

INFLUENCE OF DIFFERENT ACID TREATMENTS ON THE RADIOCARBON CONTENT SPECTRUM OF SEDIMENTARY ORGANIC MATTER DETERMINED BY RPO/ACCELERATOR MASS SPECTROMETRY

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ABSTRACT. In practice, obtaining radiocarbon (^{14}C) composition of organic matter (OM) in sediments requires first removing inorganic carbon (IC) by acid-treatment. Two common treatments are acid rinsing and fumigation. Resulting ^{14}C content obtained by different methods can differ, but underlying causes of these differences remain elusive. To assess the influence of different acid-treatments on ^{14}C content of sedimentary OM, we examine the variability in ^{14}C content for a range of marine and river sediments. By comparing results for unacidified and acidified sediments [HCl rinsing ($\text{Rinse}_{\text{HCl}}$) and HCl fumigation (Fume_{HCl})], we demonstrate that the two acid-treatments can affect ^{14}C content differentially. Our findings suggest that, for low-carbonate samples, $\text{Rinse}_{\text{HCl}}$ affects the Fm values due to loss of young labile organic carbon (OC). Fume_{HCl} makes the Fm values for labile OC decrease, leaving the residual OC older. High-carbonate samples can lose relatively old organic components during $\text{Rinse}_{\text{HCl}}$, causing the Fm values of remaining OC to increase. Fume_{HCl} can remove thermally labile, usually young, OC and reduce the Fm values. We suggest three factors should be taken into account when using acid to remove carbonate from sediments: IC abundance, proportions of labile and refractory OC, and environmental matrix.

KEYWORDS: acidification, pretreatment, radiocarbon, sediments, stable carbon isotope.

INTRODUCTION

Measuring the radiocarbon (^{14}C) content of organic carbon (OC) in sediments is useful for understanding the sources and dynamics of the sedimentary OC in the aquatic environment (Griffith et al. 2010; Blair and Aller 2012; Canuel and Hardison 2016). In practice, obtaining the ^{14}C content of OC in sediments requires first removing inorganic carbon (IC) by acid treatment. However, there is evidence that sample acidification can affect the measured total OC (Froelich 1980; Hedges and Stern 1984; Kennedy et al. 2005; Komada et al. 2008; Brodie et al. 2011) and total nitrogen (TN) contents (Kennedy et al. 2005), as well as the stable carbon (^{13}C) (Jaschinski et al. 2008; Komada et al. 2008; Brodie et al. 2011), nitrogen (^{15}N) (Kennedy et al. 2005; Brodie et al. 2011; Vafeiadou et al. 2013), sulfur (^{34}S) (Connolly and Schlacher 2013), and ^{14}C compositions (Komada et al. 2008) as a consequence of the various treatment procedures.

Two common treatments are “acid rinsing” and “acid fumigation.” The former approach involves direct acid titration using strong hydrochloric (e.g., ~1N HCl) or weak phosphoric (e.g., ~0.6 N H_3PO_4) acid and subsequent rinsing with Milli-Q water to neutralize the sample as well as remove hygroscopic salts (Komada et al. 2008; Brodie et al. 2011). After completely drying, the sample can be analyzed on an elemental analyzer or combusted for further isotopic analysis (Kennedy et al. 2005; Brodie et al. 2011). Previous studies have tested different conditions (e.g., varying concentrations of HCl used to remove IC in the sediment; Brodie et al. 2011) in order to evaluate changes in OC ^{13}C composition ($\delta^{13}\text{C}$) during acid rinsing (Jaschinski et al. 2008; Komada et al. 2008; Ramnarine et al. 2011). These studies demonstrated that some organic components may be lost during the rinsing process, thus influencing measured isotope

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ratios (Komada et al. 2008; Brodie et al. 2011). Acid fumigation exposes samples to vaporous acid in a sealed desiccator to remove IC. Prior studies have examined variations in carbon isotopic composition after acid fumigation as a function of acid exposure duration (Komada et al. 2008; Brodie et al. 2011), and concluded that isotopic compositions can vary depending on duration of fumigation as well as acid concentration. However, the question about how specific changes in OC components during the acid treatment lead to alteration of isotopic signatures remains unresolved, hindering our understanding of discrepancies in ^{14}C contents between different acid treatments and selection of optimal IC removal methods.

A recently developed analytical approach allows separation of OC components in sediments by their thermochemical stability when exposed to a linear temperature program (Rosenheim et al. 2008). This method has been successfully applied to both river and ocean sediments and holds great potential for shedding new light on ^{14}C age variations within sedimentary organic matter (OM) (Plante et al. 2013; Schreiner et al. 2014; Williams et al. 2015; Hemingway et al. 2017a; Bao et al. 2018a, 2018b). The methodology is relatively straightforward, involving ramped-pyrolysis-oxidation (RPO) followed by ^{14}C analysis of evolved CO_2 collected over user-defined temperature (time) windows. This simple yet effective approach can yield a broad spectrum of ^{14}C ages that provides novel insight into the composition and age of organic components.

In order to address changes of ^{14}C contents of OM after acidification, and to evaluate changes in the resulting OC concentrations and isotopic compositions under different acid treatments, we here apply the RPO technique to sediment residues prior to and after different acidification protocols. Focus is placed on the differences in OC ^{14}C contents between two commonly used acid treatments—rinsing and fumigation. This study represents the in-depth results of the first systematic comparison of ^{14}C contents of organic components after the two most common acid treatments.

MATERIALS AND PROCEDURES

In this study, we selected six aquatic sediment samples that represent both marine and fluvial settings (Figure 1 and Table 1). Low carbonate marine sediments were obtained from the Nantucket Mud Patch (“Nan,” fine-grained sediment; Bothner et al. 1981; Poppe et al. 1991) and Buzzards Bay (“Buzz,” silty-clay sediment; McNichol et al. 1988); high carbonate deep-sea sediments were obtained from Bermuda Rise (“Berm”), Sierra Leone Rise (“Sierra”), and Ceara Rise (“Ceara”) (Martin et al. 2000); and one river suspended particulate matter (SPM) sample was obtained from the Taunton River (“Taun”). All sample materials were freeze-dried, homogenized, and preserved in a desiccator or dry box until analysis. All sample preparation and analyses were conducted at the National Ocean Sciences Accelerator Mass Spectrometry Facility (NOSAMS) at the Woods Hole Oceanographic Institution (WHOI).

Acidification Methods

Rinse_{HCl}

The first acid treatment we used was HCl rinsing (*Rinse_{HCl}*). In this treatment, samples were first acidified and then rinsed with Milli-Q water prior to combustion. All glassware used was pre-combusted at 550°C for 5 hr prior to use. Each sample (~2–3 g dry weight) was weighed into a 60-mL glass centrifuge tube and 10 mL of 1.0 N HCl was added (Fisher Trace Metal Grade, A508-P212). After gentle agitation, the glass tubes were placed in a 60°C water bath for 1 hr. The samples were then centrifuged (2500 rpm) and the aqueous acid solutions were carefully pipetted out. The above steps were repeated until no visible dissolution was present. To remove residual acid, Milli-Q water (10 mL) was added to the centrifuge tubes, which were then

Table 1 Sample locations and results of bulk measurements.

Sample name	Carbonate (%)	OC contents ($\pm 0.11[1\sigma]$, %)	Pretreatment	Bulk	
				$\delta^{13}\text{C}$ ($\pm 0.1[1\sigma]$, ‰)	Fm
Nantucket Mud (Nan) (40°29.6'N, 70°13.6'W)	1.4	1.2	Rinse _{HCl}	−21.3	0.8236 \pm 0.0039 (n = 32)
		1.4	Fume _{HCl}	−20.9	0.8324 \pm 0.0020
			Non-acidification	−19.6	0.8434 \pm 0.0017
Buzzard's Bay (Buzz) (41°31.3'N, 70°45.7'W)	1.3	1.8	Rinse _{HCl}	−21.1	0.9121 \pm 0.0031 (n = 7)
		2.0	Fume _{HCl}	−20.9	0.9073 \pm 0.0041
			Non-acidification	−20.5	0.9244 \pm 0.0018
Taunton River (Taun) (41°52.0'N, 71°05.0'W)	1.4	0.3	Rinse _{HCl}	−27.4	0.6519 \pm 0.0017
		0.5	Fume _{HCl}	−27.5	0.7133 \pm 0.0017
			Non-acidification	−27.2	0.7521 \pm 0.0014
Bermuda Rise (Berm) (33°41.6'N, 57°36.7'W)	30.3	0.4	Rinse _{HCl}	−21.5	0.5072 \pm 0.0016
		0.4	Fume _{HCl}	−20.7	0.5284 \pm 0.0054
			Non-acidification		n.d.
Ceara Rise (Ceara) (6°0.0'N, 42°30.0'W)	41.8	0.7	Rinse _{HCl}	−19.5	0.7874 \pm 0.0022
		0.5	Fume _{HCl}	−19.5	0.7756 \pm 0.0030 (n = 2)
			Non-acidification		n.d.
Sierra Leona Rise (Sierra) (5°56.0'N, 21°26.1'W)	45.7	0.4	Rinse _{HCl}	−16.6	0.1563 \pm 0.0012
		0.7	Fume _{HCl}	−17.6	0.1619 \pm 0.0012
			Non-acidification		n.d.

Note: n.d. indicates not determined.

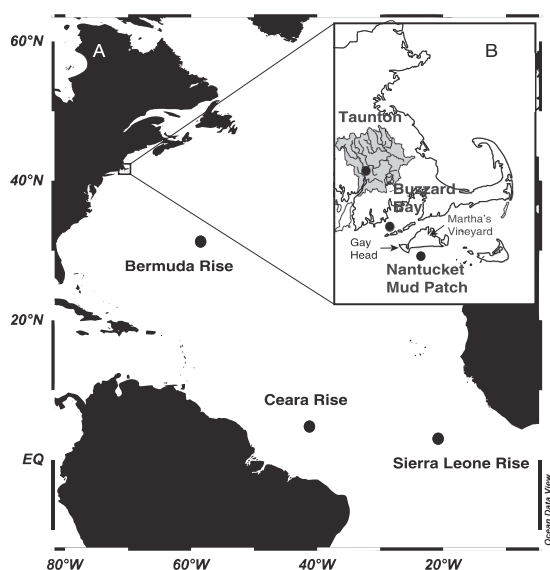


Figure 1 Locations of all six samples with high (A) and low (B) carbonate concentrations.

agitated, centrifuged, and decanted as above (repeated three times). Finally, the samples were vacuum filtered onto a pre-combusted GF/F filter (0.7 μm) using a glass funnel, placed into a petri dish, and dried (60°C, 24 hr).

Fume_{HCl}

The second acid treatment we used was HCl fumigation (Fume_{HCl}). Freeze-dried samples (~2–3 g dry weight) were weighed into 5 cm diameter pre-combusted glass petri dishes. A beaker filled with approximately 50 mL of 37% HCl (Fisher Trace Metal Grade, A508-P212) was placed at the bottom of a 250 mm ID glass desiccator, and samples were placed on a ceramic tray above the acid. The desiccator was evacuated and samples were treated at 60°C for 72 hr. To remove excess acid and residual chloride ions (that would otherwise corrode the RPO instrument), the samples were neutralized by replacing the acid beaker with ~20 g NaOH pellets in a pre-combusted petri dish after fumigation. The desiccator containing the acidified samples with NaOH pellets was again evacuated and placed in an oven (60°C, 72 hr). The acidified samples were stored in a drying oven (60°C) prior to analysis.

Bulk Measurements

Resulting total OC contents (TOC) and carbon isotopic compositions after both acid treatments (Rinse_{HCl} and Fume_{HCl}) were determined using an elemental analyzer (Costech, ECS 4010). Samples (~20 mg) were weighed into 5 × 9 mm tin capsules and combusted in the elemental analyzer at 1025°C. The generated CO₂ was trapped cryogenically, separated from the helium carrier gas, and stored for ¹³C and ¹⁴C measurements (McNichol et al. 1994). The precision (standard deviation, σ) of measured TOC content is 0.11 % (1 σ , n = 26). Approximately 7% of the gas was taken for stable isotope determination via isotope ratio mass spectrometry on either a VG

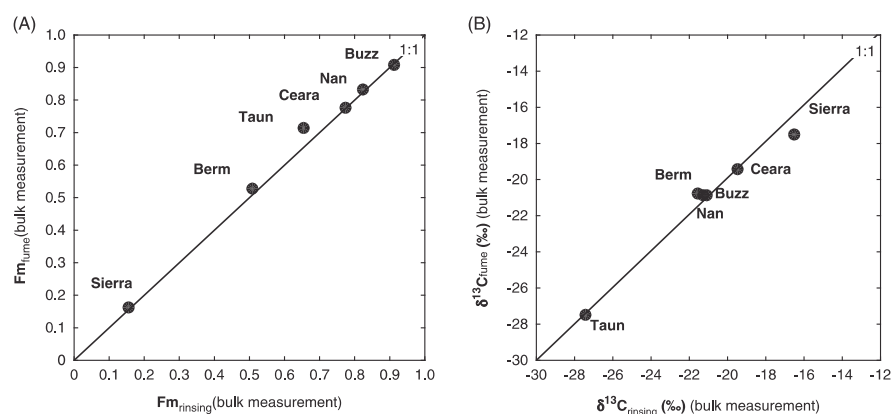


Figure 2 Cross-plots of bulk measurements (A: Fm and B: $\delta^{13}\text{C}$) between Rinse_{HCl} and Fume_{HCl}.

Optima or VG Prism dual-inlet stable isotope ratio mass spectrometer. $\delta^{13}\text{C}$ values, reported in per mille notation (‰) relative to Vienna Pee Dee Belemnite (VPDB), were determined with precision better than ± 0.1 ‰ (1 σ). The remaining CO_2 was reduced with H_2 to filamentous (graphitic) carbon using standard procedures (McNichol et al. 1992; von Reden et al. 1998) and ^{14}C analysis was conducted at NOSAMS (Longworth et al. 2015). ^{14}C data are reported using Fraction modern (Fm) notation and corresponding errors are shown in Table 1 and Figure 2.

Ramped Pyrolysis/Oxidation (RPO)

Unacidified and acidified samples were analyzed using the RPO system at NOSAMS. Pre-weighed samples (~35–400 mg) were loaded into a pre-combusted quartz reactor, and subjected to a constant rate of temperature increase (5°C min^{-1}) until reaching 900°C . Evolved gases were simultaneously oxidized and removed from the reactor using a carrier gas mixture of O_2 and He ($\sim 8\% \text{O}_2$, 35 mL min^{-1} total flow rate). Gases other than CO_2 that are deleterious to the analysis (e.g., SO_2 , vapor HCl) were subsequently removed by passage over CuO, Ag, and MnO catalyst (“chemical oven”) held at isothermal conditions ($\sim 520^\circ\text{C}$) (Froelich 1980; Fry et al. 1996). No significant isotopic fractionation was observed as a consequence of this step (see *Supplementary Material* for further details). Downstream of the chemical oven, a continuous record of evolved CO_2 was obtained via a flow-through infrared CO_2 analyzer (Sable Systems International Inc., CA-10a). The evolved CO_2 was collected within five different temperature intervals (T_n ; indicated in Table 2 and Figure 3 and 4, except that Taun sample has six thermal intervals). After isolation, the individual CO_2 fractions were further distilled and quantified using standard vacuum line techniques and sealed into combusted glass tubes with $\sim 50 \text{ mg}$ CuO and 10 mg Ag granules. Tubes were subsequently combusted (525°C , 1 hr) as a final gas purification step prior to isotopic measurement. CO_2 was then split into two aliquots for ^{13}C and ^{14}C analyses.

RESULTS AND DISCUSSION

The results from carbon isotopic analysis of bulk unacidified, Rinse_{HCl}, and Fume_{HCl} samples are listed in Table 1, with discrepancies between two acidification methods highlighted in Figure 2. The offsets of Fm values range from 0.0614 ± 0.0034 (Taun) to 0.0048 ± 0.0072 (Buzz); the offsets of $\delta^{13}\text{C}$ values range from <0.1 (Ceara) to 1.0‰ (Sierra). In low-carbonate sediments, bulk Fm

Table 2 Radiocarbon data of each thermal fraction among acidified and non-acidified samples.

Sample name	Acid treatment	Fraction modern (Fm)					
		T ₁ fraction [§] (100–255°C)	T ₂ fraction (255–332°C)	T ₃ fraction (332–433°C)	T ₄ fraction (443–558°C)	T ₅ fraction* (558–900°C)	T ₆ fraction (692–900°C)
Nan	Rinse _{HCl}	0.8970 ± 0.0019	0.8725 ± 0.0018	0.8611 ± 0.0017	0.7581 ± 0.0024	0.3854 ± 0.0030	
	Fume _{HCl}	0.9098 ± 0.0019	0.8943 ± 0.0018	0.8395 ± 0.0017	0.6753 ± 0.0016	0.2327 ± 0.0040	
	Non-acidification	0.8964 ± 0.0019	0.9046 ± 0.0019	0.8683 ± 0.0020	0.7709 ± 0.0016	0.3167 ± 0.0023	
Buzz	Rinse _{HCl}	1.0162 ± 0.0022	0.9796 ± 0.0020	0.9399 ± 0.0019	0.8293 ± 0.0019	0.3565 ± 0.0016	
	Fume _{HCl}	1.0398 ± 0.0022	1.0048 ± 0.0023	0.8767 ± 0.0019	0.5880 ± 0.0023	0.1779 ± 0.0024	
	Non-acidification	1.1581 ± 0.0023	1.0419 ± 0.0024	0.9854 ± 0.0021	0.7934 ± 0.0016	0.2854 ± 0.0016	
Taun	Rinse _{HCl}	0.9197 ± 0.0034	0.9007 ± 0.0018	0.7689 ± 0.0017	0.3950 ± 0.0016	0.1154 ± 0.0027	0.0337 ± 0.0032
	Fume _{HCl}	0.9381 ± 0.0020	0.8508 ± 0.0017	0.6566 ± 0.0015	0.4673 ± 0.0011	0.1230 ± 0.0011	0.1064 ± 0.0010
	Non-acidification	0.9851 ± 0.0020	0.9218 ± 0.0020	0.7195 ± 0.0015	0.3215 ± 0.0011	0.0742 ± 0.0010	0.0011 ± 0.0011
Berm	Rinse _{HCl}	0.6052 ± 0.0020	0.5061 ± 0.0020	0.4928 ± 0.0021	0.4854 ± 0.0034	0.1622 ± 0.0029	
	Fume _{HCl}	0.6281 ± 0.0022	0.5865 ± 0.0016	0.5160 ± 0.0014	0.3637 ± 0.0018	0.2544 ± 0.0031	
	Non-acidification	0.6716 ± 0.0027	0.6496 ± 0.0017				
Ceara	Rinse _{HCl}	0.8147 ± 0.0018	0.7986 ± 0.0017	0.8097 ± 0.0021	0.8231 ± 0.0017	0.4209 ± 0.0024	
	Fume _{HCl}	0.5653 ± 0.0341	0.7934 ± 0.0023	0.7864 ± 0.0021	0.7557 ± 0.0021	0.5086 ± 0.0036	
	Non-acidification	0.669 ± 0.0022	0.7871 ± 0.0016				
Sierra	Rinse _{HCl}	0.1672 ± 0.0010	0.1465 ± 0.0010	0.1589 ± 0.0008	0.1775 ± 0.0020	0.1007 ± 0.0048	
	Fume _{HCl}	0.2048 ± 0.0040	0.1778 ± 0.0029 [#]	0.1589 ± 0.031	0.1562 ± 0.0021 [#]	0.1615 ± 0.0014	
	Non-acidification	n.d.	0.2386 ± 0.0042				

*T₅ fraction in Taun sample is a range of temperature (558–692°C).[§]T₁ fractions in Nan, Taun, and Ceara sample start from 120°C, T₁ fraction in Sierra starts from 157°C. T₅ fractions in Sierra and Ceara sample stops at 835°C and 723°C, respectively. The non-trapped CO₂ account for <1% of total mass, which do not affect the mass balance results shown in supplementary Figure S1.[#]Indicates that results are average values (n = 2).

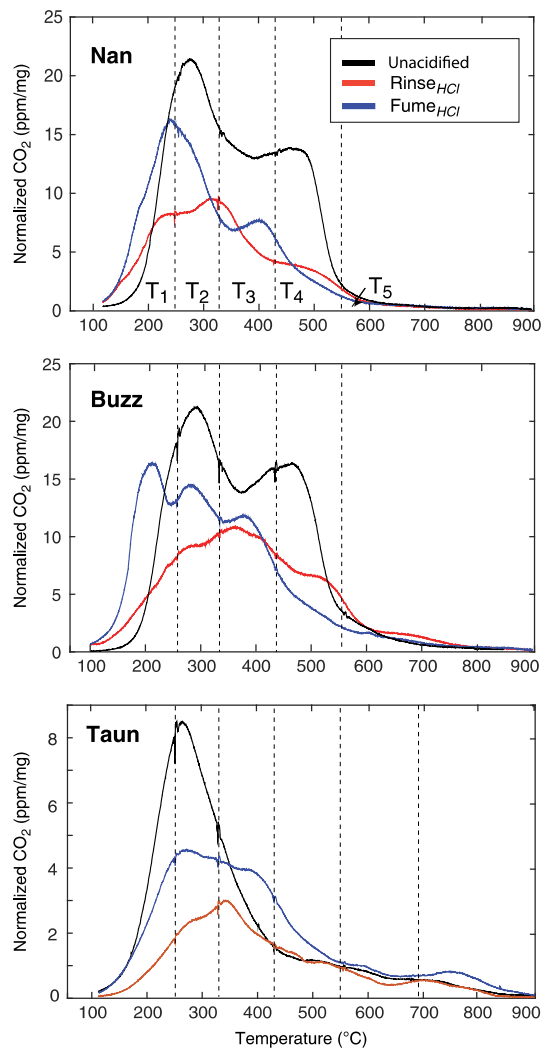


Figure 3 Thermograms displaying CO₂ evolution for the acidified and unacidified samples with low carbonate content during RPO. The dotted lines show temperature interval “windows.” The CO₂ concentrations are normalized by the mass of sediments loaded into the RPO instrument. Taking Nan sample as an example, T₁, T₂, T₃, T₄, and T₅ are labeled.

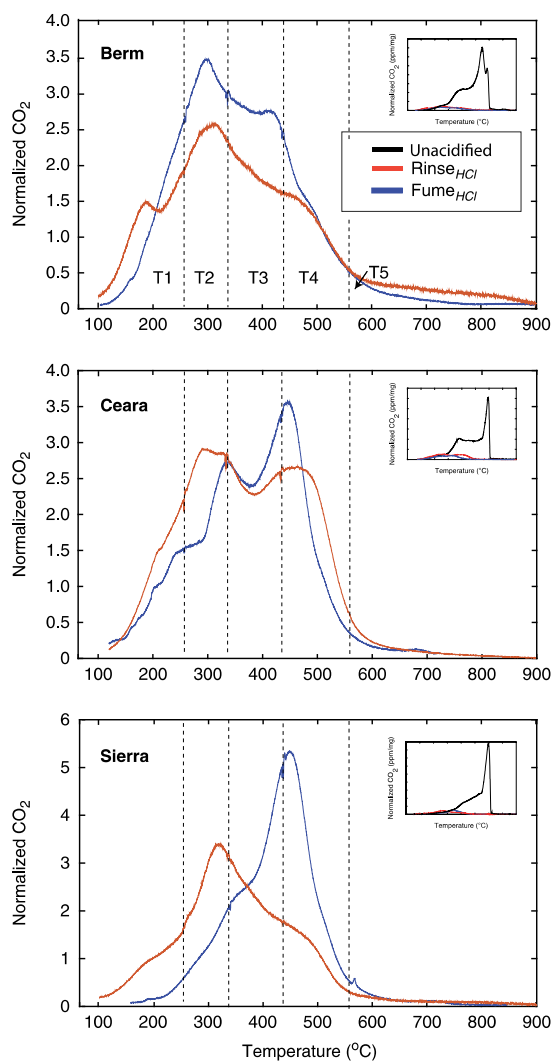


Figure 4 Thermograms displaying CO₂ evolution for the acidified and unacidified samples with high carbonate content during RPO. The dotted lines show temperature interval "windows." The inserts show the full Y axis scales. The CO₂ concentrations are normalized by the total mass. Taking Berm sample as an example, T₁, T₂, T₃, T₄, and T₅ are labeled.

and $\delta^{13}\text{C}$ values of unacidified samples are generally higher than those of sediments subjected to either acidification method (Table 1). This likely reflects the presence of biogenic IC that is enriched in ^{14}C (younger ^{14}C age) and ^{13}C (higher $\delta^{13}\text{C}$) relative to OC. Indeed, modern biogenic

Table 3 Stable carbon isotopic composition data of each thermal fraction among acidified and non-acidified samples.

Sample name	Acid treatment	$\delta^{13}\text{C}$ (± 0.1 [1 σ], ‰)					
		1 fraction	2 fraction	3 fraction	4 fraction	5 fraction	6 fraction
Nan	Rinse _{HCl}	−22.3	−21.6	−21.2	−22.8	−23.8	
	Fume _{HCl}	−23.2	−20.5	−22.2	−26.1	−23.4	
	Non-acidification	−24.3	−21.2	−19.9	−18.3	−22.3	
Buzz	Rinse _{HCl}	−21.5	−20.8	−21.2	−22.2	−23.7	
	Fume _{HCl}	−22.5	−20.1	−21.9	−25.7	−24.8	
	Non-acidification	−26.3	−22.6	−20.7	−21.2	−22.6	
Taun	Rinse _{HCl}	−30.9	−30.8	−29.2	−28.1	−26.3	−25.4
	Fume _{HCl}	−31.8	−31.3	−32.0	−27.6	−24.7	−24.1
	Non-acidification	−30.7	−28.7	−27.5	−26.2	−25.1	−25.4
Berm	Rinse _{HCl}	−21.9	−21.1	−21.8	−23.8	−26.4	
	Fume _{HCl}	−23.2	−24.2	−21.5	−31.5	−27.8	
	Non-acidification	−17.2	−14.5	−3.8	0.3	−0.4	
Ceara	Rinse _{HCl}	−21.4	−20.1	−19.4	−20.4	−22.3	
	Fume _{HCl}	−24.4	−23.0	−21.3	−29.2	n.d.	
	Non-acidification	−21.8	−14.0	−5.1	−0.3	0.7	
Sierra	Rinse _{HCl}	−21.6	−17.1	−16.5	−16.9	−22.7	
	Fume _{HCl}	−22.4	−21.4	−17.2	−18.2	−26.1	
	Non-acidification	n.d.	−13.7	−4.9	−0.1	0.0	−8.2

carbonates (e.g., mollusk shells, foraminiferal tests) in coastal and riverine settings, likely contribute to the enriched carbon isotopic compositions ($F_m > 1$, Druffel et al. 1986; McNichol and Aluwihare 2007; $\delta^{13}\text{C} = \sim 0$ ‰, Meyer 1994; Martin et al. 2000). Thus, IC in unacidified samples contributes to the enrichment in isotopic composition for bulk measurements.

However, based solely on bulk results from unacidified and/or acidified samples, it is difficult to evaluate whether or how the different acidification methods influence the ^{14}C results. In order to better understand underlying factors, we utilize RPO to examine the isotopic differences of thermally separated components of the OM before and after acidification. This study yields improved insights into changes in the content and isotopic distribution of OC introduced by different methods of IC removal. The RPO analyses of samples after Rinse_{HCl} and Fume_{HCl} and corresponding unacidified samples show different thermograms (Figure 3 and 4). In the low-carbonate samples, the Fume_{HCl} thermograms contain more carbon than those after Rinse_{HCl} (integrated area ratios of Rinse_{HCl} thermograms to Fume_{HCl} thermograms: 0.8:1 (Nan), 0.8:1 (Buzz), and 0.6:1 (Taun)). The major difference between the thermograms from the two methods occurs in the relatively low temperature windows (e.g., T_1 and T_2) (Figure 3). In contrast, for the high-carbonate samples, the greatest differences are seen in the relatively higher temperature windows (e.g., T_3 and T_4). Tables 2 and 3 summarize the variability of F_m and $\delta^{13}\text{C}$ values among thermal windows obtained from both low- and high-carbonate samples.

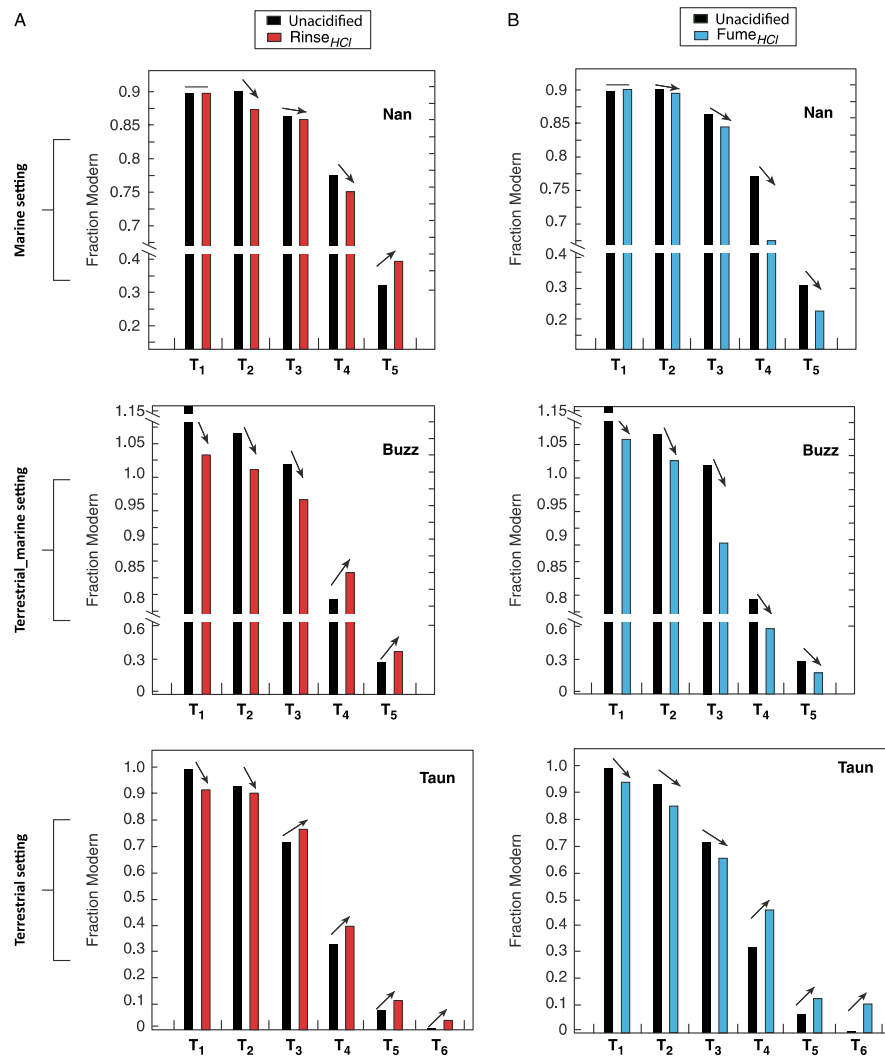


Figure 5 Comparisons between unacidified vs. Rinse_{HCl} (A panels) and unacidified vs. Fume_{HCl} (B panels) Fm values for all thermal fractions from low-carbonate samples.

Low-Carbonate Samples

We find that the Fm values of low temperature fractions following Rinse_{HCl} treatment are lower relative to those of corresponding fractions from unacidified samples (Figure 5A). It is possible that IC with higher Fm values contributes to all the thermal fractions of unacidified samples. However, this is not supported by associated $\delta^{13}\text{C}$ data, since $\delta^{13}\text{C}$ values of the lowest

temperature fractions (T_1) of unacidified Nan and Buzz samples are lower than those in the corresponding Rinse_{HCl} fractions (Table 3). The above therefore implies that influences of (residual) IC are not primarily responsible for the Fm offsets between unacidified and Rinse_{HCl} samples. The thermograms of low-carbonate samples subjected to Rinse_{HCl} produce markedly less CO₂ (i.e. the integral of CO₂ concentrations during RPO) than the corresponding unacidified samples (Figure 3). Acid treatment can lead to removal of OC in addition to IC during Rinse_{HCl}, likely either through solubilization or acid hydrolysis (Brodie et al. 2011; Harris and Juggins 2011). For example, hydrolysis, in the presence of dilute acid, can convert esters present in macromolecules into a carboxylic acid and an alcohol (Charton 1975; Li 1993); these soluble and labile compounds may be removed during the rinsing process (Komada et al. 2008). The decrease in Fm value of low temperature fractions (Figure 5A) likely reflects the removal of organic material with relatively high Fm (i.e. young) during the Rinse_{HCl} method. According to the definition of thermal stability and nature of OM from Capel et al. (2006) and reference therein, the OC decomposed at <400°C is considered as “labile OC.” The data collected here suggest that application of the Rinse_{HCl} method to low-carbonate samples can lead to the loss of young, thermally labile, OC. The amount lost will depend on the chemical characteristics of OM in the low-carbonate sample. While thermal stability of OM in sediment does not completely represent the chemical stability, the former can reflect the latter (Kleber et al. 2011). Therefore, the accuracy of OM ¹⁴C measurements using Rinse_{HCl} is related to the overall thermal, and likely chemical, lability of OM within samples.

The Fm values of the highest temperature windows for low-carbonate samples (Nan and Buzz) under Rinse_{HCl} are higher than those of the unacidified ones (Figure 5A). The $\delta^{13}\text{C}$ values of the T_5 fractions under Rinse_{HCl} are higher than those of corresponding unacidified fractions (Table 3). The finding implies a loss of old and ¹³C enriched material during Rinse_{HCl}, either carbonate or ¹³C-enriched organic material. Fm values for different thermal windows generally decrease with increasing temperature (Table 2), indicating that the thermally recalcitrant OM is older (lower Fm values). The observed changes of Fm and $\delta^{13}\text{C}$ values of the highest temperature windows indicate the loss of some older and refractory components, with relatively enriched ¹³C, during Rinse_{HCl}. These losses must be small based on the minor shift in the thermograms. It is not possible for us to distinguish if the material loss is carbonate or OM. A potential source of old carbonate near the Nan and Buzz samples is siderite from Gay Head in Martha's Vineyard. Outcrops of older sedimentary carbonate rock may be eroded and deposited in Buzzards Bay and the Nantucket Mud Patch. However, this is unlikely based on the reported absence of siderite in Nan sediments (Poppe et al. 1991).

Application of the Fume_{HCl} method to the coastal marine sediments (Nan and Buzz samples) results in lower Fm values for almost all thermal fractions relative to their unacidified counterparts (Figure 5B, the T_1 fraction from Nan sample is the exception). One potential explanation is degradation of ¹³C- and ¹⁴C-enriched OC during Fume_{HCl}. Although the Fume_{HCl} method does not include a rinsing step, there is a potential for OM to be degraded. Since HCl can react with OM, especially at the relatively high temperature used in the acidification (>60°C) (Csapá et al. 1997), we suspect that younger OC enriched in ¹³C is lost through the hydrolysis of labile OM (Trumbore and Zheng 1996; Schmidt and Gleixner 2005). Additionally, the low-carbonate samples do not reveal any discrepancy between reconstructions of CO₂ isotopic compositions from RPO mass-balance under Fume_{HCl} and corresponding bulk values (supplementary Figure S1). The $\delta^{13}\text{C}$ values for the high temperature fractions, where the influence of IC removal is expected to be the greatest, under Fume_{HCl} are lower than corresponding windows from the unacidified aliquots (Table 3), indicating that IC is effectively

removed during Fume_{HCl}. We suggest that the observed decreases of Fm values under Fume_{HCl} relative to their unacidified counterparts do not result from potential remains of IC, but from degrading younger and labile components and leaving more refractory organic parts that may be more depleted in ¹³C and ¹⁴C. As with the Rinse_{HCl} results, we find that the Fm values of the low temperature fractions following Fume_{HCl} are lower relative to the corresponding fractions in the unacidified samples. The thermograms in the low temperature range of the low carbonate samples after Fume_{HCl} generate more CO₂ than those after Rinse_{HCl} but smaller than the unacidified samples (Figure 3). We speculate that Fume_{HCl} removes OM, particularly in thermally labile fractions.

The variability in Fm values for the different treatments of the riverine sample (Taun) differs from the coastal marine sediments (Figure 5). In the higher temperature fractions (T₅, T₆), the Fm and δ¹³C values using Fume_{HCl} are both higher than those in their unacidified fractions (Table 2 and 3). We speculate that the different patterns of variability in Fm values between Nan and Buzz, and Taun samples are likely related to the environmental matrix. The OC from the marine samples is primarily marine, while the OC from the river sample is mainly terrestrial. The distinct OC sources are likely an important factor influencing the Fm values measured on OM after Fume_{HCl} (Brodie et al. 2011). A broad distinction may exist between deep oceanic vs. terrestrially-involved marginal samples in terms of their susceptibility to different acid hydrolysis methods (Roland et al. 2008) as indicated by distinct Fm values of carbohydrates and amino acids. Studies of more samples from different environmental and depositional settings will be required to fully investigate the influence of Fume_{HCl} on Fm values of refractory OC in low-carbonate samples.

Rinse_{HCl} versus Fume_{HCl} for Low-Carbonate Samples

Bulk Fm offsets between Fume_{HCl} and Rinse_{HCl} fall within 2σ of each other (standard deviation) (Figure 2A), but RPO analysis indicates the methods have different impacts on the OC (Figure 3). RPO yields for the samples treated with Fume_{HCl} are greater in the low temperature range than for those treated with Rinse_{HCl}. Rinse_{HCl} has a greater impact on labile OM than Fume_{HCl}. The Fm values of T₁ fractions after Fume_{HCl} are slightly higher (younger) than those after Rinse_{HCl} (Figure 6), yet, the offsets are not marked. This suggests that both methods have a similar impact on the Fm values of OC in samples with mostly labile and younger OC. In contrast, the highest temperature windows show marked Fm differences for Nan and Buzz samples. The Fm values of high temperature fractions after Rinse_{HCl} are higher (younger) than those after Fume_{HCl}, suggesting that Fume_{HCl} may remove the more relatively ¹⁴C-enriched components from refractory OM in marine sediment, compared with Rinse_{HCl}. This implies that samples containing more thermally stable, i.e. refractory, OC will show greater differences between the two methods. An implication of this finding is that thermally labile OC is ¹⁴C homogeneous but thermally refractory OC is more heterogeneous. Results from the riverine sample (Taun) show more modest differences, and in opposite directions to those of coastal marine sediments. Overall, these findings suggest that the application of either method to low-carbonate samples comprised mostly of labile OM will result in similar Fm values. However, samples containing a marked proportion of refractory OM may yield different Fm values depending on the method employed as well as the environmental and depositional conditions.

High-Carbonate Samples

Compared with low-carbonate samples, removing IC from high-carbonate samples is more difficult (Phillips et al. 2011). Due to the high abundance of IC in unacidified samples, their RPO thermograms are characterized by large total peak areas (Figure 4B, inserts). We did not

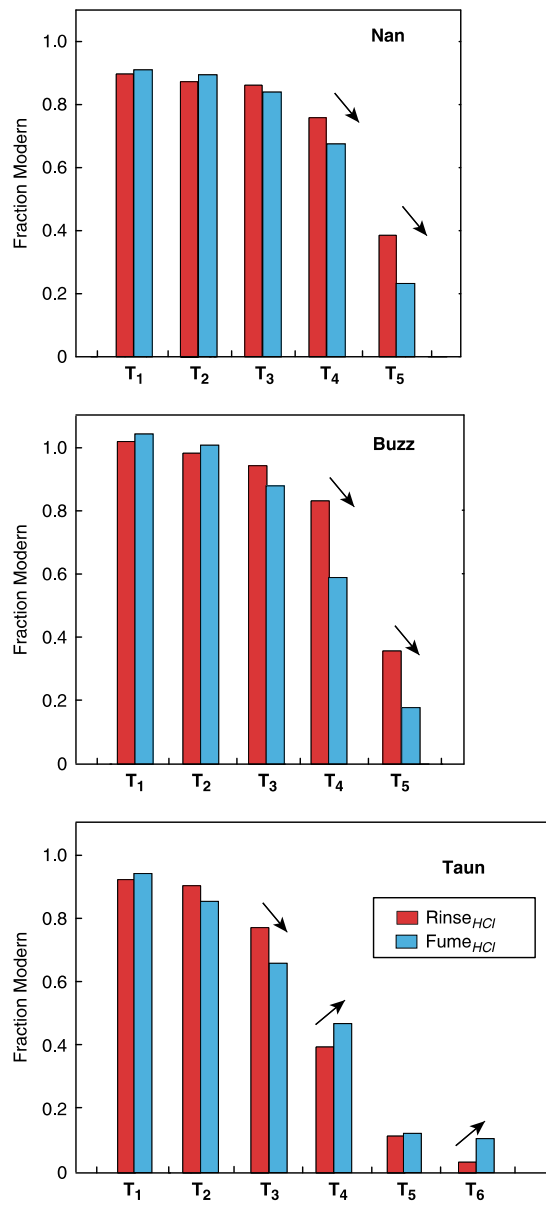


Figure 6 Comparisons of Fm values for thermal windows of low-carbonate samples under Rinse_{HCl} and Fume_{HCl}.

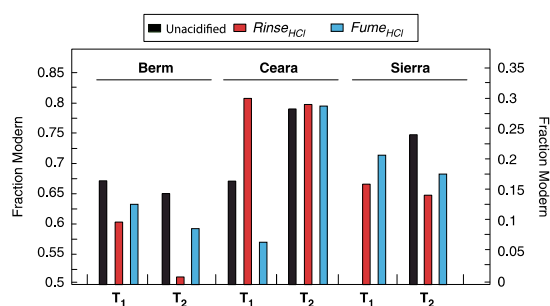


Figure 7 Comparisons of low-temperature fraction Fm values resulting from Rinse_{HCl}, Fume_{HCl}, and unacidified treatments for high-carbonate samples. Berm and Ceara samples response to left y-axis, Sierra sample responses to right y-axis.

make ^{14}C measurements on the high temperature fraction of these samples. In high carbonate samples, IC may start to decompose at lower temperatures than expected based on thermodynamics due to non-first-order decay (Rosengard 2017; Hemingway et al. 2017b). The $\delta^{13}\text{C}$ results suggest that IC can be present in even the lowest temperature interval in some instances (T₁, Berm) (Table 3). The $\delta^{13}\text{C}$ results also indicate that IC is effectively removed by both acidification methods.

We note that the T₁ window from the Ceara sample under Rinse_{HCl} has a higher Fm (0.8147 ± 0.0018) value than the same interval in the unacidified sample (0.6690 ± 0.0022 ; Figure 7 and Table 2). Due to their similar $\delta^{13}\text{C}$ values (-21.4‰ and -21.8‰ , respectively), we suggest that Rinse_{HCl} removes relatively low Fm components from the thermally labile OM (T₁, lowest temperature window) in this sample. We cannot make similar inferences for the Berm and Sierra samples, because the $\delta^{13}\text{C}$ data do not support the suggestion. In the Berm sample, the $\delta^{13}\text{C}$ value of T₁ windows of unacidified Berm sample is much higher (-17.2‰) than that of corresponding Rinse_{HCl} sample (-21.9‰), and, in the Sierra sample, we do not have the $\delta^{13}\text{C}$ data. Nevertheless, the Ceara results indicate that it is possible for high-carbonate samples to lose relatively old organic components during Rinse_{HCl} processes (Komada et al. 2008).

After Fume_{HCl}, the $\delta^{13}\text{C}$ values of the T₁ fractions are lower than after Rinse_{HCl} (Table 3). If Rinse_{HCl} completely removes IC in the T₁ windows as discussed above, we can infer that Fume_{HCl} also removes IC completely in this window. Similarly, we also note that the T₁ window from the Ceara sample under Fume_{HCl} (0.5653 ± 0.0341) has lower Fm values than the T₁ windows in the corresponding unacidified sample (0.6690 ± 0.0022 , Table 2), suggesting that Fume_{HCl} may remove OM with a relatively high Fm. It is likely that acid hydrolysis contributes to the change in the Fm value of labile OC after Fume_{HCl}. IC reacts with HCl to produce H₂O and CaCl₂ during Fume_{HCl}. Since CaCl₂ is hygroscopic (i.e., it absorbs water), this can lead to the formation of a concentrated acid pool in the petri dish containing the sample. Compared with the short duration (1 hr) of Rinse_{HCl} treatment, the markedly longer sample exposure time period during Fume_{HCl} (i.e., 72 hr) may lead to high *in situ* acid concentrations, favoring hydrolysis that can change the ^{14}C content of OC. Results from Komada et al. (2008) support this interpretation, as they indicated that fumigation time is an important factor when considering the consequences of acidification. Our results indicate that Fume_{HCl} affects the Fm results in an unpredictable manner (Table 2). In summary, Rinse_{HCl} and Fume_{HCl} both affect

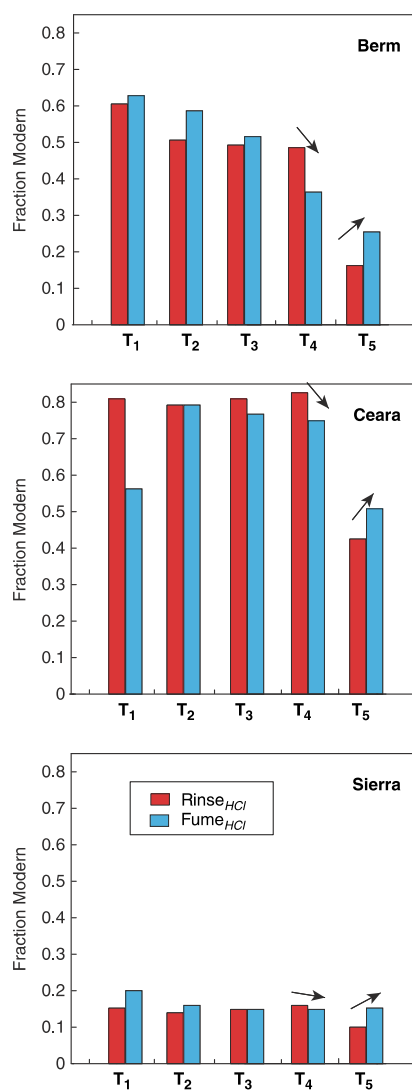


Figure 8 Comparisons of Fm values for thermal windows of high-carbonate samples under Rinse_{HCl} and Fume_{HCl}.

the Fm values of OC in the high-carbonate samples, probably causing the increasing and decreasing corresponding Fm values for labile organic components, respectively. Due to the overwhelming IC contribution in the higher temperature windows of unacidified samples, we cannot compare the Fm results in these fractions and make conclusions about the influence of two acidifications on the Fm values of refractory OM.

Rinse_{HCl} versus Fume_{HCl} for High-Carbonate Samples

We compare the Fm values of corresponding RPO thermal windows of three high-carbonate samples under Fume_{HCl} and Rinse_{HCl}. The Fm values of T₄ window after Rinse_{HCl} are higher than those after Fume_{HCl}; in contrast, the Fm values of T₅ window after Rinse_{HCl} are lower than those after Fume_{HCl} (Figure 8), suggesting that the methods have opposite effects on Fm values for the thermally refractory organic components. Since the T₄ fraction contains much more carbon than T₅, we suggest that Fume_{HCl} will produce lower Fm values for the thermally refractory OM than Rinse_{HCl}. For the low temperature fractions, the measured Fm values do not show clear a trend between the two methods (Figure 8).

Factors Influencing ¹⁴C Results during Acidification Treatment

IC abundance in the samples is an important factor differently influencing the ¹⁴C contents under Rinse_{HCl} or Fume_{HCl}. For instance, Rinse_{HCl} appears to result in greater removal of young components from labile OM pools in low-carbonate samples but old components in high-carbonate samples. Nevertheless, Fume_{HCl} can cause Fm values of labile organic components to decrease regardless of IC abundance. These differences in Fm values of OC between the two acidification methods are likely dependent on the mineralogy (Komada et al. 2008) and abundance of IC (Philips et al. 2011) in the samples. Further studies spanning a greater range of IC contents would improve our understanding of the role of IC on ¹⁴C contents following pretreatment, especially with respect to Rinse_{HCl}.

We find that the proportions of labile and refractory OC in sediment samples may influence the impact of the acidification method on bulk OC Fm values. For instance, we find no marked effect of either acidification method on measured Fm values of labile OM in low-carbonate samples, implying that samples dominated by labile OM will likely yield similar bulk OC Fm values when prepared by either acidification method. In contrast, if a sample contains mostly refractory OM (e.g., river samples with a large percentage of refractory OC; Hemingway et al. 2018), bulk Fm values under two methods will likely be different. We think that RPO can be a good screening method for choosing an appropriate acidification treatment for a suite of similar samples by defining heterogeneous ¹⁴C contents in a sediment sample. Alternative less direct methods, such as determining the C/N ratio, can be used to define OC heterogeneity before measuring ¹⁴C content. The C/N ratio can be used to distinguish between algal and land-plant origins of sedimentary OM, and selective degradation of organic components during early diagenesis (Meyers 1994).

In addition, the environmental matrix of samples should also be considered when choosing an acidification method. For low-carbonate samples, results from the marine and river samples exhibit distinct differences in Fm values under Rinse_{HCl} and Fume_{HCl} (Figure 5). This might reflect differing proportions of labile and refractory OC, with varying susceptibility to acidification conditions. Physical factors of sediment matrix can also indirectly affect the labile and refractory OC preservation (Zonneveld et al. 2010). For instance, sediment grain size (Bao et al. 2016, 2018a), density (Wakeham et al. 2009), and mineral surface area (Mayer 1994) may control the partitions of labile and refractory OC preservation in the sample. In addition, during rinsing processes under acidic condition, differing physical protections might affect the extent of labile OC lost. The potential influences of sediment matrix on carbon isotope composition during the pretreatments need be considered as well as studied further. Additionally, intrinsic chemical characteristics of different OM components might determine their susceptibility to hydrolysis during acidification (Trumbore and Zheng 1996; Schmidt and Gleixner 2005). For instance, proteins, amino acids, and

polysaccharides are particularly prone to hydrolysis and/or condensation reactions during acid-treatment (Li 1993; Sun and Cheng 2002). In summary, RPO analysis has provided insights into the impact of different acid treatments on the ^{14}C content of sedimentary OM, but further research is needed to fully understand the factors influencing the impact of acidification.

CONCLUSIONS

This study provides a systematic comparison of the influence of two common acid treatment methods on the isotopic composition of OC in sediment samples from environmental settings ranging from riverine to marine and characterized by a wide range of carbonate contents (<1.5% to >30.3%). We show that the ^{14}C contents of residual OM are affected by both acid-treatments. Based on the analytical approaches (bulk-level measurements and RPO) and range of sample types used in this study, we conclude:

- For low-carbonate samples, Rinse_{HCl} and Fume_{HCl} methods can lead to the loss of young labile OC, leaving the residual OC older.
- For high-carbonate samples, it is possible to remove relatively old OC during Rinse_{HCl} processes and increase the Fm value of remaining material. Fume_{HCl} may remove more young material than Rinse_{HCl} (e.g., labile OC) leading to lower measured Fm values on sediment.
- Overall, there appear to be multiple factors that influence the Fm values of OC under different acidification pretreatments. We identify three factors (at least) that influence the measured ^{14}C content of sedimentary OM: IC abundance, proportions of labile and refractory OC, and environmental matrix. We thus recommend taking these factors into account when selecting and applying acidification methods in order to yield consistent results and informed interpretation of resulting data.

For the determination of ^{14}C content in low-carbonate samples, Fume_{HCl} is recommended over Rinse_{HCl} because less OC is lost with this method. For high-carbonate samples, Rinse_{HCl} is recommended because of the complications introduced by high concentrations of hygroscopic salts and the absence of large differences between the results from the two methods. We also recommend choosing a straightforward pre-screening method (e.g., RPO, C/N ratio) to assess the potential ^{14}C heterogeneity of OC prior to acidification for further ^{14}C measurements.

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SUPPLEMENTARY MATERIAL

To view supplementary material for this article, please visit <https://doi.org/10.1017/RDC.2018.125>

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