Loss on ignition: a qualitative or quantitative method for organic matter and carbonate mineral content in sediments?

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Abstract

Since the publication of the paper of Dean (1974), loss on ignition (LOI) has been widely used as a method to estimate the amount of organic matter and carbonate mineral content (and indirectly of organic and inorganic carbon) in sediments. The relationships between LOI at 550 °C (LOI_{550}) and organic carbon (OC) content and between LOI at 950 °C (LOI_{950}) and inorganic carbon (IC) content are currently accepted as a standard. However, the comparison of 150 analyses of samples of diverse lithologies, collected from a single core, reveals that these relationships are affected by sediment composition (presence of clays, salts, and the variable content of organic carbon). This results in an incremental error on the estimation of carbon content from LOI values that invalidates the use of LOI values as a quantitative method for estimating carbon content. Conversely, the general trends of LOI_{550} and LOI_{950} show a good correlation with carbon content (both organic and inorganic) allowing use of LOI as a qualitative test for carbon content. Similarly, in our case, LOI at 105 °C (LOI_{105}) is a good qualitative proxy for the trends in gypsum content.

Introduction

Sequential loss on ignition (LOI) is a simple method for estimating the content of organic matter and carbonate minerals in sediments using the linear relations between LOI values and organic and inorganic carbon content. Easy implementation in the laboratory makes the method widely used (e.g., Dean 1974, 1999; Korsman et al. 1999; Dodson and Ramrath 2001; Heiri et al. 2001; Boyle 2001, 2004; Bendell-Young et al. 2002; and Beaudoin 2003).

The method is based on differential thermal analysis: organic matter begins to ignite at about 200 °C and is completely depleted at about 550 °C, and most carbonate minerals are destroyed at higher temperatures (calcite between 800 and 850 °C, dolomite between 700 and 750 °C). The organic carbon content has been experimentally calculated as about half the LOI_{550} (Dean 1974). Calculation of the inorganic carbon (IC) assumes that ignition follows a stoichiometric relationship (Dean 1974, 1999; Heiri et al. 2001), and that the amount of carbonate is $1.36 \times LOI_{950}$ (Heiri et al. 2001). This implies that $IC = 0.273 \times LOI_{950}$. Many authors (e.g., Meyers and Lallier-Verges 1999; Meyers and Teranes 2001) have remarked that certain volatile non-carbon components of the sediment increase the LOI values. One of the most influential is the lattice water in clays (Dean 1974; Ran et al. 2000; Heiri et al. 2001) that can account up to 5% in LOI. Gypsum, sulphide minerals, and metallic oxihydroxides can modify LOI values as well, via oxidation or dehydratation (Brauer et al. 2000; Rosen et al. 2002; Ralska-Jasiewiczowa et al. 2003). Additional errors come from loss of inorganic carbon at temperatures between 425 and 520 °C in minerals such as siderite, magnesite, rhodochrosite and dolomite (Heiri et al. 2001). For this reason, Meyers and Lallier-Verges (1999) and Meyers and Teranes (2001) suggested other approximations for calculating carbon contents.

In spite of the previous considerations, many calculations of carbon contents in sediments found in the literature derive from LOI_{550} and LOI_{950} values. This is particularly important because fluctuations in carbon content are often correlated to climatic or biological changes, and have been widely used in the analysis of Plio-Quaternary deposits (e.g., Ramrath et al. 1999; Brauer et al. 2000; Valero-Garcés et al. 2000; Dodson and Ramrath 2001; Battarbee et al. 2002).

We intended to revise this idea when we began a study of wetland deposits in Las Tablas de Daimiel National Park in central Spain (Figure 1) in 2001. One of our main goals was to estimate the capacity of the environment to produce and store carbon. Available time and budget restrictions required a simple, cheap, reliable method to determine organic and carbonate contents. As a methodological approach, we sampled a core and compared the results obtained using LOI (following the method proposed by Heiri et al. 2001) and by direct measurement of organic and inorganic carbon in the same samples.

Methods

The 187 cm-long core selected for high resolution sampling (Güiüela 4-2, Figure 1) includes diverse lithologies and variable contents of organic and inorganic carbon. Sampling spacing was 0.7 cm between 0 and 100 cm, and 1.1 cm from 100 cm to the bottom, making a total of 213 samples. The upper 132 samples and one of each of three of the following samples (total: 162 samples) were se-
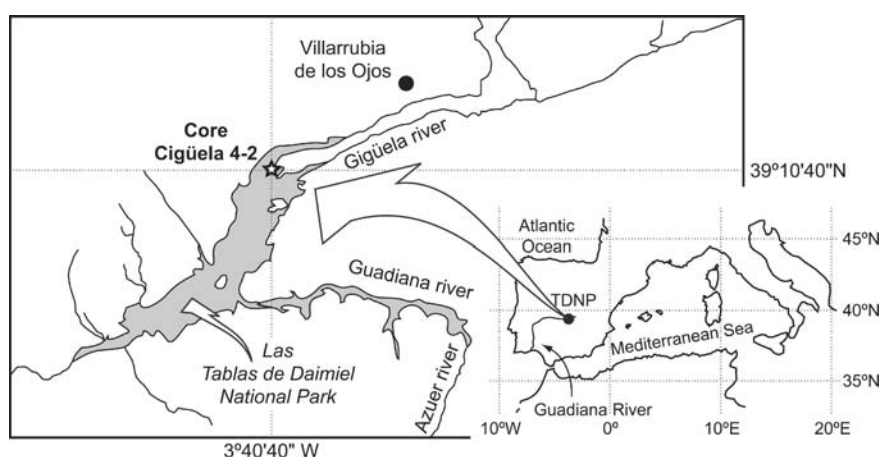

Figure 1. Location of core Güiüela 4-2. TDNP: Las Tablas de Daimiel National Park.
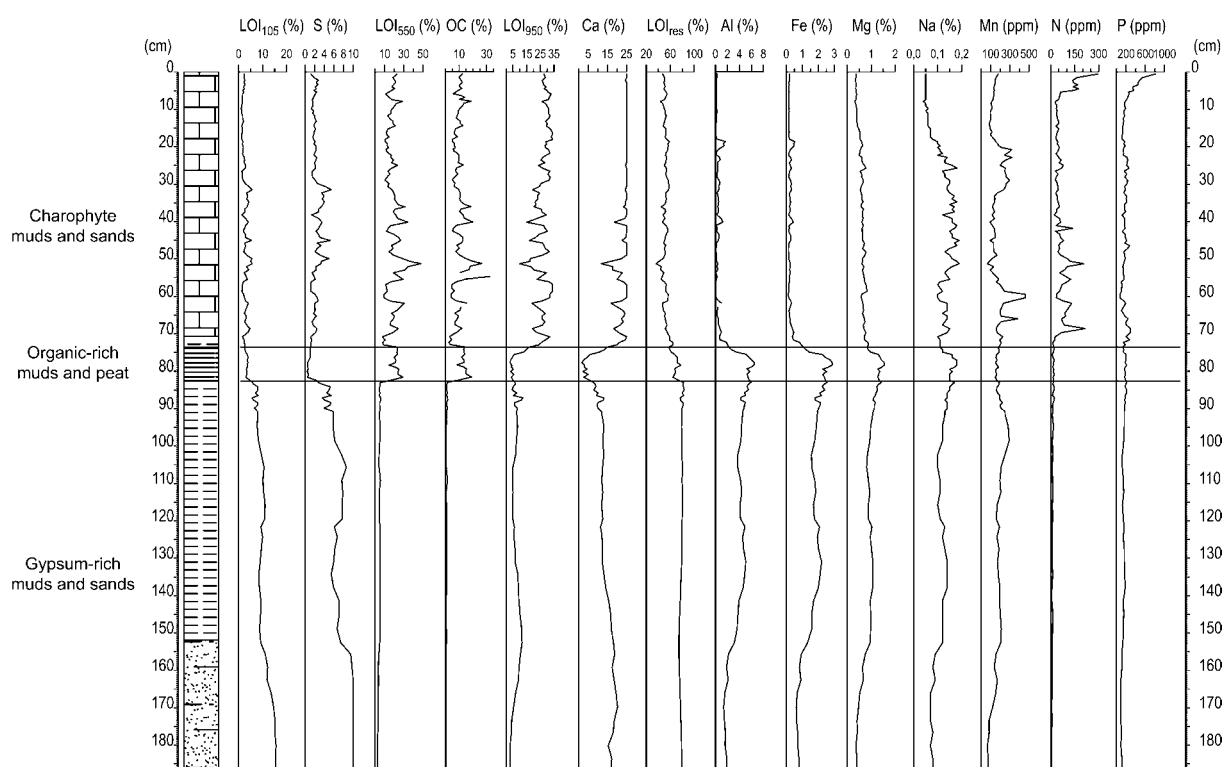
Figure 2. Stratigraphical log of core Gigüela 4-2 and main geochemical parameters analyzed in this paper.

Table 1. Statistical parameters of core Gigüela 4-2 ($n = 150$) (significance level of 0.05)

	LOI_{105}	LOI_{550}	LOI_{950}	LOI_{res}	IC	OC	Ca	S	Al	Fe	Mg	Na	Mn	P	N
Mean	4.59	14.97	19.74	60.71	5.05	7.65	19.39	3.43	1.79	0.81	0.74	0.120	175	181	47.4
Standard deviation	3.64	8.54	10.68	12.61	2.74	5.49	6.93	2.54	2.03	0.85	0.30	0.040	67.38	87.29	46.49
Variance	13.26	72.87	114.05	159.10	7.48	30.13	47.98	6.47	4.11	0.72	0.09	0.002	4540.60	7620.03	2160.95
Range	14.58	45.33	31.27	46.65	8.69	26.15	23.22	9.58	6.39	2.75	1.23	0.15	396	740	290.2
Minimum	1.00	2.63	2.79	36.48	0.31	0.21	1.78	0.42	0.06	0.11	0.31	0.04	66	70	4.8
Maximum	15.57	47.96	34.06	83.13	9	26.36	25	10	6.45	2.86	1.54	0.19	462	810	295
Confidence level (95%)	0.59	1.38	1.72	2.04	0.44	0.89	1.12	0.41	0.33	0.14	0.05	0.01	10.87	14.08	7.50

Notice that 63 samples are above 25% of Ca and 10 samples are above 10% of S (detection limits). Units in % except for Mn, P and N (in ppm).

lected for analysis by ALS Chemex Laboratories (Vancouver, Canada). Twelve samples did not weigh enough, so the total number of samples for carbon content measurement was reduced to 150. All samples underwent double analyses: sequential loss on ignition and direct measurement of total carbon and inorganic carbon.

Sequential loss on ignition followed the method proposed by Heiri et al. (2001), with the modification by Bengtsson and Enell (1986) which takes into account the loss of mass at 105 °C and the residues after ignition for the calculation of the LOI. The process was:

(1) Dry the sample 12–24 h at 105 °C. Calculate the loss on ignition at 105 °C (LOI_{105}) as $LOI_{105} = 100(WS - DW_{105})/WS$, where WS is the weight of the air-dried sample and DW_{105} is the dry weight of the sample heated at 105 °C.

Table 2. Correlation coefficients for the whole core ($n = 150$) (significance level of 0.05)

	LOI$_{105}$	LOI$_{550}$	LOI$_{950}$	LOI$_{res}$	IC	OC	Ca	S	Al	Fe	Mg	Na	Mn	P	N
LOI$_{105}$	1														
LOI$_{550}$	−0.58	1													
LOI$_{950}$	−0.79	0.31	1												
LOI$_{res}$	0.78	−0.77	−0.83	1											
IC	−0.77	0.32	0.99	−0.84	1										
OC	−0.61	0.99	0.32	−0.76	0.31	1									
Ca	−0.48	0.17	0.89	−0.73	0.90	0.15	1								
S	0.95	−0.61	−0.61	0.65	−0.58	−0.65	−0.23	1							
Al	0.49	−0.39	−0.86	0.85	−0.88	−0.37	−0.94	0.29	1						
Fe	0.47	−0.38	−0.85	0.84	−0.87	−0.35	−0.95	0.26	1.00	1					
Mg	0.23	−0.19	−0.68	0.64	−0.69	−0.19	−0.86	0.01	0.89	0.90	1				
Na	−0.01	0.27	−0.31	0.08	−0.27	0.21	−0.37	−0.10	0.32	0.32	0.61	1			
Mn	−0.10	−0.27	0.08	0.14	0.08	−0.29	0.00	−0.09	0.10	0.10	0.21	0.17	1		
P	−0.28	0.24	0.19	−0.24	0.16	0.23	0.15	−0.29	−0.13	−0.12	−0.15	−0.15	−0.04	1	
N	−0.39	0.57	0.42	−0.63	0.42	0.50	0.39	−0.35	−0.51	−0.50	−0.43	−0.10	−0.11	0.67	1

Sixty three samples above 25% of Ca and 10 samples above 10% of S (detection limits).

Table 3. Correlation coefficients for the green gypsum-rich muds and sands ($n = 41$) (significance level of 0.05)

	LOI$_{105}$	LOI$_{550}$	LOI$_{950}$	LOI$_{res}$	IC	OC	Ca	S	Al	Fe	Mg	Na	Mn	P	N
LOI$_{105}$	1														
LOI$_{550}$	−0.92	1													
LOI$_{950}$	−0.54	0.52	1												
LOI$_{res}$	−0.30	0.18	−0.64	1											
IC	−0.34	0.39	0.96	−0.79	1										
OC	−0.79	0.77	0.29	0.36	0.07	1									
Ca	0.73	−0.63	0.17	−0.85	0.38	−0.68	1								
S	0.94	−0.87	−0.34	−0.46	−0.13	−0.82	0.82	1							
Al	−0.88	0.84	0.13	0.62	−0.05	0.67	−0.91	−0.90	1						
Fe	−0.88	0.84	0.13	0.62	−0.04	0.67	−0.91	−0.91	1.00	1					
Mg	−0.96	0.88	0.35	0.46	0.16	0.74	−0.82	−0.94	0.95	0.95	1				
Na	−0.92	0.84	0.29	0.49	0.10	0.73	−0.82	−0.96	0.95	0.95	0.97	1			
Mn	−0.77	0.72	0.50	0.12	0.39	0.42	−0.45	−0.59	0.63	0.62	0.67	0.57	1		
P	−0.87	0.78	0.21	0.55	0.01	0.75	−0.84	−0.94	0.92	0.92	0.93	0.96	0.50	1	
N	−0.68	0.57	0.27	0.32	0.09	0.65	−0.57	−0.68	0.57	0.57	0.64	0.59	0.41	0.65	1

Ten samples above 10% of S (detection limit).

(2) Burn the sample at 550 °C for 4 h. Calculate $LOI_{550} = 100(DW_{105} − DW_{550})/WS$, where LOI_{550} is the percentage of loss on ignition at 550 °C and DW_{550} is the weight of the sample after heating at 550 °C.

(3) Heat the sample at 950 °C for 2 h; calculate $LOI_{950} = 100(DW_{550} − DW_{950})/WS$, where LOI_{950} is the percentage of loss on ignition at 950 °C and DW_{950} is the weight of the sample after heating at 950 °C. The remaining sample, after heating at 950 °C, is the residuum (LOI_{res}).

Direct measurement of total carbon content was achieved with a Leco© SC-444DR carbon and sulphur analyser. Inorganic carbon (IC) was measured by CO_2 coulometry with an UIC© CM140 Total Inorganic Carbon Analyser. The content in organic carbon (OC) is the difference between the previous values.

It was also important to know the influence of other minerals in LOI values. Mineralogy was determined by X-ray diffractometry (XRD) at the Department of Geology of the University of Salamanca (Spain), using a Siemens D-500 XRD

Table 4. Correlation coefficients for the organic-rich muds and peat ($n = 14$) (significance level of 0.05)

	LOI$_{105}$	LOI$_{550}$	LOI$_{950}$	LOI$_{res}$	IC	OC	Ca	S	Al	Fe	Mg	Na	Mn	P	N
LOI$_{105}$	1														
LOI$_{550}$	−0.61	1													
LOI$_{950}$	−0.74	0.16	1												
LOI$_{res}$	0.87	−0.69	−0.82	1											
IC	−0.76	0.19	1.00	−0.84	1										
OC	−0.50	0.98	0.01	−0.57	0.04	1									
Ca	−0.66	0.11	0.99	−0.79	0.99	−0.04	1								
S	0.37	−0.43	0.28	0.00	0.27	−0.47	0.40	1							
Al	0.77	−0.32	−0.98	0.90	−0.98	−0.17	−0.97	−0.27	1						
Fe	0.77	−0.33	−0.97	0.91	−0.98	−0.18	−0.97	−0.27	1.00	1					
Mg	0.77	−0.38	−0.96	0.92	−0.96	−0.23	−0.95	−0.28	0.99	0.99	1				
Na	0.70	−0.37	−0.91	0.88	−0.92	−0.23	−0.91	−0.34	0.95	0.97	0.97	1			
Mn	−0.46	−0.13	0.72	−0.45	0.72	−0.27	0.71	0.22	−0.65	−0.65	−0.61	−0.54	1		
P	0.80	−0.52	−0.80	0.88	−0.80	−0.42	−0.75	−0.01	0.84	0.85	0.85	0.85	−0.50	1	
N	−0.33	0.07	0.32	−0.27	0.33	0.04	0.28	−0.01	−0.30	−0.28	−0.31	−0.27	0.26	−0.41	1

Table 5. Correlation coefficients for the Charophyte-rich layers with vegetal lamina ($n = 95$) (significance level of 0.05)

	LOI$_{105}$	LOI$_{550}$	LOI$_{950}$	LOI$_{res}$	IC	OC	Ca	S	Al	Fe	Mg	Na	Mn	P	N
LOI$_{105}$	1														
LOI$_{550}$	0.64	1													
LOI$_{950}$	−0.90	−0.81	1												
LOI$_{res}$	−0.27	−0.87	0.42	1											
IC	−0.83	−0.81	0.94	0.46	1										
OC	0.51	0.97	−0.72	−0.89	−0.76	1									
Ca	−0.63	−0.67	0.72	0.43	0.68	−0.57	1								
S	0.78	0.40	−0.65	−0.12	−0.63	0.35	−0.15	1							
Al	0.19	−0.10	−0.33	0.49	−0.27	−0.16	−0.27	0.04	1						
Fe	0.18	−0.16	−0.29	0.53	−0.22	−0.22	−0.31	−0.04	0.94	1					
Mg	0.35	−0.03	−0.27	0.27	−0.11	−0.17	−0.32	0.07	0.42	0.46	1				
Na	0.66	0.36	−0.61	−0.06	−0.49	0.23	−0.37	0.54	0.23	0.17	0.76	1			
Mn	−0.07	−0.42	0.20	0.47	0.23	−0.47	0.14	−0.12	0.15	0.13	0.30	0.13	1		
P	0.06	0.10	−0.08	−0.09	−0.16	0.10	0.09	−0.01	−0.01	0.01	−0.36	−0.27	−0.08	1	
N	0.36	0.47	−0.36	−0.45	−0.41	0.41	−0.40	0.07	−0.13	−0.12	−0.18	−0.06	−0.14	0.68	1

Sixty three samples above 25% of Ca (detection limit).

diffractometer with a Cu anticathode and a graphite monochromator. In addition, the procedure to determine P, Al, Ca, S, Na, Mn and Fe was HF–HNO$_3$–HClO$_4$ acid digestion, HCl leach and a combination of ICP-MS and ICP-AES. Nitrogen was determined as extractable N (NH$_4$, using a Technicon Autoanalyser$^©$, and NO$_3$, colorimetrically using the CTA method) at ALS Chemex Labs.

We used the R system (Ihaka and Gentleman 1996) to perform cross-correlation and principal components analysis (Lebreton et al. 1991; Boyle 2001; Grunsky 2001) for Al, Ca, S, Na, Mn, Fe, LOI$_{105}$, LOI$_{550}$, LOI$_{950}$, LOI$_{res}$, IC, OC, N and P, both for the whole core and for each facies. We performed linear regression of the LOI data for the total core data and for each separate facies.

LOI$_{550}$ and LOI$_{950}$ results were used to determine organic (OC) and inorganic (IC) carbon contents by means of Dean's (1974, 1999) relations (OC = LOI$_{550}$/2, IC = 0.273LOI$_{950}$), and our regression equations for the whole core data. Both sets of values were compared with direct measurements of C to determine the benefit achieved by generating a new set of equations prior to LOI analyses.
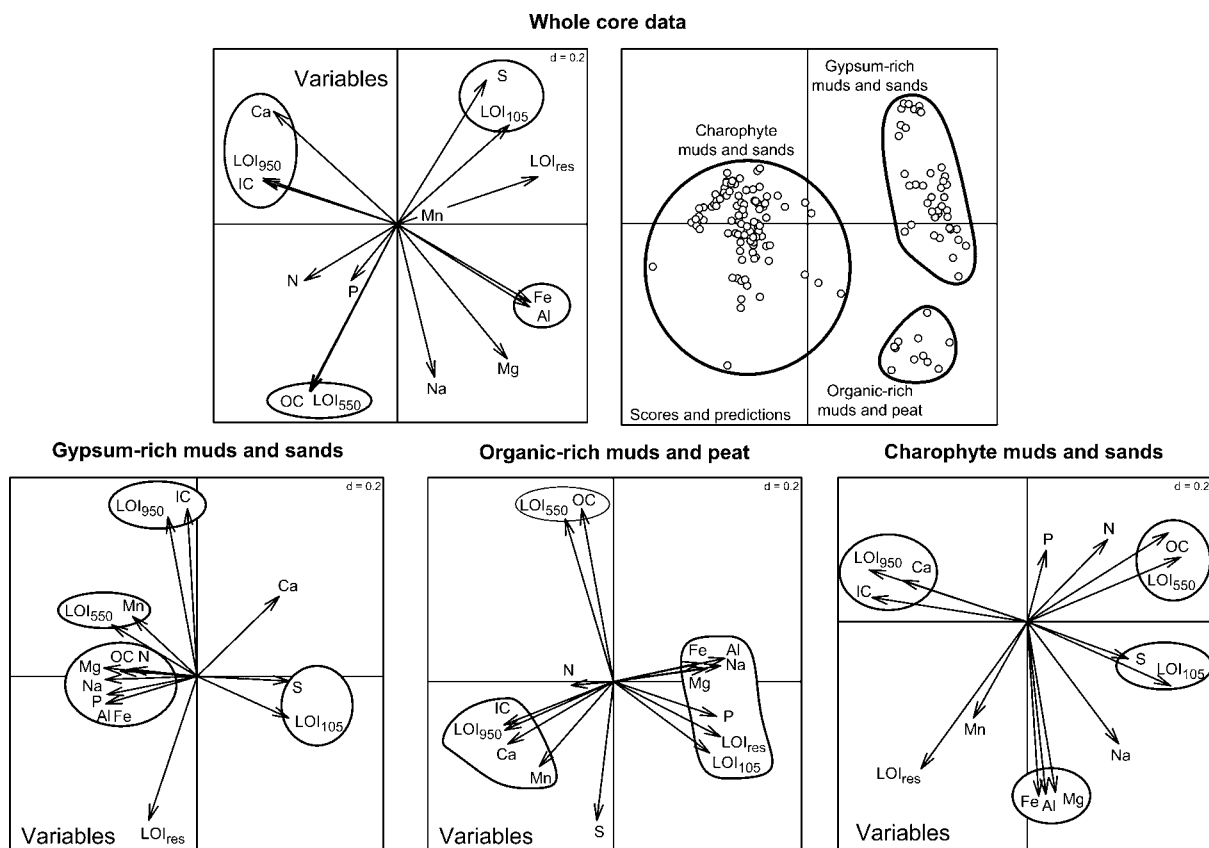
Whole core data

Figure 3. Principal components analyses. Variable relationships and scores and predictions.

Analyzed materials

The core Gigüela 4-2, Holocene in age, consists of three main facies (Figure 2): (i) Gypsum-rich siliciclastic mud and sand, (ii) organic mud and peat, and (iii) charophyte mud to sand layers with vegetal organic matter. The mineralogy of these materials is calcite (0–99%), quartz (0–17%), phyllosilicates (0–81%), gypsum (0–55%) and, as a minor component, feldspar (0–5%) in some samples. As a whole, the content of organic and inorganic carbon varies widely, as do Ca, S, Al, Mn, N and P. In contrast, Mg, Na and Fe fluctuate less (Table 1).

Discussion

Geochemical and mineralogical relationships

Correlation and principal components analyses, using LOI values and the main geochemical indi-

cators of the mineralogy, were used to confirm the dependence of LOI values on lithology. The analyses were performed for the whole core (Table 2) and for each facies (Tables 3–5) and the results are presented as principal components graphs that show the main relations among parameters (Figure 3).

Regarding the whole core, principal components analysis reveals two main factors that explain most of the sediment composition.

Factor 1 comprises IC–Ca–LOI_{950}, which represents the carbonate mineral content of the sediment, as opposed to Al–Fe which characterize the clay content. Factor 2 contains OC–LOI_{550}, corresponding to the organic content of the sediment, as opposed to S–LOI_{105} which stands for the gypsum content.

However, analysing samples as lithology groups reveals a rather different picture. For the gypsum-rich siliciclastic mud and sand, the most significant factor shows Al–Fe and OC–LOI_{550} (including Mg, Na and P) as opposed to S–LOI_{105} (Figure 3,

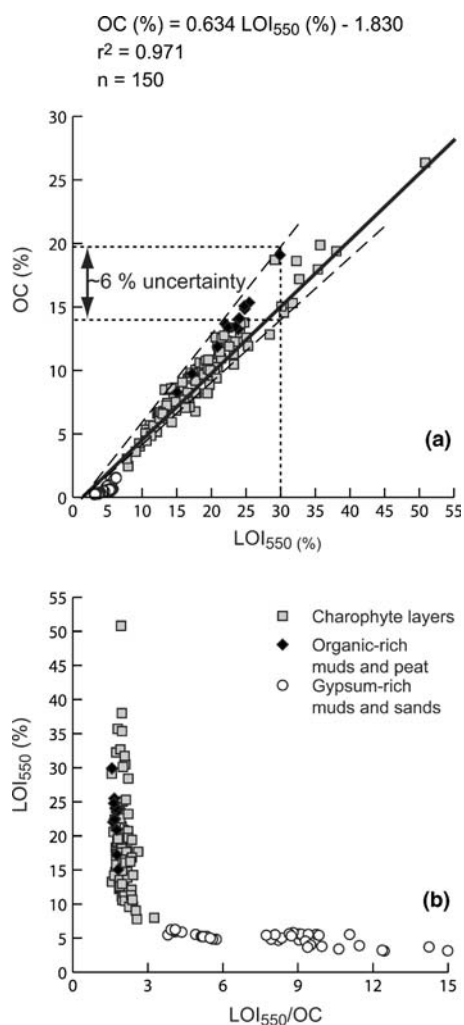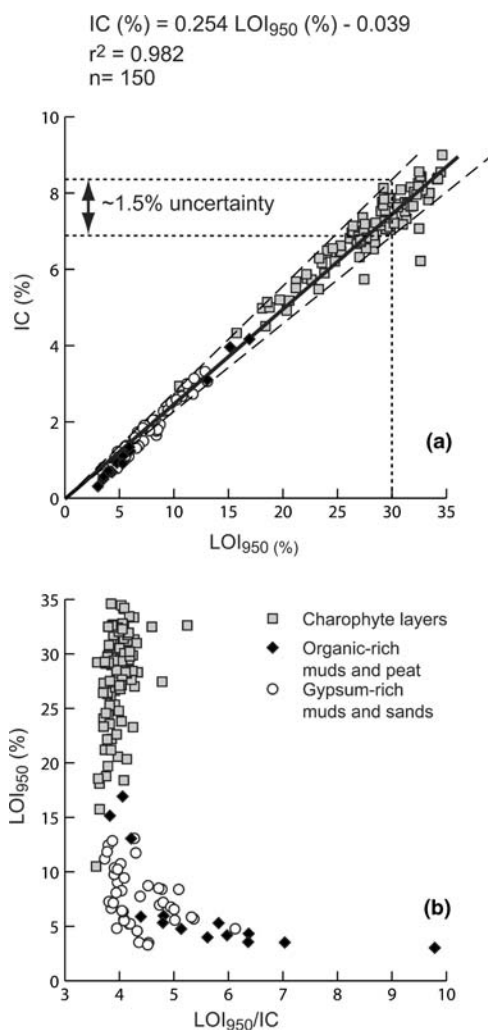$$OC (\%) = 0.634\ LOI_{550}\ (\%) - 1.830$$
$$r^2 = 0.971$$
$$n = 150$$

Figure 4. Correlation graphs between (a) LOI_{550} and organic carbon content, and (b) the variability of the LOI_{550}/OC ratios in relation to LOI values. Correlation equations are derived for the whole number of samples.

Table 3) and $IC–LOI_{950}$ versus LOI_{res} as a second factor. A main difference in the results of the whole core is the shift of Ca towards $S–LOI_{105}$ (correlation coefficient $S–Ca = 0.82$, significance level of 0.05) due to the high content of gypsum.

There is a major change in relations for the organic-rich mud and peat (Figure 3, Table 4). The main factor encloses Al–Fe as opposed to $IC–Ca–LOI_{950}$. Factor 2 is represented by $OC–LOI_{550}$ versus S, which has very little weight, but these show moderate to low correlation coefficients with the other components. The pair Al–Fe is also correlated to LOI_{res} and LOI_{105}.

For the charophyte mud to sand layers with vegetal organic matter, the main factor shows $IC–Ca–LOI_{950}$ with lower weighting on $OC–LOI_{550}$ and $S–LOI_{105}$; factor 2 is composed of Al–Fe by as opposed to LOI_{res} (Figure 3, Table 5). Al–Fe has very low correlation coefficients (−0.33 to 0.53, significance level of 0.05) with the other components reflecting the very low content in clay of this facies.

In summary, the parameters analysed can be grouped as: (1) *Al–Fe* group (with occasional influence of Na, Mg and P), which represent the clay content, (2) $OC–LOI_{550}$ group (with N and P as minor constituents) representing the organic matter content, (3) $IC–Ca–LOI_{950}$ group representing the calcite content and (4) $S–LOI_{105}$ group related to the gypsum content. Other parameters such as Mn, Mg, Na, P, N and LOI_{res} play a minor role and shift from one group to other depending on the mineralogy of the facies.

Carbon versus LOI record

A first test of the reliability of LOI data for the estimation of carbon content is direct (visual) comparison of the results obtained using LOI with direct measurements of carbon (Figure 2). As values and trends are very similar, regression analyses were performed for organic carbon (OC) versus LOI_{550} (Figure 4, Table 6) and for inorganic carbon (IC) versus LOI_{950} (Figure 5, Table 7).

There is very good numerical correlation of LOI_{550} with OC except for the gypsum-rich facies (Table 6, Figure 4a). LOI_{550}/OC ratio follows the expected behaviour: the ratio is almost constant for LOI_{550} values higher than 5% and there is no obvious relation for lower values (Figure 4b), which is interpreted to be a result of the low content in organic carbon in this facies.

More detailed analysis of this relationship reveals that as LOI_{550} values increase, the range of observed OC values widens introducing an incremental uncertainty to the OC estimations derived from LOI_{550}. For instance, OC content ranges between 13.98 and 19.74% (range: 5.76%) when LOI_{550} reaches 30% (Figure 4a) and between 18.89 and 26.6% (range: 7.7%) for a LOI_{550} value of 40%.

Regression data for IC versus LOI_{950} are better for all the data sets (Table 7, Figure 5a), but the

Table 6. Regression coefficients (OC $= a * LOI_{550} + b$) for organic carbon (OC) (significance level of 0.05)

	Equation	r^2
Whole core	$a = 0.634, b = -1.830$	0.971
Charophyte layers	$a = 0.579, b = -0.889$	0.948
Organic-rich muds	$a = 0.707, b = -2.100$	0.963
Gypsum-rich muds	$a = 0.332, b = -0.760$	0.593

Figure 5. Correlation graphs between (a) LOI_{950} and inorganic carbon content, and (b) the variability of the LOI_{950}/IC ratios in relation to LOI values. Correlation equations are derived for the whole number of samples.

range of values for the LOI_{950}/IC ratio is wider than for the LOI_{550}/OC ratio, particularly for samples of the organic-rich mud, carbonate-poor, facies (Figure 5b). As for LOI_{550}, the sample data

reveal a broad range of observed IC values for a single LOI_{950} value, which means an increasing error in IC estimation as the LOI_{950} value increases. For instance, the observed IC content varies from 6.8 to 8.4% for a LOI_{950} of 30% (Figure 5a).

Comparison with established relations

In order to check the accuracy of the LOI technique, the carbon content was calculated using Dean's (1974, 1999) relations and our own regression equations (Tables 6 and 7). These values (value$_{sim}$ in Figure 6), were compared to the carbon content obtained by direct measurement (value$_{obs}$ in Figure 6) and a percentage of variation was obtained as [100 * (value$_{obs}$ − value$_{sim}$)/value$_{obs}$]. The range of this percentage of variation is very wide (Figure 6, Table 8), reflecting the clear dependence on lithology and the regression model selected.

Regarding the OC, Dean's (1974) relation systematically overestimates the OC content, with the maximum variation (almost 560%) found in the gypsum-rich, organic-poor, facies (Figure 6). In contrast, using our equations the variations fluctuate around the 0% line. The IC estimation yields better results, as the variation for the both approaches decrease to about 165%.

The nearly constant variation of data for OC and IC does not extend to the organic-rich mud facies, where variations experience a major shift (Figure 6). This shift is striking because the IC content of the two mud facies (organic or gypsum-rich) are similar.

Normalized LOI_{550}, OC, LOI_{950} and IC data for the whole core and for every facies (Figure 7) show good agreement of trends despite the shifts of absolute values. However, closer inspection of the OC–LOI_{550} diagram reveals that some observed peaks of OC are masked on the LOI_{550} curve (Figure 7).

LOI_{105} and LOI_{res}

As expected, the sedimentary facies share strong correlations between (i) LOI_{550} and OC and (ii) LOI_{950} and IC. However, the behaviour of LOI_{105} and LOI_{res} vary depending on the lithology.
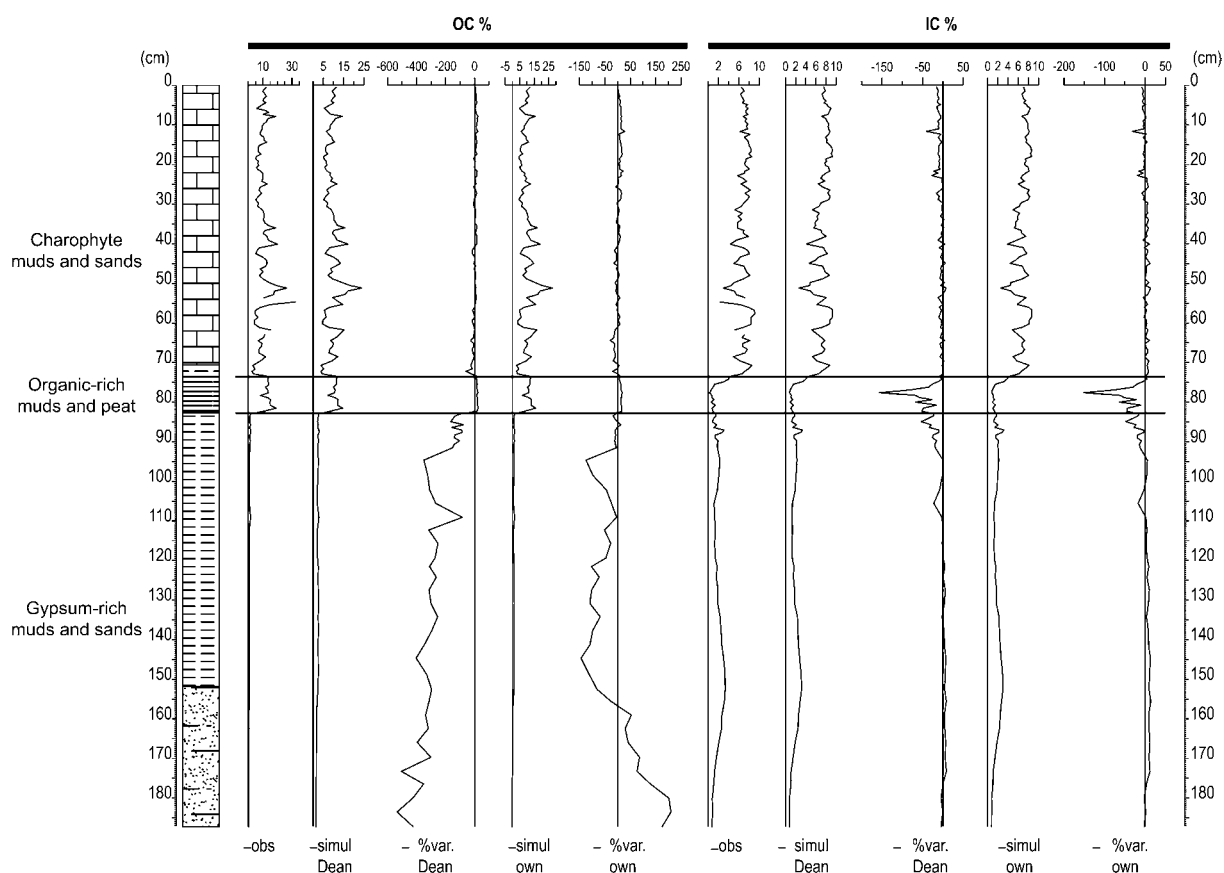
Figure 6. Comparison between observed (obs.) and simulated (sim.) carbon values and the percentage of variation between them.

Table 7. Regression coefficients (IC = $a * LOI_{950} + b$) for inorganic carbon (IC) (significance level of 0.05)

	Equation	r^2
Whole core	$a = 0.254$, $b = -0.039$	0.982
Charophyte layers	$a = 0.215$, $b = 1.137$	0.879
Organic-rich muds	$a = 0.286$, $b = -0.436$	0.995
Gypsum-rich muds	$a = 0.286$, $b = -0.170$	0.924

LOI_{105} is usually related to S except in the organic-rich mud and peat layers. LOI_{res} is related to the Al–Fe group in the organic-rich mud and peat, but it does not show clear relations with the other facies (Figure 3).

A major point is that LOI_{105} is related to water loss and, therefore, reflects the dewatering of organic matter and water-bearing minerals (in our case clay and gypsum) in addition to loss of pore waters. Thus, LOI_{105} values depend in part on the amount of such components, but it is important to remember that clays lose water over a wide range of temperatures, that surpasses 950 °C (Brindley and Le Maitre 1987). Thus, at least in theory, LOI_{105} only provides an estimate on the loss of water (pore, "organic", and lattice waters of clays and salts).

In our case, it is clear that LOI_{105} and S follow similar trends (Figure 2) and regression analysis reveals a good fit ($r^2 = 0.839$) for the whole core data (Table 9). However, r^2 is extremely variable for each facies (charophyte layers: $r^2 = 0.615$; organic-rich mud: $r^2 = 0.139$; gypsum-rich mud and sand: $r^2 = 0.912$). Regression of LOI_{105} on Al produces poorer results for the whole core data and for each facies.

Better results are obtained for regression analysis of LOI_{105} on Al + S for the whole core data ($r^2 = 0.907$, Table 9), indicating that LOI_{105} reflects loss of water of gypsum and clays. However, noticeable changes of r^2 values among facies reveal the dependence of LOI_{105} on lithology.
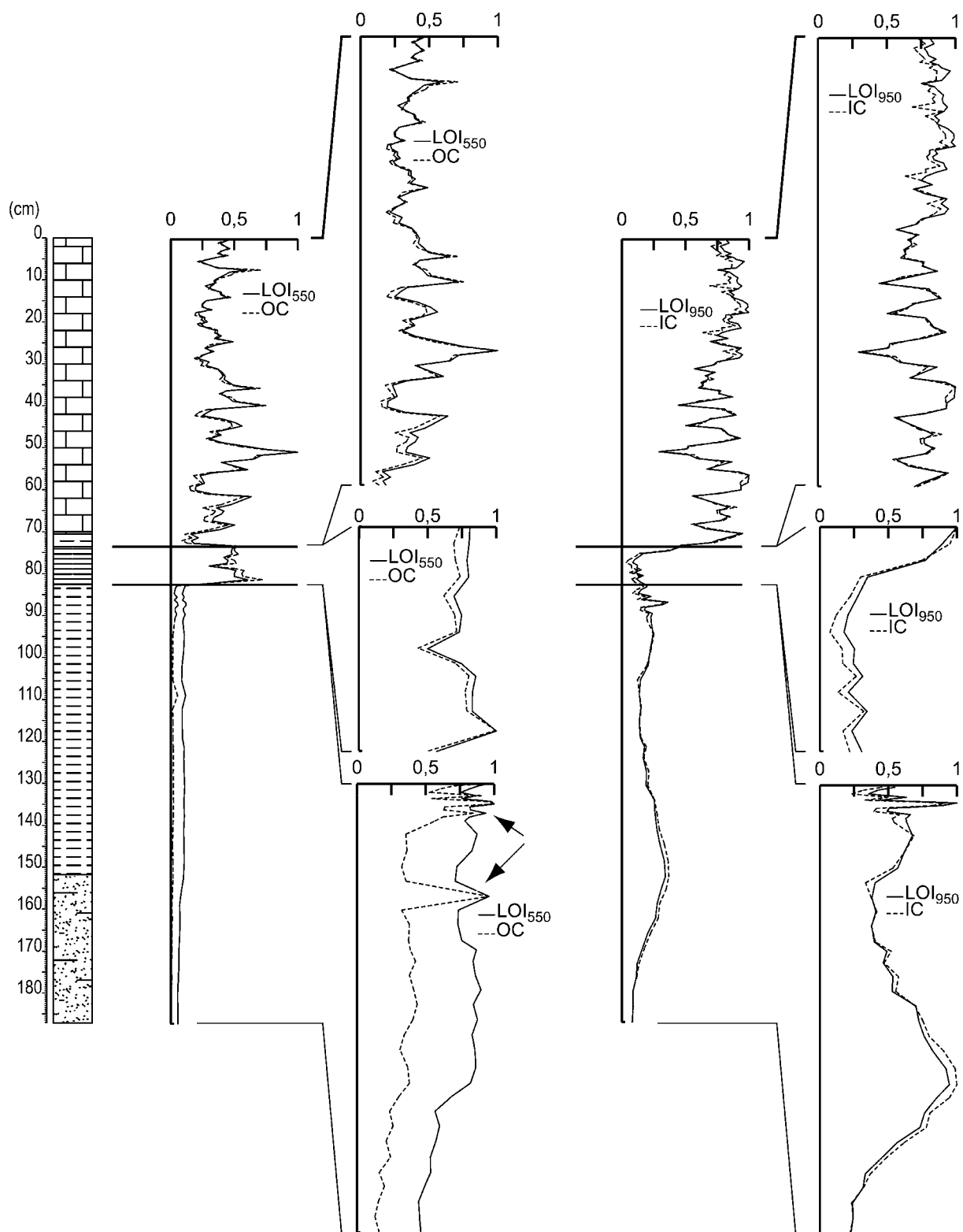
Figure 7. Normalized data for LOI$_{550}$, OC and LOI$_{950}$, IC calculated for the whole core data and for each facies. Note that two significant peaks on OC are masked on LOI$_{550}$ (arrows).

Table 8. Extreme values and range of variation for the simulation resulting from Dean's (1974, 1999) approach and our regression data

	OC			IC		
	Extreme values (%)		Range (%)	Extreme values (%)		Range (%)
Dean equations	−534.6	24.1	558.66	−156.8	8.6	165.3
Own equation	−171.1	167.2	338.32	−151.6	13.6	165.2

Table 9. Regression coefficients ($y = a * LOI_{105} + b$) for different elements in function of LOI_{105} (significance level of 0.05)

	Al		S		Al + S	
	Equation	r^2	Equation	r^2	Equation	r^2
Whole core[1]	$a = 10.274, b = 0.527$	0.243	$a = 0.669, b = 0.371$	0.839	$a = 1.158, b = 0.192$	0.907
Charophyte layers	$a = 0.069, b = 0.238$	0.037	$a = 0.628, b = 0.730$	0.615	$a = 0.697, b = 0.968$	0.615
Organic-rich muds	$a = 1.841, b = −1.191$	0.600	$a = 0.313, b = −0.180$	0.139	$a = 2.153, b = −1.371$	0.877
Gypsum-rich muds[1]	$a = −0.411, b = 7.879$	0.769	$a = 0.989, b = −2.390$	0.912	$a = 0.648, b = 4.927$	0.875

Notice that[1] 10 samples are above 10% of S (detection limit).

The value of LOI_{res} is more difficult to interpret because it includes the residues of all previous ignitions: ashes from combustion of organic matter (LOI_{550}) plus oxides resulting from decomposition of salts (LOI_{950}) plus the dewatered clays (LOI_{105}). This is corroborated by principal components analysis (Figure 3) which reveals that LOI_{res} behaves as an independent factor. Values of r^2 for regression analysis are not acceptable except for LOI_{res} on Al and on Ca for the organic-rich mud (Table 10), supporting the hypothesis that it is difficult to assign a reliable interpretation to LOI_{res} values.

Conclusions

Analysis of LOI data in a core from the Gigüela River in central Spain yields some conclusions concerning the use of LOI as a substitute method for the measurement of carbon content in sediments. Using data from the whole core, the method provides trends that largely agree with the results of direct measurements. However, the method is unreliable because the composition of sediments induce significant deviations of values. More important, deviations do not follow a predictable trend, which results in the unexpected occurrence or disappearance of peak values. This implies a loss of resolution because, to minimize errors, it would be necessary to use averaged values.

Determinations of organic carbon (OC) are strongly influenced by the content of OC in the sediment: the higher the organic content, the better the correspondence between OC and LOI_{550} values obtained via Dean's (1974) approach or regression analysis. Errors arise with very low contents in OC because large and erratic variations have been detected that prohibit any reliable quantitative comparison between facies.

With respect to the inorganic carbon (IC), the results of calculations that use the stoichiometrical relations derived from the transformation: $LOI_{950} \rightarrow CO_2 \rightarrow CO_3^{2-}$ fit very well the IC contents measured directly, but we found major deviations in facies with similar IC contents that still lack explanation. In addition, LOI_{950} is not a reliable indicator of the total amount of carbonate, because the decomposition of some carbonates begins at temperatures below 550 °C.

In addition, LOI values are influenced by the content in clay (Dean 1974), owing to the very wide range of dehydratation temperatures of clay minerals.

Analysis of relations of variables with LOI_{105} and LOI_{res} suggests that LOI_{105} is a good qualitative estimate of gypsum. The behaviour of LOI_{res} is not easy to interpret, as it does not correlate with the theoretical concept (the remains left after burning). As a general conclusion, LOI cannot be used as an accurate standalone technique for the estimation of carbon content unless the amount of carbon is known and the degree of

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Table 10. Regression coefficients ($y = a * LOI_{res} + b$) for different elements in function of LOI_{res} (significance level of 0.05)

	Al		S		Ca		Al + S + Ca	
	Equation	r^2	Equation	r^2	Equation	r^2	Equation	r^2
Whole core[1]	$a = 0.137, b = -6.525$	0.726	$a = 0.103, b = -3.076$	0.374	$a = -0.512, b = 52.589$	0.536	$a = -0.186, b = 38.552$	0.103
Charophyte layers[1]	$a = 0.045, b = -1.912$	0.236	$a = -0.024, b = 3.563$	0.014	$a = 0.357, b = 8.672$	0.121	$a = 0.378, b = 10.323$	0.150
Organic-rich muds	$a = 0.216, b = -9.584$	0.819	$a = 0.0002, b = 0.867$	7e-06	$a = -0.589, b = 45.741$	0.629	$a = -0.373, b = 37.024$	0.449
Gypsum-rich muds[2]	$a = 0.365, b = -24.88$	0.388	$a = -0.316, b = 31.078$	0.202	$a = -1.289, b = 115.04$	0.717	$a = -1.775, b = 166.05$	0.295

Notice that [1] 63 samples are above 25% of Ca and [2] 10 samples are above 10% of S (detection limits).

error is estimated. However, LOI is a useful substitute method for analysis of composition of sediments assuming that:

- It yields only qualitative data.
- It requires previous knowledge of the mineralogical composition of sediments.
- The effects of variations in lithology are adequately investigated.

Appropriate techniques of data manipulation are used to avoid the random nature of shifts in values.

Acknowledgements

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