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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

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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 CO₂ 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

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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 moraine-molasse 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

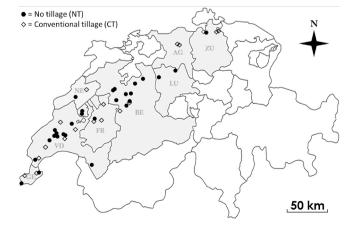


Fig. 1. Switzerland map with location of the sample fields. Diamond \Diamond : Conventional tillage. Ring \bullet : No tillage.

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 < 2 mm fractions of the soil samples to a $< 250 \, \mu m$ 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 [% 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 $\mathrm{HC.g}^{-1}$ 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 ${\rm SOC}_{\rm OX}$ 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 R^2 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 R^2 for each variable selected in the stepAIC model (Grömping, 2006). Based on the partial R^2 we selected the two first-ranking variables to adjust a simplified model for each of the dependant 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.

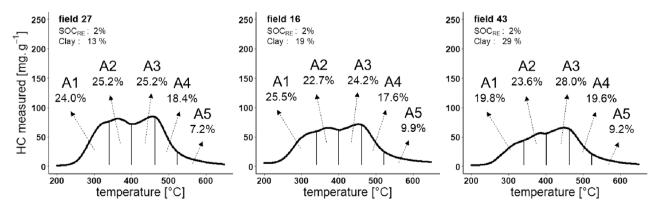


Fig. 2. Examples of hydrocarbon compound (HC) thermograms from samples of the 0–5 cm layer, with the same SOC_{RE} content and different clay content. The relative percentage of each of the five A1, A2, A3, A4 and A5 thermal pools are calculated as the surface area under the thermogram as delimited by 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 (R² = 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 ***, 0.001 *** (Student test on log-transformed data for clay, ratio SOC_{RE} :clay and HI comparisons).

Analyses and unit	Depth ranges			0-20) cm			20–4	10 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		
Analyses and unit	Depth ranges		5 cm		0 cm		20 cm		80 cm		40 cm
i mary see and anne	Type of tillage	NT	CT	NT	CT	NT	CT	NT	CT	NT	CT
000 50 0 -13	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 3.40	0.90	1.20	0.95	1.22 3.00	0.66 2.92	1.09	0.41 1.83	0.37 1.69
SOC _{RE} [% g C.g ⁻¹]	Max	4.41 3.15 *	3.40 2.53 *	3.81 2.59	3.16 2.25	3.19 2.00	2.10	2.92 1.48 *	2.55 1.76 *	0.91	1.69 1.05
SOC _{RE} [% g C.g]	Mean SD	1.16	0.82	0.98	0.70	0.78	0.72	0.65	0.62	0.91	0.38
	Min	1.61	1.37	0.90	1.24	0.78	1.12	0.69	0.02	0.44	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
Tatio Bocox.clay	SD	0.04	0.04	0.03	0.03	0.02	0.02	0.02	0.02	0.01	0.03
	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
ratio do c _{RE} .emy	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
- 1 0 - 0 1	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
HIA3 [mg HC.g ⁻¹ SOC _{RE}]	Max	73.0	64.5	64.8	59.3	51.4	54.5 50.1 *	41.8 38.9 ***	43.0 46.0 ***	37.8 31.5 **	37.0 36.2 **
	Mean	55.2	53.5	50.8	51.5	46.3*					
resistant pool	SD Min	6.0 41.3	5.3 43.2	6.0 38.4	4.8 44.1	6.0	4.0 43.5	6.6 26.8	4.2 38.6	7.3 19.7	5.8 26.9
	Max	41.3 64.9	43.2 64.3	38.4 60.8	59.3	31.3 59.1	43.5 57.2	26.8 57.6	38.6 52.4	19.7 54.8	26.9 47.6
HIA4 [mg HC.g ⁻¹ SOC _{RE}]	Mean	36.8	36.4	34.2	35.5	32.0	34.7	27.2***	32.4 32.1***	21.9*	47.6 25.0*
refractory pool	SD	4.8	3.9	4.8	4.4	5.4	3.9	5.3	3.7	5.1	4.6
remactory poor	Min	27.4	29.8	25.3	28.1	20.1	27.6	19.5	26.6	14.9	18.1
	Max	44.8	42.4	43.1	42.4	43.8	40.8	43.3	37.0	39.7	35.3
HIA5 [mg HC.g ⁻¹ SOC _{RE}]	Mean	15.3	15.7	14.9	16.5	14.7*	15.91*	14.5*	15.9*	14.7	15.7
most refractory pool	SD	1.6	1.4	1.5	4.3	1.6	1.3	2.2	1.7	1.9	1.9
most remactory 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	19.1	20.9	20.2	20.0	20.9

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 R² and adjusted R² 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 Simplified	ні	Clay + Averages depth + Tillage + Altitude + Serie + SOC _{RE} :clay Averages depth + SOC _{RE} :	0.81	0.80
Simplified	пі	clay	0.72	0.72
stepAIC	HIA1	Averages depth + Tillage + Serie + Altitude + SOC _{RE} :clay + pH	0.71	0.70
Simplified	HIA1	Averages depth $+$ SOC _{RE} : clay	0.64	0.63
stepAIC	HIA2	$SOC_{RE} + Clay + Averages$ depth + Altitude + Serie + SOC_{RE} : $clay + pH$	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} : $clay + pH$	0.79	0.78
Simplified	HIA3	Averages depth $+$ SOC _{RE} : clay	0.66	0.66
stepAIC	HIA4	Clay + Averages depth + Tillage + Altitude + Serie + SOC _{RE} :clay + rain + Silt	0.75	0.74
Simplified	HIA4	Averages depth + SOC _{RE} : clay	0.57	0.57
stepAIC	HIA5	Clay + Tillage + Altitude + Serie + Silt	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 R² 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 $R^2 = 0.30$ 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_{RE}: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 SOCRE:clay or any other available property (Table 5 & Fig. 3 E).

4. Discussion

The mean SOCOX: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 SOCRE, SOCRE: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,

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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)	108.51	9.89	< 2e ⁻¹⁶	***					16.42	< 2.2e ⁻¹⁶
	Clay	0.96	0.19	0.00	***	0.02					
	Averages depth	-1.05	0.14	0.00	***	0.34					
	Tillage	9.88	2.32	0.00	***	0.02	0.81	0.80	215		
	Altitude	-0.03	0.01	0.00	***	0.01					
	Serie	3.06	0.59	0.00	***	0.02					
	SOC _{RE} :clay	475.14	35.81	$< 2e^{-16}$	***	0.40					
	(Intercept)	36.10	6.30	0.00	***						
	Altitude	0.00	0.00	0.11		0.00					$< 2.2e^{-16}$
	Averages depth	-0.24	0.05	0.00	***	0.27					
stepAIC HIA1	Tillage	2.26	0.78	0.00	**	0.01	0.71	0.70	215	5.56	
	Serie	1.09	0.20	0.00	***	0.04					
	SOC _{RE} :clay	120.75	11.92	$< 2e^{-16}$	***	0.35					
	pН	-1.79	0.76	0.02	*	0.03					
	(Intercept)	11.64	5.67	0.04	*						
	SOC_{RE}	-3.59	1.48	0.02	*	0.22		0.83	214	4.76	
stepAIC HIA2	Clay	0.54	0.15	0.00	***	0.02					
	Averages depth	-0.35	0.04	0.00	***	0.26	0.84				< 2.2e ⁻¹⁶
steprite iiiiz	Altitude	-0.01	0.00	0.00	***	0.02	0.04				\ <u>2.2</u> c
	Serie	0.69	0.17	0.00	***	0.01					
	SOC _{RE} :clay	222.82	29.47	0.00	***	0.30					
	pН	1.72	0.69	0.01	*	0.01					
	(Intercept)	11.60	4.52	0.01	*			0.78	214		$< 2.2e^{-16}$
	SOC_{RE}	-3.46	1.41	0.01	*	0.21					
	Clay	0.72	0.14	0.00	***	0.04				4.52	
stepAIC HIA3	Averages depth	-0.35	0.04	0.00	***	0.26	0.79				
этергие типо	Tillage	2.59	0.64	0.00	***	0.02	0.7 5			1.02	
	Serie	0.76	0.16	0.00	***	0.02					
	SOC _{RE} :clay	167.64	27.99	0.00	***	0.22					
	pН	1.32	0.60	0.03	*	0.01					
	(Intercept)	21.00	2.59	0.00	***						
	Clay	0.43	0.04	$< 2e^{-16}$	***	0.10					
	Averages depth	-0.15	0.03	0.00	***	0.26					
	Tillage	2.61	0.55	0.00	***	0.03					1.0
stepAIC HIA4	Altitude	0.00	0.00	0.02	*	0.01	0.75	0.74	213	3.51	$< 2.2e^{-16}$
	Serie	0.37	0.14	0.01	*	0.01					
	SOC _{RE} :clay	82.41	7.73	$< 2e^{-16}$	***	0.33					
	rain	-0.03	0.01	0.01	*	0.00					
	Silt	-0.14	0.04	0.00	***	0.02					

Table 4Summary table of the "simplified" models with the coefficients, standard errors, significance of the different variables and their weight, R² of the model, adjusted R² 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

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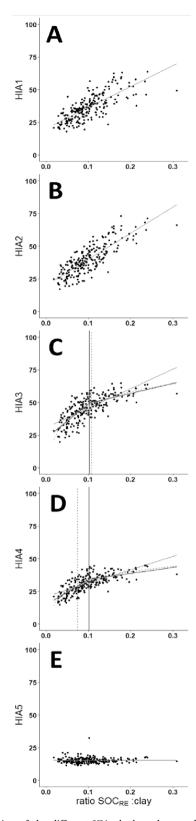


Fig. 3. Proportion of the different HIAx hydrocarbon pools in SOC_{RE} as a function of the SOC_{RE} :clay ratio: A) HIA1 = most-labile; B) HIA2 = labile; C) HIA3 = resistant; D) HIA4 = refractory; E) HIA5 = most-refractory. Fine dark grey lines represent linear regression models, dotted dark grey lines, 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	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 ~ 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	$bp(x) = 0.102 \pm 0.007$	0.61	0.60
		f(y2) = 76.24x		< 0.001	$bp(x) = 0.102 \pm 0.007$		0.00
	linear	f(y) = 102.44x	+ 21.05	< 0.001	-	0.50	0.50
HIA4 ~ SOC _{RE} :clay	log	$f(y) = \log(10.49x)$	+ 56.64	< 0.001	mcp(x) = 0.074	0.57	0.57
HIA4 ~ SOC _{RE} :Clay	broken stick	f(y1) = 191.39x	+ 14.73	< 0.001	$bp(x) = 0.101 \pm 0.007$	0.59	0.58
	DIOREII SIICK	f(y2)=46.78x		< 0.001	$bp(x) = 0.101 \pm 0.007$	0.39	0.36
$HIA5 \sim SOC_{RE}\text{:}clay$	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, 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.

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