

Soil organic matter thermal pools as influenced by depth, tillage, and soil texture – A Rock-Eval® analysis study on the cropland soils of the Swiss Plateau

Cedric Deluz, David Sebag, Eric Verrecchia, Pascal Boivin

▶ To cite this version:

Cedric Deluz, David Sebag, Eric Verrecchia, Pascal Boivin. Soil organic matter thermal pools as influenced by depth, tillage, and soil texture – A Rock-Eval® analysis study on the cropland soils of the Swiss Plateau. Geoderma, 2024, 445, pp.116871. 10.1016/j.geoderma.2024.116871. hal-04559321

HAL Id: hal-04559321 https://ifp.hal.science/hal-04559321v1

Submitted on 25 Apr 2024 $\,$

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution 4.0 International License



Contents lists available at ScienceDirect

Geoderma



journal homepage: www.elsevier.com/locate/geoderma

Soil organic matter thermal pools as influenced by depth, tillage, and soil texture – A Rock-Eval® analysis study on the cropland soils of the Swiss Plateau

Cedric Deluz^{a,b,*}, David Sebag^c, Eric Verrecchia^b, Pascal Boivin^a

^a University of Applied Sciences of Western Switzerland, HES-SO, hepia-inTNP, 150 route de Presinge, 1254 Jussy Geneva, Switzerland

^b University of Lausanne, FGSE-IDYST, Campus Mouline, CH-1015 Lausanne, Switzerland

^c IFPEN, Earth Sciences and Environmental Technologies Division, Rueil-Malmaison, France

ARTICLE INFO

Handling Editor: C. Rumpel

Keywords: Soil organic carbon Soil organic matter Organic matter pools Tillage Structure vulnerability Clay content Clay saturation Rock-Eval®

ABSTRACT

This study investigated the relationships between the soil organic matter content (SOM), SOM thermal pools, soil properties, and tillage practices, on cropland soils of the central plateau of Switzerland. Soil samples were collected in 45 no-till and conventional tillage fields in five layers from 0 to 40 cm depth. Soil organic carbon content (SOC) and hydrocarbon compound (HC) pools were analysed with Rock-Eval® thermal analysis. In addition, the clay content was determined by sedimentation.

The SOM contents were highest in 0–5 cm of no-till soils and the plough pan of tilled soils. SOM was less oxygenated and showed lower degradation under conventional tillage then no-tillage. The proportion of the thermo-stable pool was mainly explained by the SOC:clay ratio, regardless of tillage practices. Below a SOC:clay ratio of 0.08, all pools were decreasing nearly equally with decreasing SOC. Above this ratio, thermo-stable pools increased only slightly, while thermo-labile pools increased linearly with SOC:clay on the full SOC:clay range. The 0.08 SOC:clay threshold in the thermo-stable pools content corresponded to the lower threshold of structure stability determined for Swiss and UK soils, below which, on average, severely degraded structures are observed in the field. These findings suggest that a large proportion of thermo-labile pool is necessary for acceptable to high soil structure quality, to protect the thermo-stable forms from degradation, and to reach the carbon sequestration potential of the soil.

1. Introduction

The ability of soils to support agricultural production while providing many other functions is directly related to their physical, chemical, and biological properties (Karlen et al., 1997; King et al., 2020). Soil organic matter (SOM) is one of the main contributors to soil quality (Bünemann et al., 2018), despite its low proportion by mass and volume in soils. Unfortunately, cropped soil quality is increasingly considered critical worldwide, due in large part to a lack of SOM (Lal, 2004; Montanarella et al., 2016; Scholes et al., 2018). Growing interest in SOM stocks, and the cropping practices granting their increase, arose when their potential to remove CO_2 from the atmosphere was stressed (Minasny et al., 2017), which in turn has also raised many conflicting debates. Numerous considerations have fuelled the debate on the relationships between cropping practices and SOM contents, particularly regarding the SOM distribution with depth, the turnover of the various SOM pools, and the observed differences in SOM dynamics between long-term experiments and on-farm results (Dupla et al., 2022).

The reduction or abandonment of tillage induces a relocation of SOM, accumulating it at the soil surface while potentially decreasing its content in the plough pan zone (e.g. Angers and Eriksen-Hamel, 2008; Balesdent et al., 2000; de Oliveira Ferreira et al., 2013; Dimassi et al., 2014; Luo et al., 2010). SOC residence time was shown to increase with depth (Balesdent et al., 2018), with 80 % of the short-term (50-year) changes in SOC content occurring in the soil upper 30 cm. However, the links between residence time, depth, SOC content, and the quality of SOM still largely need to be deciphered, as they constitute key knowledge for both the management of soil fertility and the sequestration of atmospheric carbon in soils.

SOM quality refers to the characterization of different SOM pools. As

https://doi.org/10.1016/j.geoderma.2024.116871

Received 21 June 2023; Received in revised form 27 March 2024; Accepted 28 March 2024 Available online 5 April 2024

0016-7061/© 2024 The Author(s). Published by Elsevier B.V. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author. *E-mail address:* cedric.deluz@hesge.ch (C. Deluz).

reported in Plante (2010), "various physical, chemical and biological fractionation techniques as well as analytical and instrumental chemical techniques have been used to characterize SOM quality to varying degrees, though correlations between various methods are not frequently reported or apparent". Moreover, most characterization methods are time-consuming and expensive, which limits the availability of largescale information. Since Disnar et al. (2003) the Rock-Eval® thermal analysis method proved to be particularly fast and inexpensive (Soucémarianadin et al., 2018). It allowed us to highlight the link between the thermal properties of SOM and its stability in soils (Plante et al., 2009, 2011). Since then, several studies have demonstrated the effectiveness of the method in measuring SOM content and distinguishing its labile, resistant, and refractory thermal pools (Albrecht et al., 2015; Saenger et al., 2013; Sebag et al., 2016; Soucémarianadin et al., 2018; Zhang et al., 2023). The links between the thermal stability of the different pools and their bioavailability to soil microorganisms were discussed in a few studies (Barré et al., 2016; Gregorich et al., 2015).

The relationships between cropping practices, soil properties, SOM content, and SOM stability were investigated during the past decades. The degree of association with clay-size particles is considered the main SOM protection process (e.g. Bosatta and Ågren, 1999; Lehmann and Kleber, 2015; Manlay et al., 2007; Plante, 2010). A concept, the soil carbon saturation, was introduced by Hassink (1997) and the amount of SOC that can be complexed on clay surfaces was quantified as 10 % of the clay content (w.w⁻¹) by Dexter et al. (2008). This 10 % threshold was often referred to as SOM saturation, thus conveying the idea that there might be a maximum "efficient" SOC with respect to soil quality. This was further developed by Johannes et al. (2017) and Prout et al. (2020) who showed on a large range of Swiss and UK soils that on average the SOC:clay ratio threshold values of 0.08, 0.1 and 0.12 defined, respectively, the domains of poor, acceptable, and sustainable structure quality. These values correspond to structure vulnerability thresholds (Dupla et al., 2021), though none of these studies observed clay-particle surface saturation, a concept which was applied to clay and clay $+\ silt$ size fractions and that remains disputed (Begill et al., 2023; Cotrufo et al., 2023; Six et al., 2023; Poeplau et al., 2023).

SOM pools are assumed to vary with cropping practices and SOM content. Some studies based on the respiration method (Haynes, 2005) or the particulate organic matter (POM) separation method (von Lützow et al., 2007) suggested that labile, easy to mineralize, SOM was located in the uppermost topsoil under conservation agriculture whereas it was more present at plough pan depth under conventional tillage; Murphy et al. (2011), Salvo et al. (2010). However, the relationships between cropping practices, SOM content, and SOM biogeochemical stability remain largely unknown.

Characterizing SOM content and its relationships to cropping practices is also questioned with respect to experimental setups. Gubler et al. (2019) pointed out that most comparative studies were carried out within the framework of paired experiments, on which practices may be unrealistic compared to the practices used by farmers, thus leading to biased conclusions (Cook et al., 2013; Govaerts et al., 2009). As an illustration, long-term experiments in Switzerland tend to show that SOC content was decreasing regardless of cropping practices (Keel et al., 2019) while on-farm results show that, on average, Swiss cropland SOC was increasing (Dupla et al., 2021). It is reasonable to assume that the same contradiction could apply to the SOC pools, although the corresponding information in this context is not available.

Consequently, this study aims at documenting the relationships between SOM pools, cropping practices, and soil properties. We assumed that sampling farm fields should provide relevant information. We worked at the Swiss plateau scale to maximize the clay and SOM content range. We assumed that selecting fields cultivated either with no-till or inversion tillage practices would allow different SOM pools and profiles with depth to be observed. We used Rock-Eval® thermal analysis to characterize these pools and analysed their relationships with soil properties, depth, SOC:clay ratio, and tillage practices.

2. Materials and methods

2.1. Study area and sampled fields

The study area includes 45 fields from 8 cantons across the Swiss Plateau from Geneva to Zurich (Fig. 1), i.e. approximately the same study area as in Johannes et al. (2017). The fields were cropped for at least 10 years under conventional tillage (CT) and no tillage (NT). The distinction between CT (17 fields) and NT (28 fields) was based on farmers' claims and not on quantified criteria, though they were mainly related to tillage intensity.

The soils were "Braunerde / Sol brun" developed on mixed morainemolasse substrate according to the Swiss map of soil (Office fédéral de topographie, 1984), which corresponds to CAMBI-LUVISOL in the FAO-IUSS classification (Food and Agriculture Organisation, 2014). Clay minerals are mostly inherited, of large size, with limited cation exchange capacity and mixed mineralogy (i.e. illite, vermiculite, and interstratified; personal data) because of the post-glacial morainic origin of the geological material and the low level and rate of weathering. Average annual rainfalls range between 900 and 1100 mm and average annual temperatures between 10 and 14° C. The soil sampling was performed under temporary meadows, alfalfa, clover, or green manure. The field surface area ranged between 0.5 and 10 ha and their altitude ranged between 360 and 1020 m.

2.2. Soil sampling

The soil sampling was performed in the 0–40 cm layer from mid-October to the end of December 2018 using a gouge sampler. The plough soles, when observed, were located in the 20 to 30 cm depth layer. Composite samples were formed by collecting 20 aliquots along the diagonals of the field following the recommendations of Deluz et al. (2020). Each gouge sample was split into 5 sub-layers, namely the 0–5; 5–10; 10–20; 20–30 and 30–40 cm depths. One composite sample by depth and field was collected by mixing up all the subsamples of each sub-layer. A total of 5 composite samples per field were therefore collected, representing 225 samples in total for the 45 fields.

2.3. Soil preparation and analyses

The samples were analysed for texture, SOC content and SOM thermal pools. The texture (5 classes) was determined on the < 2 mm fraction using the standard Robinson pipette sedimentation method (ISO 11277) on the 0–20 cm and 20–40 cm depth pooled samples. The



Fig. 1. Switzerland map with location of the sample fields. Diamond \Diamond : Conventional tillage. Ring \bullet : No tillage.

structure vulnerability index was calculated as the SOC to clay content ratio (Dupla et al., 2021; Johannes et al., 2017). The SOC to clay ratio is often referred to as "clay saturation by SOC" in the literature, which we used in its literal sense, without implying that a maximum amount of carbon can be complexed on mineral particles.

The SOC and the different SOM thermal pools were analysed with a Rock-Eval® 6 analyser from Vinci Technologies, after grinding the < 2mm fractions of the soil samples to a $< 250 \,\mu\text{m}$ size. The reader can refer to Behar et al. (2001), Disnar et al. (2003) and Lafargue et al. (1998) for a detailed description of the method and its interpretation. Briefly, the Rock-Eval® thermal analysis is based on a pyrolysis phase (under N2 atmosphere from 200 to 650 °C) releasing volatile hydrocarbon compounds (HC), CO₂ and CO, followed by an oxidation phase (laboratory atmosphere from 300 to 850 °C) extracting by combustion the remaining carbon in the form of CO₂ and CO from organic and carbonated fractions. HC are quantified by flame ionization detection (FID), while CO₂ and CO are quantified by infrared detection (IRD) during both phases. The Rock-Eval® thermal analysis therefore generates five thermograms integrated at defined temperature limits to calculate the total amount of organic carbon (TOC [% g $C.g^{-1}$]), the mineral carbon (MinC $[\% \text{ g C.g}^{-1}]$) and qualitative standard parameters, namely the hydrogen index (HI [mg HC.g⁻¹ TOC]) and the oxygen index (OI [mg CO₂.g⁻¹ TOC) which respectively inform on the degree of hydrogenation and oxygenation of the SOM. They are negatively correlated, and HI informs on the chemical energy potentially available for SOM biodegradation (Disnar et al., 2003; Barré et al., 2016).

In complement to these standard parameters, Sebag et al. (2006, 2016) showed that the HC thermogram, denoted S2 in the literature, can be decomposed into five C thermal pools defined by their range of cracking temperature, by splitting the surface area of the thermogram in five areas based on cracking temperature thresholds. These pools were categorized from thermal most-labile pool (A1 between 200 and 340 $^{\circ}$ C), labile pool (A2 between 340 and 400 $^{\circ}$ C), resistant pool (A3 between 400 and 460 $^{\circ}$ C), refractory pool (A4 between 460 and 520 $^{\circ}$ C) and most-refractory pool (A5 between 520 and 650 $^{\circ}$ C) (Fig. 2).

Among the parameters that can be calculated from Rock-Eval® analysis, we focused on the HI index. HI is the most robust and reproducible parameter provided by Rock-Eval® analysis (Behar et al., 2001; Pacini et al., 2023) and is not sensitive to the presence or absence of mineral carbonates. Moreover, relatively short-term SOM changes, such as expected from changes in cropping practices over a decade, will mainly influence HI, which has therefore already been used to characterize carbon pools from natural soils in the same region or impacts of cropping practices (Delahaie et al., 2023). Furthermore, in this study we multiplied HI (mg HC.g⁻¹ TOC) by the percentage of each of its thermal pools, as suggested in Sebag et al. (2006), to distinguish within the HI the proportion of thermal most-labile, labile, resistant, refractory, and

most-refractory HC. We denoted these different HI pools HIA1, HIA2, HIA3, HIA4 and HIA5 (mg HC.g^{-1} TOC), respectively. The term HIAx refers to all HIA1 to HIA5 pools in the following sections.

As TOC determination by Rock-Eval® can wrongly attribute mineral carbon to non-carbonaceous samples and therefore overestimate the mineral carbon of the samples, the SOTHIS correction method (Hazera et al., 2023; Sebag et al., 2022) has been applied to the whole dataset. The TOC (from Rock-Eval®) corrected by the SOTHIS method will be referred to as SOC_{RE} .

To compare our findings with previously reported results, SOC was also determined on the < 2 mm fraction of the composite samples using the sulfochromic wet oxidation method (ISO 14235) derived from Walkley and Black (1934). This value will be referred to as SOC_{OX} in the following sections.

2.4. Statistical analysis

Statistical analysis was performed using R (v 4.0.3, R Development Core Team 2020). The normality of the distributions was tested using the Shapiro test. The distribution of the different soil properties in NT and CT treatments were compared at all depths using T-tests, after log transformation when necessary. When normality was not respected, we used the non-parametric Wilcoxon test.

A linear multivariate model with stepwise algorithm by Akaike information criterion (stepAIC function of the MASS package in the statistical software R) was used to select the combinations of independent variables maximizing the adjusted R² of the model (Venables and Ripley, 2002). The dependent variables included HI, HIAx and the tested independent variables included texture fractions, SOC_{RE}:clay ratio, SOC_{RE}, pH, soil tillage, depth, Rock-Eval® analytical series °n, altitude, and cumulated rainfall (mm) during the 2 weeks before sampling. The "lmg" metric from the R package relaimpo allowed determining a partial R² for each variable selected in the stepAIC model (Grömping, 2006). Based on the partial R² we selected the two first-ranking variables to adjust a simplified model for each of the dependent variables. The two models, namely with all significant independent variables and with the two major independent variables, are presented in the result section.

Linear, logarithmic, and broken-stick models were fitted to describe the relationships between the major independent variables and the hydrocarbon thermal pools. Broken-stick regression statistics (Toms and Lesperance, 2003) were fitted using the "segmented" package (Muggeo, 2008) (version 1.6–2) of the R software. A simple piecewise regression model joining two straight lines at the breakpoint was used and the statistical significance of the breakpoint was assessed using a Davies test (Davies, 2002), which tests for the difference in slope parameters in a piecewise regression. The maximum curvature point of the logarithmic models was determined by calculating the second derivative.



Fig. 2. Examples of hydrocarbon compound (HC) thermograms from samples of the 0-5 cm layer, with the same SOC_{RE} content and different clay content. The relative percentage of each of the five A1, A2, A3, A4 and A5 thermal pools are calculated as the surface area under the thermogram as delimited by the pool threshold temperature value (black vertical bars).

3. Results

The SOC contents obtained with Rock-Eval® (SOC_{RE}) and with sulfochromic wet oxidation (SOC_{OX}) were linearly correlated ($R^2 = 0.993$) with SOC_{RE} = 1.15 SOC_{OX} when the intercept was forced to 0.

In the following section, we examine the relationships between SOC_{RE} , the oxygen and hydrogen indexes, the HIAx pools, soil layer depth and tillage method.

3.1. Carbon-related indexes as a function of depth and tillage

The main properties of the composite samples at the different depths in the NT and CT treatments are presented in Table 1. Clay contents ranged from 11 to 37 % and no significant difference in clay content was observed between NT and CT samples nor between the two 0–20 and 20–40 cm depth layers. The SOC_{RE}, SOC_{RE}:clay and HC values decreased with depth in both treatments. Significant differences were observed as follows: the SOC_{RE}, SOC_{RE}:clay and HC values were higher in the 0–5 cm layer of NT fields while they were larger in CT fields in the 20–30 cm

Table 1

Summary of the properties of the sampled layers for no-till and conventional tillage fields in the 0–5, 5–10, 10–20, 20–30 and 30–40 cm depths. Soil organic carbon content analysed using Rock-Eval® (SOC_{RE}), SOC_{RE}:clay ratio, soil organic carbon content using sulfochromic wet oxidation (SOC_{OX}), SOC_{OX}:clay ratio, Hydrocarbon compounds (HC), Oxidation index OI, Hydrogen index HI and HIAx (x = 1, 2, 3, 4 or 5), corresponding to the most-labile, labile, resistant, refractory and most refractory pools, respectively. Significance level between NT and CT: 0.05 *, 0.01 *** (Student test on log-transformed data for clay, ratio SOC_{RE}:clay and HI comparisons).

	Depth ranges		0–20 cm			20–40 cm						
Analyses and unit	Type of tillage			NT	CT			NT	CT			
	n			28	17			28	17			
Clay [% g clay.g ⁻¹]	Mean			19.87	21.13			19.47	20.67			
	SD			6.63	6.54			5.64	6.61			
	Min			10.86	13.14			11.46	10.92			
	Max			36.67	32.68			33.76	33.05			
	Depth ranges	0-5	5 cm	5-1	0 cm	10-2	10–20 cm		20–30 cm		30–40 cm	
Analyses and unit	Type of tillage	NT	СТ	NT	СТ	NT	СТ	NT	CT	NT	CT	
	n	28	17	28	17	28	17	28	17	28	17	
SOC_{OX} [% g C.g ⁻¹]	Mean	2.70*	2.26*	2.23	2.00	1.77	1.92	1.31*	1.63*	0.83	0.98	
	SD	0.77	0.58	0.75	0.58	0.61	0.56	0.55	0.48	0.37	0.35	
	Min	1.53	1.43	0.90	1.20	0.95	1.22	0.66	1.09	0.41	0.37	
	Max	4.41	3.40	3.81	3.16	3.19	3.00	2.92	2.55	1.83	1.69	
SOC _{RE} [% g C.g ⁻¹]	Mean	3.15*	2.53*	2.59	2.25	2.00	2.10	1.48*	1.76*	0.91	1.05	
	SD	1.16	0.82	0.98	0.70	0.78	0.72	0.65	0.62	0.44	0.38	
	Min	1.61	1.37	0.90	1.24	0.93	1.12	0.69	0.75	0.40	0.33	
	Max	6.62	4.32	4.58	3.68	3.80	3.39	3.45	2.94	2.07	1.70	
ratio SOC _{OX} :clay	Mean	0.14*	0.11*	0.11	0.10	0.09	0.09	0.07*	0.08*	0.04	0.05	
	SD	0.04	0.04	0.03	0.03	0.02	0.02	0.02	0.02	0.01	0.02	
	Min	0.08	0.05	0.07	0.05	0.05	0.06	0.04	0.05	0.02	0.03	
	Max	0.21	0.18	0.18	0.15	0.13	0.15	0.13	0.13	0.08	0.08	
ratio SOC _{RE} :clay	Mean	0.16*	0.13*	0.13	0.11	0.10	0.10	0.08*	0.09*	0.05	0.05	
	SD	0.05	0.04	0.04	0.03	0.02	0.03	0.02	0.02	0.02	0.02	
	Min	0.08	0.06	0.07	0.06	0.06	0.06	0.04	0.05	0.02	0.03	
	Max	0.31	0.21	0.21	0.17	0.15	0.16	0.15	0.13	0.09	0.09	
HC [mg HC.g ⁻¹]	Mean	6.75*	5.20*	4.95	4.34	3.41	3.90	2.16*	2.94*	1.12	1.45	
	SD	2.91	2.03	2.25	1.72	1.62	1.65	1.21	1.17	0.73	0.65	
	Min	2.58	2.57	1.41	2.18	1.19	1.89	0.89	1.13	0.35	0.40	
	Max	14.88	9.54	11.04	7.97	7.69	7.39	6.67	4.67	3.78	2.89	
OI [mg CO ₂ .g ⁻¹ SOC _{RE}]	Mean	221.	211.3.	230	218	242*	220*	259**	231**	315**	274**	
	SD	24	25	27	28	26	29	26	30	56	47	
	Min	162	186	176	180	189	177	210	197	225	216	
	Max	250	282	271	283	291	278	309	295	505	418	
HI [mg HC.g ^{-1} SOC _{RE}]	Mean	211	203	187	190	166**	182**	141***	165***	118**	135**	
	SD	27	26	25	22	22	18	21	15	20	18	
	Min	153	157	142	154	115	155	102	140	87	107	
	Max	260	243	243	230	212	218	193	186	183	170	
HIA1 [mg HC.g ⁻¹ SOC _{RE}]	Mean	48.1	45.9	40.8	41.0	34.8	38.9	29.6*	33.9*	24.6**	28.0**	
most labile pool	SD	9.6	10.1	7.8	7.0	6.1	6.5	5.7	3.9	4.4	3.9	
	Min	31.5	26.4	28.9	26.7	24.5	27.3	20.3	25.3	17.8	22.4	
	Max	63.7	59.7	57.7	56.0	46.4	51.2	44.5	40.2	35.2	33.6	
HIA2 [mg HC.g ⁻¹ SOC _{RE}]	Mean	55.7	51.0	46.4	45.0	38.2*	42.5*	31.0***	37.0***	25.7**	29.73**	
labile pool	SD	9.6	9.1	8.3	6.1	5.8	5.6	4.9	4.3	4.9	4.4	
	Min	38.2	34.1	32.3	36.6	26.3	35.6	21.1	26.0	17.1	23.4	
	Max	73.0	64.5	64.8	59.3	51.4	54.5	41.8	43.0	37.8	37.0	
HIA3 [mg HC.g SOC _{RE}]	Mean	55.2	53.5	50.8	51.5	46.3^	50.1*	38.9***	46.0***	31.5**	36.2**	
resistant pool	SD	6.0	5.3	0.0	4.8	6.0	4.0	0.0	4.2	/.3	5.8	
	Man	41.3	43.2	38.4	44.1	31.3	43.5	26.8	38.6	19.7	26.9	
HIA4 [mg HC g ⁻¹ SOC]	Moon	04.9 36.9	04.3 36 4	24.2	39.3 25 5	39.1	37.2	37.0 37.3***	02.4 99 1***	54.8 21.0*	47.0	
refractory pool	INICALL CD	30.0 4 ۹	30.4	<u>۲۹،۵</u>	23.3 4 A	54.0	30	5.2	32.1	51	23.U 4.6	
remactory poor	Min	7.0 27 4	20.9	7.0 25.2	7.4 201	20.1	3.9 27.6	5.5 10 5	3.7 26.6	14 0	10 1	
	Max	44.8	42.0	43.5 43.1	42.1	43.8	40.8	43.3	20.0	30.7	35.3	
HIA5 [mg HC g^{-1} SOC]	Mean	15.3	15.7	14.0	16.5	14 7*	15 01*		15 9*	147	15 7	
most refractory pool	SD	16	1 4	14.9	4 3	14.7	13.51	22	17	10	10.7	
most renaciony poor	Min	13.0	13.6	12.4	13.2	11.9	14.0	11.4	12.8	11.3	12.2	
	Max	17.8	18.9	18.1	32.4	17.7	191	20.9	20.2	20.0	20.9	
		17.00	10.0	10.1		- / • /	17.1		20.2			

layer. No significant difference between tillage modalities was observed in the other layers (5–10, 10–20 and 30–40 cm).

3.2. Hydrogen and oxygen-bonded carbon

With depth, values of HI decreased, and values of OI increased (Table 1). HI and OI are inversely correlated (y = -0.5578x + 319.7; $R^2 = 0.5$; p_value < 0.01). According to the T-test, HI values were larger and OI values were smaller in CT for the 10–20, 20–30 and 30–40 cm depths, compared to NT.

3.3. HIAx pools

The proportion of the different HC pools in SOC_{RE} HIAx [mg HC g⁻¹ SOC_{RE}], tended to decrease with depth, except HIA5 which showed no change with depth (Table 1). NT and CT HIAx values were similar in the 0–5 and 5–10 cm surface layers. Except for HIA1 and HIA4 at 10–20 cm depths that show no difference, all HIAx are larger for CT at depths between 10 and 40 cm.

3.4. HI and HIAx relationship with soil properties and tillage method

The R^2 and adjusted R^2 of the StepAIC and simplified models (based on the two first-ranking independent variables as selected with the lmg metric) applied to the HI and HIAx dependent variables are presented in Table 2. Two independent variables, namely sampling depth and SOC_{RE}: clay ratio, explained from 57 to 76 % of the variance of the dependent variables, while the other variables provided little additional

Table 2

Summary of optimized model (stepAIC) and simplified model for the response HI, HIA1, HIA2, HIA3, HIA4 and HIA5 HC pools. "stepAIC" optimize the adjusted R² by removing the non-significant variables among the considered explanatory variables (SOC_{RE} ; Clay content; Averages depth; Tillage method; Mineral carbon (MinC); Altitude; Rock-Eval® analytical serie n° (Serie); SOC_{RE} : clay; annual rainfall; Silt content). The "simplified" model used the two most contributing variables from the stepAIC model.

Model	Response variable	Explanatory variables	Multiple R ²	Adjusted R ²
stepAIC	HI	Clay + Averages depth + Tillage + Altitude + Serie + SOC _{PE} :clay	0.81	0.80
Simplified	HI	Averages depth $+$ SOC _{RE} : clay	0.72	0.72
stepAIC	HIA1	Averages depth + Tillage + Serie + Altitude +	0.71	0.70
Simplified	HIA1	SOC _{RE} :clay + pH Averages depth + SOC _{RE} : clay	0.64	0.63
stepAIC	HIA2	SOC_{RE} + Clay + Averages depth + Altitude + Serie +	0.84	0.83
Simplified	HIA2	Averages depth + SOC _{RE} : clay	0.76	0.76
stepAIC	HIA3	SOC_{RE} + Clay + Averages depth + Tillage + Serie + SOC_{RE} + pH	0.79	0.78
Simplified	HIA3	Averages depth $+$ SOC _{RE} : clay	0.66	0.66
stepAIC	HIA4	Clay + Averages depth + Tillage + Altitude + Serie	0.75	0.74
Simplified	HIA4	+ SOC _{RE} : clay $+$ rain $+$ SNC Averages depth $+$ SOC _{RE} : clay	0.57	0.57
stepAIC	HIA5	Clay + Tillage + Altitude	0.22	0.20
Simplified	HIA5	Averages depth + SOC_{RE} : clay	0.01	0.00

information on the HI pools according to the StepAIC (Table 2). Only HIA5 was poorly explained by the independent variables, with a maximum R^2 of 0.22 and no effect of SOC_{RE}:clay ratio and sampling depth ($R^2 = 0.00$).

The relative contribution of the independent variables in the optimized and simplified models according to the lmg metric are presented in Table 3 and Table 4, respectively. For the simplified model (Table 4) the relative weight of the two independent variables is equivalent for HI and HIA3 (respectively R² of 0.36 and 0.33 for the two variables) and is slightly higher for the SOC_{RE}:clay ratio for the HIA1, HIA2 and HIA4 pools, compared to sample depth, with R² = 0.30 for the depth and 0.33 for the SOC_{RE}:clay ratio; 0.36 for the depth and 0.40 for the SOC_{RE}:clay ratio; 0.28 for the depth and 0.30 for the SOC_{RE}:clay ratio, respectively.

The relationships between the hydrocarbon pools and SOC_{RE}:clay are presented in Fig. 3 together with the fitted models. The broken-stick or log models are shown when they significantly fit to the experimental data better than the linear model according to the Davies test, and the corresponding equations are reported in Table 5. The most labile pools HIA1 and HIA2 presented a linear relation to SOC_{RE}:clay, i.e. they can be considered proportional to this ratio, thus decreasing or increasing with it on the full range (Fig. 3 A & B). The relationships between the HIA3 and HIA4 pools and SOC_{RF}:clay were better described by the broken stick model (with breakpoint values of 0.102 and 0.101 SOCRE:clay respectively) or the log model (with maximum curvature points at 0.108 and 0.074 SOC_{RE}:clay respectively; Fig. 3 C & D). However, the RMSE observed with the broken-stick model was equal to or slightly larger than with the logarithmic model. As reported above, HIA5 was constant in the soil samples regardless of SOC_{RE}:clay or any other available property (Table 5 & Fig. 3 E).

4. Discussion

The mean SOC_{OX}:clay ratios (Table 1) found in this study are large compared to the values reported for the Swiss Plateau in the studies of Dupla et al. (2021) and Johannes et al. (2017), particularly for CT fields. This suggests that the corresponding farmers paid more attention their soil organic carbon balance compared to the regional average. The observed SOC_{RE} profiles in NT and CT were accordant with the patterns reported in the literature (e.g. Balesdent et al., 2000; Franzluebbers, 2002; Luo et al., 2010; Martínez et al., 2016; Mary et al., 2020; Tan et al., 2007). The SOC_{RE} profile of CT fields was quite constant in the ploughed layer and decreased below the plough pan, while the SOC_{RE} profile of NT fields showed significantly larger SOC_{RE} content in the 0-5 cm layer and a more regular decrease with depth, with significantly smaller SOC_{RE} content than with CT in the 20-30 cm layer next to the plough pan. The SOC_{RE} contents were not significantly different between NT and CT below the plough pan. It is important to note, however, that this study is not a paired experiment and did not aim at quantitatively comparing the SOC contents or stocks as a function of cropping practices, and to recall the relatively large SOC contents we observed in the CT fields. The SOC_{RE}:clay profiles with depth showed similar patterns to SOC_{RE} profiles (Table 1).

The negative correlation between OI and HI accords with previous observations (e.g. Disnar et al., 2003; Gregorich et al., 2015; Sebag et al., 2016; Soucémarianadin et al., 2018).

In NT fields, the larger SOC_{RE} , SOC_{RE} :clay and hydrocarbon pool contents in the top 5 cm layer were not associated with larger oxygenation of the SOC_{RE} (OI), whereas this index was significantly larger than with CT in the 10–40 cm layer. A smaller OI is an indicator of the "freshness" of the SOM (Barré et al., 2016; Gregorich et al., 2015; Saenger et al., 2013). SOM was, therefore, fresher next to the plough limit under CT compared to NT.

According to our observations, the equilibrium between the different hydrocarbon pools is related to the level of saturation of the clay by SOC (Table 2-4 and Fig. 3). The slopes of the HIAx to SOC_{RE}:clay relationships at the lower end of SOC_{RE} :clay ratio values (Table 5) are similar,

Table 3

Summary of "stepAIC" models with the coefficients, standard errors, significance of the different variables and their weigh according to the "lmg" metric, the R^2 of the model, the adjusted R^2 of the model, the degrees of livery (DF), the residual error and the p_value of the model. Bold: the 2 variables the larger weight. Variable significance levels in the multivariate linear model are 0.05 *, 0.01 **, 0.001 ***.

Model	Variables	Estimate	Std. Error	Signif.		lmg	multiple R ²	adjusted R ²	DF	Resid. std. Error	p_value
stepAIC HI	(Intercept) Clay Averages depth Tillage Altitude Serie SOC_{RE}:clay	$108.51 \\ 0.96 \\ -1.05 \\ 9.88 \\ -0.03 \\ 3.06 \\ 475.14$	9.89 0.19 0.14 2.32 0.01 0.59 35.81	$< 2e^{-16} \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ 0.00 \\ < 2e^{-16}$	*** *** *** *** ***	0.02 0.34 0.02 0.01 0.02 0.40	0.81	0.80	215	16.42	$< 2.2e^{-16}$
stepAIC HIA1	(Intercept) Altitude Averages depth Tillage Serie SOC_{RE}:clay pH	36.10 -0.24 2.26 1.09 120.75 -1.79	6.30 0.00 0.05 0.78 0.20 11.92 0.76	$\begin{array}{c} 0.00\\ 0.11\\ 0.00\\ 0.00\\ 0.00\\ < 2e^{\cdot 16}\\ 0.02 \end{array}$	*** ** ** ** **	0.00 0.27 0.01 0.04 0.35 0.03	0.71	0.70	215	5.56	$< 2.2e^{-16}$
stepAIC HIA2	(Intercept) SOC _{RE} Clay Averages depth Altitude Serie SOC_{RE}:Clay pH	$11.64 \\ -3.59 \\ 0.54 \\ -0.35 \\ -0.01 \\ 0.69 \\ 222.82 \\ 1.72$	5.67 1.48 0.15 0.04 0.00 0.17 29.47 0.69	0.04 0.02 0.00 0.00 0.00 0.00 0.00 0.00	* * *** *** *** *** *	0.22 0.02 0.26 0.02 0.01 0.30 0.01	0.84	0.83	214	4.76	$< 2.2e^{-16}$
stepAIC HIA3	(Intercept) SOC _{RE} Clay Averages depth Tillage Serie SOC_{RE}:clay pH	$ \begin{array}{r} 11.60 \\ -3.46 \\ 0.72 \\ -0.35 \\ 2.59 \\ 0.76 \\ 167.64 \\ 1.32 \\ \end{array} $	4.52 1.41 0.14 0.04 0.64 0.16 27.99 0.60	0.01 0.01 0.00 0.00 0.00 0.00 0.00 0.00	* * *** *** *** ***	0.21 0.04 0.26 0.02 0.02 0.22 0.01	0.79	0.78	214	4.52	$< 2.2e^{-16}$
stepAIC HIA4	(Intercept) Clay Averages depth Tillage Altitude Serie SOC _{RE} :clay rain Silt	$21.00 \\ 0.43 \\ -0.15 \\ 2.61 \\ 0.00 \\ 0.37 \\ 82.41 \\ -0.03 \\ -0.14$	2.59 0.04 0.03 0.55 0.00 0.14 7.73 0.01 0.04	$\begin{array}{c} 0.00 \\ < 2e^{\cdot 16} \\ 0.00 \\ 0.00 \\ 0.02 \\ 0.01 \\ < 2e^{\cdot 16} \\ 0.01 \\ 0.00 \end{array}$	*** *** *** * * * *	0.10 0.26 0.03 0.01 0.01 0.33 0.00 0.02	0.75	0.74	213	3.51	< 2.2e ⁻¹⁶

Table 4

Summary table of the "simplified" models with the coefficients, standard errors, significance of the different variables and their weight, R^2 of the model, adjusted R^2 of the model, degrees of freedom (DF), residual standard error and the p_value of the model.

Model	Variables	Estimate	Std. Error	Signif.		lmg	multiple R ²	adjusted R ²	DF	Resid. std. Er.	p_value
stepAIC HI	(Intercept) Averages depth SOC _{RE} :clay	$156.15 \\ -1.40 \\ 362.16$	6.41 0.16 39.99	$<2e^{-16}\\ 0.00\\ <2e^{-16}$	*** ***	0.36 0.36	0.72	0.72	219	19.57	$< 2.2e^{-16}$
stepAIC HIA1	(Intercept) Averages depth SOC _{RE} :clay	$31.51 \\ -0.32 \\ 102.90$	2.01 0.05 12.55	$< 2e^{-16}$ 0.00 0.00	*** ***	0.30 0.33	0.64	0.63	219	6.14	$< 2.2e^{-16}$
stepAIC HIA2	(Intercept) Averages depth SOC _{RE} :clay	$34.26 \\ -0.41 \\ 126.86$	1.86 0.05 11.62	$<2e^{-16}\\ 0.00\\ <2e^{-16}$	*** *** ***	0.36 0.40	0.76	0.76	219	5.69	< 2.2e ⁻¹⁶
stepAIC HIA3	(Intercept) Averages depth SOC _{RE} :clay	45.42 -0.42 73.98	1.86 0.05 11.61	$<2e^{-16} \\ <2e^{-16} \\ 0.00$	*** ***	0.33 0.33	0.66	0.66	219	5.68	$< 2.2e^{-16}$
stepAIC HIA4	(Intercept) Averages depth SOC _{RE} :clay	$28.88 \\ -0.22 \\ 62.36$	1.47 0.04 9.17	$< 2e^{-16}$ 0.00 0.00	***	0.28 0.30	0.58	0.57	219	4.49	< 2.2e ⁻¹⁶

denoting a similar thermo-lability of these carbon pools for low SOC_{RE}: clay. The thermo-labile HIA1 and HIA2 pools remain proportional to SOC_{RE} :clay with increasing SOC_{RE} :clay. Oppositely, above a SOC_{RE} :clay ratio of about 0.1 (broken-stick model), HIA3 and HIA4 show limited

increase with SOC_{RE}:clay. The maximum curvature points of the logarithmic models were observed at SOC_{RE}:clay ratios of 0.11 and 0.07 for HIA3 and HIA4, respectively. Converting SOC_{RE} to SOC_{OX} yields SOC_{OX}: clay ratios breakpoint value of 0.087, thus close to the lower soil



Fig. 3. Proportion of the different HIAx hydrocarbon pools in SOC_{RE} as a function of the SOC_{RE} :clay ratio: A) HIA1 = most-labile; B) HIA2 = labile; C) HIA3 = resistant; D) HIA4 = refractory; E) HIA5 = most-refractory. Fine dark grey lines represent linear regression models, dotted dark grey lines, log models, and bold dark grey lines broken-stick models. The dotted dark grey and bold dark grey vertical lines indicate the maximum curvature point of the log model and the breakpoint of the broken-stick model, respectively.

structure vulnerability threshold (1:13) requiring short-term structure quality improvement according to Johannes et al. (2017). These authors emphasized that the structure quality follows a broken-stick pattern with respect to SOC, while it is linearly related to SOC:clay. Therefore, increased loss of HIA3 and HIA4 carbon pools observed below SOC:clay threshold suggests further investigation of the role of these carbon pools in preventing high soil structure vulnerability.

For larger SOC:clay ratios, the most labile hydrocarbon pools accumulate faster than the refractory pools with increasing SOC_{RE}:clay. This suggests that the improvement of structure vulnerability and physical properties reported in (Johannes et al., 2017) above the 0.08 SOC_{OX}:clay value was mostly promoted by the most labile hydrocarbon pools, which suggests that a high structure quality could be related to labile carbon pools and associated high biological activity.

Interestingly, the major driver of carbon pool relative contents was the clay size particle content and no significant effect of the tillage system on the HIAx pools was detected, except that the highest labile pool content was controlled by the SOC_{RE} :clay ratio which was larger on the topsoil in NT and at the plough limit in CT. Finally, the HIA5 hydrocarbon pool seemed to remain constant across a wide range of soils, SOC content and tillage systems, suggesting this pool is quite independent of soil management over decades.

These results are consistent with observations from (Gulde et al., 2008; Hermle et al., 2008; Mayer et al., 2022) that the clay mineral phase was saturated with intermediate and resistant organic matter pools while the labile pools were continuously increasing with SOC. However, the picture provided by this study is more detailed and has implications for both organic carbon thermal properties and SOC management in cropped soils. Our results agree with previous findings that the concept of saturation of clay-size particles by SOC does not apply insofar as SOC content and SOC pools increase with SOC:clay ratio on the observed range of values, including ratios > 1:10. However, above this ratio labile pools accumulate faster than refractory ones, suggesting that the latter are more dependent of the available clay surface area.

In terms of soil quality management, the accumulation of thermolabile pools compared to the refractory pools above the acceptable limit of structure vulnerability (Johannes et al., 2017) means that reaching an acceptable cropped soil quality (SOC:clay > 1:10) implies increasing the pool of most thermo-labile fractions regardless of tillage practices.

Conversely, a SOC content below the lower structure vulnerability limit indicates that a large part of the refractory – probably most ancient – pools was lost, which is the case in many intensively cropped soils (Dexter et al., 2008; Dupla et al., 2021; Prout et al., 2020).

Labile carbon pools are of uppermost interest for plant nutrition, particularly in organic farming systems (King et al., 2020). Therefore, it is in the interest of farmers and of food security to guarantee the availability of these pools, particularly in the context of mineral fertilizer reduction. According to our results, assuming that the thermo-labile pools can be considered bioavailable pools, the SOM mineralisation management objectives should accord with the structure vulnerability management objectives to increase the SOC:clay above the target value of 0.08.

Moreover, if the sequestration potential of the cropped soils, usually calculated based on a SOC:clay ratio of 0.1 or more (e.g. Chen et al., 2019; Dupla et al., 2021), was achieved, it would have to go hand in hand with an explicit increase in the content of thermo-labile carbon reservoirs. Again, under the assumption of good correspondence between thermo-labile and bioavailable pools, a larger reversibility of sequestration may be associated with these pools, which should be further studied, in particular regarding the ability of microorganisms and roots to build persistent carbon pools (Domeignoz-Horta et al., 2021; Yuan et al., 2020). This could be also related to the corresponding agri-environmental management schemes and their stability, not only to the relative stability of carbon pools, arguably. In this perspective, performing carbon sequestration in cropped land requires agri-

Table 5

Equations of the linear, logarithmic, and broken-stick models presented in Fig. 3, with their maximum curvature points (mcp) and breakpoints (bp) for the HIAx hydrocarbon pools as a function of the SOC_{RE}:clay ratio.

fonction	regression type	regression equation	intercept	p_value	max cuve point (x) / break point (x) \pm se	\mathbb{R}^2	R ² ajd.
$HIA1 \sim SOC_{RE}: clay$	linear	f(y) = 160.55x	+ 20.24	< 0.001		0.57	0.57
$HIA2 \sim SOC_{RE}:clay$	linear	f(y) = 200.20x	+ 19.93	< 0.001		0.68	0.67
HIA3 \sim SOC _{RE} :clay	linear	f(y) = 149.36x	+ 30.69	< 0.001	-	0.53	0.53
	log	$f(y) = \log(15.23x)$	+ 82.45	< 0.001	mcp(x) = 0.108	0.60	0.60
	broken stick	f(y1) = 262.27x	+ 22.64	< 0.001	$hn(\mathbf{x}) = 0.102 \pm 0.007$	0.61	0.60
	broken stick	f(y2) = 76.24x		< 0.001	$bp(x) = 0.102 \pm 0.007$		0.00
$HIA4 \sim SOC_{RE}: clay$	linear	f(y) = 102.44x	+ 21.05	< 0.001	-	0.50	0.50
	log	$f(y) = \log(10.49x)$	+ 56.64	< 0.001	mcp(x) = 0.074	0.57	0.57
	huston stick	f(y1) = 191.39x	+ 14.73	< 0.001	$hp(x) = 0.101 \pm 0.007$	0.50	0.58
	DIOKEII SUCK	f(y2) = 46.78x		< 0.001	$bp(x) = 0.101 \pm 0.007$	0.39	0.36
$HIA5 \sim SOC_{RE}: clay$	linear	f(y) = 0.72x	+ 15.18	0.81		< 0.01	< 0.01

environmental management schemes that guarantee that the corresponding practices will be applied in the long term because it must be based on large labile carbon pools. This could be seen as a weakness of this Negative Emission Technology. However, owing to the large panel of soil functions offered by a high SOC:clay ratio and corresponding cropping practices, including erosion, flood control and storage of plant available water, we argue that this should rather be considered as a virtue since it commits the society to take care of its soils in the long term.

The results presented in this study should also be commented on from the point of view of the experimental set-up. We sampled actual farm fields, not long-term paired experiments conducted in controlled conditions, therefore, quantitative comparisons of SOC contents as influenced by tillage method were not directly addressed. On the other hand, our results are assessed regardless of the large variations in soil quality, such as pH and texture, as well as in cropping practices, such as manuring and cover crop intensity and type, which are observed in the farms of the Swiss plateau. Therefore, the dependence of the HIAx pools on the SOC:clay ratio is assessed in a single sampling regardless of the many varying conditions that would not have been reproduced in a longterm experiment. This suggests that using living-lab sampling strategies in the future may prove to be a highly efficient strategy. Finally, we observe that the Rock-Eval® pyrolysis and the focus on the HI pools allow us to retrieve stimulating observations and suggest further exciting research questions with respect to structure quality and soil organic carbon pools.

5. Conclusions

As previously observed, the relative distribution of SOC with depth is influenced by tillage, with larger SOC in the top layer under no tillage (NT) and above the plough pan under conventional tillage (CT). Accordingly, the SOM was less oxygenated and thus younger above the plough pan under CT compared to NT. Conversely, the proportion of hydrocarbon compound (HC) in the SOC (HI) was larger in CT than in NT in the deeper layers. This is also observed for most HI-derived thermal pools (HIAx).

The proportion of refractory HC in the SOC appeared to be mainly driven by the SOC:clay ratio, the tillage system only influencing this proportion through the SOC:clay distribution with depth. Below the SOC_{OX} :clay ratio of 0.08, all pools were decreasing nearly equally with decreasing SOC, and above this ratio, the proportion of refractory pools in the SOC increased only slightly. While no saturation was observed with SOC and SOC pools in general, our results suggest that the proportion of most refractory pools is limited by the clay-size particles content.

The corresponding SOC_{OX}:clay threshold is close to the lower limit of structure vulnerability index reported in the literature for Swiss and UK soils, below which severely degraded structures are observed on average

in the field. These findings have implications for soil fertility and carbon sequestration management, since they suggest that a large proportion of labile carbon is necessary for soils to attain acceptable to high structure quality, to protect the refractory pools, and to reach the soil carbon sequestration potential.

CRediT authorship contribution statement

Cedric Deluz: Writing – review & editing, Writing – original draft, Software, Methodology, Investigation, Formal analysis, Conceptualization. **David Sebag:** Writing – review & editing, Validation, Methodology. **Eric Verrecchia:** Writing – review & editing, Validation. **Pascal Boivin:** Writing – review & editing, Validation, Supervision, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The authors are grateful to Victor Martin, who helped to sample the soils, Aline Chambettaz and Sylvain Mischler who performed the SOC analyses, Thierry Adatte who run the Rock-Eval® pyrolysis, Alyssa Deluz, who took part in the brainstorming sessions, Julien Clark for reviewing the English of the entire text and the many farmers who opened us the access to their fields.

The authors are also grateful to hepia of the University of Applied Sciences Western Switzerland (HES-SO) for funding the master's work that led to this publication.

References

- Albrecht, R., Sebag, D., Verrecchia, E., 2015. Organic matter decomposition: bridging the gap between rock-eval pyrolysis and chemical characterization (CPMAS 13C NMR). Biogeochemistry 122, 101–111, https://doi.org/10.1007/s10533-014-0033-8.
- Angers, D.A., Eriksen-Hamel, N.S., 2008. Full-inversion tillage and organic Carbon distribution in soil profiles: a meta-analysis. Soil Sci. Soc. Am. J. 72, 1370. https:// doi.org/10.2136/sssaj2007.0342.
- Balesdent, J., Chenu, C., Balabane, M., 2000. Relationship of soil organic matter dynamics to physical protection and tillage. Soil Tillage Res. 53, 215–230.
- Balesdent, J., Basile-Doelsch, I., Chadoeuf, J., Cornu, S., Derrien, D., Fekiacova, Z., Hatté, C., 2018. Atmosphere–soil carbon transfer as a function of soil depth. Nature 559, 599–602. https://doi.org/10.1038/s41586-018-0328-3.
- Barré, P., Plante, A.F., Cécillon, L., Lutfalla, S., Baudin, F., Bernard, S., Christensen, B.T., Eglin, T., Fernandez, J.M., Houot, S., Kätterer, T., Le Guillou, C., Macdonald, A., van

C. Deluz et al.

Oort, F., Chenu, C., 2016. The energetic and chemical signatures of persistent soil organic matter. Biogeochemistry 130, 1–12. https://doi.org/10.1007/s10533-016-0246-0.

- Begill, N., Don, A., Poeplau, C., 2023. No detectable upper limit of mineral-associated organic carbon in temperate agricultural soils. Glob. Change Biol. 29, 4662–4669. https://doi.org/10.1111/gcb.16804.
- Behar, F., Beaumont, V., Penteado, D.B.H.L., 2001. Rock-Eval 6 technology: performances and developments. Oil Gas Sci. Technol. 56, 111–134. https://doi.org/ 10.2516/ogst:2001013.
- Bosatta, E., Ågren, G.I., 1999. Soil organic matter quality interpreted thermodynamically. Soil Biol. Biochem. 31, 1889–1891. https://doi.org/10.1016/ S0038-0717(99)00105-4.
- Bünemann, E.K., Bongiorno, G., Bai, Z., Creamer, R.E., De Deyn, G., de Goede, R., Fleskens, L., Geissen, V., Kuyper, T.W., Mäder, P., Pulleman, M., Sukkel, W., van Groenigen, J.W., Brussaard, L., 2018. Soil quality – a critical review. Soil Biol. Biochem. 120, 105–125. https://doi.org/10.1016/j.soilbio.2018.01.030.
- Chen, S., Arrouays, D., Angers, D.A., Chenu, C., Barré, P., Martin, M.P., Saby, N.P.A., Walter, C., 2019. National estimation of soil organic carbon storage potential for arable soils: a data-driven approach coupled with carbon-landscape zones. Sci. Total Environ. 666, 355–367. https://doi.org/10.1016/j.scitotenv.2019.02.249.
- Cook, S., Cock, J., Oberthür, T., Fisher, M., 2013. On-Farm Experimentation. Better Crops 97, 17–20.
- Cotrufo, M.F., Lavallee, J.M., Six, J., Lugato, E., 2023. The robust concept of mineralassociated organic matter saturation: A letter to Begill et al., 2023. Glob. Change Biol. 29, 5986–5987. https://doi.org/10.1111/gcb.16921.
- Davies, R.B., 2002. Hypothesis testing when a nuisance parameter is present only under the alternative: Linear model case. Biometrika 89, 484–489. https://doi.org/ 10.1093/biomet/89.2.484.
- de Oliveira Ferreira, A., Amado, J.C.T., da Silveira Nicoloso, R., de Moraes Sá, J.C., Ernani Fiorin, J., Santos Hansel, D.S., Menefee, D., 2013. Soil carbon stratification affected by long-term tillage and cropping systems in southern Brazil. Soil Tillage Res. 133, 65–74. https://doi.org/10.1016/j.still.2013.05.011.
- Delahaie, A.A., Barré, P., Baudin, F., Arrouays, D., Bispo, A., Boulonne, L., Chenu, C., Jolivet, C., Martin, M.P., Ratié, C., Saby, N.P.A., Savignac, F., Cécillon, L., 2023. Elemental stoichiometry and Rock-Eval® thermal stability of organic matter in French topsoils. SOIL 9, 209–229. https://doi.org/10.5194/soil-9-209-2023.
- Deluz, C., Nussbaum, M., Sauzet, O., Gondret, K., Boivin, P., 2020. Evaluation of the potential for soil organic Carbon content monitoring with Farmers. Front. Environ. Sci. 8 https://doi.org/10.3389/fenvs.2020.00113.
- Dexter, A.R., Richard, G., Arrouays, D., Czyz, E.A., Jolivet, C., Duval, O., 2008. Complexed organic matter controls soil physical properties. Geoderma 144, 620–627. https://doi.org/10.1016/j.geoderma.2008.01.022.
- Dimassi, B., Mary, B., Wylleman, R., Labreuche, J., Couture, D., Piraux, F., Cohan, J.-P., 2014. Long-term effect of contrasted tillage and crop management on soil carbon dynamics during 41 years. Agr Ecosyst Environ 188, 134–146. https://doi.org/ 10.1016/j.agee.2014.02.014.
- Disnar, J.R., Guillet, B., Keravis, D., Di-Giovanni, C., Sebag, D., 2003. Soil organic matter (SOM) characterization by rock-eval pyrolysis: scope and limitations. Org Geochem. 34, 327–343. https://doi.org/10.1016/S0146-6380(02)00239-5.
- Domeignoz-Horta, L.A., Shinfuku, M., Junier, P., Poirier, S., Verrecchia, E., Sebag, D., DeAngelis, K.M., 2021. Direct evidence for the role of microbial community composition in the formation of soil organic matter composition and persistence. ISME Commun. 1, 1–4. https://doi.org/10.1038/s43705-021-00071-7.
- Dupla, X., Gondret, K., Sauzet, O., Verrecchia, E., Boivin, P., 2021. Changes in topsoil organic carbon content in the swiss leman region cropland from 1993 to present. Insights from large scale on-farm study. Geoderma 400, 115125. https://doi.org/ 10.1016/j.geoderma.2021.115125.
- Dupla, X., Lemaître, T., Grand, S., Gondret, K., Charles, R., Verrecchia, E., Boivin, P., 2022. On-Farm relationships between agricultural Practices and annual changes in organic Carbon content at a regional scale. Front. Environ. Sci. 10, 834055 https:// doi.org/10.3389/fenvs.2022.834055.
- Food and Agriculture Organisation, 2014. World reference base for soil resources 2014. Franzluebbers, A.J., 2002. Water infiltration and soil structure related to organic matter and its stratification with depth. Soil Tillage Res. 66, 197–205. https://doi.org/ 10.1016/S0167-1987(02)00027-2
- Govaerts, B., Verhulst, N., Castellanos-Navarrete, A., Sayre, K.D., Dixon, J., Dendooven, L., 2009. Conservation agriculture and soil Carbon sequestration: between myth and Farmer reality. Crit. Rev. Plant Sci. 28, 97–122. https://doi.org/ 10.1080/07352680902776358.
- Gregorich, E.G., Gillespie, A.W., Beare, M.H., Curtin, D., Sanei, H., Yanni, S.F., 2015. Evaluating biodegradability of soil organic matter by its thermal stability and chemical composition. Soil Biol. Biochem. 91, 182–191. https://doi.org/10.1016/j. soilbio.2015.08.032.
- Grömping, U., 2006. Relative importance for Linear regression in R: the package relaimpo. J. Stat. Softw. 17 https://doi.org/10.18637/jss.v017.i01.
- Gubler, A., Wächter, D., Schwab, P., Müller, M., Keller, A., 2019. Twenty-five years of observations of soil organic carbon in swiss croplands showing stability overall but with some divergent trends. Environ. Monit. Assess. 191 https://doi.org/10.1007/ s10661-019-7435-y.
- Gulde, S., Chung, H., Amelung, W., Chang, C., Six, J., 2008. Soil Carbon saturation controls labile and stable Carbon Pool dynamics. Soil Sci. Soc. Am. J. 72, 605–612. https://doi.org/10.2136/sssaj2007.0251.
- Hassink, J., 1997. The capacity of soils to preserve organic C and N by their association with clay and silt particles. Plant Soil 191, 77–87. https://doi.org/10.1023/A: 1004213929699.

- Haynes, R.J., 2005. Labile organic matter fractions as central components of the quality of agricultural soils: an overview. Advances in Agronomy 85, 221–268., Advances in Agronomy. Elsevier.
- Hazera, J., Sebag, D., Kowalewski, I., Verrecchia, E., Ravelojaona, H., Chevallier, T., 2023. Adjustments of the rock-eval® thermal analysis for soil organic and inorganic carbon quantification. Biogeosci. Discuss. 1–18 https://doi.org/10.5194/ bg-2023-66.
- Hermle, S., Anken, T., Leifeld, J., Weisskopf, P., 2008. The effect of the tillage system on soil organic carbon content under moist, cold-temperate conditions. Soil Tillage Res. 98, 94–105. https://doi.org/10.1016/j.still.2007.10.010.
- Johannes, A., Matter, A., Schulin, R., Weisskopf, P., Baveye, P.C., Boivin, P., 2017. Optimal organic carbon values for soil structure quality of arable soils. Does clay content matter? Geoderma 302, 14–21. https://doi.org/10.1016/j. geoderma.2017.04.021.
- Karlen, D.L., Mausbach, M.J., Doran, J.W., Cline, R.G., Harris, R.F., Schuman, G.E., 1997. Soil quality: a concept, definition, and framework for evaluation (a guest editorial). Soil Sci. Soc. Am. J. 61, 4. https://doi.org/10.2136/ sssaj1997.03615995006100010001x.
- Keel, S.G., Anken, T., Büchi, L., Chervet, A., Fliessbach, A., Flisch, R., Huguenin-Elie, O., Mäder, P., Mayer, J., Sinaj, S., Sturny, W., Wüst-Galley, C., Zihlmann, U., Leifeld, J., 2019. Loss of soil organic carbon in swiss long-term agricultural experiments over a wide range of management practices. Agr Ecosyst Environ 286, 106654. https://doi. org/10.1016/j.agee.2019.106654.
- King, A.E., Ali, G.A., Gillespie, A.W., Wagner-Riddle, C., 2020. Soil organic matter as catalyst of crop resource capture. Front. Environ. Sci. 8 https://doi.org/10.3389/ fenvs.2020.00050.
- Lafargue, E., Marquis, F., Pillot, D., 1998. Rock-eval 6 applications in Hydrocarbon exploration, production, and soil contamination studies. Revue De L'institut Français Du Pétrole 53, 421–437. https://doi.org/10.2516/ogst:1998036.
- Lal, R., 2004. ECOLOGY: managing soil Carbon. Science 304, 393. https://doi.org/ 10.1126/science.1093079.
- Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature. https://doi.org/10.1038/nature16069.
- Luo, Z., Wang, E., Sun, O.J., 2010. Can no-tillage stimulate carbon sequestration in agricultural soils? A meta-analysis of paired experiments. Agr Ecosyst Environ 139, 224–231. https://doi.org/10.1016/j.agee.2010.08.006.
- Manlay, R.J., Feller, C., Swift, M.J., 2007. Historical evolution of soil organic matter concepts and their relationships with the fertility and sustainability of cropping systems. Agr Ecosyst Environ 119, 217–233. https://doi.org/10.1016/j. agee.2006.07.011.
- Martínez, I., Chervet, A., Weisskopf, P., Sturny, W.G., Etana, A., Stettler, M., Forkman, J., Keller, T., 2016. Two decades of no-till in the Oberacker long-term field experiment: Part I. crop yield, soil organic carbon and nutrient distribution in the soil profile. Soil Tillage Res. 163, 141–151. https://doi.org/10.1016/j.still.2016.05.021.
- Mary, B., Clivot, H., Blaszczyk, N., Labreuche, J., Ferchaud, F., 2020. Soil carbon storage and mineralization rates are affected by carbon inputs rather than physical disturbance: evidence from a 47-year tillage experiment. Agr Ecosyst Environ 299, 106972. https://doi.org/10.1016/j.agee.2020.106972.
- Mayer, M., Krause, H.-M., Fliessbach, A., Mäder, P., Steffens, M., 2022. Fertilizer quality and labile soil organic matter fractions are vital for organic carbon sequestration in temperate arable soils within a long-term trial in Switzerland. Geoderma 426, 116080. https://doi.org/10.1016/j.geoderma.2022.116080.
- Minasny, B., Malone, B.P., McBratney, A.B., Angers, D.A., Arrouays, D., Chambers, A., Chaplot, V., Chen, Z.-S., Cheng, K., Das, B.S., Field, D.J., Gimona, A., Hedley, C.B., Hong, S.Y., Mandal, B., Marchant, B.P., Martin, M., McConkey, B.G., Mulder, V.L., O'Rourke, S., Richer-de-Forges, A.C., Odeh, I., Padarian, J., Paustian, K., Pan, G., Poggio, L., Savin, I., Stolbovoy, V., Stockmann, U., Sulaeman, Y., Tsui, C.-C., Vågen, T.-G., van Wesemael, B., Winowiecki, L., 2017. Soil carbon 4 per mille. Geoderma 292, 59–86. https://doi.org/10.1016/j.geoderma.2017.01.002.
- Montanarella, L., Pennock, D.J., McKenzie, N., Badraoui, M., Chude, V., Baptista, I., Mamo, T., Yemefack, M., Singh Aulakh, M., Yagi, K., Young Hong, S., Vijarnsorn, P., Zhang, G.-L., Arrouays, D., Black, H., Krasilnikov, P., Sobocká, J., Alegre, J., Henriquez, C.R., de Lourdes Mendonça-Santos, M., Taboada, M., Espinosa-Victoria, D., AlShankiti, A., AlaviPanah, S.K., Elsheikh, E.A.E.M., Hempel, J., Camps Arbestain, M., Nachtergaele, F., Vargas, R., 2016. World's soils are under threat. SOIL 2, 79–82. https://doi.org/10.5194/soil-2-79-2016.
- Muggeo, V.M.R., 2008. segmented: An R Package to Fit Regression Models with Broken-Line Relationships 8.
- Murphy, D.V., Cookson, W.R., Braimbridge, M., Marschner, P., Jones, D.L., Stockdale, E. A., Abbott, L.K., 2011. Relationships between soil organic matter and the soil microbial biomass (size, functional diversity, and community structure) in crop and pasture systems in a semi-arid environment. Soil Res. 49, 582. https://doi.org/ 10.1071/SR11203.
- Office fédéral de topographie, 1984. Atlas de la Suisse, 2ème édition. ed. Office fédéral de topographie.
- Pacini, L., Adatte, T., Barré, P., Boussafir, M., Bouton, N., Cécillon, L., Lamoureux-Var, V., Sebag, D., Verrecchia, E., Wattripont, A., Baudin, F., 2023. Reproducibility of Rock-Eval® thermal analysis for soil organic matter characterization. Organic Geochemistry 186, 104687. https://doi.org/10.1016/j.orggeochem.2023.104687.
- Plante, A.F., Fernández, J.M., Leifeld, J., 2009. Application of thermal analysis techniques in soil science. Geoderma 153, 1–10. https://doi.org/10.1016/j. geoderma.2009.08.016.
- Plante, A.F., Fernández, J.M., Haddix, M.L., Steinweg, J.M., Conant, R.T., 2011. Biological, chemical and thermal indices of soil organic matter stability in four grassland soils. Soil Biol. Biochem. 43, 1051–1058. https://doi.org/10.1016/j. soilbio.2011.01.024.

- Poeplau, C., Begill, N., Don, A., 2023. Response to: "The robust concept of mineralassociated organic matter saturation: A letter to Begill et al. (2023).". Glob. Change Biol. 29 https://doi.org/10.1111/gcb.16920.
- Prout, S.K.D., McGrath, S.P., Kirk, G.J.D., Haefele, S.M., 2020. What is a good level of soil organic matter? An index based on organic carbon to clay ratio. Eur. J. Soil Sci. https://doi.org/10.1111/ejss.13012.
- Saenger, A., Cécillon, L., Sebag, D., Brun, J.-J., 2013. Soil organic carbon quantity, chemistry and thermal stability in a mountainous landscape: a rock-eval pyrolysis survey. Org Geochem. 54, 101–114. https://doi.org/10.1016/j. orggeochem.2012.10.008.
- Salvo, L., Hernández, J., Ernst, O., 2010. Distribution of soil organic carbon in different size fractions, under pasture and crop rotations with conventional tillage and no-till systems. Soil Tillage Res. 109, 116–122. https://doi.org/10.1016/j. still.2010.05.008.
- Scholes, R.J., Montanarella, L., Brainich, E., Barger, N., Brink, B. ten, Cantele, M., Erasmus, B., Fisher, J., Gardner, T., Holland, T.G., Kohler, F., Kotiaho, S., Maltitz, G. von, Nangendo, G., Pandit, R., Parrotta, J., Potts, M.D., Prince, S., Sankaran, M., Willemen, L., 2018. IPBES (2018): Summary for policymakers of the assessment report on land degradation and restoration of the Intergovernmental Science- Policy Platform on Biodiversity and Ecosystem Services. Intergovernmental Science-Policy Platform on Biodiversity and Ecosystem Services.
- Sebag, D., Disnar, J.R., Guillet, B., Di Giovanni, C., Verrecchia, E.P., Durand, A., 2006. Monitoring organic matter dynamics in soil profiles by "rock-eval pyrolysis": bulk characterization and quantification of degradation. Eur. J. Soil Sci. 57, 344–355. https://doi.org/10.1111/j.1365-2389.2005.00745.x.
- Sebag, D., Verrecchia, E.P., Cécillon, L., Adatte, T., Albrecht, R., Aubert, M., Bureau, F., Cailleau, G., Copard, Y., Decaens, T., Disnar, J.-R., Hetényi, M., Nyilas, T., Trombino, L., 2016. Dynamics of soil organic matter based on new rock-eval indices. Geoderma 284, 185–203. https://doi.org/10.1016/j.geoderma.2016.08.025.

Sebag, D., Verrecchia, E.P., Adatte, T., Aubert, M., Cailleau, G., Decaëns, T., Kowalewski, I., Trap, J., Bureau, F., Hedde, M., 2022. Size fractions of organic matter pools influence their stability: application of the rock-eval® analysis to beech forest soils. Pedosphere 32, 565–575. https://doi.org/10.1016/S1002-0160(21) 60050-4.

- Six, J., Doetterl, S., Laub, M., Müller, C.R., Van De Broek, M.. The six rights of how and when to test for soil C saturation (preprint). Soils and biogeochemical cycling. http s://doi.org/10.5194/egusphere-2023-2221.
- Soucémarianadin, L., Cécillon, L., Chenu, C., Baudin, F., Nicolas, M., Girardin, C., Barré, P., 2018. Is rock-eval 6 thermal analysis a good indicator of soil organic carbon lability? – a method-comparison study in forest soils. Soil Biol. Biochem. 117, 108–116. https://doi.org/10.1016/j.soilbio.2017.10.025.
- Tan, Z., Lal, R., Owens, L., Izaurralde, R.C., 2007. Distribution of light and heavy fractions of soil organic carbon as related to land use and tillage practice. Soil Tillage Res. 92, 53–59. https://doi.org/10.1016/j.still.2006.01.003.
- Toms, J.D., Lesperance, M.L., 2003. Piecewise regression: a tool for identifying ecological thresholds. Ecology 84, 2034–2041. https://doi.org/10.1890/02-0472.
- Venables, W.N., Ripley, B.D., 2002. Random and Mixed Effects, in: Venables, W.N., Ripley, B.D. (Eds.), Modern Applied Statistics with S, Statistics and Computing. Springer, New York, NY, pp. 271–300. https://doi.org/10.1007/978-0-387-21706-2_ 10.
- von Lützow, M., Kögel-Knabner, I., Ekschmitt, K., Flessa, H., Guggenberger, G., Matzner, E., Marschner, B., 2007. SOM fractionation methods: relevance to functional pools and to stabilization mechanisms. Soil Biol. Biochem. 39, 2183–2207. https://doi.org/10.1016/j.soilbio.2007.03.007.
- Walkley, A., Black, I.A., 1934. An examination of Degtjareff method for determining soil organic matter and a proposed modification of the chromic acid titration method. Soil Sci. 1, 29–37.
- Yuan, Y., Zhang, Z., Chen, L., Yang, C., 2020. The formation of protected SOM facilitated by labile C input via artificial roots. Eur. J. Soil Biol. 100, 103231 https://doi.org/ 10.1016/j.ejsobi.2020.103231.
- Zhang, Y., Gao, Y., Zhang, Y., Huang, D., Li, X., McLaughlin, N., Zhang, X., Chen, X., Zhang, S., Gregorich, E., Liang, A., 2023. Linking rock-eval parameters to soil heterotrophic respiration and microbial residues in a black soil. Soil Biol. Biochem. 178, 108939 https://doi.org/10.1016/j.soilbio.2023.108939.