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UNDERSTANDING THE CARBON ISOTOPIC SIGNATURE IN COMPLEX ENVIRONMENTAL MATRICES

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Abstract

Elementary and isotopic analyses of carbon in environmental matrices usually integrate multiple sources having distinct concentration (wt%) and $^{13}C/^{12}C$ isotopic ratio. Interpretation necessarily needs the characterization of the diverse end-members that usually are constituted by carbonate, organic and elemental components. In this view, we developed a routine protocol based on the analytical coupling of elementary and isotopic compositions that is able to discriminate the inorganic (TIC) and organic (TOC) contributions to the total carbon (TC) content. The procedure is only based on thermal destabilization of the different carbon species and has been successfully applied on different environmental matrices (rocks, soils, biological samples) with a mean C elemental and isotopic recovery of 99% (SD = 3%) and 0.3‰ (SD = 0.3‰), respectively. The thermal speciation lead us to define precise isotopic end-members whose are unaffected by any chemical treatment of the samples. The approach allows accurate mass balance calculation that represents a powerful tool to quantify the distinct carbon species.

Keywords : *carbon, speciation, isotope, environmental matrices*

Introduction

The carbon elementary analysis in its distinct forms (inorganic, organic and elemental) is of fundamental importance for the characterization of environmental matrices. Insights on the nature of the carbon species could be provided by isotopic analyses. Consequently, in the last few decades, thanks to the advances in technology, a widespread diffusion of the Isotope Ratio Mass Spectrometry (IR MS) led to an exponential production of stable isotopes data, i.e. the $^{13}C/^{12}C$ ratio, notionally expressed as $\delta^{13}C$ ($1000*[^{13}C/^{12}C_{sample}-^{13}C/^{12}C_{standard}]/\ ^{13}C/^{12}C_{standard}$). The $\delta^{13}C$ has to be considered a fingerprint of the analyzed material, which in turn integrates distinct isotopic contributions of the different carbon components forming the bulk matrix; this fingerprint is stable over time and in a relative wide range of temperatures. A number of environmental materials identified as primary (natural) or secondary (anthropogenic) carbon sources have been analyzed in these years, thus providing an end-member database that serves as reference for qualitative characterization of samples of unknown origin (Faure, 1986; Michener and Lajtha, 2007). The carbon isotope analysis of multicomponent matrices represents therefore an useful tool that is used for the qualitative identification of their main carbon sources.

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In this framework, uncountable applications are reported in the literature, spanning diverse scientific disciplines. For example, C (wt%) and $\delta^{13}C$ analyses are widely used to examine OM sources, mixing and evolution in sediments (e.g. Meyers, 1997) and to identify nutrient sources and photosynthetic pathways in plants (e.g. C3 and C4 plant differentiation; Meyers, 2003; Sharpe, 2007). In soils these parameters provide the identifications of carbon reservoirs and dynamics in the soil-plant systems (e.g. Harris et al., 2001), and have been successfully used to identify lithogenic and pedogenic carbonates (Nordt et al., 1998), as well as the C3 vs. C4 contributions to Soil Organic Matter (SOM), that in turn give insights on climatic conditions (Morgun et al., 2008). In agronomic studies these tracers also serve to evaluate trophic levels in environmental systems (Bunn et al., 1995; Pinnegar and Polunin, 1999) as well as to understand mineralization processes (e.g. Freudenthal et al., 2001).

Unfortunately, isotopic analyses are often used for qualitative interpretation, whereas quantitative estimates are usually made with other techniques. While the Total Carbon (TC) determination is straightforward, the separation and analysis of the Total Inorganic (TIC) and Organic (TOC) carbon fractions is more complex, time-consuming, cost effective and usually requires the utilization of dangerous chemicals. To achieve these results a number of physico-chemical pre-treatments of the sample have been proposed and developed for the various environmental matrices and the associated carbon fractions, in relation to the different nature of the investigated samples (Walkley and Black, 1934, Froelich, 1980; Cachiers et al., 1989; Caughney and Barcelona, 1994; Serrano et al., 2008; Meyer et al., 2013). Unfortunately, all these analytical protocols invariably require acidification of the sample to remove the TIC prior to the determination of the TOC fraction, either when measured directly by dry combustion or by colorimetric techniques (Soon and Abboud, 1991) after wet chemical oxidation (e.g. Walkley and Black, 1934 for soils). This approach, employing acidification pre-treatment, although very popular is highly debated. Several studies investigated the effects of distinct acidification methods and acid types on distinct environmental matrices, indicating that the procedure variously lead to carbon losses, in turn resulting in a non-linear, sometimes significant, deviations in C (wt%) and $\delta^{13}C$ values (e.g. Serrano et al., 2008; Brodie et al., 2011 and reference therein; Schlacher and Connolly 2014 and reference therein).

Alternative protocols to separate TIC and TOC fractions can be based on thermal methods that exploit their distinctive decomposition temperature intervals. Boyle (2004) shows that for plants and soils most of the OM thermal destabilization occur in the interval between 200 and 500°C, whereas soil carbonates break-down at temperatures between 650-750°C. A more detailed study provided by Pallasser et al. (2013), based on soil thermogravimetric data performed by dry combustion and coupled with mass spectrometry (TGA-MS), suggested a narrower temperatures range 200-430 °C for a reliable determination of soil OC, to avoid contribution from inorganic sources progressively occurring at higher temperatures. This is in agreement with the temperature of 430°C generally suggested for OM determination in soils by Loss On Ignition (LOI; Nelson and Sommers, 1996, Chatterjee et al., 2009). Dry combustion with automated analyzers can also be utilized to determine TIC fraction in environmental matrices. In this case, the measurement involves dry combustion of samples that have to be pre-combusted to remove the OM in an O_2 stream (Rabenhorst, 1988).

In order to overcome the analytical limits (and related problems) of the existing procedures, in this contribution we describe a protocol that allows the quantitative analysis (C wt%) of the distinct forms of carbon coupled with the relative isotopic ratio (δ^{13}C ‰). In this new method the coupled C(wt%) and δ^{13}C(‰) data represent a proxy of each targeted carbon species, which can be selectively extracted on the basis of their distinctive thermal stability. The quantitative estimate of the various carbon species is cross-checked and validated by elemental-isotopic mass balance calculations between the values of TC and those of Total Organic Carbon (TOC) and Total Inorganic Carbon (TIC) fractions.

Materials and methods

The methodology has been developed by the use of an Elementar Vario Micro Cube Elemental Analyzer (EA) in line with an ISOPRIME 100 Isotopic Ratio Mass Spectrometer (IRMS). The carbon contained in the sample is extracted by combustion and transformed in gaseous CO_2. The system allows to vary the combustion module temperature up to 1050°C; this theoretically allows to extract different components having distinctive destabilization temperature and to analyze the relative C(wt%) and δ^{13}C(‰).

All carbon isotope ratios are expressed in the standard (δ) notation in per mil (‰) relative to the international Vienna Pee Dee Belemnite (VPDB) isotope standard. The precision and accuracy were controlled by the repeated analyses of laboratory standards and is ca. 10% for carbon elementary analyses, while for isotopic measurement the average standard deviation is ±0.1 for δ^{13}C.

The approach highlights a robust correlation between the combustion temperature and the measured carbon isotopic compositions, in relation to the distinct organic (decidedly negative δ^{13}C‰) and inorganic (δ^{13}C‰ approaching 0) components that are selectively destabilized. In these tests the sample weight varied from 1 to 20 mg for the different sample types, in order to obtain significant signals for accurate and precise measures of the isotopic ratio. The results of these investigations have been synthetized in a rapid analytical protocol which is applicable to a wide range of environmental matrices. The protocol consists in the repeated analysis of each sample in different analytical conditions:

1) total CO_2 stripped out burning the sample at 950 °C, hereafter defined as TC;
2) organic CO_2 stripped out burning the sample at 450 °C, hereafter defined as TOC;
3) inorganic-CO_2 stripped out burning TIC fraction (i.e. combustion residua resulting after preliminary heating of a sample aliquot at 450 °C for 5h) at 950°C.

The analyses have been repeated at least three times for each fraction in order to

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minimize inhomogeneity of the samples, to carry out a significant Standard Deviation (SD, 1σ) and to give consistency to the method. The resulting C (wt%) and δ^{13}C‰ of the TOC and TIC are elaborated by mass balance, calculating a theoretical TC fingerprint which is compared with that directly measured ($\delta^{13}C_{CT\ Measured}$).

$$\delta^{13}C_{TC\ Theoretical} = \delta^{13}C_{TOC}*X_{TOC} + \delta^{13}C_{TIC}*X_{TIC} \qquad [1]$$

where $X_{TOC}+X_{TIC} = 1$ and represent the Total Organic and Total Inorganic fractions, respectively.

The misfit between theoretical and measured bulk isotopic ratios, expressed as $\Delta^{13}C$, complements the elemental carbon recovery and is used to cross-check the reliability of the method:

$$\Delta^{13}C = \delta^{13}C_{TC\ Measured} - \delta^{13}C_{TC\ Theoretical} \qquad [2]$$

Applicative examples and analytical details will be explained and clarified in order to standardize a tool for a proper understanding of the carbon budget and related fluxes in the environmental processes.

The proposed methodology has been calibrated by the analysis of samples of known elemental and isotopic composition (Table 1).

Table 1

Mean elemental and isotopic carbon composition of end members (Carrara Marble – CC, wheat flour – Wf) and relative mixtures (MIX A = 25% CC + 75% Wf; MIX B = 75% CC + 25% Wf) used in the method calibration.

C fract.	**Sample**	**C(%)**		**δ^{13}C (‰)**	
		mean	**SD**	**mean**	**SD**
	End Members				
TC					
	CC	12.49	0.72	2.1	0.3
	Wf	41.34	1.17	-25.3	0.1
	Mixtures				
TC					
	MIX A-Theor.	*34.13*		*-22.8*	
	MIX A –Meas.	33.91	2.87	-22.7	0.5
	MIX B - Theor.	*19.70*		*-12.3*	
	MIX B - Meas.	19.82	0.78	-12.6	0.6
TIC					
	MIX A, MIX B-Theor.	*12.49*		*2.06*	
	MIX A - Meas.	12.39	0.95	1.99	0.5
	MIX B - Meas.	13.04	0.64	1.50	0.1
TOC					
	MIX A - Theor.	*31.01*		*-25.3*	
	MIX A - Meas.	31.29	0.57	-25.3	0.4
	MIX B - Theor.	*10.34*		*-25.3*	
	MIX B - Meas.	10.28	0.32	-24.3	0.2

Where: TC is Total Carbon fraction; IC is Inorganic Carbon fraction; OC is Organic Carbon fraction. The theoretical (*Theor.*) elemental and isotopic composition of the mixtures are also reported for the comparison with the relative measured (*Meas.*) carbon fraction.

The selected samples for the calibration procedure consist of powdered calcite crystals hand-picked from a carbonatic rock (CC), and wheat flour (Wf) representing two end-members having very different origin and carbon composition (totally inorganic and organic, respectively). Two samples of intermediate composition have been obtained mixing different proportions of the above mentioned end-members: MIX A = 25%CC + 75%Wf, MIX B = 75%CC + 25%Wf. The end-members and the mixtures have been repeatedly analyzed applying the proposed methodology in order to check the precision and the accuracy of the method in the TOC and TIC speciation.

The results, presented in table 1 and plotted in figure 1, show that there is a very good agreement between the expected elemental and isotopic composition of the investigated mixtures and those really measured for TC, TOC and TIC fractions.

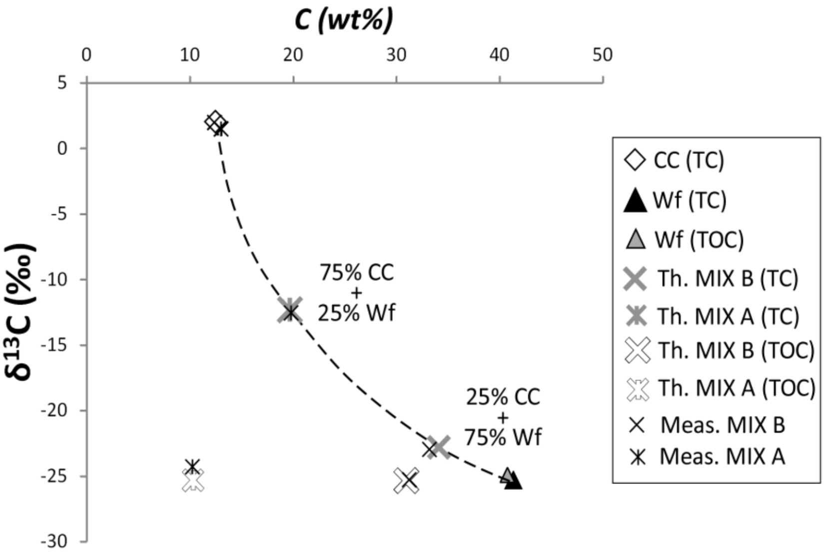

Figure 1. *C (%) – δ^{13}C binary diagram illustrating the carbon composition of end-member and mixtures of samples used for the calibration of the proposed methodology. Abbreviations as in the text and in Table 1.*

Therefore, the results of this calibration indicate that the proposed method is suitable for the carbon speciation of complex matrices. A cross-check has been provided by the analysis of a soil standard (ML-1, Vittori Antisari et al., in press) in which the carbon species (TOC and TIC) were determined by independent methods, as described by Springer and Klee (1954) for TOC and ISO 10693 (1995) for TIC; the analysis of TC gives a carbon content of 2.53% coupled with $\delta^{13}C_{CT}$ of -25.1‰ suggesting that the organic carbon fraction is preponderant in this soil. Coherently, the measure of TIC is only 0.32% ($\delta^{13}C_{TIC}$ = -6.5‰) whereas the TOC account for the remaining 2.18% ($\delta^{13}C_{TIC}$ = -26.9‰). The carbon speciation

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obtained for this sample conforms to that obtained by other laboratories with other methods (Vittori Antisari et al., 2014).

Furthermore, the reliability of the method has been tested analyzing different types of environmental samples such as sedimentary and magmatic rocks, soils and plants. In this framework, the combined analysis of carbon concentration and isotopic ratios have been carried out on two rock samples (one Carrara Marble, one carbonatic magmatic rock namely carbonatite), one plant (*Calluna vulgaris*, C3 photosynthesis pathway; Bragazza and Iacumin, 2009), one animal manure (cattle manure) and some soil samples (AR6B, AR19B, AR34B, AR16A, AR30A) from the Padanian Plain of Northern Italy taken in the surrounding of Argenta and previously studied by Di Giuseppe et al. 2014.

Results

The two rock samples exhibit similar TC content (marble: 12.32% with SD = 1.09%; carbonatite: 12.23% with SD = 0.39%), but distinct isotopic ratios (Carrara Marble: $\delta^{13}C_{TC}$ = +2.1‰ with SD = 0.1‰; carbonatite: $\delta^{13}C_{TC}$ = -6.0‰ with SD = 0.1‰) in agreement with their different genesis (Hudson, 1977; Deines, 2002). The measured TIC (Carrara Marble: 12.38% with SD = 0.08%; carbonatite: 12.23% with SD = 0.39%) is comparable with the TC content of the two rocks, as well as their respective isotopic ratios (Carrara Marble: $\delta^{13}C_{TIC}$ = 2.3‰ with SD = 0.1 ‰; carbonatite: $\delta^{13}C_{TIC}$ = -5.9‰ with SD = 0.2‰). The expected absence of organic fraction in the two rock samples is confirmed by a very low TOC, which account for 0.08% (SD = 0.01%) in the Carrara Marble and 0.06% (SD = 0.01%) in the carbonatite, that is coupled with distinctive more negative $\delta^{13}C_{TOC}$ values (Carrara Marble = -10.7‰ with SD = 0.7‰; carbonatite = -18.04‰ with SD = 3.2‰). The recovery of carbon for the rocky samples are excellent both for elementary (100%) and isotopic composition (Carrara Marble $\Delta^{13}C$= -0.1‰; carbonatite $\Delta^{13}C$ = 0.0‰).

The two biological samples show the highest TC content (plant: 54.69% with SD = 2.80%; animal manure: 44.56% with SD = 0.75%) that is associated with decidedly negative $\delta^{13}C_{TC}$ values (plant: $\delta^{13}C_{TC}$ = -27.7‰ with SD = 0.2‰; animal manure: $\delta^{13}C_{CT}$ = -24.0‰ with SD = 0.1‰). The measured TIC is significantly variable in the investigated biological samples, accounting for 2.15 % in the plant and 6.71 % (SD = 0.27%) in the animal manure. The associated isotopic values are however very similar (plant: $\delta^{13}C_{TIC}$ = -18.5‰ with SD = 0.1‰; animal manure: $\delta^{13}C_{TIC}$ = -17.2‰ with SD = 0.2‰). The measured TOC content account for 51.49 % in plant (SD = 12.85%), and 36.07 % (SD = 0.09%) in the animal manure, both of them showing an isotopic composition comparable to that of TC (plant: $\delta^{13}C_{TOC}$ = -27.7‰ with SD = 0.3‰; animal manure: $\delta^{13}C_{TOC}$ = -24.0‰ with SD = 0.4‰). The recovery of carbon for biological samples are very good both for elementary (plant = 98%; animal manure = 96%) and isotopic composition (plant $\Delta^{13}C$ = -0.4‰; animal manure $\Delta^{13}C$ = -1.0‰).

The selected soils samples are characterized by a TC content varying in the range 1.31(AR16A)-3.56 (AR30A) % and by a remarkable variations in the associated bulk isotopic composition ($\delta^{13}C_{TC}$ -5.0‰ in AR19B to -21.9 ‰ in AR16A). The measured TIC content ranges from 0.15% (AR16A) to 2.56% (AR6B) and displays $\delta^{13}C_{TIC}$ varying from -1.5‰ (AR30A) to -10.4‰ (AR16A), whereas the TOC content is in the range 0.34% (AR19B) – 1.17 % (AR30A) and is associated with carbon isotopic ratios varying from -22.0‰ (AR34B) to -25.5‰ (AR30A). The recovery for elemental carbon vary from 96% (AR34B) to 105% (AR6B), whereas the isotopic recovery ($\Delta^{13}C$) ranges from 0.0 (AR16A) to -0.5 (AR19B) ‰. The measured elemental and isotopic data for the selected soil samples are presented in figure 2, which also includes the theoretical isotopic composition obtained by mass balance calculation ($\delta^{13}C_{CT\ Theoretical}$) for a direct comparison with the measured bulk $\delta^{13}C_{CT.}$

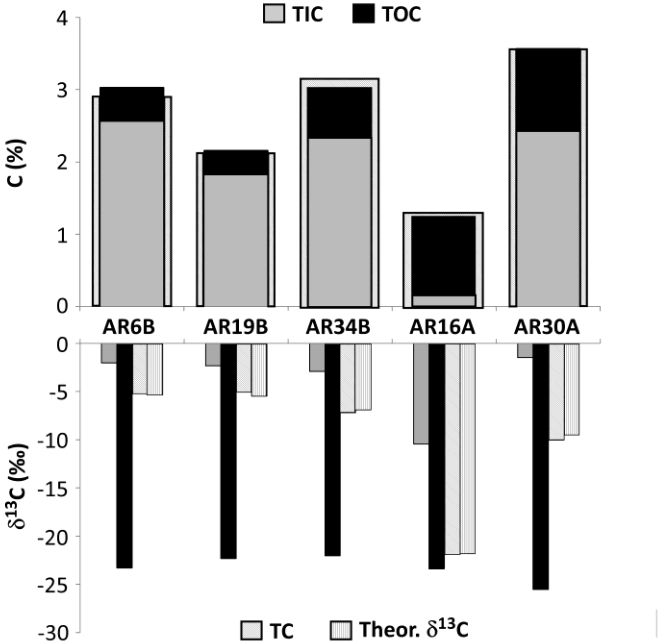

Figure 2
Carbon elemental and isotopic composition of the different carbon fraction (TC, TIC and TOC) in soils from the Padanian Plain (Di Giuseppe et al., 2014).

Discussion

TC (and TIC) content of the investigated rocks is in agreement with stoichiometrically C content (wt %) in the $Ca(CO)_3$ molecule which account for ca. 12 wt%. The $\delta^{13}C_{TC}$ values of the Carrara Marble (+2.1 ‰) is in the typical carbonate range (Hudson, 1977), and very close to the value listed in the IAEA documents for the "Carrara Marble-C1" radiocarbon reference material (+2.42 ‰), whereas the $\delta^{13}C_{TC}$ of carbonatite sample (-6.0‰) exhibit a typical Earth's mantle composition ($\delta^{13}C \sim -5$‰; Deines, 2002). The difference between $\delta^{13}C_{TC}$ and

$\delta^{13}C_{TIC}$ for these rocks (0.1-0.2 ‰) is very close the analytical error ($\delta^{13}C$ ±0.1‰), with $\delta^{13}C_{TIC}$ always less negative than $\delta^{13}C_{TC}$ values. As expected, the investigated rock samples exhibit very low, although detectable, TOC fraction (max 0.08 % detected in marble), the interpretation of which is not so straightforward, mainly because of the low signal detected on the mass spectrometer leading to discard the resulting isotopic ratio. As concerns the investigated biological samples, the measured TOC content correspond to a fraction of 0.94 and 0.81 of the TC for the C3 plant and the animal manure respectively, suggesting that inorganic carbon compounds are present in both the investigated biological matrices. The formation of a mineral fraction in biological matrices could be related to (bio)-mineralization processes that mainly lead to oxalate formation (Franceschi and Horner, 1980; Skinner and Ehrlich, 2014 and reference therein). The high TIC detection in the animal manure (0.15 of the TC) is probably due either to the presence of carbonates formed during its anaerobical store (Sommer and Husted, 1995; Chantigny et al., 2001) or to the presence of calcium-oxalates ingested with the livestock fodder (Shahack-Gross, 2011 and reference therein); future investigations will be addressed to evaluate if the combustion process here used to isolate the TIC fraction lead to the formation of secondary carbonates, as suggested by Cao and Harris (2010). The TIC isotopic ratio is distinctly less negative ($\delta^{13}C_{TIC}$ = -17.2‰) than that recorded in the TC ($\delta^{13}C_{TC}$ of -24.0‰), plausibly confirming a genesis by anaerobic degradation of acetate which lead to the production of ^{13}C-depleted CH_4 (Krzycki et al., 1987) and complementary ^{13}C-enriched CO_2 (Boehme et al., 1996) from which carbonates crystallize. On the other hand, the very low TIC measured in C3 plant (4% of TC) is probably due to biomineralization occurring within plant tissues; the associated isotopic ratio ($\delta^{13}C_{TIC}$ = -18.5‰) is consistent with the values of Ca-oxalates observed in terrestrial plants (Cailleau et al., 2011).

Summarizing, the elementary and isotopic carbon recovery efficiency for the investigated samples can be summarized as follows: rocks > plant > animal manure. In any case, the lowest elementary recovery (ca. 4%, observed for animal manure samples) is below the analytical precision.

In our view, the method is ideal to study complex matrices in which the presence of distinct carbon forms is ubiquitous. For example, the application to soils from the Padanian plain (Northern Italy; Bianchini et al., 2012) allows the precise determination of their TC, TIC and TOC which implements previous investigations and classifications in terms of textures, geomorphological setting and sampling depth (Di Giuseppe et al., 2014). The TIC tends to prevail in the soils developed from coarse sediments deposited in high energy hydrodynamic conditions. On the contrary, TOC becomes prevalent in soils developed from fine-grained sediments from low energy depositional environments. The isotopic composition of TIC recorded in the majority of the investigated soils is very similar (average $\delta^{13}C_{TIC}$ = -2.2‰, SD=0.6‰) confirming both the lithogenic nature of the measured fraction and its stability through the geological conditions. However, an exception is represented by the sample AR16A which shows $\delta^{13}C_{TIC}$ = -10.1‰ plausibly reflecting the presence of pedogenic carbonates in its inorganic fraction. In fact, the recorded $\delta^{13}C_{TIC}$ for this sample is characterized by an isotopic shift of ca. +15‰ respect to the associated soil organic matter ($\delta^{13}C_{TOC}$ = -25.5‰) conforming to the values suggested by Nordt et al., (1998) for pedogenic carbonates.

In general, the $\delta^{13}C_{TOC}$ values are significantly more negative than $\delta^{13}C_{TIC}$ clearly deriving from the thermal destabilization of the Soil Organic Matter (SOM). In particular, in all the investigated samples the isotopic composition of the TOC (average $\delta^{13}C_{TOC\,=}$ -23.3‰, SD = 1.4‰) indicates that the SOM is mainly derived from C3 photosynthetic pathway vegetation. The recorded isotopic variability of SOM in the selected samples ($\delta^{13}C_{TOC}$ from -21.6 to 25.5‰) possibly reflects isotopic fractionation originated by organic matter decomposition leading to a production of depleted ^{13}C soil respiration gases in parallel with a ^{13}C enrichment of the residual decomposition products (Winn et al., 2006). The carbon elementary recovery is usually better than 5% and appear to be not related to the $\Delta^{13}C$ which is in the range ±0.5‰. Note that positive $\Delta^{13}C$ typically denotes the samples characterized by significant SOM fraction; this means that a carbon fraction with distinctly negative isotopic signature has not been measured during the three steps of the analytical procedure. The inferred unmeasured fraction is plausibly represented by charred material known to be recalcitrant to further combustion processes, and/or by elemental carbon plausibly related to incipient SOM mineralization.

Conclusions

The presented results, although preliminary, support the development of a novel methodology that, based on the use of a coupled EA-IRMS system, is able to speciate distinct carbon fractions in different environmental solid matrices. The proposed method of carbon extraction (CO_2) exploits the different destabilization temperatures of the distinct carbon-bearing phases (having distinct $\delta^{13}C$ signature) that coexist within an environmental matrix. The validity of the approach is demonstrated by the very good (in some cases excellent) elementary recovery and isotopic mass balance.

In conclusion, the development of this rapid methodology for carbon speciation is a powerful tool to unravel distinct carbon forms and their origin in various environmental matrices. The application of mass balance is also fundamental to detect "cryptic" (difficult to analyze) carbon forms which are not directly measured.

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COMPRENDRE LA SIGNATURE DE CARBONE ISOTOPIQUE DANS DES MATRICES ENVIRONNEMENTALES COMPLEXES

Résumé

Les analyses élémentaires et isotopiques de carbone dans des matrices environnementales intègrent généralement plusieurs sources ayant une concentration distincte (% en poids) et rapport isotopique $^{13}C/^{12}C$. Interprétation nécessairement besoin de la caractérisation des finales membres divers qui sont généralement constitués par des composants carbonate, organiques et élémentaires. Dans cette optique, nous avons développé un protocole de routine basée sur le couplage analytique des compositions élémentaires et isotopiques qui est capable de discriminer les minéraux (TIC) et organiques (TOC) des contributions à le carbone total (TC) de contenu. La procédure est basée uniquement sur la déstabilisation thermique des différentes espèces de carbone et a été appliquée avec succès sur différentes matrices environnementales (roches, sols, les échantillons biologiques) avec un C récupération élémentaire et isotopique moyenne de 98,2% (SD = 1,7) et -0,5 ‰ (SD = 0,6 ‰). La spéciation de carbone à base thermiquement efficace nous a conduit à obtenir de véritables rapports ne sont pas touchés par tout traitement chimique des échantillons, qui sont essentiels pour effectuer un calcul de bilan de masse isotopique correct.

Mots-clés: *carbon, spéciation, isotope, matrices environnementales*

COMPRENDERE LA FIRMA ISOTOPICA DEL CARBONIO IN MATRICI AMBIENTALI COMPLESSE

Riassunto

L'analisi elementare ed isotopica del carbonio in matrici ambientali integra molteplici sorgenti caratterizzate da diverse concentrazioni (% in peso) e rapporti isotopici $^{13}C/^{12}C$. La loro interpretazione necessita di una caratterizzazione dei diversi end-members costituiti da componenti carbonatiche, organiche ed elementari. In quest'ottica, abbiamo sviluppato un protocollo analitico basato sull'accoppiamento dell'analisi elementare ed isotopica che è in grado di discriminare i contributi inorganici (TIC) e organici (TOC) che contribuiscono al contenuto totale di carbonio (TC). La procedura si basa sulla destabilizzazione termica delle diverse specie di carbonio presenti ed è stata applicata con successo su diverse matrici ambientali (rocce, suolo, campioni biologici) con una media del recupero di carbonio elementare ed isotopica del 98,2% (SD = 1.7) e -0.5 ‰ (SD = 0,6 ‰), rispettivamente. L'efficace speciazione del carbonio su base termica ci permette di ottenere rapporti isotopici affidabili, non modificati da trattamenti chimici dei campioni, che sono essenziali per eseguire un corretto calcolo del bilancio di massa, imprescindibile per ottenere stime corrette delle diverse forme di carbonio.

Parole chiave: *carbonio, speciazione, isotopi, matrici ambientali*