

# Chapter 14

## Approaches to Water Content Correction and Calibration for $\mu$ XRF Core Scanning: Comparing X-ray Scattering with Simple Regression of Elemental Concentrations

John F. Boyle, Richard C. Chiverrell and Dan Schillereff

**Abstract** Geochemical evaluation of sediment records traditionally exploits dry mass concentration data; the new generation of scanning XRF devices, however, are generally presented with wet sediment cores. Therefore, conversion of wet core measured XRF data to dry mass concentrations will aid the palaeoenvironmental interpretation, provided the method used is reliable and avoids loss of data quality. Here, using data from a GEOTEK/Olympus DELTA scanning  $\mu$ XRF device (approximately 5 mm resolution), we compare two methods: (1) correction by simple regression, calibrated using dry sediment elemental concentration data measured for a ‘training set’ of subsamples, and (2) a novel technique that corrects for water content estimated using X-ray scattering data obtained during scanning. We show that where sediment water contents are highly variable the regression method fails while water content correction methods can be highly effective. Where water sediment water contents are relatively constant, the elemental regression is as effective and introduces less noise.

**Keywords** Scanning XRF · Lake sediment · Chemical stratigraphy · Water content

### Introduction

The last decade has seen a proliferation in the use of high resolution or micro-scanning XRF data to discern stratigraphical changes in alluvial, lacustrine and marine sediment, work that exploits a growing family of  $\mu$ XRF equipment that includes the ITRAX core scanner (0.2 mm resolution) originally developed by Croudace, Rothwell and Cox Analytical (Croudace et al. 2006; <http://coxsys.se/>), the Avaatek XRF core scanner (0.1 mm resolution) (Richter et al. 2006; <http://www.avaatech.com/>),

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developed over the last two decades for rapid analysis of marine sediment cores, and systems that automate (e.g. GEOTEK: <http://www.geotek.co.uk/>) the application of Handheld XRF Analysers such as the Olympus Delta XRF and Thermo-Niton XL3t (3–6 mm resolution). As  $\mu$ XRF scanning becomes an increasingly popular way of measuring element composition data in sediment cores over “conventional” XRF analysis (Boyle 2000), the question is raised of whether they generate sufficiently accurate quantitative compositional data. The answer to this is far from simple, depending as much on the application or purpose of the measurements as to other considerations. The palaeoecologist with cores of wet sediment who asks whether scanning  $\mu$ XRF is as good as conventional XRF methods must first specify the question and expectations of the data. If these involve assessing the meaning of relative variations in element concentration, and considering only elements that are well-measured by  $\mu$ XRF, then the answer may be a simple, yes. However, the device will clearly not produce precise and accurate dry mass concentration values, and if these quantitative data are required then the answer is, no.

### Micro-XRF Analysis Versus Conventional XRF Analysis

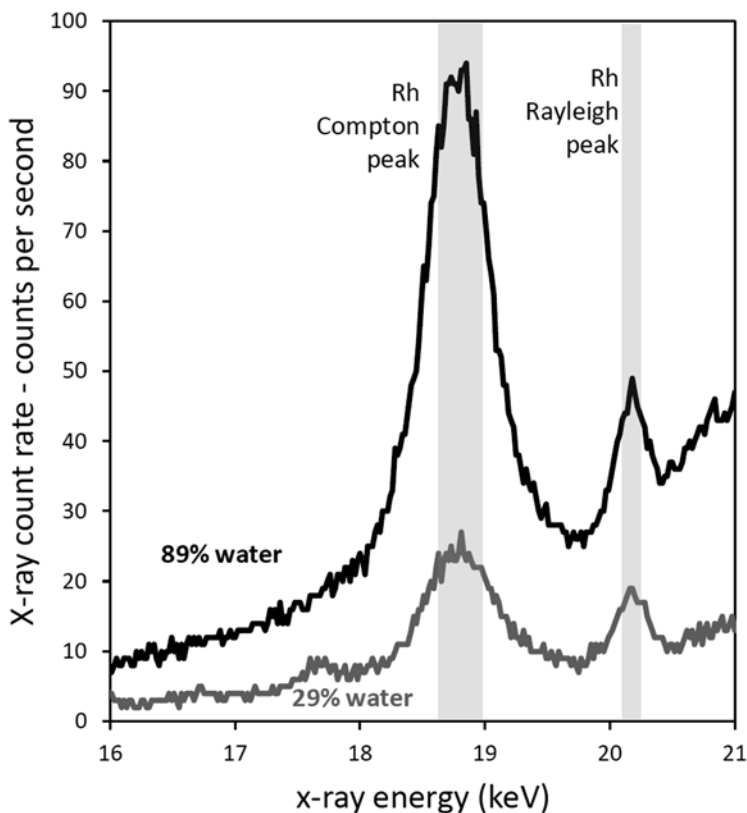
As  $\mu$ XRF scanning becomes an increasingly popular way of measuring element composition data in sediment cores over “conventional” XRF or other analysis (Boyle 2000; Croudace et al. 2006), the question is raised of whether they generate sufficiently accurate quantitative composition data. The answer to this is far from simple, depending as much on the application or purpose of the measurements as to other considerations. The palaeoecologist with cores of wet sediment who asks whether scanning  $\mu$ XRF is as good as conventional XRF methods must first specify the question and their expectations of the data. If these involve assessing the meaning of relative variations in element concentration, and considering only elements that are effectively measured by  $\mu$ XRF, then the answer may be a simple, Yes. However, the device will clearly not produce precise and accurate dry mass concentration values, and if these quantitative data are required then the answer is, No.

These two end-member cases are unlikely to change in the near future, because the issues do not arise from technological limitations. Rather, the problem is that conventional methods in sediment geochemical evaluation (Boyle 2001) are based on dry mass concentrations, where the concentration of an element,  $X$ , is defined as the mass of  $X$  divided by the dry mass of sample in which it is measured (Note this remains true even if the mass of  $X$  is expressed in molar units). It is a convenient fact of XRF analysis that such dry mass concentration values are obtained without the need to know the sample mass, provided the sample is both dry and of “infinite” thickness (Tertian 1969) relative to X-ray penetration (generally a few millimetres of dry sediment will achieve this).  $\mu$ XRF scans of wet sediment do not meet this requirement. They still measure elements as concentrations (even where reported as

X-ray count per second as with the ITRAX system, this is proportional to, and thus a measure of, concentration), but this concentration is relative to the density of wet sediment. In the case of typical organic lake sediment, where water contents may exceed 95%, the wet mass concentration may be only 5% of the dry mass concentration for a particular element.

This diluting of the concentration by water presents a challenge when interpreting wet-core  $\mu$ XRF data. Consider the case of a sediment record which contains high frequency variations in the carbonate to silicate ratio, but which also has highly variable water content. The X-ray signal for Ca, for example, will vary both with the Ca concentration in the dry matter and with the water content of the sediment. As the geochemist is interested only in the dry mass concentration component, it is necessary to process the signal to reduce the contribution of other sources of variation. The most widely used approach is to normalise the element of interest to either another element (Löwemark et al. 2011; Richter et al. 2006) or to back-scatter peaks (Kylander et al. 2012). Working with element ratios has the advantage of eliminating several unknowns; the diluting water content and surface imperfections in particular. However, as X-ray mass attenuation by water varies with photon energy, element ratios do not wholly avoid water content artefacts (Hennekam and de Lange 2012). Furthermore, when working with element ratios it is easy to overlook associated variations in major components that alter the geochemical interpretation. Furthermore, direct comparison of results with other data is difficult or impossible unless the element composition data are expressed as absolute concentrations, and ideally in dry mass form. Thus, the element ratio solution to the water content problem is far from ideal.

It would be desirable, therefore, if wet sediment core scanning XRF signals could be reliably converted to a dry sediment basis. In relatively uniform and consistent stratigraphical sequences the absence of large changes in content of water or organic matter means this conversion to a dry sediment equivalent basis can be achieved by simple correlation as demonstrated by Croudace et al. (2006) and Weltje and Tjallingii (2008). This is because under such constraints the dry and wet mass concentrations are proportional. This simple approach can be used regardless of whether the XRF output is given in concentration units (as is typical for Handheld XRF devices) or as raw X-ray count data. However, if water content in the sediment varies systematically, then simple regression will lead to an invalid correction, potentially producing an apparent chemical stratigraphy that is highly misleading. Where water content varies strongly, such as at the sediment-water interface, or across the transition from inorganic to very organic sediments in lakes during the early Holocene (Shen et al. 2008), then wet and dry mass concentrations are not proportional, and an alternative approach must be taken which is capable first of estimating the water content of the wet sediment, and then correcting the XRF signal for this. In the special case of marine sediment, it may be assumed that the Cl concentration in the sediment is a useful measure of water content and may be used for correction (Hennekam and de Lange 2012), but in freshwater sites this cannot be done. Fortunately, all energy dispersive XRF spectra contain information that is strongly associated with the water content, offering the possibility that



**Fig. 14.1** Scattering of primary rhodium x-rays as a function of sediment water content. The sediments are from the LOR3 core. The Rayleigh peak represents coherently (without loss of energy) scattered photons, while the Compton peaks represents incoherently (with partial energy loss) scattered photons. The wetter sample has a greater proportion of incoherent X-ray scattering

direct correction could be achieved. This information is contained in the part of the signal that arises from scattering of the primary x-rays rather than from fluorescence effects. Figure 14.1 shows the scattering of primary rhodium x-rays in two sediments with different water contents. Two different types of scattering can be seen. Rayleigh (or coherent) scattering leaves the photon energy unchanged, while Compton (or incoherent) scattering transfers some of the photon energy to electrons in the irradiated material, slightly lowering the energy of the photons. The amount and relative proportions of the different scattering mechanism varies with atomic number (Duvauchelle et al. 1999); high water content (thus low mean atomic number) causes more scattering and favours the Compton mechanism. If sediment water content is the primary control over mean atomic mass, then the sediment water content may be estimated using this scattering ratio.

Particle size also impacts the X-ray fluorescence signal (Finkelshtein and Brjansky 2009). We neglect this effect for two reasons. First, range of the particle size

variation in our lake sediment cores (as is typical for deep water cores) is sufficiently narrow that a large particle size effect of X-ray signal is not expected. At Lilla Öresjön particle size varies, in parallel with water content, between the late glacial sediment below 12.7 m (median size ca. 34  $\mu\text{m}$ ) and the overlying early Holocene sediment (median size ca. 10  $\mu\text{m}$ ). At Brotherswater, the median size varies through the core alternating between 17 and 27  $\mu\text{m}$  in response to palaeo-floods. Second, while the substantial water content effect can be readily corrected using information already collected (X-ray scattering), no equivalent method is available for the particle size effect.

In this paper we present a procedure for estimating dry mass concentrations for wet core sediment developed for the GEOTEK MSCL-XZ system driving an Olympus Delta XRF Analyser as a scanning  $\mu$ XRF, and we assess the implications of this for the analysis of lake sediments by comparison with parallel analysis of the sediments by conventional dry loose-powder measurements.

## The Instruments

A Bruker S2 Ranger energy dispersive X-ray fluorescence analyser (EDXRF) was used to measure the dry mass composition of sediment subsamples (freeze dried) from the scanned cores. This instrument has a Pd-target X-ray tube and Peltier-cooled silicon drift detector. The instrument was run at three different measurement conditions (20, 40 and 50 kV, typically at 0.2, 0.4 and 1 mA respectively) on loose powder under helium. Powder cups were prepared with spectroscopic grade 6  $\mu\text{m}$  polypropylene film (Chemplex Cat. No. 425). Calibration used a set of up to 18 certified reference materials (Table 14.1). Mass attenuation correction used theoretical alphas, with organic matter concentrations estimated by LOI.

The Geotek MSCL-XZ is a compact bench-top core-scanning system, located in the Central Teaching Laboratory of the University of Liverpool, that can conduct non-destructive measurements on split sediment core lengths (up to 1.55 m) obtaining multiple data sets simultaneously (XRF geochemistry, Colour photospectrometry, Magnetic Susceptibility and Line-scan high resolution imaging). The Olympus Delta is a handheld energy dispersive XRF Analyser fitted to the Geotek MSCL-XZ, which has a 4 W rhodium X-ray tube (8–40 kV 5–200  $\mu\text{A}$  excitation) and a thermoelectrically cooled, large-area silicon drift detector. The detector window is covered with a Mylar film. The XRF was run in two modes; the first (Soil mode) uses three beam conditions: 40, 40 (filtered) and 15 kV each for 20 s to optimise beam conditions for materials where the elements of interest are relatively heavy, relatively dilute, and in a matrix of lighter elements. Elements are calibrated individually on a linear basis after spectra have been normalized to the Compton scattering peak to partially correct for mass attenuation effects. For the second mode, (Mining-Plus) the spectrometer performs two measurements in succession: 40 and 15 kV beam conditions each for 20 s, and in a configuration suited to measuring the overall composition of the rock or sediment. This mode uses a fundamental param-

**Table 14.1** Data for precision and accuracy of the S2 Ranger and Olympus DELTA XRF systems. The slope (certified/measured value) and root mean square difference (RMSD) indicate accuracy and precision. The number of certified reference materials used,  $N$ , and their mean and maximum concentrations are shown

	Bruker S2 Ranger						Olympus DELTA					
	Measured v. certified RMIs <sup>a</sup>						Measured v. certified RMIs <sup>b</sup>					
	Slope	RMSD	Mean	Max	$N$		Slope	RMSD	Mean	Max	$N$	
Al	1.004	2.17	42.9	85.0	16		0.984	4.29	49.8	88.7	6	
Si	1.003	5.48	198.5	370.0	14		0.934	13.32	270.2	467.0	7	
P	0.963	0.05	1.1	4.1	11		<i>Non-significant correlation</i>					
S	0.970	0.11	0.8	2.5	12		1.326	0.04	4.8	12.6	3	
K	1.049	0.91	20.1	43.0	12		1.128	0.98	15.6	33.8	7	
Ca	0.997	1.85	51.4	300.0	16		1.160	0.68	10.6	26.0	6	
Ti	0.994	0.16	2.9	5.6	17		1.002	0.16	3.1	7.0	6	
Mn	0.993	0.03	0.7	2.5	16		1.049	0.02	0.4	1.0	7	
Fe	0.961	1.26	21.5	93.8	14		0.925	0.59	25.0	39.4	7	
Cu	0.997	5.42	108.3	247.0	18		0.891	6.87	82.1	237.0	7	
Zn	0.988	3.43	72.8	373.0	15		0.861	3.54	88.3	251.0	6	
Rb	0.999	2.23	101.1	466.0	18		1.066	3.96	81.9	175.0	7	
Sr	0.993	10.30	275.7	790.0	17		1.022	11.27	151.0	239.0	6	
Y	0.990	0.98	16.8	62.0	14		0.939	0.37	12.8	33.0	4	
Zr	0.982	6.31	146.2	370.0	14		1.206	18.93	151.2	385.0	5	
Pb	0.995	2.56	65.0	698.0	14		0.975	3.66	96.3	500.0	8	

*Reference material used:* <sup>a</sup> CRM7002 Light sandy soil, GBW7309 Stream sediment, GBW7602 Bush, branches and leaves, GBW7603 Bush, branches and leaves, GBW7604 Poplar leaves, GBW7605 Tea, LGCC6139 River clay sediment, NCSDC70302 Carbonate rock, NCSDC70309 Carbonate rock, NCSDC70314 Tibet sediment, NCSDC70317 Tibet sediment, NCSDC70319 Tibet sediment, NCSDC73301 Rock, NCSDC73302 Rock, NCSDC73303 Rock, NCSDC73309 Stream sediment, NCSDC73373 Stream sediment, NIST2709 San Joaquin Soil

<sup>b</sup> CCRM TILL-4 Till sample, MC CRM River sediment, NIES No. 2 Pond sediment, NIST 2780 Hard rock mine waste—elements, NIST2704 Buffalo River sediment, NIST2709a San Joaquin Soil, RCRA Soil standard, SiO<sub>2</sub> Specpure silica

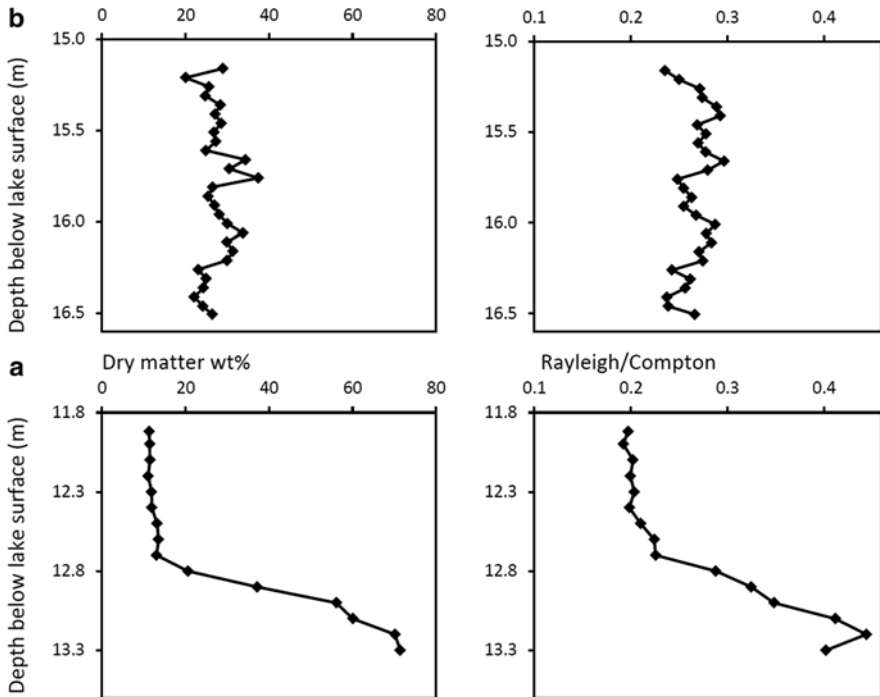
eters approach to correct for matrix effects, where the software assumes that certain elements are present in the sample and iteratively fits a model to the spectra. This approach is better suited to samples with high concentrations of the target elements (rock, or mineral-rich soil/sediment). The Olympus Delta completes a daily calibration check against a known standard (Alloy 316 Stainless Steel), and will not measure unless within tolerance. For both modes of operation local consistency checks have been made using a set of up to eight certified reference materials (Table 14.1).

## The Experiment

Two sediment cores have been investigated from lakes sites (Fig. 14.2) that were selected to exemplify the two cases of (1) systematic variation in water content, and (2) relatively uniform water content (Fig. 14.3). The sediment at Lilla Öresjön, Sweden (In the boreal forest zone, Västra Götaland, core location 57.5514°N, 12.3166°E) is predominantly organic, but with an abrupt transition at the base of the Holocene from basal high-density glacial clays to low density wet organic gyttja (Fig. 14.3). The sediment core LOR3 (1.45 m total length) taken in August 2009 (Fig. 14.2)



Fig. 14.2 Geographical location of the study sites



**Fig. 14.3** Dry matter content (wt%) for the subsamples, and coherent/incoherent backscatter ratio (Olympus DELTA scanning XRF) for the corresponding core interval for **a** Lilla Öresjön and **b** Brotherswater

samples the abyssal inflow-proximal sediments. A 1.5 m long, 70 mm diameter Russian corer was used. The core was tightly wrapped to prevent drying, and stored in darkness at 4 °C. The Brotherswater site (Cumbria, UK, 54.5066°N, -2.9249°E) was chosen for its more mineral-rich character and lack of systematic variation in water content (Fig. 14.3). The core drive BW12-9A (1.35 m total length) was extracted in October 2012 from the flat bottomed central basin using 1.5 m long, 70 mm diameter Russian corer.

The wet cores were scanned using the Olympus Delta instrument using the two measurement modes described above. The Mining-Plus mode was used for Al, Si, P, and Ca; the Soil mode was used for the other elements. For both modes the instrument automatically converts X-ray signals to elemental concentrations using factory-set calibrations. Split core lengths (up to 1.55 m length) were cleaned and covered with spectroscopic grade 6 µm polypropylene film (Chemplex Cat. No. 425) with measurements conducted at 5 mm intervals. Subsets of samples at intervals of 100 mm for Lilla Öresjön and 50 mm for Brotherswater were freeze dried, further oven dried at 50 °C to ensure constant dryness, and measured using the Bruker S2 Ranger under the conditions described above. Samples were weighed before and after drying to measure the water content of the sediment.

A series of tests were applied to the data collected.



1. Comparison of GEOTEK/Olympus DELTA XRF system wet core scanned concentrations with those measured on dried subsamples using the Bruker S2 Ranger XRF. The scanned data are compared both with (a) dry mass concentrations, and (b) calculated wet mass concentrations ( $C_{wet}$ , based on the measured percentage water content,  $W$ , of the sediment and S2 Ranger dry mass concentrations,  $C_{dry}$ , using Eq. 14.1.

$$C_{wet} = C_{dry} \times \frac{100}{(100 - W)} \quad (14.1)$$

These comparisons serve to test (a) whether  $\mu$ XRF scanning yields usually accurate wet concentration data, and (b) whether simple regression methods can be used to convert wet to dry mass concentrations.

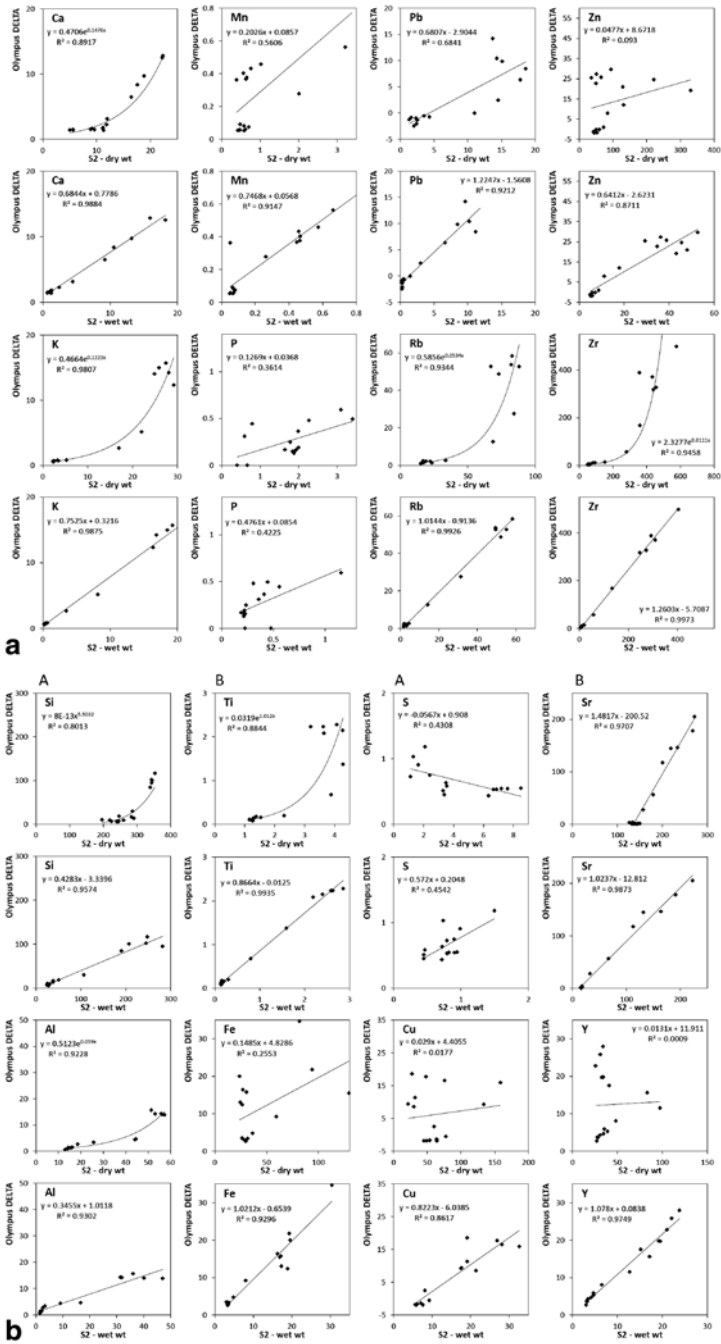
2. Comparison of the ratio of coherent to incoherent X-ray scattering (coherent/incoherent) for the main tube line (Rh  $k\alpha$ ) of the Olympus DELTA XRF with (a) water content and (b) mean atomic mass.
3. Recalculation of the scanned XRF data on a dry mass basis by (a) direct simple regression using the coefficients from test 1, and (b) calculation using the water content estimate of test 2. This is achieved using Eq. 14.1 in reverse.
4. A brief assessment of the geochemical interpretation of (a) uncorrected wet sediment concentrations, (b) dry concentrations determined by simple regression, and (c) dry concentrations determined from back-scatter estimated water contents, for two different sediment cores.

## Results

### *Correlation of GEOTEK/Olympus DELTA Scanned XRF Data with Subsample Dry and Wet Mass Concentrations*

Figure 14.4 compares the measured concentration values obtained using the Olympus DELTA XRF and the Bruker S2 Ranger for the Lilla Öresjön LOR3 core. The S2 data were measured on subsamples; the Olympus DELTA XRF data used for the comparison is the mean value of scan data for the depth corresponding to the subsample. For each element there are two graphs. The left hand graph is based on the measured S2 Ranger value for the dried subsample. The right hand graphs uses the same measurements but recalculated to a wet composition basis, making the S2 data more comparable with the Olympus DELTA XRF data. The wet and dry basis-comparisons yield very different results.

In the dry mass comparison, elements displayed highly variable responses. Si, Al, Sr, Ca, K, Rb and Zr yield strong positive relationships, all exponential in form except for Sr which showed a linear relationship. P showed a weaker but statistically significant relationship. Fe, Mn, Cu, and Zn showed generally positive but highly scattered relationships that were not statistically significant. Y and Pb showed an



**Fig. 14.4** Correlations for the Lilla Öresjön core of element concentrations (ppm) measured by Olympus DELTA and by Bruker S2 Ranger. **a** Wet core Olympus DELTA v. dry sample Bruker S2, and **b** wet core Olympus DELTA v. wet concentration calculated from Bruker S2 dry sample measurements

organised but non-linear relationship. S showed a negative relationship. In the wet mass comparison all elements showed positive straight-line relationships. All are statistically significant, though for S and P this was weak. The lighter elements (Al, Si, P and S) all have low measured values by Olympus DELTA XRF relative to the S2 Ranger, with slopes ranging 0.3–0.5. Most other elements yield slopes between 0.8 and 1.25, and have coefficients of variation ( $r^2$ ) greater than 0.9. The heavier elements (Rb, Sr, Y and Zr) have coefficients of variation close to 0.99.

The data for Brotherswater (Fig. 14.5) show some similarities with the results for LOR3, but with less striking differences between the wet and dry mass results. For most elements a stronger correlation is seen with the wet mass S2 data than for dry. However, none of the correlations are as good as for the LOR3 core. For Pb a similar degree of correlation was found for both, while for K the dry mass correlation was the better of the two.

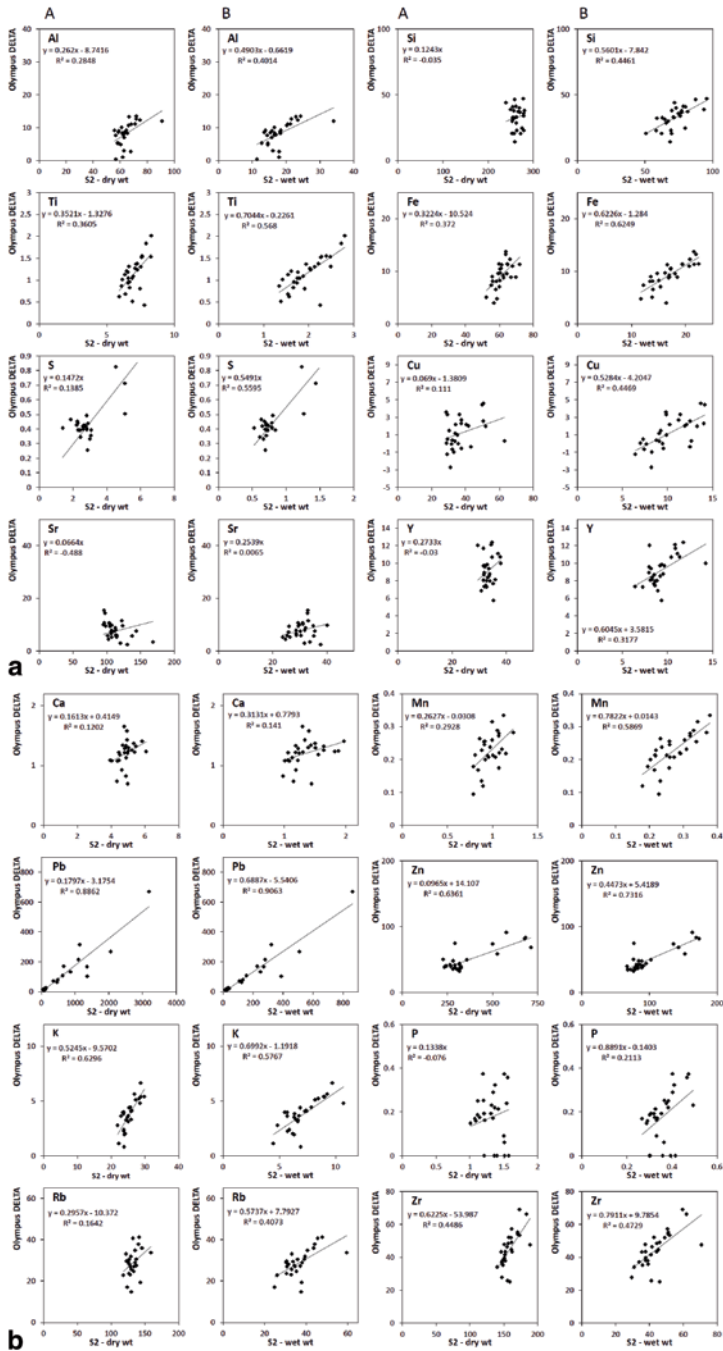
The better fit between the scanned XRF data with the calculated wet concentrations is directly analogous to the finding of Tjallingii et al. (2007) who performed a similar experiment in reverse, comparing dry scanned data with conventional XRF data on dry material. This shows that better results are obtained when concentrations are expressed in terms of the same matrix type (wet or dry).

### ***Sediment Core Water Content and X-ray Back-scattering***

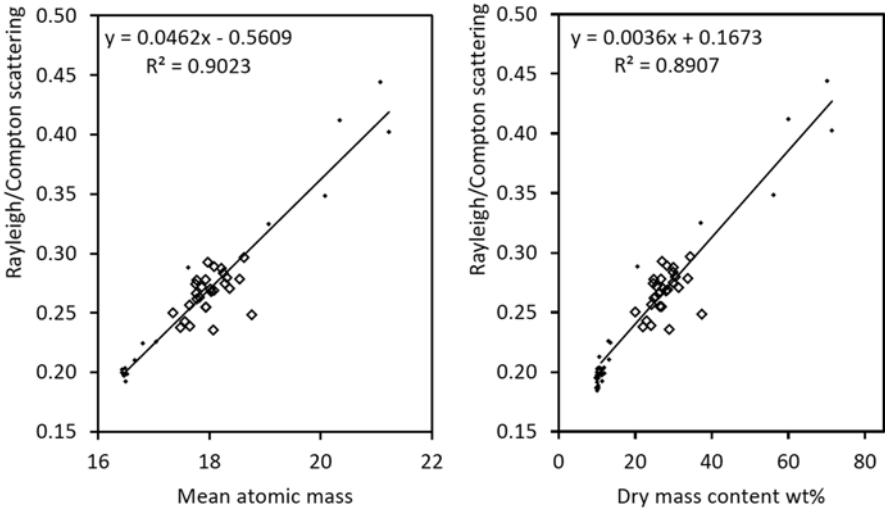
The data in Fig. 14.3 show a clear positive association between the ratio of coherent to incoherent back-scattering and the sediment dry mass concentration (wt%). Figure 14.6 shows the correlation between the dry matter concentration and the back-scatter ratio, revealing a coefficient of variation is 0.89. A linear regression line generated for the combined data sets passes through the points for both cores showing a strong similarity in the dependence of X-ray scattering on water content for these two rather different sediments. The slightly better relationship seen with mean atomic mass, as conforms with theory, shows that variations in mineral matter composition and organic matter content (which are taken into account in calculating the mean atomic mass) only marginally improves prediction of scattering properties. This shows that variation in water content is the main factor driving variations in mean atomic mass. This in turn allows the measured X-ray back-scattering to be used to estimate the water content of the sediment core material.

### ***Conversion of GEOTEK/Olympus DELTA XRF Scanned Data to Dry Mass Basis***

Figures 14.7 and 14.8 show, for the LOR3 and BW cores respectively, the dry mass concentration estimates for the two procedures, and compare these with both the uncorrected data and sub-sample dry mass concentration values.



**Fig. 14.5** Correlations for the Brotherswater core of element concentrations (ppm) measured by Olympus DELTA and by Bruker S2 Ranger. **a** Wet core Olympus DELTA v. dry sample Bruker S2, and **b** wet core Olympus DELTA v. wet concentration calculated from Bruker S2 dry sample measurements



**Fig. 14.6** Relationship between measured subsample water content and the corresponding DELTA X-ray back scatter ratios for Lilla Öresjön (points) and Brotherswater (diamonds). The regression coefficients are used to generate high resolution water content estimates for the scanned cores using the measured X-ray back scatter peaks

The simple regression correction has been applied using the coefficients ( $b_0$  and  $b_1$ ) shown on Figs. 14.4 and 14.5 according to Eq. 14.2.  $C$  is the elemental concentration measured by Olympus DELTA, the suffix indicating the sediment state (wet or dry).

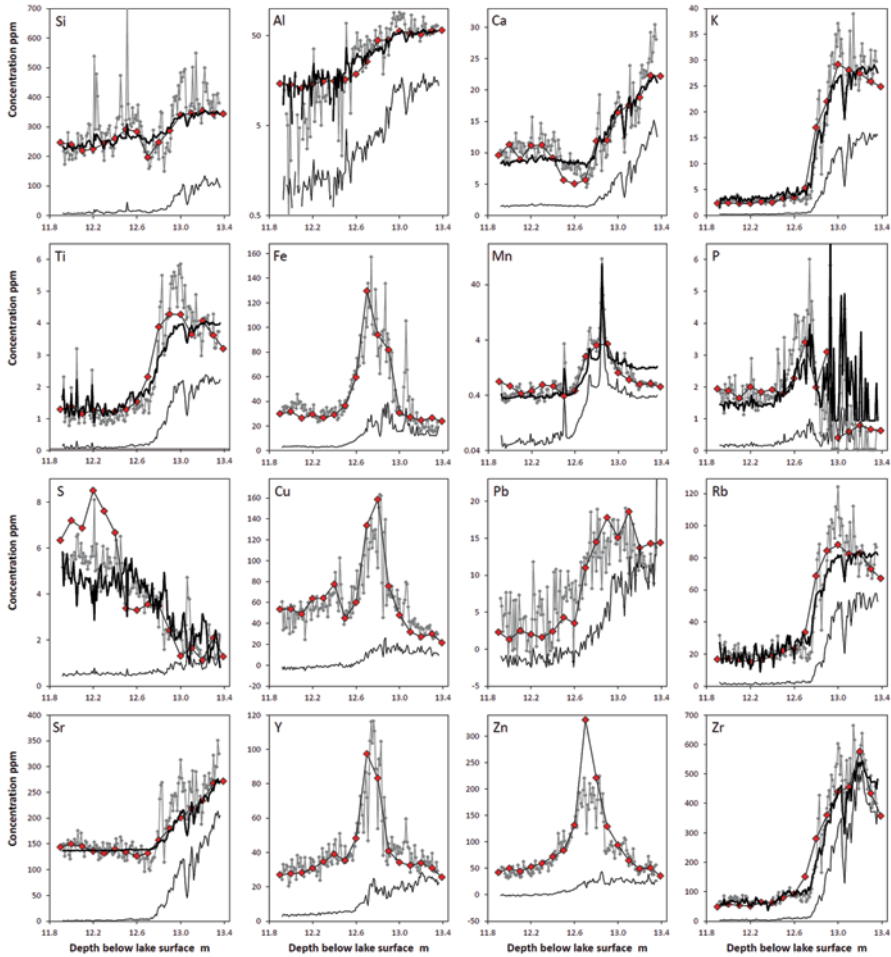
$$C_{dry} = \frac{(C_{wet} - b_0)}{b_1} \tag{14.2}$$

The water content correction was applied by combining Eqs. 14.3, 14.4 and 14.5, where the regression coefficients ( $b_0$  and  $b_1$ ) were taken from the wet-wet comparison on Figs. 14.4 and 14.5.  $W$  is the percentage water content of the sediment. “Coherent” and “incoherent” refer to measured source K-line back scatter peak heights (see Fig. 14.1), corresponding respectively to Rayleigh and Compton scattering.

$$C_{dry} = C_{wet,corrected} \frac{(100)}{(100 - W)} \tag{14.3}$$

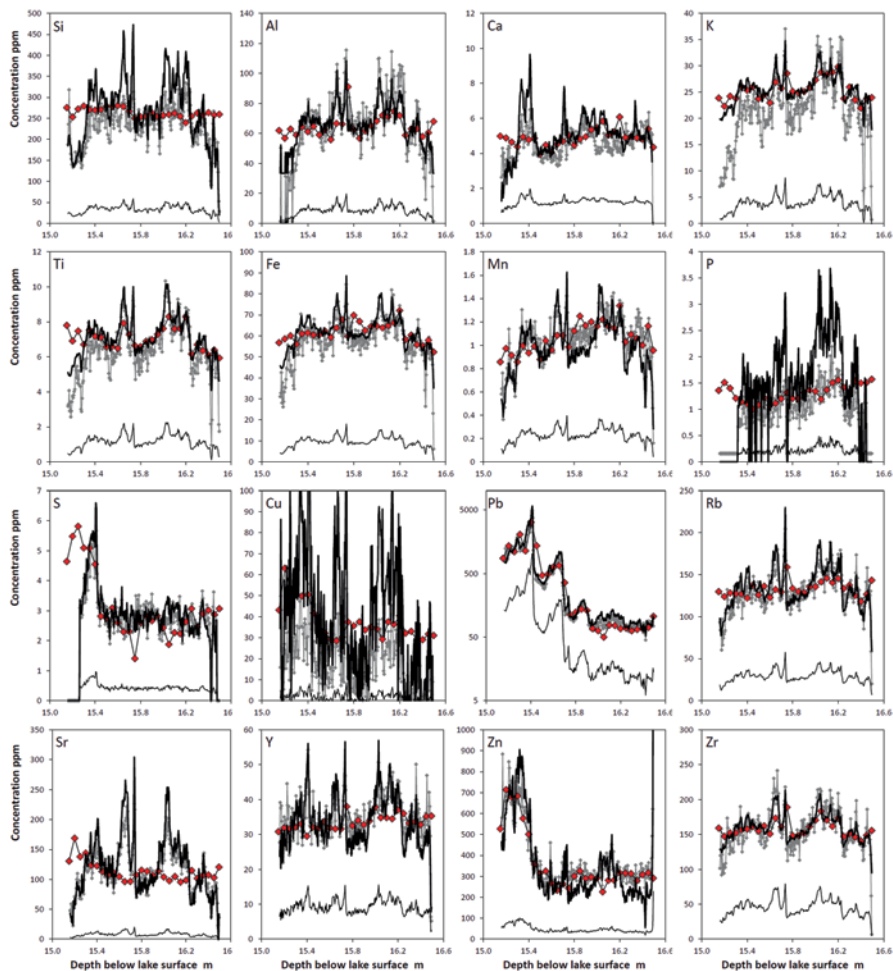
$$C_{wet,corrected} = \frac{(C_{wet} - b_0)}{b_1} \tag{14.4}$$

$$W = \frac{((\text{coherent}/\text{incoherent}) - 0.167)}{0.0036} \tag{14.5}$$



**Fig. 14.7** Lilla Öresjön element concentration data. *Red symbols* are S2 Ranger subsample data, accurate but low resolution dry mass concentration values. *Thin black line* represents Olympus DELTA uncorrected data. *Thick black line* reflects Olympus DELTA corrected by regression on dry S2 data (only shown for cases that showed statistically significant correlations). *Grey line* GEOTEK corrected using water contents inferred from back-scatter X-ray data

At Lilla Öresjön (Fig. 14.7) it can be seen that correction to dry mass basis brings the GEOTEK data in line with the subsample measurements, the uncorrected data having very much lower values. For the corrected values the elements may be divided into three classes. (1) Al and Zr show essentially identical patterns but with the simple regression (Eq. 14.2) yielding the best agreement with the subsample measurements, and very much the least noise. (2) For Si, Ca, K, Ti, Mn, P, S, Rb and Sr the two methods show similar degrees of agreement with the subsample data, though with clearly poorer capture of underlying trends for the simple regression method but rather lower noise. (3) For Fe, Cu, Pb, Y and Zn the simple regression



**Fig. 14.8** Brotherswater element concentration data. *Red symbols* are S2 Ranger subsample data, accurate but low resolution dry mass concentration values. *Thin black line* represents Olympus DELTA uncorrected data. *Thick black line* reflects Olympus DELTA corrected by regression on dry S2 data (only shown for cases that showed statistically significant correlations). *Grey line* GEOTEK corrected using water contents inferred from back-scatter X-ray data

method could not be used owing to lack of correlation, but the water content correction method works well. In this last case there is a very great difference between the uncorrected (wet) and corrected (dry) sediment concentrations.

Membership within these three classes is associated with the relationship between the element concentration profile and the water content (Fig. 14.3). Where an element correlates well with the sediment water content, positively or negatively (class 1), the simple regression method (Eq. 14.2) works well. Where these two are

uncorrelated (class 3), the relationship between wet and dry mass concentrations is weak or non-existent, and the simple regression method is inapplicable.

At Brotherswater (Fig. 14.8) the two methods yield a similar degree of fit with the subsample dry concentration values. They differ in the level of noise, which is far lower for the simple regression method.

For geochemical interpretation the two cores lead to different conclusions. At Brotherswater, the pattern of variation is similar for all three forms of the scanned data (uncorrected, and both corrected data sets). Except for considerations of magnitude (absolute dry mass concentration), the corrections have no impact on the geochemical interpretation. However, at Lilla Öresjön the situation is very different. The uncorrected and regression-corrected data both fail to show the trends of variation through the late glacial, and both fail to detect the enrichment in Fe, Cu, Zn, P and Y during the earliest Holocene, and thus fail to show a signal of substantial environmental significance (Boyle et al. 2013). Thus the successful dry mass correction obtained using the X-ray back-scatter water content estimate profoundly improves the geochemical interpretation.

## Discussion

The results from Lilla Öresjön (Fig. 14.7) show that where the correlation between wet core XRF and dry sediment XRF concentration is poor (illustrated on Fig. 14.4), then (a) failure to correct for water content will lead to highly distorted depth-concentration profiles, and (b) that water content estimation from X-ray back-scattering provides a useful degree of correction. A similar finding can be expected in any case where substantial systematic shifts in water contents are found through a core. We may also expect a comparable benefit from applying such a correction where large non-systematic shifts in water content are found; erratic signals resulting from erratic variation in water content will be reduced. However, this procedure comes at a price; the back-scatter signal is relatively noisy such that considerable noise is added to an element concentration profile through application of the method (Eqs. 14.3–14.5). Thus for any particular case, both methods should be applied. Where both reveal a similar underlying data structure, the lower noise of the direct simple regression gives it a distinct advantage. This case is well illustrated at Brotherswater (Fig. 14.8). There, it is apparent that both correction methods reveal patterns that are rather different from the subsampled dry mass data, which likely relates to imperfections in the core surface, but it is clear that the less noisy direct correction (Eq. 2) is better than the back-scatter approach (Eqs. 14.3–14.5).

The pros and cons of conversion to dry mass concentrations are also well illustrated by the two cores. The concentrations of Fe, Cu, Zn, P and Y in the mid-profile “spike” in LOR3 are exceptionally high by comparison with other lake sediments. Expressed as wet mass concentrations, element ratios or raw counts this phenomenon is much less clear. Of course, this alone could be achieved simply by measuring only the subsamples. However, it is also clear for LOR3 that considerable fine



scale compositional structure would be missed by coarse subsampling. It is similar at Brotherswater; the wet concentrations reveal very high Pb enrichment, but it is the dry mass values that can be compared with other cores and neighboring sites.

To apply dry mass correction with confidence it is necessary to analyse subsamples, ideally measured for both water content and element composition. This provides both a training set and a means of evaluating performance. There is some advantage to analyzing the subsample independently. However, our Olympus DELTA XRF produces sufficiently accurate dry mass concentration data that subsamples can be dried and presented loose-powder form (pressed into loose “pellets” in inverted XRF cups) for scanning, allowing it to be used to generate test or calibration data (Table 14.1).

The procedure we have developed for the GEOTEK system is equally applicable for other scanning XRF instruments. Even where these present results as X-ray count rather than concentration data, normalization to dry matter content estimated from X-ray scatter peaks (which can be readily extracted from the raw X-ray spectra files generated by each instrument) will correct for systematic variation in water content, and is an essential first step before recalculation of the X-ray count scans to dry mass concentration.

## Conclusions

Proliferation in the use of scanning  $\mu$ XRF has seen significant research gains in terms of resolution of analysis and examining fine structure within sediment profiles. However, reliance on elemental ratios in interpretation of count or concentration data loses important information on the dry mass concentration of elements, sometimes negating correlation between and within sites. Correction of scanned data to a ‘quantitative’ dry mass equivalent form offers potential benefits for the understanding of elemental concentrations and fluxes. Our analysis of the two cores reveals that X-ray back-scatter correction for water content can be usefully applied to convert Olympus DELTA XRF wet concentration data to a dry mass basis where large variations in water content are present. Although the correction procedure introduces noise at finer resolution, there is a very great improved accuracy in relation to the underlying trends. Where water contents are less variable, simple regression of wet and dry sediment element mass concentrations is likely the best approach.

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