COMPARISON OF LOSS ON IGNITION AND THERMAL ANALYSIS STEPWISE METHODS FOR DETERMINATION OF SEDIMENTARY ORGANIC MATTER

Gretel Frangipane[a], Mario Pistolato[b], Emanuela Molinaroli[b*], Stefano Guerzoni[a]
Davide Tagliapietra[a]

[a] CNR-Istituto di Scienze Marine, Riva VII Martiri 1364/A, 30122 Venezia, Italy

[b] Università Ca' Foscari Venezia, Dipartimento di Scienze Ambientali, Dorsoduro 2137, 30123 Venezia, Italy

* Corresponding author. Tel.: +39-041-2348583; fax +39-041-2348510.
E-mail address: molinaro@unive.it (Emanuela Molinaroli)

gretel.frangipane@gmail.com (Gretel Frangipane)
pist@unive.it (Mario Pistolato)
stefano.guerzoni@ismar.cnr (Stefano Guerzoni)
davide.tagliapietra@ve.ismar.cnr.it (Davide Tagliapietra)

ABSTRACT

1. Loss on ignition (LOI) is a widely used method to estimate organic matter (OM) in the sediment of marine and freshwater ecosystems. Thermogravimetric-differential thermal analysis (TG-DTA) of organic species provides information on thermal reactions, the amount and properties of clay structural water, organic species and carbonates.

2. The accuracy of LOI compared to TG-DTA was evaluated in 33 sediment samples from the Lagoon of Venice (Italy).

3. In all tests conducted with TG-DTA we measured the mass loss of OM and the loss of clay structural water (LCSW) on oxidized samples. The mass loss of OM at 350°C (TG-DTA 350 OM) and the total extraction of organic matter at 567°C (TEOM) calculated from the difference between natural state samples and oxidized samples highlight the presence of both thermally labile and thermally stable substances.

4. The grain size data of sediment samples from the Lagoon shows a variable distribution between slightly muddy sand and mud. Loss of clay structural water at

350°C (LCSW 350) and total extraction of clay structural water at 567°C (TECSW) both estimated by TG-DTA on oxidized samples, were found to correspond approximately to 6% and 10% respectively of the clay fraction (<4 μm). This percentage may be used to correct LOI measurements of OM in sediments with high clay content.

5. LOI 350 (loss on ignition at 350°C) and LOI 550 (loss on ignition at 550°C) proved to be ~80 % and ~200 % respectively of total extraction of mass loss at 350°C (TG-DTA 350 tot) and at 567°C (TEML) estimated by TG-DTA on natural samples, meaning that the LOI 550 value represents a significant overestimate. The difference between the LOI 550 and TEML values indicates that the mass loss excess (MLE) may be accounted for by losses due to breakdown of carbonates.

KEY WORDS**:** sediments, organic matter, thermogravimetric differential thermal analysis, loss on ignition.

INTRODUCTION

The organic content of sediments is of primary importance in studies of benthic ecosystems. Gray *et al.* (2002) emphasised the importance of the lability of the OM rather than its absolute quantity, since it is lability that determines the degree to which it stimulates microbial metabolisms.

Organic matter (OM) in surface sediments is an important source of food for benthic fauna (Gray, 1974; Pearson and Rosenberg, 1978; Lopez and Levinton, 1987; Lopez *et al.,* 1989; Cocito *et al.*, 1990; Snelgrove and Butman, 1994). Increases in the organic content of sediment may be also accompanied by increases in chemical contaminants that co-vary in relation to a common environmental factor (e.g., greater proportions of finer-grained sediment particles, which provide greater surface area for adsorption of both organic and other chemical pollutants) (Landrum and Robbins, 1990; Lamberson *et al.,* 1992; Thompson and Lowe, 2004). Several papers suggesting potentially useful indicators of benthic health have recently been published (Viaroli *et al.*, 2004; Fano *et al.*, 2003; Hyland *et al.*, 2005; Reizopoulou and Nicolaidou 2007).

There are several commonly used methods for determination of OM in sediment (Buchanan, 1984):

1. For accurate determination, total organic carbon (TOC) is estimated by CHN analyser.

2. For routine determination, a rough estimate may be obtained by measuring the mass loss on ignition (LOI).

3. For description and determination of sediment organic matter (highly amorphous and relatively condensed), thermogravimetric-differential thermal analyses (TG-DTA) may be used.

Although OM as determined by LOI is a macro-descriptor, integrating a number of components, it is suitable for studying variability in estuarine and coastal regions (Eisma *et al.*, 1991).

The wide acceptance of LOI as an alternative approach to CHN analysis in the literature on soil, ecology (Gosz *et al.*, 1976; Covington, 1981), wetlands (Craft *et al.*, 1991), and rivers (Gagnier and Bailey, 1994; Abbt-Braun and Frimmel, 1996; Van Der Perk and Van Gaans, 1997) is due to the following: (a) it is a relatively rapid and simple procedure (Luczak et al., 1997; Dodson and Ramrath, 2001; Heiri *et al.,* 2001; Boyle,

2001, 2004; Bendell-Young *et al.,* 2002; Beaudoin, 2003); (b) muffle furnaces are inexpensive in comparison with CHN analysers; (c) division of LOI by the conventional 'Von Bemmelen' factor of 1.724 (assuming that 58% of OM is organic carbon, cf., Nelson and Sommers, 1996) provides an instant estimate of organic carbon; and (d) finally, numerous studies have found very strong statistically significant regression relationships between organic carbon as determined by CHN analyser and by LOI (i.e., Spain *et al.*, 1982; Howard and Howard, 1990; Grewal *et al.*, 1991; Wang *et al.*, 1996).

There is no standardised LOI method shared by the scientific community, and differences in ignition temperature, exposure time, or even position in the furnace can cause inter-laboratory variability (Luczak *et al.*, 1997; Heiri *et al.*, 2001). However, two main sources of error have been identified, which occur during combustion: (1) potential loss of CO_2 from carbonates (inorganic matter) (Hirota and Szyper, 1975), and (2) loss of structural water from clay minerals (Ball, 1964; Mook and Hoskin, 1982; Dankers and Laane, 1983). Both losses can be erroneously attributed to OM. The first source of error can be reduced significantly by using an ignition temperature below 500°C (Hirota and Szyper, 1975). The second source of error depends on the proportion and composition of clay minerals. Clays are multi-layered crystals of silicates separated by thin layers of structural water. The mass loss due to removal of clay structural water may be negligible for sediments with low clay content. For example, studies dealing of noncalcareous soils with a broad range of OM concentrations (Ball, 1964; Goldin, 1987; Craft *et al.*, 1991) have found that organic matter determined by LOI was very similar to evaluations obtained using CHN. On the other hand, the clay content was always lower than 20%. Estuary and lagoon sediments are often characterised by high clay content, and the weight due to clay structural water can seriously affect OM estimations (Mook and Hoskin, 1982; Dankers and Laane, 1983). Although it is preferable to use TG-DTA or CHN in this case, the large numbers of samples involved, and the cost and/or availability of equipment may preclude this approach. Several recent papers concerning fluvial and marine sediments have sought to explain and reduce the variability inherent in LOI, indicating that this method is used by many laboratories (Luczac *et al.*, 1997; Sutherland, 1998; Leong and Tanner, 1999; Heiri *et al.*, 2001). Several studies have also expressed serious concerns about using LOI estimates of OM (e.g., Christensen and Malmros, 1982; Howard and Howard, 1990). Major criticisms

include: (a) with furnace temperatures of between 425 and 520°C there is potential loss of CO_2 from minerals in soils or sediments containing inorganic carbon, for example in the form of siderite ($FeCO_3$), magnesite ($MgCO_3$) or rhodochrosite ($MnCO_3$) (Weliky *et al.*, 1983); (b) conventional oven heating at temperatures of below 150°C is not sufficient to drive off hygroscopic and intercrystalline water from clays and allophane, nor does it eliminate hydroxyl groups in sesquioxides or octahedral sheets in phyllosilicate layers (Mook and Hoskin, 1982; Grewal *et al.*, 1991; Schulte *et al.*, 1991); (c) it does not take account of possible decarboxylation of organic functional groups (Grewal *et al.*, 1991); and (d) simple application of the 1.724 factor to OM values derived from LOI in order to estimate organic carbon is not appropriate, because the nature of OM varies significantly (Howard and Howard, 1990; Sutherland, 1998).

Thermogravimetric-differential thermal analyses (TG-DTA) may be useful to characterise the various OM structures, separating the labile, recalcitrant and refractory fractions and quantifying them. Schnitzer and Hoffman (1966) and Angerhn-Bettinazzi *et al.* (1988) used thermogravimetric techniques to estimate the degree of humification of organic matter in organic and mineral soils, respectively. In general, thermal techniques such as TG-DTA provide an easy and rapid means of determining significant changes in organic matter quality. TG-DTA is used to investigate the composition of amorphous and condensed soil/sediment organic matter (Cuypers *et al.,* 2002) and to determine the temperatures of the exothermic peaks in differential thermal curves of organic matter, which are dependent on the nature of the charcoal formed during the gradual heating of the samples (Yariv, 2004). This method has also been applied to investigate whether soils that developed under tropical conditions have different OM and microbial biomass dynamics than soils that developed under temperate ones (Grisi *et al.*, 1998).

During gradual heating in an oxidizing atmosphere, organic material is oxidized, giving rise to distinct exothermic peaks. Differential thermal curves are divided into three regions (1) the dehydration of the clay, (2) the thermal oxidation of the organic material and (3) the dehydroxylation of the clay (evolution of water from hydroxyls belonging to the clay structure).

The exothermic oxidation of the OM during gradual heating takes place in two steps: in the range 200–500°C, oxidation of organic hydrogen occurs, with the formation of

water and charcoal; in the range 400–750°C, oxidation of charcoal occurs, with the formation of CO_2. The exothermic peak temperatures depend on the mineral and organic compounds. During differential thermal analysis, differences in temperature between samples and an inert reference material are recorded while samples are heated at a constant rate. The decrease or increase of the sample temperature in comparison to the temperature of the reference material is attributed to endothermic or exothermic transitions occurring in the sample.

A CHN analyser is usually employed for the reference determination of total organic carbon (TOC) in sediment, after removal of inorganic carbonates and de-gassing of CO_2 (hereafter called decarbonation).

In the case of conversion from TOC to OM, Broadbent (1953) observed that the general use of the conventional 'Von Bemmelen' conversion factor of 1.724 has become established thanks to long use rather than by adequate experimental verification, and its blind acceptance may lead to errors as large as 50%. He suggested, as did Howard (1965), that the conversion factor was too low and values of 1.9 for surface soils, and 2.5 for sub-soils would be more satisfactory.

The present study focuses on the margin of error in OM measurement deriving from clay structural water and carbonate minerals. Structural water present in clay minerals is a significant hurdle for investigators unfamiliar with clay mineralogy and for those who use LOI for trophic investigations. The accuracy of LOI was tested in the Lagoon of Venice (Italy) by comparing OM values determined by LOI with those determined by TG-DTA, together with TOC as determined independently by CHN analyser.

MATERIALS AND METHODS

Sampling

The samples processed in the present study are part of a database created by ISMAR-CNR. Bottom sediment samples from the Lagoon of Venice were collected at 60 sites during field work in 2003 organized by CNR and sponsored by the *Magistrato alle Acque* (Water Management Authority). In the present study, 33 bottom sediment samples from shallow lagoon beds (average depth ~1 m) were selected, in order to

cover the Lagoon as a whole, spanning a range of textures from slightly muddy sand to mud (Flemming, 2000).

At each site, the area (a circle approximately 30 m across, with a central point fixed by geographical co-ordinates) and sample dimensions (16 sediment cores to depths of 5 cm) were defined. Integrated sampling (with cores equally distributed over the area) was carried out in order to take account of any spatial microvariability in pollution/bioavailability, according to the scheme reported in Volpi Ghirardini *et al.* (2005). The samples were taken from short cores obtained by various techniques, using an 8-cm-diameter Plexiglas corer.

Sediment grain size analysis was performed by dry sieving and Sedigraph 5000D Particle Size Analyser (Micromeritics) for sand and mud fractions respectively.

All samples were analysed with three different methods: sequential LOI, TG-DTA and CHN.

Sample preparation

Before analysis, samples were homogenised and split into two parts. One part was oxidised by hydrogen peroxide, the other part was directly analysed by LOI, CHN and TG-DTA.

The protocol for peroxide oxidation was designed to maximise the accessibility of organic matter to the oxidant. Briefly, 30 grams of air-dried sample was treated with 750 ml of 30% hydrogen peroxide (H_2O_2) using a magnetic stirrer to ensure homogeneous exposure of organic matter to oxidant. Treatments were performed at room temperature. The treatment was replicated until there was no visible frothing and finally, after complete sedimentation, the sample was washed with distilled water and dried at room temperature.

After oxidation the samples were analysed by TG-DTA.

Determination of organic matter

Loss on Ignition (LOI)

Sediment samples were first dried at 60°C until constant weight was obtained. Ten grams of sample were weighed and then split into two crucibles, heated to 350°C for 16

hours in a muffle furnace (Neytech, Vulcan A-550; precision ± 10%), after which one of the crucibles was weighed. The second one was heated for a further 16 hours at 550°C. Percentage mass loss was calculated for each replicate. Mass losses are given as percentage loss on ignition at each of the separate temperature steps (Kristensen and Andersen, 1987).

Thermogravimetric-Differential Thermal analyses (TG-DTA)

In order to determine whether mass loss during thermogravimetric analysis was due to exothermic or endothermic transitions, differential thermal analysis was performed simultaneously using a Netzsch STA 429 thermal analyser.

Samples were heated under a flux of oxidizing atmosphere (air), from room temperature to 1000°C at a rate of 5°C min^{-1}. Analyses were performed on samples before and after H_2O_2 treatment. In each case, approximately 30 mg of air-dried clay fraction sample were analysed in alumina crucibles, together with an inert reference material (calcinated kaolinite). Differential thermal values were recorded while samples were heated at a constant rate. The decrease or increase in sample temperature in comparison to the temperature of the reference material was attributed to endothermic or exothermic transitions occurring in the sample.

In this paper we use the following abbreviations: TG-DTA 350 OM as OM mass loss at 350°C calculated from the difference between the natural-state sample and the oxidized sample at 350°C and TG-DTA 350 tot as the total mass loss at 350°C estimated on natural-state sample; TEOM corresponds to the total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample at 567°C; TEML corresponds to total extraction of mass loss at 567°C estimated on natural-state sample, while LCSW 350 corresponds to loss of clay structural water at 350°C and TECSW to total extraction of clay structural water at 567°C both estimated on oxidized sample. All parameters were measured by thermogravimetric-differential thermal analyses.

CHN analyser

A CHN analyser was used for reference determination of TOC, after removal of inorganic carbonates and degassing of CO_2. Following the procedure described by

Nieuwenhuize *et al.,* (1994), 15-30 mg of sediment was acidified *in situ* with 25% HCl in silver sample cups. The organic carbon content was then measured with a Carlo Erba CHN analyser (NA-1500). Extensive testing and application has shown long-term precision of about 2% for organic carbon measurement. Percentage total organic carbon is given in table 2.

RESULTS AND DISCUSSION

Thermogravimetric-Differential Thermal analyses (TG-DTA)

Figure 1 shows the rate of mass loss and the exothermic and endothermic peaks determined by TG-DTA.

Thermogravimetric mass losses were frequently observed at temperatures of around 300, 400, 500 and 600-900°C, as evidenced by the more negative slopes in the thermogravimetric curves. These mass losses correlate well with the exothermic regions attributed to OM oxidation and the endothermic region attributed to carbonate loss. The patterns in Figure 1 are related to the decomposition of specific OM structures. Different OM constituents have different thermal stabilities, so the formation of a peak in a certain temperature range can be related to the decomposition of specific OM structures. These include a labile, a recalcitrant and a refractory pool. The labile OM fraction decomposes during thermal analysis at ~300–350°C while the more recalcitrant OM decomposes at ~400–500°C. The refractory fraction has been reported to decompose at ~450–600°C (Lopez-Capel *et al.*, 2005a, 2005b, 2006).

In the differential thermal curves, the exothermic peaks associated with the burning of specific carbon groups occur at 302°C, 401°C and 503°C (mean temperatures calculated for the 33 samples). The areas of the 350°C, 450°C and 550°C peaks were also calculated. The thermogravimetric and differential thermal curves of peroxide-treated samples showed no weight loss, and the corresponding lack of exothermic peaks reflected the prior removal of organic matter by the peroxide (Figure 1). Peroxide treatment is a common method for the removal of organic matter prior to mineralogical and particle-size analyses (Kunze and Dixon, 1986). Although mineralisation of organic matter using peroxide treatment has been found to be incomplete (Theng *et al.*, 1986,

1992; Righi *et al.,* 1995; Plante *et al.*, 2004) and the residual organic matter is considered to be refractory, our data showed a negligible residual fraction (Figure 1).

In the thermogravimetric curves, the mass loss of OM was calculated from the difference between the natural-state sample and the oxidized sample at the peak temperatures of the differential thermal curve. The loss of clay structural water corresponds to the mass loss value of the oxidized sample. We used the following equation to determine the total extraction of OM (TEOM):

$$TEOM_{(T°)} = TEML_{\text{Natural-state sample}(T°)} - TECSW_{\text{oxidized sample}(T°)}$$

where $TEOM_{(T°)}$ corresponds to the total extraction of OM. The temperature was different in each sample depending on the content and composition of OM but the mean temperature was 567°C.

$TEML_{\text{Natural-state sample}(T°)}$ is the total extraction of mass loss at 567°C and $TECSW_{\text{oxidized sample}(T°)}$ is the total extraction of clay structural water at 567°C.

The decomposition of calcite and dolomite takes place in the temperature range from 650 to 900°C.

The values of the TG-DTA parameters for the sediment samples are summarised in table 1.

Sample #9 (Figure 1A) shows a sharp exothermic peak at approximately 500°C (peak 3, solid line), indicating a significant quantity of thermally resistant OM. On the other hand, in sample #27 the highest peak is the first, at around 300°C, (solid line) indicating a greater proportion of thermally labile OM. In both samples the three exothermic peaks are not discernable in oxidized samples (dashed line) due to the prior removal of OM by the peroxide (Figure 1).

Peak 1 in samples #9 and #27 (Figure 1 A) can be assigned to the decomposition of more labile structures and relatively simple organic components. These may be include fatty acids, peptides, and carbohydrates such as monosaccharides, cellulose, and hemicellulose (Nguyen *et al.*, 1981; Angehrn-Bettinazzi *et al.*, 1988; Leinweber *et al.*, 1996; Cuypers, 2002). These are readily biodegradable and can be easily extracted with mild solvents. Schnitzer and Hoffman (1966) reported that the height of peak 1 is

inversely proportional to the degree of humification. The peak becomes broader and smaller as organic matter becomes more humified.

Peaks 2 and 3 in samples #9 and #27 (Figure 1A) correspond to recalcitrant and refractory components and correspond to more humified organic substances. Both humic and fulvic acids yield peaks in a temperature range corresponding to peaks 2 and 3, humic acids being more thermostable than fulvic acids (Shurygina *et al.*, 1971). Besides humified materials, non-humified materials may also contribute to peaks 2 and 3. Peak 3 has been associated with the decomposition of aromatic nuclei (Turner and Schnitzer, 1962; Shurygina *et al.*, 1971) and calcium-OM complexes (Schnitzer and Hoffman, 1966). However, aliphatic compounds may also contribute to peak 3, as follows from the high thermostability of humic fractions.

The endothermic peak (peak 4) in samples #9, #27 and #85 (Figure 1) was attributed to the decomposition of calcite and dolomite following Schnitzer and Hoffman (1966), Shurygina *et al.* (1971), Angehrn-Bettinazzi *et al.* (1988).

In table 1 the total mass loss at 350°C (TG-DTA 350 tot) and the total extraction of mass loss (TEML) (organic matter and clay structural water) estimated on natural-state sample are compared to LCSW 350 and the total extraction of clay structural water (TECSW) estimated on oxidized sample, together with TG-DTA 350 OM and TEOM calculated from the difference between the natural-state sample and the oxidized sample at the peak temperatures.

In two samples out of 33, TEOM was above 10%, while the mean value was 4.9%. The mean value of TG-DTA 350 OM was only 1.88. At 350°C, mean mass loss values for LCSW and OM are broadly similar.

A similar result for the thirty-three samples is shown in Figure 2. The figure shows TG-DTA 350 OM compared to TEOM. TG-DTA 350 OM is 41% of the TEOM, indicating a clear proportional relationship ($R^2 = 0.83$; $p < 0.001$) and highlighting the presence of various OM constituents. Figure 2 shows six (#25, #27, #31, #48, #53, #67) out of thirty-three samples with a high percentage of thermo-labile OM. The decomposition of the remaining OM shows the presence of more thermally stable substances (recalcitrant and refractory fractions).

Quantifying refractory forms of organic matter in sediments is important for improving estimates of carbon flux from the biosphere to the sedimentary carbon pool. Refractory

forms of organic matter, such as humic-like materials and black carbon, represent a significant sink for CO_2, since they entail the transfer of carbon from the biological-atmosphere carbon cycle to the long-term geological carbon cycle (Middelburg *et al.*, 1999; Gustafsson *et al.*, 2001).

It is also very important to know the grain size and the mineralogical composition of the analysed samples. The clay components are multi-layered silicate crystals separated by thin layers of structural water. The removal of clay structural water starts at very low temperatures above 60°C. Weight loss due to removal of clay structural water can be negligible for particulate matter with low clay content. However, lagoon sediments are often characterised by high clay content, so the presence of clay structural water can seriously affect OM estimations, and the error related to LCSW may thus be very high.

The mean LCSW 350 and TECSW were 33% and 43% of TEML respectively.

The grain size data relating to the sediment samples show a distribution ranging from slightly muddy sand to mud (Figure 3).

There was a clear relationship between the percentage of the clay fraction (<4 μm) and the LCSW as determined by TG-DTA analysis. Figure 4 shows that LCSW 350 and TECSW correspond approximately to 6% and 10% respectively of the clay fraction. The larger the clay fraction, the larger the amount of LCSW 350 and TECSW; when estimating OM therefore, is important to take account of the relative size of the clay fraction in the samples. The clay structural water percentages found by TG-DTA analysis may be used to correct LOI measurements of OM, depending on the clay fraction.

Comparison of the two methods: Thermogravimetric-Differential Thermal analyses (TG-DTA) and Loss on Ignition (LOI)

A comparison of LOI and TG-DTA shows that LOI does not distinguish the labile from the refractory OM, however, it can still prove useful as anoverall indicator of this parameter.

Table 2 shows the percentage mass loss as measured by LOI at 350°C and 550°C. The LOI 350 mass loss was between 0.4% and 9% with a mean value of 2.5%. In contrast, the LOI 550 mass loss was always greater than 10%, with the exception of three samples (#122 = 3.5%, #17 = 7.2% and #48 = 9.7%). The texture of these three

samples, together with samples #158 (LOI 550 = 11.6%) was slightly muddy sand (Figure 3), corresponding to very coarse sediments with very low mud content. Figure 4 and table 1 show that an increased muddy fraction corresponds to a rise in the OM content, confirming the findings of Mayer (1994a, 1994b). The potential incompleteness of LOI in a high-clay environment should not be disregarded (Barillè-Boyer, 2003). The mean LOI 350 and LOI 550 mass losses were 2.5% and 14.3% respectively.

The loss of OM as measured by TG-DTA was compared with the mass loss values estimated by LOI. The LOI 350 and LOI 550 values correspond to ~80% and ~200% respectively of total extraction of mass loss at 350°C (TG-DTA 350 tot) and at 567°C (TEML) estimated on natural samples. The difference between the two methods indicates that the LOI 550 value represents a considerable overestimation of mass loss. This may be related to the site-specific characteristics (clay content, sedimentological parameters, etc.) and also to the time of combustion (16 hours).

Figure 5 shows the relationship of LOI 350 to TG-DTA 350 OM and of LOI 350 to TG-DTA 350 tot. The plot shows clear positive trends, and the linear regression shows that there is a robust relationship ($R^2 = 0.82$; $p < 0.001$) between LOI 350 and TG-DTA 350 tot. The relationship of LOI 550 to TEML, with a good regression correlation coefficient ($R^2 = 0.53$; $p < 0.001$) highlights an overestimation by LOI 550. The LOI 550 values include mass loss of both OM and clay structural water and probably also the breakdown of some carbonates. Therefore, to identify the presence of carbonates we calculated the difference between the LOI 550 and TEML values. This difference corresponds to the mass loss excess (MLE) and may be accounted for by the loss resulting from the breakdown of carbonates. Comparison of the MLE with the percentage of carbonates in the sediments shows a good regression correlation coefficient ($R^2 = 0.46$; $p < 0.001$), supporting this hypothesis.

The correction proposed here, based on the loss of clay structural water as measured by TG-DTA, could be useful for correcting OM data sets based on LOI analysis of sedimentary deposits with differing clay content.

Comparison of Loss on Ignition (LOI) and Total Organic Carbon (TOC)

Table 2 shows the percentage TOC measured by CHN analyser. The ratio of mass loss measured by LOI 350 to the TOC value estimated by CHN and the ratio of TEOM

(total extraction of OM at 567°C) to TOC for each of the 33 samples are shown in Figure 6. The scatter plot shows a positive trend and a very close relationship ($R^2 = 0.93$; p< 0.001) between LOI 350 and TOC. The regression line passes close to the origin, suggesting that the values are roughly equivalent. The regression equation may be used to calculate the difference between the two sets of values. The TOC values are roughly 1/2 of the OM values calculated by LOI 350. Therefore, the LOI 350 values can be divided by a factor of 2 to convert to TOC. A good regression correlation coefficient ($R^2 = 0.56$; $p < 0.001$) is also seen between TEOM and TOC, the TOC values being ∼1/3 of the TEOM values. Similar conversion factors for marine sediments, 3 and 2, were reported by Leong and Tanner (1999) and Barillé-Boyer *et al.* (2003) respectively.

The correction factors obtained in this study are summarised in table 3 they may be provide useful operational indications for similar studies.

The correction factors presented in the study were valid for sediments from the Lagoon of Venice, but needs to be tested before being applied to other lagoon systems.

CONCLUSIONS

1. Two samples out of 33 had total extraction of organic matter (TEOM) of more than 10%, while the mean was 4.9%. At 350°C the values loss of clay structural water (LCSW) on oxidized samples and loss of OM are broadly similar.

On average, the mass loss measured by the thermogravimetric differential thermal analysis at 350°C (TG-DTA 350 OM) account for 41% of the TEOM mass loss, highlighting the presence of different constituents of OM. Six out of thirty-three samples show a high percentage of thermolabile OM. The remainder show the presence of more thermally stable substances (recalcitrant and refractory fractions).

2. The percentage mass losses of clay structural water (LCSW) at 350°C and of total extraction of clay structural water (TECSW) both estimated on oxidized samples correspond approximately to 6% and 10% respectively of the clay fraction < 4 μm. This percentage may be used to correct LOI measurements of OM depending on the amount of the clay fraction.

3. The LOI 350 and LOI 550 values correspond to ∼80% and ∼200% % respectively of total extraction of mass loss at 350°C (TG-DTA 350 tot) and at 567°C (TEML)

estimated by TG-DTA on natural samples. The difference between the two methods shows that the LOI 550 value represents a large overestimation of mass loss.

4. Comparison between the mass loss excess (MLE) and the percentage of carbonates in the sediments shows a good regression correlation coefficient ($R^2 = 0.46$). Therefore, the LOI 550 measurements may be adjusted on the basis of the carbonate content of the sediments.

5. The TOC values are about 1/2 of the OM values calculated by LOI 350 and are ~1/3 of the OM values calculated by the total extraction of organic matter (TEOM) as measured by TG-DTA.

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TABLES

Tab. 1. Percentage mass losses measured by TG-DTA at different temperatures steps in the exothermic regions attributed to: total mass losses, loss of clay structural water and loss of OM.

Sample	Natural-state sample		Oxidized samples		Natural-state sample-Oxidized sample	
	TG-DTA 350 tot[1]	TEML[2]	LCSW 350[3]	TECSW[4]	TG-DTA 350 OM[5]	TEOM[6]
2	5.33	12.30	3.23	4.55	2.10	7.75
9	8.18	17.05	3.38	5.05	4.80	12.00
17	2.08	4.25	0.70	1.00	1.38	3.25
25	11.75	21.30	2.75	4.30	9.00	17.00
27	8.00	15.42	3.40	6.00	4.60	9.42
31	4.38	7.68	2.65	4.58	1.73	3.10
48	1.15	3.15	0.30	0.65	0.85	2.50
53	5.35	9.28	1.60	2.68	3.75	6.60
59	5.33	9.25	1.58	2.65	3.75	6.60
64	3.00	8.60	1.70	3.15	1.30	5.45
67	4.67	7.29	3.19	4.74	1.48	2.55
70	3.39	7.14	2.16	4.25	1.23	2.89
74	3.23	9.57	2.83	5.82	0.40	3.75
79	1.21	2.15	0.93	1.65	0.28	0.50
85	1.71	3.57	1.12	2.13	0.59	1.44
89	2.58	6.20	0.80	1.65	1.78	4.55
98	0.75	2.20	0.10	0.35	0.65	1.85
101	2.33	8.90	1.18	2.40	1.15	6.50
103	1.85	6.00	0.70	1.55	1.15	4.45
108	3.11	7.40	1.02	2.25	2.09	5.15
113	3.15	8.66	1.00	1.75	2.15	6.91
116	3.25	7.30	1.00	1.90	2.25	5.40
119	2.15	4.65	0.50	0.90	1.65	3.75
122	0.38	1.33	0.38	0.68	0.00	0.65
125	4.30	11.50	1.15	2.00	3.15	9.50
132	2.33	5.65	0.83	1.55	1.50	4.10
139	2.50	7.35	1.25	2.30	1.25	5.05
146	1.43	4.48	0.23	0.98	1.20	3.50
152	1.75	3.85	0.45	0.85	1.30	3.00
158	0.45	1.65	0.15	0.50	0.30	1.15
166	2.34	6.90	0.88	1.75	1.46	5.15
169	1.15	4.96	0.35	0.91	0.80	4.05

| 177 | 1.45 | 3.40 | 0.55 | 0.95 | 0.90 | 2.45 |
| **Mean** | 3.21 | 7.28 | 1.33 | 2.38 | 1.88 | 4.91 |

[1] TG-DTA 350 tot = tot mass loss at 350°C estimated on natural-state sample; [2] TEML = total extraction of mass loss at 567°C estimated on natural-state sample; [3] LCSW 350 = loss of clay structural water at 350°C estimated on oxidized sample; [4] TECSW = total extraction of clay structural water at 567°C estimated on oxidized sample; [5] TG-DTA 350 OM = OM mass loss at 350°C calculated from the difference between the natural-state sample and the oxidized sample; [6] TEOM = total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample .

Table 2. Percentage of LOI mass loss at different temperature steps and total organic carbon (TOC). LOI 350 = loss on ignition at 350°C; LOI 550 = loss on ignition at 550°C.

Sample	LOI 350	LOI 550	TOC
2	4.91	16.66	2.70
9	8.13	20.93	4.21
17	2.21	7.23	1.36
25	8.50	20.89	4.35
27	9.00	19.80	3.93
31	4.00	15.80	1.79
48	0.92	9.66	0.42
53	1.58	14.60	0.87
59	1.83	16.49	0.98
64	1.58	16.14	0.90
67	3.00	18.30	1.69
70	2.60	17.10	1.37
74	2.48	16.90	1.36
79	1.00	14.10	0.78
85	1.40	14.80	0.77
89	1.53	14.50	0.77
98	0.53	13.87	0.23
101	1.28	15.57	0.83
103	1.12	12.72	0.64
108	2.38	14.78	1.31
113	3.18	12.16	1.60
116	2.46	14.90	1.25
119	1.48	11.83	2.14
122	0.39	3.50	0.14
125	3.67	12.54	1.53
132	2.13	11.97	0.98
139	2.30	13.52	1.24
146	1.29	12.54	0.67
152	1.31	12.66	0.74
158	0.61	11.95	0.22
166	1.51	15.20	0.75
169	0.75	14.31	0.47
177	1.04	14.41	0.54
Mean	2.49	14.31	1.32

Tab. 3. Conversion factors from present study

METHODS	CONVERSION FACTORS	
LOI vs TG-DTA	LOI 350[1] = 1.2 * TG-DAT 350 OM[2]	(Fig. 5)
LOI vs TG-DTA	LOI 350[1] = 0.8 * TG-DTA 350 tot[3]	(Fig. 5)
LOI vs CHN	LOI 350[1] = 1.9 * TOC[4]	(Fig. 6)
TG-DTA vs CHN	TEOM[5] = 3.3 * TOC[4]	(Fig. 6)
TG-DTA vs Grain-Size	LCWS 350[6]= 0.06 * Clay (<4μm)	(Fig. 4)
TG-DTA vs Grain-Size	TECSW[7] = 0.10 * Clay(<4μm)[8]	(Fig. 4)

[1] LOI 350 = Loss on ignition at 350°C; [2] TG-DTA 350 OM = OM mass loss at 350°C calculated from the difference between the natural-state sample and the oxidized sample; [3] TG-DTA 350 tot = tot mass loss at 350°C estimated on natural-state sample; [4] TOC = total organic carbon; [5] TEOM = total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample; [6] LCSW 350 = loss 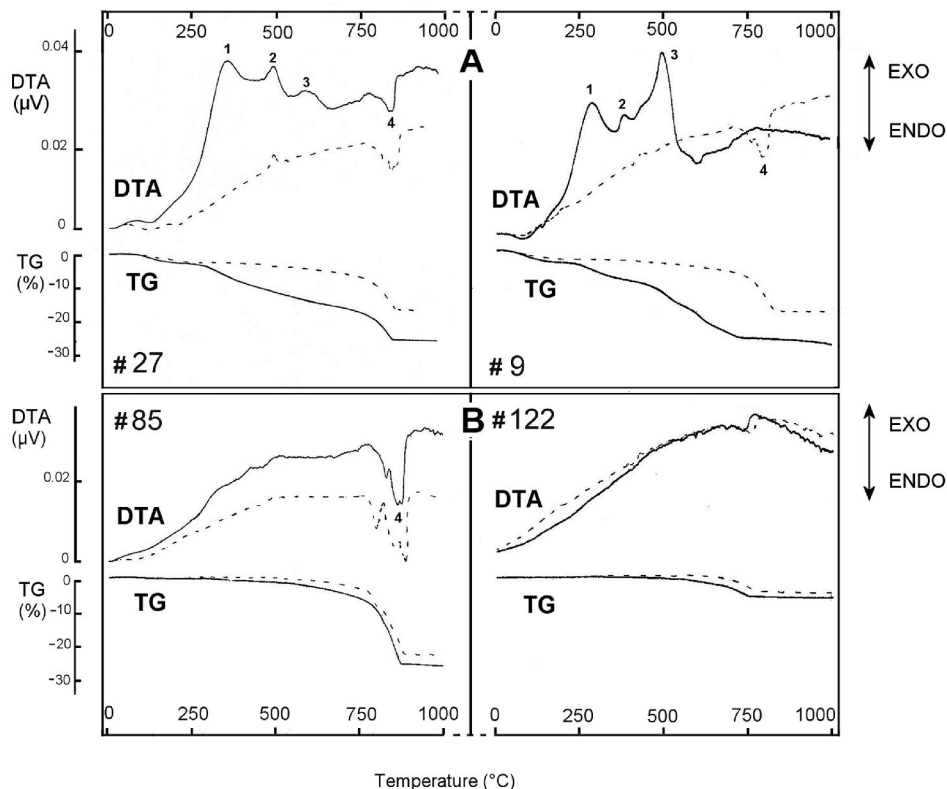of clay structural water at 350°C estimated on oxidized sample; [7] TECSW = total extraction of clay structural water at 567°C estimated on oxidized sample.

FIGURE CAPTIONS

Figure 1. Thermogravimetric (TG) and differential thermal (DTA) curves for four samples. A) Two samples with high OM content: 10.8% (sample # 27) and 13.8% (sample # 9). B) Two samples with low OM content: 1.6% (sample # 85) and 1.2% (sample # 122). The solid line represents samples in the natural state; the dashed line oxidized samples. Peak 1 is attributed to the decomposition of more labile components. Peaks 2 and 3 correspond to recalcitrant and refractory components. Peak 4 was attributed to the decomposition of carbonates.

Figure 2. Linear regression of TG-DTA 350 OM (OM mass loss at 350°C calculated from the difference between the natural-state sample and the oxidized sample) against TEOM (total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample).

Figure 3. Ternary diagrams for textural classification of sediments from Lagoon of Venice, based on sand/silt/clay ratios. Boundaries indicate different sediment types (Flemming, 2000).

Figure 4. Relationship of clay fraction (<4 μm) to LCSW 350 (loss of clay structural water at 350°C estimated on oxidized sample) and TECSW (total extraction of clay structural water at 567°C estimated on oxidized sample). LCSW 350 and TECSW were estimated by TG-DTA.

Figure 5. Scatter plot of mass losses of OM as measured by LOI 350 and TG-DTA; (∗) TG-DTA 350 OM = mass loss of OM at 350°C calculated from the difference between the natural-state sample and the oxidized sample; (●) TG-DTA 350 tot = total mass loss at 350°C estimated on natural-state sample .

Figure 6. Relationships of mass loss of OM measured by LOI 350 (□) and TEOM (total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample) estimated by TG-DTA (●) to TOC (total organic carbon) values estimated by CHN analyser.

Figure 1. Thermogravimetric (TG) and differential thermal (DTA) curves for four samples. A) Two samples with high OM content: 10.8% (sample # 27) and 13.8% (sample # 9). B) Two samples with low OM content: 1.6% (sample # 85) and 1.2% (sample # 122). The solid line represents samples in the natural state; the dashed line oxidized samples. Peak 1 is attributed to the decomposition of more labile components. Peaks 2 and 3 correspond to recalcitrant and refractory components. Peak 4 was attributed to the decomposition of carbonates.
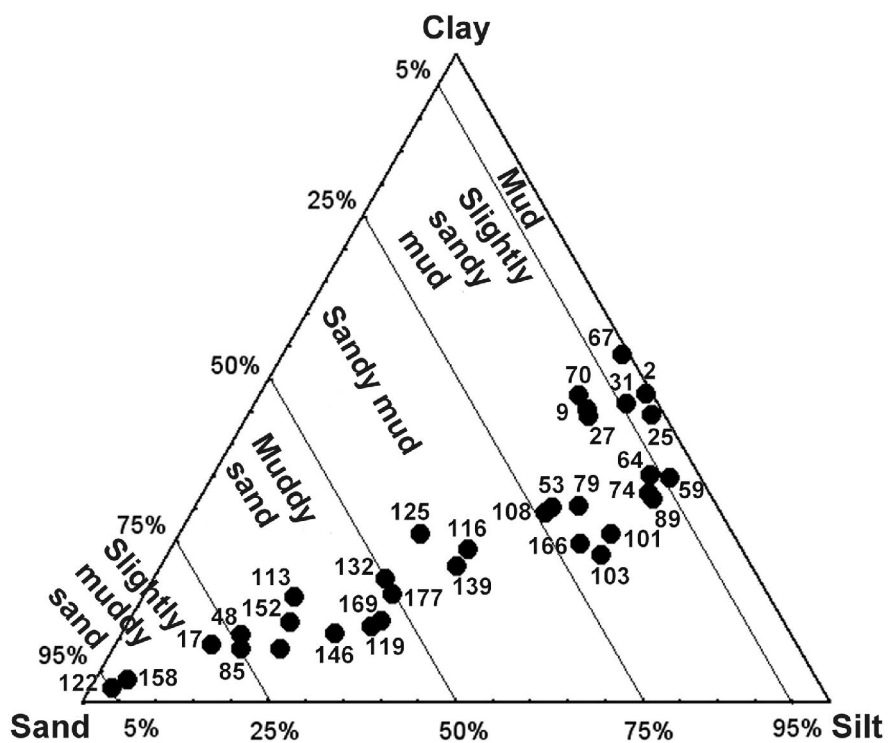105x89mm (600 x 600 DPI)
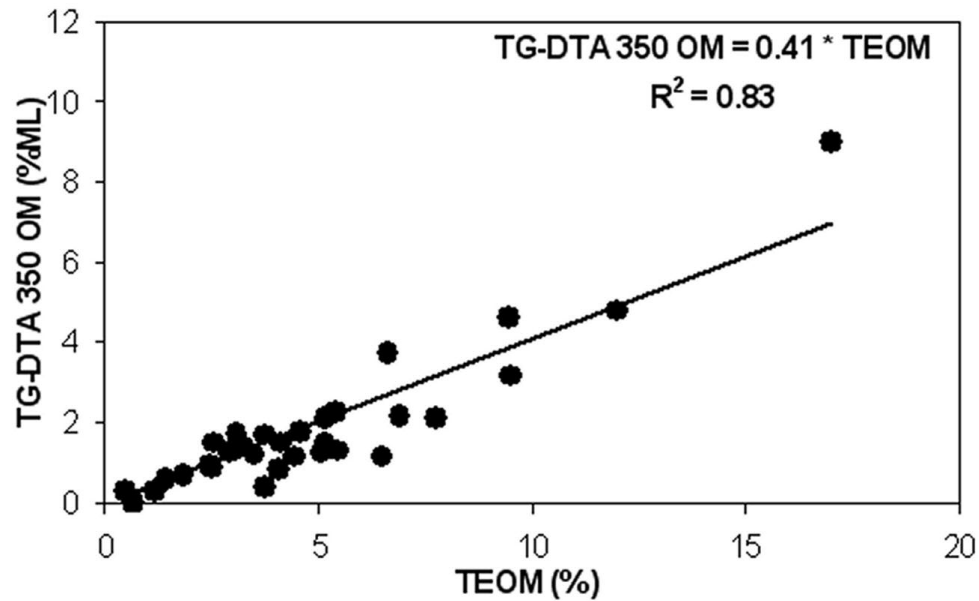
Figure 2. Linear regression of TG-DTA 350 OM (OM mass loss at 350°C calculated from the difference between the natural-state sample and the oxidized sample) against TEOM (total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample).
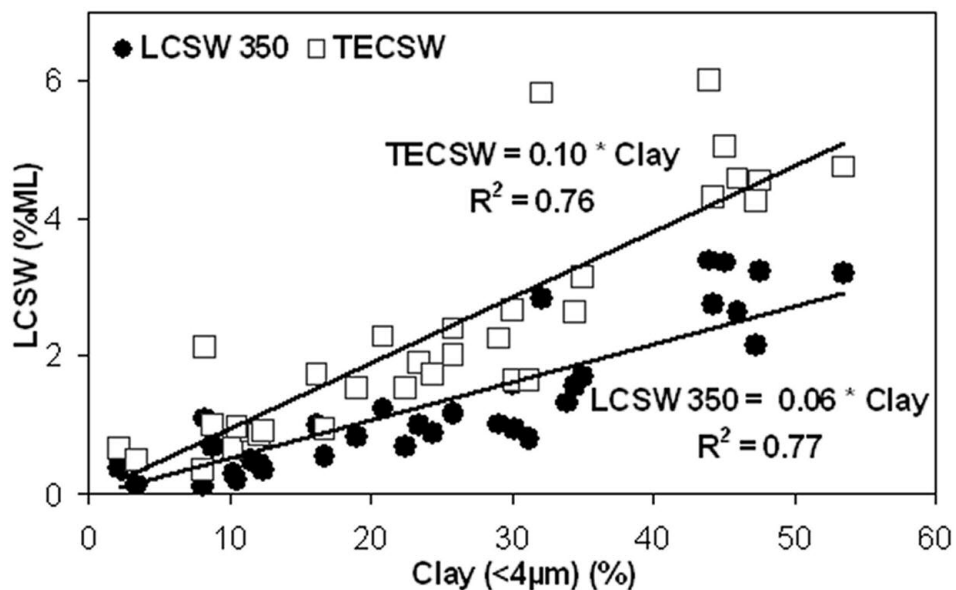56x35mm (600 x 600 DPI)

Figure 3. Ternary diagrams for textural classification of sediments from Lagoon of Venice, based on sand/silt/clay ratios. Boundaries indicate different sediment types (Flemming, 2000).
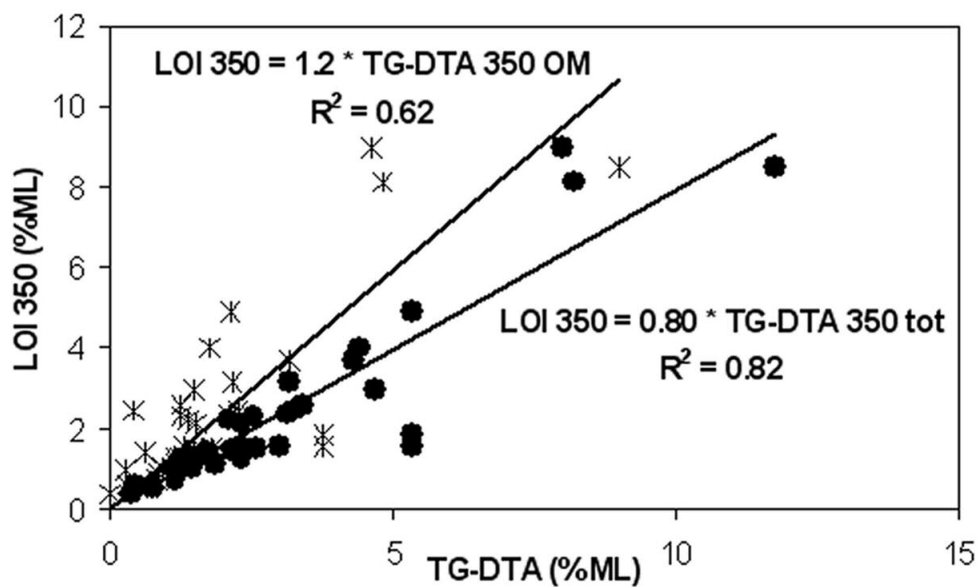91x68mm (600 x 600 DPI)

Figure 4. Relationship of clay fraction (<4 μm) to LCSW 350 (loss of clay structural water at 350°C estimated on oxidized sample) and TECSW (total extraction of clay structural water at 567°C estimated on oxidized sample). LCSW 350 and TECSW were estimated by TG-DTA.
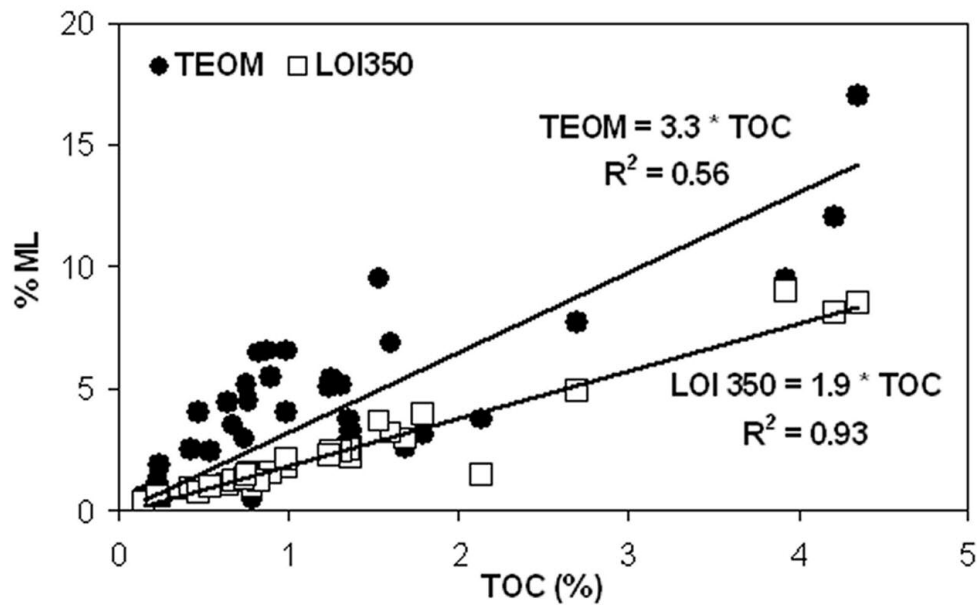55x35mm (600 x 600 DPI)

Figure 5. Scatter plot of mass losses of OM as measured by LOI 350 and TG-DTA; (*) TG-DTA 350 OM = mass loss of OM at 350°C calculated from the difference between the natural-state sample and the oxidized sample; (   ) TG-DTA 350 tot = total mass loss at 350°C estimated on natural-state sample .
52x32mm (600 x 600 DPI)

Figure 6. Relationships of mass loss of OM measured by LOI 350 (□) and TEOM (total extraction of OM at 567°C calculated from the difference between the natural-state sample and the oxidized sample) estimated by TG-DTA (●) to TOC (total organic carbon) values estimated by CHN analyser.
54x34mm (600 x 600 DPI)