

Pitfalls of acid leaching method for determining organic and inorganic carbon contents in marine sediments

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Abstract

Organic and inorganic carbon contents of marine sediments are important to reconstruct marine productivity, global carbon cycle, and climate change. A proper method to separate and determine organic and inorganic carbons is thus of great necessity. Although the best method is still disputable, the acid leaching method is widely used in many laboratories because of its ease-of-use and high accuracy. The results of the elemental analysis of sediment trap samples reveal that organic and inorganic carbon contents cannot be obtained using the acid leaching method, causing an infinitely amplified error when the carbon content of the decarbonated sample is $12\% \pm 1\%$ according to a mathematical derivation. Acid fumigation and gasometric methods are used for comparison, which indicates that other methods can avoid this problem in organic carbon analysis. For the first time, this study uncovers the pitfalls of the acid leaching method, which limits the implication in practical laboratory measurement, and recommends alternative solutions of organic/inorganic carbon determination in marine sediments.

Key words: marine sediments, organic carbon, inorganic carbon, acid leaching method, limitation

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1 Introduction

Preservation and migration of carbon in marine sediments are important processes for transferring carbon from an active surface cycle to a slower geological cycle (Keil, 2017). The marine biological pump, as an important part of the global carbon cycle, is the main mechanism for absorbing carbon from atmosphere through photosynthesis and sequestering it into the deep sea (Passow and Carlson, 2012). Carbon fixed by primary productivity is mainly transported to the deep sea by passive sinking (Castro et al., 2018). The sinking particles, the most suitable materials to study the sinking process, are mainly composed of biogenic and terrigenous components. The biogenic component mainly consists of calcareous shells (CaCO_3), siliceous shells (opal), and organic matter (Chen et al., 1998). The organic matter can be represented by organic carbon, while the CaCO_3 can be calculated by inorganic carbon (Chen et al., 2015). As a result, it highlights the importance of a precise laboratory method to determine the carbon content in marine sediments (Sun et al., 2014).

Total organic carbon (TOC) is the total amount of carbon inherent to organic matters, whereas total inorganic carbon (TIC) pertains inorganic compounds, such as carbonate or bicarbonate. The sum of TOC and TIC constitutes the total carbon (TC) of the sample (Bisutti et al., 2004; Nelson and Sommers, 1982). There are diverse methods used in different research disciplines to determine TOC and TIC (Qiu et al., 2015). In general, TOC in marine sediments can be determined by directly measure the TOC, or indirectly obtain TOC from the difference between TC

and TIC, often independently measured by other methods (Bisutti et al., 2004; Froelich, 1980). The key point is the accurate separation of organic and inorganic carbons whichever methods are used (Weliky et al., 1983). However, different experimental methods may lead to differences in separation accuracy (King et al., 1998).

The common methods of separating organic and inorganic carbons are oxidation, combustion, and acidification (Froelich, 1980; Walkley and Black, 1934). One of most remarkable issues of oxidation is that refractory organic matters in marine sediments are hard to be completely oxidized (Schwartz, 1995; Li and Xu, 1987). Moreover, the amount of oxidant is susceptible to the influence of other reducing substances in the sample (Froelich, 1980). Artificial errors are also prone to being generated because oxidation methods generally involve sensitive analytical procedures. The principle for the combustion method is the use of decomposition temperature differences between organic and inorganic matters. The major defect is that the lattice water of clays will affect the weight loss, especially for the sample with low carbonate and high clay mineral contents. In addition, some researchers proposed that the thermal decomposition temperature of organic carbon and inorganic carbon overlap near 500°C (Gibbs, 1977; Cheng et al., 2010). As a result, the organic carbon and inorganic carbon cannot be accurately separated by the combustion method.

The acidification method to separate organic and inorganic carbons is the widely acknowledged method at present. The TIC can be calculated by measuring the amount of CO_2 produced by

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the reaction of a non-oxidizing acid, most commonly HCl (Weliky et al., 1983; Bai et al., 2013), with the carbonate in the sample (Jones and Kaiteris, 1983). The TOC of the decarbonated sample can then be determined by an elemental analyzer (Bisutti et al., 2004; Byers et al., 1978). The operation of the acid leaching method is by adding excess HCl solution directly to the sample, then subsequently rinsing the residual acid away by adding deionized water and centrifuging (Ryba and Burgess, 2002). A severe drawback of the acid leaching method is the potential loss of acid-soluble organic matter during the reaction with acid, especially for sediments with high carbonate content; up to 10%–20% of organic carbon can be dissolved in the acid. This can reach 40%–50% if the acid concentration and treatment time is increased (Roberts et al., 1973; Galy et al., 2007). To eliminate the loss of acid-soluble organic matter during acidification, the acid fumigation method is utilized as a substitute (Hedges and Stern, 1984; Harris et al., 2001; Wu et al., 1999; Komada et al., 2008). This method involves placing the sample in a vacuum desiccator with concentrated HCl at the lower compartment. The carbonate from the sample is made to react with the HCl vapor completely, and then removing the residual HCl by drying at 60°C for 12 h (Lorrain et al., 2003). H_2SO_4 is used in occasional cases instead of HCl (Verardo et al., 1990). Although the acid fumigation avoids the change of original components during rinsing, problems still exist in treatment of the high carbonate sample (Schubert and Nielsen, 2000; Peng et al., 2015). An apparent problem is that the hygroscopic salts generated by the reaction (e.g., CaCl_2) remain in the sample, and Cl^- is harmful to the machines (Brodie et al., 2011).

Each method has its own advantages and disadvantages. It is still disputed which is the best analysis method for TOC and TIC separation (Komada et al., 2008; Brodie et al., 2011; Tan et al., 2018). The acid leaching method is widely used in many laboratories because of its simplicity, efficient carbonate removal, and safety to the instruments (Bai et al., 2013; Yang and Li, 2006; Zhang et al., 2009; Black et al., 2018; Tripathi et al., 2017). As TIC is destroyed by acids, it is unlikely to directly obtain the TOC value in bulk sample using the acid leaching method, and thus a conversion is needed (Wang et al., 1988). In this study, we reveal that, due to the limitation of the conversion equation, i.e., zero cannot be the denominator, the organic and inorganic carbons are unlikely to be obtained when the carbon content of the decarbonated sample is close to 12%. Several methods to measure TOC and TIC contents are also employed to re-evaluate values from the acid leaching method. This study reveals for the first time the fatal flaw of the acid leaching method and reminds that cautionary measurement should be taken when processing marine sediments with decarbonated carbon content of ~12%.

2 Materials and methods

2.1 Sample materials

Three time-series sediment traps (TJ-B16-UP, TJ-C16-MD, and TJ-G1602-UP) equipped on mooring systems were deployed in the northeastern South China Sea from May 2016 to May 2017. Among them, TJ-B16-UP and TJ-G1602-UP were deployed at water depths of ~500 m, and TJ-C16-MD was deployed at a water depth of 2 070 m. Each trap collected 21 samples of sinking particles consecutively. The bulk samples were passed through a sieve with a mesh size of 1 mm to remove coarse sand and large nekton. The <1 mm particles were filtered through 0.45- μm Whatman[®] Nuclepore[™] membranes, and then dried at 40°C for analysis. A total of 63 samples were analyzed and 4 samples with

decarbonated carbon content close to 12% (TJ-B16-UP11+12, TJ-B16-UP13, TJ-C16-MD01, and TJ-G1602-UP19, hereafter denoted as Sample #1 to #4) were focused on for this study.

2.2 Methods to measure TC, TOC and TIC

Approximately 250 mg of sediments were taken from each sample and homogenized into powders in an agate mortar and pestle. The powders were dried at 40°C for 24 h, and 10 mg powders were weighed accurately and packed into tin capsules for TC contents measurement. The TC contents were measured with a vario EL cube elemental analyzer (Elementar GmbH, Germany) at the State Key Laboratory of Marine Geology (Tongji University), Shanghai. Standard samples of acetanilide and duplicate samples were interpolated during the tests to ensure the data quality. The analytical precision is better than 0.01%, which accords with the national standard GB/T 12763.8–2007 (Li et al., 2008). The contents of TOC and TIC were obtained by the following three methods, respectively.

(1) Acid leaching method

Approximate 100 mg powders from each sample were weighed and put into the separate centrifuge tubes, and decarbonated with excess 1 mol/L HCl for 2 h. The samples were then rinsed with deionized water and centrifuged at least three times until the pH of supernatant was neutral. Loss of acid-soluble organic carbon during water rinsing is negligible. The residues were then dried at 40°C and grounded into powders. Once dried, 10 mg were then accurately weighed and put into tin capsules. The carbon contents of these decarbonated samples (denoted as OC' herein) were measured with the same elemental analyzer. The TOC and TIC contents of the original samples were calculated from TC and OC' values (Eqs (1) and (2)).

(2) Acid fumigation method

The acid fumigation method follows the experimental processes described in Blattmann et al. (2018). Bulk sample powders (10–20 mg) were weighed accurately and put into silver capsules. The silver capsules were then put into 2 mL glass vials carefully to prevent the samples from spilling. The vials were moved into a vacuum desiccator together with 12 mol/L HCl. The whole desiccator was placed in an oven at 60°C for 72 h to let HCl vapor react completely with the carbonates in the sample. The HCl in the desiccator was then replaced with excess NaOH powder and put in a 60°C oven for 72 h to neutralize the residual HCl. After the reaction was completed, the silver capsules were compacted and packed in tin capsules. The TOC contents of the original samples were then measured with the same elemental analyzer. The TIC contents were determined by subtracting TOC from the TC contents.

(3) Gasometric method

The carbonate content of a sample is proportional to pressure of CO_2 generated from the reaction of the sample with HCl in a closed instrument (Jones and Kaiteris, 1983). Assuming that all the inorganic carbon is calcium carbonate (CaCO_3), the TIC content can be derived from the carbonate content. A precise and calibrated CO_2 barometer was used herein to measure the pressure of the amount of CO_2 produced by the reaction, with a test error of less than 2%. The linear regression equation of the CaCO_3 mass and the gas volume was established based on the reaction of 3 mol/L HCl with 10 mg increments from 10 to 100 mg of CaCO_3 standards (Analytical Reagent). A total of 100 mg sample powders were placed into the reaction cup, and closed tightly with the cap. The cup was gently shaken to ensure the contact of sample with the acid. The pressure of CO_2 was read from the barometer and then substituted into the established lin-

ear regression equation to determine the relative carbonate content. The TIC content of the original sample was calculated by the carbonate content multiplied by a factor of 0.12, the carbon mass fraction in CaCO_3 . The TOC content was determined by subtracting TIC from the TC content.

3 Results

Results of the acid leaching method show that calculated TOC and TIC contents of the four samples are anomalous (Table 1). On the one hand, the TC content of Sample #1 is 12.01%, while the carbon content of its decarbonated sample is 12.70%. According to Eqs (5)–(7), the TOC, TIC, and CaCO_3 contents determined by the acid leaching method are 0.16%, 11.85%, and 98.76%, respectively. However, results from other two methods on the Sample #1 show significant differences (Table 2). The TOC content retested by the acid fumigation method is 4.95%, while the TIC content is 7.06% converting into the CaCO_3 content of 58.81%. Results of the gasometric method show that the TOC, TIC, and CaCO_3 contents are 5.2%, 6.8%, and 56.7%, respectively. For Sample #2, the TC content is slightly greater than 12.00% (~12% after rounding to two decimal places), while the TOC, TIC, and CaCO_3 contents calculated by the acid leaching method are -0.05%, 12.05%, and 100.42%, respectively. Results from acid fumigation method retest of Sample #2 show that the TOC content is 3.35%, the TIC content is 8.64%, and the CaCO_3 content is 72.03%. Results from gasometric method retest of Sample #2 show that the TOC, TIC, and CaCO_3 contents are 3.4%, 8.6%, and 71.7%, respectively. For these two samples (Samples #1 and #2), their TC contents are slightly greater than 12%. Meanwhile, their OC' values measured by the acid leaching method are also slightly greater than 12%. These TC and OC' values consequently make the calculated TOC contents to be almost zero or even negative and the TIC contents to be ~12%, resulting in CaCO_3 contents close to or exceeding 100%. However, the reasonable results are obtained by the acid fumigation method and gasometric method. Their differences of the TOC and TIC contents obtained between the two methods are about 0.2%.

On the other hand, Sample #3 has a TC content of 11.31%. The TOC, TIC, and CaCO_3 contents calculated by the acid leaching method are 19.74%, -8.43%, and -70.29%, respectively. Results from acid fumigation method retest of Sample #3 show that the TOC, TIC, and CaCO_3 contents are 6.75%, 4.55%, and 37.94%, respectively. The TOC, TIC, and CaCO_3 contents from gasometric method retests of Sample #3 are 7.0%, 4.3%, and 36.0%, re-

spectively. For Sample #4, the TC content is 11.71%, while the TOC, TIC, and CaCO_3 contents calculated by the acid leaching method are 50.52%, -38.81%, and -323.39%, respectively. Results of the acid fumigation method on Sample #4 appear more reasonable with the 6.97% TOC, 4.75% TIC, and 39.56% CaCO_3 . Results from gasometric method retest of Sample #4 show that the TOC, TIC, and CaCO_3 contents are 7.4%, 4.3%, and 36.1%, respectively. These two samples (Samples #3 and #4) have TC contents approaching 12% from the negative direction and OC' values slightly less than 12%. Consequently, the TOC contents calculated by the acid leaching method are much higher than the TC contents, resulting in negative TIC contents and thus largely negative CaCO_3 contents. The results of acid fumigation method and gasometric method show high similarity, which could be considered as actual compositions of these two samples.

4 Discussion

4.1 Limitation of acid leaching method

The pretreatment and measurement of the sample with abnormal TOC and TIC values were double-checked and repeated to make sure there is no mistake during the experimentation. In order to find the cause of the anomaly, we have considered the principle of the acid leaching method and discussed the rationale and restriction of the equations.

In the acid leaching method, the TC content of the original sample is calculated as:

$$\text{TC} = \frac{m_{\text{OC}} + m_{\text{IC}}}{M} \times 100\% = \text{TOC} + \text{TIC}, \quad (1)$$

where m_{OC} is the mass of organic carbon, m_{IC} is the mass of inorganic carbon, and M is the total mass of the original sample. The carbon content of the decarbonated sample after acid leaching is calculated as:

$$\text{OC}' = \frac{m_{\text{OC}}}{M - m_{\text{Carb}}}, \quad (2)$$

where m_{Carb} is the mass of carbonate. Here we emphasize that OC' is the decarbonated carbon, which is different from organic carbon because the latter is m_{OC}/M . Assuming the mass fraction of carbon in carbonate is k , the mass of inorganic carbon can be expressed as:

Table 1. Test datum and calculation results of the abnormal values when tested using the acid leaching method

Sample #	Sample name	TC/%	OC'/%	TOC _L /%	TIC _L /%	CaCO _{3L} /%
1	TJ-B16-UP11+12	12.01	12.70	0.16	11.85	98.76
2	TJ-B16-UP13	12.00	12.66	-0.05	12.05	100.42
3	TJ-C16-MD01	11.31	11.59	19.74	-8.43	-70.29
4	TJ-G1602-UP19	11.71	11.93	50.52	-38.81	-323.39

Note: Subscript L is the result of acid leaching method.

Table 2. Comparison of the results of three test methods

Sample #	Sample name	TOC _L /%	TIC _L /%	CaCO _{3L} /%	TOC _F /%	TIC _F /%	CaCO _{3F} /%	TOC _G /%	TIC _G /%	CaCO _{3G} /%
1	TJ-B16-UP11+12	0.16	11.85	98.76	4.95	7.06	58.81	5.2	6.8	56.7
2	TJ-B16-UP13	-0.05	12.05	100.42	3.35	8.64	72.03	3.4	8.6	71.7
3	TJ-C16-MD01	19.74	-8.43	-70.29	6.75	4.55	37.94	7.0	4.3	36.0
4	TJ-G1602-UP19	50.52	-38.81	-323.39	6.97	4.75	39.56	7.4	4.3	36.1

Note: Subscript L is the result of acid leaching method; subscript F is the result of acid fumigation method; and subscript G is the result of gasometric method.

$$m_{\text{IC}} = k \cdot m_{\text{Carb}}. \quad (3)$$

Simplifying Eq. (2) and substitute Eq. (3) into it, so OC' is expressed as:

$$\text{OC}' = \frac{m_{\text{OC}}}{M - \frac{m_{\text{IC}}}{k}} = \frac{\frac{m_{\text{OC}}}{M}}{1 - \frac{m_{\text{IC}}}{k \cdot M}} = \frac{\text{TOC}}{1 - \frac{\text{TIC}}{k}}. \quad (4)$$

Assuming all the inorganic carbon was calcium carbonate (CaCO_3), the k should be 12%. The TOC content of the original sample is calculated by substituting Eq. (1) into Eq. (4), which is:

$$\text{TOC} = \frac{12\% - \text{TC}}{12\% - \text{OC}'} \cdot \text{OC}'. \quad (5)$$

The TIC content is determined by subtracting TOC from the TC content:

$$\text{TIC} = \text{TC} - \text{TOC} = \frac{12\% \cdot (\text{TC} - \text{OC}')}{12\% - \text{OC}'}. \quad (6)$$

The carbonate content (c) is determined with the following equation:

$$c = \frac{\text{TIC}}{k} = \frac{100}{12} \text{TIC}. \quad (7)$$

The derivation above is constrained when the denominator of Eq. (5) is zero when $\text{OC}'=12\%$, making it impossible to calculate the TOC and TIC contents. This is a mathematical problem where the proportion of the two compounds, namely the inorganic and organic carbons, are calculated, given their measured contents. One of the two compounds is CaCO_3 , which is completely removed during acidification. The other is the decarbonated residue, whose carbon content is the OC' value. If the carbon content of decarbonated residue is 12%, it is identical to the carbon mass fraction of CaCO_3 . Therefore, whatever ratio of the two substances is, the carbon content of the mixture, i.e., the TC content of original sample, is always 12%. In this case, the TOC and TIC contents of the bulk sample cannot be calculated by Eqs (5)–(7).

Functional relations of TC, OC', and TOC can be obtained through Eq. (5). In the three-dimensional coordinate system with TC, OC', and TOC as the axes, the graph of Eq. (5) is approximately irregular saddle-shaped with a symmetric central point at (12, 12, 0) (Fig. 1). The position of the four samples with abnormal values from the acid leaching method in Table 1 are shown in Fig. 1. These four points are approximately distributed on the line of intersection between $\text{TC}=12\%$ and $\text{OC}'=12\%$. Meanwhile, Samples #1 and #2 are closer to the central point. Because the curvature of the surface increases as it gets closer to the central point, tremendous changes of amplitude occur when the function takes a value nearby. This can explain the cases when OC' is very close to 12%, the calculated TOC and TIC contents will also be anomalous, usually shown as large positive or negative values.

Because it is very difficult to analyze the changes of nonlinear three-dimensional graph intuitively, we transform it into plane curves by continuous sections. Since the TC content is obtained from the result of the first test without pretreatment, we believe it is empirical and accurate. By assuming the TC value is constant,

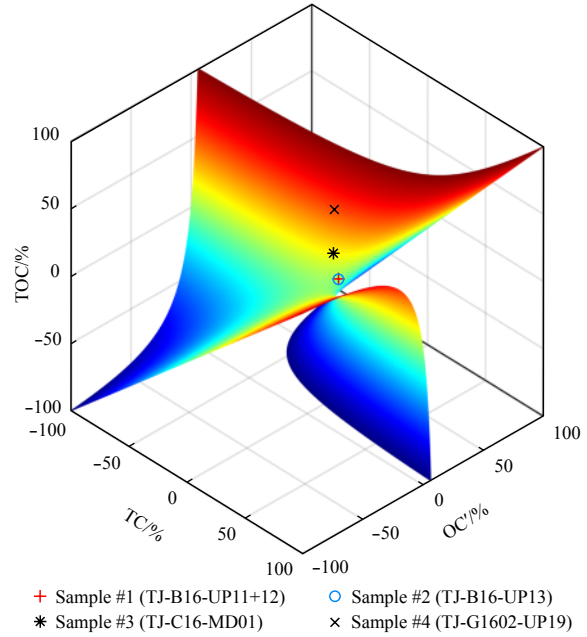


Fig. 1. The functional relations of TC, OC', and TOC.

the relative variation of TOC and OC' can be obtained by substituting it into Eq. (5), that is, the cross section perpendicular to the TC axis is made on the graph of Fig. 1 to reveal the change on the plane, where $\text{TC} \neq 12\%$.

When the TC value is constant, TOC and OC' do not have a linear relationship due to the different inorganic carbon contents of the sample. The graph of this function is a hyperbola passing through the origin. The asymptote on the vertical axis is $\text{TOC}=\text{TC}-12\%$, and the asymptote on the horizontal axis is $\text{OC}'=12\%$. The four samples with abnormal TOC values from the acid leaching method are all located near the asymptote of the horizontal axis (Fig. 2). Since the measured OC' is non-negative, we mainly discuss the variation of the function when the domain is greater than zero. When $\text{TC} < 12\%$, the TOC value is monotonically increasing on each curve, and the curvature of the curve increases gradually with the increase of TC value (Fig. 2a). When $\text{TC} > 12\%$, the function graph is axisymmetric along with graph of $\text{TC} < 12\%$ at the axis of $\text{TOC}=0$, that is the TOC value monotonically decreasing on each curve, and the curvature of curve decreasing gradually with the increase of TC value (Fig. 2b). This indicates that the closer the TC value approaches 12%, the larger curvature of the curve is and the closer the curve fits the asymptote $\text{OC}'=12\%$. This means that if the function takes the same range, its domain of definition will become smaller.

As measurements of organic and inorganic carbon contents are basic and essential analyses in marine chemistry and paleoceanography, samples with decarbonated carbon contents close to 12% are not uncommon. According to the property of the hyperbola, a slight change of OC' can lead to an obvious change of TOC as it approaches its asymptote $\text{OC}'=12\%$. Especially when the curvature of hyperbola is larger, that is, the TC is closer to 12%, the TOC calculated will be either greatly amplified, or show a negative value even if the measured OC' is only slightly erroneous. Therefore, we consider that the acid leaching method is not applicable when $\text{OC}'=12\% \pm 1\%$. This limitation theoretically exists in all experimental methods that require similar conversion to obtain TOC contents.

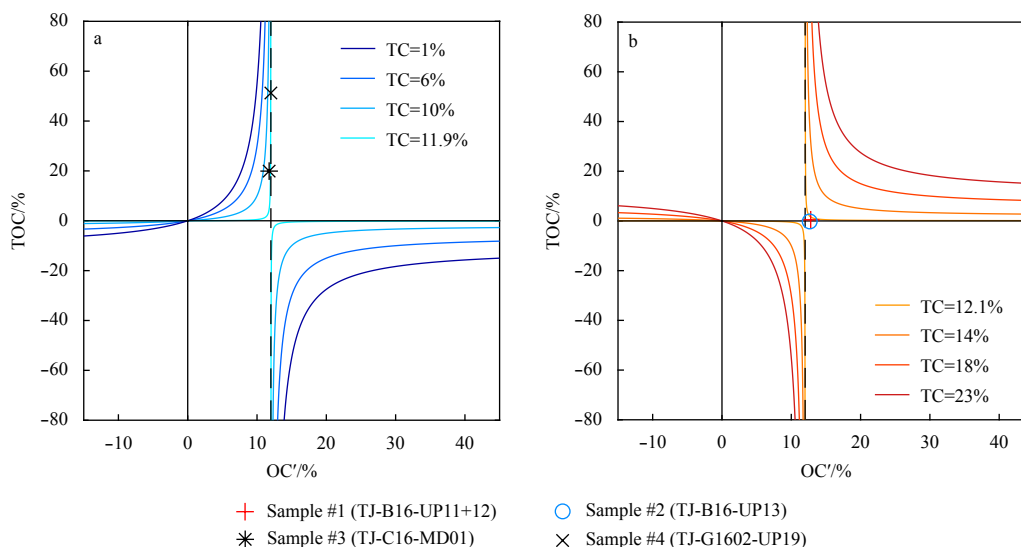


Fig. 2. The functional relations of TOC and OC'. a. When $TC < 12\%$ and b. when $TC > 12\%$.

4.2 Alternative solutions

The intermediate variable OC' in the acid leaching method is affected by multiple factors, such as TOC content of original sample, mixing ratio of organic and inorganic carbons, and loss of sample during pretreatment. As these factors are unpredictable, the acid leaching method has great uncertainty in practical use. This is especially problematic when the volume of a sample is limited, such as the sediment trap sample that has often inadequate material for a duplicate measurement. For such samples, an advisable strategy is to measure TOC and TIC using alternative methods. The experimental results shown above indicate that both acid fumigation and gasometric method can obtain robust results for the samples that are not suitable for the acid leaching method.

(1) Pretreatment by acid fumigation method to determine TOC

Although both acid leaching method and acid fumigation method aim to remove carbonate from a sample, the key difference is when the mass of sample is recorded. The former is to record the mass of sample before treatment, while the latter is to record after treatment. The acid leaching method measures the carbon content of decarbonated sample, while the acid fumigation method obtains the TOC content of original sample directly through the mass of residual carbon divided by the sample mass before fumigation. By comparing the test results in Tables 1 and 2, the difference of carbon content (OC' and TOC_F) measured by these two methods is up to about 10%. The result of acid fumigation method is more reasonable than acid leaching method as shown by the experimental results (Table 2).

There are several advantages of the acid fumigation method. Results adhere to the high accuracy of the elemental analyzer, while avoiding the limitations in the conversion process of the acid leaching method. The systematic error mainly depends on the accuracy of the elemental analyzer, which has a test error of $< 0.01\%$. Additionally, the acid fumigation process is generally less destructive to the non-carbonate components (Galy et al., 2007), and the amount of sample needed for acid fumigation method is 80% less than the sample needed for the acid leaching method. However, the proper duration of acid fumigation is still difficult to determine: if the fumigation time is too short, the reaction will be incomplete; or conversely too long, it risks destructing some

labile organic molecules (Komada et al., 2008; Peng et al., 2015).

(2) Use gasometric method to determine TIC

The organic carbon in marine sediments come in complex and diverse physical and chemical properties. However, the carbonate composition of marine sediments is mainly composed of foraminifera and other calcareous microfossils, thus can be considered as complete $CaCO_3$. Therefore, it is also feasible to calculate the TIC by accurately measuring the pressure from the amount of CO_2 generated by the reaction with an acid. The barometer used for determining the volume of CO_2 is a traditional instrument with a test error of $< 2\%$. The advantage of this method is that test results can be immediately obtained without sample pretreatment. Although the test results are almost identical with the acid fumigation method's results, the accuracy of TC and TIC contents could be compromised due to the compounding of the variations from using two different instruments for measurement.

The acid fumigation and gasometric methods are theoretically clearer and simpler, avoiding the mathematical problems that may occur in the subsequent conversion of OC' to TOC and TIC. These methods can remarkably eliminate the loss of acid-soluble organic matter, without introducing other byproducts that may change the composition of the sample. Moreover, the operations are relatively easy and fast, favoring the rapid analyses of large numbers of marine sediment samples.

5 Conclusions

In this study, three methods have been used to determine the TOC and TIC contents of marine sediments collected by sediment traps. Results of the acid leaching method show that accurate TOC and TIC contents cannot be obtained when the carbon content measured by elemental analyzer is $12\% \pm 1\%$. Reasons for the anomalies are revealed through the mathematical derivation on the calculation. The denominator in the conversion equation is close to zero when the carbon content of decarbonated sample is close to 12%. In this case, a slight deviation in the measurement will lead to tremendous wrong values of TOC and TIC contents, usually shown as very large positive or negative values. Due to this restriction, the acid leaching method is greatly limited in practical laboratory measurements.

Retesting analyses of samples verify the feasibility of acid fu-

migration method and gasometric method. Although the effect of acid fumigation and the accuracy of gasometric method are disputable, these two alternative methods are still more suitable for samples with decarbonated carbon content close to 12%. We therefore highlight that caution should be considered when using the acid leaching method to process samples with high organic matter and CaCO_3 contents, such as marine surface suspended particulate materials and sediments from estuaries, bays, and nearshore areas. The acid fumigation method and gasometric method are recommended for samples obtained from these environmental settings.

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