A COMPARATIVE STUDY BETWEEN LOSS ON IGNITION AND TOTAL CARBON ANALYSIS ON MINEROGENIC SEDIMENTS

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ABSTRACT. The present study deals with a comparison between organic and carbonate content determinations based on loss-on-ignition and step-wise total carbon analysis, and a correlation to grain-size. Although loss-on-ignition can generally be regarded as an accurate measure of the organic mater content of a sediment, the amount of fine fraction in the sediments is a limiting factor for an absolute organic determination and influences directly the correction factor. The same holds true for carbonate content determinations based on loss on ignition. In order to provide accurate organic and carbonate content determinations for a sediment, loss-on-ignition data must be corroborated by standard total carbon analysis.

Keywords: minerogenic sediments, loss-on-ignition, total carbon, Late Glacial, Atteköps mosse, Sweden.

Introduction

The sedimentological properties of lacustrine sediments can provide valuable data on the nature of former depositional environments, being useful indices of climatic and other local and regional environmental changes (Lowe & Walker, 1997).

A common way to generate a rough sediment geochemistry profile is to use the loss-on-ignition method. Numerous authors from Dean (1974) and onwards have noted that this method can be considered to be a good tool for determining the organic matter and carbonate contents of sediments, even if several uncertainties limit the absolute precision of the method (Dean, 1974; Bengtsson & Enell, 1986; Heiri et al., 2001). The relative changes of loss-on-ignition parameters throughout the analyzed core sections were regarded as very useful in interpreting the impact of changing climatic conditions on different biogeochemical processes throughout the sediment sequence, and often are sufficient for correlation between overlapping-cores.

On the other hand, total carbon determined automatically is the fundamental parameter for describing the abundance of organic and inorganic carbon in sediments. In this way, an organic matter value, via loss-on-ignition, are, presumed to be equivalent to about twice the total organic carbon values

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(Meyers & Lallier-Vergés, 1999). Total organic carbon can be both diluted by clastic sediment particles and concentrated by dissolution of carbonate minerals.

The present paper presents results of several sedimentological analyses performed upon the deepest, minerogenic core segment (~1 m long), taken on the Atteköps mosse, southwestern Sweden. The study site, which is located in Hallandsåsen area, is considered, alongside by Kullen Peninsula (Sandgren et al., 1999) one of the earlier deglaciated region in Sweden.

Therefore, the aim of this study is to assess the usefulness of the loss-on-ignition method in estimating the organic and carbonate contents in minerogenic sediments. The assumption is that the method over-estimates the organic matter and carbonate content of fine-grained sediments because of a weight loss related to various organic and inorganic sediment components. Total carbon analysis with a specific carbon analyzer is generally viewed to be a better indicator for those parameters. To test this hypothesis, conventional loss-on-ignition analysis, total carbon and grain-size measurements were performed over selected sediment intervals and compared with each other.

Introduction to the methods

Loss-on-ignition

Loss-on-ignition is a common and widely used method to estimate sediment properties (i.e., water content, organic matter, inorganic carbon and minerogenic residue), because is the quickest and cheapest among all the methods employed for determining some of those parameters (Dean, 1974; Maher, 1998).

Most sediment is composed of a mixture of clastic silicates and oxides (sand, silt and clay fractions), organic material, carbonates and water. Quantitative determinations of such sediment parameters by means of loss-on-ignition are based on the sequential heating of the samples (other techniques involve gas collecting and measuring the amount either volumetrically or chromatically (Dean, 1974)) in a muffle furnace (Heiri et al., 2001). After oven drying of the sediment to constant weight (or dry matter) and cooling to room temperature, organic matter is combusted in a first reaction to ash and carbon dioxide at temperatures between $500\text{-}550^{0}C$. The amount of organic matter is the weight difference between the dry sediment and the $550^{0}C$ ash (Dean, 1974; Maher, 1998; Heiri et al., 2001), being assumed to be derived from organic material with the formula $(CH_2O)_n$, (Snowball & Sandgren, 1996).

In a second step, the same sample is ignited at temperatures of $925^{0}C$ (Bengtsson & Enell, 1986, Heiri et al., 2001) or $1000^{0}C$ (Dean, 1974; Maher, 1998) in order to find the amount of carbon dioxide evolved from the breakdown of the carbonate minerals. The carbonate content in the original sample is then determined by multiplying the weight loss between loss-on-ignition at $550^{0}C$ and loss-on-ignition at $925^{0}C$ with 1.36, which is the ratio between the molecular weights of CO_3 (60) and CO_2 (44), according to Bengtsson & Enell (1986).

Dean (1974) and Bengtsson & Enell (1986) pointed out that the method is fast and inexpensive and thus useful for analyses of a large number of samples. It also gives a rough indication of the organic matter and carbonate contents and a good correlation with organic carbon content, despite of several uncertainties (see the Discussions chapter), which limit the precision of the method.

Grain-size distribution
Particle size distribution is a fundamental property of sedimentary material and can be used to infer the provenance and history of the sediment transport (Buckley & Cranston, 1991).

Size analysis of clay and silt-sized sediment can be inferred by a variety of automated methods based on their physical, electrical and optical properties. The Sedigraph method used by this study, measures the sedimentation speed of suspended particles by monitoring the rate at which particles settle and are removed from the monitored volume, giving in that way a cumulative size distribution of the sediments (Coakley & Syvitski, 1991).

Total carbon
Total carbon concentration is a fundamental parameter for describing the abundance of organic matter and inorganic carbon in sediments (Meyers & Lallier-Vergés, 1999).

The total organic carbon concentration is a bulk value that represents the fraction of organic matter that escaped mineralization during sedimentation processes being influenced by both initial biomass production and subsequent degree of degradation. Total organic carbon concentration often varies through the sedimentary sequence, indicating changes in organic deposition under different sedimentary conditions (Meyers & Lallier-Vergés, 1999).

Samples and analysis

Core collection and description
Multiple core segments were retrieved with a Russian peat sampler (1 m length and 10 cm diameter). The lithostratigraphy of the cores was described both in the field and in the laboratory (see the description in Table 1).

Because detailed sedimentological analyses mainly focused on the minerogenic sediments, only the lowest segment (C6-a, 767-690 cm) of core C6 was selected for further analysis in this study.

Sediment analysis
For loss-on-ignition analysis, volumetrically samples were weighed (using a Sartorius-Tillquist model H120 balance), placed in pre-weighted crucibles and dried for 12 h at 105^0C (using a Termarks oven) to determine both the water content (or loss-on-drying) and dry sediment percentages (normally 3-5 g), the latter serving as a base to which ignition losses were compared.

The weight loss during the ignitions (using a Heraeus type 170 muffle furnace) were calculated according to Bengtsson & Enell´s (1986) formula, with the exception that in the present study the weight loss is related to dry weight. Samples were gradually heated until they reached temperatures of 550^0C and 925^0C, respectively and afterwards ignited for 4 h at the respective temperatures. The samples were then put into a desiccator and weighed at room temperatures. The carbonate content was determined by multiplying the weight loss obtained between 550^0C and 925^0C with 1.36.

For the grain-size analysis a Micromeritics Sedigraph 5100 Particle Size Analysis System was used. This sedigraph uses a collimated beam of *X*-rays to sense the sedimentation speed of suspended particles with time and a device measurement of particles with diameters ranging from 100 to 0,2 micrometers (Coackley & Syvitski, 1991). The samples (2-3 cm^3) were first split to obtain a subsample of approximately 1.8 g for analysis, deflocculated in 40 ml $Na_4P_2O_7$ and dispersed by means of ultrasonic stirring. Because it had been noted that samples with high organic carbon (>10%) can hinder proper dispersion of the sample (see Coakley & Syvitski, 1991), selected intervals were used where organic matter content was low. Finally, the grain size distribution data is presented as cumulative percentages of several fractions: clay (<2 μm), fine silt (2-6 μm), medium silt (6-20 μm), coarse silt (20-60 μm) and fine sand (60-100 μm).

The organic and inorganic carbon content of the selected samples was determined by temperature-controlled combustion in pure oxygen (step-wise heating from 100 to 1000^0C) of the homogenous and dried samples with subsequent detection of carbon dioxide by infrared absorption photometry in a LECO RC 412 Multiphase Carbon Determinator. The sediments were dried (for 12h at 105^0C), finely ground and homogenized and then stirred and shaken in a tungsten ball container. Due to different amounts of material available, sample size varied between 0.12 and 0.30 g of dry weight. The carbon emitted between 105 and 650^0C is interpreted as the content of organic carbon of the samples, otherwise, the carbon evolved between 650 and 925^0C is interpreted as the carbonate content, assuming theoretical carbon contents of 12% and *c.* 40% for pure calcium carbonate and organic matter, respectively.

Results and discussion

Lithostratigraphy

The nature of sediment sequence analyzed by this study is shown in Table 1. Organic and carbonate contents for core C6-a estimated using both loss-on-ignition and total carbon analyses, are presented in Figures 1 and 3. The results of grain-size distribution analysis are summarized in Figure 4 (right). The relationship between sediment geochemical parameters and granulometry is also shown in Figure 4.

Table 1.

Lithostratigraphic units and sediment description for Core C6-a.

Unit	Layer	Depth below surface (cm)	Sediment description
VI	15	667-679	Beige grey silt gyttja.
	14	679-685	Beige grey gyttja silt sparse in FeS stains. UB-rg.
	13	685-692	Beige grey clayey silt gyttja, with cladocera remains. UB-rg. 685-688 cm more beige, 688-692 cm more dark.
V	12	692-715	Beige grey clayey silt gyttja, brown in moss rich areas, laminated by some organic matter layers. UB-rg. 696-700 cm some moss remains, 700-704,5 cm increase in moss remains, 704,5-707 cm few moss remains, 707-708 cm brown layer, rich in mosses.
IV	11	715-720	Brown to beige-grey clayey gyttja silt, organic matter decreases gradually upwards to 718 cm. UB-fs.
	10	720-722	Very disturbed layer of light grey silt, UB-fs.
	9	722-724	Dark grey coarse sand/gravels. UB-fs.
	8	724-732	Dark grey clayey silt with some coarse silt in the bottom. UB-s.
III	7	732-733,5	Beige grey clayey silt layer, abundant mosses, laminations. UB-fs.
	6	733,5-734	Light grey silt layer with some moss remains. UB-rg.
	5	734-739,5	Dark grey clayey silt with mosses (736-737 cm). UB-fs.
	4	739,5-741	Grey silt with coarse silt and organic material in the bottommost part (dark grey). UB-g.
II	3	741-754	Dark grey silty clay laminated by thin silt-layers; gravel particles at 745 and 748 cm, respectively. UB-fs.
	2	754-757	Layers of dark-grey to black silty clay laminated every 0,5 cm; calcareous particles. UB-fs.
I	1	757-767	Grey fine-sand to sand with thin silt lamination; calcareous particles and vague lamination from coarse silt to fine sand. UB-rg.

UB-upper boundary: rg-rather gradual, fs-fairly sharp, g-gradual, s-sharp.

Comparison between loss-on-ignition and total carbon

The accuracy of organic matter determination by means of loss-on-ignition seems to be hampered by some factors, which limit the precision of the method, leading to an overestimation of the true organic content. It was generally noted that for determining organic carbon content of minerogenic sediments by means of organic matter (via loss-on-ignition), the results can strongly be overestimated because of various losses, which belong to volatile salts, organic compounds (*e.g.* Bengtsson & Enell, 1986), structural water (*e.g.* Dean, 1974), sulphide oxidation (Ramrath et al., 1999) or inorganic carbon. For example, if

inorganic carbon is present it will evolve CO_2 at temperatures between 425 and 520^0C in minerals such magnesite, rhodochrosite (Heiri et al., 2001) or siderite (Hedvall, 1925, cited by Hammarlund, 1994). Moreover, as Aaby (1983, cited by Andersen, 1986) pointed out, the volume of organic matter cannot be determined exactly, as pore space enters the volume of the ignitable matter. In this case, changes in the organic content can be detected by determination of organic carbon (Andersen, 1986). On the other hand, technical factors such as sample size, exposure time, position of the sample in the furnace may affect the loss-on-ignition results, with loss on ignition at 550^0C being more susceptible to these factors than loss-on-ignition at 925^0C. As a consequence, any bias of loss-on-ignition at 550^0C will influence the results of loss-on-ignition at 925^0C (Heiri et al., 2001).

In general, the amount of organic matter determined by loss-on-ignition at 550^0C is considered to be "approximately" twice the organic carbon content (Dean, 1974, 1999; Snowball & Sandgren, 1996) of a sample. Although this converting is generally accepted and widely used, various conversion factors have been proposed for converting organic carbon to original organic matter content of a sample. For example, Dean (1974) found a conversion factor of 2.13, Zolitschka & Löhr (1999, cited by Ramrath et al., 1999) and Ramrath et al., (1999) have proposed a factor of 1.82 and 1.81, respectively, while Digerfeldt et al. (2000) obtained a factor of 1.45.

One of the major goals of this study is to test the accuracy of organic carbon determination by loss-on-ignition, since selected values from loss on ignition at 550^0C are believed to represent either typically organic matter, but also a weight loss related to various organic or inorganic sediment components. Therefore, organic carbon values determined automatically and on the same sample are regarded as representative for the organic carbon of the original sediment matter, and are compared to corresponding loss on ignition values. The results of this test are plotted in Figure 1 (left panel). Surprisingly, the resulting regression line crosses the *y*-axis at a loss-on-ignition value of 1.06%. This probably corresponds to a weight loss, which should be related to the already mentioned extra-loss generators. The true organic matter content in the analyzed samples as suggested by the equation presented in Figure 1 (left) may be obtained by multiplication of the total organic carbon determined automatically with a factor of 1.49. Though this low factor suggests a good correlation between these different organic carbon determinations, indicating that loss-on-ignition is a rather accurate measurement of the amount of organic matter in a sample, the resulting conversion factor is not in good agreement with the published factors presented above. This confirms the idea that the amplitude in difference between the results of those two methods may depend on type and chemical composition of the analyzed sediments.

In order to test the accuracy of the organic matter determination and to find out a proper correction factor (making abstraction by the factor determined by this study), the ignition loss results were compared with total organic carbon
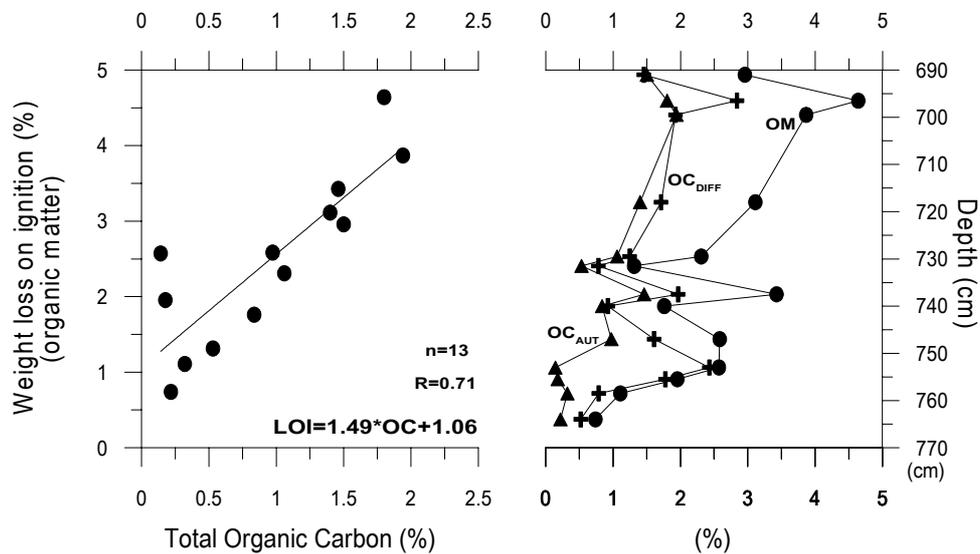
176

Figure 1. *Left: Scatter diagram of percent total organic carbon determined automatically and percent organic matter at 550 ^{0}C measured on samples from Atteköps mosse. Number of data points (n), correlation coefficient (R) and the regression line are given.*

Right: Percentage organic carbon determined automatically (OC_{AUT}-triangles), percentage organic matter (OM_{LOI}-circles), and the difference in results between those parameters (OC_{DIFF}-crosses), plotted against depth.

multiplied by different conversion factors (Fig. 2, left panel):

- A_1- automatically determined organic carbon multiplied by 2.5 (according to the chemical formula CH_2O/C)
- B_1- automatically determined organic carbon multiplied by 2.13 (according to Dean, 1974)
- C_1- automatically determined organic carbon multiplied by 1.82 (Zolitschka & Löhr, 1999 cited by Ramrath et al., 1999)
- D_1- automatically determined organic carbon multiplied by 1.81 (Ramrath et al., 1999)
- E_1- automatically determined organic carbon multiplied by 1.45 (Digerfeldt et al., 2000).

The variables that resulted as differences between loss-on-ignition at 550^0C and organic carbon multiplied by different constants are labeled from A_2 (as a variable produced by the A_1-chemical formula) to E_2 (a variable induced by the E_1- Digerfeldt et al., 2000) and plotted in Figure 2 (right). The vertical zero line implies a perfect correlation between the values. The positive trend suggests that the loss-on-ignition values at 550^0C are higher than presumably supposed, while the negative values, indicating higher values for organic carbon.

As easily may be seen from the curves in Figure 2 (right), the A_2 and B_2 variables yield generally negative values, implying in this way an overestimation of primary organic matter content determined by loss-on-ignition. The C_2 and D_2 variables are relatively close to zero, whereas E_2 leads to increased differences. To summarize these results, it is evident that the conversion factors mentioned above are strongly influenced by the type of sediment analyzed.

Moreover, if an absolute determination of the organic content is to be done, then the loss-on-ignition data must be supported by independent total organic carbon determination.
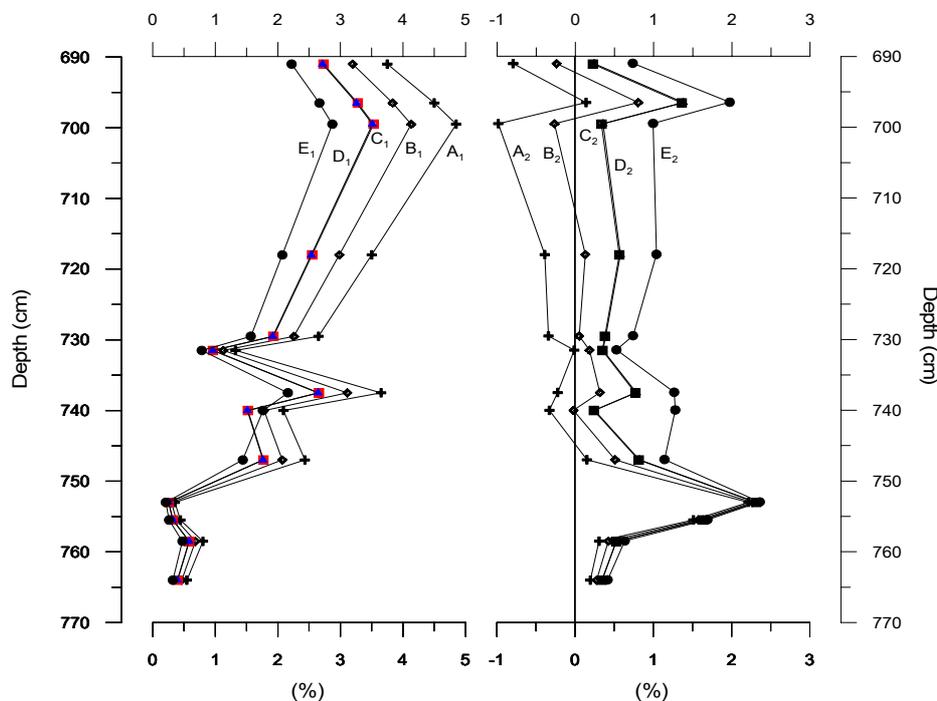

Figure 2. *Left: Organic carbon determined automatically and multiplied by various conversion factors: 2.5 (A_1-crosses), 2.13 (B_1-rhombus), 1.82 (C_1-triangles), 1.81 (D_1-squares) and 1.45 (E_1-circles) plotted against depth.*

Right: The differences (A_2, B_2, C_2, D_2, E_2), which result from a subtraction of organic carbon determined automatically and multiplied by the already mentioned factors from loss on ignition at 550 ^{0}C.

The main difference between the two methods is shown by the curves presented in Figure 3. Thus, if the carbonate content determined automatically (CC_{AUT}) in an order of <2 % is viewed as the proper carbonate content of the analyzed sediments, then the high carbonate percentages (<7%) derived from loss-on-ignition at 925^{0}C (CC_{LOI}) lead to a large difference (CC_{DIF}) between those two methods (for further discussions see Fig. 4).
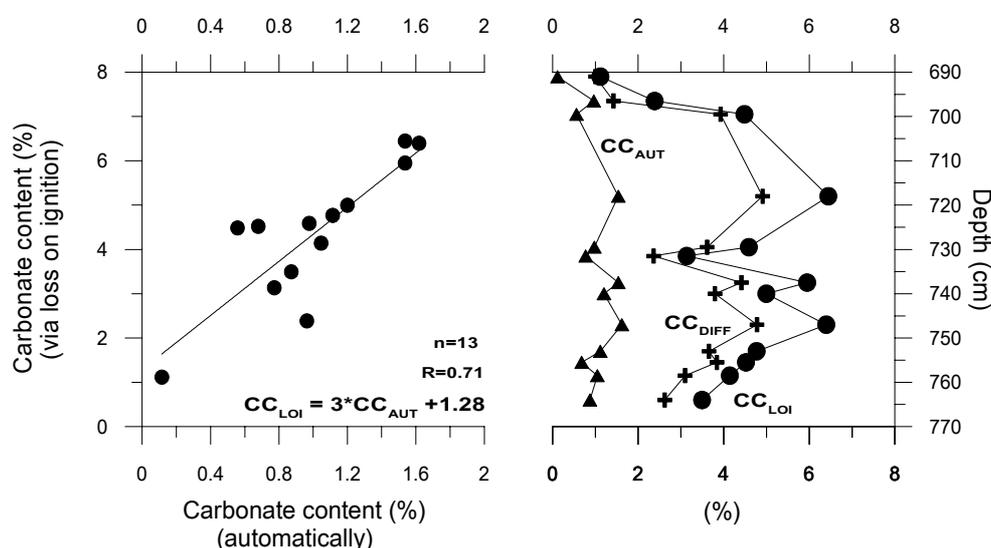
Figure 3. *Left: Scatter diagram of percent carbonate content determined automatically and percent carbonate content derived from loss-on-ignition at 925 ^0C measured on samples from Atteköps mosse. 1.36 multiplies both values. Number of data points (n), correlation coefficient (R) and the regression line are given.*

Right: Selected values of carbonate carbon determined automatically (CC_{AUT}-fill triangles), carbonate content calculated from loss-on-ignition at 925 ^0C (CC_{LOI}-fill circles) and the difference in results between those parameters (CC_{DIFF}) plotted against depth. 1.36 multiplies both carbonate contents.

In order to check the assumption that higher percentages of organic carbon are commonly associated with fine-grained sediments, because of the higher adsorption capacities of finer particles, the above discussed differences between loss-on-ignition and total carbon (see Fig. 4-left) were related to grain size data at the corresponding levels (Fig. 4-right). It is known that clays may contain up to 5% hydroxyl groups (OH)⁻ as structural water. If a fine fraction is present in relatively high quantity, but has low carbonate content, those hydroxyl groups should be liberated as water when the sample is heated up over 550^0C. In this way, part of the loss (4-5%), may result from that chemically bound water loss in such samples with high clay and low carbonate content (Maher, 1998). Thereby, the assumption that the ignition loss between 550-925^0C represents CO_2 evolved from carbonates will be in error by an amount, which is directly proportional to the amount of clay present, and inversely proportional to the amount of carbonates present (see Dean, 1974).

It is evident from Figure 4 (left) that the OC_{DIFF} curve has more or less the same trend as the curve for the finer fraction. The difference is not so large because the clay fraction is only around 20-30% (compared with 50-70% in Digerfeldt et al., 2000). For example, Ramrath et al., (1999) and Digerfeldt et al., (2000) found a weight loss related to the above-mentioned loss generators of 5.3% and 7.8%, respectively, whereas in this study the weight loss is 1.06%.
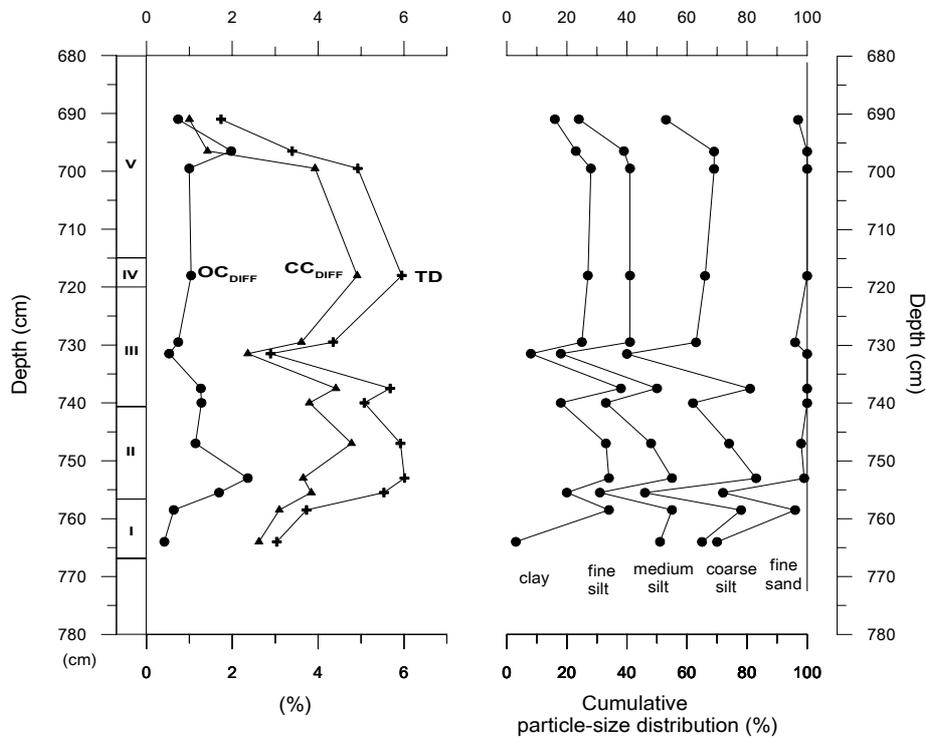
179

Figure 4. *Left: Organic carbon difference (OC_{DIFF}-circles), carbonate content difference (CC_{DIFF}-triangles) and total difference (TD-crosses). TD= OC_{DIFF}+ CC_{DIFF};*

Right: Cumulative particle size distribution (%) for selected values.

The most evident correlation between the variable features and the grain-size distribution is suggested by the CC_{DIFF} curve. It is obvious that a rise in clay content leads to a difference between the methods. This seems to be valid for fine silt as well. For example, in the lower most sample, where the clay content is extremely low and fine silt dominates the grain-size distribution, the CC_{DIFF} is in an order of ~3%. The coarse fraction (medium silt, coarse silt and fine sand) has generally the same trend as the finer fraction and seems not to influence the amplitude of the difference, at least, not as much as the fine fraction.

Total difference (TD) is a composite curve combining the values of both variables presented above. It increases where the fine fraction is high.

Concluding remarks
- Loss-on-ignition is an accurate measurement of primary organic content of sediments, if the fine fraction is present in low percentages.
- Sediment composition seems to be the main cause, which determines the value of correction factor between loss-on-ignition and total organic carbon. If an absolute organic carbon determination is to be done, loss-on-ignition data must be sustained by organic carbon determination.

- ▪ Carbonate carbon determination by means of loss-on-ignition is strongly influenced by the distribution of the fine fraction. A rise in clay content is closely followed by a rise in extra weight-loss. Care must be taken in the interpretation of carbonate content via loss-on-ignition as a paleoenvironmental indicator.

Acknowledgments

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