-watering of the upper sediments. This in turn will affect the prediction of the organic content by the moly ratio. Another reason the Blue Lake core might not be affected is that there is a drop in the organic content at the top of the core already. Dewatering of the top of the core would exaggerate the decrease in organic content predicted by the moly ratio.

4.3.2. Over-prediction of organic content

Sample 3 from Little Llangothlin shows an extreme example of over prediction of the organic content of the sediment due to the sediment being wetter than usual. The moly ratio fails to detect the thin inorganic layer in the Little Llangothlin Lagoon core at about 82 cm depth (Fig. 3). This appears to be because this sample is wetter than we might expect for an inorganic sample in this core. In the Little Llangothlin Lagoon core, inorganic samples (LOI ~ 10%) typically have a moisture content of ~40% (Fig. 4E). The sample where the moly ratio under-predicts organic content has a moisture content of closer to 70% (Fig. 4E). We did not observe this in our dataset, but we think it is possible for the moly ratio to infer a trend of increasing organic content towards the top of the core due to a decrease in density and corresponding increase in moisture content (Weller, 1959).

The upper sediments in Lake Mary are actually wetter than usual with respect to the relationship between organic content and moisture content, but there was not an effect on the prediction of organic content by the moly ratio (Fig. 5A). The only explanation we can think of for this discrepancy is that the top of the core had dried out during scanning on the Itrax. The water content measured from the sub-sample represents the high quantity of moisture still present in the entire core, whereas the Itrax only detects water on the surface. We might expect the entire core to dry out at the same rate, but the higher surface area of exposed sediment at the top of the core may accelerate drying.

4.4. Other causes for discrepancies between organic content and the moly ratio

4.4.1. Low moly ratio values without low LOI in Little Llangothlin

There is one other major discrepancy between the moly ratio and the organic content as inferred from LOI. This discrepancy occurs between 27 and 32 cm in the Little Llangothlin Lagoon core (Fig. 3). There is a decrease in the moly ratio from 3.7 to 3.2, and this would correspond to a reconstructed decrease in organic content of 3% based on the equation in Table 4. We acknowledge that we have used a measure for organic content (LOI) that can be affected by dewatering of clays in inorganic samples (Santisteban et al., 2004). This is because the water content in clay minerals can have a large effect on the LOI in inorganic sediments. Santisteban et al. (2004) found that the influence of clay minerals in LOI was not significant until the LOI was below 5% in their study, whereas the discrepancy in the Little Llangothlin core occurs when LOI is 14%.

It could still be possible that the dehydration of clay minerals has an effect on LOI when the LOI is at 14%, so the LOI is actually over estimating the organic content in this instance. However, this water in clay minerals should also affect the moly ratio.

We believe that our use of LOI as a measure for organic content is still appropriate as our interpretations are based on samples spanning a large gradient of LOI. The use of LOI as a measure of organic content also allows us to account for the total mass of water, organic and inorganic matter. This would not be possible if were to only use % carbon as a measure for organic content. We stand by our interpretation of this dataset but recommend that a future study should compare elemental concentrations for H, C, N, and O with the moly ratio. We also note that the inferred decrease in organic content inferred by the moly ratio (3%) in the Little Llangothlin core is within the bounds of the error of 4.2% on the regression between organic content and the moly ratio for this site (Table 4). We should therefore pay less attention to fluctuations in organic content inferred from the moly ratio that are less than the predictive error. The errors on the calibration functions for the moly ratio from our study cores (Table 4) also indicate that the moly ratio may not perform well for more subtle changes in organic content, i.e. changes in LOI < 5%.

4.4.2. The effect of model selection

The redundancy analysis of the residuals for organic content vs the moly ratio (Table 5) indicates that organic content explains ~ 13% of the variation in the error of prediction for the moly ratio. The regression in Fig. 5B shows there is a trend of increased under prediction of the organic content by the moly ratio with increasing organic content. All of the highly organic samples (LOI > 30%) come from the Little Llangothlin Lagoon core (Fig. 4A). In seeking a source for this trend in the errors, we examined the fit of the exponential curve to the dataset of organic content vs the moly ratio. There is a good fit for the exponential curve to the data ($r^2 = 0.92$) and we did not consider a more complicated model (e.g. a polynomial) because it only resulted in a small increase in performance ($r^2 = 0.95\%$). Model development could be based in future on an information-theoretic approach (Burnham and Anderson, 1998), where minimum models are ranked using Akaike's Information Criteria (AIC) (Akaike, 1973).

Selecting a polynomial function to explain the relationship between organic content and the moly ratio ($y = 5.3307 \times ^2 - 37.384x + 80.516$, $r^2 = 0.95$) removes the effect of LOI on the predictive error of the moly ratio. There is only a modest increase in r^2 (0.92–0.95) and reduction in RMSE (4.2%–4.1%) with the selection of the polynomial model, but it removes the tendency for the moly ratio to under-predict organic content.

The model that was used to explain the relationship between the moly ratio and organic content is not always defined in previous studies. Liu et al. (2013) showed regression plots and the selected model was linear (Table 1). Chawchai et al. (2016) and Sáez et al. (2009) did not mention the model selected, but we assumed in was a linear model (Table 1). Chawchai et al. (2016) and Sáez et al. (2009) don't mention any log transformation of the variables or a test for normality. There did not appear to be any consideration of different models that could be used to explain the relationship between the moly ratio and organic content in these previous studies. We recommend the development of a standard protocol for selection of the best model for calibrating the moly ratio with organic content in the future. A model should be selected with minimal complexity such that the explanation of trend is maximised (r^2), error is lowest and, there are no systematic trends in error along the organic content gradient.

4.4.3. What explains the other 70% of the error of prediction for the moly ratio?

In our dataset, moisture variability only explained 30% of the predictive error of the moly ratio. With consideration of model selection, we have removed the 13% explained by organic content. What could be contributing to the other 70% of the variation in the predictive of the moly ratio? We discussed the effects of sample heterogeneity in section 5.1. Sample heterogeneity can affect the apparent error in the prediction of the organic content by the moly ratio due to changes in sediment organic content in the core. Since the Itrax scans the sediment surface, and calibration sub-samples are deeper; there is a danger that the organic content measured during calibration and Itrax scanning is different.

This may not account for all of the remaining 70% of the error, but we suspect that it would account for a large proportion of it. As we mentioned in section 5.1, there are possible solutions to reduce the effect of sample heterogeneity, but it may not be completely eliminated. Reducing the effect of sample heterogeneity may be done by running repeated scans of a core along different longitudinal transects. This would reduce the effect of occasional clasts or organic detritus, but may not be so effective where clasts or organic detritus are more common. Reducing sample heterogeneity for calibration samples can be reduced by taking larger sediment samples. We recommend a future test to explore the effects of sample heterogeneity on the moly ratio. Such a study could build on the work by MacLachlan et al. (2015) which examined the effect of fine scale heterogeneity on element counts produced by the Itrax.

Grainsize variability and surface roughness can also affect Compton scattering during in-line XRF core scanning and hence the Moly ratio (Weltje and Tjallingii, 2008). Although we selected cores with minimal changes in grainsize, and hence surface roughness, these could also contribute to the error of prediction.

5. Conclusions and future directions

The results from our study demonstrate that the effect of moisture and organic content on the moly ratio is highly variable between sites. Both moisture and organic content can have a significant, independent effect on the moly ratio and its ability to accurately predict sediment organic content. Water content can affect the moly ratio due to the presence of light elements (H and O) and the attenuation of X-ray energy. It is therefore important that there is a constant relationship between organic content and moisture content in a core. Deviations from a constant relationship can cause severe over or under-prediction of the organic content by the moly ratio. It is therefore possible that decreasing water content with depth (due to compaction) could be interpreted as a decrease in organic content with depth. Preservation of the sediment water interface with sodium polyacrylate also appears to have an effect on the relationship between moisture and organic content. We recommend a future study to explore the effect of sodium polyacrylate on moisture content, bulk density and moly ratio as a proxy for organic content.

Variability in sediment water content only accounted for ~30% of the error in the prediction of organic content by the moly ratio in our dataset. Sample heterogeneity can also have a large effect on XRF core scanner results and measurements of sediment organic content in the calibration dataset. This will give the impression of large prediction errors for the moly ratio, when this discrepancy results from a different composition of sediment measured by the XRF core scanner and for total organic content. We recommend taking large ($\geq 2\,cm^3$) sediment samples for calibration of the moly ratio. Multiple core scans may be necessary to reduce the effect of sample heterogeneity on moly ratio outputs from the XRF core scanner.

In our study we used LOI as a measure for organic content. Although we argue that this is better than using organic carbon content by itself, we think our study could be improved by using another measure for total organic content. In conclusion, we believe there is a good potential for future refinement of the moly ratio as a proxy for organic content. We recommend that all studies that use it as a proxy, calibrate the moly ratio with measurements of sediment organic content and water content. This could be achieved with a reasonably small sample size such as the datasets used for Blue Lake and Lake Chappa'ai in this paper. The focus of our study was fine-grained carbonate free sediments from freshwater lakes. The results of our study are likely to be applicable to other fine-grained freshwater sediments without carbonates (e.g. alluvial deposits). Future work is required to explore the combined effect of water, organic content, grain-size and carbonates on the moly ratio. Carbonates are common in marine sediments, so bromine may be preferable to the moly ratio in this setting and this should be explored.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.quaint.2018.11.031.

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