



Technical note: Further adjustments to the Rock-Eval® thermal analysis for soil organic and inorganic carbon quantification to avoid post-hoc corrections

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Abstract. Accurate quantifications of soil organic (SOC) and inorganic (SIC) carbon are essential for a better understanding
 20 of the global carbon cycle. The procedures usually used to quantify SOC and SIC (e.g., elemental analysis after
 pretreatment) rely on various approximations and can lead to analytical errors. Ramped thermal analyses are increasingly
 investigated to quantify SOC and SIC by heating a single aliquot and continuously measuring the carbonaceous compounds
 emitted. The Rock-Eval® thermal analysis (RE) has been standardized to estimate organic and inorganic C contents of oil-
 bearing rocks through two parameters named TOC and MINC, respectively. Moreover, its pyrolysis phase before the
 25 oxidation provides the basis for calculating indices to characterize soil organic matter (SOM). However, statistical post-hoc
 corrections of TOC and MINC are needed to adjust their estimations of SOC and SIC contents because SOC and SIC
 decomposition signals overlap at the end of the pyrolysis. A new cycle with a final pyrolysis temperature of 520 °C
 (PYRO520) instead of 650°C is investigated to avoid SIC decomposition while preserving OM characterization during
 pyrolysis. The results are compared to the quantifications obtained with the standard analysis cycle (PYRO650) and by
 30 elemental analysis after pretreatments. The PYRO520 cycle corrects the misallocation of the end-of-pyrolysis signals
 between the TOC and MINC parameters and thus accurately and repeatably estimated SOC and SIC contents measured by
 EA after pretreatments without needing post-hoc corrections. Moreover, the values and interpretations of the indices
 characterizing SOM are not drastically modified by the pyrolysis modification.



1 Introduction

Two carbon (C) forms can be found in soils: soil organic carbon (SOC) and soil inorganic carbon (SIC). Since the early 1990s, only about 4% of soil C publications have addressed SIC (Raza et al., 2024). Traditionally, SIC has been viewed as inert over a human lifetime, only slightly affected by land use and agricultural practices, and thus considered irrelevant to studies on soil C sequestration and soil ecology (Dina Ebouel et al., 2024; Raza et al., 2024). However, an increasing number of studies shows that the presence of SIC can enhance SOC stabilization (Rowley et al., 2018; Qafoku et al., 2023; Shabtai et al., 2023) and may act either as a sink (Entry et al., 2004; Manning, 2008; Cailleau et al., 2011; Wang et al., 2015; Bughio et al., 2016; Raheb et al., 2017; Gao et al., 2017; Liu et al., 2018; Gatz-Miller et al., 2022; Liu et al., 2023) or as a source of atmospheric CO₂ (Emmerich, 2003; Bertrand et al., 2007; Chevallier et al., 2016; Raza et al., 2021; Zamanian et al., 2021; Guo et al., 2021; Zhao et al., 2022). Despite these findings, the influence of SIC-related processes on the global C cycle remains uncertain. Consequently, accurate quantifications of SOC and SIC are essential for completing soil C databases, improving digital mapping of SIC, and integrating SIC dynamics into global C cycle models (Sharififar et al., 2023; Dina Ebouel et al., 2024; Raza et al., 2024).

The elemental analysis (EA) remains the reference method for soil C quantification. It consists in high-temperature combustion (> 1000 °C) of the soil sample and measurement of the emitted carbon dioxide (CO₂; ISO, 1995; Bispo et al., 2017; Apesteguia et al., 2018; Shamrikova et al., 2023). Both SOC and SIC decompose at this temperature. To quantify SOC and SIC, the total carbon (TC) is first estimated by EA on one aliquot, and then either SOC or SIC is estimated on a second aliquot by removing the unwanted C form prior to EA or by using specific methods quantifying SOC (e.g., wet oxidation) or SIC (e.g., calcimetry). However, SIC removal by acidification or SOC removal by combustion can be incomplete or even alter the untargeted C form (Schlacher and Connolly, 2014; Apesteguia et al., 2018; Shamrikova et al., 2023, 2024). Moreover, specific quantification methods depend on approximations for estimating SOC yields from wet oxidation, while calcimetry is calibrated exclusively for quantifying calcium carbonate and thus misses other carbonate forms (e.g., calcium magnesium carbonate) (Apesteguia et al., 2018; Nayak et al., 2019; Shamrikova et al., 2023, 2024). The unquantified C form is then calculated using the difference (e.g., SIC = TC - SOC), leading to an increase in the measurement error of the result (e.g., $\Delta \text{SIC} = \sqrt{\Delta \text{TC}^2 + \Delta \text{SOC}^2}$). Sample heterogeneity and/or very low or high contents of one C form can also lead to inconsistencies and even negative or null values (Apesteguia et al., 2018; Shamrikova et al., 2023, 2024). The loss-on-ignition method quantifies SOC and SIC by heating a single aliquot and by measuring the mass loss during the heating. The mass loss up to 450-600 °C is usually attributed to organic matter (OM) decomposition and the mass loss up to 850-950 °C to carbonate decomposition. However, the temperature limits reported in the literature are variable, and other processes (e.g., clay dehydroxylation) can contribute to mass loss. Moreover, SOC contents are estimated by assuming that OM contains on average 58% carbon, a proportion that can vary widely between soils (from 40% to 71%; Apesteguia et al., 2018; Dina Ebouel et al., 2024; Shamrikova et al., 2024).



Thermal analyses are increasingly investigated to quantify both SOC and SIC on a single aliquot by continuously measuring the carbonaceous compounds released either during oxidation alone (Vuong et al., 2013, 2015; Apesteguia et al., 2018) or during pyrolysis and oxidation (Delahaie et al., 2023; Hazera et al., 2023; Koorneef et al., 2023). Since SIC decomposes at higher temperatures than SOC, these methods use temperature boundaries to distinguish the compounds emitted by the SOC decomposition from those emitted by the SIC decomposition. Among these methods, the Rock-Eval® thermal analysis (RE) has been standardized to estimate organic and inorganic C contents in oil-bearing rocks through two parameters named TOC and MINC, respectively. The advantage of RE is to include a pyrolysis phase before the oxidation during which hydrocarbon compounds (HC) are measured in addition to carbon monoxide (CO) and CO₂ (Lafargue et al., 1998; Behar et al., 2001). The HC measurement is used to calculate indices that are increasingly used in soil science to characterize soil OM (Disnar et al., 2003; Carrie et al., 2012; Sebag et al., 2016; Cécillon et al., 2018; Malou et al., 2023).

Nevertheless, thermal analyses are not exempt from uncertainties on temperature boundaries to be used for distinguishing the signals from SOC and SIC thermal decompositions. Recent quantifications of SOC and SIC by RE in calcareous samples showed that the sum of TOC and MINC parameters accurately estimates the TC content, while the TOC parameter underestimates the SOC content and the MINC parameter overestimates the SIC content. A proportion of SOC is accounted in the MINC parameter because of an overlap of the SOC and SIC decomposition signals at the end of the pyrolysis (Delahaie et al., 2023; Hazera et al., 2023; Koorneef et al., 2023). Indeed, SIC thermal decomposition begins at the end of the pyrolysis, while a proportion of SOC remains in the crucible. The CO₂ emitted by SIC decomposition reacts with the residual organic C to form two CO molecules (Boudouard's reaction: $\text{CO}_2 + \text{Corg} \rightarrow 2\text{CO}$). The production of CO at the end of pyrolysis (i) leads to the arbitrary halving of the CO signal between TOC and MINC parameters although the yield of the Boudouard's equilibrium depends on temperature, and (ii) increases the uncertainties on temperature boundaries to be used to distinguish SOC and SIC signals since SIC thermal decomposition usually does not produce CO ($\text{CaCO}_3 \xrightarrow{\Delta} \text{CaO} + \text{CO}_2$). Thus, distinguishing SOC and SIC decomposition signals during pyrolysis remains uncertain and likely depends on the forms of SOC and SIC in the soil sample. A post-hoc correction has been proposed consisting in subtracting a proportion of the TOC parameter (8-9%) from the MINC parameter (Sebag et al., 2022a; Hazera et al., 2023) and adding it to the TOC parameter (Disnar et al., 2003). However, this correction may not be suitable for all soil types and remains calibrated on SOC and SIC contents estimated by the reference methods, which themselves include measurement errors.

Preventing SIC thermal decomposition by reducing the final temperature of pyrolysis could avoid the need for post-hoc corrections for SOC and SIC quantification. The standard pyrolysis reaches 650 °C, a high temperature originally chosen to measure the HC emitted by the thermal decomposition of the most mature organic matters of oil-bearing rocks (Lafargue et al., 1998). However, in soils, the most persistent OM are hydrogen-depleted so their decomposition emit few HC at high temperatures (Disnar et al., 2003; Barré et al., 2016; Sebag et al., 2016). The HC emitted by soil samples at the end of the pyrolysis are rare and not relevant for the characterization of soil OM (Pacini et al., 2023; Deluz et al., 2024). Delarue et al. (2013) even suggested that the HC emitted at the end of the pyrolysis could be mainly products from secondary reactions



occurring in the pyrolysis furnace. Therefore, lowering the final temperature of pyrolysis should not compromise the
 100 characterization of soil OM through the HC-based indices. During pyrolysis, the thermal decomposition of common soil
 carbonates (e.g., calcite, dolomite) begins around 550 °C (Hazera et al., 2023), whereas some carbonates like siderite or
 oxalates start their decomposition around 520 °C (Lafargue et al., 1998). Reducing the final temperature of pyrolysis to
 520 °C offers a practical compromise: it prevents the SIC decomposition during pyrolysis while still preserving a meaningful
 HC signal for characterizing soil OM. In this approach, SIC would be quantified exclusively during the subsequent oxidation
 105 phase.

Therefore, the aim of this study was to improve the direct quantification of SOC and SIC with RE by lowering the final
 temperature of pyrolysis rather than applying post-hoc corrections on TOC and MINC parameters. To this end, 173 soils and
 nine reference materials were analyzed with both the standard analysis cycle (noted PYRO650) and a cycle with a final
 pyrolysis temperature of 520 °C (noted PYRO520). The SOC and SIC quantifications using TOC and MINC parameters
 110 directly obtained with the two cycles (i.e., without post-hoc corrections) were compared to the SOC and SIC quantifications
 by EA after pretreatments. The indices characterizing OM obtained with the two cycles were compared. We hypothesized
 that (i) TOC and MINC parameters obtained with the PYRO520 cycle were respectively higher and lower than those
 obtained with the PYRO650 cycle, (ii) TOC and MINC parameters obtained with the PYRO520 would not differ
 significantly from the SOC and SIC contents estimated by EA, and (iii) the indices characterizing OM obtained with both
 115 cycles were linearly correlated.

2 Materials and methods

2.1 Materials

A total of 173 agricultural soils of varied geographical origins, land uses, and textures were selected (Fig. 1, Table S1). The
 soils were sampled at depths ranging from 0-10 cm to 210-220 cm (Table S1). Samples were sieved to 2 mm, milled with
 120 200 µm mesh, and dried at 40 °C to constant weight before Rock-Eval® (RE) and elemental analyses (EA). The SOC
 contents measured by EA after removing SIC by acidification ranged from 1.2 g C kg⁻¹ to 68.2 g C kg⁻¹ and the SIC contents
 measured by EA after removing SOC by combustion ranged from 0.0 g C kg⁻¹ to 94.9 g C kg⁻¹ (Table S1). Among these
 soils, 26 were considered non-calcareous (SIC < 2.0 g C kg⁻¹) and 147 were calcareous, with carbonates mainly in the form
 of calcite and, to a lesser extent, dolomite (Table S1).

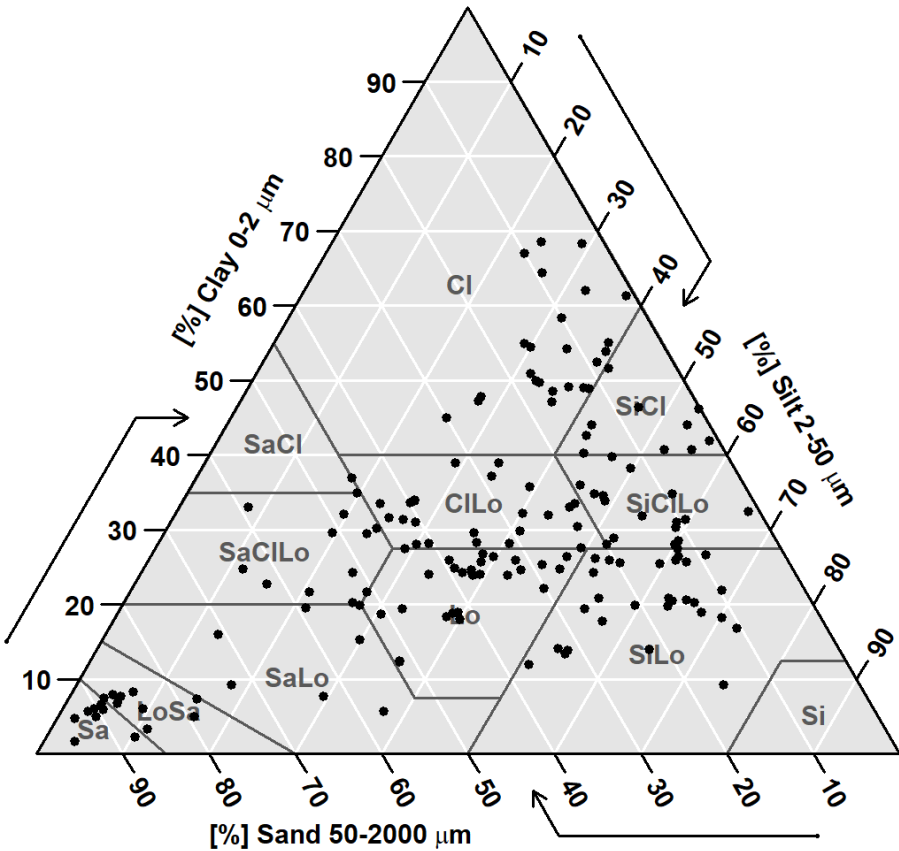


Figure 1: Particle size distributions as the proportion of sand, silt, and clay (%) of the 173 soils. Cl: clay, SiCl: silty clay, SaCl: sandy clay, CiLo: clay loam, SiCiLo: silty clay loam, SaCiLo: sandy clay loam, Lo: loam, SiLo: silty loam, SaLo: sandy loam, Si: silt, LoSa: loamy sand, Sa: sand (USDA classification).

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130 Nine reference materials from environmental agencies were also analyzed (Table 1). Their reference SOC contents ranged from 2.6 g C kg⁻¹ to 56.1 g C kg⁻¹ and their reference SIC contents ranged from 0.4 g C kg⁻¹ to 54.8 g C kg⁻¹ (Table 1).



Table 1: Name, type, environmental agency and TC, SOC, SIC reference contents (g C kg⁻¹) of the nine reference materials

Name	Type	Environmental agency	TC	SOC	SIC
SR-1	Rock	Norwegian Petroleum Directorate	36.9	22.4	14.5
NIST-8704	River sediment	National Institute of Standards and Technology USA	33.5	24.0	9.1
PACS-3	Marine sediment	National Research Council Canada	32.9	31.7	1.2
ERM- CC690	Calcareous soil	Joint Research Centre Institute for Reference Materials and Measurements	93.0	56.1	36.9
BCR-280R	Lake sediment	Joint Research Centre Institute Reference Materials and Measurements	17.4	14.1	3.4
ISE-850	Calcareous soil	Wageningen Evaluating Programs for Analytical Laboratories	68.3	2.5	65.8
AAFC-01	Calcareous soil (eroded)	Agriculture and Agri-Food Canada, Lethbridge (intern)	27.5	11.1	16.5
AAFC-02	Calcareous soil (non-eroded)	Agriculture and Agri-Food Canada, Lethbridge (intern)	20.9	13.6	7.2
Till-3	Subsoil	Natural Resources Canada (NRCan) Canadian Centre for Mineral and Energy Technology (CANMET)	11.5	11.1	0.4

135 2.2 Elemental analysis

Total carbon (TC), organic carbon (SOC), and inorganic carbon (SIC) contents were estimated on three aliquots using an elemental analyzer. The aliquots for TC quantification were analyzed directly by EA without pretreatment. Carbonates of the aliquots dedicated to SOC quantification were removed by acid treatment before EA (Table 2). SOC of the aliquots dedicated to SIC quantification was destroyed by combustion at 550 °C before EA (Table 2). The TC, SOC, and SIC contents estimated by EA are noted TC_{EA}, SOC_{HCl+EA}, and SIC_{550°C+EA}, respectively.



Table 2: Sample weight (mg), device and protocol used by the four laboratories for SOC and SIC quantification by elemental analysis (EA) or thermal ramp

Samples	Weight	Device	SOC protocol	SIC protocol
France, Italy, Tunisia (n = 113)	13-20	Elementar Vario Isotope Select	Fumigation with HCl (12 M) + EA	Muffle furnace ignition at 550 °C (6 h) + EA
Germany (n = 15)	0.2-10 (SOC) 15-800 (SIC)	Thermo Flash 2000 EA (SOC) LECO R612 (SIC)	Fumigation with HCl (12 M) + EA	Thermal ramp analysis after 550 °C
Hungary (n = 30)	2-4	Thermo Flash 2000 EA	Acidification HCl (3 M) + washing + EA	Muffle furnace ignition at 550 °C (6 h) + EA
Canada (n = 15)	5-200	Thermo Flash 2000 EA	Small-scale acidification with HCl (6 M) + EA	Muffle furnace ignition at 550 °C (6 h) + EA

145 Carbon contents were measured using EA and conducted in four laboratories. Sample weights, elemental analyzer devices, and pretreatment protocols differed among the four laboratories (Table 2). C content estimations by EA were replicated between one and five times for soil samples and at least four times for the reference materials. Each reference material was analyzed by the four laboratories (Table 2).

2.3 Rock-Eval® thermal analysis

150 2.3.1 Method description

The TC, SOC, and SIC contents were estimated on one untreated aliquot using a RE6Standard apparatus (Vinci Technologies, France). SOC and SIC contents were estimated by the TOC and MINC parameters, respectively. The TC content was estimated by the sum of the TOC and MINC parameters. Steel crucibles were filled with 60 ± 1 mg of sample and analyzed using the standard “Bulk Rock” method. The analysis consists of a pyrolysis phase under an inert atmosphere
 155 (N_2 , purity = 99.99%) during which hydrocarbon compounds (HC), carbon monoxide (CO), and carbon dioxide (CO_2) emissions are measured, followed by an oxidation phase under synthetic air (80% N_2 and 20% O_2 , purity = 99.99%) during which CO and CO_2 emissions are measured. Thus, five thermograms are obtained at the end of the analysis.

RE analyses were replicated three times for the reference materials as well as for 11 soil samples distributed across the TC content range of the studied soil samples (Table S1).



2.3.2 Calculation of the TOC and MINC parameters

Two RE cycles were performed on each sample with differing final pyrolysis temperatures: a standard pyrolysis with a final temperature of 650 °C (noted PYRO650), and a pyrolysis with a reduced final temperature of 520 °C (noted PYRO520). In both cycles, the pyrolysis started with an isotherm of 3 min at 200 °C and continued with a temperature ramp of 25 °C min⁻¹. The PYRO650 cycle ended at 650 °C without an isotherm (Behar et al., 2001), whereas the PYRO520 cycle ended with an isotherm of 5 min at 520 °C to complete the thermal pyrolysis of OM decomposing at this temperature. The sample was cooled down at the end of the pyrolysis before the oxidation phase. The oxidation phase was identical for both cycles. The oxidation started with an isotherm of 3 min at 200 °C and continued with a temperature ramp of 25 °C min⁻¹ up to an isotherm of 7 min at 850 °C to ensure the complete thermal decomposition of carbonates (Hazera et al., 2023).

The five thermograms obtained with the PYRO650 cycle were divided into nine curves: S1 and S2 refer to the HC emitted during and after the 200 °C isotherm, respectively; S3CO and S3'CO display the CO emitted during pyrolysis before and after 550°C, respectively; S3CO₂ and S3'CO₂ denote the CO₂ emitted during pyrolysis before and after 550°C, respectively; S4CO refers to the CO emitted during oxidation, and S4CO₂ and S5, to the CO₂ emitted during oxidation before and after 650°C, respectively (Table 3).

Table 3: Temperature spans (°C) and contributions to the TOC and MINC parameters (%) of the curves obtained with the PYRO650 and PYRO520 cycles (n = 173)

		PYROLYSIS						OXIDATION		
		HC		CO		CO ₂		CO	CO ₂	
		S1	S2	S3CO	S3'CO	S3CO ₂	S3'CO ₂	S4CO	S4CO ₂	S5
PYRO650										
Temperature span		200	200-650	200-550	550-650	200-550	550-650	200-650	200-650	650-850
Parameter		TOC	TOC	TOC	TOC/MINC	TOC	MINC	TOC	TOC	MINC
Contribution to the parameter		0 ± 0	11 ± 5	2 ± 1	1 ± 0/ 2 ± 3	16 ± 7	13 ± 15	4 ± 1	66 ± 6	86 ± 17
PYRO520										
Temperature span		200	200-520	200-520	-	200-520	-	200-850	200-650	650-850
Parameter		TOC	TOC	TOC	-	TOC	-	TOC	TOC	MINC
Contribution to the parameter		0 ± 0	9 ± 5	2 ± 1	-	16 ± 6	-	4 ± 1	68 ± 5	100

The parameters obtained with the PYRO650 cycle are noted TOC₆₅₀, MINC₆₅₀ (Eqs 1 and 2), and TC₆₅₀.

$$\text{TOC}_{650} = \text{S1} + \text{S2} + \text{S3CO} + \frac{1}{2} \text{S3'CO} + \text{S3CO}_2 + \text{S4CO} + \text{S4CO}_2 \quad (1)$$



$$\text{MINC}_{650} = \frac{1}{2} \text{S3}'\text{CO} + \text{S3}'\text{CO}_2 + \text{S5} \quad (2)$$

180 The S3'CO and S3'CO₂ curves obtained with the PYRO520 cycle were null (Table 3). The parameters obtained with the PYRO520 cycle are noted TOC₅₂₀, MINC₅₂₀ (Eqs 3 and 4), and TC₅₂₀.

$$\text{TOC}_{520} = \text{S1} + \text{S2} + \text{S3CO} + \text{S3CO}_2 + \text{S4CO} + \text{S4CO}_2 \quad (3)$$

$$\text{MINC}_{520} = \text{S5} \quad (4)$$

The relative errors of the TOC and MINC parameters were estimated at 1.2 % and 3.3 % respectively (Pacini et al., 2023).

185 2.3.3 Calculation of the indices characterizing organic matter

The main indices used in the literature to characterize soil OM are the hydrogen index (HI), the oxygen index (OIRE6), the I-index, and the R-index, which are directly calculated from the thermograms (e.g., Chassé et al., 2021; Deluz et al., 2024; Sebag et al., 2022). In addition, there is the proportion of stable SOC on a century scale (Cs) predicted by the Party_{SOC} model (e.g., Cécillon et al., 2018, 2021; Delahaie et al., 2024, 2023).

190 The HI corresponds to the amount of HC emitted during pyrolysis relative to the TOC (Eq 5, mg HC g⁻¹ TOC; Behar et al., 2001; Carrie et al., 2012). The OIRE6 relates to the amount of oxygen emitted as CO and CO₂ during pyrolysis of OM relative to the TOC (Eq 6, mg O₂ g⁻¹ TOC; Behar et al., 2001; Carrie et al., 2012). The HI and OIRE6 are correlated with the H:C and O:C ratios of OM, respectively (Disnar et al., 2003). The HI = f(OIRE6) diagram is used to assess the decomposition state of OM: HI generally decreases with depth, reflecting the progressive oxidation of OM, i.e.,
 195 dehydrogenation (decrease of HI) and relative oxidation (increase of OIRE6) of OM (Disnar et al., 2003; Barré et al., 2016; Sebag et al., 2022a). The HI and OIRE6 were obtained using the same calculation for both cycles of analysis but they are not equivalent as the temperature span of the S2 and S3CO₂ curves, as well as the TOC value, differ for each cycle (Table 3, Eqs 1 and 3). The HI and OIRE6 are noted HI₆₅₀, OIRE6₆₅₀, HI₅₂₀, and OIRE6₅₂₀ when obtained with the PYRO650 and the PYRO520 cycles, respectively.

$$\text{HI} = \frac{\text{S2}}{\text{TOC}} \times 100 \quad (5)$$

$$\text{OIRE6} = \frac{16}{28} \times \frac{\text{S3CO}}{\text{TOC}} \times 100 + \frac{32}{44} \times \frac{\text{S3CO}_2}{\text{TOC}} \times 100 \quad (6)$$

The I and R indices are calculated from a subdivision of the S2 curve into five areas: A1 (200-340 °C), corresponding to highly labile biopolymers, A2 (340-400 °C), labile biopolymers, A3 (400-460 °C), resistant biopolymers, A4 (460-520 °C), refractory biopolymers, and A5 (> 520 °C), highly refractory biopolymers (Sebag et al., 2016). The I and R indices
 205 correspond to the proportions of thermally labile and thermally stable OM, respectively, and are calculated from the A1, A2, A3, A4, and A5 areas expressed as percentages of the S2 curve (Eqs 7, 8, and 9). Since the A5 area does not apply with the PYRO520 cycle, the calculation of the R index was modified accordingly. The I and R indices are noted I₆₅₀ and R₆₅₀ (Eqs 7 and 8) when obtained with the PYRO650 cycle and I₅₂₀ and R₅₂₀ (Eqs 7 and 9) when obtained with the PYRO520 cycle.



$$I_{650} = \log_{10}[(A1 + A2)/A3] = I_{520} \quad (7)$$

$$R_{650} = (A3 + A4 + A5)/100 \quad (8)$$

$$R_{520} = (A3 + A4)/100 \quad (9)$$

The $I = f(R)$ diagram is used to investigate the dynamics of OM decomposition in the studied samples by comparing results with those from a conventional decomposition model, as described in Sebag et al. (2016).

215 The Cs proportion is estimated by the PARTY_{SOC} model. The PARTY_{SOC} model is a random forest machine learning model that estimates the Cs proportion of a sample from several RE parameters that have shown strong correlation with the Cs proportion of soils under bare fallow for several decades (Cécillon et al., 2018). The cycle used by Cécillon et al. (2018) was similar to the PYRO650 one but differed from it in its pyrolysis and oxidation temperature ramps: 30 °C min⁻¹ and 20 °C min⁻¹ respectively, versus 25 °C min⁻¹ for the PYRO650 cycle. Fifteen soil samples were analyzed with the cycle used
 220 by Cécillon et al. (2018) to assess the influence of these differences on the obtained Cs proportions (N° 9, 21, 23, 27, 58, 66, 69, 91, 92, 109, 151, 157, 168, 175, 177; Table S1). The *Soil Carbon* module of the Geoworks™ software (Geoworks V1.8R1, Vinci Technologies) was used to predict the Cs proportions for each soil sample and each RE analysis cycle with the PARTY_{SOC} v2.0 model (Cécillon et al., 2021). With both the PYRO650 cycle and the cycle from Cécillon et al. (2018), the Geoworks™ software integrates CO and CO₂ pyrolysis signals up to 560 °C and the CO₂ oxidation signal up to 611 °C
 225 (Cécillon et al., 2018). With the PYRO520 cycle, the HC, CO, and CO₂ pyrolysis signals were integrated across the whole pyrolysis temperature range. The Cs proportions obtained with the PYRO650, PYRO520 cycles, and the one used by Cécillon et al. (2018) are noted Cs₆₅₀, Cs₅₂₀, and Cs_{Cécillon}, respectively.

2.4 Data analysis

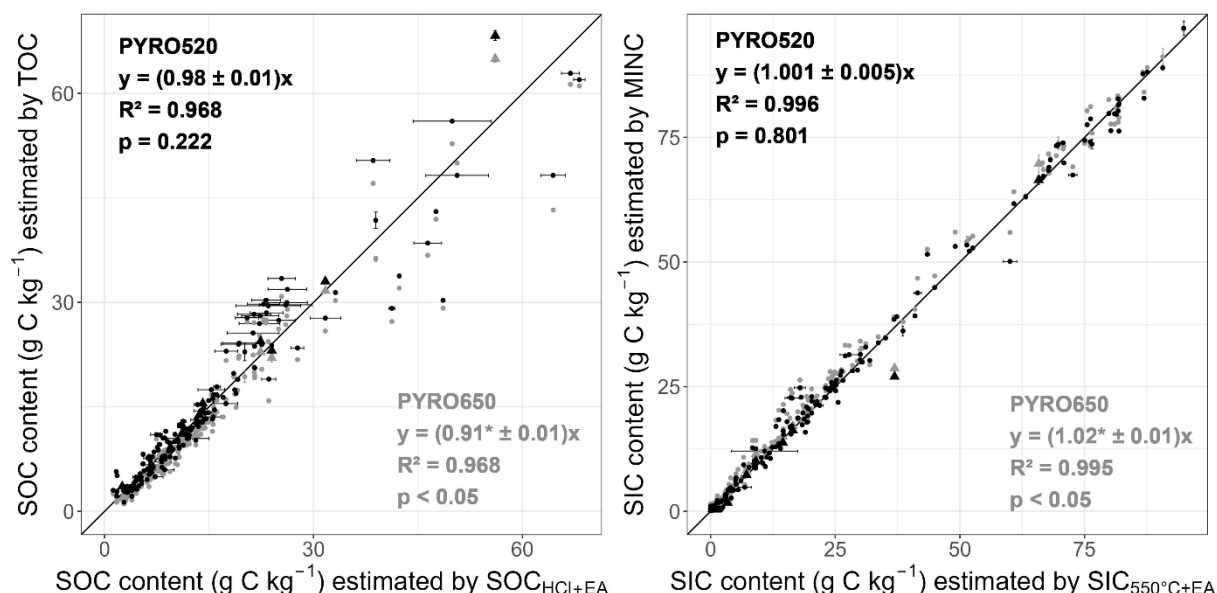
The measurement repeatability was assessed using the median of standard deviations and coefficients of variation. The
 230 measurement accuracy was evaluated using the median of the absolute values of the relative error with respect to the reference contents of standard materials. For the measurements of the SIC content, only calcareous samples (SIC ≥ 2 g C kg⁻¹) were included, specifically, this involved seven reference materials (Table 1), and 37 soil samples that were reanalyzed from the total of 147 calcareous soil samples.

The significance of the differences between the paired variables was evaluated within a 95% confidence interval using the
 235 Student's test for parametric variables (H0: the variables are not different, *t-test* function of the statistical software R, R Core Team, 2024) and the Wilcoxon's test for non-parametric variables (H0: the variables are not different, *wilcox.test* function of R). Ordinary least squares regressions between the variables were tested with the linear model fitting function (*lm* function of R) without their intercept. The overall significance of the regression was evaluated with the Fisher's test (H0: the relationship between the two variables is not significant). The coefficient of determination R^2 reflects the proportion of
 240 variance explained by the regression. The significance of the difference between the regression slope and 1 was evaluated within a 95% confidence interval using the Student's test (H0: the slope is equal to 1, *t-test* function of R). The regression slopes are given with their standard errors.

3 Results and discussion

3.1 Quantification of soil organic and inorganic carbon with the PYRO520 cycle of the Rock-Eval® device

245 TC_{EA} was well estimated by TC_{650} ($TC_{650} = (1.00 \pm 0.00) TC_{EA}$, p-value (p) < 0.001, $R^2 = 0.997$; Fig. S1), while TOC_{650} underestimated SOC_{HCl+EA} by 9% ($TOC_{650} = (0.91 \pm 0.01) SOC_{HCl+EA}$; Fig. 2) and $MINC_{650}$ overestimated $SIC_{550^\circ C+EA}$ by 2% ($MINC_{650} = (1.02 \pm 0.01) SIC_{550^\circ C+EA}$; Fig. 2).



250 **Figure 2:** SOC and SIC contents ($g C kg^{-1}$) estimated by TOC_{650} and $MINC_{650}$ (gray) and TOC_{520} and $MINC_{520}$ (black), respectively ($n = 182$ samples), vs SOC and SIC contents estimated by SOC_{HCl+EA} and $SIC_{550^\circ C+EA}$, respectively ($n = 173$ soils), and reference SOC and SIC contents ($n = 9$ reference materials). Soil samples are represented by dots, and reference materials by triangles. Error bars show the standard deviations of SOC and SIC estimations by SOC_{HCl+EA} and $SIC_{550^\circ C+EA}$ (black symbols only, $n = 117$), TOC_{650} and $MINC_{650}$ ($n = 20$ i.e., 11 soils + 9 reference materials), and TOC_{520} and $MINC_{520}$ ($n = 20$), respectively. The 1:1 line ($y = x$) is plotted as a solid black line. Regression slopes are significantly different from zero (p-value (p) < 0.001). The p-values displayed on the graph indicate whether the slope significantly differs from 1. * Slope significantly differs from 1.

The deviations between TOC_{650} and SOC_{HCl+EA} showed distributions significantly shifted towards negative values, while the deviations between $MINC_{650}$ and $SIC_{550^\circ C+EA}$ showed distributions significantly shifted towards positive values (Fig. 3).

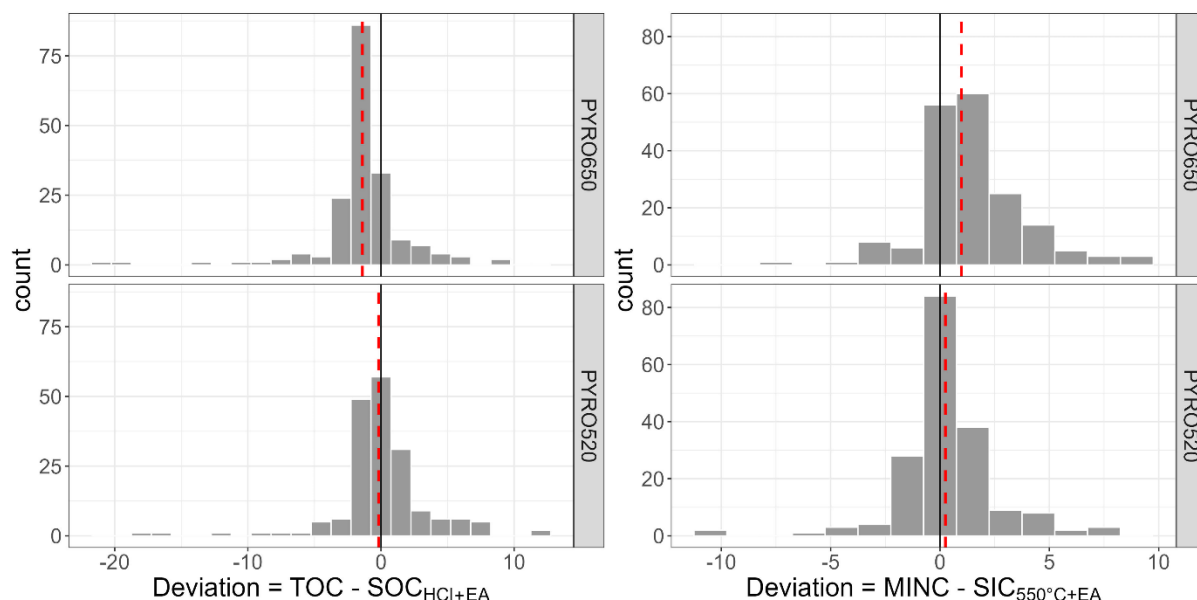


Figure 3: Distributions of deviations (g C kg^{-1}) between the SOC content estimated by TOC_{650} (top) or TOC_{520} (bottom) and by $\text{SOC}_{\text{HCl+EA}}$ or the reference SOC content (left) and between the SIC content estimated by MINC_{650} (top) and MINC_{520} (bottom) and by $\text{SIC}_{550^\circ\text{C+EA}}$ or the SIC reference content (right, $n = 182$). The zero-deviation line is plotted as a solid black line. The medians of the deviation are plotted as red dashed lines.

These results confirm that, with the PYRO650 cycle, a systematic error in the signal allocation between the TOC_{650} and MINC_{650} parameters is added to the random measurement error of the Rock-Eval® device. Delahaie et al., (2023), Hazera et al. (2023) and Stojanova et al. (2024) reported underestimations by the TOC parameter of 13%, 16%, and 8%, respectively, and overestimations by the MINC parameter of 7%, 4%, and 4%, respectively, with RE analysis cycles identical or similar to the PYRO650 cycle. The reported percentage of deviations between the EA and RE estimations are in the same range of values but vary depending on the datasets. These observations confirm that correcting these deviations with a fixed coefficient estimated on specific datasets could lead to substantial errors. Recently, this correction has been statistically modeled using machine learning algorithms to avoid errors related to the use of a fixed correction coefficient for all soils (Stojanova et al., 2024). However, this latter method was also calibrated on SOC and SIC contents estimated with the standard quantification methods (see Introduction), and only on French agricultural topsoils with a SOC content not exceeding 50 g C kg^{-1} so far.

TC_{EA} was also well estimated by TC_{520} ($\text{TC}_{520} = (1.01 \pm 0.00) \text{ TC}_{\text{EA}}$, $p < 0.001$, $R^2 = 0.997$; Fig. S1). TOC_{520} was statistically higher than TOC_{650} (Wilcoxon's test: $p < 0.05$) and was not statistically different from $\text{SOC}_{\text{HCl+EA}}$ (Wilcoxon's test: $p = 0.96$). The slope of the regression between $\text{SOC}_{\text{HCl+EA}}$ and TOC_{520} ($\text{TOC}_{520} = (0.98 \pm 0.01) \text{ SOC}_{\text{HCl+EA}}$; Fig. 2) was not statistically different from 1 (Student's test: $p = 0.222$, Fig. 2). The mean of the absolute deviations between TOC_{520} and $\text{SOC}_{\text{HCl+EA}}$ was larger for samples with $\text{SOC} \geq 40 \text{ g C kg}^{-1}$ ($8.95 \pm 5.14 \text{ g C kg}^{-1}$, $n = 11$) than for samples with $\text{SOC} < 40 \text{ g C kg}^{-1}$ ($1.66 \pm 1.78 \text{ g C kg}^{-1}$). Disnar et al. (2003) previously reported particularly large deviations between



the RE and EA estimations for “biopolymer-rich samples”. MINC₅₂₀ was statistically lower than MINC₆₅₀ (Wilcoxon’s test: $p < 0.05$) but remained statistically different from SIC_{550°C+EA} (Wilcoxon’s test: $0.01 < p < 0.05$). However, the slope of the regression between MINC₅₂₀ and SIC_{550°C+EA} (MINC₅₂₀ = (1.00 ± 0.00) SIC_{550°C+EA}; Fig. 2) was not significantly different from 1 (Student’s test: $p = 0.801$, Fig. 2). The deviations between TOC₅₂₀ and SOC_{HCl+EA}, and between MINC₅₂₀ and SIC_{550°C+EA}, showed distributions centered around zero, comparable to the distribution of random measurement errors (Fig. 3).

The repeatability of RE analyses was satisfactory. The medians of the standard deviations and the coefficients of variation obtained by RE were lower than or equivalent to the ones obtained by EA (Table 4).

Table 4: Medians of standard deviation (SD, g C kg⁻¹) and coefficient of variation (CV, %) of the total carbon (TC), organic carbon (SOC) and inorganic carbon (SIC) content estimations replicated at least 3 times on both the soil collection and the reference material sets. Median of the absolute relative errors (%) calculated with respect to the reference values given by the environmental agencies for TC, SOC and SIC content estimations. N indicates the number of samples replicated and n indicates the number of analyses used for the calculations. SIC*: standard deviations, coefficients of variation and relative errors are reported for calcareous samples only (SIC content ≥ 2 g C kg⁻¹).

C form	Method	Soil collection set				Reference material set				
		SD	CV	N	n	Relative error	SD	CV	N	n
SOC	SOC _{HCl+EA}	0.4	4.0	117	408	11.7	2.1	12.7	9	283
	TOC ₆₅₀	0.2	1.7	11	33	5.0	0.1	0.8	9	27
	TOC ₅₂₀	0.2	2.5	11	33	8.7	0.1	0.4	9	27
SIC*	SIC _{550°C+EA}	0.3	2.5	37	112	21.9	1.7	14.6	7	152
	MINC ₆₅₀	0.5	1.7	10	30	13.8	0.2	1.5	7	21
	MINC ₅₂₀	0.5	1.4	10	30	5.1	0.1	1.1	7	21
TC	TC _{EA}	0.4	1.5	50	155	2.9	1.3	4.0	9	278
	TC ₆₅₀	0.6	1.3	11	33	2.0	0.2	1.0	9	27
	TC ₅₂₀	0.4	1.0	11	33	1.4	0.1	0.3	9	27

For the reference materials, the standard deviations and the coefficients of variation of EA were calculated from the results of four laboratories, which explained their higher values compared to the ones of soils and RE analyses. Nevertheless, RE analyses exhibited the lowest standard deviations and coefficients of variation among the five laboratories (data not shown). The medians of the standard deviations and the coefficients of variation obtained with the PYRO520 cycle were comparable to the ones obtained with the PYRO650 cycle (Table 4). The repeatability of the PYRO520 cycle was equivalent to that of EA or the PYRO650 cycle.



The values obtained by RE seemed more accurate than those obtained by EA. The medians of the absolute relative errors obtained by RE were lower than the ones obtained by EA (Table 4), yet the reference values were estimated by EA. Although the medians of relative errors for TC_{EA} and $SIC_{550^{\circ}C+EA}$ were calculated from the results of four laboratories, they
 305 are consistent with the ones reported by Shamrikova et al. (2023): between 10% and 23% for TC contents ranging from 1 g C kg⁻¹ to 300 g C kg⁻¹ and between 15% and 25% for SIC contents ranging from 1 g C kg⁻¹ to 120 g C kg⁻¹. The relative errors obtained by RE were higher than the ones reported by Pacini et al. (2023) of 1.2% for TOC and 3.3% for MINC. However, the relative errors reported by Pacini et al. (2023) were calculated with respect to the mean value obtained by a set of RE devices and not with respect to a reference value. Thus, the relative errors reported by Pacini et al. (2023) reflect the
 310 inter-laboratory reproducibility of RE results rather than the accuracy of RE results. The relative errors obtained with the PYRO520 cycle were similar to the ones obtained with the PYRO650 cycle (Table 4). The accuracy of the estimations obtained with the PYRO520 cycle was finally satisfactory.

Thus, lowering the final temperature of pyrolysis at 520°C (i) corrected the misallocation of the end-of-pyrolysis signals in the TOC and MINC parameters without the need for post-hoc corrections, and (ii) improved the estimations of the SOC and
 315 SIC contents estimated by EA after acid or heating pretreatments. The TOC_{520} and $MINC_{520}$ parameters were reproducible and accurate estimators of the SOC_{HCl+EA} and $SIC_{550^{\circ}C+EA}$ values.

3.2 Consequences of the change of the analysis cycle on the indices of organic matter characterization

3.2.1 Hydrogen index and oxygen index

The hydrogen indices (HI) and oxygen indices (OIRE6) obtained with the PYRO520 and PYRO650 cycles were statistically
 320 different (Wilcoxon's tests: $p < 0.05$) but remained within similar ranges. HI_{650} range was 20-310 mg HC g⁻¹ TOC and HI_{520} range was 16-285 mg HC g⁻¹ TOC (Fig. 4a). $OIRE_{650}$ range was 216-1159 mg O₂ g⁻¹ TOC and $OIRE_{520}$ range was 256-1149 mg O₂ g⁻¹ TOC (Fig. 4b).

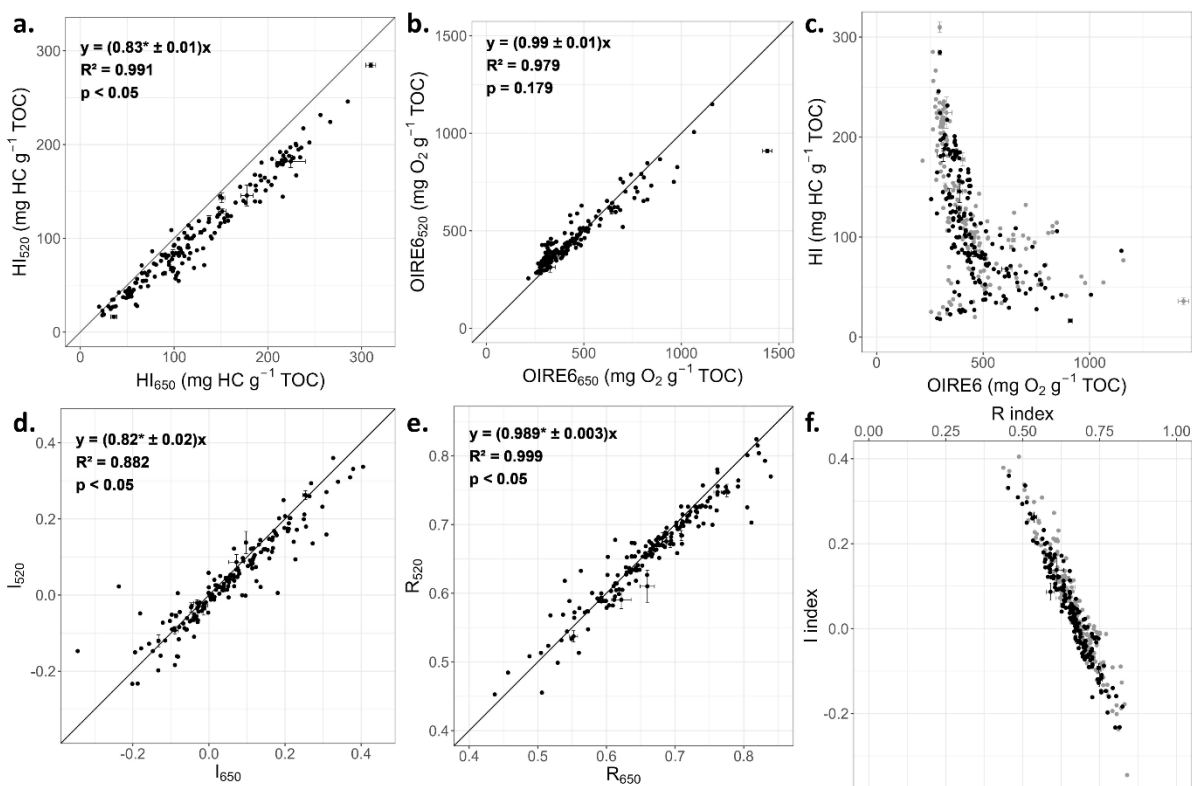


Figure 4: Comparison of the indices characterizing OM obtained with the PYRO650 and PYRO520 cycles (n = 173). a. HI₅₂₀ vs HI₆₅₀ (mg HC g⁻¹ TOC) b. OIRE₅₂₀ vs OIRE₆₅₀ (mg O₂ g⁻¹ TOC) c. HI₅₂₀ = f(OIRE₆₅₀) in black and HI₆₅₀ = f(OIRE₆₅₀) in gray. d. I₅₂₀ vs I₆₅₀. e. R₅₂₀ vs R₆₅₀. f. I₅₂₀ = f(R₅₂₀) in black and I₆₅₀ = f(R₆₅₀) in gray. The 1:1 line (y = x) is plotted as a solid black line. Regression slopes are significantly different from zero (p-value (p) < 0.001). The p-values displayed on the graph indicate whether the slope significantly differs from 1. * Slope significantly differs from 1.

Sebag et al. (2016) reported HI range of 5-400 mg HC g⁻¹ TOC and OIRE6 range of 150- 1020 mg O₂ g⁻¹ TOC for a diversity of A and B horizons (n = 527) analyzed with a cycle similar to the PYRO650 one. Delahaie et al. (2023) reported HI range of 67- 515 mg HC g⁻¹ TOC and OIRE6 range of 75- 337 mg O₂ g⁻¹ TOC for a diversity of French agricultural topsoils (n = 1891) analyzed with a cycle similar to the PYRO650 one. The HI and OIRE6 measured in this study were therefore consistent with those reported in the literature.

The HI and OIRE6 obtained with the PYRO520 cycle were linearly correlated with those obtained with the PYRO650 cycle ($R^2 \geq 0.98$, $p < 0.001$; Fig. 4a and 4b). HI₅₂₀ were on average lower than HI₆₅₀ (HI₅₂₀ = (0.83 ± 0.01) HI₆₅₀; Fig. 4a). The S2 curve integrations obtained with the PYRO520 cycle were reduced by the HC emitted between 520 °C and 650 °C thus their integrations were lower. As the TOC₅₂₀ parameter was higher than the TOC₆₅₀ parameter (Fig. 2), the S2:TOC ratio of the PYRO520 cycle used in the HI calculation (Eq. 5) was lower than the one of the PYRO650 cycle. OIRE₅₂₀ were on average close to OIRE₆₅₀ (OIRE₅₂₀ = (0.99 ± 0.01) OIRE₆₅₀; Fig. 4b). The reduction of the S3CO and S3CO₂ curves by the CO₂ emitted between 520°C and 550°C in the PYRO520 cycle was offset by the 5-minute isotherm at 520°C at the end of the



pyrolysis. The integrations of the S3CO and S3CO₂ curves obtained with the PYRO520 cycle were, on average, slightly higher than those obtained with the PYRO650 cycle (Fig. S2 and S3). As the TOC parameter was also higher with the PYRO520 cycle (Fig. 2), the S3CO:TOC and S3CO₂:TOC ratios of the PYRO520 cycle used in the OIRE6 calculation (Eq. 6) were equivalent to those of the PYRO650 cycle. Only one soil sample (No. 168, Table S1) showed a large difference
 345 between OIRE6₆₅₀ and OIRE6₅₂₀, respectively $1441 \pm 25 \text{ mg O}_2 \text{ g}^{-1} \text{ TOC}$ and $910 \pm 9 \text{ mg O}_2 \text{ g}^{-1} \text{ TOC}$. This sample, which had a very low SOC content, showed the largest relative difference between TOC₅₂₀ ($4.6 \pm 0.1 \text{ g C kg}^{-1}$) and TOC₆₅₀ ($2.1 \pm 0.0 \text{ g C kg}^{-1}$), greatly influencing the S3CO:TOC and S3CO₂:TOC ratios. Consequently, the OIRE6₆₅₀ of this sample was particularly high and aberrant compared to the OIRE6 values reported in the literature.

The general trend of the $\text{HI} = f(\text{OIRE6})$ diagram was preserved with the PYRO520 cycle (Fig. 4c). With the PYRO520
 350 cycle, HI and OIRE6 are henceforth calculated with more accurate TOC values as they are no longer influenced by the presence of SIC. Moreover, the S2, S3CO, and S3CO₂ curves are integrated over identical temperature intervals (200-520°C), contrary to HI₆₅₀ and OIRE6₆₅₀, for which the S2 curve was integrated over 200-650 °C and the S3CO and S3CO₂ curves over 200-550 °C (Table 3). Consequently, HI₅₂₀ and OIRE6₅₂₀ are more coherent for characterizing organic matter in soil samples.

3.2.2 I-index and R-index

I₅₂₀ and R₅₂₀ were statistically different from I₆₅₀ and R₆₅₀, respectively (Student's test: $p < 0.05$), but remained within similar ranges. I₆₅₀ ranged from -0.35 to +0.40 and I₅₂₀ from -0.23 to +0.36. R₆₅₀ ranged from 0.44 to 0.84 and R₅₂₀ from 0.45 to 0.82. Sebag et al. (2016) reported I indices ranging from -0.18 to +0.64 and R indices from 0.29 to 0.80 for a diversity of A and B horizons ($n = 527$) analyzed with a cycle similar to the PYRO650 one. Delahaie et al. (2023) reported I indices
 360 ranging from -0.14 to +0.39 and R indices from 0.44 to 0.77 for a diversity of French agricultural topsoils ($n = 1891$) analyzed with a cycle similar to the PYRO650 one. The I and R indices measured in this study were therefore consistent with those reported in the literature.

The indices I and R obtained with the PYRO520 cycle were linearly correlated with those obtained with the PYRO650 cycle ($R^2 \geq 0.9$, $p < 0.001$; Fig. 4d and 4e). I₅₂₀ were on average lower than I₆₅₀ ($I_{520} = (0.82 \pm 0.01) I_{650}$; Fig. 4d), whereas the R
 365 indices were on average not modified by the cycle change ($R_{520} = (0.99 \pm 0.01) R_{650}$; Fig. 6e). This was due to the modification in the contributions of the A1 to A5 areas to the S2 curve used in the calculation of the I and R indices (Eq. 7, 8, and 9, Table 5).



Table 5: Proportions (mean $\pm$ standard deviation) of the A1, A2, A3, A4, and A5 areas (% of S2 curve) obtained with the PYRO650 and PYRO520 cycles. The p-values indicate whether the difference between the proportions obtained with the PYRO650 and PYRO520 cycles is statistically significant.

	A1	A2	A3	A4	A5
PYRO650	12.3 $\pm$ 5.0	21.2 $\pm$ 3.8	28.8 $\pm$ 2.9	24.3 $\pm$ 3.4	13.3 $\pm$ 4.9
PYRO520	12.2 $\pm$ 4.6	22.0 $\pm$ 3.5	30.6 $\pm$ 2.8	35.2 $\pm$ 5.9	NA
p-value	0.25	< 0.5	< 0.5	< 0.5	NA

The absence of the A5 area in the PYRO520 cycle (approximately -13%) was offset by an increase of the A4 area contribution (approximately +10%), as it included the HC emitted during the 5-minute isotherm at 520°C at the end of pyrolysis, and by an increase of the A3 area contribution (approximately +2%; Table 5). Therefore, the ratio of the R index (Eq. 8) was not significantly altered by the modification of the pyrolysis phase. In contrast, the A1+A2:A3 ratio used in the I index calculation (Eq. 7) was slightly lower with the PYRO520 cycle because, although the contribution of the A1 area was not modified (Wilcoxon's test: $p = 0.25$; Table 4), the contribution of the A3 area increased more than the one of the A2 area (< 1%; Table 5). Since the calculation of the I index involves a logarithmic function, this slight decrease in the A1+A2:A3 ratio was amplified. However, the general trend of the $I = f(R)$ diagram was preserved with the PYRO520 cycle (Fig. 4f).

3.2.3 Cs proportion

The $Cs_{Cécillon}$ proportions were not significantly different from the Cs_{650} proportions (Student's test: $p = 0.07$, $n = 15$; Fig. S4). The differences between the PYRO650 cycle and the one used by Cécillon et al. (2018) did not affect the Cs proportions estimated by the Party_{SOC} algorithm. Cs_{520} was statistically different from Cs_{650} (Wilcoxon's test: $p < 0.05$) but remained within similar ranges. Cs_{650} ranged from 32% to 85% and Cs_{520} from 46% to 84%. Kanari et al. (2022) and Delahaie et al. (2024) reported Cs proportions ranging from 44% to 74% and from 25% to 82%, respectively, for a diversity of French agricultural topsoils analyzed with the cycle used by Cécillon et al. (2018). Therefore, the Cs proportions measured in this study were consistent with those reported in the literature.

Cs_{520} and Cs_{650} were linearly correlated ($R^2 = 0.99$, $p < 0.001$; Fig. 5). Cs_{520} were on average higher than Cs_{650} ($Cs_{520} = (1.02 \pm 0.00) Cs_{650}$; Fig. 5).

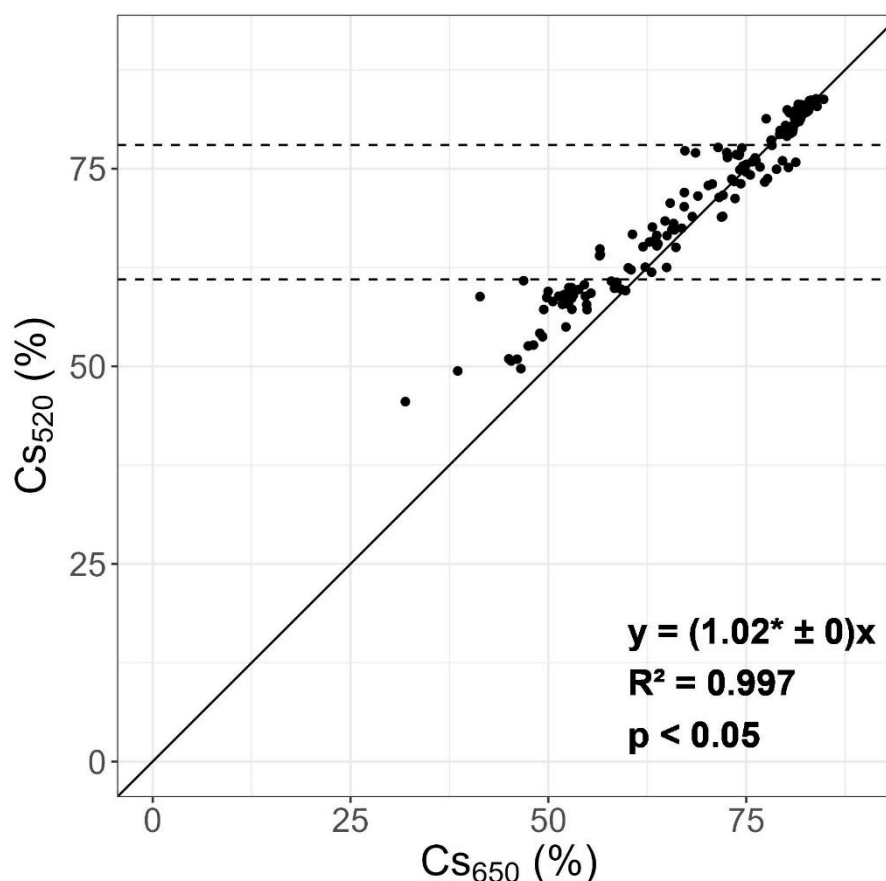


Figure 5: Proportion Cs_{520} vs proportion Cs_{650} ($n = 173$). The 1:1 line ($y = x$) is plotted as a solid black line and the $Cs_{520} = 61\%$ and $Cs_{520} = 78\%$ lines are plotted as dashed black lines. Regression slope is significantly different from zero (p -value (p) < 0.001). The p -value displayed on the graph indicates whether the slope significantly differs from 1. * Slope significantly differs from 1.

The Cs proportion showed strong negative correlations with the parameters HI, S2, and the amount of pyrolyzed carbon (Cécillon et al., 2021). These parameters were lower with the PYRO520 cycle because a part of the OM that usually decomposes during pyrolysis was decomposed during the oxidation phase. Similarly, the Cs proportion showed positive correlations with the temperatures at which 50%, 70%, and 90% of the carbon is emitted as CO_2 during the oxidation phase (Cécillon et al., 2021). These temperatures were higher with the PYRO520 cycle because the thermally stable fraction of OM that did not decompose during pyrolysis decomposed at higher temperatures during the oxidation phase. Thus, the Party_{SOC} algorithm predicted higher Cs proportions with the signals obtained with the PYRO520 cycle than with those obtained with the PYRO650 cycle. The deviation of measurements between Cs_{650} and Cs_{520} seemed to depend on the magnitude of Cs value (Fig. 5). The deviations between Cs_{650} and Cs_{520} were larger for low Cs values: on average 6% for Cs_{520} values below 61% ($n = 39$), 1% for Cs_{520} values between 61% and 78% ($n = 66$), and < 0.5% for Cs_{520} values above 78% ($n = 68$).



405 4 Conclusions

The TOC and MINC parameters obtained with the PYRO520 cycle were higher and lower than the ones obtained with the PYRO650 cycle, respectively. Lowering the final pyrolysis temperature corrected the misallocation of the end-of-pyrolysis signals between the TOC and MINC parameters and, thereby avoiding the need for post-hoc corrections. The TOC₅₂₀ and MINC₅₂₀ parameters estimated SOC and SIC contents measured by EA after pretreatments with both good repeatability and
 410 accuracy. The MINC₅₂₀ parameter provided accurate estimates of SIC contents up to 100 g C kg⁻¹. However, discrepancies between the TOC₅₂₀ parameter and the SOC_{HCl+EA} values persisted for samples rich in SOC (≥ 40 g C kg⁻¹). Specific studies should focus on rich SOC samples to improve the estimation of their SOC contents by RE.

The modification of the pyrolysis phase decreased the HI and I indices while having almost no effect on the OIRE6 and R indices. Nevertheless, the general trends of the HI = f(OIRE6) and I = f(R) diagrams were preserved with the PYRO520
 415 cycle. The proportions of Cs predicted by the Party_{SOC} algorithm with the PYRO520 signals were higher than the ones predicted with the PYRO650 signals, especially for soils with a predicted Cs₅₂₀ below 61%.

Since the HI, OIRE6, I, R indices, and the Cs proportions obtained with the two cycles were linearly correlated, the indices obtained with the PYRO650 cycle could be converted to be compared with those obtained with the PYRO520 cycle.

420 *Data availability.* The dataset is available at <https://doi.org/10.57745/AL3NVT>.

Supplement. SM1: Table S1, <https://doi.org/10.57745/AL3NVT>

SM2: Figures

Author contributions. JH, DS, TC, and IK designed the experiment. GJ, DZ, LT, RM, and JF sampled the soils. JH and HR performed the Rock-Eval measurements. GJ, DZ, FS, JF, and TC performed the elemental analysis. JH, TC, DS, IK, EV, and
 425 HR analyzed the data. JH wrote the manuscript. TC, DS, IK, EV, GJ, DZ, FS, LT, RM and, JF reviewed and edited the manuscript.

Competing interests. The authors declare that they have no conflict of interest.

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